## Functionalization and Subsequent Chemical

## Reactions of Polypnictogen Ligand Complexes

## DISSERTATION

zur Erlangung des
DOKTORGRADES DER
NATURWISSENSCHAFTEN (Dr. rer. nat.)
der Fakultät für Chemie und Pharmazie der Universtität Regensburg

vorgelegt von
Stephan Johannes Reichl
aus Traunstein

Regensburg 2022

Diese Arbeit wurde angeleitet von Prof. Dr. Manfred Scheer.

Promotionsgesuch eingereicht am: 31.08.2022
Tag der mündlichen Prüfung: $\quad 28.10 .2022$

Vorsitzender: Prof. Dr. Alkwin Slencka
Prüfungsausschuss: Prof. Dr. Manfred Scheer
Prof. Dr. Robert Wolf
Prof. Dr. Oliver Reiser
TR

## Eidesstattliche Erklärung

Ich erkläre hiermit an Eides statt, dass ich die vorliegende Arbeit „Functionalization and Subsequent Chemical Reactions of Polypnictogen Ligand Complexes" ohne unzulässige Hilfe Dritter und ohne Benutzung anderer als der angegebenen Hilfsmittel angefertigt habe; die aus anderen Quellen direkt oder indirekt übernommenen Daten und Konzepte sind unter Angabe der Literaturzitats gekennzeichnet.
$\qquad$
Stephan Reichl

This thesis was elaborated within the period from January 2019 until August 2022 in the Institute of Inorganic Chemistry at the University of Regensburg, under the supervision of Prof. Dr. Manfred Scheer.

Parts of this work have already been published or submitted:
( ${ }^{*}=$ Co-First Authorship: These authors contributed equally to this work.)

- M. Piesch*, S. Reichl*, M. Seidl*, G. Balázs, M. Scheer, Angew. Chem. Int. Ed. 2019, 58, 16563-16568.
- S. Reichl*, R. Grünbauer*, G. Balázs, M. Scheer, Chem. Commun. 2021, 57, 3383-3386.
- S. Reichl, E. Mädl, F. Riedlberger, M. Piesch, G. Balázs, M. Seidl, M. Scheer, Nat. Commun., 2021, 12, 5774.

In Addition, parts of this work have already been published as joint cooperation, however, will not discussed in detail within this work:

- R. Yadav, T. Simler, S. Reichl, B. Goswami, C. Schoo, R. Köppe, M. Scheer, P. W. Roesky, J. Am. Chem. Soc., 2020, 142, 1190-1195.
- M. Piesch, F. Dielmann, S. Reichl, M. Scheer, Chem. Eur. J., 2020, 26, 1518-1524.
- R. Yadav, B. Goswami, T. Simler, C. Schoo, S. Reichl, M. Scheer, P. W. Roesky, Chem. Commun., 2020, 56, 10207-10210.
- R. Yadav, B. Goswami, T. Simler, C. Schoo, S. Reichl, M. Scheer, P. W. Roesky, Chem. Commun., 2020, 56, 10207-10210.
- M. Piesch, S. Reichl, C. Riesinger, G. Balazs, M. Seidl, M. Scheer, Chem. Eur. J., 2021, 27, 1-13.
- M. E. Moussa, M. Fleischmann, G. Balazs, A. V. Virovets, E. Peresypkina, P. A. Shelyganov, M. Seidl, S. Reichl, M. Scheer, Chem. Eur. J., 2021, 27, 1-7.
- N. Reinfandt, N. Michenfelder, C. Schoo, R. Yadav, S. Reichl, S. N. Konchenko, A. N. Unterreiner, M. Scheer, P. W. Roesky, Chem. Eur. J., 2021, 27, 7862-7871.
- M. Piesch, S. Reichl, M. Seidl, G. Balazs, M. Scheer, Angew. Chem. Int. Ed., 2021, 60, $2-$ 10.
- M. Dietz, M. Arrowsmith, S. Reichl, L. Lugo-Fuentes, J.O.C. Jiménez-Halla, M. Scheer, H. Braunschweig, Angew. Chem. Int. Ed., 2022, e202206840.
"Heute ist die gute alte Zeit von morgen"
- Karl Valentin


## Preface

During the period of this thesis (January 2019 - August 2022) some results have already been published (vide supra). These results are also summarized in the present work and reprinted with the permission of the respective scientific publisher.

Each chapter contains the section 'author contributions', which describes the extent of involvement of every author contributing to the respective part. Here it is stated, if results from collaborations have been in part already discussed in other theses or publications.

To ensure a uniform design of this work, all chapters are subdivided intro 'Preface', 'Introduction', 'Results', 'Conclusion', 'References', as well as 'Supplementary Information' and have the same text settings, and the compound numeration begins anew. Due to different requirements of the journals and different article types, the presentation of figures for single crystal X-ray structures or the 'Supporting Information' may differ. In addition, a general introduction is given at the beginning and a comprehensive conclusion of all chapters is presented at the end of this thesis.

Dedicated ta my Family

## Table of Contents

1 Introduction ..... 1
1.1 Phosphorus - The "light-bearing" Element and its Heavier Analog Arsenic ..... 1
1.2 Functionalization of White Phosphorus - An Important Quest ..... 4
$1.3 \quad E_{n}$ Ligand Complexes ..... 5
1.4 References ..... 8
2 Research Objectives ..... 11
3 Ring Contraction by NHC-induced Pnictogen Abstraction ..... 13
3.1 Preface ..... 13
3.2 Introduction ..... 15
3.3 Results ..... 16
3.4 Conclusion ..... 23
3.5 References ..... 25
3.6 Supplementary Information ..... 27
4 Reactivity of $P_{4}$ butterfly complexes towards NHCs - Generation of a metal-bridged $P_{2}$ dumbbell complex ..... 67
4.1 Preface ..... 67
4.2 Introduction ..... 69
4.3 Results ..... 70
4.4 Conclusion ..... 76
4.5 References ..... 77
4.6 Supplementary Information ..... 79
5 Pentaphosphaferrocene mediated Synthesis of Asymmetric Organo-Phosphines Starting from White Phosphorus ..... 97
5.1 Preface ..... 97
5.2 Introduction ..... 99
5.3 Results ..... 100
5.4 Conclusion ..... 106
5.5 Methods ..... 107
5.6 References ..... 114
5.7 Supplementary Information ..... 119
6 Novel Synthetic Route for (parent) Phosphetane, Phospholane, Phosphinane and
Phosphepanes ..... 173
6.1 Preface ..... 173
6.2 Introduction ..... 175
6.3 Results ..... 176
6.4 Conclusion ..... 181
6.5 References ..... 182
6.6 Supplementary Information ..... 184
7 Controlled functionalization of one P atom in $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right]$ by successive reactions with nucleophiles and electrophiles containing functional groups ..... 221
7.1 Preface ..... 221
7.2 Introduction ..... 223
7.3 Results ..... 225
7.4 Conclusion ..... 232
7.5 References ..... 233
7.6 Supplementary Information ..... 235
8 Synthesis of the Largest Molecular Anionic Arsenic Ligand Complex ..... 289
8.1 Preface ..... 289
8.2 Introduction ..... 291
8.3 Results ..... 292
8.4 Conclusion ..... 298
8.5 References ..... 299
8.6 Supplementary Information ..... 300
9 Reactivity of $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{5}-A s_{5}\right)\right]$ towards Carbenes and Analogues ..... 323
9.1 Preface ..... 323
9.2 Introduction ..... 325
9.3 Results ..... 326
9.4 Conclusion ..... 331
9.5 References ..... 333
9.6 Supplementary Information ..... 335
10 Additional Findings ..... 355
10.1 Quenching of $\left[K(\mathrm{dme})_{2}\right]_{2}\left[\mathrm{Cp} * \mathrm{Fe}\left(\mathrm{n}^{4}-\mathrm{P}_{5}\right)\right](1)$ ..... 355
10.2 Synthesis of $\left[\left\{\mathrm{Na}(15 \mathrm{c} 5) \mathrm{thf}_{0.9}\right\}\{\mathrm{Na}(15 \mathrm{c} 5)\}\right]\left[\mathrm{Cp} * \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Te}_{2}\right)\right]$ (T7) ..... 362
10.3 Reactivity of $P_{n}$ ligand Complexes towards ${ }^{\text {Et }} \mathrm{CAAC}$ ..... 363
10.4 Reactivity of $\left[\left\{\mathrm{CpMo}(\mathrm{CO})_{2}\right\}_{2}\left(\mu, \eta^{2}: \eta^{2}-\mathrm{P}_{2}\right)\right](4)$ towards IMe and ${ }^{\mathrm{Et}} \mathrm{CAAC}$ ..... 365
10.5 Supporting Information ..... 368
10.6 References ..... 376
11 Epilogue ..... 377
11.1 Reactivity of Polypnictogen Ligand Complexes towards NHCs ..... 377
11.2 Functionalization of Pentaphosphaferrocene - Novel Synthetic Route for the Synthesize of (Asymmetric) Organo Phosphines ..... 379
11.3 Reactivity of Pentaarsaferrocene towards anionic Nucleophiles, Carbenes and Analogues 38211.4 Closing Remarks384
11.5 References ..... 385
12 Appendix ..... 387
12.1 Thematic List of Abbreviations ..... 387
12.2 Acknowledgement ..... 390

## 1 Introduction

### 1.1 Phosphorus - The "light-bearing" Element and its Heavier Analog Arsenic

### 1.1.1 Phosphorus - A Short Overview

Hamburg - 1669, the self-styled doctor and alchemist Henning Brand made a groundbreaking discovery. While trying to find the philosopher's stone, he succeeded for the first time in producing white phosphorus $\left(\mathrm{P}_{4}\right)$ by evaporating deposits of urine. ${ }^{1}$ Although Brand did not find the Philosopher's Stone, he was impressed by the mysterious glow of white phosphorus
 this eponymous phenomenon is due to the oxidation of phosphorus suboxides with atmospheric oxygen. ${ }^{2}$

Over 350 years later, phosphorus seems even more important than the Philosopher's Stone and is even referred to as "the staff of life". ${ }^{3}$ With more than one percent total of body weight and part of ATP (adenosine triphosphate) - the unique environmental energy unit, phosphorus is without any doubt one of the most relevant elements, ${ }^{3}$ which applies also to industry. ${ }^{4-7}$ Driven by the usage of white phosphorus in incendiary bombs during the Second World War, an entire industry based on (white) phosphorus was created. ${ }^{4-7}$ Nowadays, white phosphorus is obtained by the reduction of phosphate rock in continuous electric arc furnace operations. ${ }^{7,8}$ This process requires large amounts of energy, often centralized close to power sources like nuclear power plants, and relies almost exclusively on fluorapatite (Ca5 $\left(\mathrm{PO}_{4}\right)_{3} \mathrm{~F}$ ) as a limited phosphorus source. ${ }^{8,9}$ Elemental phosphorus occurs generally speaking, in three allotropic modifications, which are simplified referred as white, red, and black phosphorus. The thermodynamic stability (at room temperature) increases from white, over red to black phosphorus. Each of these allotropes forms different crystal structures, which is reflected in major differences in physical/chemical properties and reactivity such as toxicology. Since white, or sometimes referred to as "yellow", phosphorus can be converted into all the other modifications employing pressure and/or temperature (Scheme 1), this represents without any doubt the most important and versatile modification. ${ }^{8}$

White phosphorus consists of discrete $\mathrm{P}_{4}$ tetrahedra, is slightly light and highly air sensitive. With a P-P bond length of $2.21 \AA$ ( $P_{4}$ molecule in the gas phase $)^{10}$ and bond energy of $\approx 135 \mathrm{kcal} / \mathrm{mol}^{11}$ represents $\mathrm{P}_{4}$ one of the most reactive elements and a benchmark for P-P single bonds. ${ }^{12}$ The second class of phosphorus modification can be grouped as "red" phosphorus and is obtained by sintering white phosphorus at variable temperatures
(Scheme 1). ${ }^{8}$ Within this class, several types exist. The most common ones are the commercially available "type I" (red phosphorus), ${ }^{13}$ "type IV" (fibrous phosphorus), ${ }^{14}$ and "type V" (violet, or Hittdorf's phosphorus) ${ }^{15}$. Red phosphorus is formed by a polymeric network and represents an amorphous solid that does not ignite in air. ${ }^{13}$ Whereas the structure of type II and III is still unknown, type IV and $V$ consist of alternating $\mathrm{P}_{8}$ or $\mathrm{P}_{9}$ moieties, linked by a $\mathrm{P}_{2}$ unit, forming tubular polymer strands. ${ }^{14-16}$ The difference between the fibrous and Hittorf's Phosphorus lies in the arrangement of the tubes. In violet phosphorus, they are arranged orthogonally and linked in layers, while in fibrous phosphorus there are double tubes of parallel linked strands. ${ }^{14-16}$


Scheme 1. Selected allotropic modifications of phosphorus and its formation conditions. 8,17

Black phosphorus represents generally speaking the thermodynamically most stable allotrope of elemental phosphorus and includes its high-pressure modifications. The orthorhombic form can be obtained by either annealing of white phosphorus at $200^{\circ} \mathrm{C}$ and 12 kbar or heating Hittdorf's phosphorus in the presence of a suitable catalyst (like $\mathrm{Snl}_{4}$ ) at low pressure or using high pressure (Scheme 1). ${ }^{8,17}$ Adjusting an even more elevated pressure ( $p=80 \mathrm{kbar}$ ), the orthorhombic form can be converted to the rhombohedral one. ${ }^{18}$ Both modifications exhibit in contrast to red phosphorus an ordered layered structure, consisting of joint $P_{6}$ (cyclo-hexyl type) units. ${ }^{18-20}$ Their similarity, especially the rhombohedral form, to graphene is unmistakable and is utilized to obtain phosphorus monolayers (so-called phosphorenes). ${ }^{21-23}$

### 1.1.2 Arsenic - Discovery, Modifications and Usage

Unlike the Discovery of phosphorus, the finding of arsenic was less spectacular and arose little attention for the time being. It is attributed to the Bishop Albertus Magnus of Ratisbon in 1250. ${ }^{8}$ Magnus reduced the arsenic-bearing mineral Arsenolite $\left(\mathrm{As}_{2} \mathrm{O}_{3}\right)$ with coal and was able to obtain and isolate for the first time elemental arsenic. ${ }^{24}$ Its name can be traced back to the Greek term "arseniós", referring to the arsenic-containing yellow mineral Orpiment ( $\mathrm{As}_{2} \mathrm{~S}_{3}$ ) and can be translated to "manly, fearless or courageous". ${ }^{8}$

Yellow arsenic ( $\mathrm{As}_{4}$ ) is by far the most unstable form under normal conditions, but the only soluble one, and consists of discrete As4 tetrahedra, analogous to white phosphorus. ${ }^{25,26}$ Yellow arsenic autocatalytically converts already at room temperature to metallic grey arsenic (Asgr). Exposure to light drastically accelerates this process and which takes place even at very low temperatures ( $\mathrm{T}=-180^{\circ} \mathrm{C}$ ) (Scheme 2). ${ }^{25}$


Scheme 2. Selected allotropic modifications of arsenic and its formation conditions. ${ }^{8,25-29}$

Grey arsenic consists of As6 units arranged in closely packed bilayers in which each arsenic atom has a distorted octahedral environment. ${ }^{8}$ Asgr is isostructural to the high-pressure modification of black (rhombohedral) phosphorus (see above). When grey arsenic is heated to $616{ }^{\circ} \mathrm{C}$ in the absence of light and oxygen, yellow (molecular) arsenic can be obtained after additional quenching (Scheme 2). ${ }^{8,29,30}$ Metastable black arsenic (Asы) is then again isostructural to black (orthorhombic) phosphorus and can be obtained by cooling arsenic vapor in the presence of mercury (Scheme 2). ${ }^{8,27}$ In contrast to white phosphorus, yellow arsenic is more famous for its academic interest, not its industrial usage. ${ }^{29}$ In contrast, gray (and black arsenic) is more in demand than ever as a starting material in the semiconductor industry. ${ }^{8,31}$

### 1.2 Functionalization of White Phosphorus - An Important Quest

The interest in organophosphorus compounds in life science (e.g. for fertilizers or food additives), material science (e.g. insecticides or pesticides), and ligand design for catalysis is an omnipresent topic. ${ }^{3-5,9,32-36}$ Besides the use of phosphines as ligands, ${ }^{34}$ the resulting complexes are widely used as catalysts in all areas of organic and organometallic chemistry. ${ }^{37,38}$ One of the most prominent examples of a catalyst containing phosphines represents Wilkinson's catalyst [ $\left.\mathrm{RhCl}\left(\mathrm{PPh}_{3}\right)\right]$, which catalyzes e.g. Hydrogenation of olefins. The classical way to synthesize phosphines is via salt metathesis or hydrophosphination starting from $\mathrm{PCl}_{3}$ or $\mathrm{PH}_{3}$, respectively (Scheme 3). ${ }^{35,39-41}$ Moreover, both $\mathrm{PCl}_{3}$ and $\mathrm{PH}_{3}$ are synthesized from $\mathrm{P}_{4}$ either by reaction with chlorine gas or by hydrolysis in basic or acidic aqueous media. ${ }^{42}$ Since both $\mathrm{Cl}_{2}$ and $\mathrm{PH}_{3}$ are toxic gases and because the synthesis of phosphines from $\mathrm{PCl}_{3}$ is associated with large (stoichiometric) amounts of side products, a more sustainable and atom-efficient process for a direct conversion of $\mathrm{P}_{4}$ into organophosphorus reagents is desirable (Scheme 3).

aim: direct and selective functionalization

Scheme 3. Conventional approaches for the synthesis of organophosphorus compounds: Hydrophosphination of $\mathrm{PH}_{3}$; Subsequent salt metathesis of $\mathrm{PCl}_{3}$.

In Addition, the interest of organophosphorus compounds is not limited to academic- or as ligand usage. About 90 percent of the extracted phosphorus is used for the production of $\mathrm{P}_{2} \mathrm{O}_{5}$, which is the raw material for fertilizers. ${ }^{43}$ Since phosphate is a limited resource and an increasing demand for fertilizers is experienced due to the constant increase of the world population, ${ }^{9}$ it is all the more important to use the given resources sensibly - keyword sustainability. This can only be achieved by recycling ${ }^{44}$ organophosphorus compounds as well as finding alternative ${ }^{45}$ or more selective ways to functionalize white phosphorus. The latter is one of the objectives of our working group and key aspect of this work.

## 1.3 $\mathrm{E}_{\mathrm{n}}$ Ligand Complexes

### 1.3.1 Activation, Transformation and Aggregation of $E_{4}(E=P, A s)$

To functionalize white phosphorus, several approaches like fixation and functionalization in the coordination sphere of transition metals have been developed. The fascination for the chemistry of phosphorus-containing organometallic compounds was born over 50 years ago with the synthesis of the first substituent free $\mathrm{P}_{\mathrm{n}}$ ligand complex $\left[\left(\mathrm{PPh}_{3}\right)_{3} \mathrm{RhCl}\left(\mathrm{n}^{2}-\mathrm{P}_{4}\right)\right]$ (I) by Ginsberg and Lindsell. ${ }^{46}$ Another milestone in this field of chemistry was reported by Sacconi in 1979 with the synthesis of complex ([(np $\left.\mathrm{n}_{3}\right) \mathrm{Ni}\left(\mathrm{n}^{1}-\mathrm{P}_{4}\right)\left(\mathrm{np}_{3}=\right.$ tris(2-diphenylphosphinoethylamine)
(II) featuring an intact $\mathrm{P}_{4}$ tetrahedron. ${ }^{47}$ Within the last 50 years a plethora of polypnictogen $\left(E_{n}\right)$ ligand complexes have been synthesized with unit sizes varying from $n=1$ to $n=24(n=12$; for $E=A s) .{ }^{29,48,49}$ Starting from white phosphorus or yellow arsenic, respectively, to form these different $E_{n}$ moieties, degradation and aggregation of the $E_{4}$ tetrahedron have to take place. Within the coordination sphere of transition metals, a variety of different polypnictogen units have been observed and can be adapted (Scheme 4), featuring individual charges and bonding modes.


Scheme 4. Successive degradation and aggregation of an $E_{4}(E=P, A s)$ tetrahedron in the coordination sphere of transition metals. Charges and bonding modes are omitted for clarity.

Following the discovery of arsenic before that of (white) phosphorus, the first polyarsenic ligand complex ( $\left[\mathrm{Co}(\mathrm{CO})_{3}\left(\eta^{3}-\mathrm{As}_{3}\right)\right]$ (III)) was already presented by Dahl in $1969 .{ }^{50}$ Over the years a variety of Asn ligand complexes has been reported, ${ }^{29}$ however much less studied compared to the $\mathrm{P}_{\mathrm{n}}$ ligand ones.


I


II


III

Figure 1. The first $A s_{n}(\text { left })^{50}$ and $P_{n}(\text { middle })^{46}$ ligand complexes as well as the first complex featuring an intact $P_{4}$ tetrahedron (right) ${ }^{47}$.

Several general approaches for the synthesis of $E_{n}$ ligand complexes are feasible, e.g photolysis ([Cp*Nb $\left.(\mathrm{CO})_{2}\left(n^{4}-\mathrm{E}_{4}\right)\right]\left(\mathrm{E}=\mathrm{P}(\mathrm{IV}),{ }^{51} \mathrm{As}(\mathrm{V})^{52}\right)$, thermolysis $\left(\left[\mathrm{Cp}{ }^{\prime \prime \prime} \mathrm{Ni}\left(\mathrm{n}^{3}-\mathrm{E}_{3}\right)\right]\left(\mathrm{E}=\mathrm{P}(\mathrm{VI}){ }^{53} \mathrm{As}(\mathrm{VII})^{54}\right.\right.$; ( $\left.\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\mathrm{n}^{5}-\mathrm{E}_{5}\right)\right]\left(\mathrm{E}=\mathrm{P}(\mathrm{VIII}),{ }^{55} \mathrm{As}(\mathrm{IX})^{56}\right)\right)$ and reactions with unsaturated $\left(\left[\mathrm{Cp}{ }^{\prime \prime \prime} \mathrm{Co}\left(\mathrm{n}^{4}-\mathrm{P}_{4}\right)\right](\mathrm{X})^{57}\right)$ or low valent metals (Scheme 5). These unsaturated fragments are often generated in situ via radiation or heating, forming suitable precursors.


Scheme 5. Activation of $\mathrm{E}_{4}$ and formation of $\mathrm{E}_{\mathrm{n}}$ Ligand Complexes via: Photolysis, reaction with unsaturated metal fragments or thermolysis. Selected examples of Polypnictogen Ligand Complexes. ${ }^{50-56}$

### 1.3.2 Ferrocene and its isolobal complex Pentaphosphaferrocene

Pittsburgh - 1951, Kealy and Pauson made an astonishing and pioneering discovery - "A new Type of Organo-Iron Compound". ${ }^{58}$ This Iron compound, latter known as Ferrocene, exhibits remarkable stability and arose so much attention that several working groups started to identify its electronic structure. In the end, both E. O. Fischer and G. Wilkinson wone the race against the clock on their one. With the help of their individual research results in total, they were able to
elucidate the structure of the so-called Ferrocene (XI), featuring an $\eta^{5}$-coordination of two (ecliptic) cyclopentadienyl ligands towards an Iron (II) center. ${ }^{59,60}$

36 years after the groundbreaking discovery of ferrocene, the so-called (pentamethyl)pentaphosphaferrocene $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right]$ (VIII) was presented by Scherer for the first time. ${ }^{55}$ It represents another milestone in the history of $\mathrm{P}_{\mathrm{n}}$ ligand complexes and is still a constant companion in the current research around polypnictogen complexes. ${ }^{17,48,61-63} \mathrm{Its}$ cyclo$\mathrm{P}_{5}$ ligand is isobal to the cyclopentadienyl anion and illustrates very well the isolobal principle between $\{\mathrm{P}\}$ and $\{\mathrm{C}-\mathrm{H}\}$ (Scheme 6). Due to the electronic structure of the $\mathrm{P}_{5}$-unit, ${ }^{64}$ pentaphosphaferrocene, unlike its namesake ferrocene, exhibits reactivity toward nucleophiles ${ }^{65}$ and electrophiles ${ }^{66,67}$ (Scheme 6).


Scheme 6. Synthesis of [Cp*Fe( $\left.\left.\eta^{5}-\mathrm{P}_{5}\right)\right]$ (VIII) and its isolobality to Ferrocene ( $\mathrm{Cp}_{2} \mathrm{Fe}$ ) (XI) (top). Selected reactivity of (VIII) towards a) nucleophiles, $-35^{\circ} \mathrm{C}$ to r.t, $\mathrm{Et}_{2} \mathrm{O}$ or THF; ${ }^{65}$ b) potassium, r.t., DME; ${ }^{68}$ c) elektrophiles, r.t., o-DFB; ${ }^{66}$ d) Chlorosilylene, $-78^{\circ} \mathrm{C}$ to r.t; ${ }^{69}$ and e) $\left[\mathrm{Cp}{ }^{\prime \prime} \mathrm{Ta}(\mathrm{CO})_{4}\right], 190^{\circ} \mathrm{C}$, decalin. ${ }^{70}$

This phenomenal versatility is little inferior to that of ferrocene and illustrates once again why polypnictogen complexes are still a hot topic.

### 1.4 References

1 F. Krafft, Angew. Chem. Int. Ed., 1969, 8, 660-671.
2 P. A. Hamilton and T. P. Murrells, J. Phys. Chem., 1986, 90, 182-185.
3 D. M. Karl, Nature, 2000, 406, 31-33.
4 J. L. Jones, Y. G. Yingling, I. M. Reaney and P. Westerhoff, MRS Bull., 2020, 45, 7-10.
5 D. Cordell, J. O. Drangert and S. White, Glob. Environ. Chang., 2009, 19, 292-305.
6 D. R. Gard, in Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley \& Sons, Inc., Hoboken, NJ, USA, 2005.

7 H. Diskowski and T. Hofmann, Phosphorus in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, Germany, 27th edn., 2000.

8 A. F. Holleman, N. Wiberg and E. Wiberg, Lehrbuch der Anorganischen Chemie, Walter de Gruyter, Berlin, 102nd edn., 2007.

9 D. Cordell and S. White, Sustainability, 2011, 3, 2027-2049.
10 B. M. Cossairt, C. C. Cummins, A. R. Head, D. L. Lichtenberger, R. J. F. Berger, S. A. Hayes, N. W. Mitzel and G. Wu, J. Am. Chem. Soc., 2010, 132, 8459-8465.

11 W. W. Schoeller, V. Staemmler, P. Rademacher and E. Niecke, Inorg. Chem., 2002, 25, 4382-4385.

12 P. Pyykkö and M. Atsumi, Chem. - A Eur. J., 2009, 15, 186-197.
13 A. J. Smith, W. L. Roth and T. W. DeWitt, J. Am. Chem. Soc., 1947, 69, 2881-2885.
14 M. Ruck, D. Hoppe, B. Wahl, P. Simon, Y. Wang and G. Seifert, Angew. Chemie - Int. Ed., 2005, 44, 7616-7619.

15 W. Hittorf, Ann. der Phys. und Chemie, 1865, 202, 193-228.
16 H. Thurn and H. Krebs, Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem., 1969, 25, 125-135.

17 L. Giusti, V. R. Landaeta, M. Vanni, J. A. Kelly, R. Wolf and M. Caporali, Coord. Chem. Rev., 2021, 441, 213927.

18 X. Ling, H. Wang, S. Huang, F. Xia and M. S. Dresselhaus, Proc. Natl. Acad. Sci., 2015, 112, 4523-4530.
P. W. Bridgman, J. Am. Chem. Soc., 1914, 36, 1344-1363.
J. C. Jamieson, Science (80-. )., 1963, 139, 1291-1292.

21 L. Li, Y. Yu, G. J. Ye, Q. Ge, X. Ou, H. Wu, D. Feng, X. H. Chen and Y. Zhang, Nat. Nanotechnol., 2014, 9, 372-377.

22 H. Liu, A. T. Neal, Z. Zhu, Z. Luo, X. Xu, D. Tománek and P. D. Ye, ACS Nano, 2014, 8, 4033-4041.
E. S. Reich, Nature, 2014, 506, 19.
G. Süss-Fink, Chem. unserer Zeit, 2012, 46, 100-109.

25
E. H. and M. V. Unruh, ZAAC, 1902, 32, 437-452.

49 F. Dielmann, M. Sierka, A. V. Virovets and M. Scheer, Angew. Chemie - Int. Ed., 2010, 18, 1827-1833.
J. W. Retgers, ZAAC, 1894, 6, 317-320.
K. H, H. W and W. K. H., Chem. Ber., 1957, 90, 1031-1037.
H. Stöhr, ZAAC, 1939, 242, 138-144.
M. Seidl, G. Balázs and M. Scheer, Chem. Rev., 2019, 119, 8406-8434.
A. Bettendorff, Justus Liebigs Ann. Chem., 1876, 144, 110-114.
A. Yoshiasa, M. Tokuda, M. Misawa, F. Shimojo, K. Momma, R. Miyawaki, S. Matsubara, A. Nakatsuka and K. Sugiyama, Sci. Rep., 2019, 9, 1-7.
J. L. Montchamp, Acc. Chem. Res., 2014, 47, 77-87.
W. Tang and X. Zhang, Chem. Rev., 2003, 103, 3029-3069.
J. F. Teichert, Homogeneous Hydrogenation with Non-Precious Catalysts, Wiley, 2019.
S. Lühr, J. Holz and A. Börner, ChemCatChem, 2011, 3, 1708-1730.
L. Pignolet, Homogeneous Catalysis with Metal Phosphine Complexes, Springer US, Boston, MA, 1983.
H. Guo, Y. C. Fan, Z. Sun, Y. Wu and O. Kwon, Chem. Rev., 2018, 118, 10049-10293.
E. I. Musina, A. S. Balueva and A. A. Karasik, Organophosphorus Chemistry, Royal Society of Chemistry, Cambridge, 2019, vol. 48.
E. Hey-Hawkins and A. A. Karasik, in Category 5, Compounds with One Saturated Carbon Heteroatom Bond, eds. Mathey and Trost, Georg Thieme Verlag, Stuttgart, 2009, vol. 42, pp. 71-108.
A. L. Clevenger, R. M. Stolley, J. Aderibigbe and J. Louie, Chem. Rev., 2020, 120, 61246196.
N. K. Gusarova and B. A. Trofimov, Russ. Chem. Rev., 2020, 89, 225-249.
G. Bettermann, W. Krause, G. Riess and T. Hofmann, Phosphorus Compounds, Inorganic, Ullmann's Encyclopedia of Industrial Chemistry, Wiley, Weinheim, Germany, 2012.
E. Desmidt, K. Ghyselbrecht, Y. Zhang, L. Pinoy, B. Van der Bruggen, W. Verstraete, K. Rabaey and B. Meesschaert, Crit. Rev. Environ. Sci. Technol., 2015, 45, 336-384.
E. Desmidt, K. Ghyselbrecht, Y. Zhang, L. Pinoy, B. Van der Bruggen, W. Verstraete, K. Rabaey and B. Meesschaert, Crit. Rev. Environ. Sci. Technol., 2015, 45, 336-384.
M. B. Geeson and C. C. Cummins, ACS Cent. Sci., 2020, 6, 848-860.
A. P. Ginsberg and W. E. Lindsell, J. Am. Chem. Soc., 1971, 93, 2082-2084.
P. Dapporto, S. Midollini and L. Sacconi, Angew. Chemie Int. Ed. English, 1979, 18, 469469.
C. M. Hoidn, D. J. Scott and R. Wolf, Chem. - A Eur. J., 2021, 27, 1886-1902.
A. S. Foust, M. S. Foster and L. F. Dahl, J. Am. Chem. Soc., 1969, 91, 5631-5633.
O. J. Scherer, J. Vondung and G. Wolmershäuser, Angew. Chemie Int. Ed. English, 1989, 28, 1355-1357.

60 G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, J. Am. Chem. Soc., 2002, 74, 2125-2126.
J. Scherer, J. Organomet. Chem., 1989, 38, 50-53.
E. Mädl, G. Balázs, E. V. Peresypkina and M. Scheer, Angew. Chemie - Int. Ed., 2016, 55, 7702-7707.
M. Piesch, S. Reichl, C. Riesinger, M. Seidl, G. Balazs and M. Scheer, Chem. - A Eur. J., 2021, 27, 9129-9140.
O. J. Scherer and T. Brück, Angew. Chem. Int. Ed., 1987, 26, 11987.
O. J. Scherer, C. Blath and G. Wolmershäuser, J. Organomet. Chem., 1990, 387, 21-24.
F. Dielmann, A. Timoshkin, M. Piesch, G. Balázs and M. Scheer, Angew. Chem. Int. Ed., 2017, 56, 1671-1675.
T. J. KEALY and P. L. PAUSON, Nature, 1951, 168, 1039-1040.
E. O. Fischer and W. Pfab, Zeitschrift fur Naturforsch. - Sect. B J. Chem. Sci., 1952, 7, 377379.
M. Scheer, G. Balázs and A. Seitz, Chem. Rev., 2010, 110, 4236-4256.
M. Caporali, L. Gonsalvi, A. Rossin and M. Peruzzini, Chem. Rev., 2010, 110, 4178-4235.
B. M. Cossairt, N. A. Piro and C. C. Cummins, Chem. Rev., 2010, 110, 4164-4177.
H. Krauss, G. Balazs, M. Bodensteiner and M. Scheer, Chem. Sci., 2010, 1, 337-342.
E. Mädl, M. V. Butovskii, G. Balázs, E. V. Peresypkina, A. V. Virovets, M. Seidl and M. Scheer, Angew. Chemie - Int. Ed., 2014, 53, 7643-7646.

66 C. Riesinger, G. Balázs, M. Bodensteiner and M. Scheer, Angew. Chem. Int. Ed., 2020, 59, 23879-23884.

67 C. Riesinger, G. Balázs, M. Seidl and M. Scheer, Chem. Sci., 2021, 12, 13037-13044.
M. V. Butovskiy, G. Balázs, M. Bodensteiner, E. V. Peresypkina, A. V. Virovets, J. Sutter and M. Scheer, Angew. Chem. Int. Ed., 2013, 52, 2972-2976.

69 R. Yadav, T. Simler, S. Reichl, B. Goswami, C. Schoo, R. Köppe, M. Scheer and P. W. Roesky, J. Am. Chem. Soc., 2020, 142, 1190-1195.
M. Detzel, T. Mohr, O. J. Scherer and G. Wolmershäuser, Angew. Chem. Int. Ed., 1994, 33, 1110-1112.

## 2 Research Objectives

As described in the introduction, $\mathrm{E}_{\mathrm{n}}(\mathrm{E}=\mathrm{P}, \mathrm{As})$ ligand complexes represent an important class of organometallic chemistry and continue to be components of current research. Since the reactivity of polypnictogen ligand complexes towards nucleophiles and (reducing) agents was already a part of my master thesis, this research has to be continued. Furthermore, this opens the possibility to further functionalize the presented anionic complexes in subsequential salt metathesis reactions with electrophiles. In addition, it should be thereby possible to introduce functional groups such as halogens and nitriles.

Therefore, the first research objective of this work is focused on:

- The reactivity of polypnictogen ligand complexes towards organo-nucleophiles
- Quenching of the synthesized anionic $E_{n}$ ligand complexes with organo-electrophiles
- Introducing functional groups to the polypnictogen ligand

In the last decades, a variety of different approaches for the synthesize of organo-phosphorus compounds, based on transition- and main group metals have been developed. To minimize the stoichiometric amount of sideproduct or the usage of hazardous chlorine gas or $\mathrm{PH}_{3}$, a more selective and direct route is desired. To do so, the synthesized and functionalized polypnictogen ligand complexes will be used as precursors for a possible phosphine abstraction and deal as a platform for the selective synthesis of (as)symmetric substituted phosphines.

Furthermore, the second scope of this thesis should deal with:

- Investigation of the reactivity of the obtained neutral and functionalized polyphosphorus ligand complexes towards nucleophiles
- Variation of the used nucleophiles and corresponding $P_{n}$ ligand complex


## 3 Ring Contraction by NHC-induced Pnictogen Abstraction

### 3.1 Preface

The following chapter has already been published. This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License.

English version: M. Piesch, ${ }^{\S}$ S. Reichl, ${ }^{\S}$ M. Seidl, ${ }^{\S}$ G. Balázs and M. Scheer, Angew. Chem. Int. Ed. 2019, 58, 16563 -16568.
https://doi.org/10.1002/anie. 201908397
German version: M. Piesch, ${ }^{\S}$ S. Reichl, ${ }^{\S}$ M. Seidl, ${ }^{\S}$ G. Balázs and M. Scheer, Angew. Chem. 2019, 131, 16716 -16721.
https://doi.org/10.1002/ange. 201908397
${ }^{\S}$ Both authors contributed equally

Authors<br>Martin Piesch, ${ }^{1}$ Stephan Reichl, ${ }^{1}$ Michael Seidl, ${ }^{1}$ Gábor Balázs, ${ }^{1}$ Manfred Scheer ${ }^{1 *}$<br>${ }^{1}$ Institute of Inorganic Chemistry, University of Regensburg; Universitätsstraße 31, 93053 Regensburg, Germany.<br>*Corresponding author. Email: manfred.scheer@chemie.uni-regensburg.de

## Author Contribution

S.R., and M.P. conceived the experiments. M. P. and G.B. performed the computational studies. M.Se. analysed and revised the X-ray data; M.Se., G. B. and M.Sch. wrote the manuscript. M.Sch. directed and coordinated the research.

## Ring Contraction by NHC-induced Pnictogen Abstraction



Tightening one's belt: The NHC assisted pnictogen abstraction proves to be a general method to induce ring contraction reactions of polypnictogen ligands, leading to new and otherwise not accessible polypnictogen compounds. This method can be applied to sandwich complexes containing cyclo- $E_{n}$ end decks as well as triple-decker complexes ( $E=P, A s$ ) and allow to generate unprecedented anionic $\left[C p^{\prime \prime \prime} C o\left(\eta^{3}-P_{3}\right)\right]^{-}$and $\left[\left(C p^{*} M\right)_{2}\left(\mu, \eta^{5: 5}-E_{5}\right)\right]^{-}(M=M o, V ; E=P$, As).

# Ring Contraction by NHC-induced Pnictogen Abstraction 


#### Abstract

The reaction of $\left[C p^{\prime \prime \prime} \mathrm{Co}\left(\eta^{4}-P_{4}\right)\right]$ (1) $\left(\mathrm{Cp}^{\prime \prime \prime}=1,2,4-{ }^{\mathrm{t}} \mathrm{Bu} u_{3} \mathrm{C}_{5} \mathrm{H}_{2}\right)$ with ${ }^{\mathrm{Me}} \mathrm{NHC}\left({ }^{\mathrm{Me}} \mathrm{NHC}=1,3,4,5-\right.$ tetramethylimidazol-2-ylidene) leads via an NHC-induced phosphorus cation abstraction to the ring contraction product $\left[\left({ }^{\mathrm{Me}} \mathrm{NHC}\right)_{2} \mathrm{P}\right]\left[\mathrm{C} p^{\prime \prime \prime} \mathrm{Co}\left(\eta^{3}-P_{3}\right)\right]$ (2), which represents the first example of an anionic $\mathrm{CoP}_{3}$ complex. Such ring contraction reactions, induced by NHCs, are also applicable for triple-decker sandwich complexes. The complexes $\left[\left(C p^{*} \mathrm{Mo}_{2}\right)_{2}\left(\mu, \eta^{6: 6}-\mathrm{E}_{6}\right)\right](3 a, 3 b)\left(C p^{*}=C_{5} \mathrm{Me} ; E=P, A s\right)$ can be transformed to the complexes $\left[\left({ }^{M} N H C\right)_{2} E\right]\left[\left(C p^{*} M\right)_{2}\left(\mu, \eta^{3: 3}-E_{3}\right)\left(\mu, \eta^{2: 2}-E_{2}\right)\right]$ (4a, 4b), with $4 b$ representing the first structurally characterized example of a NHC-substituted As(I) cation. Further, the reaction of the vanadium complex $\left[\left(C p^{*} V\right)_{2}\left(\mu, \eta^{666}-E_{6}\right)\right]$ (5) with ${ }^{\text {Me }} \mathrm{NHC}$ results in the formation of the unprecedented complexes $\left[\left({ }^{(M e} N H C\right)_{2} P\right]\left[\left(C p^{*} V\right)_{2}\left(\mu, \eta^{6: 6}-E_{6}\right)\right](6),\left[\left({ }^{(M e} N H C\right)_{2} P\right]\left[\left(C p^{*} V\right)_{2}\left(\mu, \eta^{5: 5}-E_{5}\right)\right]$ (7) and $\left.\left[\left(C p^{*} V\right)_{2}\left(\mu, \eta^{3: 3-} P_{3}\right)\left(\mu, \eta^{1: 1}-P_{2}^{\text {Me }} N H C\right\}\right)\right]$ ( 8$)$.


### 3.2 Introduction

Ring contraction reactions are a powerful tool in organic synthesis, giving access to otherwise not or only hardly accessible products. ${ }^{[1]}$ They can be divided into different groups, which are usually defined by the conditions that are needed to induce the ring contraction (acidic, basic, oxidative, photolytic, and thermal). However, ring contraction reactions are not limited to carbocycles and heterocycles. ${ }^{[2]}$ For example, Stone et al. reported on the reaction of pentamethylcyclopentaphosphine $(\mathrm{MeP})_{5}$ with CuCl leading to the cyclotetraphosphine complex (MeP) $)_{4} \mathrm{CuCl}^{[3]}$ A further example for ring contraction reactions involving cyclopolyphosphines was reported by Hey-Hawkins et al. by the reaction of ( ${ }^{(\mathrm{Bu}} \mathrm{BP}_{5}$ ) ${ }^{\text {w }}$ with $\mathrm{SnCl}_{2}$ resulting in A (Scheme 7). ${ }^{[4]}$ Thermally induced rearrangements are another method for ring contractions, as was for instance shown for the formation of $\mathbf{B}$ (Scheme 7), which is obtained by heating a solution of $\left.\left[\mathrm{Ni}^{(t} \mathrm{Bu}_{4} \mathrm{P}_{5}\right)_{2}\right] \cdot{ }^{[5]}$ Moreover, we recently found that the complexes $\left[(\mathrm{LCo})_{2}\left(\mu_{2}, \eta^{2: 2}-\mathrm{E}_{4}\right)\right]\left(\mathrm{L}=\mathrm{CH}\{\mathrm{C}(\mathrm{Me}) \mathrm{N}(\mathrm{Dipp})\}_{2} ; \mathrm{E}=\mathrm{P}, \mathrm{As}\right)$ undergo a thermally induced elimination of a pnictogen atom leading to the triple-decker complexes [(LCo) $\left.)_{2}\left(\mu_{2}, \eta^{3: 3}-\mathrm{E}_{3}\right)\right]$ (C) with an $\mathrm{E}_{3}$ middle deck. ${ }^{[6]}$
a)

b)

c)


Scheme 7. Selected examples for ring contraction reactions of cyclopolyphosphines and polypnictogen ligand complexes.

This overview raised the question if there might be a general and more selective way avoiding harsh reaction conditions to promote ring contraction reactions to be used for the synthesis of new and otherwise not accessible compounds. Thus, in the case of polypnictogen compounds, it will lead to more desirable compounds in terms of their functionalization or the synthesis of organophosphorus compounds. ${ }^{[7]}$ Here, the thermally induced ring contractions are limited to only few polypnictogen ligand complexes. Their outcome is not predictable and combined with low yields. Therefore, in our opinion, the use of N -heterocyclic carbenes ( NHCs ) ${ }^{[7 \mathrm{c}, 8]}$ seemed to be a promising approach. It was shown by Bertrand that NHCs or cyclic (alkyl)-(amino)carbenes (CAACs) can be reacted with white phosphorus ( $\mathrm{P}_{4}$ ), leading, depending on the used carbene and stoichiometry, to $\mathrm{P}_{4}$ species ${ }^{[9]}$ fragmented into a bis $(\mathrm{NHC})$-supported $\mathrm{P}(\mathrm{I})$ cation and a formal NHC-coordinated $\mathrm{P}_{3}$ unit. The latter could only be monitored by ${ }^{31} \mathrm{P}$ NMR spectroscopy ${ }^{[96]}$ or by aggregation to an NHC-substituted $\mathrm{P}_{12}$ cage compound. ${ }^{[10]}$ Other examples for an NHC-induced phosphorus atom abstraction from cyclo-pnictines, $\mathrm{P}_{4}, \mathrm{P}_{7}{ }^{3-}$ and other polyphosphorus cages were described, ${ }^{[11]}$ but did not feature a ring contraction. E.g. Weigand et al. reported about a degradation of a cationic $\mathrm{P}_{5}$ cage into an allylic $\mathrm{P}_{3}$ and a $\mathrm{P}_{2}$ unit substituted by NHCs. ${ }^{[11 \mathrm{e}]}$ Herein, we report a general method of ring contraction reactions induced by the NHC-assisted abstraction of a pnictogen cation for a large variety of polypnictogen complexes, leading to unprecedented otherwise not accessible complexes.

### 3.3 Results

We recently showed that $\left[\mathrm{Cp}^{\prime \prime \prime} \mathrm{Co}\left(\eta^{4}-\mathrm{P}_{4}\right)\right](1){ }^{[12]}$ can be used for ring expansion reactions with the pentelidene complexes $\left[C p^{*} E\left\{W(C O)_{5}\right\}_{2}\right](E=P, A s) .{ }^{[13]}$ The release of ring strain might be a
driving force of such reactions, leading to a five-membered ring system. It was a challenge to investigate if it is also a candidate for a ring contraction reaction by increasing the ring strain.


Scheme 8. Reaction of [Cp'" $\left.\mathrm{Co}\left(\eta^{4}-\mathrm{P}_{4}\right)\right]$ (1) with MeNHC.

The addition of ${ }^{\mathrm{Me}} \mathrm{NHC}$ to a solution of 1 at $-80^{\circ} \mathrm{C}$ resulted in an immediate colour change, which is completed at room temperature. After workup, $\left[\left({ }^{(M e} N H C\right)_{2} \mathrm{P}\right]\left[\mathrm{Cp}{ }^{\prime \prime \prime} \mathrm{Co}\left(\eta^{3}-\mathrm{P}_{3}\right)\right]$ (2) was isolated in a crystalline yield of $79 \%$ (Scheme 8). The ${ }^{31}$ P NMR spectrum of the reaction mixture showed only two singlets at -111.4 ppm for the $\left[\left({ }^{\mathrm{Me}} \mathrm{NHC}\right)_{2} \mathrm{P}\right]^{+}$cation and at -313.3 ppm for the $\left[\mathrm{Cp}^{\prime \prime}{ }^{\prime} \mathrm{Co}\left(\eta^{3}-\mathrm{P}_{3}\right)\right]^{-}$anion, indicating a full conversion of the starting compounds to 2 . Compound 2 is formed by an NHC-induced phosphorus abstraction, leading to a bis(NHC)-coordinated P(I) cation and the ring contraction product $\left[\mathrm{Cp}{ }^{\prime \prime \prime} \mathrm{Co}\left(\eta^{3}-\mathrm{P}_{3}\right)\right]^{-}$. The latter is the first representative of an anionic $\mathrm{CoP}_{3}$ complex, revealing a cyclo- $\mathrm{P}_{3}$ end-deck. The tetrahedral $\mathrm{CoP}_{3}$ unit (Figure 2) is formally isolobal to $\mathrm{P}_{4}$ in which one phosphorus atom is replaced by a $15 \mathrm{VE} \mathrm{Cp}^{\prime \prime \prime} \mathrm{Co}^{-}$ fragment. The Mulliken population analysis performed on the optimized geometry of $\left[\mathrm{Cp}^{\prime \prime \prime} \mathrm{Co}\left(\eta^{3}-\mathrm{P}_{3}\right)\right]$ - shows that the negative charge is mostly located on the $\mathrm{P}_{3}$ unit $(-0.64)$ and considerably less on the $\mathrm{Cp}^{\prime \prime \prime}$ ligand ( -0.12 ) and at the Co atom as well ( -0.26 ). The P-P and Co-P bond lengths are between 2.1552(6) $\AA$ and $2.1624(6) ~ \AA$ and between $2.2596(5) ~ \AA$ and $2.2705(5) \AA$, respectively, and therefore in the range of single bonds. These distances differ slightly from the recently reported neutral complex [\{CNAr $\left.\left.{ }^{\text {Mes } 2}\right\}_{3} \mathrm{Co}\left(\eta^{3}-\mathrm{P}_{3}\right)\right]$ ( $\mathrm{Ar}^{\mathrm{Mes} 2}=2,6-(2,4,6-$ $\left.\mathrm{Me}_{3} \mathrm{C}_{6} \mathrm{H}_{2}\right)_{2} \mathrm{C}_{6} \mathrm{H}_{3}$ ) for which the Co-P bond lengths are with $2.312(1) \AA$ to $2.317(1) ~ A ̊ ~ s o m e w h a t$ elongated. ${ }^{[14]}$


Figure 2. Molecular structure of 2 in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

Since we were interested in the elucidation of the reaction pathway between 1 and ${ }^{\mathrm{Me}} \mathrm{NHC}$, we performed a temperature-depending ${ }^{31} \mathrm{P}$ NMR study, starting from $-80^{\circ} \mathrm{C}$ to room temperature (in $20^{\circ} \mathrm{C}$ steps). The spectra show several signal sets indicating the formation of different intermediates. Unfortunately, an identification of these intermediates was not possible and even numerous attempts to isolate them at low temperature failed. Nevertheless, after 18 hours at room temperature, the ${ }^{31} \mathrm{P}$ NMR spectrum of the reaction mixture shows only the signals of 2 (see Figure S4).

Since the desired $P_{n}$ ring contraction was successful for sandwich complexes such as 1 , we were interested to find out if the novel concept is applicable to triple-decker sandwich complexes containing polypnictogen middle decks ( $\mathrm{E}=\mathrm{P}, \mathrm{As}$ ), because of the challenge of a much hindered release of an atom in these compounds. Therefore, the triple-decker $\left[\left\{\mathrm{Cp}^{*} \mathrm{Mo}_{3}\right\}_{2}\left(\mu, \eta^{6: 6}-\mathrm{P}_{6}\right)\right]$ (3a) was reacted with 2 equivalents of ${ }^{\text {Me }}$ NHC (Scheme 9). The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of the reaction mixtures showed only two singlets at -112.4 ppm and -59.9 ppm , indicating a full conversion of the starting complex 3a to a bis(NHC)-supported $\mathrm{P}(\mathrm{I})$ cation ( -112.4 ppm ) and the anticipated anion $\left[\left\{\mathrm{Cp}^{*} \mathrm{Mo}_{2}\left(\mu, \eta^{5: 5}-\mathrm{P}_{5}\right)\right]^{-}\right.$(Scheme 9). After workup, 4a was isolated in $49 \%$ crystalline yield as dark green blocks. The molecular structure of 4a (see SI Figure S19/20) shows a $P_{5}$ middle deck disordered over two positions (60:40), with shorter (2.313(19) $\AA$ $2.480(12) \AA$ ) and longer ( $2.500(10) \AA$ - $2.605(11) ~ A ̊)$ P...P distances. The latter might best be described as separated $\mathrm{P}_{3}$ and $\mathrm{P}_{2}$ units instead of a cyclo- $\mathrm{P}_{5}$ middle deck. This geometry is also confirmed by DFT calculations, which reproduce well the experimental geometric parameters of the anion in 4 a (see SI ). Further, the Wiberg bond indices (WBIs) for the longer P...P distances indicate with 0.13 only weak interactions. The WBIs of the shorter P-P distances amount to 1.16 for the $\mathrm{P}_{2}$ unit and to 0.82 for the $\mathrm{P}_{3}$ unit. Very surprisingly, even at $-80^{\circ} \mathrm{C}$, only one slightly broadened singlet centered at -62.9 ppm was observed in the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum in solution, as it would be anticipated for a symmetrical $P_{5}$ middle deck. This result points to a fast rearrangement of the distorted $\mathrm{P}_{5}$ middle deck, observed for the solid state, to a symmetric cyclo- $\mathrm{P}_{5}$ unit in solution on the NMR timescale, even at low temperatures. This process probably occurs through a simultaneous P-P bond formation/bond cleavage reaction. The Mo-Mo bond distance is with $2.667(1) \AA$ in the range of a single bond, which is in accordance with the WBI of 0.70. Complex 4 a is the first example of a molybdenum triple-decker complex containing a $\mathrm{P}_{5}$ middle deck. Usually the co-thermolysis of $\left[\mathrm{Cp}^{\mathrm{R}} \mathrm{M}(\mathrm{CO})_{3}\right]_{2}$ with $\mathrm{P}_{4}$ affords for $\mathrm{M}=\mathrm{Mo}, \mathrm{W}$ the cyclo- $\mathrm{P}_{6}$ triple-decker complexes, such as 3a. Only for $\mathrm{M}=\mathrm{Cr}$, the neutral complex $\left[\left(C p^{*} C r\right)_{2}\left(\mu, \eta^{5: 5}-P_{5}\right)\right]^{[15]}$ is obtained. Although, the structure of the latter was proven crystallographically, the quality of the reported X-ray data did not allow the discussion of any bond distances.


Scheme 9. Reaction of $\left[\left\{\mathrm{Cp}^{*} \mathrm{Mo}_{2}\right\}_{2}\left(\mu, \eta^{6: 6}-\mathrm{E}_{6}\right)\right](\mathrm{E}=\mathrm{P}(3 \mathrm{a})$, $\mathrm{As}(3 \mathrm{~b}))$ with ${ }^{\text {Me }} \mathrm{NHC}$.

Complex $\left[\left\{\mathrm{Cp}^{*} \mathrm{Mo}_{2}\left(\mu, \eta^{6: 6}-\mathrm{As}\right)\right]\right.$ (3b), which is the heavier homologue of 3a, was also reacted with 2 equivalents of ${ }^{\text {Me }} \mathrm{NHC}$ to investigate if the pnictogen abstraction observed for 3 a is also possible in the case of a polyarsenic ligand. This reaction proceeds analogously to the phosphorus complex and, after workup, the product [(MeNHC) $\left.{ }_{2} \mathrm{As}\right]\left[\left\{\mathrm{Cp}^{*} \mathrm{Mo}_{2}\left(\mu, \eta^{5: 5}-\mathrm{As} 5\right)\right]\right.$ (4b) was isolated as dark green blocks in $82 \%$ yield. The cation $\left[\left({ }^{\mathrm{Me}} \mathrm{NHC}\right)_{2} A s\right]^{+}$within $\mathbf{4 b}$ is the first structurally characterized example of a doubly NHC-substituted As(I) cation and the second one known in literature. ${ }^{[16]}$ Interestingly, the only other example was reported by Märkl et al. by the reaction of 2 -chlor- N -methyl-benzthiazolium-fluoroborat with $\mathrm{As}\left(\mathrm{SiMe}_{3}\right)_{3}{ }^{[17]}$ The molecular structure of $\mathbf{4 b}$ is shown in Figure 3. The As-C bond distances for the cation $\left[\left({ }^{\mathrm{Me}} \mathrm{NHC}\right)_{2} \mathrm{As}\right]^{+}$are with $1.924(2) \AA \AA$ and $1.927(2) \AA$ A in the range of single bonds as it is predictable for an C-As-C-N torsion angle of about $43^{\circ}$, which prevents an effective overlap of the $\pi$ system on the NHC fragments with the p orbitals on As. ${ }^{[18]}$ As for the anionic part, although the Ass middle deck is disordered over three positions with occupations of 0.62 to 0.26 to 0.12 (see SI), one can again distinguish between shorter (between 2.289(14) Å and 2.463(4) Å) and longer (between 2.729(15) Å and 2.870(13) Å) As…As distances (similar to 4a). Therefore, the Ass middle deck is also best described as separate Ass and Ass ligands instead of a cyclo-Ass ligand, which is in accordance with DFT calculations (cf. SI). The neutral complex $\left[\left\{\mathrm{CpMo}_{2}\left(\mu, \eta^{5: 5}-\mathrm{As} 5\right)\right]\right.$, which was obtained by Rheingold et al. from the co-thermolysis of $\left[\mathrm{CpMo}(\mathrm{CO})_{3}\right]_{2}$ with (MeAs) $)_{5}$, features also two long and three short As $\cdots$ As distances. However, the Mo-Mo bond is with $2.764(2) \AA$ A slightly longer than for $\mathbf{4 b}$ as an anion. Further, the As-As bond length of the As2 unit is with $2.570(2) \AA$ a by 0.183 or $0.281 \AA$, respectively, longer than the comparable As-As bond in 4b. Additionally, the long As...As distances are shorter. These differences become more distinct by comparing the bond distances of the optimized structures of both complexes (cf. SI).


Figure 3. Molecular structure of 4 b (for 4 a see SI ) in the solid state with thermal ellipsoids at $50 \%$ probability level. Only the main part of the disordered $\mathrm{As}_{5}$ middle deck is depicted. Hydrogen atoms and solvent molecules are omitted for clarity.


Scheme 10. Reaction of $\left[\left\{C p^{*} \mathrm{~V}\right\}_{2}\left(\mu, \eta^{6: 6}-\mathrm{P}_{6}\right)\right](5)$ with Me NHC .

The complex $\left[\left\{\mathrm{Cp}^{*} \mathrm{~V}_{2}\left(\mu, \eta^{6: 6}-\mathrm{P}_{6}\right)\right]\right.$ (5) is one of only few examples for vanadium complexes containing polyphosphorus ligands ${ }^{[19]}$, and, so far, no vanadium triple-decker complex with a $\mathrm{P}_{5}$ middle deck is known. Therefore, 5 was reacted with ${ }^{\text {Me }} \mathrm{NHC}$ to induce the anticipated ring contraction, leading to the desired complex $\left[\left({ }^{(M e} N H C\right)_{2} P\right]\left[\left\{\mathrm{Cp}^{*} \mathrm{~V}_{3}\left(\mu, \eta^{5: 5}-\mathrm{P}_{5}\right)\right]\right.$ (7) (Scheme 10). However, the reaction did not solely result in 7, but additionally the two complexes $\left[\left({ }^{M e} N H C\right)_{2} P\right]\left[\left\{C^{*} V_{3_{2}}\left(\mu, \eta^{6: 6}-P_{6}\right)\right]\right.$ (6) and $\left[\left\{C_{p}{ }^{*} V_{2}\left(\mu, \eta^{3: 3}-P_{3}\right)\left(\mu-P^{M e} N H C\right)\right]\right.$ (8) were obtained. Complex 6 is probably formed by the reduction of the starting compound 5 . In contrast, the formation of 8 seems to involve several indistinct reaction steps, but reveals that the applied method can go further by abstracting more than one pnictogen atom (for a possible mechanism cf. SI). By monitoring this reaction by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}$ at variable temperatures $\left(20^{\circ} \mathrm{C}\right.$ steps, starting from $-80^{\circ} \mathrm{C}$ to r.t.), we tried to get insight into some of these reaction processes (Figure S17). However, at low temperatures, next to the signal of the cation $\left[\left({ }^{(N e N H C}\right)_{2} P\right]^{+}$of 7 , only two broad signals at about 320 ppm and 238 ppm are observed, which merge with the increase of the temperature to room temperature into one broad signal at 280 ppm . After two days, this signal vanished completely and only the signals for the cation $\left[\left({ }^{\mathrm{Me}} \mathrm{NHC}\right)_{2} \mathrm{P}\right]^{+}$and the products 7 and 8 were present. Unfortunately, these observations did not contribute to identifying any
intermediates involved in the reaction pathway. Since $\mathbf{8}$ is a neutral complex, it can easily be separated from the ionic complexes 6 and 7 by the extraction of the crude reaction residue with toluene (isolated yield of 8: $18 \%$ ). However, a separation of 6 and 7 is not possible, since both complexes only differ in the nature of the $P_{n}$ middle deck resulting in a similar solubility. Moreover, it was not possible to separate both compounds by fractionated crystallisation, since both compounds co-crystallise (isolated yield of 6 and 7: 49 \%). Increasing the amount of the used ${ }^{\text {Me }} \mathrm{NHC}$ from 2 equivalents to 3 equivalents leads to the increase in the formation of 8 (isolated yield $24 \%$ ). A further increase to 6 equivalents of ${ }^{M}$ NHC, however, results in the formation of not identified products.


Figure 4. Molecular structure of the anionic part of compound 6 (a) and 7 (b) in the solid state with thermal ellipsoids at 50\% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

The molecular structures of $\mathbf{6}$ and $\mathbf{7}$ are depicted in Figure 4. For clarity, the overlaying middle decks are shown as separated molecules. The distribution of the disordered middle decks was found to be 0.6 for the planar cyclo- $\mathrm{P}_{6}$ unit of 6 and 0.4 for the planar cyclo- $\mathrm{P}_{5}$ unit of 7 . A similar distribution was found in the elemental analysis of the crystals. For both compounds, the Cp * ligands and the middle deck are nearly parallel oriented. The P-P bond distances for 6 are all very similar from 2.139(4) Å to 2.161(3) Å and are therefore in the range between single and double bonds. The $V \cdots \vee$ distance is with $2.6766(6) \AA$ in the range of a single bond. ${ }^{[20]}$ However, the optimized geometries (B3LYP/def2-SVP level of theory) obtained for the anion in 6 differ slightly from the experimentally found geometries. With $2.585 \AA$, the V-V bond is shorter and the P-P distances are no longer equal and can be divided in four shorter ( $2.149 \AA$ $2.151 \AA$ Å) and two longer ( $2.283 \AA$ and $2.287 \AA$ Å) P-P distances, featuring a bis-allylic distortion of the six-membered polyphosphorus middle deck. The X-ray structure of 7 shows four short P-P distances in the range of single bonds (2.193(6) Å to 2.239(7) Å) and one long P...P distance, which is with $2.677(7) \AA$ too long for a P-P bond, featuring an open $P_{5}$ chain as middle deck. However, as for 6 , the experimentally obtained structural parameters of 7 differ from the DFT-
optimized geometry (B3LYP/def2-SVP level of theory). One difference is that, for the DFToptimized structure, the $\mathrm{Cp}^{*}$ ligands are no longer parallel. The second, more obvious difference is found at the middle deck, since the $\mathrm{P}_{5}$ ligand is no longer planar but one phosphorus atom is bent out of the plane (dihedral angle of about $14 \mathbf{0}^{\circ}$ ) (cf. SI). These discrepancies between the DFT-optimized geometries (gas phase) and the experimentally determined structural parameters of the two complexes 6 and 7 might be caused by multiple additional weak interactions in the solid state, especially since $\mathbf{6}$ co-crystallizes together with $\mathbf{7}$. Compound $\mathbf{7}$ is a diamagnetic 26 VE (valence electron) species and shows in the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum next to the signals for the $\left[\left({ }^{\mathrm{Me}} \mathrm{NHC}\right)_{2} \mathrm{P}\right]^{+}$cation, a broad signal at 611.7 ppm for the $\mathrm{P}_{5}$ middle deck and a singlet at 2.34 ppm in the ${ }^{1} \mathrm{H}$ NMR spectrum for the $\mathrm{Cp}{ }^{*}$ ligands. Regarding the acycliclike $P_{5}$ middle deck, one would expect three signals in the ${ }^{31}$ P NMR. However, only one singlet at 611.7 ppm is observed, even if the solution is cooled to $-80^{\circ} \mathrm{C}$, indicating a fast dynamic rearrangement on the NMR timescale (cf. Figure $S$ 13). In contrast to 7 compound 6 represents a paramagnetic 27 VE species, which is confirmed both in the solid state and in solution by a broad signal in the EPR at $g_{\text {iso }} \approx 2.014$ (see Figure S12) at 77 K (recorded from the mixture of 6 and 7). In the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR only the signal for the diamagnetic cation $\left[\left({ }^{\mathrm{Me}} \mathrm{NHC}\right)_{2} \mathrm{P}\right]^{+}$is detected at -110.9 ppm . In the ${ }^{1} \mathrm{H}$ NMR spectrum, next to the signal of the cationic part (singlets at 2.23 ppm and 3.50 ppm ), only one broad signal for the $\mathrm{Cp}^{*}$ ligands at 0.95 ppm is identified.


Figure 5. Resonance structures (I, II) of the NHC-phosphinidenide ligand.

It was also possible to obtain crystals (red rods) of 8 from a thf solution layered by hexane (Figure 6). The $\mathrm{Cp}^{*}$ ligands and the $\mathrm{P}_{4}$ middle deck are both planar and parallel. The $\mathrm{V}-\mathrm{V}$ bond distance is with $2.6375(8) \AA$ in a similar range as observed for 6 and 7. The P-P distances for P2-P3 and P3-P4 are with 2.159(1) Å and 2.134(1) Å, respectively, in the range between a single and a double bond, featuring an allylic $P_{3}$ ligand. The distances between P1-P2 and P1-P4 are with $3.467(1) \AA$ and $3.144(1) \AA$, respectively, far too long for any interaction. This is also in accordance with the calculated optimized geometries of 8 (B3LYP/def2-SVP level of theory) and the WBI's of 0.04 and 0.05 , respectively. Interestingly, the remaining NHC-P unit in 8 can be regarded as an NHC-phosphinidenide ligand bridging the two vanadium atoms. In the literature, only few transition metal complexes with such NHC-phosphinidenide ligands are known. ${ }^{[21]}$ In Figure 5, two possible resonance structures (I and II) for such NHC-
phosphinidenide ligands are shown. The P-C bond length of 1.804(4) Å, which is in the region of a single bond, indicates that mainly the resonance structure II contributes to the experimentally observed structure of $\mathbf{8}$. This is also in agreement with the other known NHCphosphinidenide complexes with P-C bonds between $1.797(3)$ Å and $1.824(2) ~ \AA .{ }^{[21 a, c, d]}$ Only the mercury complex [(Dipp $\left.N H C=P)_{2} \mathrm{Hg}\right]$ reported by Grützmacher et al. features a shorter P-C bond (1.754(6) Å), indicating a higher contribution of the resonance structure I. ${ }^{[21 b]}$


Figure 6. Molecular structure of compound 8 in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

The ${ }^{31} P\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}$ spectrum of 8 shows three different signals at $659.4,446.1$ and -8.7 ppm , respectively, being in accordance with the calculated values of the chemical shifts (cf. SI). The signals that originate from the $\mathrm{P}_{3}$ unit are observed at 659.4 ppm as a broad doublet with a coupling constant of 427 Hz and at -8.7 ppm as a sharp triplet of doublets $\left({ }^{1}{ }_{\mathrm{J}, \mathrm{P}}=427 \mathrm{~Hz}\right.$; ${ }^{2} \mathrm{~J}_{\mathrm{P}, \mathrm{P}}=38 \mathrm{~Hz}$ ). Therefore, the broad signal at 446.1 ppm originates from the NHC-P1 unit, which is in a similar region as the NHC-phosphinidenide complexes reported by Tamm et al. ${ }^{[21 a, c]}$ The broadening of the signals may be explained by a dynamic rearrangement of this NHCsubstituted $\mathrm{P}_{1}$ unit. This would also explain why for the $\mathrm{P}_{3}$ unit only the two outer phosphorus atoms show a broadening of the ${ }^{31} \mathrm{P}$ NMR signal. Cooling the solution to $-80^{\circ} \mathrm{C}$ does not lead to four separated ${ }^{31}$ P NMR resonances. However, a sharpening and a shift of the doublet to 645.4 ppm can be monitored (see Figure S16).

### 3.4 Conclusion

In conclusion, we showed that ring contraction reactions can be induced by NHCs to extrude a pnictogen cation from cyclo- $\mathrm{P}_{\mathrm{n}}$ and cyclo-As $\mathrm{s}_{\mathrm{n}}$ ligands, respectively, of sandwich and tripledecker sandwich complexes. This novel method is a general one, working under very mild conditions and is able to generate unprecedented complexes, which could not otherwise be obtained. By this method, three new vanadium triple-decker complexes with polyphosphorus
middle decks, unprecedented triple-decker complexes of Mo with a cyclo- $\mathrm{E}_{5}$ unit and, most important, an unprecedented anionic $\mathrm{CoP}_{3}$ complex were achievable for the first time. Future investigations will focus on examining the reaction pathway of such abstraction reactions by the isolation of intermediates, which might be feasible if different NHCs are used. Another promising goal is the use of other low-valent main group compounds such as CAACs or silylenes for such pnictogen atom abstraction reactions.

## Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) within the project Sche 384/38-1.

### 3.5 References

[1] a) D. Redmore, C. D. Gutsche, Carbocyclic Ring Contraction Reactions, Advances in Alicyclic Chemistry 1971, 3, pp.1-138; b) M. Bohle, J. Liebscher, Advances in Heterocyclic Chemistry, v. 65 (Ed.: A. R. Katritzky), Elsevier textbooks, 1996, pp. 39-92.; c) L. F. Silva, Tetrahedron 2002, 58, 9137-9161; d) L. Silva, Synlett 2014, 25, 466-476; e) S. A. Snyder, E. J. Corey, J. Am. Chem. Soc. 2006, 128, 740-742; f) Y. Kita, K. Higuchi, Y. Yoshida, K. lio, S. Kitagaki, K. Ueda, S. Akai, H. Fujioka, J. Am. Chem. Soc. 2001, 123, 3214-3222.
[2] a) M. Baudler, K. Glinka, Chem. Rev. 1993, 93, 1623-1667; b) S. S. Chitnis, H. A. Sparkes, V. T. Annibale, N. E. Pridmore, A. M. Oliver, I. Manners, Angew. Chem. Int. Ed. 2017, 56, 9536-9540.
[3] C. S. Cundy, M. Green, F. G. A. Stone, A. Taunton-Rigby, J. Chem. Soc., A 1968, 1776.
[4] A. Schisler, P. Lönnecke, T. Gelbrich, E. Hey-Hawkins, Dalton Trans. 2004, 2895.
[5] S. Gómez-Ruiz, A. Schisler, P. Lönnecke, E. Hey-Hawkins, Chem. Eur. J. 2007, 13, 7974.
[6] a) F. Spitzer, G. Balázs, C. Graßl, M. Keilwerth, K. Meyer, M. Scheer, Angew. Chem. Int. Ed. 2018, 57, 8760; b) F. Spitzer, C. Graßl, G. Balázs, E. Mädl, M. Keilwerth, E. M. Zolnhofer, K. Meyer, M. Scheer, Chem. Eur. J. 2017, 23, 2716.
[7] a) B. M. Cossairt, N. A. Piro, C. C. Cummins, Chem. Rev. 2010, 110, 4164-4177; b) M. Caporali, L. Gonsalvi, A. Rossin, M. Peruzzini, Chem. Rev. 2010, 110, 4178-4235; c) M. Scheer, G. Balázs, A. Seitz, Chem. Rev. 2010, 110, 4236-4256; d) S. Khan, S. S. Sen, H. W. Roesky, Chem. Commun. 2012, 48, 2169-2179; e) W. Huang, P. L. Diaconescu, Chem. Commun. 2012, 48, 2216-2218.
[8] V. Nesterov, D. Reiter, P. Bag, P. Frisch, R. Holzner, A. Porzel, S. Inoue, Chem. Rev. 2018, 118, 9678-9842.
[9] a) J. D. Masuda, W. W. Schoeller, B. Donnadieu, G. Bertrand, Angew. Chem. 2007, 119, 7182-7185; b) O. Back, G. Kuchenbeiser, B. Donnadieu, G. Bertrand, Angew. Chem. Int. Ed. 2009, 48, 5530-5533.
[10] J. D. Masuda, W. W. Schoeller, B. Donnadieu, G. Bertrand, J. Am. Chem. Soc. 2007, 129, 14180-14181.
[11] a) A. J. Arduengo, J. C. Calabrese, A. H. Cowley, H. V. R. Dias, J. R. Goerlich, W. J. Marshall, B. Riegel, Inorg. Chem. 1997, 36, 2151-2158; b) A. Hinz, A. Schulz, A. Villinger, Chem. Commun. 2016, 52, 6328-6331; c) M. Cicač-Hudi, J. Bender, S. H. Schlindwein, M. Bispinghoff, M. Nieger, H. Grützmacher, D. Gudat, Eur. J. Inorg. Chem. 2016, 2016, 649- 658.; d) J. E. Borger, A. W. Ehlers, M. Lutz, J. C. Slootweg, K. Lammertsma, Angew. Chem. Int. Ed. 2017, 56, 285-290; e) M. H. Holthausen, S. K. Surmiak, P. Jerabek, G. Frenking, J. J. Weigand, Angew. Chem. Int. Ed. 2013, 52, 11078-11082.
[12] F. Dielmann, A. Timoshkin, M. Piesch, G. Balázs, M. Scheer, Angew. Chem. Int. Ed. 2017, 56, 1671-1675.
[13] M. Piesch, M. Seidl, M. Stubenhofer, M. Scheer, Chem. Eur. J. 2019, 25, 6311-6316.
[14] C. Chan, A. E. Carpenter, M. Gembicky, C. E. Moore, A. L. Rheingold, J. S. Figueroa, Organometallics 2019, 38, 7, 1436-1444.
[15] O. J. Scherer, J. Schwalb, G. Wolmershäuser, W. Kaim, R. Gross, Angew. Chem. Int. Ed. Engl. 1986, 25, 363-364.
[16] a) V. Nesterov, D. Reiter, P. Bag, P. Frisch, R. Holzner, A. Porzelt, S. Inoue, Chem. Rev. 2018, 118, 9678-9842; b) T. Krachko, J. C. Slootweg, Eur. J. Inorg. Chem. 2018, 2018, 2734-2754.; c) K. Schwedtmann, G. Zanoni, J. J. Weigand, Chem. Asian J. 2018, 13, 1388-1405.
[17] G. Märkl, F. Lieb, Tetrahedron Lett. 1967, 8, 3489-3493.
[18] B. D. Ellis, C. A. Dyker, A. Decken, C. L. B. Macdonald, Chem. Commun. 2005, 19651967.
[19] a) M. Herberhold, G. Frohmader, W. Milius, Phosphorus, Sulfur and Silicon 1994, Vol. 9394, 205-208; b) M. Herberhold, G. Frohmader, W. Milius, J. Organomet. Chem. 1996, 522, 185-196; c) B. Pinter, K. T. Smith, M. Kamitani, E. M. Zolnhofer, B. L. Tran, S. Fortier, M. Pink, G. Wu, B. C. Manor, K. Meyer, M. Baik, D. J. Mindiola, J. Am. Chem. Soc. 2015, 137, 15247-15261.
[20] P. Pyykkö, M. Atsumi, Chem. Eur. J. 2009, 15, 186-197.
$[21] \quad$ a) A. Doddi, D. Bockfeld, T. Bannenberg, P. G. Jones, M. Tamm, Angew. Chem. Int. Ed. 2014, 53, 13568-13572; b) M. Bispinghoff, A. M. Tondreau, H. Grützmacher, C. A. Faradji, P. G. Pringle, Dalton Trans. 2016, 45, 5999-6003; c) M. Peters, A. Doddi, T. Bannenberg, M. Freytag, P. G. Jones, M. Tamm, Inorg. Chem. 2017, 56, 1078510793; d) O. Lemp, M. Balmer, K. Reiter, F. Weigend, C. von Hänisch, Chem. Comm. 2017, 53, 7620-7623; e) G. Hierlmeier, A. Hinz, R. Wolf, J. M. Goicoechea, Angew. Chem. Int. Ed. 2018, 57, 431-436.

### 3.6 Supplementary Information

## Ring Contraction by NHC-induced Pnictogen Abstraction

Martin Piesch, ${ }^{1}$ Stephan Reichl, ${ }^{1}$ Michael Seidl, ${ }^{1}$ Gábor Balázs ${ }^{1}$ and Manfred Scheer ${ }^{1 *}$

${ }^{1}$ Institute of Inorganic Chemistry, University of Regensburg; Universitätsstraße 31, 93053 Regensburg, Germany.
*Corresponding author. Email: Manfred.Scheer@chemie.uni-regensburg.de

## Table of Content

1. Experimental Details 28
2. Selected NMR and EPR spectra 31
3. Crystallographic Details 38
4. Possible reaction pathway for the formation of 6 and 8 49
5. Computational Details 50
6. Supplementary References 66

## 1. Experimental Details:

## General Procedures:

All manipulations were carried out under an inert atmosphere of dried argon using standard Schlenk and glove box techniques. Solvents were dried using a MB SPS-800 device of the company MBRAUN. NMR spectra were recorded on a Bruker Avance III 400 MHz NMR spectrometer. Chemical shifts were measured at ambient temperature and are given in ppm; they are referenced to TMS for 1 H and $85 \%$ H3PO4 for 31P as external standard. LIFDI-MS spectra (LIFDI = liquid injection field desorption ionization) were measured on a JEOL AccuTOF GCX. ESI-MS spectra (ESI = Electrospray ionization) were measured on an Agilent Q-TOF 6540 UHD. Elemental analysis (CHN) was determined using a Vario micro cube instrument. The X-Band EPR measurements were carried out with a MiniScope MS400 device with a frequency of 9.44 GHz and a rectangular resonator TE102 of the company Magnettech GmbH. The compounds ${ }^{\text {Me }}$ NHC (1,3,4,5-tetramethyl-imidazol-2-ylidene), ${ }^{[i]}\left[\mathrm{Cp}{ }^{\prime \prime \prime} \mathrm{Co}\left(\eta^{4}-\mathrm{P}_{4}\right)\right]$ (1) ${ }^{[i]}$ and $\left[\left\{\mathrm{Cp}^{*} \mathrm{Mo}\right\}_{2}\left(\mu, \eta^{6: 6}-\mathrm{E}_{6}\right)\right]$ (E $\left.=P(3 a){ }^{[i i i]} \mathrm{As}(3 b)^{[i V]}\right)$ were synthetized according to literature procedures. The Synthesis of $\left[\left\{\mathrm{Cp}^{*} \mathrm{~V}\right\}_{2}\left(\mu, \eta^{6: 6-} \mathrm{P}_{6}\right)\right](5)^{[\mathrm{V}]}$ was improved by using 1,4-diisopropylbenze instead of xylene as a solvent. Thereby the yield was increased from $39 \%$ to $72 \%$. Unless otherwise noted, all other materials were obtained from commercial suppliers and used without purification.

## Synthesis of [( $\left.\left.{ }^{\mathrm{Me}} \mathrm{NHC}\right)_{2} \mathrm{P}\right]\left[\mathrm{Cp}{ }^{\prime \prime \prime} \mathrm{Co}\left(\eta^{3}-\mathrm{P}_{3}\right)\right]$ (2)

MeNHC ( $65.6 \mathrm{mg}, 0.53 \mathrm{mmol}, 2.2 \mathrm{eq}$ ) in 20 mL thf was added to a stirred solution of [Cp"' $\left.\mathrm{Co}\left(\eta^{4}-\mathrm{P}_{4}\right)\right]$ (1) (100 mg, $0.24 \mathrm{mmol}, 1 \mathrm{eq})$ in thf at $-80^{\circ} \mathrm{C}$. The colour of the reaction mixtures turned immediately from red to green. The reaction mixture was allowed to warm to room temperature, while the colour changed to red. The solvent was removed in vacuo. The residue was dissolved in thf, layered with hexane and stored at $-30^{\circ} \mathrm{C}$. After a few days, 2 can be obtained as red rods. The supernatant was decanted off and the residue dried in vacuo.

Yield 2: $126 \mathrm{mg}(0.19 \mathrm{mmol}, 79 \%) .{ }^{1} \mathrm{H}$ NMR (thf- $\left.\mathrm{d}_{8}, 300 \mathrm{~K}\right): \delta[\mathrm{ppm}]=4.36\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{2}{ }^{\mathrm{t}} \mathrm{Bu}_{3}\right), 3.45\left(\mathrm{~s}, 12 \mathrm{H},{ }^{\mathrm{Me}} \mathrm{NHC}\right.$ ), $2.25\left(\mathrm{~s}, 12 \mathrm{H},{ }^{\mathrm{Me}} \mathrm{NHC}\right), 1.31\left(\mathrm{~s}, 18 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{2}{ }^{\mathrm{t}} \mathrm{Bu} u_{3}\right), 1.12\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{2}{ }^{\mathrm{t}} \mathrm{Bu}_{3}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{thf}-\mathrm{d}_{8}, 300 \mathrm{~K}\right): \delta[\mathrm{ppm}]=-111.4$
 $3 P, \mathrm{Cp}^{\prime \prime \prime} \mathrm{CoP}_{3}$ ). ${ }^{13} \mathrm{C}$ NMR (thf- $\mathrm{d}_{8}, 300 \mathrm{~K}$ ): $\delta[\mathrm{ppm}]=9.5\left(\mathrm{~s}, \mathrm{CH}_{3}\right), 31.1\left(\mathrm{~s}, \mathrm{CH}_{3}\right), 33.0\left(\mathrm{~s}, \mathrm{CH}_{3}\right), 33.3\left(\mathrm{~s}, \mathrm{CH}_{3}\right), 34.0(\mathrm{~d}$, $\left.J_{\mathrm{PC}}=8 \mathrm{~Hz}, \mathrm{CH}_{3}\right), 35.6\left(\mathrm{~s}, \mathrm{CH}_{3}\right), 73.9\left(\mathrm{~s}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 103.1(\mathrm{~s}, \mathrm{C}), 103.6(\mathrm{~s}, \mathrm{C}), 127\left(\mathrm{~d}, \mathrm{~J}_{\mathrm{PC}}=3 \mathrm{~Hz}, \mathrm{C}\right), 158.0\left(\mathrm{~d}, \mathrm{~J}_{\mathrm{PC}}=90 \mathrm{~Hz}\right.$, C). ESI-MS (anion, dme): $m / z=385.08\left(30 \%,\left[\text { Cp'"CoP }_{3}\right]^{-}\right.$). ESI-MS (cation, dme): $m / z=279.18\left(100 \%,\left[\left(\mathrm{MeNHC}_{2} \mathrm{P}\right]^{+}\right)\right.$. EA: Due to the high sensitivity of 2 towards moisture and air, it was not possible to obtain an exact elemental analysis. Although several samples from different reactions were used.

## Synthesis of $\left[\left({ }^{\mathrm{Me}} \mathrm{NHC}\right)_{2} \mathrm{P}\right]\left[\left\{\mathrm{C} p^{*} \mathrm{Mo}_{2}\left(\mu, \eta^{3: 3}-\mathrm{P}_{3}\right)\left(\mu, \eta^{2: 2}-\mathrm{P}_{2}\right)\right]\right.$ (4a)

$\left[\left\{\mathrm{Cp}^{*} \mathrm{Mo}_{2}\left(\mu, \eta^{6: 6}-\mathrm{P}_{6}\right)\right](3 \mathrm{a})(0.2 \mathrm{mmol}, 130 \mathrm{mg}, 1 \mathrm{eq})\right.$ in dme is cooled to $-50^{\circ} \mathrm{C}$. To this solution, a solution of ${ }^{\mathrm{Me}} \mathrm{NHC}$ ( $0.4 \mathrm{mmol}, 50 \mathrm{mg}, 2 \mathrm{eq}$ ) in 30 mL dme is added. The resulting brown solution is stirred for 18 hours and warmed up to room temperature. A change in colour from brown to dark green is observed. The solvent is removed in vacuo. The resulting green residue is washed with $3 \times 10 \mathrm{~mL}$ n-hexane, solved in 3 mL thf and stored at $-30^{\circ} \mathrm{C}$. Overnight $\left[\left\{\mathrm{Cp}^{*} \mathrm{Mo}_{2}\left(\mu, \eta^{3: 3}-\mathrm{P}_{3}\right)\left(\mu, \eta^{2: 2}-\mathrm{P}_{2}\right)\right]\left[\mathrm{P}^{(\mathrm{Me}} \mathrm{NHC}_{2}\right]\right](4 \mathrm{a})$ crystallized as dark green blocks, suited for X -ray analysis.

Yield 4a: $87.7 \mathrm{mg}, 0.098 \mathrm{mmol}, 49 \%{ }^{1} \mathrm{H}$ NMR ( 400 MHz , thf- $\mathrm{d}_{8}, 193 \mathrm{~K}$ ): $\delta[\mathrm{ppm}]=1.73\left(\mathrm{~s}, 30 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 2.45(\mathrm{~s}$, $\left.12 \mathrm{H},-\mathrm{NCCH}_{3}\right), 3.64\left(\mathrm{~s}, 12 \mathrm{H},-\mathrm{NCH}_{3}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 400 MHz , thf- $\mathrm{d}_{8}, 193 \mathrm{~K}$ ): $\delta[\mathrm{ppm}]=-117.1\left(\mathrm{~s}, 1 \mathrm{P},\left(\mathrm{MeNHC}_{2} \mathrm{P}\right)\right.$, 62.9 (s, 5 P, [\{Cp*Mo\} $\left.{ }_{2}\left(\mu, \eta^{5: 5}-P_{5}\right)\right] \cdot{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \operatorname{thf}-\mathrm{d}_{8}, 300 \mathrm{~K}$ ): $\delta[\mathrm{ppm}]=1.74\left(\mathrm{~s}, 30 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 2.41(\mathrm{~s}$,
$\left.12 \mathrm{H},-\mathrm{NCCH}_{3}\right), 3.63\left(\mathrm{~s}, 12 \mathrm{H},-\mathrm{NCH}_{3}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(400 \mathrm{MHz}\right.$, thf- $\left.\mathrm{d}_{8}, 300 \mathrm{~K}\right): \delta[\mathrm{ppm}]=-112.4\left(\mathrm{~s}, 1 \mathrm{P},(\mathrm{MeNHC})_{2} \mathrm{P}\right),-$ 59.9 (s, 5 P, [\{Cp* Mo $\left.\}_{2}\left(\mu, \eta^{5: 5}-P_{5}\right)\right]$.ESI-MS (dme): anion mode: $m / z=616.92\left(100 \%,[M]^{-}\right)$, cation mode: $m / z=279.18$ (100 \%, [(MeNHC) $\left.{ }_{2} \mathrm{P}\right]^{+}$). EA calculated for $\mathrm{C}_{34} \mathrm{H}_{54} \mathrm{~N}_{4} \mathrm{P}_{6} \mathrm{Mo}_{2}\left(896.54 \mathrm{~g} \cdot \mathrm{~mol}^{-1}\right)$ : C: $45.55, \mathrm{H}: 6.07, \mathrm{~N}: 6.25$; found [\%]: C: 45.36, H: 5.72, N: 6.09

## Synthesis of [( $\left.\left.{ }^{\text {Me }} \mathrm{NHC}\right)_{2} \mathrm{As}\right]\left[\left\{\mathrm{Cp}{ }^{*} \mathrm{Mo}_{2}\left(\mu, \eta^{3: 3}-\mathrm{As} 3\right)\left(\mu, \eta^{2: 2}-\mathrm{As} 2\right)\right]\right.$ (4b)

A solution of ${ }^{\mathrm{Me}} \mathrm{NHC}(0.2 \mathrm{mmol}, 25 \mathrm{mg}, 2 \mathrm{eq})$ in 10 mL thf is added to a solution of $\left[\left\{\mathrm{Cp}^{*} \mathrm{Mo}_{2}\left(\mu, \eta^{6: 6}-\mathrm{As}\right)\right]\right.$ (3b) $(0.1 \mathrm{mmol}, 91.2 \mathrm{mg}, 1 \mathrm{eq}$ ) in 20 mL thf. A change in colour from brown to dark green is observed immediately. The reaction is stirred for 3 hours. The solvent is removed under reduced pressure. The resulting green residue is washed with $3 \times 10 \mathrm{~mL}$-hexane, dissolved in 5 mL thf and layered by 10 mL of $n$-hexane. After two days, $\mathbf{4 b}$ can be obtained in form of dark green plates.

Yield 4b: $95.0 \mathrm{mg}, 0.082 \mathrm{mmol}, 82 \%{ }^{1} \mathrm{H}$ NMR ( 400 MHz , thf- $\mathrm{d}_{8}, 300 \mathrm{~K}$ ): $\delta[\mathrm{ppm}]=1.60\left(\mathrm{~s}, 30 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 2.37(\mathrm{~s}$, $\left.12 \mathrm{H},-\mathrm{NCCH}_{3}\right), 3.66$ (br, $12 \mathrm{H},-\mathrm{NCH}_{3}$ ). ESI-MS (dme): anion mode: $\mathrm{m} / \mathrm{z}=840.65\left(100 \%\right.$, [M] ${ }^{-}$), cation mode: $\mathrm{m} / \mathrm{z}=$ 323.12 (36.6 \%, [(MeNHC) $\left.\left.{ }_{2} \mathrm{As}\right]^{+}\right), \mathrm{m} / \mathrm{z}=279.18$ ( $63.4 \%,\left[{ }^{\mathrm{Me}} \mathrm{NHC}\right]^{+}$). EA calculated for $\mathrm{C}_{34} \mathrm{H}_{54} \mathrm{~N}_{4} \mathrm{As}_{6} \mathrm{Mo}_{2}$ (1160.23 g. $\mathrm{mol}^{-1}$ ): C: $35.20, \mathrm{H}: 4.69, \mathrm{~N}: 4.83$; found [\%]: C: $35.33, \mathrm{H}: 4.45, \mathrm{~N}: 4.49$

## Reaction of $\left[\left\{\mathrm{Cp}^{*} \mathrm{~V}_{3}\left(\mu, \eta^{6: 6}-\mathrm{P}_{6}\right)\right]\right.$ (5) with ${ }^{\mathrm{Me}} \mathrm{NHC}$

$\left[\left\{\mathrm{Cp}^{*} \mathrm{~V}\right\}_{2}\left(\mu, \eta^{6: 6-P_{6}}\right)\right](5)(0.2 \mathrm{mmol}, 111.6 \mathrm{mg}, 1.00 \mathrm{eq})$ is dissolved in 20 mL thf and cooled to $-80^{\circ} \mathrm{C}$. $\mathrm{A}-80^{\circ} \mathrm{C}$ cold solution of ${ }^{\mathrm{Me}} \mathrm{NHC}(0.6 \mathrm{mmol}, 75 \mathrm{mg}, 3 \mathrm{eq})$ in thf is added dropwise. The resulting dark green mixture was allowed to stir overnight and reach room temperature. Thereby the colour changed to dark red. The solvent is removed in vacuo. The residue is washed with $3 \times 10 \mathrm{~mL}$ n-hexane. A dark red solution can be extracted from the residue with $2 \times 25 \mathrm{~mL}$ of toluene, remaining a green residue. This residue is solved in 4 mL thf, layered by 4 mL of $n$-hexane and stored at $-30^{\circ} \mathrm{C}$. Dark green blocks containing the co-crystallised compounds $\left[\left({ }^{\mathrm{Me}} \mathrm{NHC}\right)_{2} \mathrm{P}\right]\left[\left\{\mathrm{Cp}{ }^{*} \mathrm{~V}\right\}_{2}\left(\mu, \eta^{6: 6}-\mathrm{P}_{6}\right)\right](6)$ and $\left[\left(\mathrm{Me}^{\mathrm{NHC}}\right)_{2} \mathrm{P}\right]\left[\left\{\mathrm{Cp}^{*} \mathrm{~V}\right\}_{2}\left(\mu, \eta^{5: 5}-\mathrm{P}_{5}\right)\right](7)$ can be obtained overnight. The solvent of the extracted red solution was removed under reduced pressure. The residue was solved in thf, layered by 5 mL of $n$-hexane and stored at $-30^{\circ} \mathrm{C}$. After three days crystals (red rods) of $\left[\left\{C p^{*} \mathrm{~V}\right\}_{2}\left(\mu, \eta^{3: 3}-\mathrm{P}_{3}\right)\left(\mu-\mathrm{P}\left\{{ }^{\mathrm{Me}} \mathrm{NHC}\right\}\right)\right]$ (8) can be obtained.

Yield mixture 6 and 7: $80.0 \mathrm{mg}, 0.097 \mathrm{mmol}, 49 \%$. ESI-MS (dme): anion mode: $\mathrm{m} / \mathrm{z}=525.99$ ( $40 \%,[7]^{-}$), 557.97 $\left(60 \%,[6]^{-}\right)$, cation mode: $m / z=279.18\left(70 \%,\left[\left({ }^{\mathrm{Me} N H C}\right)_{2} \mathrm{P}\right]^{+}\right)$, $\left(70 \%, 113.06\left(30 \%,\left[\left({ }^{\mathrm{Me} N H C}\right)^{+}\right]\right)\right.$. EA calculated for $\mathrm{C}_{34} \mathrm{H}_{54} \mathrm{~N}_{4} \mathrm{P}_{6.6} \mathrm{~V}_{2}\left(825.13 \mathrm{~g} \cdot \mathrm{~mol}^{-1}\right.$ ): C: 49.49, H: 6.60, $\mathrm{N}: 6.79$; found [\%]: C: 48.91, H: 6.48, N: 6.83.

The calculated values for the mixture of 6 and 7 are based on the distribution, which was determined by single crystal X-ray analysis.

Data for 6: ${ }^{1} \mathrm{H}$ NMR (400 MHz, thf- $\left.\mathrm{d}_{8}, 300 \mathrm{~K}\right): \delta[\mathrm{ppm}]=0.99\left(\mathrm{br}, 30 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 2.21\left(\mathrm{~s}, 12 \mathrm{H},-\mathrm{NCCH}_{3}\right), 3.46(\mathrm{~s}$, $\left.12 \mathrm{H},-\mathrm{NCH}_{3}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(400 \mathrm{MHz}, \operatorname{thf}^{2}-\mathrm{d}_{8}, 300 \mathrm{~K}\right): \delta[\mathrm{ppm}]=-111.0\left(\mathrm{~s}, 1 \mathrm{P},(\mathrm{Me} \mathrm{NHC})_{2} \mathrm{P}\right)$. EPR solid state, $77 \mathrm{~K}: g_{\text {iso }}$ $=2.014251$; thf, $77 \mathrm{~K}: g_{\text {iso }}=2.014010$

Data for 7: ${ }^{1} \mathrm{H}$ NMR ( 400 MHz, thf- $\mathrm{d}_{8}, 300 \mathrm{~K}$ ): $\delta[\mathrm{ppm}]=2.21\left(\mathrm{~s}, 12 \mathrm{H},-\mathrm{NCCH}_{3}\right), 2.34\left(\mathrm{br}, 30 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 3.45(\mathrm{~s}$, $\left.12 \mathrm{H},-\mathrm{NCH}_{3}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(400 \mathrm{MHz}\right.$, thf- $\left.\mathrm{d}_{8}, 300 \mathrm{~K}\right): \delta[\mathrm{ppm}]=611.7$ (br, $5 \mathrm{P},\left[\left\{\mathrm{Cp}^{*} \mathrm{~V}_{2}\left(\mu, \eta^{5: 5}-\mathrm{P}_{5}\right)\right]\right),-111.0(\mathrm{~s}, 1 \mathrm{P}$, $\left({ }^{\mathrm{Me}} \mathrm{NHC}\right)_{2} \mathrm{P}$ )

Yield 8: $28.8 \mathrm{mg}, 0.047 \mathrm{mmol}, 24 \%{ }^{1} \mathrm{H}$ NMR ( 400 MHz , thf- $\mathrm{d}_{8}, 300 \mathrm{~K}$ ): $\delta[\mathrm{ppm}]=1.79\left(\mathrm{~s}, 30 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 2.27(\mathrm{~s}$, $\left.6 \mathrm{H},-\mathrm{NCCH}_{3}\right), 3.11\left(\mathrm{~s}, 6 \mathrm{H},-\mathrm{NCH}_{3}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(400 \mathrm{MHz}\right.$, thf- $\left.\mathrm{d}_{8}, 193 \mathrm{~K}\right): \delta[\mathrm{ppm}]=-32.3\left(\mathrm{t}, 1 \mathrm{P},{ }^{1} \mathrm{~J}_{\mathrm{PA}, \mathrm{PX}}=427 \mathrm{~Hz}\right.$, $\left.P_{\mathrm{A}}\right), 470.7\left(\mathrm{~s}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{M}}\right), 645.4\left(\mathrm{~d}, 2 \mathrm{P},{ }^{1} \mathrm{~J}_{\mathrm{PA}, \mathrm{PX}}=427 \mathrm{~Hz}, \mathrm{P}_{\mathrm{X}}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(400 \mathrm{MHz}\right.$, thf $\left.-\mathrm{d}_{8}, 300 \mathrm{~K}\right): \delta[\mathrm{ppm}]=-8.7(\mathrm{dt}$,
$1 \mathrm{P}, 1^{1} \mathrm{JPA}, \mathrm{PX}=427 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{\mathrm{PA}, \mathrm{Pm}}=38 \mathrm{~Hz} \mathrm{P}_{\mathrm{A}}$ ), $446.1\left(\mathrm{~s}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{M}}\right), 659.4\left(\mathrm{~d}, 2 \mathrm{P},{ }^{1} \mathrm{~J}_{\mathrm{PA}, \mathrm{PX}}=427 \mathrm{~Hz}, \mathrm{P}_{\mathrm{X}}\right.$ ). LIFDI-MS (toluene): $620.13\left(70 \%,[8]^{+}\right), 125.11\left(100 \%,\left[\left({ }^{M e} \mathrm{NHCH}\right)^{+}\right]\right)$. EA calculated for $\mathrm{C}_{27} \mathrm{H}_{42} \mathrm{~N}_{2} \mathrm{P}_{4} \mathrm{~V}_{2}\left(620.41 \mathrm{~g} \cdot \mathrm{~mol}^{-1}\right): \mathrm{C}: 52.27, \mathrm{H}: 6.82$, $\mathrm{N}: 4.52$; found [\%]: C: 51.79, H: 6.94, N: 4.77

## 2. Selected NMR and EPR spectra



Figure S1. ${ }^{1} \mathrm{H}$ NMR spectrum of compound 2 (thf- $\mathrm{d}_{8}, 300 \mathrm{~K}$ ).


Figure S2. ${ }^{31}{ }^{1}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of compound 2 (thf $-\mathrm{d}_{8}, 300 \mathrm{~K}$ ).


Figure S3. ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of compound 2 (thf- $\mathrm{d}_{8}, 300 \mathrm{~K}$ ).


Figure S4. Variable temperature ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra of the reaction of 1 with ${ }^{\text {MeNHC. }}$.


Figure S5. ${ }^{1} \mathrm{H}$ NMR spectrum of compound 4 a (thf- $\mathrm{d}_{8}, 300 \mathrm{~K}$ ).


Figure S6. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of compound 4 a (thf- $\mathrm{d}_{8}, 300 \mathrm{~K}$ ).


Figure S7. ${ }^{1} \mathrm{H}$ NMR spectrum of compound 4 a (thf- $\mathrm{d}_{8}, 193 \mathrm{~K}$ ).


Figure S8. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of compound 4 a (thf- $\mathrm{d}_{8}, 193 \mathrm{~K}$ ).


Figure $\mathbf{S 9 .}{ }^{1} \mathrm{H}$ NMR spectrum of compound 4 b (thf- $\mathrm{d}_{8}, 300 \mathrm{~K}$ ).


Figure $\mathbf{S 1 0 .}{ }^{1} \mathrm{H}$ NMR spectrum of the mixture of the compounds 6 and 7 (thf- $\mathrm{d}_{8}, 300 \mathrm{~K}$ ).


Figure $\mathbf{S 1 1 .}{ }^{31}{ }^{1}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}$ spectrum of the mixture of the compounds $\mathbf{6}$ and $\mathbf{7}$ (thf- $\mathrm{d}_{8}, 300 \mathrm{~K}$ ).


Figure S12. EPR spectrum of compound 6 as a solid at 77 K (left; $g_{\text {iso }}=2.014$ ) and in thf at 77 K (right; $g_{\text {iso }}=2.014$ ).

The EPR spectrum was recorded from a mixture of co-crystallising 6 and 7 . Because 7 is diamagnetic, the above depicted spectra represent only the properties of 6.


Figure $\mathbf{S 1 3}$. Variable temperature ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}$ spectra of the mixture of 6 and 7 with traces of 8.


Figure $\mathbf{S 1 4 .}{ }^{1} \mathrm{H}$ NMR spectrum of compound 8 (thf- $\mathrm{d}_{8}, 300 \mathrm{~K}$ ).


Figure $\mathbf{S 1 5 .}{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of compound 8 (thf- $\mathrm{d}_{8}, 300 \mathrm{~K}$ ).


Figure S16. Variable temperature ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra of 8 with traces of 7 .


Figure S17. Variable temperature ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra of the reaction of 5 with ${ }^{\text {Me }} \mathrm{NHC}$.

## 3. Crystallographic details

The crystals were selected and mounted on a Gemini Ultra diffractometer equipped with an AtlasS2 CCD detector (4a, 4b, 6/7, 8) and a GV50 diffractometer equipped with a TitanS2 detector (2), respectively. All crystals were kept at $T=123(1) \mathrm{K}$ during data collection. Data collection and reduction were performed with CrysAlispro (Version 1.171.38.46 (4a), 171.39.46 (4b, 6/7, 8), 1.171.40.14a (2)). ${ }^{[v i]}$ For the compounds (4b, 6/7, 8) an analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark \& J.S. Reid.(Clark, R. C. \& Reid, J. S. (1995). Acta Cryst. A51, 887-897) was applied. For the compounds (2, 4a) a numerical absorption correction based on gaussian integration over a multifaceted crystal model and an empirical absorption correction using spherical harmonics as implemented in SCALE3 ABSPACK was applied. Using Olex2, ${ }^{\text {[vii] }}$ all structures were solved by ShelXT ${ }^{[\text {viii] }}$ and a least-square refinement on $F^{2}$ was carried out with ShelXL ${ }^{[i x]}$. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms at the carbon atoms were located in idealized positions and refined isotropically according to the riding model.
Compound 2: The asymmetric unit contains two thf molecules. One of the thf molecules is disordered over two positions with a distribution of 58:42. To describe the disorder the SADI, RIGU and SIMU restrains were applied.
Compound 4a: The asymmetric unit contains thf molecules, which are heavily disordered. A solvent mask was calculated and 284.0 electrons were found in a volume of $1148.0 \AA^{3}$ in 1 void. This is consistent with the presence of 1.8 thf molecules per formula unit, which account for 288.0 electrons. Further, the $\mathrm{P}_{5}$ middle deck is disordered over two positions with a distribution of 60:40. To describe this disorder the SIMU restrain was applied.
Compound 4b: The asymmetric unit contains 2 thf molecules, which are located at an inversion centre. Both thf molecules are disordered over 4 positions. Further, the $\mathrm{As}_{5}$ middle deck is also disordered over three positions. The distribution of the $\mathrm{As}_{5}$ middle deck over these positions was determined to be 0.62 to 0.26 to 0.12 . To describe the disorder the DEFIX, SADI, ISOR and SIMU restrains were applied.
Mixed crystals of the Compounds 6 and 7: The asymmetric unit contains two thf molecule. One of these thf molecules is heavily disordered. A solvent mask was calculated and 160 electrons were found in a volume of $652 \AA^{3}$ in 1 void. This is consistent with the presence of 1 thf per formula unit which account for 160.0 electrons. Further, the compounds 6 and 7 co-crystallise at the same position and can only be distinguished by the disordered middle deck. In the case of 6 a $P_{6}$ ligand ( $60 \%$ occupancy) and in the case of 7 a $P_{5}$ ligand ( $40 \%$ occupancy).
Compound 8: The asymmetric unit contains a thf molecule, which is heavily disordered. A solvent mask was calculated and 158.0 electrons were found in a volume of $746.0 \AA^{3}$ in 1 void. This is consistent with the presence of one thf molecule per formula unit, which account for 160.0 electrons. Further, the ${ }^{\mathrm{Me}} \mathrm{NHC}$ and one $\mathrm{Cp}^{*}$ ligand are disordered over two positions with a distribution of 63 to 37 respectively. To describe this disorder the SADI and SIMU restrains were applied.

CCDC-1938034 (2), CCDC-1938035 (4a), CCDC-1938036 (4b), CCDC-1938037 (6/7) and CCDC-1938038 (8), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table S1.

Crystallographic details of 2, 4a and 4b.

| Compound | $2 \times 2$ thf | 4a $\times 1.8$ thf | 4b $\times 2$ thf |
| :---: | :---: | :---: | :---: |
| CCDC | 1938034 | 1938035 | 1938036 |
| Formula | $\mathrm{C}_{39} \mathrm{H}_{69} \mathrm{CoN}_{4} \mathrm{O}_{2} \mathrm{P}_{4}$ | $\mathrm{C}_{41.2} \mathrm{H}_{68.4} \mathrm{Mo}_{2} \mathrm{~N}_{4} \mathrm{O}_{1.8} \mathrm{P}_{6} \mathrm{C}_{38} \mathrm{H}_{62} \mathrm{As}_{6} \mathrm{Mo}_{2} \mathrm{~N}_{4} \mathrm{O}$ |  |
| $D_{\text {calc. }} / \mathrm{g} \mathrm{cm}^{-3}$ | 1.233 | 1.422 | 1.821 |
| $\mu / \mathrm{mm}^{-1}$ | 4.753 | 6.463 | 4.976 |
| Formula Weight | 808.79 | 1026.30 | 1232.31 |
| Colour | clear dark red | clear dark green | green |
| Shape | block | block | plate |
| Size/mm ${ }^{3}$ | $0.28 \times 0.19 \times 0.17$ | $0.29 \times 0.19 \times 0.16$ | $0.23 \times 0.17 \times 0.11$ |
| T/K | 122.9(3) | 123(1) | 123(1) |
| Crystal System | triclinic | orthorhombic | monoclinic |
| Flack Parameter |  | 0.019(14) | - |
| Hooft Parameter |  | -0.018(10) | - |
| Space Group | P-1 | Pca21 | $\mathrm{P} 21 / \mathrm{n}$ |
| $a / \AA$ | 10.5055(3) | 21.6124(4) | 9.1320(2) |
| b/Å | 13.2212(4) | 12.3273(2) | 21.5901(3) |
| $c / \AA$ | 16.9043(6) | 17.9964(3) | 22.8192(4) |
| $\alpha /{ }^{\circ}$ | 79.289(3) | 90 | 90 |
| $\beta /^{\circ}$ | 80.698(3) | 90 | 92.666(2) |
| $\gamma /{ }^{\circ}$ | 71.820(3) | 90 | 90 |
| $\mathrm{V} / \AA^{3}$ | 2178.30(13) | 4794.65(14) | 4494.18(14) |
| Z | 2 | 4 | 4 |
| Z' | 1 | 1 | 1 |
| Wavelength/A | 1.54184 | 1.54184 | 0.71073 |
| Radiation type | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ | MoK ${ }_{\alpha}$ |
| $\Theta_{\text {min }} /{ }^{\circ}$ | 3.556 | 4.091 | 3.348 |
| $\Theta_{\max } /^{\circ}$ | 75.200 | 72.950 | 32.446 |
| Measured Refl. | 24546 | 15659 | 35365 |
| Independent Refl. | 8626 | 7514 | 14409 |
| Reflections with I > 2(I) | 8215 | 6792 | 11791 |
| Rint | 0.0318 | 0.0363 | 0.0280 |
| Parameters | 513 | 478 | 703 |
| Restraints | 198 | 7 | 638 |
| Largest Peak | 0.409 | 0.487 | 1.217 |
| Deepest Hole | -0.278 | -0.719 | -0.679 |
| GooF | 1.025 | 1.027 | 1.099 |
| $w R_{2}$ (all data) | 0.0878 | 0.0958 | 0.0870 |
| wR2 | 0.0853 | 0.0926 | 0.0816 |
| $R_{1}$ (all data) | 0.0357 | 0.0410 | 0.0523 |
| $R_{1}$ | 0.0335 | 0.0367 | 0.0384 |

Table S2.
Crystallographic details of 6/7 and 8 .

| Compound | $0.6 \times 6 / 0.4 \times 7 \times 2$ thf | $8 \times$ thf |
| :---: | :---: | :---: |
| CCDC | 1938037 | 1938038 |
| Formula | $\mathrm{C}_{42} \mathrm{H}_{70} \mathrm{~N}_{4} \mathrm{O}_{2} \mathrm{P}_{6.61} \mathrm{~V}_{2}$ | $\mathrm{C}_{31} \mathrm{H}_{50} \mathrm{~N}_{2} \mathrm{OP}_{4} \mathrm{~V}_{2}$ |
| $D_{\text {calc. }} / \mathrm{g} \mathrm{cm}^{-3}$ | 1.346 | 1.283 |
| $\mu / \mathrm{mm}^{-1}$ | 0.650 | 0.725 |
| Formula Weight | 969.61 | 692.49 |
| Colour | dark green | dark red |
| Shape | block | block |
| Size/mm ${ }^{3}$ | $0.62 \times 0.44 \times 0.22$ | $0.82 \times 0.32 \times 0.15$ |
| T/K | 123(1) | 123(1) |
| Crystal System | orthorhombic | monoclinic |
| Flack Parameter | 0.003(5) |  |
| Hooft Parameter | 0.014(5) |  |
| Space Group | Pca2 ${ }_{1}$ | P2 $1^{\prime}$ n |
| $a / \AA$ | 21.8599(4) | 10.4380(5) |
| b/Å | 12.2056(2) | 12.2863(4) |
| $c / \AA$ | 17.9368(3) | 28.2286(7) |
| $\alpha /{ }^{\circ}$ | 90 | 90 |
| $\beta /^{\circ}$ | 90 | 98.124(3) |
| $\gamma /{ }^{\circ}$ | 90 | 90 |
| $\mathrm{V} / \AA^{3}$ | 4785.77(14) | 3583.8(2) |
| Z | 4 | 4 |
| Z' | 1 | 1 |
| Wavelength/A | 0.71073 | 0.71073 |
| Radiation type | MoK ${ }_{\alpha}$ | MoK ${ }_{\alpha}$ |
| $\Theta_{\text {min }} /{ }^{\circ}$ | 3.338 | 3.355 |
| $\Theta_{\max } /^{\circ}$ | 32.572 | 30.033 |
| Measured Refl. | 53371 | 37711 |
| Independent Refl. | 16150 | 10476 |
| Reflections with I > 2(I) | 14021 | 8478 |
| Rint | 0.0266 | 0.0423 |
| Parameters | 533 | 502 |
| Restraints | 1 | 611 |
| Largest Peak | 0.423 | 0.678 |
| Deepest Hole | -0.395 | -1.038 |
| GooF | 1.057 | 1.113 |
| $w R_{2}$ (all data) | 0.1070 | 0.1612 |
| wR2 | 0.1023 | 0.1555 |
| $R_{1}$ (all data) | 0.0539 | 0.0938 |
| $R_{1}$ | 0.0443 | 0.0803 |



Figure S18. Molecular structure of $\mathbf{2}$ in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms and the solvent molecules are omitted for clarity.

Table S3. Selected bond length and angles of 2.

| Atom-Atom | Length [Å] |
| :---: | :---: |
| P1-P2 | $2.1552(6)$ |
| P2-P3 | $2.1635(6)$ |
| P3-P1 | $2.1624(6)$ |
| Co1-P1 | $2.2596(5)$ |


| Atom-Atom | Length [Å] |
| :---: | :---: |
| Co1-P2 | $2.2705(5)$ |
| Co1-P3 | $2.2629(5)$ |
| C18-P4 | $1.8033(18)$ |
| C25-P4 | $1.7941(17)$ |


| Atom-Atom-Atom | Angle [$]$ |
| :--- | :--- |
| P1-P2-P3 | $60.09(2)$ |
| P2-P3-P1 | $59.76(2)$ |


| Atom-Atom-Atom | Angle [ ${ }^{\circ}$ ] |
| :--- | :--- |
| P3-P1-P2 | $60.14(2)$ |
| C18-P4-C25 | $98.74(8)$ |



Figure S19: Molecular structure of 4a in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms, the solvent molecules and the second part of the disordered $\mathrm{P}_{5}$ middle deck are omitted for clarity.


Figure S20. Side (a) and top (b) view of the molecular structure of 4 a in the solid state with thermal ellipsoids at $50 \%$ probability level. The disordered $\mathrm{P}_{5}$ middle deck is highlighted green (Part 1) and blue (Part 2).

Table S4. Selected bond length of 4a.

| Atom-Atom | Length [Å] | Atom-Atom | Length [Å] | Atom-Atom | Length [Å] |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Mo1-Mo2 | $2.6669(6)$ | Mo1-P5A | 2.555(10) | Mo1-P2B | 2.503(13) |
| P6-C21 | 1.801(7) | Mo2-P1A | 2.398(5) | Mo1-P3B | 2.385(10) |
| P6-C28 | 1.801(7) | Mo2-P2A | 2.498(9) | Mo1-P4B | 2.483(17) |
| Part 1 |  | Mo2-P3A | 2.460(10) | Mo1-P5B | 2.406(10) |
| P1A-P2A | 2.500(10) | Mo2-P4A | 2.492(10) | Mo2-P1B | 2.509(8) |
| P2A-P3A | 2.480(12) | Mo2-P5A | 2.510(10) | Mo2-P2B | 2.443(14) |
| P3A-P4A | 2.605(11) | Part 2 |  | Mo2-P3B | 2.429(12) |
| P4A-P5A | 2.390(13) | P1B-P2B | 2.360(15) | Mo2-P4B | 2.414(16) |
| P5A-P1A | 2.294(10) | P2B -P3B | 2.384(14) | Mo2-P5B | 2.462(13) |
| Mo1-P1A | 2.435(4) | P3B-P4B | 2.512(14) |  |  |
| Mo1-P2A | 2.449(8) | P4B-P5B | 2.313(19) |  |  |
| Mo1-P3A | 2.522(9) | P5B-P1B | 2.511(16) |  |  |
| Mo1-P4A | 2.450(10) | Mo1-P1B | 2.463(7) |  |  |

Table S5. Selected angles of 4a.

| Atom-Atom-Atom | Angle [${ }^{\circ}$ ] |
| :---: | :---: |
| C21-P6-C28 | $97.4(3)$ |
| Part 1 |  |
| P1A-P2A-P3A | $105.2(4)$ |
| P2A-P3A-P4A | $104.3(4)$ |
| P3A-P4A-P5A | $108.9(5)$ |
| P4A-P5A-P1A | $108.0(5)$ |
| P5A-P1A-P2A | $113.2(3)$ |


| Atom-Atom-Atom | Angle [$]$ |
| :---: | :---: |
| Part 2 |  |
| P1B-P2B-P3B | $108.7(6)$ |
| P2B-P3B-P4B | $108.4(6)$ |
| P3B-P4B-P5B | $106.0(7)$ |
| P4B-P5B-P1B | $109.7(6)$ |
| P5B-P1B-P2B | $106.8(5)$ |



Figure S21. Molecular structure of 4b in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms, the solvent molecules and the other parts of the disordered $\mathrm{As}_{5}$ middle deck are omitted for clarity.


Figure S22. Side (a) and top (b) view of the anionic part of 4 b in the solid state with thermal ellipsoids at $50 \%$ probability level. The disordered $\mathrm{As}_{5}$ middle deck is highlighted green (Part 1), blue (Part 2) and orange (Part 3).

Table S6. Selected bond length of 4b.

| Atom-Atom | Length [Å] | Atom-Atom | Length [Å] | Atom-Atom | Length [Å] |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Mo1-Mo2 | 2.7220(3) | Mo2-As4A | 2.652(8) | Mo2-As5B | $2.466(4)$ |
| As6-C21 | 1.924(2) | Mo2-As5A | 2.481(4) | Part 3 |  |
| As6-C28 | 1.927(2) | Part 2 |  | As1C-As2C | 2.384(6) |
| Part 1 |  | As1B-As2B | 2.404(10) | As2C-As3C | 2.834(7) |
| As1A-As2A | 2.289(14) | As2B -As3B | 2.482(6) | As3C-As4C | $2.443(4)$ |
| As2A-As3A | 2.729(15) | As3B-As4B | 2.767(7) | As4C-As5C | 2.463(4) |
| As3A-As4A | $2.446(8)$ | As4B-As5B | 2.387(8) | As5C-As1C | $2.772(4)$ |
| As4A-As5A | $2.409(8)$ | As5B-As1B | 2.836(10) | Mo1-As1C | 2.596(3) |
| As5A-As1A | 2.870(13) | Mo1-As1B | 2.453(11) | Mo1-As2C | 2.586(5) |
| Mo1-As1A | 2.628(10) | Mo1-As2B | $2.767(6)$ | Mo1-As3C | 2.501(3) |
| Mo1-As2A | 2.570(12) | Mo1-As3B | 2.597(3) | Mo1-As4C | 2.725(4) |
| Mo1-As3A | 2.502(8) | Mo1-As4B | $2.543(6)$ | Mo1-As5C | $2.5578(19)$ |
| Mo1-As4A | $2.627(7)$ | Mo1-As5B | $2.399(4)$ | Mo2-As1C | 2.593(3) |
| Mo1-As5A | $2.469(4)$ | Mo2-As1B | 2.529(10) | Mo2-As2C | 2.575(5) |
| Mo2-As1A | 2.624(10) | Mo2-As2B | 2.831(6) | Mo2-As3C | 2.472(3) |
| Mo2-As2A | 2.573(13) | Mo2-As3B | 2.678(4) | Mo2-As4C | 2.716(4) |
| Mo2-As3A | 2.514(8) | Mo2-As4B | 2.634(6) | Mo2-As5C | 2.5399(19) |

Table S 7. Selected angles of $\mathbf{4 b}$.

| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| C21-As6-C28 | $94.53(11)$ |
| Part 1 |  |
| As1A-As2A-As3A | $109.5(6)$ |
| As2A-As3A-As4A | $110.7(4)$ |
| As3A-As4A-As5A | $105.4(3)$ |
| As4A-As5A-As1A | $111.1(3)$ |
| As5A-As1A-As2A | $103.2(5)$ |
| Part 2 |  |
| As1B-As2B-As3B | $105.5(3)$ |
| As2B-As3B-As4B | $112.6(2)$ |


| Atom-Atom-Atom | Angle [${ }^{\circ}$ ] |
| :--- | :---: |
| As3B-As4B-As5B | $104.5(2)$ |
| As4B-As5B-As1B | $106.6(3)$ |
| As5B-As1B-As2B | $110.8(4)$ |
| Part 3 |  |
| As1C-As2C-As3C | $104.3(2)$ |
| As2C-As3C-As4C | $112.32(17)$ |
| As3C-As4C-As5C | $104.44(16)$ |
| As4C-As5C-As1C | $112.31(12)$ |
| As5C-As1C-As2C | $106.58(18)$ |



Figure S23. Molecular structure of 6 and 7 in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms and the solvent molecules are omitted for clarity.
a)

b)


Figure S 24. Side (a) and top (b) view of the anionic part of mixed crystal of 6 and 7 in the solid state with thermal ellipsoids at $50 \%$ probability level. The disordered $P_{6}$ and $P_{5}$ middle deck are highlighted green (Part 1 ) and blue (Part 2).

Table S8. Selected bond length of 6 and 7.

| Atom-Atom | Length [Å] | Atom-Atom | Length [Å] |
| :---: | :---: | :---: | :---: |
| V1-V2 | $2.6766(6)$ | V2-P2A | 2.552(2) |
| P7-C21 | 1.806(4) | V2-P3A | 2.5552(17) |
| P7-C28 | 1.800(4) | V2-P4A | 2.5460(19) |
| Part 1 |  | V2-P5A | 2.5358(19) |
| P1A-P2A | 2.161(3) | V2-P6A | 2.507(3) |
| P2A-P3A | 2.149(4) | Part 2 |  |
| P3A-P4A | 2.151(5) | P1B-P2B | 2.239(7) |
| P4A-P5A | 2.139(4) | P2B-P3B | 2.215(7) |
| P5A-P6A | 2.161(3) | P3B-P4B | 2.193(6) |
| P6A-P1A | 2.139(5) | P4B-P5B | 2.212(5) |
| V1-P1A | 2.520(3) | P5B-P1B | 2.677(7) |
| V1-P2A | 2.5015(17) | V1-P1B | 2.332(4) |
| V1-P3A | 2.5178(16) | V1-P2B | 2.417(2) |
| V1-P4A | 2.5494(19) | V1-P3B | 2.455(3) |
| V1-P5A | 2.536(2) | V1-P4B | 2.423(3) |
| V1-P6A | 2.530(3) | V1-P5B | 2.325(5) |
| V2-P1A | 2.540(3) | V2-P1B | $2.306(4)$ |


| Atom-Atom | Length [Å] |
| :---: | :---: |
| V2-P2B | $2.423(3)$ |
| V2-P3B | $2.355(3)$ |
| V2-P4B | $2.453(3)$ |
| V2-P5B | $2.339(5)$ |

Table S9. Selected angles of 6 and 7.

| Atom-Atom-Atom | Angle [$]$ |
| :---: | :---: |
| C21-P7-C28 | $98.15(15)$ |
| Part 1 |  |
| P1A-P2A-P3A | $120.11(13)$ |
| P2A-P3A-P4A | $120.19(11)$ |
| P3A-P4A-P5A | $119.86(12)$ |
| P4A-P5A-P6A | $119.91(15)$ |
| P5A-P6A-P1A | $120.54(17)$ |


| Atom-Atom-Atom | Angle [${ }^{\circ}$ ] |
| :---: | :---: |
| P6A-P1A-P2A | $119.37(15)$ |
| Part 2 |  |
| P1B-P2B-P3B | $108.60(16)$ |
| P2B-P3B-P4B | $114.79(18)$ |
| P3B-P4B-P5B | $109.38(19)$ |
| P4B-P5B-P1B | $103.7(2)$ |
| P5B-P1B-P2B | $103.19(18)$ |

a)

b)


Figure S25. Molecular structure of 8 (a: side view; b: top view) in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms and the solvent molecules are omitted for clarity.

Table S10. Selected bond length of 8 .

| Atom-Atom | Length $[\AA \AA]$ |
| :---: | :---: |
| $\mathrm{V} 1-\mathrm{V} 2$ | $2.6375(8)$ |
| P2-P3 | $2.1585(14)$ |
| P3-P4 | $2.1337(14)$ |
| C21-P1 | $1.804(4)$ |


| Atom-Atom | Length [Å] |
| :---: | :---: |
| P1-V1 | $2.3082(11)$ |
| P1-V2 | $2.3143(11)$ |
| P2-V1 | $2.3552(11)$ |
| P2-V2 | $2.3530(11)$ |


| Atom-Atom | Length [Å] |
| :---: | :---: |
| P3-V1 | $2.5702(12)$ |
| P3-V2 | $2.5696(12)$ |
| P4-V1 | $2.3811(12)$ |
| P4-V2 | $2.3817(12)$ |

Table S11. Selected angles of 8.

| Atom-Atom-Atom | Angle [$]$ |
| :---: | :---: |
| $\mathrm{V} 1-\mathrm{P} 1-\mathrm{V} 2$ | $69.58(3)$ |
| $\mathrm{V} 1-\mathrm{P} 2-\mathrm{V} 2$ | $68.14(3)$ |
| $\mathrm{V} 1-\mathrm{P} 3-\mathrm{V} 2$ | $61.75(3)$ |
| $\mathrm{V} 1-\mathrm{P} 4-\mathrm{V} 2$ | $67.25(3)$ |


| Atom-Atom-Atom | Angle [${ }^{\circ}$ ] |
| :---: | :---: |
| P2-P3-P4 | $107.42(5)$ |
| $\mathrm{C} 21-\mathrm{P} 1-\mathrm{V} 1$ | $127.02(13)$ |
| $\mathrm{C} 21-\mathrm{P} 1-\mathrm{V} 2$ | $130.23(12)$ |
|  |  |

## Possible reaction pathway for the formation of 6 and 8



In a proposed reaction pathway (see above) the complex $\left[\left\{\mathrm{Cp}^{*} \mathrm{~V}_{2}\left(\mu, \eta^{6 \cdot 6}-\mathrm{P}_{6}\right)\right]\right.$ (5) reacts with two equivalents of ${ }^{\text {me }} \mathrm{NHC}$, via a NHC induced phosphorus atom abstraction, to the complex $\left[\left({ }^{M e} N H C\right)_{2} P\right]\left[\left\{\mathrm{Cp}^{*} \mathrm{~V}_{2}\left(\mu, \eta^{5: 5}-\mathrm{P}_{5}\right)\right]\right.$ (7). Complex 7 on the other hand reduces the starting compound 5 resulting formally in the complexes $\left[\left({ }^{M} N \mathrm{NHC}\right)_{2} P\right]\left[\left\{\mathrm{Cp}^{*} \mathrm{~V}\right\}_{2}\left(\mu, \eta^{6: 6}-\mathrm{P}_{6}\right)\right]$ (6) and in a neutral complex $\left[\left\{C^{*} V\right\}_{2}\left(\mu, \eta^{5 \cdot 5}-P_{5}\right)\right]$. The later was neither isolated nor spectroscopically observed. The complex $\left[\left\{\mathrm{Cp}^{*} \mathrm{~V}_{2}\left(\mu, \eta^{5: 5}-\mathrm{P}_{5}\right)\right]\right.$ is supposed to react with an excess of ${ }^{\mathrm{Me}} \mathrm{NHC}$ by several indistinct reaction steps to the neutral complex $\left[\left\{\mathrm{Cp}^{*} \mathrm{~V}\right\}_{2}\left(\mu, \eta^{3: 3}-\mathrm{P}_{3}\right)\left(\mu-\mathrm{P}^{\mathrm{Me}} \mathrm{NHC}\right)\right]$ ( 8 ). In fact, if an excess of the NHC is used the amount of $\mathbf{8}$ increases.

## 4. Computational Details

Gaussian 09 program package was used throughout. ${ }^{[x]}$ Density functional theory (DFT) in form of Becke's three-parameter hybrid functional B3LYP ${ }^{[x i]}$ with def2-SVP basis set ${ }^{[\text {[xil }}$ was employed. For solvents effects has been accounted by using the polarizable continuum model (CPM). ${ }^{\text {[xiii] }}$ For the reaction energies the SCF energies, without zero point vibration energies have been used. The dielectric constant of dichloromethane $(\varepsilon=8.93)$ has been used in all calculations. The figures for the supporting information concerning the DFT calculations were created with ChemCraft. ${ }^{[\text {[iv] }}$

For the calculation of the ${ }^{31} \mathrm{P}$ NMR chemical shifts of compound 8 and $\left({ }^{\mathrm{Me}} \mathrm{NHC}\right)_{2} \mathrm{P}^{+}$, the geometry has been optimized at the D3BJ ${ }^{[x x]}$-BP86 $6^{[x v i]} /$ def2-TZVP level of theory using a fine integration grid and tight convergence criteria. For the solvent effects has been accounted via the CPM model using the dielectric constant of THF. The ${ }^{31} \mathrm{P}$ NMR shielding tensors has been computed with the Gauge-Independent Atomic Orbital (GIAO) method ${ }^{[x v i]}$ using the $x 2 c$ TZVPall ${ }^{[\text {[vii] }}$ basis set for phosphorus and the def2-TZVP basis set for all other atoms.

Table S12. Experimental and calculated ${ }^{31} \mathrm{P}$ NMR chemical shifts for compound 8 and ( $\left.{ }^{\mathrm{Me}} \mathrm{NHC}\right)_{2} \mathrm{P}^{+}$.

| Atom | $\delta\left({ }^{31} \mathrm{P}\right)$ calc./ppm | $\delta\left({ }^{31} \mathrm{P}\right)$ exp. $(193 \mathrm{~K}) / \mathrm{ppm}$ |
| :---: | :---: | :---: |
| $\mathrm{P}^{3}$ | 459.9 | 470.7 |
| $\mathrm{P}^{4}$ | 575.3 | 645.4 |
| $\mathrm{P}^{5}$ | 646.3 | 645.4 |
| $\mathrm{P}^{6}$ | -74.6 | -32.3 |
| $(\mathrm{Me} \mathrm{NHC})_{2} \mathrm{P}^{+}$ | -109.4 | $-111.5^{\mathrm{a})}$ |

a) at room temperature in thf-d8.

Table S13. Total energies for all optimized geometries (B3LYP/def2-SVP level of theory).


|  | total energy [ Ha ] |
| :---: | :---: |
| [ $\left.\mathrm{Cp}^{\prime \prime \prime} \mathrm{CoPP}_{3}\right]^{-}$ | -3071.3970680 |
| $\left[\left(\mathrm{Cp}{ }^{*} \mathrm{Mo}_{2} \mathrm{As}_{5}\right]^{-}\right.$ | -12094.7366607 |
| [(Cp*Mo) $2^{2} \mathrm{P}_{5}{ }^{-}$ | -2622.7959840 |
| $\left[\left({ }^{\text {Me }} \mathrm{NHC}\right)_{2} \mathrm{As}\right]^{+}$ | -3001.9142360 |
| $\left[\left({ }^{\text {ene }} \mathrm{NHC}\right)_{2} \mathrm{P}\right]^{+}$ | -1107.5366457 |
| [(Cp*V) $\left.2 \mathrm{P}_{4} \mathrm{NHC}\right]$ | -4415.88217580 |
| $\left[\left(\mathrm{Cp}^{*} \mathrm{~V}\right)_{2} \mathrm{P}_{6}\right]^{-}$ | -4715.3573508 |
| [( $\left.\left.\mathrm{Cp}^{*} \mathrm{~V}\right)_{2} \mathrm{P}_{5}\right]$ (singlet) | -4374.0779531 |
| $\left.\left[\left(C p^{*}\right)\right)_{2} \mathrm{P}_{5}\right]$ (triplet) | -4374.0836442 |
| $\left[\mathrm{Cp}^{\prime \prime \prime} \mathrm{CoP}_{4}\right]$ | -3412.5655889 |
| $\left[\left(\mathrm{Cp}{ }^{*} \mathrm{Mo}\right)_{2} \mathrm{As}_{6}\right]$ | -14330.2813708 |
| $\left[\left(C p^{*} \mathrm{Mo}^{2}{ }_{2} \mathrm{P}_{6}\right]\right.$ | -2963.9547670 |
| $\left[\left(\mathrm{Cp}^{*} \mathrm{~V}\right)_{2} \mathrm{P}_{6}\right]$ | -4715.2466587 |
| MeNHC | -383.1663541 |

$\left[\mathrm{Cp}^{\prime \prime \prime} \mathrm{CoP}_{4}\right]+2{ }^{\mathrm{Me}} \mathrm{NHC}->\left[\left(\mathrm{Me}^{\mathrm{Ne}} \mathrm{NHC}\right)_{2} \mathrm{P}\right]\left[\mathrm{Cp}^{\prime \prime \prime} \mathrm{CoP}_{3}\right], \Delta \mathrm{E}=-92.99 \mathrm{~kJ} / \mathrm{mol}$
$\left[\left(\mathrm{Cp}^{*} \mathrm{Mo}\right)_{2} \mathrm{As} 6\right]++2{ }^{\mathrm{Me}} \mathrm{NHC}->\left[(\mathrm{MeNHC})_{2} \mathrm{As}\right]\left[\left(\mathrm{Cp}^{*} \mathrm{Mo}\right)_{2} \mathrm{As}_{5}\right], \Delta \mathrm{E}=-96.66 \mathrm{~kJ} / \mathrm{mol}$
$\left[\left(\mathrm{Cp}{ }^{*} \mathrm{Mo}\right)_{2} \mathrm{P}_{6}\right]++2 \mathrm{Me}^{\mathrm{NHC}}->\left[(\mathrm{Me} \mathrm{NHC})_{2} \mathrm{P}\right]\left[\left(\mathrm{Cp}{ }^{*} \mathrm{Mo}\right)_{2} \mathrm{P}_{5}\right], \Delta \mathrm{E}=-118.55 \mathrm{~kJ} / \mathrm{mol}$

## $\left[C p^{\prime \prime} \operatorname{Co}\left(\eta^{3}-P_{3}\right)\right]^{-}$



Table S14. Optimized geometries of $\left[\mathrm{Cp}^{\prime \prime \prime} \mathrm{Co}\left(\eta^{3}-\mathrm{P}_{3}\right)\right]^{-}$(anion in 2). XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.

| Co | 10.631282000 | 4.000404000 | 9.703352000 |
| :--- | :---: | :---: | :---: |
| P | 10.681355000 | 3.025810000 | 7.622739000 |
| P | 11.973365000 | 4.760380000 | 8.002607000 |
| P | 9.798341000 | 5.025525000 | 7.829920000 |
| C | 10.132214000 | 4.992050000 | 11.474971000 |
| C | 9.727102000 | 6.432937000 | 11.777158000 |
| C | 10.023802000 | 2.652230000 | 11.171767000 |
| C | 11.446371000 | 4.450826000 | 11.543293000 |
| H | 12.340419000 | 5.045235000 | 11.703585000 |
| C | 9.268992000 | 3.875043000 | 11.248185000 |
| H | 8.190314000 | 3.941974000 | 11.146239000 |
| C | 11.433471000 | 3.017129000 | 11.375873000 |
| C | 9.257656000 | 1.309763000 | 11.103465000 |
| C | 12.734031000 | 2.192812000 | 11.547876000 |
| C | 9.757762000 | 6.629908000 | 13.312722000 |
| H | 9.072129000 | 5.928081000 | 13.814902000 |
| H | 9.455056000 | 7.655530000 | 13.586152000 |
| H | 10.768950000 | 6.456016000 | 13.714463000 |
| C | 7.917876000 | 1.491831000 | 10.348077000 |
| H | 7.227487000 | 2.171686000 | 10.867685000 |
| H | 7.406581000 | 0.519171000 | 10.262468000 |
| H | 8.088238000 | 1.883774000 | 9.334182000 |
| C | 9.989703000 | 0.162695000 | 10.383084000 |
| H | 10.251636000 | 0.451193000 | 9.354379000 |
| H | 9.329712000 | -0.719186000 | 10.334113000 |


| H | 10.904299000 | -0.152048000 | 10.899288000 |
| :--- | :--- | :--- | :--- |
| C | 8.919884000 | 0.866412000 | 12.549612000 |
| H | 9.826475000 | 0.688210000 | 13.145704000 |
| H | 8.330276000 | -0.066570000 | 12.543365000 |
| H | 8.327666000 | 1.638318000 | 13.066258000 |
| C | 8.302468000 | 6.728312000 | 11.272139000 |
| H | 8.226413000 | 6.560458000 | 10.187262000 |
| H | 8.031423000 | 7.776409000 | 11.481733000 |
| H | 7.554897000 | 6.089652000 | 11.769071000 |
| C | 13.170393000 | 1.451850000 | 10.263464000 |
| H | 12.428026000 | 0.725759000 | 9.917244000 |
| H | 14.114448000 | 0.908102000 | 10.442472000 |
| H | 13.332587000 | 2.170509000 | 9.446879000 |
| C | 13.911919000 | 3.126702000 | 11.915538000 |
| H | 14.107685000 | 3.864756000 | 11.123153000 |
| H | 14.828084000 | 2.528465000 | 12.045236000 |
| H | 13.732426000 | 3.669008000 | 12.856606000 |
| C | 12.597493000 | 1.190974000 | 12.718250000 |
| H | 12.312927000 | 1.710242000 | 13.647916000 |
| H | 13.557957000 | 0.679077000 | 12.898647000 |
| H | 11.845131000 | 0.415902000 | 12.524838000 |
| C | 10.702001000 | 7.434514000 | 11.126998000 |
| H | 11.735961000 | 7.279839000 | 11.473656000 |
| H | 10.418775000 | 8.469569000 | 11.383060000 |
| H | 10.695844000 | 7.331061000 | 10.031554000 |

Table S15. Mulliken charges for the complex $\left[\mathrm{Cp}^{\prime \prime \prime} \mathrm{Co}\left(\eta^{3}-\mathrm{P}_{3}\right)\right]$ -

| Cp"' | -0.12 |
| :--- | :--- |
| Co | -0.24 |
| $C^{\prime \prime \prime} C o$ | -0.36 |
| $P_{3}$ | -0.64 |

$\left[\left(\mathrm{Cp}^{*} \mathrm{Mo}_{2}\left(\mu, \eta^{3: 3}-\mathrm{As}_{3}\right)\left(\mu, \eta^{2: 2}-\mathrm{As}_{2}\right)\right]^{-}\right.$


Table S16. Optimized geometries of $\left[\left(\mathrm{Cp}^{*} \mathrm{Mo}\right)_{2}\left(\mu, \eta^{3: 3}-\mathrm{As}_{3}\right)\left(\mu, \eta^{2: 2}-\mathrm{As}_{2}\right)\right]$ - (anion in 4 b$)$. XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.

| Mo | -1.369822000 | 0.004333000 | 0.000423000 | C | 3.511034000 | 2.776735000 | -0.126835000 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Mo | 1.369822000 | 0.004374000 | -0.000466000 | H | 3.128135000 | 3.170827000 | -1.078701000 |
| As | -0.005253000 | 1.945762000 | -1.180911000 | H | 4.567238000 | 3.091131000 | -0.035378000 |
| As | 0.001559000 | -0.895510000 | -1.930526000 | H | 2.945987000 | 3.265847000 | 0.679817000 |
| As | 0.000069000 | -2.424274000 | -0.000043000 | C | -3.557290000 | 0.781152000 | 2.621382000 |
| As | 0.005201000 | 1.945666000 | 1.181016000 | H | -3.147964000 | 0.012246000 | 3.291970000 |
| As | -0.001513000 | -0.895538000 | 1.930473000 | H | -4.618602000 | 0.931235000 | 2.893809000 |
| C | -3.422631000 | 0.383365000 | 1.180142000 | H | -3.022800000 | 1.718591000 | 2.832162000 |
| C | 3.422668000 | 0.383766000 | -1.180025000 | C | -3.634706000 | -2.199812000 | 1.487123000 |
| C | -3.419708000 | 0.498091000 | -1.142324000 | H | -3.226232000 | -3.083343000 | 0.976611000 |
| C | 3.391133000 | 1.281504000 | -0.059813000 | H | -4.707638000 | -2.390520000 | 1.674460000 |
| C | 3.448431000 | -0.952859000 | -0.671177000 | H | -3.135870000 | -2.124857000 | 2.464174000 |
| C | -3.448506000 | -0.953058000 | 0.670791000 | C | 3.622703000 | -2.046671000 | 1.700801000 |
| C | -3.391056000 | 1.281526000 | 0.060271000 | H | 3.183736000 | -1.845131000 | 2.688405000 |
| C | -3.445383000 | -0.882536000 | -0.768562000 | H | 4.694394000 | -2.273171000 | 1.851400000 |
| C | 3.445288000 | -0.882861000 | 0.768208000 | H | 3.143403000 | -2.955685000 | 1.309727000 |
| C | 3.419721000 | 0.497627000 | 1.142485000 | C | -3.510873000 | 2.776741000 | 0.127811000 |
| C | -3.622923000 | -2.046027000 | -1.701534000 | H | -3.128087000 | 3.170468000 | 1.079872000 |
| H | -3.184809000 | -1.843849000 | -2.689384000 | H | -4.567043000 | 3.091232000 | 0.036305000 |
| H | -4.694615000 | -2.272984000 | -1.851427000 | H | -2.945672000 | 3.266106000 | -0.678581000 |
| H | -3.142894000 | -2.954987000 | -1.311226000 | C | 3.634438000 | -2.199402000 | -1.487870000 |
| C | -3.552797000 | 1.041264000 | -2.535383000 | H | 3.224131000 | -3.082716000 | -0.978446000 |
| H | -3.002501000 | 1.985791000 | -2.652776000 | H | 4.707425000 | -2.391283000 | -1.673685000 |
| H | -4.612806000 | 1.236243000 | -2.783747000 | H | 3.137139000 | -2.123342000 | -2.465616000 |
| H | -3.161853000 | 0.337230000 | -3.283873000 | C | 3.552911000 | 1.040249000 | 2.535747000 |
| C | 3.557322000 | 0.782222000 | -2.621087000 | H | 3.003089000 | 1.985019000 | 2.653418000 |
| H | 3.148496000 | 0.013415000 | -3.292086000 | H | 4.612989000 | 1.234615000 | 2.784295000 |
| H | 4.618591000 | 0.932984000 | -2.893297000 | H | 3.161533000 | 0.336147000 | 3.283947000 |
| H | 3.022359000 | 1.719468000 | -2.831527000 |  |  |  |  |



Figure S26. Selected frontier orbitals of the complex $\left[\left(\mathrm{Cp}^{*} \mathrm{Mo}\right)_{2}\left(\mu, \eta^{3: 3}-\mathrm{As}_{3}\right)\left(\mu, \eta^{\left.2: 2-A s_{2}\right)}\right]^{-}\right.$(anion in 4b).

## $\left[\left(\mathrm{Cp}^{*} \mathrm{Mo}_{2}\left(\mu, \eta^{3: 3}-\mathrm{As}_{3}\right)\left(\mu, \eta^{2: 2}-\mathrm{As} 2\right)\right]\right.$ (neutral)



Table S17. Optimized geometries of $\left[\left(\mathrm{Cp}^{*} \mathrm{Mo}_{2}\left(\mu, \eta^{3: 3}-\mathrm{As}_{3}\right)\left(\mu, \eta^{2: 2}-\mathrm{As} 2\right)\right]\right.$ (neutral). XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.

| Mo | -1.418686000 | 0.020561000 | -0.002586000 |
| :--- | :---: | :---: | :---: |
| Mo | 1.418691000 | 0.020413000 | 0.002924000 |
| As | 0.002836000 | 1.755182000 | -1.271677000 |
| As | 0.003935000 | -0.851596000 | -1.975330000 |
| As | -0.000130000 | -2.309064000 | -0.002509000 |
| As | -0.002618000 | 1.753602000 | 1.273125000 |
| As | -0.004053000 | -0.855726000 | 1.973384000 |
| C | -3.447273000 | 0.344656000 | 1.195712000 |
| C | 3.447470000 | 0.349540000 | -1.193556000 |
| C | -3.438711000 | 0.599341000 | -1.114545000 |
| C | 3.412142000 | 1.310538000 | -0.126977000 |
| C | 3.487070000 | -0.959356000 | -0.609401000 |
| C | -3.487110000 | -0.961727000 | 0.605986000 |
| C | -3.411889000 | 1.310184000 | 0.133242000 |
| C | -3.480276000 | -0.805146000 | -0.824017000 |
| C | 3.480012000 | -0.808831000 | 0.821262000 |
| C | 3.438740000 | 0.594411000 | 1.117735000 |
| C | -3.665281000 | -1.907876000 | -1.826428000 |
| H | -3.224000000 | -1.652589000 | -2.799957000 |
| H | -4.739892000 | -2.104956000 | -1.989467000 |
| H | -3.204540000 | -2.847180000 | -1.489132000 |
| C | -3.570211000 | 1.218797000 | -2.475921000 |
| H | -3.092562000 | 2.207462000 | -2.521795000 |
| H | -4.635519000 | 1.351464000 | -2.736698000 |
| H | -3.114697000 | 0.591363000 | -3.255109000 |
| C | 3.581728000 | 0.661461000 | -2.655964000 |
| H | 3.135881000 | -0.124656000 | -3.281377000 |
| H | 4.647112000 | 0.745622000 | -2.935849000 |
| H | 3.095149000 | 1.611888000 | -2.916630000 |


| C | 3.520592000 | 2.800289000 | -0.281658000 |
| :--- | ---: | ---: | ---: |
| H | 3.089677000 | 3.144158000 | -1.232370000 |
| H | 4.580436000 | 3.111263000 | -0.265084000 |
| H | 3.006887000 | 3.334825000 | 0.530036000 |
| C | -3.581408000 | 0.650379000 | 2.659446000 |
| H | -3.135088000 | -0.138139000 | 3.281488000 |
| H | -4.646794000 | 0.732830000 | 2.939832000 |
| H | -3.095292000 | 1.599959000 | 2.924034000 |
| C | -3.679221000 | -2.251537000 | 1.350840000 |
| H | -3.301310000 | -3.112130000 | 0.781613000 |
| H | -4.752480000 | -2.427338000 | 1.544502000 |
| H | -3.165056000 | -2.243055000 | 2.322480000 |
| C | 3.664459000 | -1.915734000 | 1.819175000 |
| H | 3.222050000 | -1.664710000 | 2.793317000 |
| H | 4.738970000 | -2.113121000 | 1.982486000 |
| H | 3.204375000 | -2.853740000 | 1.477425000 |
| C | -3.520087000 | 2.799264000 | 0.294283000 |
| H | -3.088008000 | 3.139085000 | 1.245920000 |
| H | -4.579926000 | 3.110370000 | 0.280205000 |
| H | -3.007258000 | 3.337113000 | -0.515775000 |
| C | 3.679249000 | -2.245987000 | -1.359723000 |
| H | 3.302650000 | -3.109157000 | -0.793544000 |
| H | 4.752415000 | -2.420208000 | -1.555313000 |
| H | 3.163972000 | -2.234023000 | -2.330745000 |
| C | 3.570163000 | 1.208037000 | 2.481740000 |
| H | 3.091648000 | 2.196068000 | 2.532131000 |
| H | 4.635454000 | 1.340560000 | 2.742668000 |
| H | 3.115587000 | 0.576718000 | 3.258330000 |
|  |  |  |  |



Figure S27. Selected frontier orbitals of the neutral complex $\left[\left(\mathrm{Cp}^{*} \mathrm{Mo}\right)_{2}\left(\mu, \eta^{3: 3}-\mathrm{As}_{3}\right)\left(\mu, \eta^{2: 2}-\mathrm{As}_{2}\right)\right]$.
$\left[\left(C p^{*} \mathrm{Mo}_{2}\right)_{2}\left(\mu, \eta^{3: 3}-\mathrm{P}_{3}\right)\left(\mu, \eta^{2: 2}-\mathrm{P}_{2}\right)\right]^{-}$


Table S18. Optimized geometries of $\left[\left(C p^{*} M o\right)_{2}\left(\mu, \eta^{3: 3}-P_{3}\right)\left(\mu, \eta^{2: 2}-P_{2}\right)\right]^{-}$(anion in $\left.4 a\right) . X Y Z$ coordinated in angstroms. B3LYP/def2-SVP level of theory.

| Mo | -1.343801000 | -0.021794000 | 0.003421000 |
| :--- | :---: | :---: | :---: |
| Mo | 1.343794000 | -0.021774000 | -0.003419000 |
| P | -0.009639000 | -0.985346000 | -1.771800000 |
| P | 0.000270000 | 1.838489000 | -1.063897000 |
| P | -0.000305000 | 1.838438000 | 1.063976000 |
| P | 0.000073000 | -2.339376000 | -0.000025000 |
| P | 0.009610000 | -0.985419000 | 1.771783000 |
| C | -3.403601000 | 0.533058000 | 1.127011000 |
| C | -3.355982000 | 1.283382000 | -0.095687000 |
| C | -3.442827000 | -0.856363000 | 0.788947000 |
| C | -3.535981000 | 1.116962000 | 2.504213000 |
| H | -3.174286000 | 0.422683000 | 3.276338000 |
| H | -4.593173000 | 1.345709000 | 2.734844000 |
| H | -2.963293000 | 2.050142000 | 2.605287000 |
| C | -3.501824000 | 0.719492000 | -2.645337000 |
| H | -2.970996000 | 1.657059000 | -2.864302000 |
| H | -4.557600000 | 0.854742000 | -2.945661000 |
| H | -3.071677000 | -0.061073000 | -3.289064000 |
| C | -3.622073000 | -1.996577000 | 1.750145000 |
| H | -3.145199000 | -2.916190000 | 1.381198000 |
| H | -4.693507000 | -2.218868000 | 1.907435000 |
| H | -3.182141000 | -1.772051000 | 2.732238000 |
| C | 3.403668000 | 0.532306000 | -1.127318000 |
| C | 3.441243000 | -0.963232000 | 0.649517000 |
| C | 3.356019000 | 1.283416000 | 0.094898000 |
| C | -3.623449000 | -2.228879000 | -1.437799000 |
| H | -3.088382000 | -2.189898000 | -2.397749000 |
| H | -4.692185000 | -2.404115000 | -1.659702000 |
| H | -3.252955000 | -3.107102000 | -0.890310000 |
|  |  |  |  |


|  |  |  |  |
| :--- | ---: | ---: | :---: |
| C | 3.396335000 | 0.358797000 | 1.192136000 |
| C | -3.396349000 | 0.358058000 | -1.192332000 |
| C | 3.435440000 | 2.779384000 | 0.199160000 |
| H | 2.854727000 | 3.271860000 | -0.594281000 |
| H | 4.481966000 | 3.125057000 | 0.112395000 |
| C | 3.442809000 | -0.856893000 | -0.788358000 |
| C | 3.621980000 | -1.997764000 | -1.748792000 |
| H | 3.144427000 | -2.916916000 | -1.379565000 |
| H | 4.693382000 | -2.220698000 | -1.905378000 |
| H | 3.182699000 | -1.773585000 | -2.731256000 |
| C | -3.435369000 | 2.779283000 | -0.200892000 |
| H | -2.854679000 | 3.272229000 | 0.592274000 |
| H | -4.481892000 | 3.125023000 | -0.114368000 |
| H | -3.044179000 | 3.137938000 | -1.163296000 |
| C | 3.623304000 | -2.228028000 | 1.439208000 |
| H | 3.088360000 | -2.188402000 | 2.399201000 |
| H | 4.692044000 | -2.403288000 | 1.661076000 |
| H | 3.252611000 | -3.106515000 | 0.892273000 |
| C | 3.536143000 | 1.115399000 | -2.504853000 |
| H | 3.174805000 | 0.420573000 | -3.276651000 |
| H | 4.593314000 | 1.344316000 | -2.735412000 |
| H | 2.963227000 | 2.048369000 | -2.606582000 |
| C | -3.441319000 | -0.963619000 | -0.648859000 |
| C | 3.501849000 | 0.721147000 | 2.644907000 |
| H | 2.971140000 | 1.658920000 | 2.863282000 |
| H | 4.557642000 | 0.856447000 | 2.945147000 |
| H | 3.071592000 | -0.058941000 | 3.289137000 |

## $\left[\left({ }^{\mathrm{Me}} \mathrm{NHC}\right)_{2} \mathrm{As}\right]^{+}$



Table S19. Optimized geometries of $\left[\left({ }^{(N e N H C}\right)_{2} A s\right]^{+}$. XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.

| As | 1.763677000 | 11.019196000 | 11.519128000 | H | -1.112027000 | 7.776916000 | 10.595233000 |
| :--- | ---: | ---: | :--- | :--- | :--- | :--- | :--- |
| N | 0.582815000 | 9.755165000 | 13.896108000 | C | 4.837129000 | 6.879386000 | 9.529576000 |
| N | 0.040877000 | 8.622340000 | 12.125432000 | H | 5.732867000 | 6.980096000 | 10.164688000 |
| N | 2.92886000 | 9.977513000 | 9.017245000 | H | 5.176659000 | 6.637739000 | 8.514301000 |
| N | 3.400528000 | 8.641535000 | 10.654249000 | H | 4.258445000 | 6.019458000 | 9.904060000 |
| C | 2.706844000 | 9.770658000 | 10.346638000 | C | -0.675738000 | 8.567426000 | 15.744920000 |
| C | -0.269949000 | 8.736854000 | 14.319776000 | H | 0.188895000 | 8.360280000 | 16.396765000 |
| C | 0.773958000 | 9.686085000 | 12.551785000 | H | -1.376019000 | 7.728092000 | 15.843654000 |
| C | -0.599478000 | 8.010791000 | 13.204715000 | H | -1.175593000 | 9.469574000 | 16.133404000 |
| C | 4.020654000 | 8.127517000 | 9.514025000 | C | 3.540561000 | 8.080845000 | 11.990215000 |
| C | 3.719464000 | 8.981014000 | 8.484485000 | H | 3.471992000 | 8.896123000 | 12.721869000 |
| C | -1.460081000 | 6.801668000 | 13.056107000 | H | 4.519315000 | 7.595026000 | 12.082036000 |
| H | -2.350419000 | 7.002356000 | 12.437334000 | H | 2.754681000 | 7.339939000 | 12.201562000 |
| H | -1.809994000 | 6.464141000 | 14.040023000 | C | 2.351584000 | 11.083929000 | 8.246388000 |
| H | -0.911838000 | 5.967031000 | 12.589843000 | H | 1.492398000 | 11.495961000 | 8.792522000 |
| C | 4.121701000 | 8.952011000 | 7.048598000 | H | 2.021383000 | 10.723730000 | 7.263509000 |
| H | 3.251490000 | 8.847476000 | 6.379861000 | H | 3.101160000 | 11.877138000 | 8.105509000 |
| H | 4.791733000 | 8.103755000 | 6.858491000 | C | 1.171738000 | 10.751607000 | 14.780744000 |
| H | 4.654223000 | 9.872387000 | 6.758813000 | H | 1.486406000 | 10.276061000 | 15.718650000 |
| C | -0.116650000 | 8.214563000 | 10.737020000 | H | 0.450873000 | 11.551556000 | 15.007299000 |
| H | 0.642541000 | 7.473099000 | 10.445342000 | H | 2.046513000 | 11.188777000 | 14.280850000 |
| H | -0.017503000 | 9.101084000 | 10.097530000 |  |  |  |  |

## $\left[\left({ }^{\text {e }} \mathrm{NHC}\right)_{2} \mathrm{P}\right]^{+}$



Table S20. Optimized geometries of $\left[\left({ }^{\mathrm{Me}} \mathrm{NHC}\right)_{2} \mathrm{P}\right]^{+}$. XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.

| P | -5.879805000 | 0.070211000 | -0.250002000 |
| :--- | ---: | ---: | ---: |
| N | -3.645570000 | -1.713221000 | -0.680222000 |
| N | -5.149598000 | -2.478426000 | 0.690901000 |
| N | -3.615130000 | 1.592073000 | 0.705299000 |
| N | -4.666547000 | 2.505822000 | -0.964187000 |
| C | -3.244317000 | -3.000645000 | -0.318759000 |
| C | -4.810573000 | -1.387669000 | -0.051233000 |
| C | -4.633983000 | 1.393484000 | -0.178636000 |
| C | -4.202961000 | -3.488638000 | 0.530634000 |
| C | -2.997085000 | 2.820211000 | 0.462794000 |
| C | -3.672843000 | 3.403207000 | -0.577434000 |
| C | -6.333723000 | -2.587255000 | 1.531658000 |
| H | -6.700398000 | -1.575574000 | 1.749928000 |
| H | -6.077100000 | -3.094742000 | 2.470513000 |
| H | -7.127778000 | -3.153149000 | 1.021588000 |
| C | -3.283156000 | 0.703756000 | 1.808978000 |
| H | -4.204131000 | 0.224019000 | 2.165441000 |
| H | -2.843291000 | 1.287185000 | 2.626160000 |
| H | -2.567370000 | -0.074094000 | 1.503572000 |
| C | -2.969756000 | -0.883490000 | -1.666243000 |
| H | -2.259177000 | -0.188489000 | -1.194305000 |
| H | -3.723244000 | -0.306493000 | -2.218275000 |

## $\left[\left(\mathrm{Cp}^{*} \mathrm{~V}_{2} \mathrm{P}_{4} \mathrm{NHC}\right]\right.$



Table S21. Optimized geometries of $\left[\left(\mathrm{Cp}^{*} \mathrm{~V}\right)_{2}\left(\mu, \eta^{3: 3}-\mathrm{P}_{3}\right)\left(\mu-\mathrm{P}\left({ }^{\mathrm{Me}} \mathrm{NHC}\right)\right](8)\right.$. XYZ coordinated in angstroms. B3LYP/def2SVP level of theory.

| V | -1.084499000 | 1.219329000 | -0.084773000 |
| :--- | ---: | ---: | ---: |
| V | -0.800036000 | -1.376263000 | -0.075779000 |
| P | 0.867842000 | 0.109888000 | -0.715105000 |
| P | -2.186413000 | -0.232739000 | -1.612908000 |
| P | -1.507429000 | -0.150168000 | 1.781257000 |
| P | -3.144425000 | -0.279279000 | 0.326376000 |
| N | 3.650851000 | 0.311771000 | -1.119652000 |
| N | 3.174429000 | 0.310090000 | 0.997615000 |
| C | 2.610443000 | 0.249894000 | -0.240678000 |
| C | -0.122091000 | 3.303033000 | -0.076305000 |
| C | -0.891672000 | 3.187201000 | 1.125860000 |
| C | -1.593442000 | -3.426437000 | 0.728728000 |
| C | -0.243404000 | -3.255671000 | 1.165825000 |
| C | -2.352048000 | 3.112382000 | -0.675116000 |
| C | -1.031397000 | 3.257384000 | -1.187776000 |
| C | -2.265434000 | 3.062489000 | 0.755648000 |
| C | 3.535547000 | 0.280766000 | -2.570868000 |
| H | 4.085919000 | -0.579415000 | -2.978445000 |
| H | 3.939866000 | 1.206289000 | -3.005664000 |
| H | 2.473855000 | 0.189847000 | -2.831546000 |
| C | 2.455913000 | 0.278375000 | 2.262119000 |
| H | 1.383875000 | 0.207461000 | 2.049688000 |
| H | 2.657612000 | 1.193694000 | 2.836921000 |
| H | 2.769583000 | -0.591505000 | 2.857123000 |
| C | 0.591389000 | -3.209898000 | 0.003759000 |
| C | -1.596210000 | -3.498928000 | -0.703326000 |
| C | 1.341554000 | 3.634779000 | -0.152929000 |
| H | 1.903535000 | 3.205862000 | 0.689547000 |
| H | 1.500579000 | 4.728732000 | -0.127339000 |
| H | 1.799192000 | 3.258944000 | -1.079472000 |
| C | -0.250038000 | -3.363361000 | -1.149753000 |
| C | 4.560817000 | 0.406957000 | 0.898182000 |
| C | 4.861345000 | 0.407889000 | -0.439461000 |
| C | 0.223969000 | -3.283217000 | 2.593259000 |
| H | 1.175421000 | -2.746895000 | 2.723336000 |
| H | 0.387101000 | -4.321230000 | 2.937190000 |
| H | -0.509730000 | -2.821847000 | 3.270429000 |
| C | -3.427619000 | 3.042153000 | 1.705326000 |
| H | -4.310639000 | 2.565260000 | 1.256843000 |
|  |  |  |  |

$\left.\begin{array}{lrrr} & & -3.714864000 & 4.070063000\end{array}\right) 1.993716000$ H

## $\left[\left(\mathrm{Cp}^{*}\right)_{2}\left(\mu, \eta^{6: 6}-\mathrm{P}_{6}\right)\right]$



Table S22. Optimized geometries of $\left[\left(C p^{*} V_{2}\right)_{2}\left(\mu, \eta^{6: 6-P} P_{6}\right)\right]^{-}(6)$. XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.

| V | 1.291735000 | -0.008207000 | 0.000920000 | H | -3.003386000 | 3.292575000 | 0.111533000 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| V | -1.293452000 | -0.000015000 | 0.010356000 | H | -4.494176000 | 2.902832000 | -0.776220000 |
| C | 3.261616000 | 0.970787000 | -0.747557000 | H | -2.921458000 | 2.868439000 | -1.604426000 |
| C | -3.274668000 | 0.090245000 | -1.217442000 | C | 3.388797000 | 2.161770000 | -1.653342000 |
| C | 3.278295000 | -0.400093000 | -1.154294000 | H | 2.971199000 | 1.960610000 | -2.650539000 |
| C | -3.278996000 | 1.181829000 | -0.293838000 | H | 4.448873000 | 2.447511000 | -1.788694000 |
| C | 3.266925000 | 1.007873000 | 0.683254000 | H | 2.859633000 | 3.039063000 | -1.251253000 |
| C | 3.287334000 | -0.339727000 | 1.160772000 | C | 3.438006000 | -0.754909000 | 2.596228000 |
| C | -3.397103000 | 0.195539000 | -2.710207000 | H | 2.888244000 | -0.084446000 | 3.273465000 |
| H | -2.978153000 | 1.140334000 | -3.086083000 | H | 4.499940000 | -0.741190000 | 2.906181000 |
| H | -4.455559000 | 0.151097000 | -3.028857000 | H | 3.058055000 | -1.772180000 | 2.768740000 |
| H | -2.864131000 | -0.621098000 | -3.219658000 | C | -3.440596000 | 1.426989000 | 2.302146000 |
| C | -3.282641000 | 0.640782000 | 1.031891000 | H | -2.965704000 | 0.921974000 | 3.155925000 |
| C | 3.295477000 | -1.210320000 | 0.025291000 | H | -4.508823000 | 1.568394000 | 2.553053000 |
| C | -3.281957000 | -0.786185000 | 0.925349000 | H | -2.986682000 | 2.425841000 | 2.224787000 |
| C | -3.276810000 | -1.125214000 | -0.465383000 | C | -3.414377000 | -2.506125000 | -1.039191000 |
| C | 3.399331000 | 2.242756000 | 1.526857000 | H | -2.866081000 | -2.608936000 | -1.987647000 |
| H | 2.874151000 | 3.100029000 | 1.079602000 | H | -4.474577000 | -2.749308000 | -1.240663000 |
| H | 4.460626000 | 2.530057000 | 1.648569000 | H | -3.023963000 | -3.272509000 | -0.353774000 |
| H | 2.979892000 | 2.094130000 | 2.532541000 | C | -3.437751000 | -1.756968000 | 2.060714000 |
| C | 3.474093000 | -2.701780000 | 0.063720000 | H | -2.893889000 | -2.694827000 | 1.874020000 |
| H | 3.023058000 | -3.146969000 | 0.962365000 | H | -4.501333000 | -2.017286000 | 2.218597000 |
| H | 4.547292000 | -2.971183000 | 0.066511000 | H | -3.056906000 | -1.343833000 | 3.005788000 |
| H | 3.015846000 | -3.192734000 | -0.806983000 | P | -0.010680000 | -1.145745000 | -1.804381000 |
| C | 3.417244000 | -0.890837000 | -2.566859000 | P | -0.005092000 | 1.141400000 | -1.802664000 |
| H | 3.019278000 | -1.908933000 | -2.686279000 | P | 0.009958000 | 1.133410000 | 1.820795000 |
| H | 4.478032000 | -0.911293000 | -2.880517000 | P | 0.012359000 | 2.296691000 | 0.011023000 |
| H | 2.876057000 | -0.246496000 | -3.275431000 | P | 0.004718000 | -1.149182000 | 1.819174000 |
| C | -3.428202000 | 2.631483000 | -0.657386000 | P | -0.006592000 | -2.305770000 | 0.007497000 |

## $\left[\left(C p^{*} \mathrm{~V}\right)_{2}\left(\mu, \eta^{5: 5}-\mathrm{P}_{5}\right)\right]^{-}$

The DFT calculations reveal that the ground state in the gas phase possess a bent $\mathrm{P}_{5}$ ligand independent on the used functional (B3LYP, BP86, PBE, PBE1PBE, wB97XD). All used functionals deliver almost the same results. The calculations result in a bent middle deck with a dihedral angle between 138 and $151{ }^{\circ}$, while the structure in the solid state reveals an almost planar middle deck (dihedral angle of approx. $174^{\circ}$ ). The $\mathrm{V}-\mathrm{V}$ distances are compared to the structure in the solid state a bit elongated. Further, packing effects can explain the structure in the solid state, especially since $\mathbf{7}$ co-crystallizes with complex 6 , which is bearing a planar cyclo- $\mathrm{P}_{6}$ middle deck.

| fuctional | spin state | total energy [Ha] | dihedral angle [ ${ }^{\circ}$ ] $P_{5}$ ligand | V-V distance [Å] | energy difference singlet triplet [Ha] | energy <br> difference singlet triplet [kJ/mol] |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| structure in the solid state |  |  | 174 | 2.676 |  |  |
| $\begin{aligned} & \text { B3LYP } \\ & \text { B3LYP } \end{aligned}$ | singlet <br> triplet | $\begin{aligned} & -4374.0779531 \\ & -4374.0836442 \end{aligned}$ | $\begin{aligned} & 140 \\ & 138 \end{aligned}$ | $\begin{aligned} & 2.77 \\ & 2.86 \end{aligned}$ | 0.0056911 | 14.94 |
| $\begin{aligned} & \text { BP86 } \\ & \text { BP86 } \end{aligned}$ | singlet <br> triplet | $\begin{aligned} & -4374.5087424 \\ & -4374.5045868 \end{aligned}$ | $\begin{aligned} & 147 \\ & 147 \end{aligned}$ | $\begin{aligned} & 2.77 \\ & 2.74 \end{aligned}$ | -0.0041556 | -11.53 |
| $\begin{aligned} & \hline \text { PBE } \\ & \text { PBE } \end{aligned}$ | singlet triplet | $\begin{aligned} & \hline-4371.8195033 \\ & -4371.8151127 \end{aligned}$ | $\begin{aligned} & \hline 151 \\ & 149 \end{aligned}$ | $\begin{aligned} & \hline 2.76 \\ & 2.74 \end{aligned}$ | -0.0043906 | -11.53 |
| PBE1PBE PBE1PBE | singlet triplet | $\begin{aligned} & \hline-4372.0434891 \\ & -4372.0507890 \end{aligned}$ | $\begin{aligned} & 147 \\ & 147 \end{aligned}$ | $\begin{aligned} & \hline 2.72 \\ & 2.82 \end{aligned}$ | 0.0072999 | 19.17 |
| $\begin{aligned} & \text { wB97XD } \\ & \text { wB97XD } \end{aligned}$ | singlet <br> triplet | $\begin{aligned} & -4373.7603244 \\ & -4373.7675124 \end{aligned}$ | $\begin{aligned} & 146 \\ & 144 \end{aligned}$ | $\begin{aligned} & \hline 2.72 \\ & 2.83 \end{aligned}$ | 0.0071880 | 18.87 |



Table S23. Optimized geometries of $\left[\left(C p^{*} V\right)_{2}\left(\mu, \eta^{5: 5}-P_{5}\right)\right]^{-}$(anion in 7) (singlet). XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.

|  |  |  |  |
| :--- | ---: | ---: | ---: |
| V | -1.387533000 | 0.015509000 | -0.034075000 |
| V | 1.383325000 | 0.005699000 | -0.029426000 |
| C | -3.260286000 | -0.248672000 | 1.359841000 |
| C | 3.297751000 | -1.146591000 | 0.654680000 |
| C | -3.348173000 | -1.219605000 | 0.317075000 |
| C | 3.211260000 | 0.065231000 | 1.411968000 |
| C | -3.303977000 | 1.048634000 | 0.759155000 |
| C | -3.430873000 | 0.876807000 | -0.659661000 |
| C | 3.357438000 | -2.538315000 | 1.215436000 |
| H | 2.800758000 | -2.619523000 | 2.160253000 |
| H | 4.401128000 | -2.845403000 | 1.415627000 |
| H | 2.925408000 | -3.276320000 | 0.523051000 |
| C | 3.335683000 | 1.167710000 | 0.508833000 |
| C | -3.449022000 | -0.526499000 | -0.932267000 |
| C | 3.484135000 | 0.636986000 | -0.810618000 |
| C | 3.458598000 | -0.791383000 | -0.719944000 |
| C | -3.375634000 | 2.359960000 | 1.487127000 |
| H | -2.872641000 | 2.311205000 | 2.463544000 |
| H | -4.424764000 | 2.661110000 | 1.666971000 |
| H | -2.895022000 | 3.168614000 | 0.916380000 |
| C | -3.660004000 | -1.156659000 | -2.280118000 |
| H | -3.208837000 | -0.556314000 | -3.084529000 |
| H | -4.736225000 | -1.259302000 | -2.513428000 |
| H | -3.212943000 | -2.160023000 | -2.333352000 |
| P | 0.443165000 | 0.069794000 | -2.105938000 |
| C | -3.427926000 | -2.705735000 | 0.514751000 |
| H | -3.090821000 | -3.253491000 | -0.377168000 |
| H | -4.465442000 | -3.023629000 | 0.727885000 |
| H | -2.802237000 | -3.036368000 | 1.357167000 |


|  |  |  |  |
| :--- | ---: | ---: | ---: |
| C | 3.123365000 | 0.158573000 | 2.908047000 |
| H | 2.630830000 | 1.088997000 | 3.226542000 |
| H | 4.127159000 | 0.138423000 | 3.373108000 |
| H | 2.548734000 | -0.678421000 | 3.331972000 |
| C | -3.242683000 | -0.543160000 | 2.832891000 |
| H | -2.744423000 | -1.499979000 | 3.045747000 |
| H | -4.269225000 | -0.605421000 | 3.240895000 |
| H | -2.712548000 | 0.236477000 | 3.399345000 |
| C | -3.690359000 | 1.971501000 | -1.655797000 |
| H | -3.190188000 | 2.908573000 | -1.371536000 |
| H | -4.773096000 | 2.183301000 | -1.738437000 |
| H | -3.333959000 | 1.705381000 | -2.662105000 |
| C | 3.427621000 | 2.617315000 | 0.890181000 |
| H | 3.095265000 | 3.273750000 | 0.072350000 |
| H | 4.466777000 | 2.902906000 | 1.139623000 |
| H | 2.802053000 | 2.848024000 | 1.765090000 |
| C | 3.663800000 | -1.753522000 | -1.855269000 |
| H | 3.125162000 | -2.698381000 | -1.689007000 |
| H | 4.733382000 | -2.002914000 | -1.985508000 |
| H | 3.305720000 | -1.338278000 | -2.809107000 |
| C | 3.748131000 | 1.441210000 | -2.051730000 |
| H | 3.460457000 | 0.892442000 | -2.960444000 |
| H | 4.820681000 | 1.69213000 | -2.144955000 |
| H | 3.188678000 | 2.388985000 | -2.051925000 |
| P | -0.240067000 | -1.845994000 | -1.084123000 |
| P | 0.037332000 | -1.479539000 | 1.109604000 |
| P | 0.054108000 | 1.440067000 | 1.189961000 |
| P | -0.235614000 | 1.927731000 | -0.976905000 |



Table S24. Optimized geometries of $\left[\left(C p^{*} V\right)_{2}\left(\mu, \eta^{5.5}-P_{5}\right)\right]^{-}$(anion in 7) (triplet). XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.

| V | -1.438125000 | 0.000094000 | -0.034385000 |
| :--- | ---: | ---: | :---: |
| V | 1.418194000 | -0.000418000 | -0.038721000 |
| C | -3.218973000 | -0.078291000 | 1.441135000 |
| C | 3.313415000 | -0.946340000 | 0.960582000 |
| C | -3.341124000 | -1.183472000 | 0.540774000 |
| C | 3.252694000 | 0.433279000 | 1.332735000 |
| C | -3.329447000 | 1.126764000 | 0.677389000 |
| C | -3.518700000 | 0.764501000 | -0.697809000 |
| C | 3.383626000 | -2.111823000 | 1.904910000 |
| H | 2.862749000 | -1.901777000 | 2.850254000 |
| H | 4.433928000 | -2.356735000 | 2.151548000 |
| H | 2.923729000 | -3.014960000 | 1.477861000 |
| C | 3.380235000 | 1.216807000 | 0.141802000 |
| C | -3.526780000 | -0.661272000 | -0.781530000 |
| C | 3.519778000 | 0.324037000 | -0.967669000 |
| C | 3.468874000 | -1.012257000 | -0.460419000 |
| C | -3.382734000 | 2.523046000 | 1.227997000 |
| H | -2.845704000 | 2.603317000 | 2.183415000 |
| H | -4.427579000 | 2.840682000 | 1.403759000 |
| H | -2.929420000 | 3.251999000 | 0.539606000 |
| C | -3.808015000 | -1.463435000 | -2.020760000 |
| H | -3.423883000 | -0.965815000 | -2.924128000 |
| H | -4.895074000 | -1.608020000 | -2.166091000 |
| H | -3.345873000 | -2.460386000 | -1.975613000 |
| C | -3.394266000 | -2.633679000 | 0.926911000 |
| H | -2.983705000 | -3.280477000 | 0.137080000 |
| H | -4.434984000 | -2.958834000 | 1.112826000 |
| H | -2.815866000 | -2.830419000 | 1.840939000 |
| C | 3.216965000 | 0.963995000 | 2.736664000 |
|  |  |  |  |


|  |  |  |  |
| :--- | ---: | ---: | ---: |
| H | 2.703829000 | 1.935003000 | 2.789891000 |
| H | 4.238786000 | 1.102916000 | 3.137212000 |
| C | 2.691773000 | 0.277792000 | 3.417493000 |
| H | -2.086817000 | -0.172154000 | 2.934882000 |
| H | -4.075633000 | -0.240148000 | 3.232215000 |
| H | -2.573359000 | 0.707220000 | 3.350548000 |
| C | -3.792328000 | 1.709386000 | -1.833965000 |
| H | -3.382424000 | 2.710138000 | -1.636143000 |
| H | -4.878806000 | 1.823400000 | -2.007930000 |
| H | -3.346197000 | 1.355822000 | -2.775989000 |
| C | 3.481943000 | 2.714661000 | 0.080000000 |
| H | 3.091698000 | 3.113421000 | -0.868269000 |
| H | 4.533882000 | 3.045210000 | 0.166334000 |
| H | 2.916477000 | 3.193292000 | 0.892442000 |
| C | 3.648750000 | -2.268330000 | -1.265395000 |
| H | 3.102907000 | -3.116119000 | -0.826208000 |
| H | 4.714586000 | -2.557822000 | -1.321377000 |
| H | 3.288437000 | -2.147451000 | -2.297587000 |
| C | 3.814139000 | 0.727152000 | -2.384705000 |
| H | 3.498264000 | -0.044154000 | -3.101884000 |
| H | 4.897425000 | 0.893467000 | -2.533762000 |
| H | 3.300420000 | 1.660292000 | -2.661257000 |
| P | -0.292640000 | -1.887211000 | -1.092580000 |
| P | 0.101552000 | -1.603847000 | 1.046385000 |
| P | 0.106383000 | 1.583516000 | 1.077268000 |
| P | -0.290311000 | 1.904717000 | -1.056034000 |
| P | 0.350915000 | 0.016172000 | -2.127884000 |
|  |  |  |  |

## [ $\left.\mathrm{Cp}{ }^{\prime \prime}{ }^{\prime} \mathrm{Co}\left(\eta^{4}-\mathrm{P}_{4}\right)\right]$



Table S25. Optimized geometries of [Cp" $\left.{ }^{\prime \prime} \mathrm{Co}\left(\eta^{4}-\mathrm{P}_{4}\right)\right]$ (1). XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.

| Co | -0.419784000 | -0.554453000 | -0.016443000 |
| :--- | ---: | :---: | :---: |
| P | -2.395830000 | -1.784752000 | 0.364434000 |
| P | -0.571900000 | -2.441910000 | 1.372582000 |
| P | 0.410418000 | -2.677648000 | -0.572985000 |
| P | -1.413695000 | -1.998807000 | -1.578773000 |
| C | -1.091836000 | 1.429210000 | 0.083280000 |
| C | -0.277870000 | 1.084020000 | 1.201595000 |
| C | 1.046501000 | 0.701290000 | 0.779740000 |
| C | 1.046481000 | 0.781943000 | -0.685786000 |
| C | -0.275502000 | 1.212569000 | -1.063191000 |
| C | -2.463678000 | 2.094781000 | 0.107301000 |
| C | -2.206282000 | 3.618478000 | -0.021249000 |
| C | -3.340793000 | 1.635593000 | -1.072747000 |
| C | -3.202109000 | 1.826163000 | 1.431142000 |
| C | 2.161786000 | 0.460573000 | 1.825783000 |
| C | 1.594893000 | 0.610769000 | 3.257255000 |
| C | 2.800992000 | -0.943618000 | 1.763055000 |
| C | 3.243382000 | 1.556043000 | 1.662442000 |
| C | 2.136915000 | 0.718858000 | -1.781078000 |
| C | 2.673362000 | 2.164198000 | -1.958070000 |
| C | 3.318959000 | -0.229044000 | -1.514739000 |
| C | 1.524270000 | 0.274247000 | -3.131889000 |
| H | -0.611758000 | 1.112305000 | 2.232903000 |
| H | -0.601717000 | 1.365772000 | -2.086897000 |
| H | -1.573450000 | 3.985936000 | 0.801914000 |
| H | -3.161032000 | 4.167767000 | 0.010436000 |


| -1.704279000 | 3.861414000 | -0.970937000 |
| :---: | :---: | :---: |
| -2.858203000 | 1.825199000 | -2.043867000 |
| -4.295087000 | 2.185678000 | -1.066589000 |
| -3.567574000 | 0.561072000 | -1.006299000 |
| -3.369076000 | 0.749417000 | 1.584624000 |
| -4.183313000 | 2.326168000 | 1.418950000 |
| -2.645841000 | 2.218362000 | 2.296749000 |
| 1.207321000 | 1.622826000 | 3.448990000 |
| 2.401142000 | 0.424301000 | 3.982991000 |
| 0.794775000 | -0.117099000 | 3.458804000 |
| 2.069932000 | -1.710398000 | 2.060173000 |
| 3.644522000 | -0.994989000 | 2.470568000 |
| 3.178089000 | -1.205451000 | 0.771119000 |
| 3.795545000 | 1.468717000 | 0.718680000 |
| 3.975817000 | 1.480898000 | 2.481854000 |
| 2.795283000 | 2.561585000 | 1.702130000 |
| 3.147372000 | 2.541518000 | -1.040892000 |
| 1.862683000 | 2.858612000 | -2.228334000 |
| 3.424850000 | 2.189730000 | -2.763683000 |
| 3.990641000 | -0.213712000 | -2.387160000 |
| 2.975445000 | -1.264186000 | -1.373926000 |
| 3.920103000 | 0.063687000 | -0.646357000 |
| 2.321430000 | 0.214585000 | -3.888442000 |
| 0.773402000 | 0.978643000 | -3.516427000 |
| 1.055424000 | -0.717816000 | -3.053045000 |

## $\left[\left(\mathrm{Cp}^{*} \mathrm{Mo}_{2}\right)_{2}\left(\mu, \eta^{6: 6-\mathrm{As}} \mathbf{6}\right)\right]$



Table S26. Optimized geometries of $\left[\left(\mathrm{Cp}^{*} \mathrm{Mo}_{2}\left(\mu, \eta^{6: 6-} \mathrm{As}_{6}\right]\right.\right.$ (3b). XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.

| Mo | -1.344576000 | -0.002684000 | -0.004509000 |
| :--- | ---: | ---: | :---: |
| Mo | 1.344442000 | 0.000633000 | -0.004295000 |
| As | 0.001652000 | -1.326920000 | -2.004341000 |
| As | 0.000224000 | -2.397260000 | 0.146579000 |
| As | 0.000176000 | -1.070432000 | 2.149758000 |
| As | -0.000442000 | 1.328809000 | 2.000986000 |
| As | -0.002969000 | 2.399616000 | -0.149213000 |
| As | 0.002091000 | 1.071556000 | -2.151398000 |
| C | -3.377971000 | -0.658359000 | -1.029700000 |
| C | -3.374596000 | -1.183818000 | 0.307525000 |
| C | -3.369621000 | -0.074697000 | 1.220189000 |
| C | -3.370012000 | 1.135558000 | 0.447581000 |
| C | -3.375259000 | 0.775429000 | -0.942664000 |
| C | -3.573207000 | -1.460149000 | -2.284080000 |
| C | -3.544617000 | 2.522267000 | 0.994006000 |
| C | -3.564623000 | 1.727907000 | -2.087291000 |
| C | 3.379232000 | -0.824916000 | -0.899189000 |
| C | 3.369481000 | -1.113359000 | 0.507737000 |
| C | 3.366479000 | 0.135421000 | 1.217142000 |
| C | 3.371689000 | 1.196306000 | 0.248763000 |
| C | 3.380383000 | 0.602488000 | -1.059447000 |
| C | 3.571153000 | -1.834503000 | -1.993619000 |
| C | 3.541637000 | -2.468904000 | 1.128828000 |
| C | 3.537753000 | 0.298678000 | 2.699262000 |
| C | 3.575756000 | 1.339568000 | -2.352763000 |
| H | -3.119793000 | -0.972088000 | -3.157935000 |
| H | -4.651037000 | -1.581614000 | -2.494172000 |
| H | -3.138280000 | -2.465779000 | -2.199514000 |
| H | -3.077619000 | 2.634002000 | 1.982827000 |


|  |  |  |  |
| :--- | ---: | ---: | ---: |
| H | -4.618388000 | 2.756736000 | 1.104711000 |
| H | -3.105809000 | 3.281397000 | 0.331099000 |
| H | -3.178845000 | 1.316755000 | -3.030297000 |
| H | -3.059978000 | 2.688033000 | -1.909507000 |
| H | -4.639080000 | 1.939962000 | -2.232284000 |
| H | 3.171691000 | -1.479802000 | -2.953789000 |
| H | 3.081245000 | -2.790155000 | -1.759959000 |
| H | 4.647057000 | -2.040176000 | -2.137271000 |
| H | 3.116696000 | -3.264181000 | 0.500318000 |
| H | 3.059337000 | -2.530409000 | 2.114677000 |
| H | 4.614472000 | -2.691911000 | 1.268695000 |
| H | 3.053608000 | -0.514048000 | 3.259002000 |
| H | 3.114505000 | 1.247513000 | 3.057665000 |
| H | 4.610394000 | 0.291497000 | 2.962875000 |
| H | 3.144287000 | 0.795171000 | -3.204091000 |
| H | 4.653496000 | 1.472406000 | -2.556127000 |
| H | 3.118937000 | 2.338665000 | -2.328138000 |
| C | 3.554974000 | 2.655058000 | 0.552369000 |
| H | 3.084334000 | 2.937595000 | 1.504616000 |
| H | 4.630327000 | 2.896102000 | 0.629266000 |
| H | 3.127672000 | 3.294185000 | -0.232901000 |
| C | -3.554782000 | -2.625026000 | 0.687586000 |
| H | -3.128036000 | -3.304030000 | -0.063677000 |
| H | -3.080312000 | -2.855201000 | 1.651820000 |
| H | -4.629247000 | -2.864130000 | 0.780594000 |
| C | -3.545846000 | -0.159146000 | 2.708124000 |
| H | -3.133361000 | -1.092032000 | 3.117099000 |
| H | -3.055725000 | 0.677323000 | 3.226136000 |
| H | -4.619145000 | -0.127613000 | 2.967592000 |
|  |  |  |  |

$\left[\left(\mathrm{Cp}^{*} \mathrm{Mo}\right)_{2}\left(\mu, \boldsymbol{\eta}^{\left.\left.6: 6-\mathrm{P}_{6}\right)\right]}\right.\right.$


Table S27. Optimized geometries of $\left[\left(C p^{*} \mathrm{Mo}_{2}\left(\mu, \eta^{6: 6-} \mathrm{P}_{6}\right)\right]\right.$ (3a). XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.

| Mo | 0.337640000 | 0.606495000 | 1.145919000 | H | 3.428745000 | 3.439148000 | 2.519571000 |
| :--- | ---: | :---: | :---: | ---: | ---: | ---: | ---: |
| P | -1.985711000 | -0.505227000 | 0.848683000 | H | 3.758949000 | 2.090429000 | 1.409510000 |
| P | -1.701375000 | 1.399818000 | -0.251654000 | C | 0.113711000 | -0.592927000 | 4.411501000 |
| P | 0.284383000 | 1.904472000 | -1.101251000 | H | 0.702374000 | -1.499032000 | 4.211873000 |
| C | 1.790806000 | 2.061310000 | 2.311761000 | H | 0.283752000 | -0.312043000 | 5.466137000 |
| C | 0.500552000 | 0.539512000 | 3.504608000 | H | -0.948541000 | -0.855573000 | 4.308631000 |
| C | 1.815833000 | 0.792252000 | 2.984868000 | C | 0.025875000 | 3.964145000 | 1.987161000 |
| C | 0.460760000 | 2.593655000 | 2.418056000 | H | -1.042169000 | 3.990975000 | 1.729318000 |
| C | -0.336912000 | 1.652990000 | 3.154016000 | H | 0.189459000 | 4.691646000 | 2.801785000 |
| C | 3.038668000 | -0.037897000 | 3.249974000 | H | 0.589022000 | 4.315379000 | 1.111133000 |
| H | -3.778791000 | -0.053989000 | -2.442760000 | H | -2.289311000 | 0.923216000 |  |
| H | 3.526139000 | 0.286968000 | 4.186332000 | H | -1.754560000 | 2.383871000 | 4.73565900 |
| H | 2.793988000 | -1.103922000 | 3.357108000 | H | -2.315704000 | 2.495253000 | 2.914442000 |
| C | 2.979581000 | 2.786064000 | 1.750448000 |  |  |  |  |

$\left[\left(C p^{*}\right)_{2}\left(\mu, \eta^{6: 6}-P_{6}\right)\right]$


Table S28. Optimized geometries of $\left[\left(C p^{*} \mathrm{~V}\right)_{2}\left(\mu, \eta^{6: 6}-\mathrm{P}_{6}\right)\right](5)$. XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.

| V | 1.297283000 | -0.003800000 | -0.005364000 |
| :--- | ---: | ---: | ---: |
| V | -1.297246000 | 0.003698000 | -0.005315000 |
| P | 0.084996000 | 1.162443000 | -1.766185000 |
| P | -0.085064000 | -1.16146000 | -1.766592000 |
| P | 0.083863000 | -2.365463000 | -0.017424000 |
| P | -0.082486000 | -1.170380000 | 1.738510000 |
| P | 0.082546000 | 1.169622000 | 1.738899000 |
| P | -0.083966000 | 2.365341000 | -0.016606000 |
| C | 3.267147000 | 0.251774000 | 1.200325000 |
| C | 3.247182000 | -1.056111000 | 0.624029000 |
| C | 3.249794000 | -0.912613000 | -0.804116000 |
| C | 3.273340000 | 0.485267000 | -1.106704000 |
| C | 3.277453000 | 1.203516000 | 0.132271000 |
| C | 3.411696000 | 0.557716000 | 2.662642000 |
| H | 4.476496000 | 0.540849000 | 2.956835000 |
| C | 3.386616000 | -2.344825000 | 1.381243000 |
| C | 3.389968000 | -2.029137000 | -1.797648000 |
| C | 3.445155000 | 1.083007000 | -2.472877000 |
| C | 3.428988000 | 2.689611000 | 0.282982000 |
| C | -3.277660000 | -1.203743000 | 0.129202000 |
| C | -3.273544000 | -0.482331000 | -1.107906000 |
| C | -3.249641000 | 0.914755000 | -0.801748000 |
| C | -3.246870000 | 1.054621000 | 0.626768000 |
| C | -3.267076000 | -0.254737000 | 1.199700000 |
| C | -3.429456000 | -2.69019000 | 0.276224000 |
| H | -4.498871000 | -2.968058000 | 0.278410000 |
| C | -3.445421000 | -1.076394000 | -2.475666000 |
| C | -3.389560000 | 2.033806000 | -1.792485000 |
| C | -3.386026000 | 2.341451000 | 1.387216000 |


| C | -3.411937000 | -0.564432000 | 2.661200000 |
| :--- | ---: | ---: | :---: |
| H | 2.885546000 | -0.178691000 | 3.287129000 |
| H | 3.015460000 | 1.551106000 | 2.916076000 |
| H | 2.939954000 | -3.190834000 | 0.839246000 |
| H | 2.906631000 | -2.293339000 | 2.369206000 |
| H | 4.453275000 | -2.582346000 | 1.543897000 |
| H | 2.948619000 | -1.769597000 | -2.770409000 |
| H | 2.903519000 | -2.952019000 | -1.449475000 |
| H | 4.456190000 | -2.262498000 | -1.969014000 |
| H | 3.036338000 | 2.101912000 | -2.530649000 |
| H | 2.948328000 | 0.481460000 | -3.247596000 |
| H | 4.516776000 | 1.142749000 | -2.735379000 |
| H | 2.993757000 | 3.054096000 | 1.224225000 |
| H | 2.948751000 | 3.238055000 | -0.539912000 |
| H | 4.498331000 | 2.967749000 | 0.284933000 |
| H | -2.950098000 | -3.236679000 | -0.548473000 |
| H | -2.993503000 | -3.057227000 | 1.216144000 |
| H | -3.037523000 | -2.095520000 | -2.535956000 |
| H | -2.947782000 | -0.473269000 | -3.248636000 |
| H | -4.517001000 | -1.134473000 | -2.738707000 |
| H | -2.948500000 | 1.776454000 | -2.765965000 |
| H | -2.902645000 | 2.955639000 | -1.442155000 |
| H | -4.455717000 | 2.268018000 | -1.963083000 |
| H | -2.905675000 | 2.287549000 | 2.374871000 |
| H | -4.452621000 | 2.578588000 | 1.550847000 |
| H | -2.939572000 | 3.188790000 | 0.847127000 |
| H | -3.015487000 | -1.558336000 | 2.912275000 |
| H | -4.476835000 | -0.548643000 | 2.955105000 |
| H | -2.886220000 | 0.170540000 | 3.287732000 |
|  |  |  |  |

## ${ }^{\text {Me }}$ NHC



Table S29. Optimized geometries of MeNHC. XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.

| N | -3.640835000 | 1.647430000 | 0.755302000 |
| :--- | ---: | ---: | ---: |
| N | -4.650890000 | 2.490460000 | -0.917477000 |
| C | -4.668973000 | 1.393405000 | -0.105676000 |
| C | -2.996527000 | 2.862389000 | 0.495764000 |
| C | -3.646365000 | 3.404768000 | -0.580450000 |
| C | -3.263266000 | 0.743429000 | 1.826220000 |
| H | -3.936450000 | -0.121703000 | 1.791877000 |
| H | -3.354161000 | 1.228969000 | 2.811170000 |
| H | -2.224919000 | 0.394047000 | 1.708266000 |
| C | -5.582348000 | 2.679023000 | -2.014505000 |
| H | -6.251971000 | 1.810916000 | -2.042848000 |

## 5. Supplementary References

[i] N. Kuhn, T. Kratz, Synthesis 1993, 6, 561-562.
[ii] F. Dielmann, A. Timoshkin, M. Piesch, G. Balázs, M. Scheer, Angew. Chem. Int. Ed. 2017, 56, 1671-1675.
[iii] O. J. Scherer, H. Sitzmann, G. Wolmershäuser, Angew. Chem. Int. Ed. 1985, 24, 351-353.
[iv] O. J. Scherer, H. Sitzmann, G. Wolmershäuser, Angew. Chem 1989, 101, 214-215.
[v] O. J. Scherer, J. Schwalb, H. Swarowsky, G. Wolmershäuser, W. Kaim, R. Gross, Chem. Ber. 1988, 121, 443-449.
[vi] CrysAlisPro Software System, Rigaku Oxford Diffraction, (2018).
[vii] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, Olex2, J. Appl. Cryst., 2009, 42, 339-341.
[viii] G. M. Sheldrick, ShelXT-Integrated space-group and crystal-structure determination, Acta Cryst., 2015, A71, 3-8.
[ix] G. M. Sheldrick, Crystal structure refinement with ShelXL, Acta Cryst. 2015, C27, 3-8.
[x] Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.
[xi] a) A. D. Becke, J. Chem. Phys. 1993, 98, 5648-5652; b) C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 1988, 37, 785-789; c) S. H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 1980, 58, 1200-1211; d) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, J. Phys. Chem. 1994, 98, 11623-11627.
[xii] a) F. Weigend, R. Ahlrichs, Phys. Chem. Chem. Phys. 2005, 7, 3297-3305; b) D. Andrae, U. Häußermann, M. Dolg, H. Stoll, H. Preuß, Theor. Chim. Acta 1990, 77, 123-141.
[ixiii] a) G. Scalmani, M. J. Frisch, J. Chem. Phys. 2010, 132, 114110. b) J. Tomasi, B. Mennucci, R. Cammi, Chem. Rev. 2005, 105, 2999-3093.
[xiv] Chemcraft - graphical software for visualization of quantum chemistry computations. https://www.chemcraftprog.com.
[xv] S. Grimme, S. Ehrlich, L. Goerigk, J. Comput. Chem. 2011, 32, 1456-1465.
[xvi] a) A. D. Becke, Phys. Rev. 1988, A 38, 3098; b) J. P. Perdew, Phys. Rev. 1986, B 33, 8822.
[xvii] a) F. London, J. Phys. Radium, 1937, 8, 397-409; b) R. McWeeny, Phys. Rev., 1962, 126, 1028; c) R. Ditchfield, Mol. Phys., 1974, 27, 789-807; d) K. Wolinski, J. F. Hilton, and P. Pulay, J. Am. Chem. Soc., 1990, 112, 825160; e) J. R. Cheeseman, G. W. Trucks, T. A. Keith, and M. J. Frisch, J. Chem. Phys., 1996, 104, 5497-509.
[xviii] P. Pollak, F. Weigend, J. Chem. Theory Comput., 2017, 13, 3696-3705.

## 4 Reactivity of $\mathbf{P}_{4}$ butterfly complexes towards NHCs Generation of a metal-bridged $\mathbf{P}_{\mathbf{2}}$ dumbbell complex

### 4.1 Preface

The following chapter has already been published. The article is reprinted with permission of RSC:
S. Reichl, ${ }^{\S}$ R. Grünbauer, ${ }^{\S}$ G. Balázs and M. Scheer, Chem. Commun., 2021, 57, 3383.

DOI: 10.1039/D1CC00615K
${ }^{\text {§ }}$ Both authors contributed equally

## Authors

Stephan Reichl, ${ }^{1}$ Rebecca Grünbauer, ${ }^{1}$ Gábor Balázs, ${ }^{1}$ Manfred Scheer ${ }^{1 *}$
${ }^{1}$ Institute of Inorganic Chemistry, University of Regensburg; Universitätsstraße 31, 93053 Regensburg, Germany.
*Corresponding author. Email: manfred.scheer@chemie.uni-regensburg.de

## Author Contribution

S.R. and R.G. conceived the experiments. G.B. performed the computational studies. S.R. and R.G. analysed and revised the X-ray data; S.R., R.G., G. B. and M.Sch. wrote the manuscript. M.Sch. directed and coordinated the research.

## Reactivity of $\mathbf{P}_{4}$ butterfly complexes towards NHCs -

## Generation of a metal-bridged $\mathrm{P}_{2}$ dumbbell complex



# Reactivity of $\mathbf{P}_{4}$ butterfly complexes towards NHCs - 

## Generation of a metal-bridged $\mathbf{P}_{2}$ dumbbell complex


#### Abstract

The reactivity of the $P_{4}$ butterfly complexes $\left[\left\{\mathrm{Cp} p^{\prime \prime} \mathrm{Fe}(\mathrm{CO})_{2}\right\}_{2}\left(\mu, \eta^{1: 1}-\mathrm{P}_{4}\right)\right]\left(\mathrm{A}, \mathrm{Cp}^{\prime \prime \prime}=\mathrm{C}_{5} \mathrm{H}_{2}{ }^{t} \mathrm{Bu}_{3}\right)$ and $\left[\left\{\mathrm{Cp}^{*} \mathrm{Cr}(\mathrm{CO})_{3}\right\}_{2}\left(\mu, \eta^{1: 1}-\mathrm{P}_{4}\right)\right]\left(\mathrm{B}, \mathrm{Cp}^{*}=\mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right)$ towards the N -heterocyclic carbene $\mathrm{IMe}(1,3,4,5-$ tetramethyl-imidazol-2-ylidene) is reported. The reaction of $\mathbf{A}$ affords $\left[\mathrm{P}(\mathrm{IMe})_{2}\right]\left[\mathrm{Fe}(\mathrm{CO})_{2} \mathrm{Cp}^{\prime \prime \prime}\right](1)$ or $\left[P(I M e)_{2}\right]\left[\left\{\mathrm{Cp}^{\prime \prime} \mathrm{Fe}\right\}_{2}\left(\mu, \eta^{3: 3}-\mathrm{P}_{3}\right)\right](2)$, the latter possessing a $\mathrm{P}_{3}$-allylic moiety. In contrast, the reaction of B yields $\left[\mathrm{P}(\mathrm{IMe})_{2}\right]\left[\mathrm{Cr}(\mathrm{CO})_{3} \mathrm{Cp}^{*}\right]$ (3) and $\left[\left\{\mathrm{Cp}^{*} \mathrm{Cr}(\mathrm{CO})_{2}\right\}\left(\eta^{2}-\mathrm{P}_{2} 1 \mathrm{Me} \mathrm{e}_{2}\right)\right]\left[\mathrm{Cr}(\mathrm{CO})_{3} \mathrm{Cp}^{*}\right]$ (4), featuring a novel metal-bridged $P_{2}$ dumbbell.


### 4.2 Introduction

The reactivity of polyphosphorus $\left(P_{n}\right)$ ligand complexes $(n \leq 4)$ has been intensively studied over the last decades. ${ }^{1-4}$ The goal of these studies is to develop a more sustainable, economical and safer generation of phosphorus-containing compounds on both an academic and industrial scale. One common feature of all polyphosphorus ligands is the vast opportunity for coordination originating from the accessible lone pairs on every P atom. Due to this coordination potential, $\mathrm{P}_{\mathrm{n}}$ ligands are mostly stabilized in the coordination sphere of unsaturated organometallic ${ }^{1,2}$ or main group ${ }^{3,4}$ moieties. However, in most cases, the resulting $\mathrm{P}_{\mathrm{n}}$ ligand complexes nevertheless possess additional electron lone pairs rendering them available for further coordination processes. Within this field, the tetraphosphabicyclo[1.1.0]butane ligand is of major interest as it represents a $\mathrm{P}_{4}$ scaffold obtained after the first reductive $\mathrm{P}-\mathrm{P}$ bond cleavage during the conversion of the $\mathrm{P}_{4}$ tetrahedron. ${ }^{5}$ $\left.\left[\left\{\mathrm{Cp}^{\prime \prime \prime} \mathrm{Fe}(\mathrm{CO})_{2}\right\}_{2}\left(\mu, \eta^{1: 1}-\mathrm{P}_{4}\right)\right]\left(\mathrm{A}, \mathrm{Cp}^{\prime \prime \prime}=\mathrm{C}_{5} \mathrm{H}_{2}{ }^{t} \mathrm{Bu}\right)_{3}\right)$ and $\left[\left\{\mathrm{Cp}^{*} \mathrm{Cr}(\mathrm{CO})_{3}\right\}_{2}\left(\mu, \eta^{1: 1}-\mathrm{P}_{4}\right)\right]\left(\mathrm{B}, \mathrm{Cp}^{*}=\mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right)$, two prominent examples of the class of so called $P_{4}$ butterfly compounds (due to the intrinsic geometry of the central $P_{4}$ unit), are accessible in remarkably high yields (>95\%). ${ }^{6,7}$ Consequently, $\mathbf{A}$ and $\mathbf{B}$ are excellent starting materials to study the reactivity of the $\mathrm{P}_{4}$ butterfly unit towards various Lewis acids. ${ }^{8-10}$ Within these studies, we were able to demonstrate the successful coordination of the intact $\mathrm{P}_{4}$ butterfly moiety as well as isomerisation and fragmentation processes (Scheme 1).


II


III


Iv
v
$\mathrm{M}=$ metal fragmen
$[\mathrm{M}]=$ modified metal fragmen
$R=$ substituent of the original $\mathrm{P}_{4}$ butterfly compound
$\mathrm{R}^{\prime}=2,6-\mathrm{Pr}^{\prime}{ }_{2} \mathrm{C}_{6} \mathrm{H}_{3}$ or $2,4,6-\mathrm{Me}_{3} \mathrm{C}_{6} \mathrm{H}_{2}$

Scheme 1. Structural motifs obtained after coordination, rearrangement and fragmentation of the $\mathrm{P}_{4}$ butterfly complex upon the reaction with various Lewis acids II - IV as well as the first NHC-stabilized $\mathrm{P}_{2}$ dumbbell (V).

Early investigations concerning the coordination chemistry of the $P_{4}$ butterfly unit with monovalent coinage metal salts afforded a tetraphosphametalla-tricyclo[1.1.1.0 $0^{2,4}$ ]pentane type I compound (Scheme 1) and a homoleptic spiro complex (Scheme 1, type II). ${ }^{8}$ Herein, the geometric properties of the $\mathrm{P}_{4}$ butterfly scaffold mainly stay unaltered while the wing-tip P atoms coordinate towards the Lewis-acidic fragment in a chelating fashion. Next to this bidentate coordination, an isomerisation of the $\mathrm{P}_{4}$ butterfly unit yielding a planar $6 \pi$-aromatic $\mathrm{R}_{2} \mathrm{P}_{4}$ ligand can be observed when reacting A with $\left.\left[\mathrm{Fe}\left(\mathrm{CH}_{3} \mathrm{CN}\right)_{6}\right][\mathrm{PF}]_{6}\right]_{2}$ (Scheme 1, type III). ${ }^{9}$ In contrast, the quantitative formation of bidentate coordination products according to type I is observed, if $\mathbf{A}$ and $\mathbf{B}$ are reacted with $\mathrm{FeBr}_{2} \cdot \mathrm{dme}$ (dme $=1,2$-dimethoxyethane). ${ }^{9}$ Consequently, the reaction pathway is strongly dependent on the nature of the Lewis acid and its intrinsic acidity. Lastly, the reaction of A with tetracarbonyl fragments of $\mathrm{Cr}, \mathrm{Mo}$ and W (obtained from $\left[\mathrm{M}(\mathrm{CO})_{4}(\mathrm{nbd})\right] ;$ nbd = norbornadiene) selectively afforded type I compounds. ${ }^{[10]}$ For the reaction of B with $\left[\mathrm{W}(\mathrm{CO})_{4}(\mathrm{nbd})\right]$, an analog type I complex was obtained, while the reaction with $\left[\mathrm{Cr}(\mathrm{CO})_{4}\right]$ and $\left[\mathrm{Mo}(\mathrm{CO})_{4}\right]$ fragments resulted in a rearrangement yielding a bent cyclo- $\mathrm{P}_{4}$ moiety which undergoes subsequent $\mathrm{P}_{1} / \mathrm{P}_{3}$-fragmentation under special reaction conditions (Scheme 1, type IV). ${ }^{10}$

### 4.3 Results

In view of the fact that the reactivity of the $\mathrm{P}_{4}$ butterfly complexes towards Lewis acids, which shows remarkable differences between compounds $\mathbf{A}$ and $\mathbf{B},{ }^{9,10}$ has been well investigated, the question arises as to whether the opposite reaction pathway, the reaction with nucleophiles, is feasible as well. Possible nucleophiles are NHCs, which are known to stabilize unsubstituted main group element moieties (e.g. formal $\mathrm{C}(0)$, $\mathrm{Si}(0)$ or $\mathrm{Ge}(0)$ species). ${ }^{11}$ Recently, we applied NHCs as reactants towards polypnictogen metalcomplexes, resulting in stable but also metastable adducts. ${ }^{12,13}$ Within the phosphorus
chemistry, one special field of application for NHCs is the stabilisation of the gaseous $\mathrm{P}_{2}$ allotrope. In contrast to its heavier homolog, $\mathrm{N}_{2}$ is highly reactive and prone to aggregation. ${ }^{14}$ In 2008, Robinson et al. reported on the first NHC-stabilized $\mathrm{P}_{2}$ dumbbells for which a bisphosphinidene structure was proclaimed (Scheme 1, V), ${ }^{15}$ which is in contrast to the $\mathrm{P} \equiv \mathrm{P}$ triple bond present in the free $\mathrm{P}_{2}$ moiety. In view of the pronounced donor properties of the compounds $\mathbf{A}$ and $\mathbf{B}$, the question arises as to whether they react with donors such as NHCs and, if so, which unprecedented products can be obtained. Herein, we report on the unique fragmentation of the $P_{4}$ unit in $A$ and $B$ to yield novel compounds containing a neutral $\mathrm{P}_{3}$-allylic as well as an unprecedented $\mathrm{P}_{2}$ dumbbell as ligands.


Scheme 2. Reactions of $\mathbf{A}$ and $\mathbf{B}$ with IMe at different reaction conditions. Isolated yields are given in parentheses.

When sterically more demanding NHCs such as IDipp (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) are reacted with $\mathbf{A}$ or $\mathbf{B}$, no reaction of the starting materials was detected by NMR spectroscopic methods. However, when employing the rather small IMe (1,3,4,5-tetramethylimidazol-2-ylidene), a reproducible reaction outcome was found. When reacting A with IMe at room temperature, $\left[\mathrm{P}(\mathrm{IMe})_{2}\right]\left[\mathrm{Fe}(\mathrm{CO})_{2} \mathrm{Cp}{ }^{\prime \prime \prime}\right](1$, Scheme 2$)$ is obtained selectively alongside an insoluble red precipitate (most likely polyphosphorus species). In contrast, $\left[\mathrm{P}(\mathrm{IMe})_{2}\right]\left[\left\{\mathrm{Cp}^{\prime \prime \prime} \mathrm{Fe}\right\}_{2}\left(\mu, \mathrm{\eta}^{3: 3}-\mathrm{P}_{3}\right)\right]$ (2, Scheme 2$)$ is formed exclusively, if the reaction is performed
starting at $-80^{\circ} \mathrm{C}$. The monophosphorus cation $\left[\mathrm{P}(\mathrm{IMe})_{2}\right]^{+}$has already been reported for various anions. ${ }^{11,12,16,17}$ However, the fact that the reaction of $\mathbf{A}$ with IMe affords different anions depending on the reaction temperature is intriguing. This suggests that $\mathbf{2}$ is the first formed product, but unstable under room temperature reaction conditions, where 1 is the favored compound. Through the addition of IMe , one P atom of A is abstracted affording the $\left[\mathrm{P}(\mathrm{IMe})_{2}\right]^{+}$ cation. At low temperatures, the remaining $P_{3}$ scaffold of the former $P_{4}$ butterfly unit rearranges under carbonyl extrusion yielding the $\left[\left\{\mathrm{Cp}^{\prime \prime \prime} \mathrm{Fe}\right\}_{2}\left(\mu, \eta^{3: 3}-\mathrm{P}_{3}\right)\right]^{-}$anion of 2 , which incorporates an unusual bridging allylic $P_{3}$ unit. At higher temperatures, the organometallic substituent of $A$ evolves into the $\left[\mathrm{Cp}{ }^{\prime \prime \prime} \mathrm{Fe}(\mathrm{CO})_{2}\right]^{-}$anion of 1 , while the residual P atoms of the $\mathrm{P}_{4}$ butterfly unit aggregate and form an insoluble precipitate.

When B is reacted with IMe at low temperatures, the two products $\left[\mathrm{P}(\mathrm{IMe})_{2}\right]\left[\mathrm{Cp}{ }^{*} \mathrm{Cr}(\mathrm{CO})_{3}\right](3$, Scheme 2) and $\left[\left\{\mathrm{Cp}^{*} \mathrm{Cr}(\mathrm{CO})_{2}\right\}\left(\eta^{2}-\mathrm{P}_{2} \mid \mathrm{Me}_{2}\right)\right]\left[\mathrm{Cp}{ }^{*} \mathrm{Cr}(\mathrm{CO})_{3}\right]$ (4, Scheme 2) are obtained simultaneously in low isolated crystalline yields next to an insoluble yellow precipitate (most likely polyphosphorus compounds). The amount of $\mathbf{3}$ and 4 as well as the conversion of B depends from the stoichiometry used. A ratio of B:IMe of 1:6 leads exclusively to 3 , while 4 is best obtained in a 1:2 ratio (cf. SI). Compound 3 is the isovalence-electronic species of 1 , containing the cation $\left[\mathrm{P}(\mathrm{IMe})_{2}\right]^{+} .{ }^{11,12,16,17}$ To the best of our knowledge, 4 represents a novel structural motif: the first $P_{2}$ dumbbell stabilized by two terminal NHCs and one bridging organometallic fragment. The cation of 3 is isostructural to those of 1 and is formed analogously: one P atom of the $\mathrm{P}_{4}$ butterfly unit of $\mathbf{B}$ is abstracted by two IMe molecules affording the $\left[P(I M e)_{2}\right]^{+}$cation, while the organometallic substituent of $B$ evolves into the $\left[\mathrm{Cp}^{*} \mathrm{Cr}(\mathrm{CO})_{3}\right]^{-}$anion and the remaining P atoms aggregate forming a polyphosphorus precipitate and $\mathrm{P}_{4}$ (detected by ${ }^{31}$ P NMR spectroscopy). However, during the formation of 4, a rearrangement occurs after the initial abstraction of one $P$ atom from the $P_{4}$ butterfly unit. The residual phosphorus scaffold reacts with two molecules of IMe affording an NHC-substituted $\mathrm{P}_{2}$ dumbbell, which is additionally stabilized by a $\left\{\mathrm{Cp}{ }^{*} \mathrm{Cr}(\mathrm{CO})_{2}\right\}$ fragment. Again, a polyphosphorus precipitate and $\mathrm{P}_{4}$ can be detected as byproducts of this reaction. They arise as aggregates formed from the redundant $P$ atoms extruded from the $P_{4}$ butterfly moiety during the concurrent formations of $\mathbf{3}$ and 4. Previous experiments showed that B is more likely to decompose or rearrange than A . With a dissociation energy of $142.91 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1}$, the cleavage of the $\mathrm{Fe}-\mathrm{P}$ bonds in A is considerably disfavored in comparison to the corresponding fragmentation of $\mathbf{B}\left(67.47{\left.\mathrm{~kJ} \cdot \mathrm{~mol}^{-1}\right)}\right.$ (cf. SI). Consequently, the $\left\{\mathrm{Cp}{ }^{\prime \prime \prime} \mathrm{Fe}(\mathrm{CO})_{2}\right\}$ substituent is less likely to detach, rearrange and reattach to a modified $P_{n}$ moiety. However, the detachment of the organometallic substituent of $\mathbf{B}$ and the rearrangement affording a bridging $\left\{\mathrm{Cp}^{*} \mathrm{Cr}(\mathrm{CO})_{2}\right\}$ fragment are essential to the formation of 4. Consequently, the fact that the organometallic fragment of $A$ is less likely to rearrange might explain why no iron analog of 4 can be observed
for the reaction of A with IMe . As $\mathbf{3}$ and 4 are formed simultaneously and due to very similar properties as regards solubility and crystallization as well as the fast decomposition during chromatographic workup, analytical investigations could only be performed for a mixture of crystals of 3 and 4.

Compounds $\mathbf{1}$ and $\mathbf{3}$ crystalize in the triclinic space group $\mathbf{P \overline { 1 }}$ as clear orange and yellow plates, respectively. In contrast, $\mathbf{2}$ crystalizes in the form of dark pink blocks in the monoclinic space group $P 2_{1} / n$. The $\left[P(I M e)_{2}\right]^{+}$cation incorporated in 1,2 and 3 is known and was already characterized in the presence of different counter anions, revealing the expected bond lengths and angles. ${ }^{11,12,16,17}$



Figure 1. Molecular structure of 2 and cationic part of 4 in the solid state. H atoms are omitted for clarity and CO as well as Cp ligands are drawn in a wire frame model; thermal ellipsoids are drawn at $50 \%$ probability.

The $\left[\left\{\mathrm{Cp}{ }^{\prime \prime \prime} \mathrm{Fe}\right\}_{2}\left(\mu, \eta^{3: 3}-\mathrm{P}_{3}\right)\right]$ anion (Fig. 1) found in 2 represents the reduced version of the neutral complex $\left[\left\{\mathrm{Cp}^{\prime \prime \prime} \mathrm{Fe}\right\}_{2}\left(\mu, \eta^{3: 3}-\mathrm{P}_{3}\right)\right]$ (C): the first binuclear complex incorporating a triphosphaallyl unit. ${ }^{18}$ However, whereas in $\mathbf{C}$ a symmetric $P_{3}$ unit is present, in 2 , it is not symmetric. With $2.1601(8) \AA$ and $2.1897(8) \AA$, the $\mathrm{P}-\mathrm{P}$ bonds in 2 are shortened in comparison to a usual P-P single bond $(2.209(5) \AA \AA) .{ }^{20}$ Yet, they are slightly elongated in comparison to the respective $\mathrm{P}-\mathrm{P}$ bonds in C (2.148(1) Å). The Fe-Fe distance in $2(2.8236(4) \AA$ ) is remarkably elongated in comparison to the corresponding existing bond in the neutral complex C (2.589(1) $\AA$ ). ${ }^{18}$ According to DFT calculations, no Fe-Fe bond is present in 2. Consequently, the formal reduction of $\mathbf{C}$ to 2 results in an enlargement of the structural scaffold. In contrast, the $\mathrm{P}-\mathrm{P}-\mathrm{P}$ angle of $2\left(95.21(3)^{\circ}\right)$ is slightly smaller than the angle reported for the neutral compound $\mathbf{C}$ (100.71(7) ${ }^{\circ}$ ). The ${ }^{31} \mathrm{P}$ NMR spectra of 1, 2 and 3 confirm the previously reported signal for $[\mathrm{P}(\mathrm{IMe} 2)]^{+}(\mathrm{s}, \delta=-114 \mathrm{ppm})$. Moreover, the ${ }^{31} \mathrm{P}$ NMR spectrum of 2 reveals two additional sets of signals attributed to the $\left[\left\{\mathrm{Cp}{ }^{\prime \prime \prime} \mathrm{Fe}\right\}_{2}\left(\mu, \eta^{3: 3}-\mathrm{P}_{3}\right)\right]^{-}$anion: a doublet at $\delta=638.6 \mathrm{ppm}$ (P1 and P3)
and a triplet at $\delta=-384.1 \mathrm{ppm}\left(\mathrm{P} 2\right.$, labeling according to Fig. 2). The simulation of the ${ }^{31}$ P NMR spectrum of 2 confirmed a ${ }^{1}$ Jpp coupling constant of 353 Hz . Hence, a P-P bond order in between a single and a double bond can be stated in accordance with the single crystal X -ray diffraction data.

Compound 4 crystallizes alongside 3 in the form of brown blocks in the monoclinic space group $P 2{ }_{1} / \mathrm{n}$ (Fig. 1). However, these crystals break easily and the debris cannot be distinguished from crystalline 3 under the microscope. Hence, an optical separation of 3 and 4 could not be achieved. In the solid state, the $\mathrm{P}-\mathrm{P}$ bond length of the central $\mathrm{P}_{2}$ dumbbell of 4 amounts to $2.1246(8) \AA$. It is elongated in comparison to the corresponding $\mathrm{P}-\mathrm{P}$ bond in $\left[\left\{\mathrm{Cp}^{*} \operatorname{Cr}(\mathrm{CO})_{2\} 2}\left\{\mu, \eta^{2: 2}-\mathrm{P}_{2}\right\}\right]\left(2.060(1) \AA\right.\right.$ ) in which the $\mathrm{P}_{2}$ dumbbell is coordinated by two $\left\{\mathrm{Cp}^{*} \mathrm{Cr}(\mathrm{CO})_{2}\right\}$ fragments, forming a tetrahedron. ${ }^{19}$ However, it is shorter than a regular $\mathrm{P}-\mathrm{P}$ single bond, given at $2.209(5) ~ \AA .{ }^{20}$ Consequently, a bond order in between a $P-P$ single and $P=P$ double bond can be proposed. In contrast, solely NHC-stabilized $\mathrm{P}_{2}$ dumbbells by Robinson and coworkers (see Scheme 1, type V ) incorporate $\mathrm{P}-\mathrm{P}$ bond lengths in the range of a regular $\mathrm{P}-\mathrm{P}$ single bond. ${ }^{15}$ In addition, the two P-C bonds in 4 (1.835(3) $\AA$ and $1.842(3) \AA$ ) are slightly elongated indicating a weaker interaction comparable to a $\mathrm{P}-\mathrm{C}$ single bond. One outstanding observation regarding the molecular structure of 4 is the fact that the $\left\{\mathrm{Cp}{ }^{*} \mathrm{Cr}(\mathrm{CO})_{2}\right\}$ fragment coordinates the $\mathrm{P}_{2}$ dumbbell in an asymmetrical fashion. The central Cr atom is shifted slightly towards one of the P atoms resulting in two different $\mathrm{P}-\mathrm{Cr}$ bond lengths of $2.3954(7) \AA$ and $2.4480(7) \AA$ as well as two differing P-P-Cr angles of $65.26(3)^{\circ}$ and $62.71(2)^{\circ}$. Due to the intrinsic asymmetry of 4 , which is introduced by the sloping coordination mode of the $\left\{\mathrm{Cp}^{*} \mathrm{Cr}(\mathrm{CO})_{2}\right\}$ fragment, two doublets at $\delta=-52.0 \mathrm{ppm}$ and $\delta=-82.1 \mathrm{ppm}$ are recorded in the ${ }^{31}$ P NMR spectrum of 4 for the inequivalent $P$ atoms. This confirms that the $P_{2}$ dumbbell maintains the asymmetrical $\eta^{2}$-coordination towards the $\left\{\mathrm{Cp}^{*} \mathrm{Cr}(\mathrm{CO})_{2}\right\}$ fragment in solution. The ${ }^{1} \mathrm{~J}_{\mathrm{PP}}$ coupling constant of $4(338 \mathrm{~Hz})$ is larger than the one recorded for [IMesP-PIDipp] ( ${ }^{1} \mathrm{~J}_{\mathrm{PP}}=$ 249 Hz ) for which a $P-P$ single bond is proposed. ${ }^{21}$ However, the $P=P$ double bond incorporating [IMesP-PIDipp] ${ }^{2+}$ displays a ${ }^{1} \mathrm{Jpp}_{\text {p }}$ coupling constant of $543 \mathrm{~Hz} .{ }^{21}$ Consequently, for 4, a P-P bond order in between a single and a double bond is reasonable. ${ }^{20}$

To gain further insight into the electronic structure of 4, the compound was investigated by DFT calculations at the B3LYP/def2-TZVP level of theory. The natural population analysis (NPA) shows that the Cr atom is negatively charged ( -0.86 ), while the $\mathrm{Cp}^{*}$ ligand and the CO groups are slightly positively charged ( 0.15 and 0.36 ), resulting in an overall negative charge of -0.35 for the $\left\{\mathrm{Cp}^{*} \mathrm{Cr}(\mathrm{CO})_{2}\right\}$ fragment. The central $\mathrm{P}_{2}$ unit and the two NHC fragments bear a positive charge of $0.37,0.51$ and 0.47 , respectively, resulting in a $\left\{\mathrm{P}_{2} \mathrm{IMe}{ }_{2}\right\}$ fragment with an overall positive charge of 1.35. The Wiberg Bond Index (WBI) of the P-P bond (1.14) confirms
only a weak double bond character, while the WBls of the C-P bonds ( 0.98 and 1.01) are characteristic for single bonds. The NBO analysis illustrates the presence of only one lone pair of electrons on each P atom in an approximate $\mathrm{sp}^{0.5}$ hybrid orbital, along with two weakly polarized $\mathrm{Cr}-\mathrm{P}$ bonds in which the P atoms participate in almost pure p orbitals ( $\mathrm{sp}^{11}$ and $\mathrm{sp}^{7.2}$ ). This description of the electronic structure of 4 is in line with the localized molecular orbitals (cf. Si Fig. S3). The AIM analysis of the electron density in 4 allowed the detection of bond critical points (BCPs) along the $\mathrm{P}-\mathrm{P}$ and $\mathrm{Cr}-\mathrm{P}$ bonds (Fig. 2). The locations of BCPs corresponding to the $\mathrm{Cr}-\mathrm{P}$ bonds point towards a metallacyclopropane-like bonding. However, the relatively high ellipticity at the BCPs 1-3 ( $\mathrm{P}_{2} \mathrm{Cr}$ core) indicates a deformation of the electron density in this plane, hence the presence of a $\mathrm{P}-\mathrm{P}$ double bond.


Figure 2. Locations and labeling of selected Bond Critical Points (BCP, green) and Ring Critical Points (RCP, violet) in the electron density of 4 .

Although the Laplacian of the electron density is positive at the BCPs corresponding to the Cr $P$ bonds, the relatively high electron density and high energy density at the BCPs clearly show the $\mathrm{Cr}-\mathrm{P}$ bonds (Fig. 3). Additionally, the ratio of the potential energy density $\mid \mathrm{V}_{\mathrm{c}}$ and the kinetic energy density $\mathrm{G}_{\mathrm{c}}$ at the bond critical point for the $\mathrm{P}-\mathrm{P}$ and $\mathrm{P}-\mathrm{C}$ bonds is characteristic of covalent interactions ( $|\mathrm{V}| / \mathrm{G}>2$ ), while those of the $\mathrm{Cr}-\mathrm{P}$ bonds are characteristic of intermediate interactions between typical covalent and closed shell, for which the |V|/G ratio lies between 1 and 2. Based on these results, the electronic structure of the $P_{2}$ dumbbell in 4 can be described as being within a single to a double bond.


Figure 3. Contour plot of the electron density (left) and the Laplacian of the electron density (right) in the $\mathrm{P}_{2^{-}}{ }^{-}$ Chromium plane of 4. Positive values in black; negative values in red. The position of bond critical points are marked with blue dots.

One compelling difference in the composition of the $\left[\left\{\mathrm{Cp}{ }^{*} \mathrm{Cr}(\mathrm{CO})_{2}\right\}\left(n^{2}-\mathrm{P}_{2} \mathrm{IMe} 2\right)\right]^{+}$cation of 4 in comparison to the $\left[\mathrm{P}(\mathrm{IMe})_{2}\right]^{+}$cation found in 1,2 and 3 is the intrinsic phosphorus/ NHC ratio. Whereas a 1:2 ratio is found in $\left[\mathrm{P}(\mathrm{IMe})_{2}\right]^{+}$, a 1:1 ratio is present in $\left[\left\{\mathrm{Cp}{ }^{*} \mathrm{Cr}(\mathrm{CO})_{2}\right\}\left(\mathrm{n}^{2}-\mathrm{P}_{2} \mid \mathrm{Me} 2\right)\right]^{+}$. Therefore, it can be assumed that the formation of 3 would be favored over the synthesis of 4, if the amount of IMe reacted with B is increased. ${ }^{31}$ P NMR spectroscopic studies validated this proposed effect of a stoichiometry variation in the starting materials on the product ratio (cf. Si Fig. S6), even though traces of B are still detectable. Smaller amounts of IMe still afford the formation of the desired products 3 and 4, however, considerable amounts of $\mathbf{B}$ are not converted.

### 4.4 Conclusion

In summary, the reaction of the $\mathrm{P}_{4}$ butterfly compound A with IMe leads to the degradation of the $\mathrm{P}_{4}$ scaffold to give selectively, depending on the reaction temperature, either an allylic $\mathrm{P}_{3}$ compound $\left[\mathrm{P}(\mathrm{IMe})_{2}\right]\left[\left\{\mathrm{Cp}{ }^{\prime \prime \prime F}\right\}_{2}\left(\mu, \mathrm{r}^{3: 3}-\mathrm{P}_{3}\right)\right]$ (2) or a $\mathrm{P}_{1}$ unit in $\left[\mathrm{P}(\mathrm{IMe})_{2}\right]\left[\mathrm{Cp}{ }^{\prime \prime \prime} \mathrm{Fe}(\mathrm{CO})_{2}\right]$ (1). In contrast, the reaction of the chromium derivative $\mathbf{B}$ with IMe afforded a higher degradation of the $\mathrm{P}_{4}$ unit to give the $\mathrm{P}_{1}$ product $\left[\mathrm{Me}{ }_{2} \mathrm{P}\right]\left[\mathrm{Cp}{ }^{*} \mathrm{Cr}(\mathrm{CO})_{3}\right]$ (3) and an unprecedented $\mathrm{P}_{2}$ unit in $\left[\left\{\mathrm{Cp}^{*} \mathrm{Cr}(\mathrm{CO})_{2}\right\}\left(\eta^{2}-\mathrm{P}_{2} \mathrm{Me} 2\right)\right]\left[\mathrm{Cp}{ }^{*} \mathrm{Cr}(\mathrm{CO})_{3}\right](4) .\left[\left\{\mathrm{Cp}^{\prime \prime \prime} \mathrm{Fe}\right\}_{2}\left(\mu, \eta^{3: 3}-\mathrm{P}_{3}\right)\right]^{-}(2)$ represents a novel anion of a triphosphaallyl unit in a binuclear complex, however, with no Fe-Fe bond as found in the neutral derivative. ${ }^{18}$ Moreover, the cationic $\mathrm{P}_{2}$ dumbbell in 4 represents a novel class of compounds accessible from B by a preferred cleavage and rearrangement of $\mathrm{Cr}-\mathrm{P}$ bonds. Comprehensive DFT calculations delineate a weak double bond character for the $\mathrm{P}_{2}$ dumbbell with one localized lone pair of electrons on each $P$ atom, while the $\left\{\mathrm{Cp}^{*} \mathrm{Cr}(\mathrm{CO})_{2}\right\}$ fragment bears the formal negative charge. Consequently, the $P_{4}$ butterfly chemistry is not limited to the previously reported bidentate coordination pattern but offers a great variety of reaction pathways.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

S.R is grateful to the Studienstiftung des Deutschen Volkes and R.G to the Fonds der Chemischen Industrie for their PhD fellowships.

### 4.5 References

1 B. M. Cossairt, N. A. Piro and C. C. Cummins, Chem. Rev. 2010, 110, 4164-4177.
2 M. Caporali, L. Gonsalvi, A. Rossin and M. Peruzzini, Chem. Rev. 2010, 110, 4178-4235.
3 M. Scheer, G. Balázs and A. Seitz, Chem. Rev. 2010, 110, 4236-4256.
4 N. A. Giffin and J. D. Masuda, Coord. Chem. Rev. 2011, 255, 1342-1359.
5 O. J. Scherer, G. Schwarz and G. Wolmershäuser, Z. Anorg. Allg. Chem. 1996, 622, 951957.

6 O. J. Scherer, T. Hilt, G. Wolmershäuser, Organometallics 1998, 17, 4110-4112.
7 C. Schwarzmaier, A. Y. Timoshkin, G. Balázs and M. Scheer, Angew. Chem. Int. Ed. 2014, 53, 9077-9081.

8 C. Schwarzmaier, S. Heinl, G. Balázs and M. Scheer, Angew. Chem. Int. Ed. 2015, 54, 13116-13121.

9 (a) J. Müller, S. Heinl, C. Schwarzmaier, G. Balázs, M. Keilwerth, K. Meyer and M. Scheer, Angew. Chem. Int. Ed. 2017, 56, 7312-7317; (b) J. Müller and M. Scheer, Chem. Eur. J. 2021, 27, 3675-3681; (c) J. Müller, G. Balázs and M. Scheer, Chem. Commun. 2021, 57, 2257-2260.

10 M. Scheer, R. Grünbauer and G. Balazs, Chem. Eur. J. 2020, 26, 11722-11726.
11 V. Nesterov, D. Reiter, P. Bag, P. Frisch, R. Holzner, A. Porzelt, S. Inoue, Chem. Rev. 2018, 118, 9678-9842.

12 M. Piesch, S. Reichl, M. Seidl, G. Balázs and M. Scheer, Angew. Chem. Int. Ed. 2019, 58, 16563-16568.

13 F. Riedlberger, S. Todisco, P. Mastrorilli, A. Y. Timoshkin, M. Seidl and M. Scheer, Chem. Eur. J. 2020, 26, 16251-16255.

14 A. F. Hollemann, E. Wiberg, Lehrbuch Für Anorganische Chemie, 2007, Walter de Gruyter, Berlin.

15 (a) Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer, P. V. R. Schleyer and G. H. Robinson, J. Am. Chem. Soc. 2008, 130, 14970-14971. For charged $P_{2}$ species cf.:
(b) O. Back, B. Donnadieu, P. Parameswaran, G. Frenking and G. Bertrand, Nat. Chem. 2010, 2, 369-373.
(c) J. B. Waters, T. A. Everitt, W. K. Myers and J. M. Goicoechea, Chem. Sci. 2016, 7, 6981-6987.

16 C. L. B. Macdonald, J. F. Binder, A. Swidan, J. H. Nguyen, S. C. Kosnik and B. D. Ellis, Inorg. Chem. 2016, 55, 7152-7166.

17 A. Hinz, A. Schulz and A. Villinger, Chem. Commun. 2016, 52, 6328-6331. M. Scheer, S. Deng, O. J. Scherer and M. Sierka, Angew. Chem. Int. Ed. 2005, 44, 37553758.
L. Y. Goh, C. K. Chu, R. C. S. Wong and T. W. Hambley, Dalton Trans. 1989, 1951-1956. P. Pyykkö and M. Atsumi, Chem. Eur. J. 2009, 15, 12770-12779.
A. Doddi, D. Bockfeld, M. K. Zaretzke, C. Kleeberg, T. Bannenberg and M. Tamm, Dalton Trans. 2017, 46, 15859-15864.

### 4.6 Supplementary Information

## Reactivity of $\mathrm{P}_{4}$ butterfly complexes towards NHCs - generation of a metal-bridged $P_{2}$ dumbbell complex

Stephan Reichl, ${ }^{1}$ Rebecca Grünbauer, ${ }^{1}$ Gábor Balázs, ${ }^{1}$ Manfred Scheer ${ }^{1 *}$<br>${ }^{1}$ Institute of Inorganic Chemistry, University of Regensburg; Universitätsstraße 31, 93053 Regensburg, Germany.<br>*Corresponding author. Email: manfred.scheer@chemie.uni-regensburg.de

## Table of Content

1. General remarks 80
2. Synthesis 80
3. NMR spectroscopic experiments 82
4. DFT calculations 86
5. Crystallographic details 91
6. Additional Information 95
7. References 96

## 1. General remarks

All experiments were carried out under an atmosphere of dry argon or nitrogen using glovebox and Schlenk techniques. Residues of oxygen and water were removed from the inert gas by passing it over a BASF R 3-11 $\left(\mathrm{CuO} / \mathrm{MgSiO}_{3}\right)$ catalyst, concentrated $\mathrm{H}_{2} \mathrm{SO}_{4}$ and finally granulated silica gel. Dry solvents were collected from a Braun SPS Apparatus and degassed prior to use. The deuterated solvents thf- $\mathrm{d}_{8}$ and toluene- $\mathrm{d}_{8}$ were degassed and dried by stirring with $\mathrm{Na} / \mathrm{K}$ alloy, followed by distillation.
 were prepared according to literature procedures. $\mathrm{LiNMe}_{2}$ and $\mathrm{LiCH}_{2} \mathrm{SiMe}_{3}$ are commercially available and were used without further modification.

NMR spectra were recorded at the NMR department of the University Regensburg using a Bruker Advance 300 or 400 spectrometer. Samples are referenced against TMS $\left({ }^{1} \mathrm{H}\right)$ or $85 \% \mathrm{H}_{3} \mathrm{PO}_{4}\left({ }^{31} \mathrm{P}\right)$ as external standards. Chemical shifts ( $\delta$ ) are reported in ppm and coupling constants (J) in Hz. The spectra were processed using the TopSpin 3.5 software (Bruker) and the WIN-DAISY module of this software was used to perform simulations. ${ }^{\text {[vi] }}$

Mass spectrometry was performed by the MS department of the University Regensburg. ESI-MS spectra were recorded on a Q-TOF 6540 UHD (Agilent) spectrometer. The observed fragments were assigned according to the mass/charge ( $\mathrm{m} / \mathrm{z}$ ) ratio and the isotope pattern.

## 2. Synthesis

## Synthesis of $\left[\mathrm{P}(\mathrm{IMe})_{2}\right]\left[\mathrm{Cp}{ }^{\prime \prime} \mathrm{Fe}(\mathrm{CO})_{2}\right]$ (1)

A colourless solution of $\mathrm{IMe}(149.0 \mathrm{mg}, 1.2 \mathrm{mmol}, 4.0 \mathrm{eq})$ in 10 mL thf is added to a red solution of $\mathrm{A}(244.3 \mathrm{mg}$, $0.3 \mathrm{mmol}, 1.0 \mathrm{eq}$ ) in 10 mL thf. Thereby, the red colour intensified and a red solid is formed. The solution is stirred for one hour and subsequently the solvent is removed under reduced pressure. The orange residue is washed with cold toluene ( $3 \times 10 \mathrm{~mL},-30^{\circ} \mathrm{C}$ ), dissolved again in thf and stored at room temperature. Compound 1 is obtained in the form of dark orange plates suitable for single crystal X-ray diffraction analysis after three days.

## Analytical data for 1

Yield: $255.2 \mathrm{mg}(0.41 \mathrm{mmol}, 68 \%) .{ }^{1} \mathrm{H}$ NMR (thf- $\left.\mathrm{d}_{8}, 300 \mathrm{~K}\right): ~ \delta[p p m]=1.12\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{2}{ }^{\mathrm{t}} \mathrm{Bu}_{3}\right), 1.30\left(\mathrm{~s}, 18 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{2}{ }^{\mathrm{t}} \mathrm{Bu}_{3}\right.$ ), $2.25\left(\mathrm{~s}, 12 \mathrm{H}, \mathrm{N}-\mathrm{CH}_{3}\right), 3.44\left(\mathrm{~s}, 12 \mathrm{H}, \mathrm{C}-\mathrm{CH}_{3}\right), 3.93\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{C}_{5} \underline{\mathrm{H}}_{2}{ }^{\mathrm{t}} \mathrm{Bu}_{3}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{thf}-\mathrm{d}_{8}, 300 \mathrm{~K}\right): \delta \quad[\mathrm{ppm}]=-$ 114.9 (s, 1P, $\left.\left[\mathrm{P}(\mathrm{IMe})_{2}\right]^{+}\right) .{ }^{31} \mathrm{P}$ NMR (thf- $\left.\mathrm{d}_{8}, 300 \mathrm{~K}\right): \delta[\mathrm{ppm}]=-114.9\left(\mathrm{~s}, 1 \mathrm{P},\left[\mathrm{P}(\mathrm{IMe})_{2}\right]^{+}\right)$. ESI- $\mathrm{MS}(\mathrm{dme}) \mathrm{m} / \mathrm{z}=345.15$ $\left[\mathrm{Fe}(\mathrm{CO})_{2} \mathrm{Cp}^{\prime \prime \prime}\right]^{-}(100 \%) . \mathrm{ESI}^{+}-\mathrm{MS}(\mathrm{dme}) \mathrm{m} / \mathrm{z}=279.18\left[\mathrm{P}(\mathrm{IMe})_{2}\right]^{+}(100 \%)$. IR (solid) $\tilde{v}_{\mathrm{co}}\left[\mathrm{cm}^{-1}\right]=1836.63(\mathrm{~m}), 1767.95$ (m).

## Synthesis of $\left[P(I M e)_{2}\right]\left[\left\{\mathrm{Cp}{ }^{\prime \prime} \mathrm{Fe}_{2}\left(\mu, \boldsymbol{\eta}^{3: 3}-\mathrm{P}_{3}\right)\right]\right.$ (2)

A red solution of $\mathbf{A}(760.6 \mathrm{mg}, 0.8 \mathrm{mmol}, 1.0 \mathrm{eq})$ in thf is cooled to $-80^{\circ} \mathrm{C} . \mathrm{A}-80^{\circ} \mathrm{C}$ cold solution of $\mathrm{IMe}(198.7 \mathrm{mg}$, $1.6 \mathrm{mmol}, 2.0 \mathrm{eq}$ ) in 10 mL thf is added. The mixture is stirred overnight and allowed to reach room temperature. Thereby, the colour changes to reddish-purple. The solvent is removed in vacuo. A dark red solution is extracted with toluene ( $3 \times 10 \mathrm{~mL}$ ) from the residue. The solvent is reduced under reduced pressure and stored at $8^{\circ} \mathrm{C}$. Compound $\mathbf{2}$ can be obtained in the form of dark red blocks suitable for single crystal X-ray diffraction analysis after one week.

## Analytical data for 2

Yield: 720.0 mg ( $0.76 \mathrm{mmol}, 95 \%$ ). ${ }^{1} \mathrm{H}$ NMR (tol- $\mathrm{d}_{8}, 300 \mathrm{~K}$ ) $\delta[\mathrm{ppm}]=1.43\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{2}{ }^{\mathrm{t}} \mathrm{Bu}_{3}\right), 1.58(\mathrm{~s}, 18 \mathrm{H}$, $\mathrm{C}_{5} \mathrm{H}_{2}{ }^{\mathrm{t}} \underline{B u}_{3}$ ), $1.84\left(\mathrm{~s}, 12 \mathrm{H}, \mathrm{N}-\mathrm{CH}_{3}\right), 2.88\left(\mathrm{~s}, 12 \mathrm{H}, \mathrm{C}-\mathrm{CH}_{3}\right), 3.82\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{2}{ }^{\mathrm{t}} \mathrm{Bu}_{3}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{tol}-\mathrm{d}_{8}, 300 \mathrm{~K}\right) \delta[\mathrm{ppm}]=$ $638.6\left(\mathrm{~d}, 2 \mathrm{P},{ }^{1} \mathrm{~J}_{\mathrm{AX}}=352.6 \mathrm{~Hz}, \mathrm{P}_{\mathrm{A}}\right),-114.2\left(\mathrm{~s}, 1 \mathrm{P},\left[\mathrm{P}(\mathrm{IMe})_{2}\right]^{+}\right),-348.1\left(\mathrm{t}, 1 \mathrm{P},{ }^{1} \mathrm{~J}_{\mathrm{Ax}}=352.6 \mathrm{~Hz}, \mathrm{P}_{\mathrm{X}}\right) .{ }^{31} \mathrm{P} \mathrm{NMR}\left(\mathrm{tol}^{2} \mathrm{~d}_{8}, 300\right.$ K) $\delta[\mathrm{ppm}]=638.6\left(\mathrm{~d}, 2 \mathrm{P},{ }^{1} \mathrm{~J}_{\mathrm{AX}}=352.6 \mathrm{~Hz}, \mathrm{P}_{\mathrm{A}}\right),-114.2\left(\mathrm{~s}, 1 \mathrm{P},\left[\underline{\mathrm{P}}(\mathrm{IMe})_{2}\right]^{+}\right),-348.1\left(\mathrm{t}, 1 \mathrm{P},{ }^{1} \mathrm{~J}_{\mathrm{AX}}=352.6 \mathrm{~Hz}, \mathrm{P}_{\mathrm{X}}\right) . \mathrm{ESI}-\mathrm{MS}$ (dme) $\mathrm{m} / \mathrm{z}=671.24\left[\left\{\mathrm{Cp}{ }^{\prime \prime \prime} \mathrm{Fe}\right\}_{2}\left(\mu, \eta^{3: 3}-\mathrm{P}_{3}\right)\right]^{-}$(100\%). ESI+-MS (dme) m/z = 279.18 [P(IMe) $]^{+}$(100\%). Elemental Analysis calcd. for $\left[\mathrm{C}_{48} \mathrm{H}_{82} \mathrm{~N}_{4} \mathrm{P}_{4} \mathrm{Fe}_{2}\right]\left(950.78 \mathrm{~g} \cdot \mathrm{~mol}^{-1}\right) \mathrm{C} 60.64, \mathrm{H} 8.69, \mathrm{~N} 5.89$; found: C 61.08, H 8.05, N 5.97 .

## Synthesis of $\left[\mathrm{P}(\mathrm{IMe})_{2}\right]\left[\mathrm{Cr}(\mathrm{CO})_{3} \mathrm{Cp}^{*}\right](3)$ and $\left[\left\{\mathrm{Cp}^{*} \mathrm{Cr}(\mathrm{CO})_{2}\right\}\left(\eta^{2}-\mathrm{P}_{2} \mid \mathrm{Me}_{2}\right)\right]\left[\mathrm{Cr}(\mathrm{CO})_{3} \mathrm{Cp}^{*}\right](4)$

An orange-brown solution of $\mathbf{B}(66 \mathrm{mg}, 0.1 \mathrm{mmol}, 1.0 \mathrm{eq}$.$) in thf ( 5 \mathrm{~mL}$ ) and a colorless solution of $\mathrm{IMe}(30 \mathrm{mg}$, $0.24 \mathrm{mmol}, 2.4 \mathrm{eq}$.) in thf ( 5 mL ) are cooled to $-90^{\circ} \mathrm{C}$. Slowly, the solution of IMe is added to the solution of $\mathbf{B}$ while stirring. The solution is brought to room temperature overnight and hereby a color change to a dark brown solution and the formation of yellow precipitate is observed. The brown solution is filtered via a canula, diluted with additional 5 mL of thf and layered with n-pentane. After a few days two kinds of crystals suitable for single crystal X-ray diffraction are obtained: small yellowish blocks of 3 and dark brown blocks of 4.

Crystalline Yield of the mixture of 3 and 4: 14.0 mg . For product ratio of $3: 1$ (as found in by NMR spectroscopic studies): 3: 11.2 mg ( $0.009 \mathrm{mmol}, 9 \%$ ). 4: $2.8 \mathrm{mg}(0.003 \mathrm{mmol}, 3 \%)$.

Analytical data for $3:{ }^{1} \mathrm{H}$ NMR (thf- $\left.\mathrm{d}_{8}, 300 \mathrm{~K}\right) ~ \delta[p p m]=1.83\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{Cp}^{*}\right), 2.24\left(\mathrm{~s}, 12 \mathrm{H}, \mathrm{N}-\mathrm{CH}_{3}\right), 3.44\left(\mathrm{~s}, 12 \mathrm{H}, \mathrm{C}-\mathrm{CH}_{3}\right)$. ${ }^{31} \mathrm{P}$ NMR (thf- $\mathrm{d}_{8}, 300 \mathrm{~K}$ ) $\delta[\mathrm{ppm}]=-114.8\left(\mathrm{~s}, 1 \mathrm{P},\left[\mathrm{P}(\mathrm{IMe})_{2}\right]^{+}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR (thf- $\left.\mathrm{d}_{8}, 300 \mathrm{~K}\right) \delta[\mathrm{ppm}]=-114.8$ (s, 1 P , $\left.\left[\underline{\mathrm{P}}(\mathrm{IMe})_{2}\right]^{+}\right) . \mathrm{ESI}-\mathrm{MS}\left(\mathrm{CH}_{3} \mathrm{CN}\right) \mathrm{m} / \mathrm{z}=271.04\left[\mathrm{Cr}(\mathrm{CO})_{3} \mathrm{Cp}^{*}\right]^{-}(100 \%) . \mathrm{ESI}{ }^{+}-\mathrm{MS}\left(\mathrm{CH}_{3} \mathrm{CN}\right) \mathrm{m} / \mathrm{z}=279.18\left[\mathrm{P}(\mathrm{IMe})_{2}\right]^{+}(100 \%)$.

Analytical data for $4:{ }^{1} \mathrm{H}$ NMR (thf- $\left.\mathrm{d}_{8}, 300 \mathrm{~K}\right) \delta[\mathrm{ppm}]=1.83\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{Cp}^{*}\right), 2.18\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{N}-\mathrm{CH}_{3}\right), 2.24\left(\mathrm{~s}, 12 \mathrm{H}, \mathrm{N}-\underline{\mathrm{CH}}_{3}\right)$, $3.85\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{C}-\mathrm{CH}_{3}\right), 4.06\left(\mathrm{br}, \mathrm{s}, 6 \mathrm{H}, \mathrm{C}-\mathrm{CH}_{3}\right) .{ }^{31} \mathrm{P} \mathrm{NMR}\left(\mathrm{thf}-\mathrm{d}_{8}, 300 \mathrm{~K}\right) \delta[\mathrm{ppm}]=-52.0\left(\mathrm{~d},{ }^{1}{ }^{\mathrm{JpP}}=388 \mathrm{~Hz}, 1 \mathrm{P}\right),-82.1(\mathrm{~d}$, $\left.{ }^{1} \mathrm{~J}_{\mathrm{PP}}=388 \mathrm{~Hz}, 1 \mathrm{P}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}$ (thf $\left.-\mathrm{d}_{8}, 300 \mathrm{~K}\right) \delta[\mathrm{ppm}]=-52.0\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{PP}}=388 \mathrm{~Hz}, 1 \mathrm{P}\right),-82.1\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{PP}}=388 \mathrm{~Hz}, 1 \mathrm{P}\right)$. ESI $-\mathrm{MS}\left(\mathrm{CH}_{3} \mathrm{CN}\right) \mathrm{m} / \mathrm{z}=271.04\left[\mathrm{Cr}(\mathrm{CO})_{3} \mathrm{Cp}^{*}\right]^{-}(100 \%) . \mathrm{ESI}{ }^{+}-\mathrm{MS}\left(\mathrm{CH}_{3} \mathrm{CN}\right) \mathrm{m} / \mathrm{z}=533.20\left[\left\{\mathrm{Cp}^{*} \mathrm{Cr}(\mathrm{CO})_{2}\right\}\left(\eta^{2}-\mathrm{P}_{2} \mathrm{IMe} 2\right)\right]^{+}$ (100\%).

## 3. NMR spectroscopic experiments



Figure $\mathrm{S} 1 .{ }^{1} \mathrm{H}$ NMR spectrum of 1 (recorded in thf- $\mathrm{d}_{8}{ }^{*}$ at 300 K ).


Figure S2. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of 1 (recorded in thf- $\mathrm{d}_{8}$ at 300 K ).


Figure S3. ${ }^{1} \mathrm{H}$ NMR spectrum of 2 (recorded in tol- $\mathrm{d}_{8}{ }^{*}$ at 300 K ).


Figure S4. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of 2 (recorded in tol- $\mathrm{d}_{8}$ at 300 K ); inset: comparison of experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of the anionic entity of 2.

The simulation of the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of the anionic entity of 2 was carried out on the basis of an $\mathrm{A}_{2} \mathrm{X}$ spin system with a $\mathrm{C}_{1}$ symmetry.

Table S1. Experimental and simulated values for the chemical shifts and coupling constants in the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}$ spectrum of 2 (recorded in tol- $\mathrm{d}_{8}$ at 300 K ).

| experimental values |  |  |  | simulated values |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\delta_{\text {A }}$ | 638.6 ppm | ${ }^{1} J_{A X}$ | 353 Hz | $\delta_{\text {A }}$ | 638.6 ppm | ${ }^{1} J_{\text {AX }}$ | 352.6 Hz |
| $\delta_{x}$ | $-384.1$ <br> ppm |  |  | $\delta x$ | -348.1 <br> ppm |  |  |



Figure S5. Experimental ${ }^{1} \mathrm{H}$ NMR (top) and ${ }^{31} \mathrm{P}$ NMR (bottom) spectrum of the crystal mixture of 3 and 4 (ratio 3/1, recorded in thf- $\mathrm{d}_{8}$ at 300 K ).


Figure S6. Experimental ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra of the reaction solution obtained from the reaction of $\mathbf{B}$ with various equivalents of IMe in thf (recorded with $\mathrm{C}_{6} \mathrm{D}_{6}$ capillary at 300 K ; peak marked with asterisk is attributed to the common side product $\left[\mathrm{Cp}{ }^{*} \mathrm{Cr}(\mathrm{CO})_{2}\left(\eta^{3}-\mathrm{P}_{3}\right)\right]$ ).

Table S2. Relative integrals of the signals obtained from the experimental ${ }^{31}$ P NMR spectra (Fig. S6) of reactions of $B$ with varying equivalents of IMe (recorded in thf with $\mathrm{C}_{6} \mathrm{D}_{6}$ capillary at 300 K ).


## 4. DFT calculations

The geometry of the molecules has been optimized using the TURBOMLE program package ${ }^{[v i a i a-d]}$ at the RI-[viiia-b]B3LYP ${ }^{[i x a-e]}$ level together with the def2-TZVP basis set for all atoms. ${ }^{[x a-d]}$ To speed up the calculations, the Coulomb part was evaluated by using the Multipole Accelerated Resolution of Identity method (MARI-J) ${ }^{[x i a-b]}$ along with optimized auxiliary basis sets on all atoms. ${ }^{[x i i]}$ The natural bond orbital analysis (NBO) has been performed with NBO $6.0^{[x i i i]}$ on the wave function obtained at the B3LYP/def2-TZVP level of theory. The topological analysis of the electron density obtained from the DFT calculations, according to the Atoms in Molecules theory ${ }^{[x i i i a-b]}$ has been performed with the MultiWFN program (version 3.6). ${ }^{[x i v a-b]}$ The reaction energies have been calculated using the SCF energies without further corrections.

In order to clarify, why the reaction of 4 with nucleophiles leads to the cleavage of the $\mathrm{Cr}-\mathrm{P}$ bonds, DFT calculations have been performed by Dr. Gábor Balázs (University Regensburg) for the uncoordinated $\mathrm{P}_{4}$ butterfly ligand $\left[\left(C p^{*} \mathrm{Cr}(\mathrm{CO})_{3}\right\}_{2}\left(\mu, \eta^{1: 1}-\mathrm{P}_{4}\right)\right]$ (1) on the BP86/def2-TZVP level. The calculations show that the homolytic cleavage of one $\mathrm{Cr}-\mathrm{P}$ bond in 1 leads to a spontaneous dissociation of the second $\mathrm{Cp}^{*} \mathrm{Cr}(\mathrm{CO})_{3}$ fragment which results in the formation of two $\mathrm{Cp}^{*} \mathrm{Cr}(\mathrm{CO})_{3}$ radicals and $\mathrm{P}_{4}$ with an endothermic dissociation energy of $67.47 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1}$. With a dissociation energy of $142.91 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1}$ the dissociation of the iron analogue $\left[\left(\mathrm{Cp}{ }^{\cdots}{ }^{\prime} \mathrm{Fe}(\mathrm{CO})_{2}\right\}_{2}\left(\mu, \eta^{1: 1-} \mathrm{P}_{4}\right)\right]$ into two $\mathrm{Cp}{ }^{\cdots}{ }^{\mathrm{Fe}}(\mathrm{CO})_{2}$ radicals and $\mathrm{P}_{4}$ is considerably more endothermic. Consequently, the assumption that the $\mathrm{Fe}-\mathrm{P}$ bond in $\mathbf{A}$ is more stable than the corresponding $\mathrm{Cr}-\mathrm{P}$ bond in $\mathbf{B}$ based on the different reactivities towards Grignard reagents, could be confirmed. Moreover, $\left[\left(C p^{*} \mathrm{Cr}(\mathrm{CO})_{3}\right\}_{2}\left(\mu, \eta^{1: 1}-\mathrm{P}_{4}\right)\right]$, the hypothetical $\mathrm{Cp}{ }^{\cdots}$ derivative of $\mathbf{B}$, possesses an even less stable $\mathrm{P}-\mathrm{Cr}$ bond with a corresponding dissociation energy of $32.64 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1}$. Consequently, this compound is expected to be even more likely to dissociate in the presence of a nucleophile.

Table S3. Total SCF energies of A, B, $\left.\left[\mathrm{Cp}{ }^{\prime \prime \prime} \mathrm{Cr}(\mathrm{CO})_{3}\right\}_{2} \mathrm{P}_{4}\right]$ and its corresponding fragments.

| Compound | Total SCF energies [Hartree] |
| :--- | ---: |
| $\left[\mathrm{Cp}^{\prime \prime \prime} \mathrm{Fe}(\mathrm{CO})_{23} 3_{2} \mathrm{P}_{4}\right]$ | -5678.390385 |
| $\left[\mathrm{Cp}{ }^{*} \mathrm{Cr}(\mathrm{CO})_{32} \mathrm{P}_{4}\right]$ | -4916.068238 |
| $\left[\mathrm{Cp}{ }^{\prime \prime \prime} \mathrm{Cr}(\mathrm{CO})_{32} \mathrm{P}_{2}\right]$ | -5466.561083 |
| $\mathrm{Cp}{ }^{\prime \prime \prime} \mathrm{Fe}(\mathrm{CO})_{2}$ | -2156.323069 |
| $\mathrm{Cp}{ }^{*} \mathrm{Cr}(\mathrm{CO})_{3}$ | -1775.176361 |
| $\mathrm{Cp}{ }^{\prime \prime \prime} \mathrm{Cr}(\mathrm{CO})_{3}$ | -2050.429417 |
| $\mathrm{P}_{4}$ | -1365.689817 |

Table S4. Cartesian coordinates of the optimized geometry of $\mathbf{B}$ at the B3LYP/def2-TZVP level ( $\mathrm{E}=-4916.068238$ a.u.).


| Atom | X | Y | Z | Atom | X | Y | Z |
| :--- | ---: | ---: | ---: | ---: | ---: | ---: | ---: |
| Cr | 1.606012700 | -2.263775500 | -2.754572600 | H | 3.987600400 | -2.474684400 | -5.459181500 |
| Cr | -1.818973700 | 3.037472000 | 1.649977500 | H | 3.206162700 | -4.064541700 | -5.470883900 |
| P | 0.637885700 | -0.911879400 | -0.792755700 | C | 2.249757600 | -5.506435800 | -3.130307500 |
| P | -0.659942400 | 0.924895200 | 0.753211700 | H | 3.036544000 | -6.264576900 | -2.982248000 |
| P | -1.164431100 | 0.273110500 | -1.344413500 | H | 1.979784900 | -5.515744000 | -4.193959500 |
| P | 0.722629000 | 1.334948800 | -0.942681700 | H | 1.368994200 | -5.830480700 | -2.561459600 |


| C | -0.050459100 | -2.958632400 | -2.318251500 | C | 2.111966200 | -4.325846100 | -0.144871200 |
| :--- | ---: | ---: | ---: | :--- | ---: | ---: | ---: |
| C | 0.928419700 | -2.601260400 | -4.421549800 | H | 2.910332500 | -4.847009600 | 0.408351000 |
| C | 1.518555200 | -0.538422500 | -3.423369300 | H | 1.357246000 | -5.073261900 | -0.419512500 |
| C | -0.008630500 | 3.160450600 | 2.003689200 | H | 1.642072100 | -3.612315900 | 0.545907300 |
| C | -1.519590800 | 4.806641000 | 1.285936700 | C | 3.738141600 | -1.603598000 | -0.105188800 |
| C | -2.214663300 | 3.064347000 | -0.159665100 | H | 4.636847100 | -2.033811300 | 0.367724900 |
| O | -1.064861100 | -3.480493800 | -2.080377100 | H | 2.932210200 | -1.620269600 | 0.640756700 |
| O | 0.499967800 | -2.826933000 | -5.481850500 | H | 3.955744300 | -0.553942900 | -0.338076900 |
| O | 1.538260200 | 0.502666100 | -3.944276800 | C | -4.308748300 | 5.053799000 | 2.667473800 |
| O | 1.109933500 | 3.296580800 | 2.300837900 | H | -5.167311200 | 5.081136000 | 3.358305800 |
| O | -1.329238500 | 5.935280300 | 1.065409600 | H | -4.695890400 | 5.218917900 | 1.653927800 |
| O | -2.552087800 | 3.175366400 | -1.268465600 | H | -3.657838300 | 5.900690000 | 2.917151100 |
| C | 3.858914800 | -2.121168600 | -2.658089800 | C | -1.919538800 | 4.384399400 | 4.691007500 |
| C | 3.469976100 | -3.218889800 | -3.494835900 | H | -2.493235600 | 4.376262700 | 5.632578200 |
| C | 2.732516400 | -4.157164300 | -2.689183500 | H | -1.914480600 | 5.416437600 | 4.317828800 |
| C | 2.673571700 | -3.634152200 | -1.350255800 | H | -0.884062400 | 4.114105600 | 4.933801000 |
| C | 3.389097200 | -2.388923300 | -1.330603700 | C | -1.293443500 | 1.241024500 | 4.443964300 |
| C | -3.594843500 | 3.740146800 | 2.785613200 | H | -1.826320200 | 0.764922700 | 5.283255400 |
| C | -2.525124700 | 3.436175700 | 3.699900300 | H | -0.506643100 | 1.876566700 | 4.869118000 |
| C | -2.245904000 | 2.028583200 | 3.595807900 | H | -0.805656400 | 0.443569300 | 3.866474900 |
| C | -3.154425200 | 1.468052900 | 2.634655100 | C | -3.338970500 | 0.008919200 | 2.357372800 |
| C | -3.969620300 | 2.527772100 | 2.117929300 | H | -4.002835000 | -0.432690800 | 3.119336600 |
| C | 4.742547100 | -0.978993200 | -3.061013500 | H | -2.389027900 | -0.541528700 | 2.387938900 |
| H | 5.801357600 | -1.235550600 | -2.892712900 | H | -3.796200400 | -0.168093900 | 1.376029000 |
| H | 4.526890700 | -0.071964200 | -2.482466100 | C | -5.120729700 | 2.365963800 | 1.171123900 |
| H | 4.628678400 | -0.730850600 | -4.123603900 | H | -6.041980900 | 2.123279400 | 1.725735300 |
| C | 3.903138600 | -3.424599300 | -4.915903100 | H | -4.946745000 | 1.556842000 | 0.450634800 |
| H | 4.892144500 | -3.910534600 | -4.943235400 | H | -5.311446700 | 3.283694500 | 0.601055700 |
|  |  |  |  |  |  |  |  |

Table S5. Cartesian coordinates of the optimized geometry of $\mathbf{A}$
 at the B3LYP/def2-TZVP level ( $\mathrm{E}=-5678.390385$ a.u.).

| Atom | m X | Y | Z | Atom X |  | Y | Z |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Fe | 3.6563096 | -0.0573871 | -0.5344296 | H | 7.6377924 | 2.7903500 | -0.5509510 |
| Fe | -3.5734605 | 0.0642978 | -0.4911500 | H | 8.5438083 | 2.0613872 | -1.8966510 |
| P | 1.4346193 | -0.0654399 | 0.2647336 | H | 6.7850493 | 2.4750614 | -3.5719375 |
| P | 0.0423094 | -1.0594926 | -1.1801880 | H | 5.8471505 | 3.3681932 | -2.3737814 |
| P | 0.0415403 | 1.1307841 | -1.0388112 | H | 5.0870636 | 2.0499933 | -3.3009071 |
| P - | -1.3489100 | -0.0406703 | 0.2657766 | H | 7.3352290 | -0.6948350 | -1.9324396 |
| O | 2.8109966 | 0.6288459 | -3.2347408 | H | 7.4898786 | 0.3059170 | -3.3783840 |
| 0 | 3.3927000 | -2.8855592 | -1.1742666 | H | 5.9127854 | -0.4046799 | -2.9636918 |
| 0 | -3.3668258 | 2.9682208 | -0.5831879 | H | 5.9367037 | 4.1649204 | -0.5919544 |
| O | -2.6867526 | -0.1596906 | -3.2559047 | H | 5.7572355 | 4.0176707 | 1.1692580 |
| C | 5.5102127 | 1.0350403 | -0.6010401 | H | 4.8615185 | 5.2707712 | 0.2795022 |
| C | 4.5086423 | 1.8167075 | 0.1559351 | H | 2.9807581 | 4.6707130 | -1.2462119 |
| C | 4.1304033 | 0.9963559 | 1.2720522 | H | 2.3195471 | 3.0230693 | -1.2954248 |
| C | 4.8289777 | -0.2409639 | 1.2718196 | H | 3.8271194 | 3.4015196 | -2.1467764 |
| C | 5.6617437 | -0.2020968 | 0.1037312 | H | 2.6899265 | 4.6250201 | 1.1179420 |
| C | -4.7127112 | -1.7776976 | -0.4803460 | H | 3.5149461 | 3.4894502 | 2.2012933 |
| C | -5.6180990 | -0.6223178 | -0.6132905 | H | 2.1487486 | 2.9386790 | 1.1871007 |
| C | -5.3989513 | 0.1760080 | 0.5583415 | H | 5.8911864 | -1.3700029 | 4.3377614 |
| C | -4.4397767 | -0.4243692 | 1.4361342 | H | 5.3939735 | 0.2796575 | 3.8877167 |
| C | -4.0204704 | $-1.6087487$ | 0.7701563 | H | 6.8071465 | -0.4675789 | 3.1056735 |
| C | 6.4837770 | 1.3450573 | -1.7587498 | H | 2.8002232 | -1.9516453 | 2.2666923 |
| C | 7.7968236 | 1.8612014 | -1.1138994 | H | 3.0202808 | -0.5828058 | 3.3718845 |
| C | 6.0084302 | 2.3725379 | -2.7996436 | H | 3.5635348 | -2.2006666 | 3.8573883 |
| C | 6.8180991 | 0.0549650 | -2.5451511 | H | 5.5142523 | -3.3004139 | 2.7837633 |
| C | 3.4730836 | -1.7579433 | -0.9018176 | H | 6.4993007 | -2.4831566 | 1.5600557 |
| C | 3.1198023 | 0.3824773 | -2.1415637 | H | 4.8658777 | -3.0650574 | 1.1481827 |
| C | -3.4183000 | 1.8080024 | -0.5349206 | H | -6.5934491 | -3.7909561 | -0.6688380 |
| C | -3.0194488 | -0.0880064 | -2.1445757 | H | -5.3363035 | -4.2194209 | 0.5111276 |
| C | 4.0139968 | 3.2765072 | 0.0584701 | H | -5.4500268 | -5.1048754 | -1.0292124 |
| C | 5.2192597 | 4.2314600 | 0.2340569 | H | -5.8597797 | -2.8098966 | -2.9903965 |
| C | 3.2505116 | 3.6038173 | -1.2412143 | H | -4.6679604 | -4.1010278 | -3.1473749 |
| C | 3.0364269 | 3.5865582 | 1.2161150 | H | -4.1449514 | -2.4133092 | -3.2660181 |
| C | 4.8767901 | -1.2604866 | 2.4029248 | H | -3.0469792 | -4.6213463 | -1.6207549 |
| C | 5.7989346 | -0.6650447 | 3.4980009 | H | -2.8991709 | -3.9243773 | -0.0056567 |
| C | 3.4825907 | -1.5096892 | 3.0051671 | H | -2.3715230 | -2.9883253 | -1.4236062 |
| C | 5.4728452 | -2.6007301 | 1.9365130 | H | -8.6706415 | -1.0485071 | -2.2299937 |
| C | -4.5625208 | -3.1191714 | -1.2285756 | H | -8.1946882 | -1.5367034 | -0.5871796 |
| C | -5.5495885 | -4.1136225 | -0.5620716 | H | -7.4536480 | -2.3146521 | -2.0012323 |
| C - | -4.8311948 | -3.0913229 | -2.7429043 | H | -8.2306953 | 1.2896249 | -1.8949907 |


| C | -3.1341998 | -3.6854571 | -1.0509118 | H | -6.7516595 | 1.8996080 | -1.1353807 |
| :--- | ---: | ---: | ---: | ---: | ---: | ---: | ---: |
| C | -6.7373342 | -0.2551977 | -1.6128545 | H | -7.9239280 | 0.9427621 | -0.1835729 |
| C | -7.8199530 | -1.3606072 | -1.6060930 | H | -5.6870027 | -0.8376556 | -3.4757343 |
| C | -7.4438476 | 1.0464173 | -1.1671987 | H | -5.5799140 | 0.8824708 | -3.0725129 |
| C | -6.2385368 | 0.0039946 | -3.0497165 | H | -7.0992093 | 0.2087608 | -3.7045329 |
| C | -4.1407382 | 0.0091335 | 2.8667694 | H | -5.7591044 | -1.2596361 | 3.6487168 |
| C | -5.4366332 | -0.2090204 | 3.6878872 | H | -6.2610666 | 0.4145341 | 3.3131417 |
| C | -3.7484030 | 1.4975101 | 2.9384466 | H | -5.2629214 | 0.0557806 | 4.7415912 |
| C | -3.0170797 | -0.8418571 | 3.4844882 | H | -3.6225188 | 1.8021326 | 3.9881379 |
| H | 3.3910026 | 1.2798022 | 2.0127792 | H | -4.5180015 | 2.1450145 | 2.4944692 |
| H | 6.3260392 | -1.0031998 | -0.2004338 | H | -2.8014818 | 1.6799189 | 2.4124878 |
| H | -5.9090101 | 1.1108168 | 0.7640857 | H | -3.2899000 | -1.9071261 | 3.5191295 |
| H | -3.2751462 | -2.2967939 | 1.1529159 | H | -2.8312844 | -0.5145814 | 4.5179538 |
| H | 8.2165244 | 1.1159085 | -0.4233977 | H | -2.0787274 | -0.7395847 | 2.9208763 |

Table S6. Cartesian coordinates of the optimized geometry of
 [Cp'" $\mathrm{Cr}(\mathrm{CO})_{3} 3_{2} \mathrm{P}_{4}$ ] at the B3LYP/def2-TZVP level
( $\mathrm{E}=-5678.390385$ a.u.).

| Atom | m X | Y | Z | Atom | m X | Y | Z |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Cr | 3.1458758 | -2.5049025 | -0.4663258 | H | 5.4791294 | -5.7944156 | -0.3584641 |
| Cr | -2.1239157 | 3.1003545 | -1.2984781 | H | 4.4838558 | -7.2140705 | -0.0320310 |
| P | 1.2402315 | -0.7813435 | -0.1712300 | H | 3.8286485 | -5.8943521 | -1.0180371 |
| P -0. | -0.6928364 | 1.0784640 | -0.4857389 | C | 5.6351434 | 0.5371900 | 0.4393518 |
| P | 0.1531819 | -0.3003237 | -2.0558393 | H | 4.9183964 | 0.7211529 | -0.3709223 |
| P | 1.4345590 | 1.2384199 | -1.1461223 | H | 5.1598458 | 0.8173485 | 1.3902028 |
| C | 1.5627692 | -3.3674565 | -0.8841603 | H | 6.4903405 | 1.2122063 | 0.2908639 |
| C | 3.6487683 | -3.4331418 | -1.9645366 | C | 6.8648887 | -1.2343615 | -0.8583658 |
| C | 3.4436006 | -1.1685455 | -1.7046147 | H | 7.7161079 | -0.5481662 | -0.9757653 |
| C | -0.6727071 | 3.7303537 | -0.3437112 | H | 7.2668067 | -2.2575721 | -0.8668044 |
| C | -1.5845611 | 4.5505345 | -2.2768021 | H | 6.2122674 | -1.1132293 | -1.7320879 |
| C - | -1.5767303 | 2.2681390 | -2.8584445 | C | 7.1185525 | -1.0940123 | 1.6344387 |
| 0 | 0.6098060 | -3.9674480 | -1.1817343 | H | 6.6346040 | -0.8755961 | 2.5971567 |
| O | 3.9672273 | -3.9880837 | -2.9378351 | H | 7.5140322 | -2.1190428 | 1.6761308 |
| 0 | 3.7331548 | -0.4045538 | -2.5375284 | H | 7.9671375 | -0.4044435 | 1.5135735 |
| $\bigcirc$ | 0.2057572 | 4.2260891 | 0.2414095 | H | 3.5133439 | -0.7059770 | 1.8693087 |
| O | -1.2096895 | 5.4746789 | -2.8804256 | H | 5.7517304 | -3.8068385 | -0.1333303 |
| 0 | -1.2861639 | 1.8377359 | -3.9011770 | C | -2.7312710 | 5.1275549 | 2.1531628 |
| C | 4.9866375 | -1.9015318 | 0.7141117 | H | -3.4537139 | 5.8577219 | 1.7610677 |
| C | 4.9906514 | -3.2973135 | 0.4480604 | H | -2.6005931 | 5.3408669 | 3.2239587 |
| C | 3.8866115 | -3.9598429 | 1.0926161 | H | -1.7661515 | 5.2947016 | 1.6583172 |
| C | 3.1361783 | -2.9088086 | 1.7851934 | C | -2.2351470 | 2.7086201 | 2.6319423 |
| C | 3.8236442 | -1.6773133 | 1.5013358 | H | -2.1519551 | 2.9359316 | 3.7049585 |
| C | -4.2957576 | 3.5472909 | -1.7021866 | H | -2.5628407 | 1.6636967 | 2.5404885 |
| C | -3.8286218 | 4.2524040 | -0.5341020 | H | -1.2333223 | 2.7878087 | 2.1908345 |
| C | -3.4718730 | 3.3461176 | 0.5045819 | C | -4.6015947 | 3.5434616 | 2.6797538 |
| C | -3.6661473 | 2.0522588 | -0.0478172 | H | -5.3470280 | 4.2200903 | 2.2377731 |
| C | -4.1894525 | 2.1229575 | -1.3843154 | H | -4.9862312 | 2.5163715 | 2.6049143 |
| C | 6.1250390 | -0.9217631 | 0.4552710 | H | -4.5011385 | 3.7943823 | 3.7461842 |
| C | 3.8748608 | -5.5046179 | 1.1491797 | C | -4.8231405 | 0.8000474 | -3.5591474 |
| C | 2.0096806 | -2.9434863 | 2.8497147 | H | -3.8350916 | 0.9349920 | -4.0173385 |
| C | -4.9572461 | 4.3215865 | -2.8679292 | H | -5.1994733 | -0.1845662 | -3.8729616 |
| C | -3.2280354 | 3.6820205 | 1.9719444 | H | -5.5070641 | 1.5492572 | -3.9705221 |
| C | -4.7480707 | 0.8299438 | -2.0231835 | C | -6.1743768 | 0.6306994 | -1.4440866 |
| C | 1.7551935 | -1.5234999 | 3.4095737 | H | -6.6074329 | -0.2997535 | -1.8407628 |
| H | 1.4119182 | -0.8285698 | 2.6308228 | H | -6.1454396 | 0.5519489 | -0.3479966 |
| H | 0.9633173 | -1.5836691 | 4.1697715 | H | -6.8469806 | 1.4572761 | -1.7052141 |
| H | 2.6485492 | -1.1042970 | 3.8947821 | C | -3.9100280 | -0.4014464 | -1.6100415 |
| C | 2.4744793 | -3.7936323 | 4.0569600 | H | -3.9050422 | -0.5726139 | -0.5259530 |
| H | 1.7427470 | -3.6946495 | 4.8724318 | H | -4.3442019 | -1.2989169 | -2.0730517 |
| H | 2.5617228 | -4.8597016 | 3.8222681 | H | -2.8693053 | -0.3185380 | -1.9494429 |
| H | 3.4473134 | -3.4450611 | 4.4336897 | C | -6.4643483 | 3.9686467 | -2.9151006 |
| C | 0.6496454 | -3.4547145 | 2.3308930 | H | -6.9700814 | 4.6210894 | -3.6421719 |
| H | 2.0366689 | -5.9173171 | 2.3082965 | H | -6.6482084 | 2.9324307 | -3.2190837 |
| H | -0.0570381 | -3.5235362 | 3.1719524 | H | -6.9367698 | 4.1258279 | -1.9344364 |
| H | 0.2279385 | -2.7519704 | 1.5993424 | C | -4.8867465 | 5.8456976 | -2.6120569 |
| C | 2.4970152 | -6.1601672 | 1.3455548 | H | -3.8538214 | 6.2098876 | -2.5346934 |
| H | 1.8006081 | -5.8794457 | 0.5443715 | H | -5.3531637 | 6.3663472 | -3.4603085 |
| H | 2.6165879 | -7.2531353 | 1.3124508 | H | -5.4348262 | 6.1382127 | -1.7050329 |
| H | 0.7084017 | -4.4394140 | 1.8604301 | C | -4.3133721 | 4.0828293 | -4.2502763 |


| C | 4.8154725 | -5.9220346 | 2.3111562 | H | -3.3055142 | 4.5136497 | -4.2925940 |
| :--- | ---: | ---: | ---: | ---: | ---: | ---: | ---: |
| H | 4.4775000 | -5.5333043 | 3.2793007 | H | -4.2368122 | 3.0260827 | -4.5156991 |
| H | 4.8572682 | -7.0194167 | 2.3796094 | H | -4.9189651 | 4.5807531 | -5.0227304 |
| H | 5.8370203 | -5.5539609 | 2.1384089 | H | -3.4755957 | 1.1249065 | 0.4823527 |
| C | 4.4532269 | -6.1209447 | -0.1454723 | H | -3.7900245 | 5.3317937 | -0.4459988 |

Table S7. Cartesian coordinates of the optimized geometry of 4 at the B3LYP/def2-TZVP level ( $\mathrm{E}=-3110.31259080507$ a.u.).

| Atom | x | y | z |
| :--- | ---: | ---: | ---: |
|  |  |  |  |
| Cr | 2.169143400 | 0.017355100 | 1.185933300 |
| P | -0.061701000 | -0.001879400 | 2.237046400 |
| P | -0.052956500 | 0.034879300 | 0.083201200 |
| N | -1.453430900 | 2.666767800 | 0.034608300 |
| N | -0.250691400 | -2.444639900 | 3.649602500 |
| N | -1.728437900 | -2.410116400 | 2.078091400 |
| N | -0.322523100 | 2.118529900 | -1.721696400 |
| O | 2.516394500 | -2.829156100 | 2.010026900 |
| O | 2.776562500 | -1.100895200 | -1.528502600 |
| C | -0.630184900 | 1.710997500 | -0.462395300 |
| C | -0.706333600 | -1.700086000 | 2.614728100 |
| C | -1.647815600 | 3.678659300 | -0.905401500 |
| C | -0.933144800 | 3.334277600 | -2.009191600 |
| C | -1.886860100 | -3.618712600 | 2.754836500 |
| C | -0.958814700 | -3.635480100 | 3.748129600 |
| C | 4.283693500 | 0.611921100 | 1.364548700 |
| C | 3.754509300 | 0.566798600 | 2.688876500 |
| C | 2.351721000 | -1.730017900 | 1.687230600 |
| C | -2.502398000 | 4.866512000 | -0.634008100 |
| H | -3.534581100 | 4.583333600 | -0.414188400 |
| H | -2.519857800 | 5.521844700 | -1.502137400 |
| H | -2.132113100 | 5.449439000 | 0.212896900 |
| C | 2.512417900 | -0.677422900 | -0.488803500 |
| C | -2.126323200 | 2.672529000 | 1.327530600 |
| H | -1.772011300 | 1.837343500 | 1.922046100 |
| H | -3.204830200 | 2.591707800 | 1.185477000 |
| H | -1.908420900 | 3.601339900 | 1.853514100 |
| C | 3.594921600 | 1.647841200 | 0.654631900 |
| C | 0.783475800 | -2.047808000 | 4.596230500 |
| H | 1.278478200 | -1.157856300 | 4.223835800 |
| H | 1.517779500 | -2.843966500 | 4.695111500 |
| H | 0.337094200 | -1.834084600 | 5.568112800 |
| C | -0.652263900 | -4.662916000 | 4.779351900 |
| H | 0.362267600 | -5.053087500 | 4.667355600 |
| H | -1.340604700 | -5.500797300 | 4.692767300 |
| H | -0.745234700 | -4.261835800 | 5.791402300 |
| C | 0.518711300 | 1.376589300 | -2.657150700 |
|  |  |  |  |


| Atom | X | y |  |
| :---: | :---: | :---: | :---: |
| H | 1.574044000 | 1.563552900 | -2.466059400 |
| H | 0.275974300 | 1.683664200 | -3.670178800 |
| H | 0.328345700 | 0.310336400 | -2.554672800 |
| C | 2.756086700 | 1.578064000 | 2.799516300 |
| C | -2.906015100 | -4.632987000 | 2.370336000 |
| H | -3.925860900 | -4.264946900 | 2.508870000 |
| H | -2.794044400 | -5.523257400 | 2.985616600 |
| H | -2.799395600 | -4.937252800 | 1.326689600 |
| C | 2.644441100 | 2.234659500 | 1.542602000 |
| C | -2.605639500 | -1.993149500 | 0.989414000 |
| H | -2.659084200 | -0.910852700 | 0.964051000 |
| H | -3.599075600 | -2.397227300 | 1.168941600 |
| H | -2.234823300 | -2.348836800 | 0.029151700 |
| C | -0.768343600 | 4.036517200 | -3.311380700 |
| H | 0.282179400 | 4.234754500 | -3.535477300 |
| H | -1.286223100 | 4.993030100 | -3.287857800 |
| H | -1.183180500 | 3.459145600 | -4.141399100 |
| C | 4.312787700 | -0.249574800 | 3.815947000 |
| H | 3.582732600 | -0.410604500 | 4.609077600 |
| H | 5.167509400 | 0.263540700 | 4.267544000 |
| H | 4.661080300 | -1.226251200 | 3.481415600 |
| C | 2.080649600 | 2.009602700 | 4.064036900 |
| H | 1.063819000 | 2.361233500 | 3.891222800 |
| H | 2.639662300 | 2.831366200 | 4.523420300 |
| H | 2.031093400 | 1.206542500 | 4.798515200 |
| C | 3.975123900 | 2.177611900 | -0.695200100 |
| H | 4.307442100 | 1.390528100 | -1.371580800 |
| H | 4.798563900 | 2.892607200 | -0.601013900 |
| H | 3.148395000 | 2.705366200 | -1.171317800 |
| C | 5.477269000 | -0.150253100 | 0.872199400 |
| H | 5.546256700 | -1.136540400 | 1.330642400 |
| H | 6.400095300 | 0.387504100 | 1.112593900 |
| H | 5.455617000 | -0.291799300 | -0.208060400 |
| C | 1.842381400 | 3.473114400 | 1.280979500 |
| H | 1.577014600 | 3.576675700 | 0.229113200 |
| H | 2.414651200 | 4.365005400 | 1.557230900 |
| H | 0.922010300 | 3.492217300 | 1.865208000 |

The AIM analysis of the electron density in 4 allowed the detection of bond critical points (BCPs) along the $\mathrm{P}-\mathrm{P}$ and $\mathrm{Cr}-\mathrm{P}$ bonds (Figure S 7 ). The locations of BCPs corresponding to the $\mathrm{Cr}-\mathrm{P}$ bonds point towards a metallacyclopropane-like bonding. However, the relatively high ellipticity at the BCPs 1-3 (P2Cr core) indicates a deformation of the electron density in this plane, hence the presence of a $\mathrm{P}-\mathrm{P}$ double bond.


Figure S7. Locations and labeling of selected Bond Critical Points (BCP, green) and Ring Critical Points (RCP, violet) in the electron density of 4 .

Table S8. Properties of selected critical points in the electron density of 4. $\rho(\mathrm{r})=$ electron density at CP; $\nabla^{2} \rho(r)=$ Laplacian of electron density; $H(r)=$ energy density; $G(r)=$ Lagrangian kinetic energy; $V(r)=$ potential energy density; $\varepsilon(r)=$ ellipticity of electron density at $C P\left(\varepsilon(r)=\left[\lambda_{1}(r) / \lambda_{2}(r)\right]-1\right.$; where $\lambda_{1}$ and $\lambda_{2}$ are the lowest and the second lowest eigenvalues of Hessian matrix of $\rho$, respectively); $\eta(r)=$ eta index $\left(\eta(r)=\left|\lambda_{1}(r)\right| / \lambda_{3}(r)\right.$, where $\lambda_{1}$ and $\lambda_{3}$ are the lowest and the highest eigenvalues of Hessian matrix of $\rho$, respectively); Bond degree, $B D=H(B C P) / \rho(B C P)$ (the more positive the BD , the weaker the interaction).

|  | $\rho(r)$ | $\nabla^{2} \rho(r)$ | $H(r)$ | $G(r)$ | $\mathrm{V}(r)$ | $\|V\| / G$ | $\varepsilon(r)$ | $\eta(r)$ | 1.548 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| BCP-1 | 0.122 | -0.145 | -0.069 | 0.033 | -0.101 | 3.118 | 0.399 | -0.566 |  |
| BCP-2 | 0.059 | 0.098 | -0.016 | 0.040 | -0.056 | 1.390 | 0.331 | 0.263 | -0.265 |
| BCP-3 | 0.055 | 0.117 | -0.013 | 0.042 | -0.055 | 1.306 | 0.334 | 0.182 |  |
| BCP-7 | 0.331 | -1.009 | -0.511 | 0.259 | -0.769 | 2.975 | -0.235 | 0.224 | 1.962 |
| BCP-6 | 0.330 | -1.002 | -0.505 | 0.254 | -0.759 | 2.985 | 0.223 | 1.972 | -1.542 |
| BCP-4 | 0.142 | 0.003 | -0.119 | 0.119 | -0.238 | 1.993 | 0.185 | 0.537 | -0.838 |
| BCP-5 | 0.141 | 0.001 | -0.117 | 0.118 | -0.235 | 1.998 | 0.234 | 0.551 | -0.835 |
| BCP-8 | 0.329 | -0.998 | -0.502 | 0.253 | -0.755 | 2.987 | 0.216 | 1.968 |  |
| BCP-9 | 0.329 | -1.008 | -0.499 | 0.247 | -0.746 | 3.020 | 0.212 | 1.997 | -1.519 |
| RCP | 0.051 | 0.114 | -0.011 | 0.040 | -0.051 | 1.284 | - | - | - |

To gain further insight in the electronic structure of 4, the compound has been investigated by DFT calculations at the B3LYP/def2-TZVP level. The natural population analysis (NPA) shows that the Cr atom is negatively charged ( -0.86 ), while the $\mathrm{Cp}^{*}$ ligand and the CO groups are slightly positively charged ( 0.15 and 0.36 , respectively) resulting in an overall negative charge of -0.35 for the $\left\{\mathrm{Cp}^{*} \mathrm{Cr}(\mathrm{CO})_{2}\right\}$ fragment. The central $\mathrm{P}_{2}$ unit and the two NHC fragments bear a positive charge of $0.37,0.51$ and 0.47 , respectively, resulting in a $\left\{\mathrm{P}_{2} \mid \mathrm{Me}_{2}\right\}$ fragment with an overall positive charge of 1.35. The Wiberg Bond Index (WBI) of the P-P bond (1.14) confirms only a weak double bond character, while the WBls of the C-P bonds ( 0.98 and 1.01) are characteristic for single bonds. The NBO analysis illustrates the presence of only one lone pair of electrons on each P atom in an approximate $\mathrm{sp}^{0.5}$ hybrid orbital, alongside to two weakly polarized $\mathrm{Cr}-\mathrm{P}$ bonds in which the P atoms participate with almost pure p orbitals ( $\mathrm{sp}^{11}$ and $\mathrm{sp}^{7.2}$ ). This description of the electronic structure of 4 is in line with the localized molecular orbitals. In Figure S 7 the localized molecular orbitals corresponding to the $\mathrm{C}-\mathrm{P}$ bond, the $\mathrm{P}-\mathrm{P}$ bond, the lone pair of electrons on the P atom and the $\mathrm{Cr}-\mathrm{P}$ bond are depicted.

Figure S8. Selected localized molecular orbitals of 4.


## 5. Crystallographic details

$\left[\mathrm{P}(\mathrm{IMe})_{2}\right]\left[\mathrm{Cp}{ }^{\prime \prime \prime} \mathrm{Fe}(\mathrm{CO})_{2}\right](1)$
Compound 1 crystalizes in the form of dark orange plates from a saturated solution in thf at room temperature after 3 days. A suitable crystal with dimensions $0.29 \times 0.20 \times 0.08 \mathrm{~mm}^{3}$ was selected and mounted on a Xcalibur, AtlasS2, Gemini ultra diffractometer. The crystal was kept at a steady $T=123(1) \mathrm{K}$ during data collection. The structure was solved with the ShelXT 2018/2 (Sheldrick, 2018) solution program using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with SheIXL 2018/3 (Sheldrick, 2015) using full matrix least squares minimization on $F^{2}$. The asymmetric unit contains one molecule of 1.
$\left[P(I M e)_{2}\right]\left[\left\{C p^{\prime \prime \prime} \mathrm{Fe}\right\}_{2}\left(\mu, \mathrm{r}^{\left.\left.3: 3-\mathrm{P}_{3}\right)\right](2)}\right.\right.$
Compound 2 crystalizes in the form of dark red blocks from a saturated solution in toluene after one week. A suitable crystal with dimensions $0.42 \times 0.16 \times 0.05 \mathrm{~mm}^{3}$ was selected and mounted on a GV50, TitanS2 diffractometer. The crystal was kept at a steady $T=123.01(10) \mathrm{K}$ during data collection. The structure was solved with the SheIXT 2018/2 (Sheldrick, 2018) solution program using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL 2018/3 (Sheldrick, 2015) using full matrix least squares minimization on $F^{2}$. The asymmetric unit contains one molecule of 2 .
$\left[\mathrm{P}(\mathrm{IMe})_{2}\right]\left[\mathrm{Cp}{ }^{*} \mathrm{Cr}(\mathrm{CO})_{3}\right]$ (3)
Compound 3 crystalizes in the form of clear yellow blocks after layering a saturated reaction solution in thf with npentane after a few days. A suitable crystal with dimensions $0.10 \times 0.05 \times 0.04 \mathrm{~mm}^{3}$ was selected and mounted on a GV50, TitanS2 diffractometer. The crystal was kept at a steady $T=123.1(3) \mathrm{K}$ during data collection. The structure was solved with the SheIXT 2018/2 (Sheldrick, 2018) solution program using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with SheIXL 2018/3 (Sheldrick, 2015) using full matrix least squares minimization on $F^{2}$. Due to poor quality of the obtained crystals only preliminary values can be given for the structural parameters (table S9). The asymmetric unit contains two anionic and cationic fragments of 3.

$$
\left[\left\{\mathrm{Cp}^{*} \mathrm{Cr}(\mathrm{CO})_{2}\right\}\left(\eta^{2}-\mathrm{P}_{2} \mathrm{Me}_{2}\right)\right]\left[\mathrm{Cp}^{*} \mathrm{Cr}(\mathrm{CO})_{3}\right] \text { (4) }
$$

Compound 4 crystalizes in the form of dark brown blocks after layering a saturated reaction solution in thf with n pentane after a few days. A suitable crystal with dimensions $0.17 \times 0.14 \times 0.10 \mathrm{~mm}^{3}$ was selected and mounted on a GV50, TitanS2 diffractometer. The crystal was kept at a steady $T=123.00$ (16) K during data collection. The structure was solved with the SheIXT 2018/2 (Sheldrick, 2018) solution program using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with SheIXL 2018/3 (Sheldrick, 2015) using full matrix least squares minimization on $F^{2}$. The asymmetric unit contains one molecule of 4 .

CCDC-2060507 (1), CCDC-2060508 (2) and CCDC-2060509 (4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html

Table S9. Selected parameters for the single crystal X-ray diffraction experiments of 1, 2, 3 and 4.

| Compound | 1 | 2 | 3 | 4 |
| :---: | :---: | :---: | :---: | :---: |
| CCDC | 2060507 | 2060508 |  | 2060509 |
| Formula | $\mathrm{C}_{33} \mathrm{H}_{53} \mathrm{FeN}_{4} \mathrm{O}_{2} \mathrm{P}$ | $\mathrm{C}_{48} \mathrm{H}_{82} \mathrm{Fe}_{2} \mathrm{~N}_{4} \mathrm{P}_{4}$ | $\mathrm{C}_{54} \mathrm{H}_{78} \mathrm{Cr}_{2} \mathrm{~N}_{8} \mathrm{O}_{6} \mathrm{P}_{2}$ | $\mathrm{C}_{39} \mathrm{H}_{54} \mathrm{Cr}_{2} \mathrm{~N}_{4} \mathrm{O}_{5} \mathrm{P}_{2}$ |
| $D_{\text {calc. }} / \mathrm{g} \mathrm{cm}^{-3}$ | 1.203 | 1.269 | 1.266 | 1.318 |
| $\mu / \mathrm{mm}^{-1}$ | 4.198 | 6.156 | 4.047 | 5.399 |
| Formula Weight | 624.61 | 950.75 | 1101.18 | 824.80 |
| Colour | orange | dark pink | yellow | dark brown |
| Shape | plate | block | plate | block |
| Size/mm ${ }^{3}$ | $0.29 \times 0.20 \times 0.08$ | $0.42 \times 0.16 \times 0.05$ | $0.10 \times 0.05 \times 0.04$ | $0.17 \times 0.14 \times 0.10$ |
| T/K | 123(1) | 123.01(10) | 123.1(3) | 123.00(16) |
| Crystal System | triclinic | monoclinic | triclinic | monoclinic |
| Space Group | $P \overline{1}$ | $P 2_{1} / n$ | $P \overline{1}$ | $P 2{ }_{1} / n$ |
| $a / \AA$ | 10.8194(4) | 13.7995(2) | 8.9241(12) | 14.7956(3) |
| b/A | 12.5965(6) | 22.0551(3) | 18.0574(17) | 8.60807(16) |
| $c / \AA$ | 15.1388(6) | 16.5807(2) | 18.8286(14) | 32.9425(6) |
| $\alpha /{ }^{\circ}$ | 106.563(4) | 90 | 106.662(7) | 90 |
| $\beta /^{\circ}$ | 98.875(3) | 99.5490(10) | 91.003(9) | 97.7244(16) |
| $\gamma /{ }^{\circ}$ | 113.707(4) | 90 | 95.628(9) | 90 |
| $\mathrm{V} / \AA^{3}$ | 1723.64(14) | 4976.40(12) | 2889.4(5) | 4157.52(13) |
| Z | 2 | 4 | 2 | 4 |
| Z' | 1 | 1 | 1 | 1 |
| Wavelength/Å | 1.54184 | 1.54184 | 1.54184 | 1.54184 |
| Radiation type | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ |
| $\Theta_{\text {min }} /{ }^{\circ}$ | 4.151 | 3.365 | 4.035 | 3.467 |
| $\boldsymbol{O}_{\text {max }} /^{\circ}$ | 72.873 | 74.005 | 62.387 | 75.267 |
| Measured Refl's. | 12167 | 20961 | 49308 | 35858 |
| Ind't Refl's | 6639 | 9772 | 9187 | 8355 |
| Refl's with I > 2(I) | 6295 | 9039 | 3895 | 7041 |
| $R_{\text {int }}$ | 0.0194 | 0.0395 | 0.3119 | 0.0616 |
| Parameters | 387 | 579 | 676 | 679 |
| Restraints | 0 | 57 | 0 | 314 |
| Largest Peak | 0.530 | 0.713 | 0.809 | 0.479 |
| Deepest Hole | -0.232 | -1.177 | -0.775 | -0.459 |
| GooF | 1.030 | 1.063 | 1.088 | 1.040 |
| $w R_{2}$ (all data) | 0.0887 | 0.1239 | 0.4240 | 0.1261 |
| $w R_{2}$ | 0.0871 | 0.1203 | 0.3433 | 0.1180 |
| $R_{1}$ (all data) | 0.0363 | 0.0520 | 0.2256 | 0.0548 |
| $\mathrm{R}_{1}$ | 0.0339 | 0.0488 | 0.1401 | 0.0456 |



1



2



3

Figure S9. Molecular structure of 1, 2 and 3 in the solid state; H atoms are omitted for clarity and CO as well as Cp ligands are drawn in a wire frame model; thermal ellipsoids are drawn at $50 \%$ probability.



Figure S10. Molecular structure of 4 in the solid state; H atoms are omitted for clarity and CO as well as $\mathrm{Cp}^{*}$ ligands are drawn in a wire frame model (only one part of the disordered $\mathrm{Cp}^{*}$ ligand is depicted); thermal ellipsoids are drawn at 50\% probability.

Table S10. Selected bond lengths $[\AA \AA]$ and angles $\left[{ }^{\circ}\right]$ of the $\left[\mathrm{P}(\mathrm{IMe})_{2}\right]^{+}$cation of $\mathbf{1 , 2} 2$ and $\mathbf{3}$ in the solid state.

|  |  | P-C [Å] | C-P-C [ ${ }^{\circ}$ ] | Twist angle [ $\left.{ }^{\circ}\right]^{[1]}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{1}$ | $1.8049(17)$ | $1.8054(18)$ | $95.79(8)$ | $42.10(8)$ | $44.75(8)$ |
| $\mathbf{2}$ | $1.802(2)$ | $1.797(2)$ | $102.65(10)$ | $26.08(10)$ | $49.42(10)$ |
| $\mathbf{3}^{[2]}$ | $1.805(13)$ | $1.787(11)$ | $98.3(6)$ | $35.9(7)$ | $44.9(7)$ |
|  | $1.817(13)$ | $1.792(12)$ | $96.9(6)$ | $36.3(7)$ | $46.7(7)$ |

${ }^{[1]}$ Distortion angle between the $\mathrm{PC}^{\text {Carbene }}{ }_{2}$ plane and the planes spanned by the NHC ring systems.
${ }^{\text {[2] }}$ Preliminary values due to poor single crystal X-ray diffraction data.
 state.

|  | $d / \AA$ |  | $\alpha /{ }^{\circ}$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Fe1-P1 | $2.1942(6)$ | Fe2-P3 | $2.1971(6)$ | Fe1-P1-Fe2 | 79.94(2) |
| Fe1-P2 | $2.4221(6)$ | P1-P2 | $2.1601(8)$ | Fe1-P2-Fe2 | $71.315(18)$ |
| Fe1-P3 | $2.1931(6)$ | P2-P3 | $2.1897(8)$ | Fe1-P3-Fe2 | $80.06(2)$ |
| Fe2-P1 | $2.2015(6)$ | Fe1-Fe2 | $2.8236(4)$ | P1-P2-P3 | $95.21(3)$ |
| Fe2-P2 | $2.4217(6)$ |  |  |  |  |

Table S12. Selected bond lengths [ $\AA \AA$ ] and angles [ ${ }^{\circ}$ ] of 4 in the solid state.

|  | $d / \AA$ |  | $\alpha /^{\circ}$ |  |  |
| :--- | :---: | :--- | :---: | :---: | :---: |
| Cr1-P1 | 2.3954(7) | P1-Cr1-P2 | 52.02(2) | P1-Cr1-P2-C8 | 93.98(8) |
| Cr1-P2 | 2.4480(7) | P2-P1-Cr1 | 65.26(3) | P2-Cr1-P1-C1 | 93.37(8) |
| P1-P2 | $2.1246(8)$ | P1-P2-Cr1 | 62.71(2) |  |  |
| P1-C | $1.842(3)$ | C1-P1-Cr1 | 114.09(8) |  |  |
| P2-C | $1.835(3)$ | C8-P2-Cr1 | 112.90(8) |  |  |

## 6. Additional Information

Initial studies showed that reactions of the $\mathrm{P}_{4}$ butterfly compounds $\mathbf{A}$ and $\mathbf{B}$ with nucleophiles like $\mathrm{LiNMe}_{2}$, $\mathrm{LiCH}_{2} \mathrm{SiMe}_{3}, \mathrm{KCHPh}_{2}$ at various reaction conditions result in either uncontrollable decomposition of the starting materials or no conversion at all.

Table S13. Comparison of structural parameters of the $\left[\left\{C p^{\prime \prime \prime F e}\right\}_{2}\left(\mu, \eta^{3: 3}-P_{3}\right)\right]^{-}$anion found in 2 and the neutral $\left[\left\{\mathrm{Cp}^{\prime \prime \prime F e}\right\}_{2}\left(\mu, \eta^{3: 3}-\mathrm{P}_{3}\right)\right](\mathrm{C})^{[16]}$ in the solid state.

|  | d/A |  |  |  | $\alpha 1^{\circ}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 2 | C |  | 2 | C |  | 2 | c |
| Fe1-P1 | 2.1942(6) | 2.225(1) | P1-P2 | $2.1601(8)$ | 2.148(1) | Fe1-P1-Fe2 | 79.94(2) | 71.51(4) |
| Fe1-P2 | 2.4221(6) | 2.2446(1) | P2-P3 | 2.1897 (8) | 2.148(1) | Fe1-P2-Fe2 | 71.315(18) | 63.92(4) |
| Fe1-P3 | 2.1931(6) | 2.225(1) | Fe1-Fe2 | $2.8236(4)$ | 2.589(1) | Fe1-P3-Fe2 | 80.06(2) | 71.51(4) |
| Fe2-P1 | 2.2015(6) | 2.225(1) |  |  |  | P1-P2-P3 | $95.21(3)$ | 100.71(7) |
| Fe2-P2 | 2.4217(6) | 2.2446(1) |  |  |  |  |  |  |
| Fe2-P3 | 2.1971(6) | 2.225(1) |  |  |  |  |  |  |

## 7. Supplementary References

[i] C. Schwarzmaier, A. Y. Timoshkin, G. Balázs, M. Scheer, Angew. Chem. Int. Ed. 2014, 53, 9077-9081.
[ii] (a) R. B. King, J. Organomet. Chem. 1967, 8, 139-148.
(b) P. Leoni, A. Landi, M. Pasquali, J. Organomet. Chem. 1987, 321, 365-369.
(c) T. J. Jaeger, M. C. Baird, Organometallics 1988, 7, 2074-2076.
(d) C. Schwarzmaier, A. Y. Timoshkin, G. Balázs, M. Scheer, Angew. Chem. Int. Ed. 2014, 53, 9077-9081.
[iii] N. Kuhn, T. Kratz, Syntheses 1993, 6, 561-562.
[iii] A. J. Arduengo, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marschall, M. Unverzagt, Tetrahedron 1999, 55, 14523-14534.
[iv] M. Schlosser, J. Hartmann, Angew. Chem. 1973, 85, 544-545; Angew. Chem. Int. Ed. Engl. 1973, 12, 508-509.
[v] TopSpin 3.0, Bruker BioSpin GmbH
[vi] (a) F. Furche, R. Ahlrichs, C. Hättig, W. Klopper, M. Sierka, F. Weigend, WIREs Comput. Mol. Sci. 2014, 4, 91100.
(b) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, Chem. Phys. Lett. 1989, 162, 165-169.
(c) O. Treutler, R. Ahlrichs, J. Chem. Phys. 1995, 102, 346-354.
(d) TURBOMOLE V6.4, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, http://www.turbomole.com.
[vii] (a) K. Eichkorn, O. Treutler, H. Oehm, M. Häser, R. Ahlrichs, Chem. Phys. Lett. 1995, 242, 652-660.
(b) K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, Theor. Chem. Acc. 1997, 97, 119.
[viii] (a) A. D. Becke, J. Chem. Phys. 1993, 98, 5648-5652.
(b) C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 1988, 37, 785-789.
(c) A. D. Becke, Phys. Rev. A 1988, 38, 3098-3100.
(d) S. H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 1980, 58, 1200-1211.
(e) J. C. Slater, Phys. Rev. 1951, 81, 385-390.
[ix] (a) A. Schäfer, C. Huber, R. Ahlrichs, J. Chem. Phys. 1994, 100, 5829.
(b) K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, Theor. Chem. Acc. 1997, 97, 119.
(c) F. Weigend, R. Ahlrichs, Phys. Chem. Chem. Phys. 2005, 7, 3297.
(d) F. Weigend, Phys. Chem. Chem. Phys. 2006, 8, 1057.
[x] (a) K. Eichkorn, O. Treutler, H. Ohm, M. Häser, R. Ahlrichs, Chem. Phys. Lett. 1995, 242, 652-660.
(b) M. Sierka, A. Hogekamp, R. Ahlrichs, J. Chem. Phys. 2003, 118, 9136-9148.
[xi] F. Weigend, Phys. Chem. Chem. Phys. 2006, 8, 1057-1065.
[xii] NBO 6.0. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, F. Weinhold (Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2013); http://nbo6.chem.wisc.edu/
[xiii] (a) R. F. W. Bader, Atoms in Molecules: A Quantum Theory, Oxford University Press, 1994.
(b) R. F. W. Bader, Chem. Rev. 1991, 91, 893-928.
[xiv] (a) T. Lu, F. Chen, J. Comput. Chem. 2012, 33, 580-592.
(b) http://sobereva.com/multiwfn.

## 5 Pentaphosphaferrocene mediated Synthesis of Asymmetric Organo-Phosphines Starting from White Phosphorus

### 5.1 Preface

The following chapter has already been published: The article is an open access article distributed under the terms of the Creative Commons CC BY license:
S. Reichl, E. Mädl, F. Riedlberger, M. Piesch, G. Balázs, M. Seidl and M. Scheer, Nat. Commun., 2021, 12, 1-9.
https://doi.org/10.1038/s41467-021-26002-7

## Authors

Stephan Reichl, ${ }^{1}$ Eric Mädl, ${ }^{1}$ Felix Riedlberger, ${ }^{1}$ Martin Piesch, ${ }^{1}$ Gábor Balázs, ${ }^{1}$ Michael Seidl, ${ }^{1}$ Manfred Scheer ${ }^{1 *}$<br>${ }^{1}$ Institute of Inorganic Chemistry, University of Regensburg; Universitätsstraße 31, 93053 Regensburg, Germany.<br>*Corresponding author. Email: manfred.scheer@chemie.uni-regensburg.de

## Author Contribution

S.R., E.M., F.R. and M.P. conceived the experiments. G.B. performed the computational studies. M.Se. analysed and revised the X-ray data; S.R., G. B. and M.Sch. wrote the manuscript. M.Sch. directed and coordinated the research.

Pentaphosphaferrocene mediated Synthesis of Asymmetric Organo-Phosphines Starting from White Phosphorus


# Pentaphosphaferrocene mediated Synthesis of Asymmetric Organo-Phosphines Starting from White Phosphorus 


#### Abstract

The synthesis of phosphines is based on white phosphorus, which is usually converted to $\mathrm{PCl}_{3}$, to be afterwards substituted step by step in a non-atomic efficient manner. Herein, we describe an alternative efficient transition metal-mediated process to form asymmetrically substituted phosphines directly from white phosphorus. Thereby, $\mathrm{P}_{4}$ is converted to $\left[C p^{*} F e\left(\eta^{5}-P_{5}\right)\right](1)$ in which one of the phosphorus atoms is selectively functionalized to the 1,1-diorgano-substituted complex $\left[C p^{*} F e\left(\eta^{4}-P_{5} R^{\prime} R^{\prime \prime}\right)\right]$ (3). In a subsequent step, the phosphine $P R^{\prime} R^{\prime \prime} R^{\prime \prime \prime}\left(R^{\prime} / R^{\prime \prime} / R^{\prime \prime \prime}=\right.$ alky, aryl) (4) is released by reacting it with a nucleophile $R^{\prime \prime \prime} M(M=$ alkali metal) as racemates. The starting material 1 can be regenerated with $\mathrm{P}_{4}$ and can be reused in multiple reaction cycles without isolation of the intermediates, and only the phosphine is distilled off.


### 5.2 Introduction

The interest in organophosphorus compounds in life science, material science, and especially in ligand design for catalysis is an omnipresent topic ${ }^{1-5}$. Besides the use of phosphines as ligands ${ }^{4-6}$, the resulting complexes are widely used as catalysts in all areas of organic and organometallic chemistry ${ }^{7}$. One of the most prominent examples of a catalyst containing phosphines represents the Wilkinson's catalyst $\left[\mathrm{RhCl}\left(\mathrm{PPh}_{3}\right)\right]^{8}$, which catalyses e.g. Hydrogenation of olefins. Over the last decades, a plethora of organophosphorus compounds were synthesised and investigated ${ }^{9-13}$. Although organophosphorus chemistry is a wellestablished area, the synthesis of asymmetrically substituted organophosphorus compounds is a crucial and challenging topic ${ }^{2,6,14,15}$. Its importance in catalysis was awarded e.g. with the Nobel prize ${ }^{16}$. The classical way to synthesise phosphines is via salt metathesis or hydrophosphination starting from $\mathrm{PCl}_{3}$ or $\mathrm{PH}_{3}$, respectively (Figure 1) ${ }^{12,13,17}$. In both cases, the targeted variation of the organic substituents is synthetically very challenging. Moreover, both $\mathrm{PCl}_{3}$ and $\mathrm{PH}_{3}$ are synthesised from $\mathrm{P}_{4}$ either by reaction with chlorine gas or by hydrolysis in basic or acidic aqueous media ${ }^{18}$. Note that, aryl phosphines cannot be synthesized via hydrophosphination ${ }^{19}$. Interestingly, first attempts to synthesise organophosphorus compounds directly from phosphates have already been made by reduction with $\mathrm{HSiCl}_{3}$ followed by reaction with $\mathrm{RCl}^{20}$, although this development is still in its infancy ${ }^{21}$. Since both $\mathrm{Cl}_{2}$ and $\mathrm{PH}_{3}$ are toxic gases and because the synthesis of phosphines from $\mathrm{PCl}_{3}$ is associated with large (stoichiometric) amounts of side products, a more sustainable and atom-efficient
process for a direct conversion of $\mathrm{P}_{4}$ into organophosphorus reagents is desirable. Besides these classical synthetic strategies, a few protocols have been developed for the direct synthesis of phosphines from $\mathrm{P}_{4}$. The first one of these protocols involves the generation of aryl radicals from aryl halides induced by an unsaturated Ti (III) complex ${ }^{22}$. The fundamental synthetic approach of all these protocols involves either an electrochemical approach ${ }^{23}$ or, more often, the generation of organo radicals from the corresponding halides induced by transition metal complexes ${ }^{22,24-26}$ as well as, quite recently, organotin-compounds ${ }^{27}$. These radical-promoted routes can be divided into stochiometric ${ }^{22,24,27}$ and/or (photo)catalytic approaches ${ }^{25,26}$.


Figure 1. Different approaches for the synthesis of ternary phosphines. Left: conventional way, hydrophosphination and salt metathesis. Right: Radical promoted, stochiometric and catalytic, as well as semi catalytic transition metal (TM) mediated synthesis of ternary phosphines.

The major drawback to all of these processes is that they do not lead to the formation of asymmetrically substituted phosphines, which are crucial for catalysis. In this report, we present a conceptually innovative strategy for a controlled and directed synthesis of symmetrically and asymmetrically substituted phosphines starting from $\mathrm{P}_{4}$ and carbon-centred nucleophiles and electrophiles by using $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right](1)\left(\mathrm{Cp}^{*}=\eta^{5}-\mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right)$ as a P-atom carrier.

### 5.3 Results

## Synthesis and structural characterization of the mono-substiituted complexes $2 \mathrm{c}-\mathrm{e}$

In our previous works, we were able to show that $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right]$ (1) readily reacts with maingroup nucleophiles such as $\mathrm{Me}_{3} \mathrm{SiCH}_{2}{ }^{-}$or $\mathrm{Me}_{2} \mathrm{~N}^{-}$via the formation of a $\mathrm{P}-\mathrm{C} / \mathrm{P}-\mathrm{N}$ bond ${ }^{28}$, leading to the complexes $\left[C p^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{R}^{\prime}\right)\right]^{-}\left(\mathrm{R}^{\prime}=\mathrm{CH}_{2} \mathrm{SiMe}_{3}(2 \mathrm{a}), \mathrm{NMe}_{2}(2 \mathrm{~b})\right)$. However, we found now that the nucleophile used can be freely varied, and basically any alkali metal organyl can be used (Figure 2). The reaction of [Cp*Fe( $\left.\left.\eta^{5}-\mathrm{P}_{5}\right)\right]$ (1) with MeLi, ${ }^{\text {t }} \mathrm{BuLi}$ and PhLi , respectively, at $-80^{\circ} \mathrm{C}$ leads to an immediate color change from green to brown. After workup, the complexes
$\left[\mathrm{Li}(\mathrm{dme})_{3}\right]\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Me}\right)\right] \quad(2 \mathrm{c}), \quad\left[\mathrm{Li}(12 \mathrm{c} 4)_{2}\right]\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}{ }^{\text {t }} \mathrm{Bu}\right)\right] \quad(2 \mathrm{~d}), \quad[\mathrm{Li}(12 \mathrm{c} 4)(\mathrm{thf})]\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\mathrm{n}^{4}-\right.\right.$ $\left.\left.\mathrm{P}_{5} \mathrm{Ph}\right)\right](2 \mathrm{e})$ can be isolated in crystalline yields of 84,86 and $75 \%$, respectively.


Figure 2. Synthesis of asymmetric phosphines 4, via successive nucleophilic, electrophilic, nucleophilic attack. Synthesis of the anionic precursor complexes 2 by nucleophilic attack; Electrophilic quenching of 2 (synthesis of 3); asymmetric phosphine abstraction by nucleophiles (synthesis of 4, 5); Regeneration of 1 by thermolysis with $\mathrm{P}_{4}$; Alternative synthesis of 3 by electrophilic quenching of 1 '.

The single crystal X -ray structure analysis of 2 shows anionic complexes with a folded $\mathrm{P}_{5} \mathrm{R}^{\prime}$ ligand in an envelope conformation (Figure 1, Supplementary Figure 40-43). The four coordinating phosphorus atoms of the $\mathrm{P}_{5} \mathrm{R}^{\prime}$ ligand build a nearly square planar $\mathrm{P}_{4}$ unit which coordinates symmetrically to the $\mathrm{Cp}{ }^{*} \mathrm{Fe}$ fragment. The P 1 atom to which the organic group is attached (P1-C1 bond length of 1.849(2) $\AA(2 \mathrm{c}), 1.898(3) \AA(2 \mathrm{~d})$ and $1.841(3) \AA(2 \mathrm{e})$ ) deviates from this plane. All P2-P5 bond lengths (1.993(13) $\AA$ - $2.1575(10) A ̊)$ ) are in the range between a single and a double bond ${ }^{29,30}$.




5

Figure 3. Molecular structures of the anions in 2d, 5 and of the neutral complexes $3 \mathrm{f}, 4 \mathrm{a}$ ' in the solid state with thermal ellipsoids at $50 \%$ probability level. Cations and hydrogen atoms are omitted for clarity. The Cp* ligands are drawn in a wire frame model.


Figure 4. Electrostatic potential mapped on electron density (isovalue $=0.001$ ) for 3 c. Colour code (blue $=$ positive, red $=$ negative) in $\mathrm{kJ} \cdot \mathrm{mol}^{-1}$.

## Reactivity of 2 towards electrophiles

The presence of the negative charge renders the compounds 2 nucleophilic, which is why they can be quenched with electrophiles such as alkyl or aryl halides. Thus, the compounds 2 were treated with alkyl halides $\mathrm{R} " \mathrm{X}\left(\mathrm{R}^{\prime \prime}=\mathrm{Me},{ }^{\text {' }} \mathrm{Pr} ; \mathrm{X}=\mathrm{Br}, \mathrm{I}\right)$ as common carbon-centered electrophiles. Indeed, the neutral organo-substituted polyphosphorus complexes [Cp*Fe(n $\left.\left.{ }^{4}-\mathrm{P}_{5} \mathrm{R}^{\prime} \mathrm{R}^{\prime \prime}\right)\right]$ (3; Figure 2) were obtained in almost quantitative yields according to ${ }^{31} \mathrm{P}$ NMR spectroscopy. The isolated compounds $\mathbf{2}$ and $\mathbf{3}$ were characterized by NMR spectroscopy (Supplementary Figure 1-9; 17-26), mass spectrometry, elemental analysis, and single-crystal XRD (Figure 3,

Supplementary Figure 40-50). The latter shows that, in 3 , the folded $\eta^{4}-P_{5}$ unit remains intact and the introduced electrophile is attached to the phosphorus atom, which bears the first organo-substituent (former nucleophiles; R', Figure 3), leading to a 1,1 -substitution pattern with a P1-C2 bond length (1.785(5) $\AA-1.922(11) \AA$ ) corresponding to single bonds ${ }^{29}$. The functionalized phosphorus atoms P1 carry two organic substituents and possess a phosphonium ion-like character (Figure 4). Of particular interest are the compounds 3a,b and $3 f$ since they represent precursors for quite rare asymmetrically substituted organo-phosphine derivatives ${ }^{2,31}$. Due to the large diversity of alkali metal organyls and electrophilic organo halides, the shown procedure gives access to the synthesis of a plethora of complexes of type 3. An alternative way for the synthesis of $\mathbf{3}$ is the reaction of the doubly reduced derivative of $\mathbf{1}$, $\left[\mathrm{K}(\mathrm{dme})_{2}\right]_{2}\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\mathrm{n}^{4}-\mathrm{P}_{5}\right)\right]\left(1^{\prime}\right)^{32}$, with alkyl halides. This was demonstrated by the synthesis of 3c and $3 \mathbf{e}$, which proceeds according to ${ }^{31}$ P NMR in a quantitative manner (Supplementary Figure 69, S70) and shows that possible limitations of organolithium reagents needed in the former procedure can be avoided. The reaction of 1 ' with two equivalents of Mel leads smoothly to 3c, while the addition of one equivalent of ${ }^{t}$ Bul followed by the addition of one equivalent of Mel leads to the formation of $3 e$ (Figure 2). In the ${ }^{31} \mathrm{P}$ NMR spectra of 2 (Supplementary Figure 1720) and 3 (Supplementary Figure 21-26), AMM'XX' spin systems were detected from which the coupling constants were obtained by simulations (Supplementary Table 1-10). The related signals of the phosphorus atoms P1 of $\mathbf{3}$ are downfield shifted compared to 2 . This is in agreement with the phosphonium-like nature of the phosphorus atom P1 in 3.

## Synthesis of (a)symmetric phosphines - Reactivity of 3 towards nucleophiles

The electrostatic potential surface of compound 3c (B3LYP/def2-TZVPP level of theory; Figure 4) shows a rather localized positive potential on the phosphorus atom bearing the organo-substituents (P1). Therefore, the attack of a nucleophile is expected to occur at the position P1. Indeed, the reactions of 3d with benzyl potassium lead to the formation of the asymmetrically substituted phosphine $\mathrm{PMe}^{i} \operatorname{PrBnz}$ (4a) in 82 \% yield (Supplementary Figure 61) and the anion $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\mathrm{n}^{4}-\mathrm{P}_{4}\right)\right]^{-}$(Supplementary Figure 55). This strategy can be extended for the synthesis of a series of asymmetric phosphines, with PR'R"R'" (4a-c (a: R' = Me, R" = 'Pr, R"' = $\left.B n z ; b: R^{\prime}={ }^{t} B u, R^{\prime \prime}=M e, R^{\prime \prime}=B n z ; c: R^{\prime}=P h, R^{\prime \prime}=M e, R^{\prime \prime \prime}=B n z\right)$ ) being isolated as air-sensitive viscous liquids in $82 \%(4 a), 55 \%(4 b), 80 \%(4 c)$ yields, respectively. The identity of the phosphine was proven by NMR spectroscopy and, after oxidation with sulphur to the corresponding phosphine sulphides (Supplementary Figure 10-16; 27-32; 34-39), also by single crystal X-ray diffraction analysis (Figure 3, Supplementary Figure 51-54). Furthermore, by changing the nucleophile to MeLi and ${ }^{n} \mathrm{BuLi}$, the corresponding phosphines $\mathrm{PMe}_{3}$ and $\mathrm{PMe}_{2}{ }^{\mathrm{n}} \mathrm{Bu}$
can be obtained in the reaction with 3c (Supplementary Figure 56, 57). The latter is less selective, $\mathrm{PMe}_{3}$, however, can be synthesized via this route in $84 \%$ yield (according to NMR).

To identify potential intermediates in the reaction of 3 with nucleophiles, the reaction of 3c with MeLi at $-80^{\circ} \mathrm{C}$ in THF-d8 was monitored by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy at this temperature. The ${ }^{31} \mathrm{P}$ NMR spectrum clearly shows the full conversion of 3 and quantitative formation of 4 and 5 (Figure 5A, Supplementary Figure 68). These very fast reactions agree with the results of the DFT calculations which show a very low activation barrier for this process (Figure 5B, S71).


B


Figure 5. Identification of the reaction pathway of phosphine abstraction. A) Experimental ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(242.90 \mathrm{MHz}, \mathrm{THF}-\mathrm{d}_{8}\right.$ ) spectrum of the crude reaction solution (low temperature reaction) of 3 c with KBnz at 180 K . B) Gibbs free energy profile of the reaction of 3 c with KBnz, calculated at the B3LYP-D3(BJ)/def2-TZVPP (PCM $=$ THF) level of theory.

The other product of the reaction of 3 with nucleophiles, i.e. $[\mathrm{M}]\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{4}\right)\right]\left(\mathrm{M}=\mathrm{K}(\mathrm{dme})_{3} ; 5\right)$ is a rare representative of the anionic complexes with a cyclo- $\mathrm{P}_{4}$ ligand as an end-deck ${ }^{33-35}$. The addition of 18 -crown-6 considerably increases its stability and 5 can be isolated in $81 \%$ crystalline yield, which is a major improvement over the previously reported complex $[K(18 c 6)]\left[\mathrm{Cp}^{\mathrm{Ar}} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{4}\right)\right]^{-}\left(\mathrm{Cp}^{\mathrm{Ar}}=\mathrm{C}_{5}\left(\mathrm{C}_{6} \mathrm{H}_{4}-4-\mathrm{Et}\right)_{5}\right)$ obtained in $4 \%$ yield ${ }^{33}$. In the solid state, the anion $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{4}\right)\right]^{-}$(Figure 3, Supplementary Figure 55) features a square planar cyclo- $\mathrm{P}_{4}$ ligand with bond lengths between 2.1666(13) and 2.175(13) Å, which are in the range between a single ${ }^{29}$ and a double bond ${ }^{30}$. In the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of 5 , a singlet is observed at
118.9 ppm (Supplementary Figure 39). The lithium derivative of 5 can be detected in all reactions of 3 b -e with organolithium reagents but decomposes partly over time in solution.

## Formation of phosphines and regeneration of the carrier platform $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\mathrm{n}^{5}-\mathrm{P}_{5}\right)\right]$ (1) in a 'semicatalytic' cyclic process

The phosphines generated in the reaction of 3 with nucleophiles can be easily isolated either by extraction with hexanes ( 5 is not soluble in hexane) or, in the case of volatile phosphines, by condensation. That is why we were interested in designing a closed-cycle-process for the generation of phosphines in which 1 represents the platform for the phosphorus atom transfer. To close the circle, 5 was reacted with one equivalent of $\mathrm{P}_{4}$ with 1 being formed in almost quantitative yield, among $\mathrm{KP}_{5}$, which partly decomposes to polyphosphides ${ }^{36}$ (Supplementary Figure 65). After workup, 1 can be isolated in 81 \% crystalline yield (Figure 6). If required, KP can be transformed into the corresponding pentaphosphaferrocene by reacting with $\left[\mathrm{Cp}{ }^{*} \mathrm{FeBr}\right]{ }_{2}{ }^{37}$ to increase the atom efficiency of this process. Moreover, it is possible to perform a larger scale synthesis of the phosphines in a one-pot reaction to easily reuse 1 and to avoid the workup of the reaction solution. In a one-pot reaction, compound 1 was dissolved in 2,5,8,11,14-pentaoxapentadecane (tetraglyme) and stoichiometric amounts of MeLi and Mel were successively added at r.t. with five minutes stirring in between (Figure 6, steps I and II). Subsequently, the solution was cooled to $-30^{\circ} \mathrm{C}$ and one equivalent of KBnz in tetraglyme was added (Figure 6, step III). The cooling bath was removed, the formed phosphine $\mathrm{PMe}_{2} \mathrm{Bnz}$ was distilled off under reduced pressure ( $1 \cdot 10^{-3} \mathrm{mbar}, 55^{\circ} \mathrm{C}$ ) and was obtained in $87 \%$ yield (Figure 6, step III, Supplementary Figure 67). To the remaining solution, one equivalent of white phosphorus was added and heated under reflux for one hour at $275{ }^{\circ} \mathrm{C}$ (IV). The ${ }^{31} \mathrm{P}$ NMR spectrum (Supplementary Figure 63) shows the almost quantitative regeneration of 1 . The same protocol was repeated two more times on the same reaction solution (see Supplementary Figure 64). The phosphine $\mathrm{PMe}_{2} \mathrm{Bnz}$ was isolated in $82 \%$ to $67 \%$ yield (overall isolated yield 79 \%, see Supplementary Figure 67, Supplementary Table 40). After these three cycles, 1 can be isolated from the reaction solution in 69 \% yield (Supplementary Figure 66), indicating that this process could be carried on for many more cycles.






3

Figure 6. 'Semi-catalytic' cycle for the synthesis of asymetric phosphines. One-pot reaction of [Cp*Fe( $\left.\left.\eta^{5}-P_{5}\right)\right]$ (1) with MeLi (I, R' $=\mathrm{Me}$ ), quenching with $\operatorname{Mel}\left(\mathbf{I I}, \mathrm{R}^{\prime \prime}=\mathrm{Me}\right)$, reaction with $\mathrm{KBnz}\left(\mathrm{IIII}, \mathrm{R}^{\prime \prime \prime}=\mathrm{Bnz}\right.$ ) and subsequent thermolysis with white phosphorus (IV).

### 5.4 Conclusion

In summary the polyphosphorus compound [ $\left.\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\mathrm{n}^{5}-\mathrm{P}_{5}\right)\right]$ (1) can be used as a recyclable platform for the targeted synthesis of symmetric or asymmetric phosphines, via a sequence of nucleophilic-electrophilic-nucleophilic reactions, directly from white phosphorus, avoiding the use of intermediate products such as $\mathrm{PCl}_{3}$ or $\mathrm{PH}_{3}$. With this modular system, asymmetric phosphines are obtained in high yields in significant preparative scales and 1 can be regenerated and reused in a 'semi-catalytic' cyclic process, which can be run for several cycles in a one-pot reaction. The presented results pave the way for a selective and easy synthetic route to asymmetric and (in future work potential) chiral phosphines based on white phosphorus. This conceptual innovative approach avoids radicals and is not limited to aryl or alkyl substituents, but phosphines with a variety of different substitution patterns are now accessible in high yields by a very simple approach.

### 5.5 Methods

## General methods

All manipulations were carried out under an inert atmosphere of dried argon using standard Schlenk and glove box techniques. 1,2-dimethoxyethane (DME), 2,5,8,11-tetraoxadodecane (triglyme) and 2,5,8,11,14pentaoxapentadecane (tetraglyme) were dried and deoxygenated by distillation under argon atmosphere from sodium (DME) or calcium hydride. All other solvents were dried using a MB SPS-800 device of the company MBRAUN and stored over molecular sieve. NMR spectra were recorded on a Bruker Avance III 400/600 MHz NMR spectrometer. Chemical shifts were measured at ambient temperature and are given in ppm; they are referenced to TMS for ${ }^{1} \mathrm{H}$ and $85 \% \mathrm{H}_{3} \mathrm{PO}_{4}$ for ${ }^{31} \mathrm{P}$ as external standard. Signal multiplicities are described using common abbreviations: $s$ (singlet), $d$ (doublet), $t$ (triplet), $q$ (quartet), quint (quintet), $m$ (multiplet) and br (broad). LIFDI-/FD-/EI-MS spectra (LIFDI = liquid injection field desorption ionization, FD = field desorption, EI = electron ionization) were measured on a JEOL AccuTOF GCX. ESI-MS spectra (ESI = Electrospray ionization) were measured on an Agilent Q-TOF 6540 UHD. Elemental analysis (CHN) was determined using a Vario micro cube instrument. A glass stirring bar was used in reactions with potassium benzyl. DFT calculations were carried out using the Gaussian 16 program ${ }^{38}$. The geometries were optimised using the B3LYP ${ }^{39-41}$ functional together with the def2-TZVPP basis set $^{43}$. Solvation effects were incorporated via the polarizable continuum model ${ }^{44}$ using the dielectric constant of THF. Dispersion effects were incorporated via Grimme's correction with Becke-Johnson damping ${ }^{45}$.

Unless otherwise stated, all other chemicals were obtained from commercial sources.
Crystals suitable for single crystal X-ray diffraction analysis were obtained as described in the corresponding synthetic protocols below. The diffraction data were collected either on a Gemini Ultra diffractometer equipped with an Atlas ${ }^{52}$ CCD detector and with a fine-focus sealed $\mathrm{Cu}-\mathrm{K}_{\alpha}$ X-ray tube, on a XtaLAB Synergy R, DW system diffractometer equipped with a HyPix-Arc 150 detector and a rotating-anode $\mathrm{Cu}-\mathrm{K}_{\alpha} \mathrm{X}$-ray tube or a GV50 diffractometer equipped with a Titan ${ }^{52}$ CCD detector and a micro-focus $\mathrm{Cu}-\mathrm{K}_{\alpha} \mathrm{X}$-ray tube. Data collection and reduction were performed with CrysAlisPro software package. The structures were solved with Olex2 ${ }^{48}$, using SheIXT ${ }^{49}$ and a least-square refinement on $F^{2}$ was carried out with SheIXL ${ }^{50}$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms at the carbon atoms were located in idealized positions and refined with isotropic displacement parameters according to the riding model. The images of the molecular structures were made using Olex2 ${ }^{48}$.

## Synthetic protocols

## Synthesis of $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right](1)^{47}$

The complex $\left[\mathrm{Cp}^{*} \mathrm{Fe}(\mathrm{CO})_{2}\right]_{2}(10 \mathrm{~g}, 20.0 \mathrm{mmol})$ and white phosphorus ( $7 \mathrm{~g}, 56.5 \mathrm{mmol}$ ) are dissolved in 1,3diisopropylbenzene ( 500 ml ) and heated to reflux for 7 hours. The solvent was removed in vacuo. The residue was dissolved in dichloromethane, silica was added and the solvent was removed under reduced pressure. The preabsorbed reaction mixture was purified via column chromatography $\left(\mathrm{SiO}_{2}\right.$, hexane, $\left.10 \times 3 \mathrm{~cm}\right)$. Using $n$-hexane, compound 1 ( $12.3 \mathrm{~g}, 35.6 \mathrm{mmol}, 89$ \%) can be eluted as a dark green fraction. Complex 1 can be obtained after one day from a concentrated solution stored at $-30^{\circ} \mathrm{C}$ as green needles.

## Synthesis of $\left[K(d m e)_{2}\right]_{2}\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\mathrm{n}^{4}-\mathrm{P}_{5}\right)\right]\left(\mathbf{1}^{\prime}\right)^{32}$

A solution of $1(0.4 \mathrm{~g}, 1.16 \mathrm{mmol}, 1 \mathrm{eq})$ in DME ( 30 ml ) was added to potassium ( $0.136 \mathrm{~g}, 3.47 \mathrm{mmol}, 3 \mathrm{eq}$ ). The solution was stirred at ambient temperature for 4 hours. The solution was filtered, the product was extracted from
an insoluble residue with DME ( 70 ml ). The volume of the combined solution was reduced to ca. 30 ml and $\mathrm{Et}_{2} \mathrm{O}$ ( 30 ml ) was added. The suspension was stirred overnight and the product was collected on a frit, washed with $\mathrm{Et}_{2} \mathrm{O}$ $(30 \mathrm{ml})$ and dried in vacuum to give $1^{\prime}(0.74 \mathrm{~g}, 0.95 \mathrm{mmol})$ as dark brown-green powder.

## Synthesis of $\left[\mathrm{Li}(\mathrm{thf})_{3}\right]\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{NMe}_{2}\right)\right](2 \mathrm{a})^{28}$

To a solution of $1(176 \mathrm{mg}, 0.51 \mathrm{mmol})$ in 5 mL THF a solution of $\mathrm{LiNMe}_{2}(26 \mathrm{mg}, 0.51 \mathrm{mmol})$ was added at $-35^{\circ} \mathrm{C}$. The colour of the solution turned immediately from green to brown. The reaction mixture was stirred over 20 hours, the solvent was concentrated to 3 mL and finally layered with $n$-hexane. After 4 days on room temperature light brown square shaped crystals of 2 a ( $150 \mathrm{mg}, 0.25 \mathrm{mmol}, 50 \%$ ) were formed.

## Synthesis of $\left[\mathrm{Li}(\mathrm{dme})_{3}\right]\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)\right](2 \mathrm{~b})^{28}$

To a solution of ((trimethylsilyl)methyl)lithium ( $68 \mathrm{mg}, 0.72 \mathrm{mmol}$ ) in $\mathrm{Et}_{2} \mathrm{O}(5 \mathrm{~mL})$ at $-35^{\circ} \mathrm{C}$ was added a solution of 1 ( $250 \mathrm{mg}, 0.72 \mathrm{mmol}$ ) in $\mathrm{Et}_{2} \mathrm{O}$ ( 15 mL ). Immediate colour change was observed. The solution was slowly warmed up to ambient temperature and volume of the reaction mixture was reduced to ca. 15 mL and layered with $n$-hexane $(20 \mathrm{~mL})$. Black crystals of $\mathbf{2 b}$ ( $342 \mathrm{mg}, 0.66 \mathrm{mmol}, 92 \%$ ) were formed after 2 days at $0^{\circ} \mathrm{C}$.

## Synthesis of $\left[\mathrm{Li}(\mathrm{dme})_{3}\right]\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Me}\right)\right]$ (2c)

To a solution of $138.0 \mathrm{mg}(0.4 \mathrm{mmol}, 1 \mathrm{eq})$ of $1 \mathrm{in} \mathrm{DME} \mathrm{at}-60^{\circ} \mathrm{C}$, a 1.6 molar solution of $\mathrm{MeLi}(0.4 \mathrm{mmol}, 0.27 \mathrm{~mL}$, 1 eq ) in $\mathrm{Et}_{2} \mathrm{O}$ (diethylether) was added and an immediate colour change to brown could be observed. The solution was stirred for 4 hours, the solvent was reduced to 5 mL and layered with $n$-hexane ( 25 mL ). [Li(dme) $\left.)_{3}\right]\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\mathrm{n}^{4}-\right.\right.$ $\left.\left.\mathrm{P}_{5} \mathrm{Me}\right)\right](2 \mathrm{c})$ was isolated as black truncated prisms. Yield: $216.0 \mathrm{mg}(0.34 \mathrm{mmol}, 83 \%)^{1} \mathrm{H}$ NMR (thf- $\left.\mathrm{d}_{8}, 293 \mathrm{~K}\right)$ : $\delta[\mathrm{ppm}]=1.49\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 0.39\left(\mathrm{~m}, 3 \mathrm{H},-\left(\mathrm{CH}_{3}\right)\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{thf}-\mathrm{d}_{8}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=71.3\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 13.7$ ( $\mathrm{m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}$ ), $71.5\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\left.\mathrm{x}, \mathrm{x}^{\prime}\right) .}{ }^{31} \mathrm{P}\right.$ NMR (thf- $\mathrm{d}_{8}, 293 \mathrm{~K}$ ): $\delta[\mathrm{ppm}]=71.3\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 13.7\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}\right),-71.5(\mathrm{~m}$, 2 P, $\mathrm{P}_{\mathrm{x}, \mathrm{x}}$ ); For coupling constants, see Supplementary Table 1-10. ESI-MS (anion, DME): $m / z=360.95$ (6 \%, [M] ${ }^{-}$), 376.94 ( $8 \%,[\mathrm{MO}]^{-}$), 392.93 ( $100 \%,\left[\mathrm{MO}_{2}\right]^{-}$); analysis (calcd., found for $\mathrm{C}_{23} \mathrm{H}_{48} \mathrm{FeLiO}_{6} \mathrm{P}_{5}$ ): C (43.28, 42.84), H (7.58, 7.42).

## Synthesis of $\left[\mathrm{Li}(12 \mathrm{c} 4)_{2}\right]\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\right)\right](2 \mathrm{~d})$

Compound 1 ( $0.2 \mathrm{mmol}, 69.2 \mathrm{mg}, 1 \mathrm{eq}$ ) was dissolved in 10 mL THF (tetrahydrofuran) and cooled to $-80^{\circ} \mathrm{C} . \mathrm{A} 1.7$ molar solution of ${ }^{\text {t }} \mathrm{BuLi}(0.2 \mathrm{mmol}, 0.12 \mathrm{~mL}, 1 \mathrm{eq})$ in $n$-pentane was added dropwise. An immediate change in colour from green to brown occurred. The mixture was allowed to stir overnight and reach room temperature. 12-crown-4 (12c4) ( $0.4 \mathrm{mmol}, 0.07 \mathrm{~mL}, 2 \mathrm{eq}$ ) was added to the brown solution and stirred for 30 minutes at room temperature. The solvent was removed under reduced pressure. The brown residue was washed with $2 \times 10 \mathrm{~mL} n$-hexane, dissolved in 2 mL THF and layered with 5 mL toluene. The mixture was stored at $8^{\circ} \mathrm{C}$. Compound 2 c was isolated after one day as dark green plates. Yield: $110.2 \mathrm{mg}(0.17 \mathrm{mmol}, 86 \%) .{ }^{1} \mathrm{H}$ NMR (THF-d ${ }_{8}, 293 \mathrm{~K}$ ): $\delta[\mathrm{ppm}]=3.78$ (s, $33 \mathrm{H}, 12 \mathrm{c} 4), 1.45\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 0.03\left(\mathrm{~d}, 9 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{p}-\mathrm{H}}=10.8 \mathrm{~Hz},-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{THF}-\mathrm{d}_{8}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]$ $=105.6\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 19.6\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}}\right),-70.2\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\left.\mathrm{x}, \mathrm{x}^{\prime}\right)}{ }^{31}{ }^{31} \mathrm{P}\right.$ NMR (THF- $\left.\mathrm{d}_{8}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=105.6\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right)$, 19.6 (m, 2 P, $\mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}$ ), -70.2 (m, 2 P, $\mathrm{P}_{\mathrm{x}, \mathrm{x}^{\prime}}$ ); (For coupling constants, see Supplementary Table 2, 3). ESI-MS (anion, DME): $\mathrm{m} / \mathrm{z}=403.00\left(100 \%,[\mathrm{M}]^{-}\right.$); analysis (calcd., found for $\mathrm{C}_{30} \mathrm{H}_{56} \mathrm{FeLiO}_{8} \mathrm{P}_{5}$ ): $\mathrm{C}(47.26,47.61), \mathrm{H}(7.40,7.49)$.

## Synthesis of [Li(12c4)(thf)][Cp*Fe(n $\left.\left.{ }^{4}-\mathrm{P}_{5} \mathrm{Ph}\right)\right]$ (2e)

Compound 1 ( $0.2 \mathrm{mmol}, 69.2 \mathrm{mg}, 1 \mathrm{eq}$ ) was dissolved in THF, cooled to $-80^{\circ} \mathrm{C}$ and a 1.9 molar solution of PhLi in dibutyl ether ( $0.2 \mathrm{mmol}, 0.11 \mathrm{~mL}, 1 \mathrm{eq}$ ) was added. A colour change from green to brown occurred. Two equivalents of 12 -crown- $4(0.4 \mathrm{mmol}, 0.12 \mathrm{~mL})$ were added and the solution was stirred overnight and allowed to reach room
temperature. The solvent was removed under reduced pressure. The resulting brownish-green residue was washed with 10 mL of $n$-hexane and again dissolved with 3 mL of THF layered with 10 mL of $n$-hexane and stored at room temperature. Dark green blocks of 2 e were isolated after one week. Yield: $102.0 \mathrm{mg}\left(0.15 \mathrm{mmol}, 75 \%\right.$ ). ${ }^{1} \mathrm{H}$ NMR (THF-d $\mathrm{d}_{8} 293 \mathrm{~K}$ ): $\delta[\mathrm{ppm}]=6.56\left(\mathrm{~m}, 5 \mathrm{H},-\mathrm{C}_{6} \mathrm{H}_{5}\right), 3.72(\mathrm{~s}, 17 \mathrm{H}, 12 \mathrm{c} 4), 3.60\left(\mathrm{~m}, 3 \mathrm{H}, \mathrm{THF}-\mathrm{H}_{8}\right), 1.77\left(\mathrm{~m}, 3 \mathrm{H}, \mathrm{THF}-\mathrm{H}_{8}\right)$, $\left.1.51\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{\underline{5}}\right) .{ }^{31} \mathrm{P}_{\{ }{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=79.3\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 21.1\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}\right),-61.84(\mathrm{~m}, 2 \mathrm{P}$, $\left.\mathrm{P}_{\mathrm{x}, \mathrm{x}^{\prime}}\right)^{31}{ }^{31} \mathrm{PNMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=79.3\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 21.1\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}}\right)$, -61.84 (m, $2 \mathrm{P}, \mathrm{P}_{\mathrm{x}, \mathrm{x}}$ ); (For coupling constants, see Supplementary Table 4). ESI-MS (anion, DME): no signal can be assigned; analysis (calcd., found for $\left.\mathrm{C}_{28} \mathrm{H}_{44} \mathrm{FeP}_{5} \mathrm{LiO}_{5}\right)$ : C (49.58, 49.80), H (6.54, 6.53).

## Synthesis of $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\mathrm{n}^{4}-\mathrm{P}_{5}\left(\mathrm{NMe}_{2}\right) \mathrm{Me}\right\}\right]$ (3a)

Compound 2a ( $0.3 \mathrm{mmol}, 168.0 \mathrm{mg}, 1 \mathrm{eq}$ ) was dissolved in 50 mL THF. A 1.11 molar solution of Mel in diethylether $(0.3 \mathrm{mmol}, 0.27 \mathrm{~mL}, 1 \mathrm{eq}$ ) was added. The mixture was allowed to stir overnight. The solvent was removed under reduced pressure and a brown solution was extracted with $20 \mathrm{~mL} n$-hexane and filtered over diatomaceous earth. The solvent was reduced to 5 mL and stored at $-30^{\circ} \mathrm{C}$. 3a was formed as dark prisms after one day. Yield: 69.1 mg ( $0.17 \mathrm{mmol}, 57 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}$ ): $\delta[\mathrm{ppm}]=1.86\left(\mathrm{dt}, 3 \mathrm{H}^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=11.7 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=5.8 \mathrm{~Hz},-\left(\mathrm{CH}_{3}\right), 1.53\left(\mathrm{~d},{ }^{3} J_{\mathrm{P}-\mathrm{H}}\right.\right.$ $\left.=10.4 \mathrm{~Hz}, 6 \mathrm{H}, \mathrm{N}\left(\mathrm{CH}_{3}\right)_{2}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=130.8\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right),-65.1\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{x}, \mathrm{x}^{\prime}}\right), 37.7(\mathrm{~m}, 2 \mathrm{P}$, $\left.\mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}\right){ }^{31} \mathrm{P}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=130.8\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right),-65.1\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{x}, \mathrm{x}^{\prime}}\right), 37.7\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}\right) ;($ For coupling constants, see Supplementary Table 4). LIFDI-MS (toluene): 405.02 (100 \%, [M] ${ }^{+}$); analysis (calcd., found for $\left.\mathrm{C}_{13} \mathrm{H}_{24} \mathrm{FeP}_{5} \mathrm{~N}\right)$ : $\mathrm{C}(38.55,38.14), \mathrm{H}(5.97,6.03)$.

## Synthesis of $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\mathrm{n}^{4}-\mathrm{P}_{5}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right) \mathrm{Me}\right\}\right]$ (3b)

Compound 2b ( $1.33 \mathrm{mmol}, 686.0 \mathrm{mg}$, 1 eq ) was dissolved in 100 mL THF. 1.2 mL of a 1.110 molar solution of Mel in $\mathrm{Et}_{2} \mathrm{O}(1.33 \mathrm{mmol}, 1 \mathrm{eq})$ was added under strong stirring at room temperature and the solution was stirred overnight. The formation of a white precipitate was observed on the glass wall. The solvent was removed, 3b extracted with 40 mL of $n$-hexane and filtered over diatomaceous earth. The solvent was reduced to 10 mL . Complex $\mathbf{3 b}$ was isolated as black plates. Crystals for X -ray structure analysis were obtained from a concentrated $n$-hexane solution at $-30{ }^{\circ} \mathrm{C}$. Yield: $426 \mathrm{mg}(0.94 \mathrm{mmol}, 71 \%) .{ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=1.80\left(\mathrm{dt}, 3 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=11.9 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=\right.$ $\left.5.8 \mathrm{~Hz},-\mathrm{CH}_{3}\right), 1.67\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 0.25\left(\mathrm{~d}, 2 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=14.9 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{3}\right),-0.18\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{CH}_{2} \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{3}\right)_{3}$. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=129.4\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 37.0\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}}\right),-96.7\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\left.\mathrm{x}, \mathrm{x}^{\prime}\right)}\right){ }^{31} \mathrm{P}$ NMR ( $\mathrm{C}_{6} \mathrm{D}_{6}$, $293 \mathrm{~K}): \delta[\mathrm{ppm}]=129.4\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 37.0\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}\right)$, -96.7 (m, $2 \mathrm{P}, \mathrm{P}_{\mathrm{x}, \mathrm{x}^{\prime}}$ ); (For coupling constants, see Supplementary Table 5). LIFDI-MS (toluene): 448.03 ( $100 \%$, [M] ${ }^{+}$); analysis (calcd., found for $\mathrm{C}_{15} \mathrm{H}_{29} \mathrm{FeP}_{5} \mathrm{Si}$ ): C (40.20, 39.64), H (6.52, 6.48).

## Synthesis of $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\mathrm{n}^{4}-\mathrm{P}_{5} \mathrm{Me}_{2}\right)\right]$ (3c)

Method A: Compound $2 \mathrm{c}(3.53 \mathrm{mmol}, 2.26 \mathrm{~g}, 1 \mathrm{eq})$ was dissolved in DME and 3.18 mL of a 1.11 molar solution of $\mathrm{Mel}(3.53 \mathrm{mmol}, 1 \mathrm{eq})$ in $\mathrm{Et}_{2} \mathrm{O}$ was added at room temperature and stirred overnight. The solvent was removed in vacuo, a brown residue was extracted with $n$-hexane and filtered over silica gel. The solvent was removed under reduced pressure, dissolved in 5 mL of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$, layered with 20 mL of acetonitrile and stored at $-30^{\circ} \mathrm{C}$. Dark green blocks of 3 c were isolated after one week. Yield: 938 mg ( $2.49 \mathrm{mmol}, 71 \%$ ). Method B : $\left[\mathrm{K}(\mathrm{dme})_{2}\right]_{2}\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\mathrm{n}^{4}-\mathrm{P}_{5}\right)\right]\left(\mathbf{1}^{\prime}\right)$ ( $0.2 \mathrm{mmol}, 165.9 \mathrm{mg}$, 1 eq ) was dissolved in 10 mL THF and 0.36 mL of a 1.11 molar solution of Mel ( $0.4 \mathrm{mmol}, 2 \mathrm{eq}$ ) in $\mathrm{Et}_{2} \mathrm{O}$ was added at room temperature. The reaction mixture was stirred for five minutes and the solvent was partly reduced in vacuo. The performed ${ }^{31}{ }^{21}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}$ experiment (Supplementary Figure 69) of the reaction in THF/C6D ${ }_{6}$ capillary matches the spectroscopic data of method $A$ and shows a quantitative formation of $3 c .{ }^{1} H N M R\left(C_{6} D_{6}\right.$,
$293 \mathrm{~K}): \delta[\mathrm{ppm}]=1.61\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{\underline{5}}\right), 1.51\left(\mathrm{dt}, 3 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=11.1 \mathrm{~Hz},{ }^{3} J_{\mathrm{P}-\mathrm{H}}=5.5 \mathrm{~Hz},-\mathrm{CH}_{3}(\mathrm{exo})\right), 0.06\left(\mathrm{~d}, 3 \mathrm{H},{ }^{2} J_{\mathrm{P}-\mathrm{H}}\right.$ $=11.5 \mathrm{~Hz},-\mathrm{CH}_{3}$ (endo)). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=117.2\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 35.4\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}}\right),-122.7(\mathrm{~m}, 2 \mathrm{P}$, $\left.\mathrm{P}_{\mathrm{x}, \mathrm{x}^{\prime}}\right)^{31}{ }^{31} \mathrm{PNMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=117.2\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 35.4\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}}\right)^{\prime}$, -122.7(m,2 P, $\left.\mathrm{P}_{\mathrm{x}, \mathrm{x}}\right)^{\prime}$ ); (For coupling constants, see Supplementary Table 6). LIFDI-MS (toluene): 376.97 ( $100 \%$, $[\mathrm{M}]^{+}$), 360.95 ( $40 \%,[\mathrm{M}]^{+}-\mathrm{CH}_{3}$ ), 345.92 (20 \%, [M] $\left.{ }^{+}-\left(\mathrm{CH}_{3}\right)_{2}\right), 314.95\left(10 \%[\mathrm{M}]^{+}-\mathrm{P}\left(\mathrm{CH}_{3}\right)_{2}\right)$; analysis (calcd., found for $\left.\mathrm{C}_{12} \mathrm{H}_{21} \mathrm{FeP}_{5}\right)$ : $\mathrm{C}(38.33,38.37), \mathrm{H}(5.63$, 5.63).

## Synthesis of $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\boldsymbol{\eta}^{4}-\mathrm{P}_{5} \mathrm{Me}{ }^{i} \mathrm{Pr}\right)\right](3 \mathrm{~d})$

To a solution of $2 \mathrm{c}(0.15 \mathrm{mmol}, 90 \mathrm{mg}, 1 \mathrm{eq})$ in 10 mL DME. 0.03 mL of isopropyl iodide ( $0.15 \mathrm{mmol}, 1 \mathrm{eq})$ was added. The brownish solution was stirred overnight, all volatiles were removed in vacuum and the brown residue was dissolved in $n$-hexane and filtered through a frit. The resulting solution was concentrated to 3 mL and stored at $30^{\circ} \mathrm{C}$. Dark red blocks of [ $\left.\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}{ }^{\text {i }} \mathrm{PrMe}\right)\right](3 \mathrm{~d})$ could be isolated after two days. Yield: 43 mg , ( $0.106 \mathrm{mmol}, 72 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}$ ): $\delta[\mathrm{ppm}]=2.40\left(\mathrm{~m}, 1 \mathrm{H},-\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.59\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 1.01\left(\mathrm{dd}, 6 \mathrm{H},-\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right.$, $\left.{ }^{3} J_{\mathrm{H}-\mathrm{H}}=7.1 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=15.0 \mathrm{~Hz}\right), 0.05\left(\mathrm{~d}, 3 \mathrm{H},-\mathrm{CH}_{3}, J_{\mathrm{P}-\mathrm{H}}=10.5 \mathrm{~Hz}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=151.8(\mathrm{~m}$, $\left.1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 33.3\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}\right),-135.8\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\left.\mathrm{x}, \mathrm{x}^{\prime}\right)} .{ }^{31} \mathrm{P}\right.$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=151.8\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 33.3(\mathrm{~m}, 2 \mathrm{P}$, $\left.P_{M, M^{\prime}}\right),-135.8$ (m, 2P, $P_{x, x^{\prime}}$ ); (For coupling constants see Supplementary Table 7). FD-MS (toluene): 404.00 (100 \%, $[\mathrm{M}]^{+}$); analysis (calcd., found for $\mathrm{C}_{14} \mathrm{H}_{25} \mathrm{FeP}_{5}$ ): $\mathrm{C}(41.61,41.60), \mathrm{H}(6.24,6.11)$.

## Synthesis of $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}{ }^{\text {t }} \mathrm{BuMe}\right)\right]$ (3e)

Method A: A solution of 2d ( $0.2 \mathrm{mmol}, 152.5 \mathrm{mg}, 1 \mathrm{eq}$ ) in 10 mL THF was cooled to $-80^{\circ} \mathrm{C}$ and a 1.005 molar solution of Mel in DME ( $0.2 \mathrm{mmol}, 0.20 \mathrm{~mL}, 1 \mathrm{eq}$ ) was added. A colour change from green to brown occurred and a colourless solid was formed. The mixture was allowed to stir overnight and reach room temperature. The solvent was removed under reduced pressure and a brown solution was extracted with 10 mL toluene and filtered over diatomaceous earth. The solvent was removed in vacuo. The brown residue was dissolved in 2 mL THF, layered with 4 mL n-hexane and stored at $-30^{\circ} \mathrm{C}$. $\left[\mathrm{C} \mathrm{p}^{*} \mathrm{Fe}\left(n^{4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{BuMe}\right)\right] 3 \mathrm{e}$ was formed as dark green blocks after one day. Yield: 71.1 mg ( $0.17 \mathrm{mmol}, 85 \%$ ).

Method B: $\left[K(d m e)_{2}\right]_{2}\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\mathrm{n}^{4}-\mathrm{P}_{5}\right)\right]\left(1^{\prime}\right)(0.4 \mathrm{mmol}, 313.8 \mathrm{mg}, 1 \mathrm{eq})$ was dissolved in 10 mL THF, cooled to $-80^{\circ} \mathrm{C}$ and 0.05 mL t Bul ( $0.4 \mathrm{mmol}, 1 \mathrm{eq}$ ) was added. The reaction mixture was stirred for ten minutes and 0.18 mL of a 1.11 molar solution of $\mathrm{Mel}(0.2 \mathrm{mmol}, 1 \mathrm{eq})$ in $\mathrm{Et}_{2} \mathrm{O}$ was added. The resulting brown solution was stirred overnight and the solvent was partly reduced in vacuo. The performed ${ }^{31} P\left\{{ }^{1} \mathrm{H}\right\}$ NMR experiment (Supplementary Figure 70) of the reaction in $\mathrm{THF} / \mathrm{C}_{6} \mathrm{D}_{6}$-capillary matches the spectroscopic data of method A and shows a quantitative formation of $3 \mathrm{e} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=1.74\left(\mathrm{~m}, 3 \mathrm{H},-\mathrm{CH}_{3}\right), 1.62\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 0.26\left(\mathrm{~d}, 9 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=14.5 \mathrm{~Hz},-\right.$ $\left.\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=151.9\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 47.0\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}}\right),-117.2\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\left.\mathrm{x}, \mathrm{x}^{\prime}\right)}\right) .{ }^{31} \mathrm{P}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=151.9\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 47.0\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}\right),-117.2\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{x}, \mathrm{x}^{\prime}}\right)$ : (For coupling constants, see Supplementary Table 8). LIFDI-MS (toluene): 418.02 (100 \%, [M] ${ }^{+}$); analysis (calcd., found for $\mathrm{C}_{15} \mathrm{H}_{27} \mathrm{FeP}_{5}$ ): C (43.09, 43.63), H (6.51, 6.36).

## Synthesis of $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{PhMe}\right)\right]$ (3f)

Compound $1(0.4 \mathrm{mmol}, 138.4 \mathrm{mg}, 1 \mathrm{eq})$ was dissolved in 20 mL of DME, cooled to $-50^{\circ} \mathrm{C}$ and 0.22 mL of a 1.9 molar solution of $\mathrm{PhLi}(0.4 \mathrm{mmol}, 1 \mathrm{eq})$ in dibutyl ether was added. The solution was stirred for two hours and allowed to reach room temperature. To the brown solution, a 1.11 molar solution of $\mathrm{Mel}(0.4 \mathrm{mmol}, 0.36 \mathrm{~mL}, 1 \mathrm{eq})$ in $\mathrm{Et}_{2} \mathrm{O}$ was added. The solution was stirred for 18 hours, the solvent removed under reduced pressure, the remaining brown residue extracted with $3 \times 5 \mathrm{~mL}$ of $n$-hexane and filtered over diatomaceous earth. The volume was reduced in vacuo
and the solution stored at $-30^{\circ} \mathrm{C}$. Compound 3 f was isolated after three days as dark green plates. Yield: 132.0 mg ( $0.30 \mathrm{mmol}, 75 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}$ ): $\delta[\mathrm{ppm}]=6.82\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{C}_{6} \mathrm{H}_{5}\right),=6.71\left(\mathrm{~m}, 3 \mathrm{H},-\mathrm{C}_{6} \mathrm{H}_{5}\right), 1.95\left(\mathrm{dt}, 3 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=\right.$ $\left.10.8 \mathrm{~Hz},{ }^{3} \mathrm{JP}_{-\mathrm{H}}=5.4 \mathrm{~Hz},-\mathrm{CH}_{3}\right), 1.64\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=117.7\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 40.5$ ( $\mathrm{m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}$ ), -109.5 (m, $\left.2 \mathrm{P}, \mathrm{P}_{\left.\mathrm{X}, \mathrm{x}^{\prime}\right)}\right)^{31} \mathrm{P}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=117.7\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 40.5\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}\right),-109.5$ ( $m, 2$ P, $P_{x, x}$ ); (For coupling constants, see Supplementary Table 9). LIFDI-MS (toluene): 437.96 (100 \%, [M] ${ }^{+}$); analysis (calcd., found for $\mathrm{C}_{17} \mathrm{H}_{23} \mathrm{FeP}_{5}$ ): $\mathrm{C}(46.61,47.09), \mathrm{H}(5.29,5.26)$.

## Synthesis of PR'R"R"' (4a-c)

Compound 3d ( $0.1 \mathrm{mmol}, 40.4 \mathrm{mg}, 1 \mathrm{eq}$ ), $3 \mathrm{e}(0.2 \mathrm{mmol}, 83.6 \mathrm{mg}, 1 \mathrm{eq})$ or $3 \mathrm{f}(0.1 \mathrm{mmol}, 43.8 \mathrm{mg}, 1 \mathrm{eq})$ were dissolved in DME and cooled to $-50^{\circ} \mathrm{C}$. To the brownish-green solution, a $-50^{\circ} \mathrm{C}$ cold solution of $\mathrm{KBnz}(0.1 \mathrm{mmol} / 0.2 \mathrm{mmol}$ for $3 \mathrm{e}, 13.0 \mathrm{mg} / 26.0 \mathrm{mmol}$ for $3 \mathrm{e}, 1 \mathrm{eq}$ ) in DME was added. The colour changed to dark red and rapidly back to brownish-green. The solution was stirred overnight and allowed to reach room temperature. The solvent was slowly removed under reduced pressure (note: in order to avoid the loss of the desired phosphine by removal of the solvent, lower boiling solvents like THF can be used for the reaction). The oily residue was extracted with $n$-pentane ( 3 x 5 mL ) and decanted of the remaining solid (compound 5, see below). The solvent was removed in vacuo and compound 4a-c (a: $\mathrm{R}^{\prime}=\mathrm{Me}, \mathrm{R}^{\prime \prime}={ }^{i} \mathrm{Pr}, \mathrm{R}^{\prime \prime \prime}=\mathrm{Bnz} ; \mathrm{b}: \mathrm{R}^{\prime}={ }^{t} \mathrm{Bu}, \mathrm{R}^{\prime \prime}=\mathrm{Me}, \mathrm{R}^{\prime \prime \prime}=\mathrm{Bnz} ; \mathrm{c}: \mathrm{R}^{\prime}=\mathrm{Ph}, \mathrm{R}^{\prime \prime}=\mathrm{Me}, \mathrm{R}^{\prime \prime}=\mathrm{Bnz}$ ) can be isolated as a viscous liquid. Yield: 4a: 14.8 mg ( $0.082 \mathrm{mmol}, 82 \%$ ), 4 b : 21.5 mg ( $0.11 \mathrm{mmol}, 55 \%$ ), 4c: 17.1mg ( 0.08 mmol, $80 \%$ ).
${ }^{1} \mathrm{H}$ NMR: $4 \mathrm{a}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=7.07\left(\mathrm{~m}, 5 \mathrm{H},-\mathrm{CH}_{2}-\mathrm{C}_{6} \mathrm{H}_{5}\right), 2.75\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=13.14 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{H}-\mathrm{H}}=3.51 \mathrm{~Hz},-\mathrm{CH}_{\underline{2}} \underline{-}^{-}\right.$ $\mathrm{Ph}), 2.41\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=13.18 \mathrm{~Hz},{ }^{3} J_{\mathrm{H}-\mathrm{H}}=1.69 \mathrm{~Hz},-\mathrm{CH}_{2}-\mathrm{Ph}\right), 1.28\left(\mathrm{~m}, 1 \mathrm{H},-(\mathrm{CH})-\mathrm{CH}_{3}\right), 0.99\left(\mathrm{dd}, 3 \mathrm{H},{ }^{3} J_{\mathrm{P}-\mathrm{H}}=14.1 \mathrm{~Hz}\right.$, ${ }^{2} J_{\mathrm{H}-\mathrm{H}}=7.0 \mathrm{~Hz},-(\mathrm{CH})-\left(\mathrm{CH}_{3}\right)_{2}, 0.91\left(\mathrm{dd}, 3 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=12.2 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{\mathrm{H}-\mathrm{H}}=6.9 \mathrm{~Hz},-(\mathrm{CH})-\left(\mathrm{CH}_{3}\right)_{2}\right), 0.73\left(\mathrm{~d}, 9 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=3.5 \mathrm{~Hz}\right.$, $\left.-\mathrm{CH}_{3}\right) ; \mathbf{4 b}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=7.13\left(\mathrm{~m}, 8 \mathrm{H},-\mathrm{CH}_{2}-\mathrm{C}_{6} \mathrm{H}_{5}\right), 2.76\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=12.2 \mathrm{~Hz},{ }^{3} J_{\mathrm{H}-\mathrm{H}}=3.9 \mathrm{~Hz},-\mathrm{CH}_{2}-\mathrm{Ph}\right)$, $2.33\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=13.0 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{H}-\mathrm{H}}=4.1 \mathrm{~Hz},-\mathrm{CH}_{2}-\mathrm{Ph}\right), 0.94\left(\mathrm{~d}, 9 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=11.2 \mathrm{~Hz},-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.71\left(\mathrm{~d}, 3 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=\right.$ $\left.3.5 \mathrm{~Hz},-\mathrm{CH}_{3}\right) ; 4 \mathrm{c}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=7.21\left(\mathrm{~m}, 5 \mathrm{H},-\mathrm{CH}_{2}-\mathrm{C}_{6} \mathrm{H}_{5}\right), 7.21\left(\mathrm{~m}, 5 \mathrm{H},-\mathrm{CH}_{2}-\mathrm{C}_{6} \mathrm{H}_{5}\right), 2.95\left(\mathrm{dd}, 2 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=\right.$ $\left.13.2 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{H}-\mathrm{H}}=2.9 \mathrm{~Hz},-\mathrm{CH}_{2}-\mathrm{Ph}\right), 2.79\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=13.0 \mathrm{~Hz},-\mathrm{CH}_{\underline{2}}-\mathrm{Ph}\right), 1.10\left(\mathrm{~d}, 3 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=4.0 \mathrm{~Hz},-\mathrm{CH}_{\underline{3}}\right)$;
${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR: $4 \mathrm{a}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=-18.5 ; 4 \mathrm{~b}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=-7.00(\mathrm{~s}) ; 4 \mathrm{c}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=$ -29.6.
${ }^{31} \mathrm{P}$ NMR: $4 \mathrm{a}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=-18.5 ; 4 \mathrm{~b}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=-7.00(\mathrm{~s}, \mathrm{br}) ; 4 \mathrm{c}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=$ -29.6 (s, br).
${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR: $4 \mathrm{a}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=138.5\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{p}-\mathrm{C}}=4.1 \mathrm{~Hz}, \mathrm{Ph}\right), 129.1\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{\mathrm{p}-\mathrm{c}}=5.4 \mathrm{~Hz}, \mathrm{Ph}\right), 128.2(\mathrm{~s}, \mathrm{Ph}), 125.5$ (d, $\left.{ }^{4} J_{\mathrm{P}-\mathrm{C}}=2.1 \mathrm{~Hz}, \mathrm{Ph}\right), 34.8\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{p}-\mathrm{C}}=18.64 \mathrm{~Hz},-\left(\underline{\mathrm{CH}} \mathrm{H}_{2}\right)-\mathrm{Ph}\right), 26.6\left(\mathrm{~d},{ }^{2} J_{\mathrm{P}-\mathrm{C}}=11.71 \mathrm{~Hz},-(\mathrm{CH})-\left(\mathrm{CH}_{3}\right)_{2}\right), 19.2\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{p}-\mathrm{C}}=\right.$ $\left.17.1 \mathrm{~Hz},-(\mathrm{CH})-\left(\mathrm{CH}_{3}\right)_{2}\right), 18.3\left(\mathrm{~d},{ }^{2} J_{\mathrm{p}-\mathrm{c}}=12.8 \mathrm{~Hz},-(\mathrm{CH})-\left(\mathrm{CH}_{3}\right)_{2}\right), 8.1\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{p}-\mathrm{c}}=20.2 \mathrm{~Hz},-\mathrm{CH}_{3}\right) ; 4 \mathrm{~b}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]$ $=139.1\left(\mathrm{~d},{ }^{2} J_{\mathrm{P}-\mathrm{C}}=6.9 \mathrm{~Hz}, \mathrm{Ph}\right), 129.3\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{\mathrm{P}-\mathrm{c}}=6.3 \mathrm{~Hz}, \mathrm{Ph}\right), 128.3\left(\mathrm{~d},{ }^{5} \mathrm{~J}_{\mathrm{P}-\mathrm{c}}=0.7 \mathrm{~Hz}, \mathrm{Ph}\right), 125.5\left(\mathrm{~d},{ }^{4} \mathrm{~J}_{\mathrm{P}-\mathrm{c}}=2.3 \mathrm{~Hz}, \mathrm{Ph}\right)$, $33.0\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{p}-\mathrm{C}}=20.8 \mathrm{~Hz},-\left(\mathrm{CH}_{2}\right)-\mathrm{Ph}\right), 27.0\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{c}}=13.6 \mathrm{~Hz},-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 26.5\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=13.6 \mathrm{~Hz},-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 6.2\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{p}-\mathrm{C}}=\right.$ $\left.23.0 \mathrm{~Hz},-\mathrm{CH}_{3}\right) ; 4 \mathrm{c}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=140.1\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{p}-\mathrm{c}}=17.9 \mathrm{~Hz}, \mathrm{Ph}\right), 137.7\left(\mathrm{~d},{ }^{2} J_{\mathrm{p}-\mathrm{c}}=4.5 \mathrm{~Hz}, \mathrm{Ph}\right), 131.6\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{p}-\mathrm{C}}=\right.$ $18.6 \mathrm{~Hz}, \mathrm{Ph}), 129.1\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=5.4 \mathrm{~Hz}, \mathrm{Ph}\right), 128.2\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{c}}=11.2 \mathrm{~Hz}, \mathrm{Ph}\right), 128.1(\mathrm{~s}, \mathrm{Ph}), 128.1(\mathrm{~s}, \mathrm{Ph}), 125.7\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=\right.$ $5.4 \mathrm{~Hz}, \mathrm{Ph}), 38.3\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=17.1 \mathrm{~Hz},-\left(\mathrm{CH}_{2}\right)-\mathrm{Ph}\right), 10.2\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=17.1 \mathrm{~Hz},-\mathrm{CH}_{3}\right)$.

## Synthesis of SPR'R"R"' (4a'-c')

Compound 4a-c ( $0.1 \mathrm{mmol}, 1 \mathrm{eq}$ ) were synthesized according to the previous procedure, dissolved in 10 mL of $n$-pentane, respectively, added to a solution of sulfur ( $0.1 \mathrm{mmol}, 3.2 \mathrm{mg}, 1 \mathrm{eq}$ ) in $10 \mathrm{~mL} n$-pentane and stirred for 4 hours at room temperature. The volume was reduced under reduced pressure and stored at $-30^{\circ} \mathrm{C}$. Colourless
crystals of $4 a^{\prime}-c^{\prime}\left(a: R^{\prime}=M e, R^{\prime \prime}=i P r, R^{\prime \prime \prime}=B n z ; b: R^{\prime}=t B u, R^{\prime \prime}=M e, R^{\prime \prime \prime}=B n z ; c: R^{\prime}=P h, R^{\prime \prime}=M e, R^{\prime \prime \prime}=B n z\right)$ were formed after two days. Yield: 4a': 16.0 mg ( $0.089 \mathrm{mmol}, 89 \%$ ), 4b': 17.5 mg ( $0.08 \mathrm{mmol}, 80 \%$ ), 4c': 17.1mg ( $0.08 \mathrm{mmol}, 80 \%$ ).
${ }^{1} \mathrm{H}$ NMR: $4 \mathrm{a}^{\prime}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=7.05\left(\mathrm{~m}, 5 \mathrm{H},-\mathrm{CH}_{2}-\mathrm{C}_{6} \mathrm{H}_{5}\right), 2.89\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{p}-\mathrm{H}}=14.7 \mathrm{~Hz},-\mathrm{CH}_{2}-\mathrm{Ph}\right), 2.74(\mathrm{dd}, 1 \mathrm{H}$, $\left.{ }^{3} \int_{\mathrm{P}-\mathrm{H}}=13.8 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{H}-\mathrm{H}}=1.8 \mathrm{~Hz},-\mathrm{CH}_{2}-\mathrm{Ph}\right), 1.39\left(\mathrm{~m}, 1 \mathrm{H},-(\mathrm{CH})-\mathrm{CH}_{3}\right), 0.99\left(\mathrm{dd}, 3 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=17.8 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{\mathrm{H}-\mathrm{H}}=7.0 \mathrm{~Hz},-\right.$ ( CH ) $\left.-\left(\mathrm{CH}_{3}\right)_{2}\right), 0.97\left(\mathrm{~d}, 9 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=11.9 \mathrm{~Hz},-\mathrm{CH}_{3}\right), 0.84\left(\mathrm{dd}, 3 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=17.5 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{\mathrm{H}-\mathrm{H}}=6.9 \mathrm{~Hz},-(\mathrm{CH})-\left(\mathrm{CH}_{3}\right)_{2}\right) ; 4 \mathrm{~b}^{\prime}$ $\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=7.27\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{CH}_{2}-\mathrm{C}_{6} \mathrm{H}_{5}\right), 7.12\left(\mathrm{~m}, 3 \mathrm{H},-\mathrm{CH}_{2}-\mathrm{C}_{6} \mathrm{H}_{5}\right), 2.79\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{CH}_{2}-\mathrm{Ph}\right), 0.97(\mathrm{~d}, 3 \mathrm{H}$, $\left.{ }^{2} J_{\mathrm{P}-\mathrm{H}}=11.8 \mathrm{~Hz},-\mathrm{CH}_{3}\right), 0.95\left(\mathrm{~d}, 9 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=15.5 \mathrm{~Hz},-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right) ; 4 \mathrm{c}^{\prime}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=7.60(\mathrm{~m}, 2 \mathrm{H},-\mathrm{Ph}), 7.00(\mathrm{~m}$, $6 \mathrm{H},-\mathrm{Ph}), 6.91(\mathrm{~m}, 2 \mathrm{H},-\mathrm{Ph}), 3.01\left(\mathrm{~d}, 2 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=14.1 \mathrm{~Hz},-\mathrm{CH}_{2}-\mathrm{Ph}\right), 1.39\left(\mathrm{~d}, 3 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=12.7 \mathrm{~Hz},-\mathrm{CH}_{2}-\mathrm{Ph}\right)$.
${ }^{31}{ }^{2}\left\{{ }^{1} \mathrm{H}\right\}$ NMR: $4 \mathrm{a}^{\prime}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=51.3 ; 4 \mathrm{~b}^{\prime}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=58.6(\mathrm{~s}) ; 4 \mathrm{c}^{\prime}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=$ 38.0.
${ }^{31}$ P NMR: $4 \mathrm{a}^{\prime}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=51.3(\mathrm{~s}, \mathrm{br}) ; 4 \mathrm{~b}^{\prime}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=58.6(\mathrm{~m}) ; 4 \mathrm{c}^{\prime}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=$ 38.0 (m).
${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR: 4a' $\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=132.7$ (d, $\left.{ }^{2} \mathrm{~J}_{\mathrm{p}-\mathrm{c}}=7.9 \mathrm{~Hz}, \mathrm{Ph}\right), 129.7\left(\mathrm{~d},{ }^{3} J_{\mathrm{p}-\mathrm{c}}=4.9 \mathrm{~Hz}, \mathrm{Ph}\right), 128.2\left(\mathrm{~d},{ }^{4}{ }^{\mathrm{J}} \mathrm{p}-\mathrm{c}=\right.$ $2.8 \mathrm{~Hz}, \mathrm{Ph}), 126.8\left(\mathrm{~d},{ }^{3} J_{\mathrm{p}-\mathrm{C}}=3.3 \mathrm{~Hz}, \mathrm{Ph}\right), 39.4\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{p}-\mathrm{C}}=45.1 \mathrm{~Hz},-\left(\mathrm{CH}_{2}\right)-\mathrm{Ph}\right), 28.7\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{p}-\mathrm{C}}=52.3 \mathrm{~Hz},-(\mathrm{CH})-\left(\mathrm{CH}_{3}\right)_{2}\right), 15.6$ $\left(\mathrm{d},{ }^{2} \mathrm{~J}_{\mathrm{p}-\mathrm{C}}=21.3 \mathrm{~Hz},-(\mathrm{CH})-\left(\mathrm{CH}_{3}\right)_{2}\right), 15.5\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{p}-\mathrm{C}}=52.5 \mathrm{~Hz},-\mathrm{CH}_{3} 15.3\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{p}-\mathrm{C}}=26.8 \mathrm{~Hz},-(\mathrm{CH})-\left(\mathrm{CH}_{3}\right)_{2}\right) ; 4 \mathrm{~b}^{\prime}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right)\right.$ : $\delta[\mathrm{ppm}]=132.9\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{p}-\mathrm{C}}=7.8 \mathrm{~Hz}, \mathrm{Ph}\right), 130.6\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{\mathrm{p}-\mathrm{c}}=5.7 \mathrm{~Hz}, \mathrm{Ph}\right), 127.1\left(\mathrm{~d},{ }^{5} \mathrm{~J}_{\mathrm{p}-\mathrm{C}}=2.9 \mathrm{~Hz}, \mathrm{Ph}\right), 127.1\left(\mathrm{~d},{ }^{4} \mathrm{~J}_{\mathrm{p}-\mathrm{C}}=3.2 \mathrm{~Hz}\right.$, Ph), $36.1\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{p}-\mathrm{c}}=43.1 \mathrm{~Hz},-\left(\underline{\mathrm{C}} \mathrm{H}_{2}\right)-\mathrm{Ph}\right), 33.3\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{p}-\mathrm{C}}=49.4 \mathrm{~Hz},-\underline{\mathrm{C}}\left(\mathrm{CH}_{3}\right)_{3}\right), 24.6\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{p}-\mathrm{C}}=1.4 \mathrm{~Hz},-\mathrm{C}\left(\underline{\mathrm{C}} \mathrm{H}_{3}\right)_{3}\right), 13.4(\mathrm{~d}$, $\left.{ }^{1} J_{\mathrm{p}-\mathrm{C}}=50.8 \mathrm{~Hz},-\mathrm{CH}_{3}\right) ; 4 \mathrm{c}^{\prime}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=131.0\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{p}-\mathrm{C}}=9.9 \mathrm{~Hz}, \mathrm{Ph}\right), 130.8\left(\mathrm{~d},{ }^{4} \mathrm{~J}_{\mathrm{p}-\mathrm{C}}=2.8 \mathrm{~Hz}, \mathrm{Ph}\right), 130.0(\mathrm{~d}$, $\left.{ }^{3} J_{\mathrm{P}-\mathrm{C}}=5.2 \mathrm{~Hz}, \mathrm{Ph}\right), 126.8\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=3.7 \mathrm{~Hz}, \mathrm{Ph}\right), 43.8\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=49.0 \mathrm{~Hz},-\left(\mathrm{CH}_{2}\right)-\mathrm{Ph}\right), 18.9\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=57.3 \mathrm{~Hz},-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right)$.

4a': El-MS $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right): 212.08\left(37 \%,[\mathrm{M}]^{+}\right)$, $91.05\left(100 \%[\mathrm{Bnz}]^{+}\right), 170.03\left(46 \%\left[\mathrm{M}-\mathrm{C}_{3} \mathrm{H}_{6}\right]^{+}\right)$.
4b': GC-MS ( $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ): $226.09\left(20 \%,[\mathrm{M}]^{+}\right)$, $91.06\left(100 \%[\mathrm{Bnz}]^{+}\right), 170.03\left(44 \%\left[\mathrm{M}-{ }^{-} \mathrm{Bu}+\mathrm{H}\right]^{+}\right)$.

4c': EI-MS ( $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ): $246.06\left(44 \%,[\mathrm{M}]^{+}\right), 155.01$ (100 \% [M-Bnz] ${ }^{+}$), $91.06\left(25 \%[B n z]^{+}\right)$.

## Targeted synthesis of $[K(18 c 6)($ thf $)]\left[C p^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{4}\right)\right]$ (5)

Compound 3c ( $0.2 \mathrm{mmol}, 75.2 \mathrm{mg}, 1 \mathrm{eq}$ ), KBnz ( $0.2 \mathrm{mmol}, 26.0 \mathrm{mg}, 1 \mathrm{eq}$ ) and $18-\mathrm{crown}-6(0.2 \mathrm{mmol}, 52.9 \mathrm{mg}, 1 \mathrm{eq})$ were dissolved separately in THF and cooled to $-80^{\circ} \mathrm{C}$. The potassium benzyl solution is added to compound $3 \mathbf{c}$, stirred for two minutes and 18 c 6 is added afterwards. The mixture was allowed to stir overnight and reach room temperature. The solvent of the resulting brown solution was removed in vacuo. The by-product $\mathrm{PMe}_{2} \mathrm{Bnz}$ was removed by washing the oily residue three times with 5 mL of $n$-pentane, resulting a greenish powder, which was dissolved in THF and layered with n-hexane. The solution was stored at $-30^{\circ} \mathrm{C}$ and compound 5 was isolated as highly air sensitive green/turquoise plates/blocks after one week. Yield: $111.9 \mathrm{mg}(0.16 \mathrm{mmol}, 81 \%) .{ }^{1} \mathrm{H}$ NMR (THF-d $8,293 \mathrm{~K}$ ): $\delta[\mathrm{ppm}]=3.73$ (s, $26 \mathrm{H}, 18-\mathrm{crown}-6$ ), 2.26 (s, $\left.\left.15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right) .{ }^{31}{ }^{\mathrm{P}\{ }{ }^{1} \mathrm{H}\right\}$ NMR (THF- $\mathrm{d}_{8}, 293 \mathrm{~K}$ ): $\delta$ [ppm] $=118.9$ (s), ${ }^{31}$ P NMR (THF- $\mathrm{d}_{8}, 293 \mathrm{~K}$ ): $\delta$ [ppm] = 118.9 (s). ESI-MS (anion, DME): $\mathrm{m} / \mathrm{z}=314.95$ ( $100 \%,[\mathrm{M}]^{-}$); analysis (calcd., found for $\mathrm{C}_{22} \mathrm{H}_{39} \mathrm{FeP}_{4} \mathrm{KO}_{6} \cdot(\mathrm{THF})_{0.75}: \mathrm{C}(44.65,44.28), \mathrm{H}(6.74,6.67)$.

## Synthesis of $\mathrm{PMe}_{2} \mathrm{Bnz}$ and regeneration of $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right]$ (1) in a cyclic process

Compound $1(3.00 \mathrm{mmol}, 1.04 \mathrm{~g}, 1 \mathrm{eq})$ was dissolved in 100 mL tetraglyme, 1.88 mL of a 1.6 molar solution of MeLi ( $3.00 \mathrm{mmol}, 1 \mathrm{eq}$ ) in $\mathrm{Et}_{2} \mathrm{O}$ was added and the resulting solution was allowed to stir for five minutes. To the reaction mixture, 2.80 mL of a 1.07 molar solution of $\mathrm{Mel}(3.00 \mathrm{mmol}, 1 \mathrm{eq})$ in $\mathrm{Et}_{2} \mathrm{O}$ was slowly added at room temperature
and stirred for five minutes. The diethylether of the stock solutions was removed under reduced pressure. The reaction mixture was cooled to $-30^{\circ} \mathrm{C}$, a solution of $\mathrm{KBnz}(3.00 \mathrm{mmol}, 390.7 \mathrm{mg}, 1 \mathrm{eq})$ in 50 mL tetraglyme was added and the reaction was stirred for 30 minutes. The cooling bath was removed and the phosphine $\mathrm{PMe}_{2} \mathrm{Bnz}$ was distilled off under reduced pressure ( $1 \cdot 10^{-3} \mathrm{mbar}, 55^{\circ} \mathrm{C}$ ). White phosphorus ( $3.00 \mathrm{mmol}, 371.7 \mathrm{mg}, 1 \mathrm{eq}$ ) was added to the remaining solution and the reaction mixture was heated under reflux for one hour at $275^{\circ} \mathrm{C}$. The described steps were repeated two more times. The starting material 1 was isolated after column chromatographic workup (silica gel, $n$-hexane, $20 \times 2 \mathrm{~cm}$ ) in overall $69 \%$ yield ( $2.07 \mathrm{mmol}, 2.07 \mathrm{~g}$ ) (Supplementary Figure 66). The phosphine $\mathrm{PMe}_{2} \mathrm{Bnz}$ was isolated as a pyrophoric colourless liquid in an overall yield of $79 \%(2.37 \mathrm{mmol}, 315.0 \mathrm{mg}$ ) (see Supplementary Figure 67, Supplementary Table 40).

### 5.6 References

1 Montchamp, J. L. Phosphinate chemistry in the 21st century: A viable alternative to the use of phosphorus trichloride in organophosphorus synthesis. Acc. Chem. Res. 47, 77-87 (2014).

2 Tang, W. \& Zhang, X. New chiral phosphorus ligands for enantioselective hydrogenation. Chem. Rev. 103, 3029-3069 (2003).

3 Karl, D. M. Phosphorus, the staff of life. Nature 406, 31-33 (2000).
4 Kamer, P. C. J. \& Leeuwen, P. W. N. van. Phosphorus(III)Ligands in Homogeneous Catalysis: Design and Synthesis. (Wiley, 2012).

5 Pignolet, L. Homogeneous Catalysis with Metal Phosphine Complexes. Modern Inorganic Chemistry (Springer US, 1983).

6 Teichert, J. F. Homogeneous Hydrogenation with Non -Precious Catalysts. (Wiley, 2019).
7 Guo, H., Fan, Y. C., Sun, Z., Wu, Y. \& Kwon, O. Phosphine Organocatalysis. Chem. Rev. 118, 10049-10293 (2018).

8 Osborn, J. A., Wilkinson, G. \& Mrowca, J. J. Tris(triphenylphosphine)halorhodium(I). in Inorganic Syntheses 67-71 (John Wiley \& Sons, Ltd, 1967).

9 Märkl, G. Heterocycles Containing Phosphorus. Angew. Chemie - Int. Ed. 4, 1023-1038 (1965).

10 Baudler, M. et al. ${ }^{\text {t }} \mathrm{Bu}_{6} \mathrm{P}_{8}$ and ${ }^{\mathrm{t}} \mathrm{Bu}_{6} \mathrm{As}_{8}$-Two New Element-Homologous Bicyclic Compounds of Different Structure. Angew. Chem. Int. Ed. Engl. 20, 406-408 (1981).
11. Gómez-Ruiz, S. \& Hey-Hawkins, E. The unusual coordination chemistry of phosphorusrich linear and cyclic oligophosphanide anions. Coord. Chem. Rev. 255, 1360-1386 (2011).

12 Musina, E. I., Balueva, A. S. \& Karasik, A. A. Phosphines: preparation, reactivity and applications. in Organophosphorus Chemistry Vol. 48 1-439 (The Royal Society of Chemistry, 2019).

13 Hey-Hawkins, E. \& Karasik, A. A. Product Class 4: Alkylphosphines. in Category 5, Compounds with One Saturated Carbon Heteroatom Bond (eds. Mathey \& Trost) vol. 42 71-108 (Georg Thieme Verlag, 2009).

14 Lühr, S., Holz, J. \& Börner, A. The Synthesis of Chiral Phosphorus Ligands for use in Homogeneous Metal Catalysis. ChemCatChem 3, 1708-1730 (2011).

15 L. Clevenger, A., M. Stolley, R., Aderibigbe, J. \& Louie, J. Trends in the Usage of Bidentate Phosphines as Ligands in Nickel Catalysis. Chem. Rev. 120, 6124-6196 (2020).

16 The Nobel Prize in Chemistry 2001. https://www.nobelprize.org/prizes/chemistry/2001/summary/.

17 Gusarova, N. K. \& Trofimov, B. A. Organophosphorus chemistry based on elemental phosphorus: advances and horizons. Russ. Chem. Rev. 89, 225-249 (2020).

18 Bettermann, G., Krause, W., Riess, G. \& Hofmann, T. Phosphorus Compounds, Inorganic, Ullmann's Encyclopedia of Industrial Chemistry. (Wiley, 2012).

19 Svara, J., Weferling, N. \& Hofmann, T. Phosphorus Compounds, Organic, Ullmann's Encyclopedia of Industrial Chemistry. (Wiley, 2006).

Geeson, M. B. \& Cummins, C. C. Phosphoric acid as a precursor to chemicals traditionally synthesized from white phosphorus. Science 359, 1383-1385 (2018).

21 Geeson, M. B. \& Cummins, C. C. Let's Make White Phosphorus Obsolete. ACS Cent. Sci. 6, 848-860 (2020).

22 Cossairt, B. M. \& Cummins, C. C. Radical synthesis of trialkyl, triaryl, trisilyl and tristannyl phosphines from P4. New J. Chem. 34, 1533-1536 (2010).

23 Yakhvarov, D. G., Gorbachuk, E. V., Kagirov, R. M. \& Sinyashin, O. G. Electrochemical reactions of white phosphorus. Russ. Chem. Bull. 61, 1300-1312 (2012).

24 Ghosh, S. K., Cummins, C. C. \& Gladysz, J. A. A direct route from white phosphorus and fluorous alkyl and aryl iodides to the corresponding trialkyl- and triarylphosphines. Org. Chem. Front. 5, 3421-3429 (2018).

Arockiam, P. B. et al. Versatile Visible-Light-Driven Synthesis of Asymmetrical Phosphines and Phosphonium Salts. Chem. Eur. J. 26, 16374-16382 (2020).

26 Lennert, U. et al. Direct catalytic transformation of white phosphorus into arylphosphines and phosphonium salts. Nat. Catal. 2, 1101-1106 (2019).

27 Scott, D. J., Cammarata, J., Schimpf, M. \& Wolf, R. Synthesis of monophosphines directly from white phosphorus. Nat. Chem. 13, 458-464 (2021).

28 Mädl, E. et al. Functionalization of a cyclo- $\mathrm{P}_{5}$ ligand by main-group element nucleophiles. Angew. Chem. Int. Ed. 53, 7643-7646 (2014).

29 Pyykkö, P. \& Atsumi, M. Molecular single-bond covalent radii for elements 1-118. Chem. Eur. J. 15, 186-197 (2009).

30 Pyykkö, P. \& Atsumi, M. Molecular Double-Bond Covalent Radii for Elements Li-E112. Chem. Eur. J. 15, 12770-12779 (2009).

Riegel, S. D., Burford, N., Lumsden, M. D. \& Decken, A. Synthesis and characterization of elusive cyclo-di- and -tri-phosphino-1,3-diphosphonium salts: Fundamental frameworks in catena-organophosphorus chemistry. Chem. Commun. 793, 4668-4670 (2007).

Butovskiy, M. V. et al. Ferrocene and pentaphosphaferrocene: A comparative study regarding redox chemistry. Angew. Chem. Int. Ed. 52, 2972-2976 (2013).

Chakraborty, U. et al. Mono- and dinuclear tetraphosphabutadiene ferrate anions. Dalt. Trans. 47, 3693-3697 (2018).

Hoidn, C. M., Maier, T. M., Trabitsch, K., Weigand, J. J. \& Wolf, R. [3+2] Fragmentation of a Pentaphosphido Ligand by Cyanide. Angew. Chem. Int. Ed. 58, 18931-18936 (2019).

Mandla, K. A., Neville, M. L., Moore, C. E., Rheingold, A. L. \& Figueroa, J. S. Dianionic Mononuclear Cyclo-P4 Complexes of Zero-Valent Molybdenum: Coordination of the Cyclo- $\mathrm{P}_{4}$ Dianion in the Absence of Intramolecular Charge Transfer. Angew. Chem. Int. Ed. 58, 15329-15333 (2019).

Baudler, M. \& Etzbach, T. Beiträge zur Chemie des Phosphors, 215. Einfache Darstellung des Pentaphosphacyclopentadienid-lons,cyclo- $\mathrm{P}_{5}$; durch Abbau von rotem Phosphor mit Kaliumdihydrogenphosphid. Chem. Ber. 124, 1159-1160 (1991).
Miluykov, V. A., Sinyashin, O. G., Scherer, O. J. \& Hey-Hawkins, E. Reactions of the pentaphospholide anion with half-sandwich complexes of iron: a new route to pentaphosphaferrocenes. Mendeleev Commun., 12, 1-2 (2002).

39 Becke, A. D. Density - functional thermochemistry . III . The role of exact exchange Density-functional thermochemistry . III . The role of exact exchange. J. Chern. Phys. 98, 5648-5652 (2005).

40 Vosko, S. H., Wilk, L. \& Nusair, M. Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. Can. J. Phys. 58, 1200-1211 (1980).

41 Lee, C., Yang, W. \& Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys. Rev. B 37, 785-789 (1988).

42 Stephen, P. J., Devlin, F. J., Chabalowski, C. F. \& Frisch, M. J. Ab Initio Calculation of Vibrational Absorption. J. Phys. Chem. 98, 11623-11627 (1994).
43 Weigend, F. \& Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn : Design and assessment of accuracy. Phys. Chem. Chem. Phys. 7, 3297-3305 (2005).

44 Tomasi, J., Mennucci, B. \& Cammi, R. Quantum mechanical continuum solvation models. Chem. Rev. 105, 2999-3093 (2005).

45 Grimme, S., Ehrlich, S. \& Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. J. Comput. Chem. 32, 1456-1465 (2011).

46 A, E. S. S., Lochmann, L. \& Trekoval, J. Li-K Exchange in alkyllithium / pottasium tpentoxides systems XIV. J. Organomet. Chem. 326, 1-7 (1987).

47 O. J. Scherer and T. Brück, Angew. Chem. Int. Ed. 26, 11987 (1987).
48 Bourhis, L. J., Dolomanov, O. V, Gildea, R. J., Howard, J. A. K. \& Puschmann, H. Olex2: a complete structure solution, refinement and anlysis program. J. Appl. Crystallogr. 42, 339-341 (2009).

49 Sheldrick, G. M. SHELXT - Integrated space-group and crystal-structure determination. Acta Crystallogr. Sect. A 71, 3-8 (2015).

50 Sheldrick, G. M. Crystal structure refinement with ShelXL. Acta Crystallogr. Sect. C 71, 38 (2015).

## Figure legends

Figure 1. Different approaches for the synthesis of ternary phosphines. Left: conventional way, hydrophosphination and salt metathesis. Right: Radical promoted, stochiometric and catalytic, as well as semi catalytic transition metal (TM) mediated synthesis of ternary phosphines.

Figure 2. Synthesis of asymmetric phosphines 4, via successive nucleophilic, electrophilic, nucleophilic attack. Synthesis of the anionic precursor complexes 2 by nucleophilic attack; Electrophilic quenching of $\mathbf{2}$ (synthesis of 3); asymmetric phosphine abstraction by nucleophiles (synthesis of 4, 5); Regeneration of 1 by thermolysis with $\mathrm{P}_{4}$; Alternative synthesis of 3 by electrophilic quenching of $1^{\prime}$.

Figure 3. Molecular structures of the anions in 2d, 5 and of the neutral complexes $\mathbf{3 f}$, $4 \mathbf{a}^{\prime}$ in the solid state with thermal ellipsoids at $50 \%$ probability level. Cations and hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligands are drawn in a wire frame model.

Figure 4. Electrostatic potential mapped on electron density (isovalue $=0.001$ ) for $3 c$. Colour code (blue $=$ positive, red $=$ negative) in $\mathrm{kJ} \cdot \mathrm{mol}^{-1}$.

Figure 5. Identification of the reaction pathway of phosphine abstraction. A) Experimental ${ }^{31}$ P\{ $\left.{ }^{1} \mathrm{H}\right\}$ NMR $\left(242.90 \mathrm{MHz}\right.$, THF- $\mathrm{d}_{8}$ ) spectrum of the crude reaction solution (low temperature reaction) of 3 c with KBnz at 180 K . B) Gibbs free energy profile of the reaction of 3 c with KBnz, calculated at the B3LYP-D3(BJ)/def2-TZVPP (PCM = THF) level of theory.

Figure 6. 'Semi-catalytic' cycle for the synthesis of asymetric phosphines. One-pot reaction of [Cp*Fe( $\left.\left.\eta^{5}-P_{5}\right)\right](1)$ with MeLi (I, $\left.R^{\prime}=\mathrm{Me}\right)$, quenching with $\mathrm{Mel}\left(\mathrm{II}, \mathrm{R}^{\prime \prime}=\mathrm{Me}\right)$, reaction with KBnz (III, $\mathrm{R}^{\prime \prime \prime}=\mathrm{Bnz}$ ) and subsequent thermolysis with white phosphorus (IV).

## Data Availability

The X-ray crystallographic coordinates for structures reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers CCDC-2041977 (2c), CCDC-2041978(2d), CCDC-2083624 (2e), CCDC-2041979 (3a), CCDC2041980 (3b), CCDC-2083625 (3c), CCDC-2083626 (3d), CCDC-2041981 (3e), CCDC2083627 (3f), CCDC-2083628 (4a'), CCDC-2083629 (4b'), CCDC-2083630 (44') and CCDC2083631 (5). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif. All other data are available in the main text or in the Supplementary Information.

## Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft within the project Sche 384/38-1. The authors thank J. Gramüller (group of R. Gschwind, University of Regensburg) for the low-temperature NMR experiment. S.R. is grateful to the Studienstiftung des Deutschen Volkes and M.P. to the Fonds der Chemischen Industrie for their PhD fellowships.

## Author contributions

S.R., E.M., F.R. and M.P. conceived the experiments. G.B. performed the computational studies. M.Se. analysed and revised the X-ray data; S.R., G. B. and M.Sch. wrote the manuscript. M.Sch. directed and coordinated the research.

## Competing interests

The authors declare no competing interests.

### 5.7 Supplementary Information

## Pentaphosphaferrocene mediated Synthesis of Asymmetric OrganoPhosphines Starting from White Phosphorus

Stephan Reichl, ${ }^{1}$ Eric Mädl, ${ }^{1}$ Felix Riedlberger, ${ }^{1}$ Martin Piesch, ${ }^{1}$ Gábor Balázs, ${ }^{1}$ Michael Seidl, ${ }^{1}$ Manfred Scheer ${ }^{1 *}$

${ }^{1}$ Institute of Inorganic Chemistry, University of Regensburg; Universitätsstraße 31, 93053 Regensburg, Germany.
*Corresponding author. Email: Manfred.Scheer@chemie.uni-regensburg.de

Table of Content

1. NMR spectroscopic characterization 120
2. Crystallographic details 145
3. Data availability 164
4. Computational details 170
5. Supplementary References 172

## 1. NMR spectroscopic characterization

${ }^{1} \mathrm{H}$ NMR Spectra:
$\left[\mathrm{Li}(\mathrm{dme})_{3}\right]\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\mathbf{\eta}^{4}-\mathrm{P}_{5} \mathrm{Me}\right)\right]$ (2c)


## Supplementary Figure 1.

Experimental ${ }^{1} \mathrm{H}$ NMR ( 400.13 MHz, THF- $\mathrm{d}_{8}$ ) spectrum of $\mathbf{2 c}$ ( ${ }^{*}=$ THF).
$\left[\mathrm{Li}(12 \mathrm{c} 4)_{2}\right]\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\right)\right]$ (2d)


Supplementary Figure 2.
Experimental ${ }^{1} \mathrm{H}$ NMR ( 400.13 MHz, THF- $\mathrm{d}_{8}$ ) spectrum of $\mathbf{2 d}$ ( ${ }^{*}=$ THF).

## $[\mathrm{Li}(12 \mathrm{c} 4)($ thf $)]\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Ph}\right)\right]$ (2e)



Supplementary Figure 3.
Experimental ${ }^{1} \mathrm{H}$ NMR (400.13 MHz, THF- $\mathrm{d}_{8}$ ) spectrum of $2 \mathrm{e}\left({ }^{*}=\mathrm{THF}\right)$.
$\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{NMe}_{2} \mathrm{Me}\right)\right]$ (3a)


Supplementary Figure 4.
Experimental ${ }^{1} \mathrm{H}$ NMR (400.13 MHz, $\left.\mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 3 a ( ${ }^{*}=\mathrm{THF}$ ).

## $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right) \mathrm{Me}\right\}\right]$ (3b)



## Supplementary Figure 5.

Experimental ${ }^{1} \mathrm{H}$ NMR (400.13 MHz, $\mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of $\mathbf{3 b}$ ( ${ }^{*}=$ traces of I$)$.
$\left[C p^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Me}_{2}\right)\right](3 \mathrm{c})$


Supplementary Figure 6.
Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of 3 c .

## $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\mathrm{n}^{4}-\mathrm{P}_{5} \mathrm{Me}^{\mathrm{iPr}}\right)\right]$ (3d)



## Supplementary Figure 7.

Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of 3 d .
$\left[C p^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{BuMe}\right)\right](3 \mathrm{e})$


## Supplementary Figure 8.

Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{THF}-\mathrm{d}_{8}$ ) spectrum of 3 e (* $=$ residual solvent).

## $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{PhMe}\right)\right]$ (3f)



Supplementary Figure 9.
Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of 3 f .

## PMeiPrBnz (4a)



## Supplementary Figure 10.

Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of 4 a ( ${ }^{*}=1,2$-diphenylethane: decomposition product of KBnz ).

PtBuMeBnz (4b)
$\stackrel{\text { 은 }}{\stackrel{\rightharpoonup}{~}}$




## Supplementary Figure 11.

Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of $\mathbf{4 b}$ ( $^{*}=$ starting material 3 e ).

PPhMeBnz (4c)


## Supplementary Figure 12.

Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of 4 c .

## SPMe'PrBnz (4a')



## Supplementary Figure 13.

Experimental ${ }^{1} \mathrm{H}$ NMR (400.13 MHz, $\mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of $4 \mathrm{a}^{\prime}$.

## SPBuMeBnz (4b')



## Supplementary Figure 14.

Experimental ${ }^{1} \mathrm{H}$ NMR (400.13 MHz, $\mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of $4 \mathrm{~b}^{\prime}$ (* = grease; " = unidentified side product).

## SPPhMeBnz (4c')



## Supplementary Figure 15.

Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of $4 \mathrm{c}^{\prime}$.
$[K(18 c 6)($ thf $)]\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{4}\right)\right](5)$


Supplementary Figure 16.
Experimental ${ }^{1} \mathrm{H}$ NMR ( 400.13 MHz, THF- $\mathrm{d}_{8}$ ) spectrum of 5 ( ${ }^{*}=$ grease $)$.

## ${ }^{31}$ P NMR Spectra:

## $\left[\mathrm{Li}(\mathrm{dme})_{3}\right]\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Me}\right)\right](2 \mathrm{c})$






110

-70
[ppm]

## Supplementary Figure 17.

Experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 161.98 MHz , THF- $\mathrm{d}_{8}$ ) spectrum of 2c.

## Supplementary Table 1.

Chemical shifts and coupling constants obtained from the simulation ( R -factor $=1.59 \%$ ) in Supplementary Figure 17.


## $\left[\mathrm{Li}(12 \mathrm{c} 4)_{2}\right]\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\right)\right](2 \mathrm{~d})$




## Supplementary Figure 18.

Experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}(161.98 \mathrm{MHz}$, THF-d ) spectrum of 2d.

## Supplementary Table 2.

Chemical shifts and coupling constants obtained from the simulation ( R -factor $=0.66 \%$ ) in Supplementary Figure 18.

| $J$ [ Hz ] |  |  |  | $\delta$ [ppm] |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{1} \mathrm{JPA}, \mathrm{PX}$ | 339.07 | ${ }^{1} \mathrm{JPM}, \mathrm{PX}$ | 384.46 | X, $\mathrm{X}^{\prime}$ | -70.2 |
| ${ }^{1} J_{\text {PA, PX }}{ }^{\prime}$ | 337.80 | ${ }^{1} \mathrm{PMM}^{\prime}$ 'PX ${ }^{\prime}$ | 365.20 |  |  |
| ${ }^{2} J_{\text {PA, PM }}{ }^{\prime}$ | -33.88 | ${ }^{2} J_{\text {PM }}$ 'PX | -13.62 | $\mathrm{M}, \mathrm{M}^{\prime}$ | 19.6 |
| ${ }^{2} J_{\text {PA, PM }}$ | -34.26 | ${ }^{2} J_{\text {PM, PX }}$ | 5.03 |  |  |
| ${ }^{1} J_{\mathrm{PM}, \mathrm{PM}}{ }^{\prime}$ | 420.91 | ${ }^{2} J_{\text {PX, PX' }}$ | -59.74 | A | 105.6 |



## Supplementary Figure 19.

Experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}$ NMR ( $161.98 \mathrm{MHz}, \mathrm{THF}-\mathrm{d}_{8}$ ) spectrum of 2d.

## Supplementary Table 3.

Chemical shifts and coupling constants obtained from the simulation ( R -factor $=1.52 \%$ ) in Supplementary Figure 19.

| $J$ [ Hz ] |  |  |  | $\delta$ [ppm] |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{1} \mathrm{JPA}, \mathrm{PX}$ | 338.11 | ${ }^{1} J_{\text {PM , PX }}$ | 384.20 | X, $\mathrm{X}^{\prime}$ | -70.2 |
| ${ }^{1} \int_{\text {PA, PX' }}$ | 338.76 | ${ }^{1} \mathrm{JPM}^{\prime} \mathrm{PK}^{\prime}$ | 365.48 |  |  |
| ${ }^{2} J_{\text {PA, PM }}{ }^{\prime}$ | -33.45 | ${ }^{2} J_{\text {PM }}$ 'PX | -15.01 | $\mathrm{M}, \mathrm{M}^{\prime}$ | 19.6 |
| ${ }^{2} J_{\text {PA,PM }}$ | -34.79 | ${ }^{2} J_{\text {PM PXX }}$, | 6.50 |  |  |
| ${ }^{1} \mathrm{JPM}, \mathrm{PM}$ | 420.73 | ${ }^{2} J_{\text {PX, PX }}$ | -59.41 | A | 105.6 |
| ${ }^{3} J_{\text {PA, }}$ | 10.76 |  |  |  |  |

## $[\mathrm{Li}(12 \mathrm{c} 4)(\mathrm{thf})]\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\mathrm{n}^{4}-\mathrm{P}_{5} \mathrm{Ph}\right)\right](2 \mathrm{e})$




## Supplementary Figure 20.

Experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}$ NMR ( 161.98 MHz, THF- $\mathrm{d}_{8}$ ) spectrum of $\mathbf{2 e}$.

## Supplementary Table 4.

Chemical shifts and coupling constants obtained from the simulation ( R -factor $=4.89 \%$ ) in Supplementary Figure 20.

| J [Hz] |  |  |  | $\delta$ [ppm] |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{1} \mathrm{JPA}, \mathrm{PX}$ | 315.77 | ${ }^{1} J_{\text {PM, PX }}$ | 382.18 | X, $\mathrm{X}^{\prime}$ | -61.8 |
| ${ }^{1} J_{\text {PA, PX }}$ | 318.37 | ${ }^{1} J_{\text {PM }}{ }^{\prime}$ PX ${ }^{\prime}$ | 368.96 |  |  |
| ${ }^{2} J_{\text {PA, PM }}{ }^{\text {a }}$ | 40.09 | ${ }^{2} J_{\text {PM }}$ 'PX | -4.06 | $\mathrm{M}, \mathrm{M}^{\prime}$ | 21.1 |
| ${ }^{2} J_{\text {PA,PM }}$ | 21.56 | ${ }^{2} J_{\mathrm{PM}, \mathrm{PX}}$ | -12.65 |  |  |
| ${ }^{1}{ }_{\text {PM PMM }}{ }^{\text {a }}$ | 417.53 | ${ }^{2} J_{\text {PX, PX' }}$ | 55.50 | A | 79.3 |

## $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{NMe}_{2} \mathrm{Me}\right)\right]$ (3a)




## Supplementary Figure 21.

Experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 3a.

## Supplementary Table 5.

Chemical shifts and coupling constants obtained from the simulation ( R -factor $=1.36$ \%) in Supplementary Figure 21.

| $J$ [ Hz ] |  |  |  | $\delta[\mathrm{ppm}]$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{1} J_{\text {PA, PX }}$ | 426.72 | ${ }^{1} J_{\text {PM, PX }}$ | 412.85 | X, $\mathrm{X}^{\prime}$ | -64.5 |
| ${ }^{1} \int_{\text {PA, PX' }}$ | 427.57 | ${ }^{1} J_{\text {PM }}{ }^{\prime} \mathrm{PX}^{\prime}$ | 415.74 |  |  |
| ${ }^{2} J_{\text {PA, PM }}{ }^{\prime}$ | 18.52 | ${ }^{2} J_{\text {PM }}$; PX | -38.01 | M, M ${ }^{\prime}$ | 37.2 |
| ${ }^{2} \int_{\text {PA, PM }}$ | 13.55 | ${ }^{2} J_{\text {PM, }}$ PX ${ }^{\text {P }}$ | -31.93 |  |  |
| ${ }^{1} \mathrm{JPM}, \mathrm{PM}{ }^{\prime}$ | 377.81 | ${ }^{2} J_{\text {PX, PX' }}$ | 15.37 | A | 131.0 |

$\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right) \mathrm{Me}\right\}\right]$ (3b)




## Supplementary Figure 22.

Experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of $\mathbf{3 b}$.

## Supplementary Table 6.

Chemical shifts and coupling constants obtained from the simulation ( R -factor $=2.83$ \%) in Supplementary Figure 22.

| $J$ [ Hz ] |  |  |  | $\delta$ [ppm] |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{1} J_{\text {PA,PX }}$ | 372.47 | ${ }^{1} \mathrm{JPM}, \mathrm{PX}$ | 403.22 | X, $\mathrm{X}^{\prime}$ | -96.7 |
| ${ }^{1} \int_{\text {PA, PX }}$, | 372.16 | ${ }^{1} \mathrm{PMM}^{\prime} \mathrm{PX}^{\prime}$ | 404.16 |  |  |
| ${ }^{2} J_{\text {PA, PM }}{ }^{\prime}$ | 13.00 | ${ }^{2} J_{\text {PM }}{ }^{\prime}$ PX | -35.26 | $\mathrm{M}, \mathrm{M}^{\prime}$ | 37.0 |
| ${ }^{2} J_{\text {PA,PM }}$ | 13.00 | ${ }^{2} J_{\text {PM, PX }}$ | -37.74 |  |  |
| ${ }^{1} J_{\text {PM }, ~} \mathrm{PM}^{\prime}$ | 377.21 | ${ }^{2} J_{P X, P X}$ | 1.63 | A | 129.4 |

$\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Me}_{2}\right)\right](3 \mathrm{c})$




## Supplementary Figure 23.

Experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 3 c .

## Supplementary Table 7.

Chemical shifts and coupling constants obtained from the simulation (R-factor = 3.46 \%) in Supplementary Figure 23.

| $J[\mathrm{~Hz}]$ |  |  |  | $\delta$ [ppm] |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{1} \mathrm{JPA}, \mathrm{PX}$ | 379.70 | ${ }^{1} J_{\text {PM, PX }}$ | 404.49 | X, $\mathrm{X}^{\prime}$ | -122.7 |
| ${ }^{1} J_{\text {PA, PX }}$ ' | 380.34 | ${ }^{1} J_{\text {PM }} /$ PX ${ }^{\prime}$ | 396.47 |  |  |
| ${ }^{2} J_{\text {PA,PM }}$ ' | 11.47 | ${ }^{2} J_{\text {PM }}$ 'PX | -32.84 | $\mathrm{M}, \mathrm{M}^{\prime}$ | 35.4 |
| ${ }^{2} J_{\text {PA,PM }}$ | 11.55 | ${ }^{2} J_{\mathrm{PM}, \mathrm{PX}}$ | -43.00 |  |  |
| ${ }^{1} \mathrm{JPM}, \mathrm{PM}{ }^{\text {d }}$ | 379.62 | ${ }^{2} J_{\text {PX, PX }}$, | 4.89 | A | 117.2 |

$\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\mathrm{n}^{4}-\mathrm{P}_{5} \mathrm{Me}^{\mathrm{iPr}}\right)\right](3 \mathrm{~d})$



## Supplementary Figure 24.

Experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of 3d.

## Supplementary Table 8.

Chemical shifts and coupling constants obtained from the simulation ( R -factor $=2.38 \%$ ) in Supplementary Figure 24.

| $J[\mathrm{~Hz}]$ |  |  |  | $\delta$ [ppm] |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{1} J_{\text {PA, PX }}$ | 389.45 | ${ }^{1} \mathrm{JPM}, \mathrm{PX}$ | 404.39 | X, $\mathrm{X}^{\prime}$ | -135.8 |
| ${ }^{1} J_{\text {PA, PX }}$ | 388.89 | ${ }^{1} \mathrm{JPM}^{\prime} \mathrm{PX}^{\prime}$ | 395.77 |  |  |
| ${ }^{2} J_{\text {PA, PM }}{ }^{\prime}$ | -12.56 | ${ }^{2} J_{\text {PM }}{ }^{\prime}$ PX | -33.85 | M, M ${ }^{\prime}$ | 33.3 |
| ${ }^{2} J_{\text {PA, PM }}$ | -9.93 | ${ }^{2} J_{\text {PM, PX }}$ ' | -41.00 |  |  |
| ${ }^{1} J_{\mathrm{PM}, \mathrm{PM}}{ }^{\text {a }}$ | 377.57 | ${ }^{2} J_{\text {PX, PX' }}$ | -0.60 | A | 151.8 |

## $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{BuMe}\right)\right](3 \mathrm{e})$



Fe


155



## Supplementary Figure 25.

Experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 3 e .

## Supplementary Table 9.

Chemical shifts and coupling constants obtained from the simulation ( R -factor $=0.95$ \%) in Supplementary Figure 25.

| $J[\mathrm{~Hz}]$ |  |  |  | $\delta[\mathrm{ppm}]$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{1} \mathrm{JPA}, \mathrm{PX}$ | 405.50 | ${ }^{1} \mathrm{JPM}, \mathrm{PX}$ | 405.50 | X, X' | -117.2 |
| ${ }^{1} J_{\text {PA, PX }}$ | 404.47 | ${ }^{1} J_{\text {PM }}{ }^{\prime}$ PX ${ }^{\prime}$ | 404.47 |  |  |
| ${ }^{2} J_{\text {PA, PM }}{ }^{\prime}$ | 14.32 | ${ }^{2} J_{\text {PM }}{ }^{\prime}$ PX | -39.50 | $\mathrm{M}, \mathrm{M}^{\prime}$ | 47.0 |
| ${ }^{2} J_{\text {PA, PM }}$ | 14.32 | ${ }^{2} J_{\text {PM, }}$ PX | -39.50 |  |  |
| ${ }^{1} \mathrm{JPM}, \mathrm{PM}{ }^{\text {a }}$ | 384.75 | ${ }^{2} \int_{\text {PX, PX' }}$ | 4.18 | A | 151.89 |

$\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\mathbf{\eta}^{4}-\mathrm{P}_{5} \mathrm{PhMe}\right)\right]$ (3f)




## Supplementary Figure 26.

Experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 3 f .

## Supplementary Table 10.

Chemical shifts and coupling constants obtained from the simulation ( R -factor $=2.69$ \%) in Supplementary Figure 26.

| $J[\mathrm{~Hz}]$ |  |  |  | $\delta$ [ppm] |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{1} \mathrm{JPA}, \mathrm{PX}$ | 400.22 | ${ }^{1} J_{\text {PM, PX }}$ | 414.76 | X, $\mathrm{X}^{\prime}$ | -109.5 |
| ${ }^{1} J_{\text {PA, PX }}$, | 400.10 | ${ }^{1} J_{\text {PM }}{ }^{\prime}$ PX' ${ }^{\prime}$ | 388.69 |  |  |
| ${ }^{2} J_{\text {PA,PM }}{ }^{\prime}$ | 13.53 | ${ }^{2} J_{\text {PM }}$ 'PX | -26.77 | $\mathrm{M}, \mathrm{M}^{\prime}$ | 40.5 |
| ${ }^{2} J_{\text {PA,PM }}$ | 10.84 | ${ }^{2} J_{\mathrm{PM}, \mathrm{PX}}$ | -52.55 |  |  |
| ${ }^{1} \mathrm{JPM}, \mathrm{PM}{ }^{\text {d }}$ | 383.76 | ${ }^{2} J_{\text {PX, PX' }}$ | 2.39 | A | 117.7 |

## PMeiPrBnz (4a)



## Supplementary Figure 27.

Experimental ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of $\mathbf{4 a}$.

## $P^{t}$ BuMeBnz (4b)



| O |
| :--- |
|  |
|  |



## Supplementary Figure 28.

Experimental ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of $\mathbf{4 b}$ ( ${ }^{*}=$ starting material 3e).

PPhMeBnz (4c)




## Supplementary Figure 29.

Experimental ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of 4 c .

SPMe ${ }^{i} \operatorname{PrBnz}\left(4 a^{\prime}\right)$



## Supplementary Figure 30.

Experimental ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of $4 \mathrm{a}^{\prime}$.

## SP'BuMeBnz (4b')




## Supplementary Figure 31.

Experimental ${ }^{31}{ }^{\mathrm{P}}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of $4 \mathrm{~b}^{\prime}$.

## SPPhMeBnz (4c')



## Supplementary Figure 32.

Experimental ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of $4 \mathrm{c}^{\prime}$.

## $[K(18 c 6)($ thf $)]\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\mathrm{n}^{4}-\mathrm{P}_{4}\right)\right](5)$




Supplementary Figure 33.
Experimental ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 161.98 MHz , THF-d $\mathrm{d}_{8}$ ) spectrum of 5 .

## ${ }^{13} \mathrm{C}$ NMR Spectra:

PMeiPrBnz (4a)


## Supplementary Figure 34.

Experimental ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $100.61 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of 4 a ( ${ }^{*}=1,2$-diphenylethane: decomposition product of KBnz).

## $P^{t}$ BuMeBnz (4b)



## Supplementary Figure 35.

Experimental ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $100.61 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of 4 b ( ${ }^{*}=$ starting material 3e).

PPhMeBnz (4c)


Supplementary Figure 36.
Experimental ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $\left.100.61 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 4 c .

## SPMe'PrBnz (4a')



## Supplementary Figure 37.

Experimental ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(100.61 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of $4 \mathrm{a}^{\prime}$.

## SP'BuMeBnz (4b')



## Supplementary Figure 38.

Experimental ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $100.61 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of $4 \mathbf{b}^{\prime}$.

SPPhMeBnz (4c')


## Supplementary Figure 39.

Experimental ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(100.61 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 4 c .

## 2. Crystallographic details

Suitable single crystals were selected and measured on a Xcalibur Gemini Ultra diffractometer equipped with an AtlasS2 CCD detector (2c, 2d, 3b), on a XtaLAB Synergy R DW system equipped with a HyPix-Arc 150 detector (2e, 3c, 3f, 4c), on a SuperNova diffractometer equipped with an Atlas CCD detector (3a), on a GV50 diffractometer equipped with a TitanS2 CCD detector (3d, 3e, 5), on a Xcalibur Gemini Ultra diffractometer equipped with a TitanS2 CCD detector (4a) or on a SuperNova Dualflex diffractometer equipped with a TitanS2 CCD detector (4b). The crystals were kept at $T=123(1) \mathrm{K}$ or 203(2) K (2c) during data collection. Data collection and reduction were performed with CrysAlisPro. Using Olex2, the structures were solved with SheIXT and a least-square refinement on $F^{2}$ was carried out with SheIXL. All non-hydrogen atoms were refined anisotropically unless stated otherwise. Hydrogen atoms at the carbon atoms were located in idealized positions and refined isotropically according to the riding model. Figures were created with Olex2.
$\left[\mathrm{Li}(\mathrm{dme})_{3}\right]\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Me}\right)\right](2 \mathrm{c})$ : The asymmetric unit contains one molecule of $\mathbf{2 c}$. The $\mathrm{P}_{5}$ middle deck is disordered over two positions with a distribution of 95:5. To describe the disorder the SADI and SIMU restrains were applied. Further, is one of the DME molecules, which are coordinated to the lithium ion, disordered over two positions with an occupancy refined to 67:33. To describe this disorder the SIMU restrain was applied. The structure in the solid state is given in Supplementary Figure 40 and S41. Crystallographic and refinement data are summarized in Supplementary Table 11.
$\left[\mathrm{Li}(12 \mathrm{c} 4)_{2}\right]\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\right)\right](2 \mathrm{~d})$ : The asymmetric unit contains one molecule of 2 d without any disorder. The structure in the solid state is given in Supplementary Figure 42. Crystallographic and refinement data are summarized in Supplementary Table 11.
$[\mathrm{Li}(12 \mathrm{c} 4)($ thf $)]\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Ph}\right)\right]$ (2e): The asymmetric unit contains one molecule of 2 e without any disorder. Compound $\mathbf{2 e}$ crystalizes in the acentric spacegroup Pn with a flack parameter of -0.004(3). The structure in the solid state is given in Supplementary Figure 43. Crystallographic and refinement data are summarized in Supplementary Table 11.
[Cp*Fe\{n4- $\left.\left.\mathrm{P}_{5}\left(\mathrm{NMe}_{2}\right) \mathrm{Me}\right\}\right]$ (3a): The asymmetric unit contains two molecules of 3a without any disorder. The structure in the solid state is given in Supplementary Figure 44. Crystallographic and refinement data are summarized in Supplementary Table 11.
[Cp*Fe\{n $\left.\left.{ }^{4}-\mathrm{P}_{5}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right) \mathrm{Me}\right\}\right]$ (3b): The asymmetric unit contains one molecule of 3 b . The $\mathrm{Cp}^{*}$ ligand and the $\mathrm{P}_{5}$ middle deck with the methyl substituent and the $\mathrm{CH}_{2} \mathrm{SiMe}_{3}$ substituent are disordered over two positions with a distribution of approximately $66: 34$. To describe these disorders the restraints SADI and SIMU were applied. The structure in the solid state is given in Supplementary Figure 45 and S46. Crystallographic and refinement data are summarized in Supplementary Table 11.
[Cp*Fe( $\left.\left.\eta^{4}-\mathrm{P}_{5} \mathrm{Me}_{2}\right)\right](3 \mathrm{c})$ : The asymmetric unit contains three molecules of 3 c . One of them without any disorder, its structure in the solid state is given in Supplementary Figure 47. The other two show disorder: The $\mathrm{P}_{5}$ middle deck is disordered over two positions with a distribution of 83:17 / 91:9, respectively. To describe the disorder the SADI and SIMU restrains were applied. Crystallographic and refinement data are summarized in Supplementary Table 12.
[Cp*Fe( $\left.\eta^{4}-\mathrm{P}_{5} \mathrm{Me}^{i} \mathrm{Pr}\right)$ ] (3d): The asymmetric unit contains one molecule of 3d without any disorder. Since the measured crystal was twinned, a HKLF 5 refinement was applied (twin law: -0.9993 0.0012 0.0018 0.0018-0.9987 0.00410 .09310 .03771 .0006 ; BASF $0.263(2))$. The structure in the solid state is given in Supplementary Figure 48. Crystallographic and refinement data are summarized in Supplementary Table 12.
$\left[C p^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{BuMe}\right)\right]$ (3e): The asymmetric unit contains half a molecule of 3d without any disorder. Compound 3d crystalizes in the acentric space group Im with a flack parameter of 0.000(3). The structure in the solid state is given in Supplementary Figure 49. Crystallographic and refinement data are summarized in Supplementary Table 12.
[Cp*Fe( $\left.\left.\eta^{4}-P_{5} \mathrm{PhMe}\right)\right](3 f)$ : The asymmetric unit contains two molecules of 3 f without any disorder. The structure in the solid state of one molecule is depicted in Supplementary Figure 50. Crystallographic and refinement data are summarized in Supplementary Table 12.

SPMe'PrBnz (4a'): The asymmetric unit contains one molecule of 4a'. The $\mathrm{P}(\mathrm{S}) \mathrm{Me}{ }^{i} \operatorname{Pr}$ unit is disordered over two positions with a distribution of 93:7. Due to the low occupancy of the second part, were only the sulphur and the phosphorus atoms anisotropically refined. The structure in the solid state is given in Supplementary Figure 51 and S52. Crystallographic and refinement data are summarized in Supplementary Table 12.

SP'BuMeBnz ( $4 \mathbf{b}^{\prime}$ ): The asymmetric unit contains one molecule of $\mathbf{4 b}$ ' without any disorder. Since the measured crystal was twinned, a HKLF 5 refinement was applied (twin law: -0.5569 0.0005 0.4439-0.0003-1.0008-0.0001 $1.5524-0.00020 .5587$; BASF $0.1610(7))$ The structure in the solid state is given in Supplementary Figure 53. Crystallographic and refinement data are summarized in Supplementary Table 13.

SPPhMeBnz ( $4 c^{\prime}$ ): The asymmetric unit contains one molecule of $4 \mathbf{c}^{\prime}$ without any disorder. The structure in the solid state of one molecule is depicted in Supplementary Figure 54. Crystallographic and refinement data are summarized in Supplementary Table 13.
$[K(18 c 6)($ thf $)]\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{4}\right)\right]$ (5): The asymmetric unit contains half a molecule of 5 . The symmetry of the molecule is lower than the site symmetry (mirror plane), which causes the disorder of the $\mathrm{Cp}^{*}$ ligand and one THF molecule over two positions. The complete structure in the solid state is given in Supplementary Figure 55. Crystallographic and refinement data are summarized in Supplementary Table 13.

The X-ray crystallographic coordinates for structures reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers CCDC-2041977 (2c), CCDC-2041978 (2d), CCDC2083624 (2e), CCDC-2041979 (3a), CCDC-2041980 (3b), CCDC-2083625 (3c), CCDC-2083626 (3d), CCDC2041981 ( 3 e ), CCDC-2083627 (3f), CCDC-2083628 (4a'), CCDC-2083629 (4b'), CCDC-2083630(4c') and CCDC2083631 (5). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

## Supplementary Table 11.

Crystallographic details of 2c, 2d, 2e, 3a and 3b.

| Compound | 2c | 2d | 2e | 3a | 3b |
| :---: | :---: | :---: | :---: | :---: | :---: |
| CCDC | 2041977 | 2041978 | 2083624 | 2041979 | 2041980 |
| Formula | $\mathrm{C}_{23} \mathrm{H}_{48} \mathrm{FeLiO}_{6} \mathrm{P}_{5}$ | $\mathrm{C}_{30} \mathrm{H}_{56} \mathrm{FeLiO}_{8} \mathrm{P}_{5}$ | $\mathrm{C}_{28} \mathrm{H}_{44} \mathrm{FeLiO}_{5} \mathrm{P}_{5}$ | $\mathrm{C}_{13} \mathrm{H}_{24} \mathrm{FeNP}_{5}$ | $\mathrm{C}_{15} \mathrm{H}_{29} \mathrm{FeP}_{5} \mathrm{Si}$ |
| $D_{\text {calc. }} / \mathrm{g} \mathrm{cm}^{-3}$ | 1.235 | 1.326 | 1.393 | 1.433 | 1.353 |
| $\mu / \mathrm{mm}^{-1}$ | 5.980 | 5.507 | 6.366 | 10.388 | 9.407 |
| Formula Weight | 638.25 | 762.38 | 678.27 | 405.03 | 448.17 |
| Colour | black | dark green | dark green | black | black |
| Shape | truncated prism | block | block-shaped | prism | plate |
| Size/mm ${ }^{3}$ | $0.40 \times 0.15 \times 0.10$ | $0.46 \times 0.30 \times 0.12$ | $0.27 \times 0.17 \times 0.13$ | $0.18 \times 0.12 \times 0.08$ | $0.34 \times 0.25 \times 0.04$ |
| T/K | 203(2) | 123.35(10) | 123.01(10) | 123(2) | 122.9(5) |
| Crystal System | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic |
| Flack Parameter | 1 | 1 | -0.004(3) | 1 | 1 |
| Hooft Parameter | 1 | 1 | -0.0039(8) | 1 | 1 |
| Space Group | P2 $1_{1} / \mathrm{c}$ | P2 $1_{1 / n}$ | Pn | P2 $1_{1} / \mathrm{c}$ | $P 2_{1} / n$ |
| $a / A ̊$ | 15.7568(2) | 9.9189(3) | 9.30050(10) | 14.3059(2) | 8.32648(12) |
| $b / \AA$ | 13.1533(2) | 19.7484(5) | 9.66730(10) | 29.8376(4) | $9.12374(11)$ |
| $c / A ̊$ | 16.9675(2) | 19.5371(7) | 18.5722(2) | 8.86570(10) | $29.0199(4)$ |
| $\alpha 1^{\circ}$ | 90 | 90 | 90 | 90 | 90 |
| $\beta 1^{\circ}$ | 102.5080(10) | 93.863(3) | 104.4500(10) | 97.1750(10) | 93.6816(12) |
| $\gamma /{ }^{\circ}$ | 90 | 90 | 90 | 90 | 90 |
| V/A ${ }^{3}$ | 3433.12(8) | 3818.3(2) | 1617.02(3) | 3754.72(8) | 2200.05(5) |
| z | 4 | 4 | 2 | 8 | 4 |
| $Z^{\prime}$ | 1 | 1 | 1 | 2 | 1 |
| Wavelength/Å | 1.54178 | 1.54184 | 1.54184 | 1.54178 | 1.54184 |
| Radiation type | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ |
| $\theta_{\text {min }}{ }^{\circ}$ | 4.292 | 4.478 | 4.574 | 4.299 | 5.083 |
| $\theta_{\text {max }} 1{ }^{\circ}$ | 66.704 | 73.095 | 74.468 | 74.224 | 66.767 |
| Measured Refl's. | 25941 | 14979 | 26196 | 19702 | 25018 |
| Ind't Refl's | 6042 | 7468 | 5149 | 7371 | 3882 |
| Refl's with l > $2 \sigma$ (l) | 4741 | 5663 | 5093 | 6535 | 3568 |
| $R_{\text {int }}$ | 0.0273 | 0.0404 | 0.0183 | 0.0168 | 0.0485 |
| Parameters | 439 | 414 | 366 | 377 | 389 |
| Restraints | 82 | 0 | 2 | 0 | 139 |
| Largest Peak | 0.367 | 0.570 | 0.411 | 0.252 | 0.693 |
| Deepest Hole | -0.221 | -0.379 | -0.179 | -0.322 | -0.547 |
| GooF | 0.966 | 1.018 | 1.084 | 1.013 | 1.083 |
| $w R_{2}$ (all data) | 0.0754 | 0.1329 | 0.0694 | 0.0549 | 0.1134 |
| $w \mathrm{R}_{2}$ | 0.0738 | 0.1199 | 0.0692 | 0.0543 | 0.1093 |
| $R_{1}$ (all data) | 0.0372 | 0.0737 | 0.0256 | 0.0238 | 0.0438 |
| $R_{1}$ | 0.0290 | 0.0510 | 0.0253 | 0.0208 | 0.0400 |

Supplementary Table 12.
Crystallographic details of $3 \mathrm{c}, 3 \mathrm{e}, 3 \mathrm{e}, 3 \mathrm{f}$ and $4 \mathrm{a}^{\prime}$.

| Compound | 3c | 3d | 3 e | 3 f | $4 a^{\prime}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| CCDC | 2083625 | 2083626 | 2041981 | 2083627 | 2083628 |
| Formula | $\mathrm{C}_{12} \mathrm{H}_{21} \mathrm{FeP}_{5}$ | $\mathrm{C}_{14} \mathrm{H}_{25} \mathrm{FeP}_{5}$ | $\mathrm{C}_{15} \mathrm{H}_{27} \mathrm{FeP}_{5}$ | $\mathrm{C}_{17} \mathrm{H}_{23} \mathrm{FeP}_{5}$ | $\mathrm{C}_{11} \mathrm{H}_{17} \mathrm{PS}$ |
| $D_{\text {calc. }} / \mathrm{g} \mathrm{cm}^{-3}$ | 1.471 | 1.401 | 1.382 | 1.456 | 1.210 |
| $\mu / \mathrm{mm}^{-1}$ | 11.427 | 10.168 | 9.711 | 9.800 | 3.382 |
| Formula Weight | 375.99 | 404.04 | 418.06 | 438.05 | 212.27 |
| Colour | dark green | dark red | metallic dark green | dark green | clear colourless |
| Shape | block | block | block | plate-shaped | needle-shaped |
| Size/mm ${ }^{3}$ | $0.20 \times 0.10 \times 0.07$ | $0.20 \times 0.08 \times 0.07$ | $0.23 \times 0.11 \times 0.06$ | $0.20 \times 0.12 \times 0.10$ | $0.21 \times 0.07 \times 0.04$ |
| T/K | 123.00(10) | 123.01(11) | 123.01(10) | 123.01(10) | 123.00(10) |
| Crystal System | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic |
| Flack Parameter | 1 | $/$ | 0.000(2) |  |  |
| Hooft Parameter | 1 | 1 | 0.0067(13) |  |  |
| Space Group | $\mathrm{P} 2{ }_{1} / \mathrm{c}$ | $P 2{ }_{1} / n$ | Cm | $P 2{ }_{1} / \mathrm{c}$ | $P 2_{1} / \mathrm{c}$ |
| $a / \AA$ | 19.5498(3) | 7.8177(3) | 7.86145(10) | 14.33040(10) | 11.6109(14) |
| b/A | 9.20470 (10) | 9.1917(4) | 12.31599(13) | 31.3940(3) | 6.2158(7) |
| c/A | 28.3406(4) | 26.6502(9) | 10.48456(11) | 8.90470(10) | 16.623(2) |
| $\alpha 1^{\circ}$ | 90 | 90 | 90 | 90 | 90 |
| $\beta /{ }^{\circ}$ | 93.0600(10) | 90.614(3) | 98.3685(10) | 94.1640(10) | 103.810(13) |
| $\gamma /{ }^{\circ}$ | 90 | 90 | 90 | 90 | 90 |
| $\mathrm{V} / \AA^{3}$ | 5092.62(12) | 1914.92(13) | 1003.86(4) | 3995.55(7) | 1165.0(3) |
| Z | 12 | 4 | 2 | 8 | 4 |
| Z' | 3 | 1 | 0.5 | 2 | 1 |
| Wavelength/A | 1.54184 | 1.54184 | 1.54184 | 1.54184 | 1.54184 |
| Radiation type | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ |
| $\theta_{\text {min }} /{ }^{\circ}$ | 2.263 | 3.317 | 5.576 | 2.815 | 3.921 |
| $\theta_{\max } /^{\circ}$ | 75.411 | 74.131 | 74.027 | 74.510 | 66.762 |
| Measured Refl's. | 39361 | 17620 | 10956 | 32976 | 5824 |
| Ind't Refl's | 10304 | 5931 | 1997 | 8063 | 2042 |
| Refl's with l > $2 \sigma$ (l) | 8981 | 5184 | 1978 | 7219 | 1679 |
| $R_{\text {int }}$ | 0.0609 | 0.1457 | 0.0359 | 0.0257 | 0.0466 |
| Parameters | 601 | 190 | 110 | 426 | 154 |
| Restraints | 127 | 0 | 26 | 0 | 0 |
| Largest Peak | 0.999 | 0.850 | 0.268 | 1.105 | 0.250 |
| Deepest Hole | -0.767 | -0.584 | -0.229 | -0.739 | -0.389 |
| GooF | 1.054 | 1.070 | 1.057 | 1.035 | 1.045 |
| $w R_{2}$ (all data) | 0.1527 | 0.2104 | 0.0539 | 0.1023 | 0.1109 |
| $w \mathrm{R}_{2}$ | 0.1463 | 0.2002 | 0.0538 | 0.0986 | 0.1042 |
| $R_{1}$ (all data) | 0.0601 | 0.0714 | 0.0204 | 0.0458 | 0.0543 |
| $R_{1}$ | 0.0537 | 0.0667 | 0.0203 | 0.0402 | 0.0432 |

## Supplementary Table 13.

## Crystallographic details of $4 b^{\prime}, 4 c^{\prime}$ and 5.

| Compound | $4 b^{\text {c }}$ | $4 c^{\prime}$ | 5 |
| :---: | :---: | :---: | :---: |
| CCDC | 2083629 | 2083630 | 2083631 |
| Formula | $\mathrm{C}_{12} \mathrm{H}_{19} \mathrm{PS}$ | $\mathrm{C}_{14} \mathrm{H}_{15} \mathrm{PS}$ | $\mathrm{C}_{26} \mathrm{H}_{47} \mathrm{FeKO}_{7} \mathrm{P}_{4}$ |
| $D_{\text {calc. }} / \mathrm{g} \mathrm{cm}^{-3}$ | 1.170 | 1.291 | 1.352 |
| $\mu / \mathrm{mm}^{-1}$ | 3.098 | 3.193 | 6.773 |
| Formula Weight | 226.30 | 246.29 | 690.46 |
| Colour | colourless | colourless | light green |
| Shape | block | needle-shaped | plate |
| Size/mm ${ }^{3}$ | $0.20 \times 0.18 \times 0.14$ | $0.24 \times 0.03 \times 0.02$ | $0.14 \times 0.13 \times 0.02$ |
| T/K | 123.00(10) | 123.01(10) | 122.97(12) |
| Crystal System | monoclinic | triclinic | orthorhombic |
| Flack Parameter | $/$ |  | / |
| Hooft Parameter | 1 |  | 1 |
| Space Group | $\mathrm{P} 2{ }_{1} / \mathrm{n}$ | P-1 | Pnnm |
| $a / A ̊$ | 11.3685(4) | 6.2144(2) | 10.9945(2) |
| b/Å | 6.3729(2) | 9.3867(3) | 25.8230(4) |
| c/Å | 18.2100(6) | 11.7876(5) | 11.9441(2) |
| $\alpha{ }^{\circ}$ | 90 | 108.326(3) | 90 |
| $\beta 1^{\circ}$ | 103.385(4) | 98.328(3) | 90 |
| $\gamma /{ }^{\circ}$ | 90 | 97.786(3) | 90 |
| V/Å ${ }^{3}$ | 1283.48(8) | 633.74(4) | 3391.06(10) |
| Z | 4 | 2 | 4 |
| Z' | 1 | 1 | 0.5 |
| Wavelength/Å | 1.54184 | 1.54184 | 1.54184 |
| Radiation type | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ |
| $\theta_{\text {min }}{ }^{\circ}$ | 4.194 | 4.032 | 3.423 |
| $\theta_{\text {max }}{ }^{\circ}$ | 66.947 | 74.326 | 73.841 |
| Measured Refl's. | 19609 | 8650 | 19093 |
| Ind't Refl's | 4201 | 2532 | 3563 |
| Refl's with l> $2 \sigma$ (I) | 3679 | 2206 | 3277 |
| $R_{\text {int }}$ | 0.0525 | 0.0260 | 0.0459 |
| Parameters | 132 | 146 | 258 |
| Restraints | 0 | 0 | 34 |
| Largest Peak | 0.359 | 0.471 | 0.543 |
| Deepest Hole | -0.366 | -0.413 | -0.429 |
| GooF | 1.041 | 1.049 | 1.150 |
| $w R_{2}$ (all data) | 0.1067 | 0.0990 | 0.1190 |
| $w R_{2}$ | 0.1044 | 0.0936 | 0.1170 |
| $R_{1}$ (all data) | 0.0405 | 0.0431 | 0.0573 |
| $R_{1}$ | 0.0362 | 0.0364 | 0.0531 |

## $\left[\mathrm{Li}(\mathrm{dme})_{3}\right]\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\mathrm{n}^{4}-\mathrm{P}_{5} \mathrm{Me}\right)\right](2 \mathrm{c})$



## Supplementary Figure 40.

Molecular structure of $\mathbf{2 c}$ in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms and disordered solvents molecules are omitted for clarity. The $\mathrm{Cp}^{*}$ ligand and the cation $\left[\mathrm{Li}(\mathrm{dme})_{3}\right]^{+}$are drawn in a wire frame model.


## Supplementary Figure 41.

Top view of the molecular structure of 2 c in the solid state with thermal ellipsoids at $50 \%$ probability level. The disordered $\mathrm{P}_{5}$ middle deck is highlighted blue (Part 1) and green (Part 2). The $\mathrm{Cp}^{*}$ ligands are drawn in a wire frame model.

## Supplementary Table 14.

Selected bond length of 2c.

| Atom-Atom | Length [Å] |
| :---: | :---: |
| Part 1 |  |
| P1-P2 | $2.050(14)$ |
| P2-P3 | $2.048(14)$ |
| P3-P4 | $2.041(13)$ |
| P4-P5 | $1.993(13)$ |
| P1-P5 | $2.009(14)$ |
| P1-C1 | $2.081(15)$ |
| P1A-P2A | $2.1576(10)$ |
| P2A-P3A | $2.1458(14)$ |
| P3A-P4A | $2.1277(15)$ |
| P4A-P5A | $2.1397(12)$ |
| P1A-P5A | $2.1521(10)$ |
| P1A-C1 | $1.849(2)$ |


| Atom-Atom | Length [Å] |
| :---: | :---: |
| Part 1 |  |
| Fe1-P2 | $2.321(13)$ |
| Fe1-P3 | $2.217(12)$ |
| Fe1-P4 | $2.185(9)$ |
| Fe1-P5 | $2.146(11)$ |
| Fe1-P1 | $3.028(14)$ |
| Part 2 |  |
| Fe1-P2A | $2.3056(7)$ |
| Fe1-P3A | $2.3166(7)$ |
| Fe1-P4A | $2.3357(7)$ |
| Fe1-P5A | $2.3222(6)$ |
| Fe1-P1A | $3.1817(7)$ |
| R |  |

## Supplementary Table 15.

Selected angles of 2c.

| Atom-Atom-Atom | Angle [ ${ }^{\circ}$ ] |
| :---: | :---: |
| Part 1 |  |
| P1-P2-P3 | 102.8(8) |
| P2-P3-P4 | 106.8(7) |
| P4-P5-P1 | 110.4(7) |
| P2-P1-C1 | 98.2(7) |
| Part 2 |  |
| P1A-P2A-P3A | 105.73(4) |
| P2A-P3A-P4A | 103.51(4) |
| P4A-P5A-P1A | 106.53(4) |


| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| Part 1 |  |
| P3-P4-P5 | $99.4(7)$ |
| P5-P1-P2 |  |
| P5-P1-C1 | $113.0(7)$ |
| P3A 2 |  |
| P5A-P1A-P5A | $102.79(4)$ |
| P5A-P1A-C1 | $92.11(3)$ |
| P2A-P1A-C1 | $107.66(9)$ |
| $108.17(9)$ |  |

## $\left[\mathrm{Li}(12 \mathrm{c} 4)_{2}\right]\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\mathbf{\eta}^{4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\right)\right](2 \mathrm{~d})$



## Supplementary Figure 42.

Molecular structure of 2d in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligand and the cation $\left[\mathrm{Li}(12 \mathrm{c} 4)_{2}\right]^{+}$are drawn in a wire frame model.

## Supplementary Table 16.

Selected bond length of 2d.

| Atom-Atom | Length [Å] |
| :---: | :---: |
| P1-P2 | $2.1564(12)$ |
| P2-P3 | $2.1552(12)$ |
| P3-P4 | $2.1279(12)$ |
| P4-P5 | $2.1590(12)$ |
| P1-P5 | $2.1510(11)$ |
| P1-C1 | $1.898(3)$ |


| Atom-Atom | Length [Å] |
| :---: | :---: |
| Fe1-P2 | $2.3149(9)$ |
| Fe1-P3 | $2.3234(10)$ |
| Fe1-P4 | $2.3191(10)$ |
| Fe1-P5 | $2.3225(10)$ |
| Fe1-P1 | $3.1302(10)$ |
|  |  |

## Supplementary Table 17.

Selected angles of 2d.

| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| P1-P2-P3 | $108.99(5)$ |
| P2-P3-P4 | $103.59(5)$ |
| P4-P5-P1 | $109.45(5)$ |
| P2-P1-C1 | $113.91(11)$ |


| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| P3-P4-P5 | $103.22(5)$ |
| P5-P1-P2 | $93.14(4)$ |
| P5-P1-C1 | $113.40(12)$ |
|  |  |

## [ Li(12c4)(thf)][Cp*Fe(n $\left.\left.{ }^{4}-\mathrm{P}_{5} \mathrm{Ph}\right)\right](2 \mathrm{e})$



## Supplementary Figure 43.

Molecular structure of $\mathbf{2 e}$ in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligand is drawn in a wire frame model.

## Supplementary Table 18

Selected bond length of $\mathbf{2 e}$.

| Atom-Atom | Length [Å] |
| :---: | :---: |
| P1-P2 | $2.1554(12)$ |
| P2-P3 | $2.1474(15)$ |
| P3-P4 | $2.1300(16)$ |


| Atom-Atom | Length $[\AA ̊]$ |
| :---: | :---: |
| P4-P5 | $2.1463(14)$ |
| P1-P5 | $2.1671(11)$ |
| P1-C1 | $1.841(3)$ |

## Supplementary Table 19.

Selected angles of $\mathbf{2 e}$.

| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| P1-P2-P3 | $107.94(5)$ |
| P2-P3-P4 | $103.55(5)$ |
| P4-P5-P1 | $107.37(5)$ |
| P2-P1-C1 | $111.35(11)$ |


| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| P3-P4-P5 | $103.27(5)$ |
| P5-P1-P2 | $92.65(4)$ |
| P5-P1-C1 | $111.92(9)$ |
|  |  |

## $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{NMe}_{2} \mathrm{Me}\right)\right]$ (3a)



## Supplementary Figure 44.

Molecular structure of 3a in the solid state with thermal ellipsoids at 50\% probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligand is drawn in a wire frame model.

## Supplementary Table 20.

Selected bond length of 3a

| Atom-Atom | Length [Å] |
| :---: | :---: |
| P1-P2 | $2.1347(5)$ |
| P2-P3 | $2.1342(5)$ |
| P3-P4 | $2.1519(6)$ |
| P4-P5 | $2.1360(5)$ |
| P1-P5 | $2.1426(5)$ |
| P1-N1 | $1.6779(12)$ |


| Atom-Atom | Length $[\AA \AA]$ |
| :---: | :---: |
| $\mathrm{Fe} 1-\mathrm{P} 2$ | $2.3303(4)$ |
| $\mathrm{Fe} 1-\mathrm{P} 3$ | $2.3198(4)$ |
| $\mathrm{Fe} 1-\mathrm{P} 4$ | $2.3399(4)$ |
| $\mathrm{Fe} 1-\mathrm{P} 5$ | $2.3168(4)$ |
| $\mathrm{Fe} 1-\mathrm{P} 1$ | $2.9843(7)$ |
| $\mathrm{P} 1-\mathrm{C} 13$ | $1.8168(14)$ |

## Supplementary Table 21.

Selected angles of 3a.

| Atom-Atom-Atom | Angle [$\left.{ }^{\circ}\right]$ |
| :---: | :---: |
| P1-P2-P3 | $102.06(2)$ |
| P2-P3-P4 | $105.44(2)$ |
| P4-P5-P1 | $101.54(2)$ |
| P2-P1-N1 | $117.53(5)$ |
| P5-P1-N1 | $122.92(5)$ |


| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| P3-P4-P5 | $105.14(2)$ |
| P5-P1-P2 | $100.084(19)$ |
| N1-P1-C13 | $103.77(7)$ |
| P2-P1-C13 | $104.76(5)$ |
| P5-P1-C13 | $106.16(5)$ |

## $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right) \mathrm{Me}\right\}\right]$ (3b)



## Supplementary Figure 45.

Molecular structure of 3b in the solid state with thermal ellipsoids at 50\% probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligand is drawn in a wire frame model.


## Supplementary Figure 46.

Side view of the molecular structure of $\mathbf{3 b}$ in the solid state with thermal ellipsoids at $50 \%$ probability level. The disorder is highlighted blue (Part 1) and green (Part 2). Hydrogen atoms are omitted for clarity.

## Supplementary Table 22.

Selected bond length of 3b.

| Atom-Atom | Length [Å] |
| :---: | :---: |
| Part 1 |  |
| P1-P2 | $2.089(3)$ |
| P2-P3 | $2.132(3)$ |
| P3-P4 | $2.135(3)$ |
| P4-P5 | $2.142(3)$ |
| P1-P5 | $2.164(2)$ |
| P1-C11 | $1.785(5)$ |
| Part 2 |  |
| P1-P2A | $2.230(6)$ |
| P2A-P3A | $2.128(5)$ |
| P3A-P4A | $2.130(5)$ |
| P4A-P5A | $2.131(5)$ |
| P1-P5A | $2.108(4)$ |
| P1-C11A | $1.922(11)$ |


| Atom-Atom | Length [Å] |
| :--- | :---: |
| Part 1 |  |
| Fe1-P2 | $2.376(3)$ |
| Fe1-P3 | $2.3679(15)$ |
| Fe1-P4 | $2.3250(15)$ |
| Fe1-P5 | $2.288(2)$ |
| Fe1-P1 | $3.0848(8)$ |
| P1-C12 | $1.796(3)$ |
| Part 2 |  |
| Fe1-P2A | $2.189(6)$ |
| Fe1-P3A | $2.272(3)$ |
| Fe1-P4A | $2.373(3)$ |
| Fe1-P5A | $2.352(3)$ |
| Fe1-P1 | $3.0848(8)$ |
| P1-C12 | $1.796(3)$ |

## Supplementary Table 23.

Selected angles of $\mathbf{3 b}$.

| Atom-Atom-Atom | Angle [ ${ }^{\circ}$ ] |
| :---: | :---: |
| Part 1 |  |
| P1-P2-P3 | 98.85(13) |
| P2-P3-P4 | 105.01(11) |
| P4-P5-P1 | 98.07(10) |
| P2-P1-C12 | 122.20(13) |
| P2-P1-C11 | 111.3(2) |
| P5-P1-C11 | 108.2(2) |
| Part 2 |  |
| P1-P2A-P3A | 94.7(2) |
| P2A-P3A-P4A | 104.1(2) |
| P4A-P5A-P1 | 95.45(16) |
| P2A-P1-C11A | 100.4(4) |
| C12-P1-C11A | 113.3(4) |


| Atom-Atom-Atom |  |
| :---: | :---: |
| Part 1 |  |
| Angle [] |  |
| P3-P4-P5 | $103.97(9)$ |
| P5-P1-P2 | $97.79(10)$ |
| P5-P1-C12 |  |
| C12-P1-C11 |  |
| P1-C12-Si1 | $113.76(12)$ |
| P3A-P4A-P5A | $116.76(18)$ |
| P5A-P1-P2A | $104.85(16)$ |
| P5A-P1-C12 | $94.80(17)$ |
| P2A-P1-C12 | $125.48(16)$ |
| P1-C12-Si1A | $129.50(18)$ |
| P5A-P1-C11A | $102.3(4)$ |

$\left[C p^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Me}_{2}\right)\right]$ (3c)


## Supplementary Figure 47.

Molecular structure of $3 c$ in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligand is drawn in a wire frame model.

## Supplementary Table 24.

Selected bond length of $3 c$.

| Atom-Atom | Length [Å] |
| :---: | :---: |
| P1-P2 | $2.1398(12)$ |
| P1-P5 | $2.1336(12)$ |
| P1-C11 | $1.818(3)$ |
| P1-C12 | $1.816(4)$ |


| Atom-Atom | Length [Å] |
| :---: | :---: |
| P2-P3 | $2.1420(16)$ |
| P5-P4 | $2.1370(17)$ |
| P3-P4 | $2.1472(19)$ |
|  |  |

## Supplementary Table 25.

Selected angles of 3c.

| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| P5-P1-P2 | $98.20(5)$ |
| C11-P1-P2 | $120.43(13)$ |
| C11-P1-P5 | $119.27(13)$ |
| C12-P1-P2 | $106.54(15)$ |
| C12-P1-P5 | $107.20(15)$ |


| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| P1-P2-P3 | $99.53(6)$ |
| P1-P5-P4 | $98.69(6)$ |
| P2-P3-P4 | $104.10(6)$ |
| P5-P4-P3 | $105.21(6)$ |
| C12-P1-C11 | $104.21(19)$ |

## $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Me}^{\mathrm{i} P r}\right)\right](3 \mathrm{~d})$



## Supplementary Figure 48.

Molecular structure of 3d in the solid state with thermal ellipsoids at 50\% probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligand is drawn in a wire frame model.

## Supplementary Table 26.

Selected bond length of $3 \mathbf{c}$.

| Atom-Atom | Length [Å] |
| :---: | :---: |
| P5-P1 | $2.1490(19)$ |
| P5-P4 | $2.143(2)$ |
| P1-P2 | $2.138(2)$ |
| P1-C12 | $1.840(6)$ |


| Atom-Atom | Length [Å] |
| :---: | :---: |
| P1-C11 | $1.811(6)$ |
| P2-P3 | $2.137(2)$ |
| P4-P3 | $2.158(3)$ |
|  |  |

## Supplementary Table 27.

Selected angles of 3d.

| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| P4-P5-P1 | $98.96(9)$ |
| P2-P1-P5 | $97.86(8)$ |
| C12-P1-P5 | $107.3(2)$ |
| C12-P1-P2 | $108.0(2)$ |
| C11-P1-P5 | $119.5(2)$ |


| Atom-Atom-Atom | Angle [ ${ }^{\circ}$ ] |
| :---: | :---: |
| C11-P1-P2 | $117.7(2)$ |
| C11-P1-C12 | $105.8(3)$ |
| P3-P2-P1 | $98.88(9)$ |
| P5-P4-P3 | $104.31(8)$ |
| P2-P3-P4 | $104.75(9)$ |

$\left[C p^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{BuMe}\right)\right]$ (3e)


## Supplementary Figure 49.

Molecular structure of 3 e in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligand is drawn in a wire frame model.

## Supplementary Table 28.

Selected bond length of 3 e .

| Atom-Atom | Length [Å] |
| :---: | :---: |
| P1-P2 | $2.1462(8)$ |
| P2-P3 | $2.1360(1)$ |
| P3-P4 | $2.1476(16)$ |
| P4-P5 | $2.1360(1)$ |
| P1-P5 | $2.1462(8)$ |
| P1-C1 | $1.828(4)$ |


| Atom-Atom | Length [Å] |
| :---: | :---: |
| Fe1-P2 | $2.3301(6)$ |
| Fe1-P3 | $2.3390(8)$ |
| Fe1-P4 | $2.3390(8)$ |
| Fe1-P5 | $2.3301(6)$ |
| $\mathrm{P} 1-\mathrm{C} 2$ | $1.863(4)$ |
|  |  |

## Supplementary Table 29.

Selected angles of $3 \mathbf{e}$.

| Atom-Atom-Atom | Angle [ ${ }^{\circ}$ ] |
| :---: | :---: |
| P1-P2-P3 | $101.40(4)$ |
| P2-P3-P4 | $105.20(3)$ |
| P4-P5-P1 | $101.40(4)$ |
| P2-P1-C1 | $105.20(9)$ |
| C1-P1-C2 | $106.04(19)$ |


| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| P3-P4-P5 | $105.20(3)$ |
| P5-P1-P2 | $99.15(5)$ |
| P5-P1-C1 | $105.20(9)$ |
| P2-P1-C2 | $119.84(7)$ |
| P5-P1-C2 | $119.84(7)$ |

## $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{PhMe}\right)\right]$ (3f)



## Supplementary Figure 50.

Molecular structure of 3 f in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligand is drawn in a wire frame model.

## Supplementary Table 30.

Selected bond length of 3 f.

| Atom-Atom | Length [Å] |
| :---: | :---: |
| P1-P2 | $2.1498(10)$ |
| P2-P3 | $2.1433(11)$ |
| P3-P4 | $2.1454(11)$ |
| P1-C2 | $1.819(3)$ |


| Atom-Atom | Length [Å] |
| :---: | :---: |
| P4-P5 | $2.1420(11)$ |
| P1-P5 | $2.1444(10)$ |
| P1-C1 | $1.812(3)$ |

## Supplementary Table 31.

Selected angles of $3 \mathbf{f}$.

| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| P1-P2-P3 | $99.65(4)$ |
| P2-P3-P4 | $104.87(4)$ |
| P4-P5-P1 | $99.84(4)$ |
| P2-P1-C1 | $106.27(12)$ |
| C1-P1-C2 | $105.52(14)$ |


| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| P3-P4-P5 | $104.89(4)$ |
| P5-P1-P2 | $98.20(4)$ |
| P5-P1-C1 | $107.55(13)$ |
| P2-P1-C2 | $120.76(10)$ |
| P5-P1-C2 | $117.59(10)$ |

## SPMe'PrBnz (4a')



## Supplementary Figure 51.

Molecular structure of 4a' in the solid state with thermal ellipsoids at 50\% probability level. Hydrogen atoms are omitted for clarity.


## Supplementary Figure 52.

Molecular structure of $4 \mathbf{a}^{\prime}$ in the solid state with thermal ellipsoids at $50 \%$ probability level. The disorder is highlighted blue (Part 1) and green (Part 2) (grey = Part 0). Hydrogen atoms are omitted for clarity.

## Supplementary Table 32.

Selected bond length of 4a'.

| Atom-Atom | Length $[\AA \AA]$ |
| :---: | :---: |
| Part 1 |  |
| $\mathrm{P} 1_{\mathrm{A}}-\mathrm{S} 1_{\mathrm{A}}$ | $1.9615(15)$ |
| $\mathrm{P} 1_{\mathrm{A}}-\mathrm{C} 1$ | $1.833(3)$ |
| Part 2 |  |
| $\mathrm{P} 1_{\mathrm{B}}-\mathrm{S} 1_{\mathrm{B}}$ | $1.91(2)$ |
| $\mathrm{P} 1_{\mathrm{A}}-\mathrm{C} 8_{\mathrm{B}}$ | $1.84(7)$ |


| Atom-Atom | Length [Å] |  |
| :---: | :---: | :---: |
| Part 1 |  |  |
| $\mathrm{P} 1_{\mathrm{A}}-\mathrm{C} 9_{\mathrm{A}}$ | $1.830(3)$ |  |
| $\mathrm{P} 1_{\mathrm{A}}-\mathrm{C} 8_{\mathrm{A}}$ | $1.797(3)$ |  |
| Part 2 |  |  |
| $\mathrm{P} 1_{\mathrm{A}}-\mathrm{C} 9_{\mathrm{B}}$ | $1.84(4)$ |  |
|  |  |  |

## Supplementary Table 33.

Selected angles of 4a'.

| Atom-Atom-Atom | Angle [ ${ }^{\circ}$ ] |
| :---: | :---: |
| Part 1 |  |
| $\mathrm{C} 1-\mathrm{P} 1_{\mathrm{A}}-\mathrm{S} 1_{\mathrm{A}}$ | $114.79(10)$ |
| $\mathrm{C} 9_{\mathrm{A}}-\mathrm{P} 1_{\mathrm{A}}-\mathrm{S} 1_{\mathrm{A}}$ | $112.86(11)$ |
| $\mathrm{C} 9_{\mathrm{A}}-\mathrm{P} 1_{\mathrm{A}}-\mathrm{C} 1$ | $103.15(12)$ |
| Part 2 |  |
| $\mathrm{C} 1-\mathrm{P} 1_{\mathrm{B}}-\mathrm{S} 1_{\mathrm{B}}$ | $112.6(9)$ |
| $\mathrm{C} 9_{\mathrm{B}}-\mathrm{P} 1_{\mathrm{B}}-\mathrm{S} 1_{\mathrm{B}}$ | $113.8(14)$ |
| $\mathrm{C} 9_{\mathrm{B}}-\mathrm{P} 1_{\mathrm{B}}-\mathrm{C} 1$ | $98.7(14)$ |


| Atom-Atom-Atom | Angle [ ${ }^{\circ}$ ] |
| :---: | :---: |
| Part 1 |  |
| $\mathrm{C} 8_{\mathrm{A}}-\mathrm{P} 1_{\mathrm{A}}-\mathrm{S} 1_{\mathrm{A}}$ |  |
| Part 2 |  |
| $\mathrm{C} 8_{\mathrm{A}}-\mathrm{P} 1_{\mathrm{A}}-\mathrm{C} 1$ | $12.80(12)$ |
| $\mathrm{C} 8_{\mathrm{A}}-\mathrm{P} 1_{\mathrm{A}}-\mathrm{C} \mathrm{A}_{\mathrm{A}}$ | $106.32(14)$ |
| $\mathrm{C} 8_{\mathrm{B}}-\mathrm{P} 1_{\mathrm{B}}-\mathrm{S} 1_{\mathrm{B}}$ | $113(2)$ |
| $\mathrm{C} 8_{\mathrm{B}}-\mathrm{P} 1_{\mathrm{B}}-\mathrm{C} 1$ | $110(2)$ |
| $\mathrm{C} 8_{\mathrm{B}}-\mathrm{P} 1_{\mathrm{B}}-\mathrm{C} 9_{\mathrm{B}}$ | $107(3)$ |

## SPtBuMeBnz (4b')



## Supplementary Figure 53.

Molecular structure of 4b' in the solid state with thermal ellipsoids at 50\% probability level. Hydrogen atoms are omitted for clarity.

## Supplementary Table 34.

Selected bond length of $\mathbf{4 b}$ '.

| Atom-Atom | Length [Å] |
| :---: | :---: |
| P1-S1 | $1.9563(7)$ |
| P1-C1 | $1.855(2)$ |
| P1-C5 | $1.828(2)$ |


| Atom-Atom | Length $[\AA \AA]$ |
| :---: | :---: |
| C6-C11 | $1.388(3)$ |
| C6-C5 | $1.512(3)$ |
| P1-C12 | $1.805(2)$ |

## Supplementary Table 35.

Selected angles of 4b'.

| Atom-Atom-Atom | Angle [$]$ |
| :---: | :---: |
| C1-P1-S1 | $113.03(7)$ |
| C5-P1-S1 | $113.52(7)$ |
| C5-P1-C1 | $105.43(9)$ |
| $\mathrm{C} 12-\mathrm{P} 1-\mathrm{S} 1$ | $111.69(8)$ |
| $\mathrm{C} 12-\mathrm{P} 1-\mathrm{C} 1$ | $107.32(10)$ |


| Atom-Atom-Atom | Angle [ ${ }^{\circ}$ ] |
| :---: | :---: |
| C12-P1-C5 | $105.28(10)$ |
| C3-C1-P1 | $108.42(14)$ |
| C4-C1-P1 | $110.89(14)$ |
| C2-C1-P1 | $108.48(13)$ |
| C6-C5-P1 | $114.37(14)$ |

## SPPhMeBnz (4c')



## Supplementary Figure 54.

Molecular structure of $4 \mathrm{c}^{\prime}$ in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity.

## Supplementary Table 36.

Selected bond length of $4 \mathrm{c}^{\prime}$.

| Atom-Atom | Length $[\AA ̊]$ |
| :---: | :---: |
| P1-S1 | $1.9595(6)$ |
| P1-C8 | $1.8186(19)$ |


| Atom-Atom | Length $[\AA ̊]$ |
| :---: | :--- |
| P1-C1 | $1.8280(19)$ |
| P1-C14 | $1.7987(18)$ |

## Supplementary Table 37.

Selected angles of $\mathbf{4 c}$ '.

| Atom-Atom-Atom | Angle [ ${ }^{\circ}$ ] | Atom-Atom-Atom | Angle [ ${ }^{\circ}$ ] |
| :---: | :---: | :---: | :---: |
| C1-P1-S1 | 112.95(6) | C1-P1-C8 | 112.78(6) |
| C14-P1-S1 | 113.08(6) | C8-P1-S1 | 105.85(9) |
| C1-P1-C14 | 106.10(9) | C14-P1-C8 | 105.43(9) |

## $[K(18 c 6)($ thf $)]\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\mathrm{n}^{4}-\mathrm{P}_{4}\right)\right](5)$



## Supplementary Figure 55.

Molecular structure of 5 in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligand is drawn in a wire frame model.

## Supplementary Table 38.

Selected bond length of 5 .

| Atom-Atom | Length $[\AA ̊]$ |
| :---: | :--- |
| Fe1-P1 | $2.3139(15)$ |
| Fe1-P3 | $2.3191(14)$ |
| $\mathrm{Fe}^{\mathrm{F}-\mathrm{P} 2^{1}}$ | $2.3129(11)$ |
| $\mathrm{Fe} 1-\mathrm{P} 2$ | $2.3130(11)$ |
| $\mathrm{K} 1-\mathrm{P} 1$ | $3.3850(16)$ |
| ${\mathrm{K} 1-\mathrm{P} 2^{1}}$ | $3.7722(13)$ |


| Atom-Atom | Length [Å] |
| :---: | :---: |
| K1-P2 | 3.7722(13) |
| P1-P2 | 2.1751(13) |
| P1-P2 ${ }^{1}$ | 2.1752(13) |
| P3-P2 | $2.1666(13)$ |
| P3-P2 ${ }^{1}$ | 2.1667(13) |
|  |  |

## Supplementary Table 39.

Selected angles of 5.

| Atom-Atom-Atom | Angle [ ${ }^{\circ}$ ] |
| :---: | :---: |
| P2-P1-P2 ${ }^{1}$ | $89.25(7)$ |
| ${\mathrm{P} 2-\mathrm{P} 3-\mathrm{P}^{1}}^{1}$ | $89.69(7)$ |


| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| P3-P2-P1 | $90.53(5)$ |
| $\mathrm{P}^{\circ}-\mathrm{P}^{1}-\mathrm{P} 1$ | $90.53(5)$ |

$\qquad$

## 3. Data availability

Reaction of 3c with MeLi (Supplementary Figure 56) and n-BuLi (Supplementary Figure 57):
[internal standard

## Supplementary Figure 56.

Experimental ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 161.98 MHz , DME|tol- $\mathrm{d}_{8}$ capillary with $\mathrm{PPh}_{3}$ as internal standard; $\mathrm{c}=0.2 \mathrm{~mol} / \mathrm{L}$ ) spectrum of the reaction of 3 c with MeLi after five hours. ${ }^{[i]}$


## Supplementary Figure 57.

Experimental ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $161.98 \mathrm{MHz}, \mathrm{DME} \mid \mathrm{C}_{6} \mathrm{D}_{6}$ capillary) spectrum of the reaction of 3 c with $n$-BuLi after one hour. ${ }^{[i i]}$

## Reaction of 3e with KBnz:




## Supplementary Figure 58.

${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}$ ( 161.98 MHz , THF- $\mathrm{d}_{8}$, 298 K ) spectrum of the reaction of 3 e with 1.5 eq of $\mathrm{KBnz} / 18 \mathrm{c} 6$ and after (partial) extraction of the phosphine.


## Supplementary Figure 59.

Cutout of ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{THF}^{2} \mathrm{~d}_{8}, 298 \mathrm{~K}\right)$ spectrum of the reaction of 3 e (Supplementary Figure 59) with 1.5 eq of $\mathrm{KBnz} / 18 \mathrm{c} 6$ and after (partial) extraction of the phosphine and postulated side products.


## Supplementary Figure 60.

Section of ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{THF}-\mathrm{d}_{8}, 298 \mathrm{~K}\right)$ spectrum of the reaction of 3e (Supplementary Figure 59) with 1.5 eq of $\mathrm{KBnz} / 18 \mathrm{c} 6$ and after (partial) extraction of the phosphine and postulated side products.

Reaction of 3b, 3c, 3d and 3e with; KBnz overview:


## Supplementary Figure 61.

Experimental ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 161.98 MHz , THF- $\mathrm{d}_{8}$ ) spectra of the reaction solutions of $\mathbf{3 b}, 3 \mathrm{c}, 3 \mathrm{~d}$ and $\mathbf{3 e}$ with KBnz $\left(^{*}=\right.$ NMR yield, according to $0.2 \mathrm{~mol} / \mathrm{L} \mathrm{PPh}_{3}$ capillary as internal standard).

## Reaction of in situ generated $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Et} \mathrm{t}^{\mathrm{P}}\right)\right]$ (1 with 1. EtLi, 2. 2-lodopropane) with KBnz:

```
[Cp*Fe(\eta}\mp@subsup{n}{}{4}-\mp@subsup{P}{6}{EEtPr})
```




## Supplementary Figure 62.

Experimental ${ }^{31}{ }^{1}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectra of the reaction of 1 with 1. EtLi, 2. 2-Iodopropane (top); Reaction of $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Et} \mathrm{P}^{\text {Pr }}\right)\right]$ with KBnz (bottom).

Reaction of 3 c with KBnz and subsequent thermolysis with white phosphorus in tetraglyme:


## Supplementary Figure 63.

Experimental ${ }^{31}{ }^{21}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}\right.$, tetraglyme|tol- $\mathrm{d}_{8}$ capillary with $\mathrm{PPh}_{3}$ as internal standard; $\mathrm{c}=0.2 \mathrm{~mol} / \mathrm{L}$ ) spectrum of the one-pot reaction of 1 with 1. MeLi, 2 . Mel, 3. KBnz; after thermolysis with white phosphorus: first cycle. ${ }^{\text {[i] }}$

## Supplementary Table 40.

Number of cycles in the reaction of 1 with 1. MeLi, 2. Mel, 3. Bnz, 4. $\mathrm{P}_{4}$ and the corresponding yield of the distilled phosphine ( $\mathrm{PMe}_{2} \mathrm{Bnz}$ ).

| Cycle | Yield (PMe2Bnz) [\%] |  |
| :---: | :---: | :---: |
| 1 |  | 87 |
| 2 |  | 82 |
| 3 | 1 | 67 |

third cycle

$$
\mathrm{PPh}_{3} \text { capillary }
$$

$\mathrm{P}_{4}$
second cycle

first cycle


## Supplementary Figure 64.

Experimental ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 161.98 MHz , tetraglyme $\mid \mathrm{C}_{6} \mathrm{D}_{6} /$ tol-d $\mathrm{d}_{8}$ capillary with $\mathrm{PPh}_{3}$ as internal standard; $\mathrm{c}=0.2 \mathrm{~mol} / \mathrm{L}$ ) spectrum of the reaction of 1 with $1 . \mathrm{MeLi}, 2 . \mathrm{Mel}, 3 . \mathrm{KBnz}$; after thermolysis with white phosphorus.

Reaction of $3 \mathbf{c}$ with KBnz and subsequent thermolysis with white phosphorus in triglyme:


## Supplementary Figure 65.

Experimental ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 161.98 MHz , triglyme|tol $-\mathrm{d}_{8}$ capillary with $\mathrm{PPh}_{3}$ as internal standard; $\mathrm{c}=0.2 \mathrm{~mol} / \mathrm{L}$ ) spectrum of the reaction of 1 with 1 . MeLi, 2. Mel, 3 . KBnz; after thermolysis with white phosphorus ( ${ }^{*}=$ unidentified polyphosphides, " = $\mathrm{PMe}_{3}$ ).


## Supplementary Figure 66.

Experimental ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of 1; obtained from the reaction of 1 with 1 . MeLi, 2. Mel, 3. KBnz; after the thermolysis white phosphorus and chromatographic workup.


## Supplementary Figure 67.

Experimental ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of the reaction of 3 c with KBnz after the thermolysis white phosphorus and distillation of $\mathrm{PMe}_{2} \mathrm{Bnz}$ (signal at $34.9 \mathrm{ppm}=\mathrm{OPMe}_{2} \mathrm{Bnz}$ ).


Supplementary Figure 68.
Experimental ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $(242.90 \mathrm{MHz} \text {, THF-d })_{8}$ ) spectrum of the crude reaction solution (low temperature reaction) of 3 c with KBnz at 180 K .


Supplementary Figure 69.
Experimental ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $161.98 \mathrm{MHz}, \mathrm{THF} \mid \mathrm{C}_{6} \mathrm{D}_{6}$ capillary) spectrum of the reaction mixture of $1^{\prime}$ with 2 eq Mel.
$3 e$


## Supplementary Figure 70.

Experimental ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{THF} \mid \mathrm{C}_{6} \mathrm{D}_{6}\right.$ capillary) spectrum of the reaction mixture of 1 ' with $1 .{ }^{\text {tBul }}$ and 2. Mel.

## 4. Computational details

## Supplementary Table 41.

Thermodynamic parameters of selected compounds calculated at D3(BJ)-B3LYP/def2TZVPP level of theory.

|  | $\mathrm{Bnz}^{-}$ | $\mathrm{PMe}_{2} \mathrm{Bnz}$ | $\left[\mathrm{Cp}^{*} \mathrm{FeP}_{4}\right]^{-}$ | $\left[\mathrm{Cp}^{*} \mathrm{FeP}_{5} \mathrm{Me}_{2}\right]$ | [Cp $\left.^{*} \mathrm{FeP}_{5} \mathrm{Me}_{2} \mathrm{Bnz}\right]^{-}(\mathrm{TS})$ |
| :--- | :---: | :---: | :---: | :---: | :---: |
| Sum of electronic and zero- <br> point Energies [Ha] <br> Sum of electronic and | -271.031677 | -692.166444 | -3019.60713 | -3440.715264 | -3711.755175 |
| thermal Energies [Ha] | -271.025692 | -692.155524 | -3019.58813 | -3440.691006 | -3711.724149 |
| Sum of electronic and <br> thermal Enthalpies [Ha] <br> Sum of electronic and | -271.024748 | -692.15458 | -3019.58719 | -3440.690062 | -3711.723204 |
| thermal Free Energies [Ha] <br> Zero-point vibrational <br> energy [J/Mol] | -271.060933 | -692.203688 | -3019.65461 | -3440.767184 | -3711.816824 |



## Supplementary Figure 71.

Gibbs free energy profile of the reaction of 3 c with KBnz, calculated at the B3LYP-D3(BJ)/def2-TZVPP (PCM $=$ THF) level of theory.


0.0


29


60

## Supplementary Figure 72.

Top: Electrostatic potential mapped on electron density (isovalue $=0.001$ ) for 2 c . Colour code (blue $=$ positive, red $=$ negative) in $\mathrm{kJ} \cdot \mathrm{mol}^{-1}$; Bottom: Optimised geometries of selected isomers of 3 c and their relative energy in $\mathrm{kJ} \cdot \mathrm{mol}^{-1}$. Calculated at the B3LYP-D3(BJ)/def2-TZVPP (PCM $=$ THF) level of theory.

Supplementary Table 42. Cartesian coordinates of the optimized geometry of Bnz.

| Atom | X | Y | Z | Atom |  | X | Y |
| :--- | ---: | ---: | ---: | ---: | ---: | ---: | ---: |
| H | -1.410854000 | 0.228519000 | 2.005526000 | C | 0.222591000 | -1.327070000 | -0.547811000 |
| C | -0.436567000 | 2.592105000 | 1.070860000 | C | -0.569729000 | -1.127914000 | 0.593133000 |
| H | -1.045908000 | 2.737939000 | 1.953960000 | C | -0.789444000 | 0.127552000 | 1.121427000 |
| H | 0.004613000 | 3.468873000 | 0.613645000 | H | 1.038776000 | 1.931081000 | -1.120388000 |
| C | -0.224698000 | 1.324357000 | 0.545470000 | H | 1.404949000 | -0.294548000 | -2.023712000 |
| C | 0.580163000 | 1.079798000 | -0.627479000 | H | 0.388859000 | -2.314764000 | -0.955344000 |
| C | 0.786146000 | -0.185447000 | -1.137982000 | H | -1.027092000 | -1.984486000 | 1.079360000 |

Supplementary Table 43. Cartesian coordinates of the optimized geometry of $\mathrm{PMe}_{2} \mathrm{Bnz}$.

| Atom |  | X | Y | Z | Atom |  | X |
| :--- | ---: | ---: | :--- | :--- | :--- | ---: | ---: |
| P | -0.030046000 | -0.118633000 | -0.039984000 | H | -2.289439000 | -0.959515000 | 0.100986000 |
| C | 1.495706000 | -1.150022000 | 0.085844000 | C | -1.316607000 | -2.275570000 | -1.284207000 |
| H | 1.644871000 | -1.697955000 | -0.843574000 | C | -0.718157000 | -3.535848000 | -1.318208000 |
| H | 1.442335000 | -1.861441000 | 0.912367000 | C | -0.671713000 | -4.273816000 | -2.495971000 |
| H | 2.355645000 | -0.497172000 | 0.235636000 | C | -1.223228000 | -3.760416000 | -3.664286000 |
| C | -0.176269000 | 0.444937000 | 1.713170000 | C | -1.821651000 | -2.504219000 | -3.643858000 |
| H | 0.622736000 | 1.153283000 | 1.932355000 | C | -1.864935000 | -1.769811000 | -2.465551000 |
| H | -0.113402000 | -0.387160000 | 2.417124000 | H | -0.287891000 | -3.943062000 | -0.412249000 |
| H | -1.128185000 | 0.957161000 | 1.853669000 | H | -0.205819000 | -5.250321000 | -2.499531000 |
| H | -2.328754000 | -0.791640000 | -2.457906000 | H | -1.189855000 | -4.333419000 | -4.580979000 |
| C | -1.329246000 | -1.463218000 | -0.022776000 | H | -2.255838000 | -2.096324000 | -4.547043000 |
| H | -1.171707000 | -2.100771000 | 0.849271000 |  |  |  |  |

Supplementary Table 44. Cartesian coordinates of the optimized geometry of [ $\left.\mathrm{Cp}^{*} \mathrm{FeP}_{5} \mathrm{Me}_{2} \mathrm{Bnz}\right]^{-}$(TS).

| Atom | X | Y | Z | Atom | X | Y | Z |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Fe | 1.928627000 | -0.429941000 | 22.755086000 | C | 4.036762000 | -0.209700000 | 25.180011000 |
| P | 1.730448000 | -2.728201000 | 20.482216000 | H | 4.408150000 | -1.217454000 | 24.996081000 |
| P | 3.195071000 | -2.267506000 | 22.079020000 | H | 4.097104000 | -0.026735000 | 26.256918000 |
| P | 3.872499000 | -0.335975000 | 21.463288000 | H | 4.714101000 | 0.484338000 | 24.685764000 |
| P | 2.073043000 | 0.575156000 | 20.655060000 | C | 2.772231000 | 2.432921000 | 23.909112000 |
| P | 0.572066000 | -0.930434000 | 20.923965000 | H | 3.826808000 | 2.277979000 | 23.686495000 |
| C | 2.659406000 | -3.100257000 | 18.964065000 | H | 2.707770000 | 3.063852000 | 24.800317000 |
| H | 2.893209000 | -2.156618000 | 18.474677000 | H | 2.339910000 | 2.986802000 | 23.077516000 |
| H | 2.099521000 | -3.739551000 | 18.288444000 | C | -0.300073000 | 1.828940000 | 23.269623000 |
| H | 3.594275000 | -3.578363000 | 19.261087000 | H | 0.186443000 | 2.596484000 | 22.670379000 |
| C | 0.984972000 | -4.256100000 | 21.128432000 | H | -0.855558000 | 2.329081000 | 24.068340000 |
| H | 1.780694000 | -4.955272000 | 21.383817000 | H | -1.024898000 | 1.325205000 | 22.630895000 |
| H | 0.323138000 | -4.700325000 | 20.391831000 | H | -1.709748000 | -5.167956000 | 19.322824000 |
| H | 0.429254000 | -4.010471000 | 22.032043000 | C | -0.476267000 | -2.872026000 | 18.568758000 |
| C | 1.616358000 | -1.046959000 | 24.740351000 | H | -1.201625000 | -2.708471000 | 19.354232000 |
| C | 0.418411000 | -0.485403000 | 24.212049000 | H | -0.129938000 | -1.986058000 | 18.052549000 |
| C | 0.693939000 | 0.864136000 | 23.827989000 | C | -0.428799000 | -4.115576000 | 17.924254000 |
| C | 2.637141000 | -0.048945000 | 24.684466000 | C | 0.339864000 | -4.344183000 | 16.737472000 |
| C | 2.067507000 | 1.132854000 | 24.117634000 | C | 0.459658000 | -5.596651000 | 16.164181000 |
| C | 1.758795000 | -2.412322000 | 25.328577000 | C | -0.175323000 | -6.715727000 | 16.712696000 |
| H | 1.087334000 | -3.124462000 | 24.851413000 | C | -0.952722000 | -6.524407000 | 17.860326000 |
| H | 1.524224000 | -2.399923000 | 26.397333000 | C | -1.082258000 | -5.278911000 | 18.445459000 |
| H | 2.773021000 | -2.790220000 | 25.214980000 | H | 0.834284000 | -3.498643000 | 16.273005000 |
| C | -0.913311000 | -1.158834000 | 24.150646000 | H | 1.056545000 | -5.707356000 | 15.265310000 |
| H | -1.507666000 | -0.790961000 | 23.316369000 | H | -0.079034000 | -7.692358000 | 16.258689000 |
| H | -1.481299000 | -0.981049000 | 25.068872000 | H | -1.472493000 | -7.368323000 | 18.300967000 |
| H | -0.810119000 | -2.236135000 | 24.030445000 |  |  |  |  |

Supplementary Table 45. Cartesian coordinates of the optimized geometry of [ $\mathrm{Cp}{ }^{*} \mathrm{FeP}_{5} \mathrm{Me}_{2}$ ].

| Atom | X | Y | Z | Atom | X | Y | Z |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Fe | 6.845963000 | 1.173527000 | 17.434821000 | H | 6.975856000 | 2.920092000 | 20.477880000 |
| P | 8.061706000 | -0.999535000 | 19.212215000 | H | 6.786085000 | 4.553838000 | 19.850051000 |
| P | 8.985547000 | 0.725627000 | 18.329035000 | H | 8.254198000 | 3.640160000 | 19.509362000 |
| P | 8.653404000 | 0.277803000 | 16.249292000 | C | 4.437409000 | 1.959767000 | 19.474998000 |
| P | 6.794668000 | -0.809458000 | 16.193325000 | H | 3.848943000 | 1.065832000 | 19.279419000 |
| P | 6.146987000 | -0.931349000 | 18.243413000 | H | 3.742305000 | 2.776752000 | 19.688240000 |
| C | 8.975225000 | -2.571586000 | 19.179665000 | H | 5.021832000 | 1.781678000 | 20.376049000 |
| H | 9.162981000 | -2.842984000 | 18.143248000 | C | 8.242616000 | 3.963375000 | 16.654113000 |
| H | 8.380226000 | -3.349309000 | 19.658778000 | H | 9.037820000 | 3.827821000 | 17.386240000 |
| H | 9.923521000 | -2.456495000 | 19.704582000 | H | 8.039366000 | 5.035334000 | 16.583746000 |
| C | 7.799405000 | -0.635008000 | 20.976046000 | H | 8.621714000 | 3.631680000 | 15.689470000 |
| H | 8.761937000 | -0.537260000 | 21.475294000 | C | 6.147133000 | 2.610026000 | 14.661710000 |
| H | 7.233919000 | -1.443482000 | 21.436003000 | H | 7.180072000 | 2.620509000 | 14.318835000 |
| H | 7.245334000 | 0.295716000 | 21.070519000 | H | 5.648055000 | 3.490397000 | 14.248207000 |
| C | 6.537721000 | 3.023668000 | 18.378523000 | H | 5.668816000 | 1.727515000 | 14.240791000 |
| C | 5.309849000 | 2.306859000 | 18.314153000 | C | 3.795618000 | 1.362001000 | 16.423629000 |
| C | 5.017860000 | 2.047538000 | 16.938721000 | H | 3.972374000 | 0.916364000 | 15.446753000 |
| C | 7.011501000 | 3.213349000 | 17.042346000 | H | 2.966046000 | 2.067360000 | 16.325274000 |
| C | 6.070325000 | 2.609833000 | 16.152472000 | H | 3.472679000 | 0.567809000 | 17.095765000 |
| C | 7.174866000 | 3.558163000 | 19.618522000 |  |  |  |  |

Supplementary Table 46. Cartesian coordinates of the optimized geometry of $\left[\mathrm{Cp}^{*} \mathrm{FeP}_{4}\right]^{-}$.

| Atom | X | Y | Z | Atom | X | Y | Z |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Fe | 0.224383000 | -0.012924000 | 0.168183000 | H | 2.202964000 | -2.269948000 | 1.906224000 |
| P | 2.242601000 | 0.829041000 | -0.669842000 | H | 0.954900000 | -3.050636000 | 2.874728000 |
| P | 1.499327000 | -1.037371000 | -1.508980000 | H | 0.998128000 | -3.281537000 | 1.126767000 |
| P | 0.403023000 | 1.828806000 | -1.266914000 | C | 1.729360000 | 0.375118000 | 3.010866000 |
| P | -0.341354000 | -0.038103000 | -2.101826000 | H | 1.957394000 | 1.427937000 | 2.852616000 |
| C | -1.548383000 | -0.025731000 | 1.208389000 | H | 1.573804000 | 0.226674000 | 4.084472000 |
| C | -0.591703000 | 0.779427000 | 1.903426000 | H | 2.610282000 | -0.196024000 | 2.722245000 |
| C | 0.525781000 | -0.046435000 | 2.231938000 | C | -0.755616000 | 2.217255000 | 2.276200000 |
| C | 0.264796000 | -1.362031000 | 1.742096000 | H | -1.391701000 | 2.740656000 | 1.564601000 |
| C | -1.017614000 | -1.352345000 | 1.108033000 | H | -1.208128000 | 2.318963000 | 3.267951000 |
| C | -1.702823000 | -2.530878000 | 0.496479000 | H | 0.203123000 | 2.733975000 | 2.297248000 |
| H | -0.982779000 | -3.233393000 | 0.078552000 | C | -2.888302000 | 0.424881000 | 0.724462000 |
| H | -2.302508000 | -3.071848000 | 1.235503000 | H | -3.207237000 | -0.148779000 | -0.144319000 |
| H | -2.366939000 | -2.224813000 | -0.310183000 | H | -3.651656000 | 0.307109000 | 1.500312000 |
| C | 1.150866000 | -2.551956000 | 1.919944000 | H | -2.872682000 | 1.475039000 | 0.435453000 |

## 5. Supplementary References

[i] Kühl, O. Phosphorus-31 NMR Spectroscopy. Phosphorus-31 NMR Spectroscopy (Springer Berlin Heidelberg, 2009).
[ii] Quin, L. D., Gordon, M. D. \& Lee, S. O. Effects of some phosphorus substituents on the carbon13 chemical shifts of alkyl chains. Org. Magn. Reson. 6, 503-507 (1974).

# 6 Novel Synthetic Route for (parent) Phosphetane, Phospholane, Phosphinane and Phosphepanes 

### 6.1 Preface

The following chapter is about to be submitted.
S. Reichl, G. Balázs and M. Scheer, manuscript in preparation.

Authors<br>Stephan Reichl, ${ }^{1}$ Gábor Balázs, ${ }^{1}$ Manfred Scheer ${ }^{1 *}$<br>${ }^{1}$ Institute of Inorganic Chemistry, University of Regensburg; Universitätsstraße 31, 93053 Regensburg, Germany.<br>*Corresponding author. Email: manfred.scheer@chemie.uni-regensburg.de

## Author Contribution

S.R. conceived the experiments. S.R. analysed and revised the X-ray data;
S.R., G. B. and M.Sch. wrote the manuscript. M.Sch. directed and coordinated the research.

Novel Synthetic Route for (parent) Phosphetane, Phospholane, Phosphinane and Phosphepanes


# Novel Synthetic Route for (parent) Phosphetane, Phospholane, <br> <br> Phosphinane and Phosphepanes 

 <br> <br> Phosphinane and Phosphepanes}


#### Abstract

A novel synthetic route for (parent) phosphorus containing cycloalkanes i.e. phosphetanes, phospholanes and phosphinanes is reported. By using $\left[K(d m e)_{2}\right]_{2}\left[C p^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}\right)\right]$ (I) in combination with $\alpha, \omega$-dibromoalkanes $\mathrm{C}_{n} \mathrm{H}_{2 n} \mathrm{Br}_{2}(\mathrm{n}=3,4,5,6$ ), unique phosphet, phosphol-, phosphin- and phosphepane precursors $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\mathrm{P}_{5}\left(\mathrm{C}_{n} \mathrm{H}_{2 n}\right)\right](2-5)\right.$ can be synthesised. They act as a P -atom carrier and the corresponding phosphetane, phospholane, phosphinane and phosphepanes (6-9) can be released by nucleophiles i.e., potassium benzyl (KBnz) or $\mathrm{LiAlH}_{4}$. The letter enables the selective synthesis of secondary phosphines, in an easy and straightforward way, including the first known parent phospholane (10).


### 6.2 Introduction

Heterocyclic chemistry is one of the prime topics in organic and inorganic chemistry, with billions of heterocyclic compounds synthesized and part of them widely used, e.g in pharmaceutical industry. ${ }^{1}$ On the other hand, phosphines are widely used in (asymmetric) organocatalysis, ${ }^{2,3}$ which is still a major field and was rewarded with two Nobel prices within the last two decades years. ${ }^{4,5}$ To customize and tune (transition)metal complexes, used in catalysis, a variety of phosphines have been and are still synthesized. ${ }^{6-8}$

While phosphorus-heterocycles are in, with some acceptions like the Wittig Reaction, academic interests, ${ }^{9}$ bidentate ${ }^{7}$ and caged ${ }^{10}$ phosphines are on the rise as tuneable ligands in catalysis and Wittig-type reactions are widely used in industry. ${ }^{11}$ The importance of specific phosphorusheterocycles in transition-metal-assisted (asymmetric) catalysis is still remarkable, e.g. like the usage of phosphetanes in DuPhos or BPE, representing chiral ligands for asymmetric catalysis (Scheme 1). ${ }^{12}$

The synthesis of cyclic phosphines is anything but trivial. Generally, special reaction conditions such as liquid ammonia as solvent, ${ }^{13}$ slow fractional distillation for work-up or tedious multistep syntheses are necessary. ${ }^{6,12,14}$ This is accompanied by a lack of selectivity and low yields. In addition, sterically demanding substituents such as tert-butyl groups in the carbon backbone or phenyl groups attached to the phosphorus atom in the starting materials are necessary to stabilize the phosphorus-containing heterocycles by these approaches, which makes the access to the corresponding parent (P-H) compounds even more difficult. ${ }^{15,16}$ Very recently, Cummins
reported the synthesis of the parent phosphirane $\left(\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{P}\right)$, without the coordination towards $\mathrm{W}(\mathrm{CO})_{5,}{ }^{17}$ based on a multistep Nickel-catalzyed transfer reaction of tri-tertbutylphosphatetrahedrane. ${ }^{18}$ Other (parent) phosphorus containing heterocycles are usually accessable by low yields or less selective. ${ }^{19,20}$ Specifically, secondary cyclic phosphines are prepared by hydrolysis of sylilated or protonation of suitable precursors. ${ }^{18,21,22}$ However, the latter usually also have to be synthesized in a complex manner, using unselective conventional routes. ${ }^{21,22}$


BPE
bis(dimethylphospholano)ethane
DuPhos
cyclophoshamide cytostatic



oxaphosphetane transition state in Wittig reactions R, R', R", R"' = alkyl, aryl

this work

Scheme 1. Selected phosphorus heterocycles used in organocatalysis, ${ }^{12}$ pharamacy, ${ }^{23}$ industry ${ }^{11}$ as well as the parent phospholane.

Herein we report the synthesis of the precursor compounds [Cp*Fe\{n4-P5(CH2)n\}] (2: $\mathrm{n}=3 ; 3: \mathrm{n}=4 ; 4: \mathrm{n}=5 ; 5: \mathrm{n}=6$ ) and the easy and selective synthesis of cyclo-monophosphines of different ring size - phosphetane (6), phosphoane (7), phosphinane (8) and phosphepane (9), via nucleophilic phosphine abstraction by a pentaphosphaferrocene mediated route. ${ }^{24}$ The reaction of the spiro compounds 2-5 with nucleophiles leads to the formation of unprecedented heterocyclic parent phosphines 6-11.

### 6.3 Results

When reacting $\left[\mathrm{K}(\mathrm{dme})_{2}\right]_{2}\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\mathrm{n}^{5}-\mathrm{P}_{5}\right)\right]$ (I) with two equivalents of 1,3-dibromopropane, the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of the reaction solution exhibits sets of signals corresponding to two different $A M M^{\prime} X X$ ' spin systems. Chromatographic workup under inert conditions lead to the isolation of two complexes, $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left\{\mathrm{n}^{4}-\mathrm{P}_{5}\left(\mathrm{C}_{3} \mathrm{H}_{6} \mathrm{Br}\right)_{2}\right\}\right]$ (1) and $\left[C p^{*} F e\left\{\eta^{4}-P_{5}\left(C_{3} H_{6}\right)\right\}\right]$ (2) (Scheme 2). Complex 1 represents the expected reaction product and the molecular structure in the solid state exhibits, a $\eta^{4}-P_{5}$ moiety, bearing two 4-bromo-n-propyl substituents (Figure 1 and Fig. S42). XRD analysis of compound

2 reveals the formation of a phosphetane like ligand system (Figure 1). The formation can be explained by the initial formation of the ionic compound $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\mathrm{P}_{5}-\mathrm{C}_{3} \mathrm{H}_{6} \mathrm{Br}\right]^{-}\right.$, followed by an intramolecular salt metathesis reaction. This side reaction competes with the formation of 1 . However, the formation of 1 cannot be supressed by using a 1:1 stochiometric ratio between I and 1,3-dibromopropane. By using a 1:2 ratio, the yields of both products $\mathbf{1}$ and $\mathbf{2}$ are similar (cf. SI).

To be noted, the use of 1,2-dibromoethane does lead in a redox process, to the formation of $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right]\left(\mathrm{I}^{\prime}\right), \mathrm{KCl}$ and ethene.

When I is reacted with 1,4-dibromobutane, without using dilation conditions, [Cp*Fe\{n $\left.\left.{ }^{4}-\mathrm{P}_{5}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)\right\}\right]$ (3) can be isolated in 71 \% yield (Scheme 2). This shows that there is an intrinsic driving force to form homocyclic products than monosubstituted bromofunctional alkyl derivatives. The structure in the solid state was proven by XRD (Fig. S44) and reveals a spirocyclic phospholane-type ligand. When reacting I with one equivalent of 1,5 -dibromopentane (Scheme 2), the ${ }^{31} P\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of the reaction solution exhibits, in analogy to the reaction of I with 1,3-dibromopropane, two different (AMM'XX') spin systems in a ratio of $10: 1$, whereas the major compound can be assigned to complex 4 (Fig. S52). After chromatographic workup, solely complex $\left[C p^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}\left(\mathrm{C}_{5} \mathrm{H}_{10}\right)\right\}\right]$ (4) can be isolated in $61 \%$ yield. A second product (minor component) cannot be isolated and decomposes during the chromatographic workup. An investigation of the reaction mixture, before workup, by mass spectrometry revealed no relevant, additional $\mathrm{Cp}^{*} \mathrm{FeP}_{\mathrm{n}}$-containing species. Similarely, I reacts with one equivalent of 1,6-dibromohexane (scheme 2), leading to $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}\left(\mathrm{C}_{6} \mathrm{H}_{12}\right)\right\}\right]$ (5), which was isolated in $30 \%$ yield. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of the reaction solution shows the formation of two other $\mathrm{Cp}^{*} \mathrm{FeP}_{\mathrm{n}}$-containing species with spin systems of higher order (Fig. S53) in an overall ratio of 1:1 to complex 5 . Mass spectrometric analysis of the reaction solution in combination with ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR data (Fig. S53) of the reaction mixture, strongly suggests the additional formation of $\left[\left\{\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}\right)\right\}_{2}\left(\mathrm{C}_{6} \mathrm{H}_{12}\right)\right]$ in which the two $\left\{\mathrm{Cp}^{*} \mathrm{FeP}_{5}\right\}$ moieties are bridged via two $n$-hexyl units. Unfortunately, the second compound decomposes during chromatographic workup and could not be isolated and further characterised.


Scheme 2. Reactivity of I towards: a) 1,3-dibromopropane; b) 1,4-dibromobutane; c) 1,5-dibromopentane; d) 1,6dibromohexane. (Yields are given in parenthesis)


Figure 1. Molecular structure of 2 - 5 in the solid state; Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at 50\% probability; Cp ligands are drawn in a wire frame model.

Compounds 2-5 were fully characterized by XRD, Mass spectrometry, NMR spectroscopy and elemental analysis. They represent complexes of a rare class of phosphet-, phosphol-, phosphine- and phosphepanes-like spirocyclic ligand containing complexes which can be easily synthesised.

Knowing that a double substituted phosphorus atom can be removed from the $\mathrm{P}_{5}$ unit of the Cp*Fe fragment, ${ }^{24}$ this strategy was also applied for compounds 2 - 5. It paved the way for a novel synthetic route for substituted phosphet-, phosphol- and phosphirane derivatives, starting from white phosphorus, where the side product $[\mathrm{K}]\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{4}\right)\right]$ can be recycled in a "semi-catalytic-cyclic-process". ${ }^{24}$ When reacting compound 2-5 with one equivalent of potassium benzyl (KBnz) at $-80^{\circ} \mathrm{C}$ in THF, the corresponding phosphetane (PBnz\{( $\left.\left.\mathrm{CH}_{2}\right)_{3}\right\}$; 6), phospholane (PBnz\{(CH2)4\}; 7), phosphinane $\left(\operatorname{PBnz}\left\{\left(\mathrm{CH}_{2}\right)_{5}\right\} ;\right.$ 8) and phosphepane (PBnz\{( $\left.\left.\mathrm{CH}_{2}\right)_{6}\right\}$; 9) (Scheme 2) can be isolated as colourless viscous liquids after extraction with $n$-pentane and slow removal of the solvent under reduced pressure in yields of $60-80 \%$ (Scheme 2). The identity of the phosphines was proven by NMR spectroscopy and, after oxidation with sulphur to the corresponding phosphine sulphides (cf. compounds 6' - 9'), also by single crystal X-ray diffraction analysis (Figure 2 and S47-50). Via this procedure compounds 6-9 can be easily and selectively synthesised without the need of bulky substituents on the phosphorus atom or special starting materials, also in much better overall yields.

2. $n=1$
2. $n=1$
3: $n=2$

4: $n=3$
5: $n=4$

6
$(60 \%)$


6
$80 \%)$


6
$73 \%)$


6
$(80 \%)$

Scheme 2. Reactivity of 2 - 5 towards KBnz. (Yields are given in parenthesis; *NMR yield with $\mathrm{PPh}_{3}$ capillary as internal standard; cf. SI ; Note that the yields given in parenthesis are not optimized).

Furthermore, we were interested whether it is possible to use other nucleophiles than KBnz to cleave off the phosphine. It has to be noted that MeLi and PhLi does not lead to the formation of the corresponding phosphines. However, using KPh shows the formation of phenylphospholane ${ }^{15}$ in the reaction of 3 with KPh. An interesting class of substances are secondary phosphines, representing functionalizeable compounds which can be converted to many different products e.g. phosphanides or act as ligands itself. As stated before, in order to synthesize cyclic secondary phosphines harsh or cumbersome reactions conditions are needed. And even then, the reactions are not very selective, limited in its scope and long-lasting workup by fractional distillation is necessary. Therefore, $\mathrm{LiAlH}_{4}$ was used as a hydride source to cleave of the $\mathrm{R}_{2} \mathrm{P}$ unit from 2-5. The reaction of compound 4 and 5 with $\mathrm{LiAlH}_{4}$ leads to the formation of the desired parent-phosphinine $\left(\mathrm{HP}\left(\mathrm{C}_{5} \mathrm{H}_{10}\right)\right)$ in $71 \%$ and -phosphepane $\left(\mathrm{HP}\left(\mathrm{C}_{6} \mathrm{H}_{12}\right)\right)$ in $73 \%$ yield, respectively, according to NMR spectroscopy (Fig. S56 and S57). The ${ }^{31} \mathrm{P} /{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR
data are in agreement with those products reported in the literature. ${ }^{21,22}$ To our surprise, (parent-)phospholane $\left(\mathrm{HP}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)\right)$ has not been reported so far. To validate the versatility of this synthetic procedure, we reacted 3 with $\mathrm{LiAlH}_{4}$ in THF - $\mathrm{d}_{8}$ (Scheme 3), leading to the parent phospholane $\left(\mathrm{HP}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)\right)(10 \mathrm{~b})$, which can be distilled off from the reaction mixture $\left(1 \cdot 10^{-3} \mathrm{mbar}\right.$, $60^{\circ} \mathrm{C}, 30$ minutes) and isolated as a THF- $\mathrm{d}_{8}$ solution in $68 \%$ yield.


Scheme 3. Reactivity of 3 towards $\mathrm{LiAlH}_{4}$.

The ${ }^{31} \mathrm{P}$ NMR spectra (THF- $\mathrm{d}_{8}$ ) of 10 b shows a doublet of triplet at $\delta=-70.8 \mathrm{ppm}$ $\left({ }^{1} \mathrm{JP}_{\mathrm{P}-\mathrm{H}}=187 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=21 \mathrm{~Hz}\right.$ ) (Fig. S25 and S26). To determine its molecular structure, compound 10b was reacted with $\left[(\mathrm{PhCN})_{2} \mathrm{Cl}_{2} \mathrm{Pt}\right]$, leading to complex 11 (Scheme 3). The molecular structure of $\mathbf{1 1}$ in the solid state (Figure 2) reveals the expected formation of the parent phospholane 10b, coordinating to a $\left[\mathrm{PtCl}_{2}\right]$ unit in a $\eta^{1}$-fashion, forming the square planar complex $\left[\left(\left\{\mathrm{C}_{4} \mathrm{H}_{8}\right\} \mathrm{PH}\right)_{2} \mathrm{PtCl}_{2}\right]$ (11) (Figure 2).


Figure 2. Molecular structure of $8^{\prime}$ (left) and 11 (right) in the solid state; Hydrogen atoms of 8' are omitted for clarity; thermal ellipsoids are drawn at $50 \%$ probability.

The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right)$ of 11 shows a singulet at $\delta=-15.4 \mathrm{ppm}$ with ${ }^{195} \mathrm{Pt}$ satellites ( ${ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{Pt}}=3384 \mathrm{~Hz}$ ). The corresponding ${ }^{31} \mathrm{P}$ NMR spectrum $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right)$ of 11 ' shows a doublet (at $\delta=-15.4 \mathrm{ppm}$ ) with a ${ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}$ coupling constant of 377 Hz . The NMR data are in agreement with similar secondary phosphines, coordinating to platinum ${ }^{25}$ and proves in combination with the corresponding FD-MS data of 11 unarguably the identity of the parentphospholane $\mathrm{HP}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)(10 b)$. It has to be noted that the reaction of 2 with $\mathrm{LiAlH}_{4}$ leads presumable to the formation of the desired (parent-)phosphetane ( $\mathrm{HP}\left(\mathrm{C}_{3} \mathrm{H}_{6}\right)$ ). According to ${ }^{31} \mathrm{P}$ NMR spectroscopy, this cyclic phosphine (10a) is formed ( $\delta=-29.1 \mathrm{ppm}\left({ }^{1}{ }_{\mathrm{P}-\mathrm{H}}=164 \mathrm{~Hz}\right.$, ${ }^{2} J_{\mathrm{P}-\mathrm{H}}=18 \mathrm{~Hz}$ ) (Fig. S54) in $42 \%$ yield alongside with unidentified volatile sideproduct, which can unfortunately not be separated from 10a. ${ }^{31}$ P NMR spectra of the distillate suggest the formation of an asymmetric secondary di-phosphine alongside of 10a (Fig. S58).

### 6.4 Conclusion

In summary, the reaction of the dianionic polyphosphorus complex I with 1,3-dibromopropane yields the functionalize-able complex $\mathbf{1}$ as well as the phosphetane-like ligand complex $\mathbf{2}$. When increasing the chain length of the di-bromoalkanes, the formation of the analog two-fold substituted 1 is not observed. Instead, the intramolecular salt metathesis reaction is favoured and the corresponding free phospholane- and phosphinane-type spirocyclic ligands are obtained in high to moderate yields, respectively. When reacting I with 1,6-dibromo-hexane, a rare seven membered phosphepane-like ligand complex 5 can be isolated. Given the different alkyl chain lengths, the trend is given to yield functionalization and ring formation for 1,3-dibromopropane, exclusively cyclisation when using 1,4-dibromobutane and ring formation and (presumable) linkage of two $\mathrm{Cp}^{*} \mathrm{FeP}_{5}$ moieties with longer alkyl chains. Moreover, the complexes 2-5 represents very versatile precursors for the synthesis of the corresponding free phosphines, by a nucleophilic phosphine abstraction reaction. The presented synthetic route offers a great variability towards different reagents and can easily be extended, without the usage of large steric substituents. By this way, the parent phosphetane, phospholane, phosphinane and phosphepane ( $6-9$ ) ring compounds could be synthesized in good yields. This procedure can be easily extended to other organo substituted ring compounds. In addition to this we demonstrated that it is also possible to synthesis secondary phosphines via this route, as represented by the parent-phosphetane $\mathrm{HP}\left(\mathrm{C}_{3} \mathrm{H}_{6}\right)(10 \mathrm{a})$ as well as parent-phospholane $\mathrm{HP}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)(10 b)$, which have been synthesized for the very first time. This strategy paves the way for having access to secondary phosphines, as a whole class of substances, in a straight forward way. This work was supported by the Deutsche Forschungsgemeinschaft within the project Sche 384/38-2. S.R is grateful to the Studienstiftung des Deutschen Volkes for PhD fellowship.

## Conflicts of interest

There are no conflicts to declare.

## Author Contributions

Conceptualization: SR, GB, MS
Investigation: SR
Visualization: SR
Funding acquisition: MS
Project administration: GB, MS
Supervision: GB, MS
Writing - original draft: SR
Writing - review \& editing: SR, GB, MS

### 6.5 References

L. D. Quin and J. A. Tyrell, Fundamentals of Heterocyclic Chemistry: Importance in Nature and in the Synthesis of Pharmaceuticals, Wiley \& Sons Lfd, 1st edn., 2010.
H. Guo, Y. C. Fan, Z. Sun, Y. Wu and O. Kwon, Chem. Rev., 2018, 118, 10049-10293.
L. Pignolet, Homogeneous Catalysis with Metal Phosphine Complexes, Springer US, Boston, MA, 1983.

The Nobel Prize in Chemistry 2001, https://www.nobelprize.org/prizes/chemistry/2001/summary/.
The Nobel Prize in Chemistry 2021, https://www.nobelprize.org/prizes/chemistry/2021/summary/.
P. C. J. Kamer and P. W. N. van Leeuwen, Phosphorus(III) Ligands in Homogeneous Catalysis: Design and Synthesis, John Wiley \& Sons, Ltd, Chichester, UK, 2012.
A. L. Clevenger, R. M. Stolley, J. Aderibigbe and J. Louie, Chem. Rev., 2020, 120, 61246196.
J. F. Teichert, Homogeneous Hydrogenation with Non-Precious Catalysts, Wiley, 2019.
K. Dimroth, in Comprehensive Heterocyclic Chemistry, eds. A. R. Katritzky and C. W. B. T.-C. H. C. Rees, Elsevier, Oxford, 1984, pp. 493-538.
H. Shet, U. Parmar, S. Bhilare and A. R. Kapdi, Org. Chem. Front., 2021, 8, 1599-1656. BASF, DBP 954247, 1956.
A. Marinetti and D. Carmichael, Chem. Rev., 2002, 102, 201-230.
R. I. Wagner, L. D. Freeman, H. Goldwhite and D. G. Rowsell, J. Am. Chem. Soc., 1967, 89, 1102-1104.
R. Emrich and P. W. Jolly, Synthesis (Stuttg)., 1993, 39-40.
R. A. Baber, M. F. Haddow, A. J. Middleton, A. G. Orpen, P. G. Pringle, A. Haynes, G. L. Williams and R. Papp, Organometallics, 2007, 26, 713-725.
F. Mathey and M. Regitz, in Comprehensive Heterocyclic Chemistry II, Elsevier, 1996, pp. 277-304.
A. A. Khan, P. Junker, G. Schnakenburg, A. Espinosa Ferao and R. Streubel, Chem. Commun., 2019, 55, 9987-9990.
M.-L. Y. Riu, A. K. Eckhardt and C. C. Cummins, J. Am. Chem. Soc., 2022, 144, 75787582.
K. Issleib and S. Häusler, Chem. Ber., 1961, 94, 113-117.
F. Mathey, in Category 5, Compounds with One Saturated Carbon Heteroatom Bond, eds. Mathey and Trost, Georg Thieme Verlag, Stuttgart, 2009.
D. M. Schubert and A. D. Norman, Inorg. Chem., 1984, 23, 4130-4131.

22
D. M. Schubert, M. L. J. Hackney, P. F. Brandt and A. D. Norman, Phosphorus, Sulfur Silicon Relat. Elem., 1997, 123, 141-160.

23 A. Emadi, R. J. Jones and R. A. Brodsky, Nat. Rev. Clin. Oncol., 2009, 6, 638-647.
24 S. Reichl, E. Mädl, F. Riedlberger, M. Piesch, G. Balázs, M. Seidl and M. Scheer, Nat. Commun., 2021, 12, 5774.

25 M. R. Eberhard, E. Carrington-Smith, E. E. Drent, P. S. Marsh, A. G. Orpen, H. Phetmung and P. G. Pringle, Adv. Synth. Catal., 2005, 347, 1345-1348.

### 6.6 Supplementary Information

# Novel Synthetic Route for (parent) Phosphet-, Phosphol-, Phosphinand Phosphepanes 

Stephan Reichl, ${ }^{1}$ Gábor Balázs, ${ }^{1}$ Manfred Scheer ${ }^{1 *}$<br>${ }^{1}$ Institute of Inorganic Chemistry, University of Regensburg; Universitätsstraße 31, 93053 Regensburg, Germany. *Corresponding author. Email: manfred.scheer@chemie.uni-regensburg.de

Table of Content

1. Experimental details 185
2. NMR spectroscopic characterization 190
3. Crystallographic details 208
4. Additional Information 218
5. References 220

## 1. Experimental details

## General methods:

All manipulations were carried out under an inert atmosphere of dried argon using standard Schlenk and glove box techniques. 1,2-dimethoxyethane (DME) was dried and deoxygenated by distillation under argon atmosphere from sodium. Ortho-diflourobenze (o-DFB) was dried and deoxygenated by distillation under argon atmosphere from $\mathrm{P}_{2} \mathrm{O}_{5}$. All other solvents were dried using a MB SPS-800 device of the company MBRAUN and stored over molecular sieve. NMR spectra were recorded on a Bruker Avance III $400 / 600 \mathrm{MHz}$ NMR spectrometer. Chemical shifts were measured at ambient temperature and are given in ppm; they are referenced to TMS for ${ }^{1} \mathrm{H}$ and $85 \% \mathrm{H}_{3} \mathrm{PO}_{4}$ for ${ }^{31} \mathrm{P}$ as external standard. Signal multiplicities are described using common abbreviations: $s$ (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet) and br (broad). LIFDI-/FD-/EI-MS spectra (LIFDI = liquid injection field desorption ionization, $\mathrm{FD}=$ field desorption, $\mathrm{EI}=$ electron ionization) were measured on a JEOL AccuTOF GCX. Elemental analysis (CHN) was determined using a Vario micro cube instrument. A glass stirring bar was used in reactions with potassium benzyl.

The compounds potassium benzyl $\left(\mathrm{KBnz}, \mathrm{KC}_{7} \mathrm{H}_{7}\right)$ and $\left[\mathrm{K}(\mathrm{dme})_{2}\right]_{2}\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}\right)\right]$ (I) were synthesized according to literature procedures. ${ }^{[i, i i]} \mathrm{LiAlH}_{4}$ was purified by extraction with $\mathrm{Et}_{2} \mathrm{O}$ and filtration over diatomaceous earth. Modified Synthesis of I: Reduction of I' with $\mathrm{KC}_{8}$ in DME or THF and used insitu.

Unless otherwise noted, all other materials were obtained from commercial suppliers and used without purification.
Crystals suitable for single crystal X-ray diffraction analysis were obtained as described below. The diffraction data were collected either on a Gemini Ultra diffractometer equipped with an Atlas ${ }^{52}$ CCD detector and with a fine-focus sealed $\mathrm{Cu}-\mathrm{K}_{\alpha} \mathrm{X}$-ray tube, on a XtaLAB Synergy R, DW system diffractometer equipped with a HyPix-Arc 150 detector and a rotating-anode $\mathrm{Cu}-\mathrm{K}_{\alpha} \mathrm{X}$-ray tube or a GV50 diffractometer equipped with a Titan ${ }^{\mathrm{S} 2} \mathrm{CCD}$ detector and a micro-focus $\mathrm{Cu}-\mathrm{K}_{\alpha} \mathrm{X}$-ray tube. Data collection and reduction were performed with CrysAlisPro software package. The structures were solved with Olex 2 , ${ }^{\text {[ii] }]}$ using SheIXT ${ }^{[i v]}$ and a least-square refinement on $F^{2}$ was carried out with ShelXL ${ }^{[v]}$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms at the carbon atoms were located in idealized positions and refined with isotropic displacement parameters according to the riding model. The images of the molecular structures were made using Olex2. ${ }^{\text {[iii] }}$ All NMR simulations were conducted with the WinDaisy application within the NMR software Top Spin 4.1.1 by Bruker.

## Synthetic protocols:

## Reaction of $\left[\mathrm{K}(\mathrm{dme})_{2}\right]_{2}\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}\right)\right]$ (I) with 1,3-dibromopropane:

A solution of insitu generated $I\left(\left[C p^{*} F e\left(\eta^{5}-P_{5}\right)\right]\left(I^{\prime}\right): 2 \mathrm{mmol}, 691.9 \mathrm{mg}, 1 \mathrm{eq} ; \mathrm{KC}_{8}: 2.2 \mathrm{mmol}, 593.8 \mathrm{mg}, 2.2 \mathrm{eq}\right.$, $)$ in DME was slowly added to a 0.917 molar solution of 1,3 -dibromopropane in DME ( $2 \mathrm{mmol}, 2.2 \mathrm{~mL}, 1 \mathrm{eq}$ ) at $-50^{\circ} \mathrm{C}$. A colour change from brown to green occurred and a colourless solid was formed. The mixture was stirred for three hours. The solvent was removed under reduced pressure. The residue was dissolved in dichloromethane, silica is added and the solvent was removed in vacuo. The preabsorbed reaction mixture was purified via column chromatography ( $\mathrm{SiO}_{2}$, hexane, $8 \times 2 \mathrm{~cm}$ ). Using a mixture of $n$-hexane/dichloromethane (10:1), a first green fraction of $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\mathrm{n}^{4}-\mathrm{P}_{5}\left(\mathrm{C}_{3} \mathrm{H}_{6}\right)\right\}\right]$ (2), followed by a brown one of $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left\{n^{4}-\mathrm{P}_{5}\left(\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br}\right)_{2}\right\}\right]$ (1) can be eluted, changing increasing the dichloromethane/ $n$-hexane ratio to $1: 1$. The solvent of both fractions was removed under reduced pressure. $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left\{\mathrm{n}^{4}-\mathrm{P}_{5}\left(\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br}\right)_{2}\right\}\right]$ (1) can be isolated as dark green blocks after one week via layering a
dichloromethane ( 3 mL ) solution with acetonitrile ( 7 mL ) and stored at $-30^{\circ} \mathrm{C}$. $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left\{\mathrm{n}^{4}-\mathrm{P}_{5}\left(\mathrm{C}_{3} \mathrm{H}_{6}\right)\right\}\right]$ (2) can be obtained analogous as red/greenish plates.

## Data for $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\boldsymbol{n}^{4}-\mathrm{P}_{5}\left(\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br}\right)_{2}\right\}\right](1)$ :

Yield: $310.1 \mathrm{mg}(0.526 \mathrm{mmol}, 26 \%) .{ }^{1} \mathrm{H} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=2.90\left(\mathrm{t}, 2 \mathrm{H}, \mathrm{J}_{\mathrm{H}-\mathrm{H}}=6.20 \mathrm{~Hz},-\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{2}-\mathrm{Br}\right)$, $2.45\left(\mathrm{t}, 2 \mathrm{H}, \mathrm{J}_{\mathrm{H}-\mathrm{H}}=6.35 \mathrm{~Hz},-\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{2}-\mathrm{Br}\right), 2.14\left(\mathrm{~m}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{3}-\mathrm{Br}\right), 1.84\left(\mathrm{~m}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{3}-\mathrm{Br}\right), 1.61\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right)_{5}$, $1.03\left(\mathrm{~m}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{3}-\mathrm{Br}\right), 0.47\left(\mathrm{~m}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{3}-\mathrm{Br}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=136.0\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 36.4(\mathrm{~m}$, $\left.2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}\right),-131.4\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\left.\mathrm{x}, \mathrm{x}^{\prime}\right) .}{ }^{31} \mathrm{P}\right.$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=136.0\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 36.4\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}\right),-131.4(\mathrm{~m}$, $\left.2 P, P_{x, x^{\prime}}\right)$. For coupling constants, see Table S1. LIFDI-MS (toluene): $m / z=589.86\left(100 \%,[M]^{+}\right)$. analysis (calcd., found for $\left.\mathrm{C}_{16} \mathrm{H}_{27} \mathrm{FeBr}_{2} \mathrm{P}_{5}\right): \mathrm{C}(32.58,33.09), \mathrm{H}(4.61,4.58)$.

## Data for $\left[C p^{*} \mathrm{Fe}\left\{\mathrm{n}^{4}-\mathrm{P}_{5}\left(\mathrm{C}_{3} \mathrm{H}_{6}\right)\right\}\right]$ (2):

Yield: $232.3 \mathrm{mg}(0.599 \mathrm{mmol}, 30 \%) .{ }^{1} \mathrm{H} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=2.74\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}_{5}\left(\mathrm{C}_{3} \mathrm{H}_{6}\right)\right), 1.58(\mathrm{~s}, 15 \mathrm{H}$, $\left.\mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 1.42\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}_{5}\left(\mathrm{C}_{3} \mathrm{H}_{6}\right)\right), 0.88\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}_{5}\left(\mathrm{C}_{3} \mathrm{H}_{6}\right)\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=125.4\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right)$, $43.5\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}\right),-89.3\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{X}, \mathrm{K}^{\prime}}\right) .{ }^{31} \mathrm{P}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=125.4\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 43.5\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}\right)$, -89.3 ( $m, 2$ P, $P_{x, x^{\prime}}$ ). For coupling constants, see Table S2. FD-MS (toluene): $m / z=387.97$ (100 \%, [M] $]^{+}$. analysis (calcd., found for $\mathrm{C}_{13} \mathrm{H}_{21} \mathrm{FeP}_{5}$ ): $\mathrm{C}(40.24,40.39)$, $\mathrm{H}(5.46,5.32)$.

The usage of two equivalents of 1,3-dibromopropane in the analog reaction setup does lead to complex 1 in $25 \%$ and complex 2 in $27 \%$ yield, respectively.

## Reaction of I with 1,4-dibromobutane:

A solution of insitu generated $I\left(\left[C p^{*} F e\left(\eta^{5}-P_{5}\right)\right]\left(I^{\prime}\right): 2 \mathrm{mmol}, 691.9 \mathrm{mg}, 1 \mathrm{eq} ; \mathrm{KC}_{8}: 2.2 \mathrm{mmol}, 593.8 \mathrm{mg}, 2.2 \mathrm{eq}\right.$, in THF was cooled to $-80^{\circ} \mathrm{C}$ and slowly added to a 0.9263 molar solution of 1,4 -dibromobutane in DME ( $8 \mathrm{mmol}, 8.6 \mathrm{~mL}$, 4 eq). A colour change from brown to green occurred and a colourless solid was formed. The mixture was stirred for 12 hours. The solvent was removed under reduced pressure. The residue was dissolved in dichloromethane, silica is added and the solvent was removed in vacuo. The preabsorbed reaction mixture was purified via column chromatography $\left(\mathrm{SiO}_{2}\right.$, hexane, $\left.10 \times 3 \mathrm{~cm}\right)$. Using a mixture of $n$-hexane/dichloromethane ( $8: 1$ ), a green/brownish fraction of $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)\right\}\right]$ (3), followed by a very small brown one can be eluted. The second one showed decomposition during the column chromatography and workup and could not be identified. The solvent of the first fraction was removed under reduced pressure. Compound 3 can be isolated as dark green prism after one week via layering a dichloromethane $(3 \mathrm{~mL})$ solution with acetonitrile $(7 \mathrm{~mL})$ and stored at $-30^{\circ} \mathrm{C}$.

## Data for $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left\{\mathrm{n}^{4}-\mathrm{P}_{5}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)\right\}\right]$ (3)

Yield: $570.9 \mathrm{mg}(1.42 \mathrm{mmol}, 71 \%) .{ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=2.34\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}_{5}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)\right), 1.64\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right)$, $1.14\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}_{5}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)\right), 0.79\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}_{5}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)\right), 0.43\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}_{5}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=$ $145.4\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 38.3\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}\right),-117.4\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{x}, \mathrm{X}^{\prime}}\right) .{ }^{31} \mathrm{P} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=145.4\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right)$,
 (100 \%, [M] ${ }^{+}$). analysis (calcd., found for $\mathrm{C}_{14} \mathrm{H}_{23} \mathrm{FeP}_{5}$ ): $\mathrm{C}(41.82,42.27), \mathrm{H}(5.77,5.73)$.

## Reaction of I with 1,5-dibromopentane:

A solution of insitu generated I ([Cp*Fe( $\left.\left.\eta^{5}-\mathrm{P}_{5}\right)\right]\left(\mathrm{I}^{\prime}\right): 2 \mathrm{mmol}, 691.9 \mathrm{mg}, 1 \mathrm{eq} ; \mathrm{KC}_{8}: 2.2 \mathrm{mmol}, 593.8 \mathrm{mg}, 2.2 \mathrm{eq}$, in THF was cooled to $-80{ }^{\circ} \mathrm{C}$ and slowly added to a 1.6053 molar solution of 1,5 -dibromopentane in DME ( $2 \mathrm{mmol}, 1.2 \mathrm{~mL}, 1 \mathrm{eq}$ ). The workup is analogous to the reaction above. $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left\{\mathrm{n}^{4}-\mathrm{P}_{5}\left(\mathrm{C}_{5} \mathrm{H}_{10}\right)\right\}\right]$ (4) can be isolated as
dark green blocks after one week via layering a dichloromethane $(2 \mathrm{~mL})$ solution with acetonitrile $(10 \mathrm{~mL})$ and stored at $-30^{\circ} \mathrm{C}$.

## Data for $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\mathrm{n}^{4}-\mathrm{P}_{5}\left(\mathrm{C}_{5} \mathrm{H}_{10}\right)\right\}\right]$ (4):

Yield: $507.6 \mathrm{mg}(1.22 \mathrm{mmol}, 61 \%) .{ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=2.08\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}_{5}\left(\mathrm{C}_{5} \mathrm{H}_{10}\right)\right), 1.64(\mathrm{~s}, 15 \mathrm{H}$, $\left.\mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 1.57\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}_{5}\left(\mathrm{C}_{5} \mathrm{H}_{10}\right)\right), 0.71\left(\mathrm{~m}, 4 \mathrm{H},-\mathrm{P}_{5}\left(\mathrm{C}_{5} \mathrm{H}_{\underline{10}}\right)\right)^{*}, 0.52\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}_{5}\left(\mathrm{C}_{5} \mathrm{H}_{10}\right)\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right):$ $\delta[\mathrm{ppm}]=127.4\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 33.0\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}\right),-136.0\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{x}, \mathrm{X}^{\prime}}\right) .{ }^{31} \mathrm{P} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=127.4(\mathrm{~m}, 1$
 416.06 (100 \%, [ M$]^{+}$). analysis (calcd., found for $\mathrm{C}_{15} \mathrm{H}_{25} \mathrm{FeP}_{5}$ ): $\mathrm{C}(43.30,42.90), \mathrm{H}(6.06,6.09)$.
*: overlay of two signals

## Reaction of I with 1,6-dibromohexane:

A solution of insitu generated $\mathrm{I}\left(\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\mathrm{n}^{5}-\mathrm{P}_{5}\right)\right]\left(\mathrm{I}^{\prime}\right): 2 \mathrm{mmol}, 691.9 \mathrm{mg}, 1 \mathrm{eq} ; \mathrm{KC}_{8}: 2.2 \mathrm{mmol}, 593.8 \mathrm{mg}, 2.2 \mathrm{eq}\right.$, ) in THF was cooled to $-80^{\circ} \mathrm{C}$ and slowly added to a 0.1064 molar solution of 1,6 -dibromohexane in DME ( $2 \mathrm{mmol}, 18.8 \mathrm{~mL}$, 1 eq). The workup is analogous to the reaction above. [ $\left.\mathrm{Cp}{ }^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}\left(\mathrm{C}_{6} \mathrm{H}_{12}\right)\right\}\right]$ (5) can be isolated as dark red plates after one week via layering a dichloromethane $(2 \mathrm{~mL})$ solution with acetonitrile $(10 \mathrm{~mL})$ and stored at $-30^{\circ} \mathrm{C}$.

## Data for $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\mathrm{n}^{4}-\mathrm{P}_{5}\left(\mathrm{C}_{6} \mathrm{H}_{12}\right)\right\}\right]$ (5):

Yield: $257.6 \mathrm{mg}(0.599 \mathrm{mmol}, 30 \%) .{ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=2.46\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}_{5}\left(\mathrm{C}_{6} \mathrm{H}_{12}\right)\right), 1.66(\mathrm{~s}, 15 \mathrm{H}$, $\left.\mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 1.52\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}_{5}\left(\mathrm{C}_{6} \mathrm{H}_{12}\right)\right), 1.14\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}_{5}\left(\mathrm{C}_{6} \mathrm{H}_{\underline{12}}\right)\right), 0.87\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}_{5}\left(\mathrm{C}_{6} \mathrm{H}_{12}\right)\right), 0.75\left(\mathrm{~m}, 4 \mathrm{H},-\mathrm{P}_{5}\left(\mathrm{C}_{6} \mathrm{H}_{12}\right)\right)^{*}$. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=145.0\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 34.8\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}\right),-128.5\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{x}, \mathrm{X}^{\prime}}\right) .{ }^{31} \mathrm{P}$ NMR ( $\mathrm{C}_{6} \mathrm{D}_{6}$, $293 \mathrm{~K}): \delta[\mathrm{ppm}]=145.0\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 34.8\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}\right),-128.5\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{X}, \mathrm{X}^{\prime}}\right)$. For coupling constants, see Table S5. FD-MS (toluene): $m / z=430.07\left(100 \%,[M]^{+}\right)$. analysis (calcd., found for $\left.\mathrm{C}_{16} \mathrm{H}_{27} \mathrm{FeP}_{5}\right)$ : $\mathrm{C}(44.68,44.85), \mathrm{H}(6.33,6.43)$.
*: overlay of two signals
General Synthesis of 1-Benzylphosphetane (6), 1-Benzylphospholane (7), 1-Benzylphosphinane (8) and 1-Benzylphosphepane (9):

Compound 2 ( $0.15 \mathrm{mmol}, 58.2 \mathrm{mg}, 1 \mathrm{eq}), \mathbf{3}(0.15 \mathrm{mmol}, 60.3 \mathrm{mg}, 1 \mathrm{eq}), 4(0.15 \mathrm{mmol}, 62.4 \mathrm{mg}, 1 \mathrm{eq})$ or $5(0.1 \mathrm{mmol}$, 43.0 mg , 1 eq ) were dissolved in THF and cooled to $-80^{\circ} \mathrm{C}$. To the solution, a $-80^{\circ} \mathrm{C}$ cold solution of $\mathrm{KBnz}(0.15$ $\mathrm{mmol} / 19.5 \mathrm{mg}$ for $\mathbf{2 - 4 , ~} 0.1 \mathrm{mmol} / 13.0 \mathrm{mg}$ for $5,1 \mathrm{eq}$ ) in THF was added, respectively. The colour changed to dark red and rapidly back to brownish-green. The solution was stirred overnight and allowed to reach room temperature. The solvent was slowly removed under reduced pressure. The oily residue was extracted with $n$-pentane ( $3 \times 5 \mathrm{~mL}$ ) and filtered over diatomaceous earth. The solvent was removed in vacuo and compounds 6-9 can be isolated as viscous liquids.

## Data for 1-Benzylphosphetane (6):

Yield: $14.8 \mathrm{mg}(0.09 \mathrm{mmol}, 60 \%) .{ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=7.06(\mathrm{~m}, 5 \mathrm{H}, \mathrm{Ph}), 2.82\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{p}-\mathrm{H}}=73.7 \mathrm{~Hz}, 2 \mathrm{H},-\right.$ $\left.\mathrm{CH}_{2}-\mathrm{Ph}\right), 1.65\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}\left(\mathrm{C}_{3} \mathrm{H}_{6}\right)\right.$ ), $1.36\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}\left(\mathrm{C}_{3} \mathrm{H}_{6}\right)\right), 0.87\left(\mathrm{~m}, 4 \mathrm{H},-\mathrm{P}\left(\mathrm{C}_{3} \mathrm{H}_{6}\right)\right)^{*} .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]$ $=14.1(\mathrm{~s}) .{ }^{31} \mathrm{P}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=14.1(\mathrm{~m}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=128.9\left(\mathrm{~d}, \mathrm{~J}_{\mathrm{p}-\mathrm{c}}=5.2 \mathrm{~Hz}\right.$, Ph), $128.4\left(\mathrm{~d}, \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=1.5 \mathrm{~Hz}, \mathrm{Ph}\right), 128.3\left(\mathrm{~d}, \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=20.4 \mathrm{~Hz}, \mathrm{Ph}\right), 37.7\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=20.9 \mathrm{~Hz},-\left(\mathrm{CH}_{2}\right)-\mathrm{Ph}\right), 23.1\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=\right.$ $\left.2.0 \mathrm{~Hz},-\mathrm{P}\left(\underline{C}_{3} \mathrm{H}_{6}\right)\right), 18.8\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=5.1 \mathrm{~Hz},-\mathrm{P}\left(\underline{C}_{3} \mathrm{H}_{6}\right)\right)$.
*: overlay of two signals

## Data for 1-Benzylphospholane (7):

Yield: $21.4 \mathrm{mg}(0.12 \mathrm{mmol}, 80 \%) .{ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=7.07(\mathrm{~m}, 5 \mathrm{H}, \mathrm{Ph}), 2.42\left(\mathrm{~s}, \mathrm{br},-\mathrm{CH}_{2}-\mathrm{Ph}\right), 1.53(\mathrm{~m}$, $\left.2 \mathrm{H},-\mathrm{P}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)\right), 1.37\left(\mathrm{~m}, 6 \mathrm{H},-\mathrm{P}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=-16.3(\mathrm{~s}) .{ }^{31} \mathrm{P}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta$ $[p p m]=-16.3(\mathrm{~s}, \mathrm{br}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=139.2\left(\mathrm{~d}, \mathrm{~J}_{\mathrm{p}-\mathrm{c}}=5.3 \mathrm{~Hz}, \mathrm{Ph}\right), 129.1\left(\mathrm{~d}, \mathrm{~J}_{\mathrm{p}-\mathrm{c}}=5.7 \mathrm{~Hz}, \mathrm{Ph}\right)$, $128.4\left(\mathrm{~d}, J_{\mathrm{P}-\mathrm{c}}=1.3 \mathrm{~Hz}, \mathrm{Ph}\right), 125.6\left(\mathrm{~d}, J_{\mathrm{P}-\mathrm{c}}=2.4 \mathrm{~Hz}, \mathrm{Ph}\right), 35.5\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=21.9 \mathrm{~Hz},-\left(\mathrm{CH}_{2}\right)-\mathrm{Ph}\right), 27.5\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=\right.$ $4.1 \mathrm{~Hz},-\mathrm{P}\left(\underline{\mathrm{C}}_{4} \mathrm{H}_{8}\right)$ ), $25.1\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=15.4 \mathrm{~Hz},-\mathrm{P}\left(\underline{\mathrm{C}}_{4} \mathrm{H}_{8}\right)\right.$ ).

## Data for 1-Benzylphosphinane (8):

Yield: $21.1 \mathrm{mg}(0.11 \mathrm{mmol}, 73 \%) .{ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=7.08(\mathrm{~m}, 5 \mathrm{H}, \mathrm{Ph}), 2.66\left(\mathrm{~s}, \mathrm{br},-\mathrm{CH}_{2}-\mathrm{Ph}\right), 1.67(\mathrm{~m}$, $2 \mathrm{H},-\mathrm{P}\left(\mathrm{C}_{5} \mathrm{H}_{\underline{10}}\right)$ ), $1.52\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}\left(\mathrm{C}_{5} \mathrm{H}_{\underline{10}}\right)\right), 1.43\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}\left(\mathrm{C}_{5} \mathrm{H}_{\underline{10}}\right)\right), 1.32\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}\left(\mathrm{C}_{5} \mathrm{H}_{\underline{10}}\right)\right), 1.11\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}\left(\mathrm{C}_{5} \mathrm{H}_{10}\right)\right)^{*}$. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=-35.0(\mathrm{~s}) .{ }^{31} \mathrm{P}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=-35.0(\mathrm{~s}, \mathrm{br}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}\right.$, $293 \mathrm{~K}): \delta[\mathrm{ppm}]=138.5\left(\mathrm{~d}, J_{\mathrm{P}-\mathrm{c}}=4.9 \mathrm{~Hz}, \mathrm{Ph}\right), 129.0\left(\mathrm{~d}, \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=5.4 \mathrm{~Hz}, \mathrm{Ph}\right), 128.3\left(\mathrm{~d}, \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=1.3 \mathrm{~Hz}, \mathrm{Ph}\right), 125.5\left(\mathrm{~d}, \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=\right.$ $2.3 \mathrm{~Hz}, \mathrm{Ph}), 34.4\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=18.9 \mathrm{~Hz},-\left(\mathrm{CH}_{2}\right)-\mathrm{Ph}\right), 27.8\left(\mathrm{~d},{ }^{2} J_{\mathrm{P}-\mathrm{C}}=2.1 \mathrm{~Hz},-\mathrm{P}\left(\underline{\mathrm{C}}_{5} \mathrm{H}_{10}\right)\right), 24.2\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=14.5 \mathrm{~Hz},-\mathrm{P}\left(\underline{\mathrm{C}}_{5} \mathrm{H}_{10}\right)\right)$, 23.3 ( $\mathrm{d},{ }^{3} J_{\mathrm{P}-\mathrm{C}}=3.5 \mathrm{~Hz},-\mathrm{P}\left(\mathrm{C}_{5} \mathrm{H}_{10}\right)$ ).

## Data for 1-Benzylphosphepane (9):

Yield: $16.5 \mathrm{mg}(0.08 \mathrm{mmol}, 80 \%) .{ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=7.07(\mathrm{~m}, 5 \mathrm{H}, \mathrm{Ph}), 2.52\left(\mathrm{~s}, \mathrm{br},-\mathrm{CH}_{2}-\mathrm{Ph}\right), 1.65(\mathrm{~m}$, $\left.4 \mathrm{H},-\mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{12}\right)\right), 1.51\left(\mathrm{~m}, 4 \mathrm{H},-\mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{12}\right)\right), 1.32\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{12}\right)\right), 1.13\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{12}\right)\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right):$ $\delta[\mathrm{ppm}]=-26.4(\mathrm{~s}) .{ }^{31} \mathrm{P}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=-26.5(\mathrm{~m}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=138.7(\mathrm{~s}, \mathrm{br}$, Ph), 129.1 (d, JP-C $=5.4 \mathrm{~Hz}, \mathrm{Ph}), 128.2\left(\mathrm{~d}, J_{\mathrm{P}-\mathrm{C}}=1.1 \mathrm{~Hz}, \mathrm{Ph}\right), 125.5\left(\mathrm{~d}, \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=2.1 \mathrm{~Hz}, \mathrm{Ph}\right), 36.8\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=15.9 \mathrm{~Hz},-\left(\mathrm{CH}_{2}\right)-\right.$ Ph), $\left.29.0\left(\mathrm{~d},{ }^{1} J_{P-C}=16.1 \mathrm{~Hz},-\mathrm{P}^{\left(\mathrm{C}_{6}\right.} \mathrm{H}_{12}\right)\right), 28.1\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=4.5 \mathrm{~Hz},-\mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{12}\right)\right), 25.9\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=9.4 \mathrm{~Hz},-\mathrm{P}\left(\underline{C}_{6} \mathrm{H}_{10}\right)\right)$.

## Synthesis of Phospholane (10b):

Complex 3 ( $0.1 \mathrm{mmol}, 40.2 \mathrm{mg}, 1 \mathrm{eq}$ ) and $\mathrm{LiAlH}_{4}(0.12 \mathrm{mmol}, 4.5 \mathrm{mg}, 1.2 \mathrm{eq})$ were dissolved separately in 1 mL THF- $\mathrm{d}_{8} . \mathrm{LiAlH}_{4}$ is added to compound 3. The solution was stirred overnight, resulting in a colour change from greenish/brown to red. The formed phosphine 10 b was distilled of under reduced pressure $\left(1 \cdot 10^{-3} \mathrm{mbar}, 60^{\circ} \mathrm{C}\right.$, 30 min.$)$.

Yield: $0.068 \mathrm{mmol}, 69 \%^{*} .{ }^{1} \mathrm{H}$ NMR (THF- $\left.\mathrm{d}_{8}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=2.91(\mathrm{~m}, 1 \mathrm{H},-\mathrm{PH}), 2.47\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{HP}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)\right), 1.89(\mathrm{~m}$, $\left.2 \mathrm{H}, \mathrm{HP}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)\right), 1.73\left(\mathrm{~m}, 13 \mathrm{H}, \mathrm{HP}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)\right)^{\#}, 1.41\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{HP}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}$ (THF- $\left.\mathrm{d}_{8}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=-70.8$ (s). ${ }^{31} \mathrm{P}$ NMR (THF-d ${ }_{8}, 293 \mathrm{~K}$ ): $\delta[\mathrm{ppm}]=-70.8\left(\mathrm{dt},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=180.3 \mathrm{~Hz},{ }^{1} \mathrm{~J}_{\mathrm{p}-\mathrm{H}}=21.7 \mathrm{~Hz}\right.$ ). ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta$ $[p p m]=30.1\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{p}-\mathrm{C}}=5.5 \mathrm{~Hz}, \mathrm{HP}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)\right), 19.3\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=9.3 \mathrm{~Hz}, \mathrm{HP}\left(\underline{C}_{4} \mathrm{H}_{8}\right)\right)$.

* according to NMR via internal standard of $\mathrm{PPh}_{3}$ capillary in toluene $-\mathrm{d}_{8}\left(\mathrm{c}=0.2 \mathrm{~mol} \cdot \mathrm{~L}^{-1}, \mathrm{v}=0.07 \mathrm{~mL}\right.$ ).
\# overlap of solvent- and product-signal causes wrong integral
Synthesis of secondary phosphines 10a,c,d according to previous reaction setup - Synthesis of Phospholane (10b).


## General Synthesis of 6'-9':

Compound 6-9 ( 0.15 mmol for 6-8, 1 eq; 0.1 mmol for $9,1 \mathrm{eq}$ ) were synthesized according to the previous procedure insitu, dissolved in 5 mL of $n$-pentane, respectively, added to a solution of sulfur ( $0.15 \mathrm{mmol}, 4.8 \mathrm{mg}$, 1 eq for 6-8; $0.1 \mathrm{mmol}, 3.2 \mathrm{mg}$ for $9,1 \mathrm{eq}$ ) in 5 mL n-pentane and stirred for 2 hours at room temperature. The volume was reduced in vacuo and stored at $-30^{\circ} \mathrm{C}$. Colourless crystals of $6^{\prime}-9^{\prime}$ were formed after one day.

## Data for 6':

Yield: $21.6 \mathrm{mg}(0.11 \mathrm{mmol}, 73 \%) .{ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=7.02(\mathrm{~m}, 5 \mathrm{H}, \mathrm{Ph}), 2.94\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=13.1 \mathrm{~Hz}, 2 \mathrm{H},-\right.$ $\left.\mathrm{CH}_{2}-\mathrm{Ph}\right), 2.06\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}\left(\mathrm{C}_{3} \mathrm{H}_{6}\right)\right), 1.87\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}\left(\mathrm{C}_{3} \mathrm{H}_{6}\right)\right), 0.88\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}\left(\mathrm{C}_{3} \mathrm{H}_{6}\right)\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]$ $=58.2(\mathrm{~s}) .{ }^{31} \mathrm{P}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=58.2(\mathrm{~m}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=129.4\left(\mathrm{~d}, \mathrm{~J}_{\mathrm{p}-\mathrm{c}}=5.1 \mathrm{~Hz}\right.$, Ph), 128.4 ( $\left.\mathrm{d}, \mathrm{J}_{\mathrm{P}-\mathrm{C}}=3.1 \mathrm{~Hz}, \mathrm{Ph}\right), 126.9\left(\mathrm{~d}, \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=3.5 \mathrm{~Hz}, \mathrm{Ph}\right), 41.5\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=31.7 \mathrm{~Hz},-\left(\mathrm{CH}_{2}\right)-\mathrm{Ph}\right), 34.2\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=\right.$ $\left.47.1 \mathrm{~Hz},-\mathrm{P}\left(\mathrm{C}_{3} \mathrm{H}_{6}\right)\right), 13.2\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=21.4 \mathrm{~Hz},-\mathrm{P}\left(\mathrm{C}_{3} \mathrm{H}_{6}\right)\right)$. EI-MS $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right): \mathrm{m} / \mathrm{z}=63.9\left(100 \%,[\mathrm{~S}]^{+}\right), 191.83\left(56 \%,\left[\mathrm{~S}_{6}\right]^{+}\right)$, $127.89\left(24 \%,\left[\mathrm{~S}_{4}\right]^{+}\right)$. analysis (calcd., found for $\left.\mathrm{C}_{10} \mathrm{H}_{13} \mathrm{PS}\right)$ : $\mathrm{C}(61.20,63.72), \mathrm{H}(6.68,7.74), \mathrm{S}(16.34,16.36)$.

## Data for 7':

Yield: $23.1 \mathrm{mg}(0.11 \mathrm{mmol}, 73 \%) .{ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=7.03(\mathrm{~m}, 5 \mathrm{H}, \mathrm{Ph}), 2.87\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=14.0 \mathrm{~Hz}, 2 \mathrm{H},-\right.$ $\left.\mathrm{CH}_{2}-\mathrm{Ph}\right), 1.57\left(\mathrm{~m}, 4 \mathrm{H},-\mathrm{P}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)\right), 1.37\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)\right), 0.91\left(\mathrm{~m}, 4 \mathrm{H},-\mathrm{P}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]$ $=61.9$ (s). ${ }^{31} \mathrm{P}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=61.9(\mathrm{~s}, \mathrm{br}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=132.9\left(\mathrm{~d}, \mathrm{~J}_{\mathrm{p}-\mathrm{c}}=8.2 \mathrm{~Hz}\right.$, Ph), 129.7 ( $\mathrm{d}, \mathrm{J}_{\mathrm{P}-\mathrm{C}}=5.1 \mathrm{~Hz}, \mathrm{Ph}$ ), 128.3 ( $\left.\mathrm{d}, J_{\mathrm{P}-\mathrm{C}}=3.0 \mathrm{~Hz}, \mathrm{Ph}\right), 126.9\left(\mathrm{~d}, J_{\mathrm{P}-\mathrm{C}}=3.5 \mathrm{~Hz}, \mathrm{Ph}\right), 42.0\left(\mathrm{~d},{ }^{1} J_{\mathrm{P}-\mathrm{C}}=40.3 \mathrm{~Hz},-\left(\mathrm{CH}_{2}\right)-\right.$ $\mathrm{Ph}), 32.1\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=51.7 \mathrm{~Hz},-\mathrm{P}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)\right)$, $25.4\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=6.1 \mathrm{~Hz},-\mathrm{P}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)\right) . \mathrm{El}-\mathrm{MS}\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right): \mathrm{m} / \mathrm{z}=210.06\left(83 \%,[\mathrm{M}]^{+}\right)$, $91.05\left(100 \%,\left[\mathrm{C}_{7} \mathrm{H}_{7}\right]^{+}\right), 119.01\left(99 \%,\left[\mathrm{M}-\mathrm{C}_{7} \mathrm{H}_{7}\right]^{+}\right)$. analysis (calcd., found for $\left.\mathrm{C}_{11} \mathrm{H}_{15} \mathrm{PS}\right)$ : C (62.83, 62.80), H (7.19, 7.49), S (15.25, 15.60).

## Data for 8':

Yield: $29.2 \mathrm{mg}(0.13 \mathrm{mmol}, 87 \%) .{ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=7.08(\mathrm{~m}, 5 \mathrm{H}, \mathrm{Ph}), 2.84\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{p}-\mathrm{H}}=14.0 \mathrm{~Hz}, 2 \mathrm{H},-\right.$ $\left.\mathrm{CH}_{2}-\mathrm{Ph}\right), 1.81\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}\left(\mathrm{C}_{5} \mathrm{H}_{10}\right)\right), 1.42\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}\left(\mathrm{C}_{5} \mathrm{H}_{10}\right)\right), 1.24\left(\mathrm{~m}, 4 \mathrm{H},-\mathrm{P}\left(\mathrm{C}_{5} \mathrm{H}_{10}\right)\right), 1.09\left(\mathrm{~m}, 1 \mathrm{H},-\mathrm{P}\left(\mathrm{C}_{5} \mathrm{H}_{10}\right)\right), 0.70(\mathrm{~m}$, $1 \mathrm{H},-\mathrm{P}\left(\mathrm{C}_{5} \mathrm{H}_{10}\right)$ ). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=36.8(\mathrm{~s}) .{ }^{31} \mathrm{P}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=36.8(\mathrm{~m})$. ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=132.0\left(\mathrm{~d}, \mathrm{~J}_{\mathrm{p}-\mathrm{C}}=8.0 \mathrm{~Hz}, \mathrm{Ph}\right), 129.9\left(\mathrm{~d}, J_{\mathrm{P}-\mathrm{C}}=5.0 \mathrm{~Hz}, \mathrm{Ph}\right), 128.2\left(\mathrm{~d}, J_{\mathrm{P}-\mathrm{c}}=3.0 \mathrm{~Hz}\right.$, Ph), $126.8\left(\mathrm{~d}, \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=3.5 \mathrm{~Hz}, \mathrm{Ph}\right), 40.2\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=45.4 \mathrm{~Hz},-\left(\mathrm{CH}_{2}\right)-\mathrm{Ph}\right), 29.9\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=48.4 \mathrm{~Hz},-\mathrm{P}\left(\mathrm{C}_{5} \mathrm{H}_{10}\right)\right), 26.1\left(\mathrm{~d}, \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=\right.$ 6.0 Hz, $-\mathrm{P}\left(\underline{\mathrm{C}}_{5} \mathrm{H}_{10}\right)$ ), $21.3\left(\mathrm{~d}, J_{\mathrm{P}-\mathrm{C}}=5.8 \mathrm{~Hz},-\mathrm{P}\left(\underline{\mathrm{C}}_{5} \mathrm{H}_{10}\right)\right)$. )). EI-MS $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right): \mathrm{m} / \mathrm{z}=224.08\left(66 \%,[\mathrm{M}]^{+}\right), 91.05(100 \%$, $\left.\left[\mathrm{C}_{7} \mathrm{H}_{7}\right]^{+}\right), 133.02\left(78 \%,\left[\mathrm{M}-\mathrm{C}_{7} \mathrm{H}_{7}\right]^{+}\right), 99.05\left(34 \%,\left[\mathrm{P}\left(\mathrm{C}_{5} \mathrm{H}_{8}\right)\right]^{+}\right)$, $192.11\left(23 \%,\left[\mathrm{BnzP}\left(\mathrm{C}_{5} \mathrm{H}_{10}\right)\right]^{+}\right)$. analysis (calcd., found for $\left.\mathrm{C}_{12} \mathrm{H}_{17} \mathrm{PS}\right): \mathrm{C}(64.26,62.80), \mathrm{H}(7.64,7.49), \mathrm{S}(14.30,15.60)$.

## Data for 9':

Yield: $16.7 \mathrm{mg}(0.07 \mathrm{mmol}, 70 \%) .{ }^{1} \mathrm{H} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=7.08(\mathrm{~m}, 5 \mathrm{H}, \mathrm{Ph}), 2.82\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=13.8 \mathrm{~Hz}, 2 \mathrm{H},-\right.$ $\left.\mathrm{CH}_{\underline{2}}-\mathrm{Ph}\right), 1.75\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{\underline{12}}\right)\right), 1.45\left(\mathrm{~m}, 4 \mathrm{H},-\mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{\underline{12}}\right)\right), 1.19\left(\mathrm{~m}, 4 \mathrm{H},-\mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{\underline{12}}\right)\right), 1.04\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{\underline{12}}\right)\right)$. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=48.9(\mathrm{~s}) .{ }^{31} \mathrm{P}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=48.9(\mathrm{~s}, \mathrm{br}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}\right.$, $293 \mathrm{~K}): \delta$ [ppm] = 129.9 (d, Jp-c $=4.8 \mathrm{~Hz}, \mathrm{Ph}), 128.2\left(\mathrm{~d}, \mathrm{~J}_{\mathrm{P}-\mathrm{c}}=2.9 \mathrm{~Hz}, \mathrm{Ph}\right), 126.8\left(\mathrm{~d}, \mathrm{~J}_{\mathrm{p}-\mathrm{c}}=3.3 \mathrm{~Hz}, \mathrm{Ph}\right), 42.0(\mathrm{~d}$, $\left.{ }^{1} J_{\mathrm{P}-\mathrm{C}}=45.6 \mathrm{~Hz},-\left(\underline{\left(\mathrm{CH}_{2}\right)}\right)-\mathrm{Ph}\right), 32.6\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{p}-\mathrm{C}}=48.1 \mathrm{~Hz},-\mathrm{P}\left(\underline{\mathrm{C}}_{6} \mathrm{H}_{12}\right)\right), 28.4\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{p}-\mathrm{C}}=0.8 \mathrm{~Hz},-\mathrm{P}\left(\underline{C}_{6} \mathrm{H}_{12}\right)\right), 21.4\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{\mathrm{p}-\mathrm{C}}=\right.$ $\left.3.7 \mathrm{~Hz},-\mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{10}\right)\right)$. EI-MS $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right): m / z=238.09\left(54 \%,[\mathrm{M}]^{+}\right)$, $91.05\left(100 \%,\left[\mathrm{C}_{7} \mathrm{H}_{7}\right]^{+}\right), 147.04\left(64 \%,\left[\mathrm{M}-\mathrm{C}_{7} \mathrm{H}_{7}\right]^{+}\right)$, $113.05\left(17 \%,\left[\mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{10}\right)\right]^{+}\right)$. Elemental analysis failed after several attempts of the isolated crystals.

## Synthesis of $\left[\left(\left\{\mathrm{C}_{4} \mathrm{H}_{8}\right\} \mathrm{PH}\right)_{2} \mathrm{PtCl}_{2}\right]$ (11):

An insitu solution of compound 10 b ( $0.2 \mathrm{mmol}, 2.67 \mathrm{eq}$ ) in 3 mL THF was synthesized according to the previous procedure, added to a solution of $\left[(\mathrm{PhCN})_{2} \mathrm{PtCl}_{2}\right](0.075 \mathrm{mmol}, 35.4 \mathrm{mg}, 1 \mathrm{eq})$ in 3 mL THF and stirred for 1 hour at room temperature. The volume was removed in vacuo, the colourless residue was dissolved in 2 mL of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$, layered with 10 mL of $\mathrm{Et}_{2} \mathrm{O}$ and stored at room temperature. Colourless crystals of 11 were formed after one day.

Yield: $0.041 \mathrm{mmol}, 53 \%{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=5.32\left(\mathrm{t}, \mathrm{br}, \mathrm{J}_{\mathrm{p}-\mathrm{H}}=2.03 \mathrm{~Hz}, 1 \mathrm{H},-\mathrm{PH}\right), 2.36(\mathrm{~m}, 1 \mathrm{H}$, $\left.\mathrm{HP}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)\right)^{\#}, 2.28\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{HP}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)\right)^{\#}, 2.08\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{HP}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)\right)^{\#}, 1.88\left(\mathrm{~m}, 3 \mathrm{H}, \mathrm{HP}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)\right)^{\#} .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right.$,
$293 \mathrm{~K}): \delta[\mathrm{ppm}]=-15.4(\mathrm{~s}) .{ }^{31} \mathrm{P}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=-15.4\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{p}-\mathrm{H}}=377.1 \mathrm{~Hz}\right) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}\right.$, $293 \mathrm{~K}): \delta[\mathrm{ppm}]=27.7\left(\mathrm{~s}, \mathrm{HP}\left(\underline{\mathrm{C}}_{4} \mathrm{H}_{8}\right)\right.$ ), $21.1\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{p}-\mathrm{c}}=42.4 \mathrm{~Hz}, \mathrm{HP}\left(\underline{C}_{4} \mathrm{H}_{8}\right)\right)$. LIFDI-MS (o-DFB): $\mathrm{m} / \mathrm{z}=442.00(100 \%$, $\left.[\mathrm{M}]^{+}\right)$. Elemental analysis failed after several attempts of the isolated crystals due to
\# overlap of solvent- and product-signal causes wrong integral

## 2. NMR spectroscopic characterization

## ${ }^{1} \mathrm{H}$ NMR Spectra:

## $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\mathrm{n}^{4}-\mathrm{P}_{5}\left(\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br}\right)_{2}\right\}\right](1)$



Fig. S1. Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of 1 .
$\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left\{\mathrm{n}^{4}-\mathrm{P}_{5}\left(\mathrm{C}_{3} \mathrm{H}_{6}\right)\right\}\right](2)$


Fig. S2. Experimental ${ }^{1} \mathrm{H}$ NMR $\left(400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of $2\left(^{*}=\mathrm{I}^{\prime}\right)$.

## $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)\right\}\right](3)$



Fig. S3. Experimental ${ }^{1} \mathrm{H}$ NMR $\left(400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 3.
$\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}\left(\mathrm{C}_{5} \mathrm{H}_{10}\right)\right\}\right](4)$


Fig. S4. Experimental ${ }^{1} \mathrm{H}$ NMR $\left(400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 4 .
$\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}\left(\mathrm{C}_{6} \mathrm{H}_{12}\right)\right\}\right](5)$


Fig. S5. Experimental ${ }^{1} \mathrm{H}$ NMR $\left(400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 5 .

## PBnz\{(CH2 $\left.)_{3}\right\}(6)$



Fig. S6. Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of 6 ( ${ }^{*}=$ unknown sideproduct, not visible in ${ }^{31} \mathrm{P}$ NMR).
PBnz\{(CH2 $\left.)_{4}\right\}(7)$


Fig. S7. Experimental ${ }^{1} \mathrm{H}$ NMR $\left(400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 7.
$\operatorname{PBnz}\left\{\left(\mathrm{CH}_{2}\right)_{5}\right\}(8)$


Fig. S8. Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of 8 .

## PBnz $\left\{\left(\mathrm{CH}_{2}\right)_{6}\right\}$ (9)



Fig. S9. Experimental ${ }^{1} \mathrm{H}$ NMR $\left(400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of $9\left(^{*}=5\right)$.
$\mathrm{HP}\left\{\left(\mathrm{CH}_{2}\right)_{4}\right\}$ (10b)


Fig. S10. Experimental ${ }^{1} \mathrm{H}$ NMR ( 400.13 MHz, THF- $\mathrm{d}_{8}$ ) spectrum of 10 b (' = integral wrong due to solvent signal overlap with product signal).

SPBnz\{( $\left.\left.\mathrm{CH}_{2}\right)_{3}\right\}\left(6^{\prime}\right)$


Fig. S11. Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of 6'.

SPBnz\{( $\left.\left.\mathrm{CH}_{2}\right)_{4}\right\}\left(\mathbf{7}^{\prime}\right)$


Fig. S12. Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of $\mathrm{7}^{\prime}$.
$\operatorname{SPBnz}\left\{\left(\mathrm{CH}_{2}\right)_{5}\right\}\left(8^{\prime}\right)$


Fig. S13. Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of $\mathbf{8}^{\prime}$.
SPBnz\{( $\left.\left.\mathrm{CH}_{2}\right)_{6}\right\}\left(9^{\prime}\right)$


Fig. S14. Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of $9^{\prime}\left(^{*}=5\right)$.

## $\left[\left(\left\{\mathrm{C}_{4} \mathrm{H}_{8}\right\} \mathrm{PH}\right)_{2} \mathrm{PtCl}_{2}\right](11)$



Fig. S15. Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{CH}_{2} \mathrm{Cl}_{2}$ ) spectrum of 11 (* = grease; \# = unidentified sideproduct(s)).

## ${ }^{31} \mathrm{P}$ NMR Spectra:

$\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}\left(\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br}\right)_{2}\right\}\right](1)$



Fig. S16. Experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 1.

Table S1. Chemical shifts and coupling constants obtained from the simulation ( R -factor $=1.13$ \%) in Figure S16.

| $J[\mathrm{~Hz}]$ |  |  |  | $\delta$ [ppm] |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{1} \mathrm{JPA}, \mathrm{PX}$ | 397.93 | ${ }^{1} \mathrm{JPM,PX}$ | 391.62 | X, X' | -131.4 |
| ${ }^{1} J_{\text {PA, PX }}$ | 398.58 | ${ }^{1} J_{\text {PM }}{ }^{\prime} \mathrm{PX}^{\prime}$ | 405.29 |  |  |
| ${ }^{2} J_{\text {PA,PM }}$ | -11.40 | ${ }^{2} J_{\text {PM }}{ }^{\prime}$ PX | -32.39 | $\mathrm{M}, \mathrm{M}^{\prime}$ | 36.4 |
| ${ }^{2} J_{\text {PA,PM }}$, | -12.33 | ${ }^{2} J_{\text {PM, PX }}$ | -45.34 |  |  |
| ${ }^{1} J_{\text {PM, PM }}{ }^{\prime}$ | 379.55 | ${ }^{2} J_{\text {PX,PX' }}$ | -1.08 | A | 136.0 |

$\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left\{\mathrm{n}^{4}-\mathrm{P}_{5}\left(\mathrm{C}_{3} \mathrm{H}_{6}\right)\right\}\right](2)$




Fig. S17. Experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 2.

Table S2. Chemical shifts and coupling constants obtained from the simulation ( R -factor $=2.72 \%$ ) in Figure S17.

| $J[\mathrm{~Hz}]$ |  |  |  | $\delta$ [ppm] |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{1}{ }_{\text {PA, PX }}$ | 431.20 | ${ }^{1}{ }_{\text {PM }}$ PX | 404.0 | X, X' | -89.3 |
| ${ }^{1} J_{\text {PA,PX }}$ | 430.90 | ${ }^{1} J_{\text {PM }}{ }^{\prime}$ PX' | 412.0 |  |  |
| ${ }^{2} J_{\text {PA,PM }}$ | 15.36 | ${ }^{2} J_{\text {PM }}{ }^{\prime}$ PX | -35.32 | M, M ${ }^{\prime}$ | 43.5 |
| ${ }^{2} J_{\text {PA,PM }}$, | 16.74 | ${ }^{2} J_{\text {PM, PX }}$ | -42.30 |  |  |
| ${ }^{1} j_{\text {PM PM }}{ }^{\prime}$ | 388.0 | ${ }^{2} J_{\text {PX, PX }}$ | 9.47 | A | 125.4 |

$\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\boldsymbol{\eta}^{4}-\mathrm{P}_{5}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)\right\}\right](3)$


Fig. S18. Experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 3.
Table S3. Chemical shifts and coupling constants obtained from the simulation ( R -factor $=3.86$ \%) in Figure S18.

| $J[\mathrm{~Hz}]$ |  |  |  | $\delta[\mathrm{ppm}]$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{1} \mathrm{JPA}, \mathrm{PX}$ | 403.23 | ${ }^{1} \mathrm{JPM}, \mathrm{PX}$ | 408.00 | $\mathrm{X}, \mathrm{X}^{\prime}$ | -117.4 |
| ${ }^{1} \mathrm{JPA}, \mathrm{PX}$ | 403.18 | ${ }^{1} J_{P M}{ }^{\prime} \mathrm{PX}^{\prime}$ | 400.51 |  |  |
| ${ }^{2} J_{\text {PA,PM }}$ | 14.30 | ${ }^{2} J_{\text {PM }}$ 'PX | -41.46 | $\mathrm{M}, \mathrm{M}^{\prime}$ | 38.3 |
| ${ }^{2} J_{\text {PA, PM }}$, | 13.60 | ${ }^{2} J_{\text {PM, PX }}$ | -34.16 |  |  |
| ${ }^{1} \mathrm{JPM}, \mathrm{PM}{ }^{\text {d }}$ | 382.76 | ${ }^{2} J_{\mathrm{PX}, \mathrm{PX}}$ ' | 9.47 | A | 145.4 |

$\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}\left(\mathrm{C}_{5} \mathrm{H}_{10}\right)\right\}\right]$ (4)




Fig. S19. Experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 4.
Table S4. Chemical shifts and coupling constants obtained from the simulation ( R -factor $=3.86 \%$ ) in Figure S19.

| $J[H z]$ |  |  |  | $\delta[\mathrm{ppm}]$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{1} \mathrm{JPA}, \mathrm{PX}$ | 389.10 | ${ }^{1} \mathrm{~J}_{\mathrm{PM}, \mathrm{PX}}$ | 396.66 | $\mathrm{X}, \mathrm{X}^{\prime}$ | -136.0 |
| ${ }^{1} J_{\text {PA, PX' }}$ | 388.90 | ${ }^{1} J_{\text {PM }}{ }^{\prime}$ PX ${ }^{\prime}$ | 402.12 |  |  |
| ${ }^{2} J_{\text {PA,PM }}$ | 11.83 | ${ }^{2} J_{\text {PM }}{ }^{\prime}$ PX | -34.40 | M, M' | 33.0 |
| ${ }^{2} J_{\text {PA, PM }}$, | 11.20 | ${ }^{2} J_{\text {PM, PX }}$ | -40.48 |  |  |
| ${ }^{1} \mathrm{JPM}, \mathrm{PM}{ }^{\text {a }}$ | 380.94 | ${ }^{2} J_{\text {PX, PX }}$ ' | 5.27 | A | 127.4 |

$\left[C p^{*} \mathrm{Fe}\left\{\mathrm{n}^{4}-\mathrm{P}_{5}\left(\mathrm{C}_{6} \mathrm{H}_{12}\right)\right\}\right](5)$


Fig. S20. Experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 5 .

Table S5. Chemical shifts and coupling constants obtained from the simulation ( R -factor = 3.86 \%) in Figure S20.

| $J[\mathrm{~Hz}]$ |  |  |  | $\delta[\mathrm{ppm}]$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{1} J_{\text {PA, PX }}$ | 384.49 | ${ }^{1}{ }_{\text {PM }}$ PX | 407.78 | X, $\mathrm{X}^{\prime}$ | -128.5 |
| ${ }^{1} \mathrm{JPA}, \mathrm{PX}$ | 384.59 | ${ }^{1} J_{\text {PM }}{ }^{\prime}$ PX ${ }^{\prime}$ | 392.43 |  |  |
| ${ }^{2} J_{\text {PA, PM }}$ | 11.65 | ${ }^{2} J_{\text {PM }}$ 'PX | -45.00 | M, M' | 34.8 |
| ${ }^{2} J_{\text {PA, PM }}{ }^{\prime}$ | 12.96 | ${ }^{2} J_{\text {PM }}$ PX' | -29.61 |  |  |
| ${ }^{1} \mathrm{JPM}, \mathrm{PM}{ }^{\prime}$ | 380.03 | ${ }^{2} J_{\text {PX, PX }}$ | 3.36 | A | 145.0 |

## $\operatorname{PBnz}\left\{\left(\mathrm{CH}_{2}\right)_{3}\right\}(6)$



Fig. S21. ${ }^{31}{ }^{\mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 6 .

## PBnz\{(CH2) $)_{4}$ (7)



Fig. S22. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 7 .
$\operatorname{PBnz}\left\{\left(\mathrm{CH}_{2}\right)_{5}\right\}(8)$


Fig. S23. $\left.{ }^{31}{ }^{\mathrm{P}\{ }{ }^{1} \mathrm{H}\right\} \mathrm{NMR} 161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of 8 .
$\qquad$

## PBnz\{(CH2 $\left.)_{6}\right\}(9)$



Fig. S24. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of $9\left({ }^{*}=5\right)$.
$\mathrm{HP}\left\{\left(\mathrm{CH}_{2}\right)_{4}\right\}$ (10b)


Fig. S25. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of $10 \mathrm{~b}\left({ }^{*}=\mathrm{OHP}\left\{\left(\mathrm{CH}_{2}\right)_{4}\right\}\right)$.


Fig. S26. ${ }^{31} \mathrm{P}$ NMR (top) and ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR (button) ( $161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of 10 b .

SPBnz\{( $\left.\left.\mathrm{CH}_{2}\right)_{3}\right\}\left(6^{\prime}\right)$


Fig. S27. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR (161.98 MHz, $\left.\mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 6'.
SPBnz\{(CH2 $\left.)_{4}\right\}\left(7^{\prime}\right)$


Fig. S28. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR (161.98 MHz, $\left.\mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 7 '.
SPBnz\{( $\left.\left.\mathrm{CH}_{2}\right)_{5}\right\}\left(8^{\prime}\right)$


Fig. S29. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR (161.98 MHz, $\left.\mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of $\mathbf{8}$.

## SPBnz\{( $\left.\left.\mathrm{CH}_{2}\right)_{6}\right\}$ (9')



Fig. S30. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $\left.161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of $9^{\prime}\left(^{*}=5\right.$; \# = OPBnz $\left\{\left(\mathrm{CH}_{2}\right)_{6}\right\}$ ).
$\left[\left(\left\{\mathrm{C}_{4} \mathrm{H}_{8}\right\} \mathrm{PH}\right)_{2} \mathrm{PtCl}_{2}\right]$ (11)


Fig. S31. ${ }^{31} \mathrm{P}$ (top) and ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ (buttom) $\mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right.$ ) spectra (zoom-in) of 11.

## ${ }^{13} \mathrm{C}$ NMR Spectra:

PBnz $\left\{\left(\mathrm{CH}_{2}\right)_{3}\right\}(6)$


Fig. S32. Experimental ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(100.61 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 6.
$\operatorname{PBnz}\left\{\left(\mathrm{CH}_{2}\right)_{4}\right\}(7)$


Fig. S33. Experimental ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $\left.100.61 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 7.

## PBnz\{( $\left.\left.\mathrm{CH}_{2}\right)_{5}\right\}$ (8)



Fig. S34. Experimental ${ }^{13} C^{1}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $\left.100.61 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 8.

## $\operatorname{PBnz}\left\{\left(\mathrm{CH}_{2}\right)_{6}\right\}(9)$



Fig. S35. Experimental $\left.{ }^{13} \mathrm{C}^{\{ }{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(100.61 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 8 .

## $\mathrm{HP}\left\{\left(\mathrm{CH}_{2}\right)_{4}\right\}(10 b)$



Fig. S36. Experimental ${ }^{13}{ }^{1}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $\left.100.61 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 10 b .

## $\operatorname{SPBnz}\left\{\left(\mathrm{CH}_{2}\right)_{3}\right\}\left(6^{\prime}\right)$



Fig. S37. Experimental $\left.{ }^{13} \mathrm{C}^{1}{ }^{1} \mathrm{H}\right\}$ NMR ( $\left.100.61 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 6'.

SPBnz\{(CH2 $\left.)_{4}\right\}\left(7^{\prime}\right)$


Fig. S38. Experimental ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $100.61 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of $\mathrm{7}^{\prime}$.
$\operatorname{SPBnz}\left\{\left(\mathrm{CH}_{2}\right)_{5}\right\}\left(8^{\prime}\right)$


Fig. S39. Experimental $\left.{ }^{13} \mathrm{C}^{1} \mathrm{H}\right\}$ NMR $\left(100.61 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 8 '.
SPBnz\{( $\left.\left.\mathrm{CH}_{2}\right)_{6}\right\}\left(9^{\prime}\right)$


Fig. S40. Experimental ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(100.61 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 9'.
$\left[\left(\left\{\mathrm{C}_{4} \mathrm{H}_{8}\right\} \mathrm{PH}\right)_{2} \mathrm{PtCl}_{2}\right](11)$


Fig. S41. Experimental $\left.{ }^{13} \mathrm{C}^{1}{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(100.61 \mathrm{MHz}, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$ spectrum of 11 .

## 3. Crystallographic details

$\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}\left(\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br}\right)_{2}\right\}\right]$ (1): The asymmetric unit contains one molecule of 1 without any disorder. The structure in the solid state is given in Figure S42. Crystallographic and refinement data are summarized in Table S6.
$\left[C p^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}\left(\mathrm{C}_{3} \mathrm{H}_{6}\right)\right\}\right]$ (2): The asymmetric unit contains one molecule of 2 without any disorder. The structure in the solid state is given in Figure S43. Crystallographic and refinement data are summarized in Table S6.
$\left[C p^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)\right\}\right]$ (3): The asymmetric unit contains two molecules of 3 without any disorder. The structure in the solid state is given in Figure S44. Crystallographic and refinement data are summarized in Table S6.
[Cp*Fe\{n4- $\left.\left.\mathrm{P}_{5}\left(\mathrm{C}_{5} \mathrm{H}_{10}\right)\right\}\right]$ (4): The asymmetric unit contains one molecule of 4 without any disorder. The structure in the solid state is given in Figure S45. Crystallographic and refinement data are summarized in Table S6.
$\left[C p^{*} F e\left\{\eta^{4}-P_{5}\left(\mathrm{C}_{6} \mathrm{H}_{12}\right)\right\}\right]$ (5): The asymmetric unit contains one molecule of 5 . One $\mathrm{Cp}^{*}$ ligand and three carbon atoms of the cyclo-hexyl substituent at the phosphorus ligand are disordered over two positions with a distribution of 57:43, respectively. To describe the disorders the SIMU restrain is applied. The structure in the solid state is given in Figure S46. Crystallographic and refinement data are summarized in Table S6.

SPBnz\{ $\left.\left(\mathrm{CH}_{2}\right)_{3}\right\}$ (6'): The asymmetric unit contains two molecules of 6 ' without any disorder. The structure in the solid state is given in Figure S47. Crystallographic and refinement data are summarized in Table S7.

SPBnz\{( $\left.\left.\mathrm{CH}_{2}\right)_{4}\right\}$ (7'): The asymmetric unit contains one molecule of 7 ' without any disorder. The structure in the solid state is given in Figure S48. Crystallographic and refinement data are summarized in Table S7.
$\operatorname{SPBnz}\left\{\left(\mathrm{CH}_{2}\right)_{5}\right\}$ ( $\left.8^{\prime}\right)$ : The asymmetric unit contains two molecules of $8^{\prime}$ without any disorder. Since the measured crystal was twinned, a HKLF5 refinement was applied (BASF 0.444). The structure in the solid state is given in Figure S49. Crystallographic and refinement data are summarized in Table S7.

SPBnz\{( $\left.\left.\mathrm{CH}_{2}\right)_{6}\right\}$ (9'): The asymmetric unit contains four molecules of 9 ' without any disorder. Since the measured crystal was twinned, a HKLF5 refinement was applied (BASF 0.171). The structure in the solid state is given in Figure S50. Crystallographic and refinement data are summarized in Table S7.
$\left[\left(\left\{\mathrm{C}_{4} \mathrm{H}_{8}\right\} \mathrm{PH}\right)_{2} \mathrm{PtCl}_{2}\right](11):$
The asymmetric unit contains half molecule of 11. The platinum atom is located at the inversion center and is disordered over two positions (52:48). The structure in the solid state is given in Figure S51. Crystallographic and refinement data are summarized in Table S7.

Table S6. Crystallographic details of 1-5.

| Compound | 1 | 2 | 3 | 4 | 5 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| CCDC <br> Formula | $\stackrel{/}{\mathrm{C}_{16} \mathrm{H}_{27} \mathrm{Br}_{2} \mathrm{FeP}_{5}}$ | $\stackrel{/}{\mathrm{C}_{13} \mathrm{H}_{21} \mathrm{FeP}_{5}}$ | $\stackrel{/}{\mathrm{C}_{14} \mathrm{H}_{23} \mathrm{FeP}_{5}}$ | $\stackrel{/}{\mathrm{C}_{15} \mathrm{H}_{25} \mathrm{FeP}_{5}}$ | $\stackrel{/}{\mathrm{C}_{16} \mathrm{H}_{27} \mathrm{FeP}_{5}}$ |
| $D_{\text {calc. }} / \mathrm{g} \mathrm{cm}^{-3}$ | 1.738 | 1.505 | 1.467 | 1.422 | 1.433 |
| $\mu / \mathrm{mm}^{-1}$ | 9.596 | 11.350 | 10.697 | 10.036 | 9.800 |
| Formula Weight | 589.89 | 388.00 | 402.02 | 416.05 | 430.07 |
| Colour | dark green | green | dark green | dark green | red |
| Shape | block-shaped | plate-shaped | prism-shaped | block-shaped | plate-shaped |
| Size/mm ${ }^{3}$ | $0.69 \times 0.28 \times 0.22$ | $0.31 \times 0.23 \times 0.08$ | $0.80 \times 0.26 \times 0.20$ | $0.15 \times 0.13 \times 0.07$ | $0.25 \times 0.17 \times 0.07$ |
| T/K | 123.2(3) | 123.00(10) | 123.00(10) | 123.01(10) | 122.99(10) |
| Crystal System | monoclinic | orthorhombic | triclinic | orthorhombic | orthorhombic |
| Flack Parameter | / | -0.010(3) | / | 0.003(2) | 0.011(4) |
| Hooft Parameter | / | -0.0120(17) | / | -0.0053(15) | 0.0033(14) |
| Space Group | P2 $1^{\prime} \mathrm{C}$ | P2 $2212{ }_{1}$ | P-1 | $\mathrm{P} 2{ }_{1} \mathrm{~L}_{1} \mathrm{C}_{1}$ | P2 $1_{21}{ }_{1}{ }_{1}$ |
| $a / \AA$ | 13.35480(10) | 8.47550(10) | 9.4353(2) | 9.17120(10) | 9.2930(3) |
| b/A | 14.71550(10) | 8.84210(10) | 13.7981(3) | 14.22010(10) | 14.8439(5) |
| $c / \AA$ | 11.90660(10) | 22.8473(3) | 15.3668(4) | 14.9030(2) | 14.4562(5) |
| $\alpha /{ }^{\circ}$ | 90 | 90 | 69.087(2) | 90 | 90 |
| $\beta /^{\circ}$ | 105.4910(10) | 90 | 77.735(2) | 90 | 90 |
| $\gamma /{ }^{\circ}$ | 90 | 90 | 89.910(2) | 90 | 90 |
| $\mathrm{V} / \mathrm{A}^{3}$ | 2254.91(3) | 1712.20(4) | 1820.09(8) | 1943.58(4) | 1994.14(12) |
| Z | 4 | 4 | 4 | 4 | 4 |
| Z' | 1 | 1 | 2 | 1 | 1 |
| Wavelength/A | 1.39222 | 1.54184 | 1.54184 | 1.54184 | 1.54184 |
| Radiation type | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ |
| $\Theta_{\text {min }} /{ }^{\circ}$ | 4.121 | 3.870 | 3.161 | 4.297 | 4.269 |
| $\Theta_{\text {max }} /{ }^{\circ}$ | 75.867 | 73.258 | 73.907 | 74.432 | 74.771 |
| Measured Refl's. | 32647 | 8327 | 23461 | 20511 | 15527 |
| Ind't Refl's | 6367 | 3197 | 6987 | 3935 | 4030 |
| Refl's with I > 2(I) | 6143 | 3167 | 6827 | 3896 | 3953 |
| Rint | 0.0743 | 0.0258 | 0.0262 | 0.0303 | 0.0273 |
| Parameters | 222 | 177 | 371 | 195 | 329 |
| Restraints | 0 | 0 | 0 | 0 | 312 |
| Largest Peak | 1.320 | 0.448 | 0.684 | 0.218 | 0.498 |
| Deepest Hole | -1.068 | -0.422 | -0.804 | -0.307 | -0.518 |
| GooF | 1.053 | 1.036 | 1.058 | 1.076 | 1.200 |
| $w R_{2}$ (all data) | 0.1335 | 0.0739 | 0.0978 | 0.0592 | 0.1093 |
| $w R_{2}$ | 0.1321 | 0.0737 | 0.0971 | 0.0590 | 0.1091 |
| $R_{1}$ (all data) | 0.0491 | 0.0274 | 0.0362 | 0.0271 | 0.0468 |
| $R_{1}$ | 0.0480 | 0.0272 | 0.0355 | 0.0267 | 0.0462 |

Table S7. Crystallographic details of 6'-9' and 11.

| Compound | 6' | 7 | 8' | 9' | 11 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| CCDC | / | / | / | / | / |
| Formula | $\mathrm{C}_{10} \mathrm{H}_{13} \mathrm{PS}$ | $\mathrm{C}_{11} \mathrm{H}_{15} \mathrm{PS}$ | $\mathrm{C}_{12} \mathrm{H}_{17} \mathrm{PS}$ | $\mathrm{C}_{13} \mathrm{H}_{19} \mathrm{PS}$ | $\mathrm{C}_{8} \mathrm{H}_{18} \mathrm{Cl}_{2} \mathrm{P}_{2} \mathrm{Pt}$ |
| $D_{\text {calc. }} / \mathrm{g} \mathrm{cm}^{-3}$ | 1.302 | 1.282 | 1.252 | 1.245 | 2.277 |
| $\mu / \mathrm{mm}^{-1}$ | 3.898 | 3.615 | 3.342 | 3.156 | 11.502 |
| Formula Weight | 196.23 | 210.26 | 224.28 | 238.31 | 442.15 |
| Colour | colourless | colourless | colourless | colourless | colourless |
| Shape | plate-shaped | needle-shaped | needle-shaped | block-shaped | block-shaped |
| Size/mm ${ }^{3}$ | $0.25 \times 0.16 \times 0.04$ | $0.22 \times 0.04 \times 0.03$ | $0.21 \times 0.05 \times 0.03$ | $0.34 \times 0.06 \times 0.05$ | $0.08 \times 0.05 \times 0.04$ |
| T/K | 123.00(10) | 122.98(10) | 122.97(11) | 100.02(10) | 100.01(12) |
| Crystal System | monoclinic | orthorhombic | monoclinic | monoclinic | tetragonal |
| Flack Parameter | / | -0.04(5) | -0.01(3) | 0.171(15) | -0.013(3) |
| Hooft Parameter | / | -0.101(13) | -0.009(5) | -0.003(4) | 0.0048(16) |
| Space Group | $\mathrm{P} 2_{1} / \mathrm{c}$ | Pna21 | Pc | P2 ${ }_{1}$ | $1-4 c 2$ |
| a/Å | 16.77790(10) | 16.0552(8) | 19.0300(5) | 12.92590(10) | 11.67740(10) |
| b/Å | 10.42680(10) | 10.9392(5) | 6.1666(2) | 9.99760(10) | 11.67740(10) |
| $c / \AA$ | 11.69300(10) | 6.2040(3) | 10.2233(2) | 19.73260(10) | 18.9131(2) |
| $\alpha /{ }^{\circ}$ | 90 | 90 | 90 | 90 | 90 |
| $\beta{ }^{\circ}$ | 101.7780(10) | 90 | 97.346(2) | 94.2160(10) | 90 |
| $\gamma /{ }^{\circ}$ | 90 | 90 | 90 | 90 | 90 |
| $\mathrm{V} / \mathrm{A}^{3}$ | 2002.50(3) | 1089.61(9) | 1189.86(6) | 2543.10(3) | 2579.02(5) |
| Z | 8 | 4 | 4 | 8 | 8 |
| Z' | 2 | 1 | 2 | 4 | 0.5 |
| Wavelength/Å | 1.54184 | 1.54184 | 1.54184 | 1.54184 | 0.71073 |
| Radiation type | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ | $\mathrm{MoK}_{\alpha}$ |
| $\left.\Theta_{\text {min }}\right)^{\circ}$ | 2.690 | 4.892 | 2.341 | 2.245 | 2.467 |
| $\Theta_{\max } /{ }^{\circ}$ | 74.370 | 74.471 | 74.906 | 74.952 | 32.546 |
| Measured Refl's. | 34643 | 8454 | 6716 | 54571 | 192001 |
| Ind't Refl's | 4062 | 1811 | 6716 | 10219 | 2350 |
| Refl's with I > 2(I) | 3934 | 1706 | 6045 | 9952 | 2300 |
| $R_{\text {int }}$ | 0.0226 | 0.0444 | . | 0.0377 | 0.0693 |
| Parameters | 217 | 118 | 254 | 542 | 69 |
| Restraints | 0 | 1 | 2 | 1 | 0 |
| Largest Peak | 0.455 | 0.535 | 1.014 | 0.603 | 1.857 |
| Deepest Hole | -0.293 | -0.465 | -0.408 | -0.452 | -0.412 |
| GooF | 1.049 | 1.108 | 1.057 | 1.027 | 1.081 |
| $w R_{2}$ (all data) | 0.0751 | 0.1467 | 0.1704 | 0.1018 | 0.0499 |
| $w R_{2}$ | 0.0746 | 0.1439 | 0.1648 | 0.1013 | 0.0495 |
| $R_{1}$ (all data) | 0.0279 | 0.0539 | 0.0654 | 0.0364 | 0.0200 |
| $R_{1}$ | 0.0272 | 0.0514 | 0.0599 | 0.0358 | 0.0195 |

## $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\mathrm{n}^{4}-\mathrm{P}_{5}\left(\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br}\right)_{2}\right\}\right]$ (1)



Fig. S42. Molecular structure of 1 in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligand is drawn in a wire frame model. Table S8. Selected bond lengths of 1.

| Atom | Atom | Length $[\AA \AA]$ | Atom | Atom | Length $[\AA \AA]$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| Br1 | C13 | $1.954(3)$ | P1 |  | $1.825(3)$ |
| Br2 | C16 | $1.967(3)$ | P4 | P5 | $2.1509(10)$ |
| P2 | P1 | $2.1451(8)$ | P4 | P3 | $2.1540(10)$ |
| P2 | P3 | $2.1478(9)$ | P1 | C14 | $1.822(3)$ |
| P1 | P5 | $2.1423(8)$ |  |  |  |

Table S9. Selected angles of 1.

| Atom | Atom | Atom | Angle [ ${ }^{\circ}$ ] | Atom | Atom | Atom | Angle [ $\left.{ }^{\circ}\right]$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| P3 | P4 | Fe1 | $62.62(3)$ | C11 | P1 | P2 | 106.44(9) |
| P1 | P5 | Fe1 | $86.71(3)$ | C11 | P1 | P5 | 109.93(9) |
| P1 | P5 | P4 | $96.93(3)$ | P5 | P4 | Fe1 | $62.09(2)$ |
| P4 | P5 | Fe1 | $62.98(3)$ | P5 | P4 | P3 | $105.06(4)$ |
| P2 | P3 | Fe1 | $62.65(3)$ | P4 | P3 | Fe1 | $62.60(3)$ |
| P2 | P3 | P4 | $104.37(4)$ |  |  |  |  |

## $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left\{\mathrm{n}^{4}-\mathrm{P}_{5}\left(\mathrm{C}_{3} \mathrm{H}_{6}\right)\right\}\right]$ (2)



Fig. S43. Molecular structure of 2 in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligand is drawn in a wire frame model.

Table S10. Selected bond lengths of 2.

| Atom | Atom | Length $[\AA ̊]$ | Atom | Atom | Length $[\AA \AA]$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| P2 | P1 | $2.1261(12)$ | C11 | C12 | $1.524(6)$ |
| P2 | P3 | $2.1358(12)$ | C13 | C12 | $1.536(5)$ |
| P1 | P5 | $2.1384(12)$ | P4 | P5 | $2.1396(12)$ |
| P1 | C11 | $1.865(3)$ | P3 | P4 | $2.1392(12)$ |
| P1 | C13 | $1.835(4)$ |  |  |  |

Table S11. Selected angles of 2.

| Atom | Atom | Atom | Angle [ ${ }^{\circ}$ ] | Atom | Atom | Atom | Angle [ $\left.{ }^{\circ}\right]$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| P1 | P2 | P3 | $102.31(5)$ | C13 | P1 | P5 | 107.67(13) |
| P2 | P1 | P5 | $101.66(4)$ | C13 | P1 | C11 | $78.86(17)$ |
| C11 | P1 | P2 | $126.19(14)$ | P2 | P3 | P4 | $106.16(5)$ |
| C11 | P1 | P5 | $126.09(14)$ | C12 | C11 | P1 | $88.9(2)$ |
| C13 | P1 | P2 | $111.56(13)$ | C12 | C13 | P1 | $89.7(2)$ |
| C11 | C12 | C13 | $100.3(3)$ |  |  |  |  |

$\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)\right\}\right]$ (3):


Fig. S44. Molecular structure of 3 in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The $C p^{*}$ ligand is drawn in a wire frame model. Table S12. Selected bond lengths of 3.

| Atom | Atom | Length $[\AA ̊]$ | Atom | Atom | Length $[\AA ̊]$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| P5 | P4 | $2.1385(8)$ | C14 | C13 | $1.536(3)$ |
| P5 | P1 | $2.1383(8)$ | C11 | C12 | $1.526(3)$ |
| P4 | P3 | $2.1498(9)$ | C13 | C12 | $1.527(3)$ |
| P1 | P2 | $2.1388(8)$ | P1 | C11 | $1.843(2)$ |
| P1 | C14 | $1.841(2)$ | P2 | P3 | $2.1434(9)$ |

Table S13. Selected angles of 3.

| Atom | Atom | Atom | Angle [ ${ }^{\circ}$ ] | Atom | Atom | Atom | Angle [ ${ }^{\circ}$ ] |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| C13 | C14 | P1 | $105.91(16)$ | C14 | P1 | C11 | $94.84(11)$ |
| C12 | C11 | P1 | $104.40(16)$ | C11 | C12 | C13 | 106.9(2) |
| C12 | C13 | C14 | $107.25(19)$ |  |  |  |  |

$\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}\left(\mathrm{C}_{5} \mathrm{H}_{10}\right)\right\}\right]$ (4)


Fig. S45. Molecular structure of 4 in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligand is drawn in a wire frame model.

Table S14. Selected bond lengths of 4 .

| Atom | Atom | Length $[\AA ̊]$ | Atom | Atom | Length $[\mathrm{A}]$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| P1 | P5 | $2.1409(12)$ | P2 |  | $2.1465(13)$ |
| P1 | P2 | $2.1360(12)$ | P4 | P3 | $2.1529(17)$ |
| P1 | C15 | $1.816(3)$ | C15 | C14 | $1.534(5)$ |
| P1 | C11 | $1.816(4)$ | C11 | C12 | $1.533(5)$ |
| P5 | P4 | $2.1380(14)$ | C14 | C13 | $1.517(6)$ |
| C12 | C13 | $1.518(7)$ |  |  |  |

Table S15. Selected angles of 4.

| Atom | Atom | Atom | Angle [ ${ }^{\circ}$ ] | Atom | Atom | Atom | Angle [ $\left.{ }^{\circ}\right]$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| C14 | C15 | P1 | $111.3(3)$ | P2 | P1 | P5 | $98.92(5)$ |
| C12 | C11 | P1 | $110.6(2)$ | C15 | P1 | P5 | $106.82(13)$ |
| C13 | C14 | C15 | $113.3(4)$ | C15 | P1 | P2 | $109.28(13)$ |
| C13 | C12 | C11 | $112.0(3)$ | C11 | P1 | P5 | $119.20(13)$ |
| C14 | C13 | C12 | $113.9(4)$ | C11 | P1 | P2 | $119.99(13)$ |
| C11 | P1 | C15 | $102.05(18)$ |  |  |  |  |

$\left[C p^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}\left(\mathrm{C}_{6} \mathrm{H}_{12}\right)\right\}\right](5)$


Fig. S46. Molecular structure of 5 (left part) in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The disorder is highlighted blue (Part 1) and green (Part 2) (right part).

Table S16. Selected bond lengths of 5 .

| Atom | Atom | Length [Å] | Atom | Atom | Length [Å] |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | Part 1 - 5 |  | Part 2 - 5 |  |  |
| C12 | C13A | 1.40(4) | C13B | C14B | 1.49(4) |
| C14A | C15A | 1.51(3) | C15B | C14B | 1.54(2) |
| C14A | C13A | 1.59(4) | C16 | C15B | 1.61(2) |
| C16 | C15A | 1.46(2) | C12 | C13B | 1.60(3) |
| P1 | P5 | $2.139(3)$ | C12 | C11 | $1.538(11)$ |
| P1 | C16 | 1.819(7) | P3 | P4 | 2.153(3) |
| P1 | C11 | 1.823(7) | P5 | P4 | 2.140(3) |
| P2 | P3 | 2.143(3) | P1 | P2 | 2.143(2) |

Table S17. Selected angles of 5 .

| Atom | Atom | Atom | Angle [ ${ }^{\circ}$ ] | Atom | Atom | Atom | Angle [ ${ }^{\circ}$ ] |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Part 1-5 |  |  | Part 2 - 5 |  |  |  |
| C15A | C16 | P1 | 119.0(11) | C15B | C16 | P1 | 113.4(9) |
| C13A | C12 | C11 | 122.0(14) | C11 | C12 | C13B | 112.3(13) |
| C15A | C14A | C13A | 115.1(17) | C14B | C13B | C12 | 118(2) |
| C16 | C15A | C14A | 115.8(17) | C14B | C15B | C16 | 113.7(13) |
| C12 | C13A | C14A | 115(2) | C13B | C14B | C15B | 114.4(14) |
| C12 | C11 | P1 | 112.4(5) |  |  |  |  |

SPBnz\{( $\left.\left.\mathrm{CH}_{2}\right)_{3}\right\}\left(6^{\prime}\right)$


Fig. S47. Molecular structure of 6 ' in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity.

Table S18. Selected bond lengths of 6'.

| Atom | Atom | Length $[\AA \AA]$ | Atom | Atom | Length $[\AA ̊]$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| P1 | S1 | $1.9538(5)$ | C8 |  | $1.554(2)$ |
| P1 | C1 | $1.8273(13)$ | C10 | C9 | $1.560(2)$ |
| P1 | C10 | $1.8251(14)$ | P1 | C8 | $1.8232(14)$ |

Table S19. Selected angles of 6'.

| Atom | Atom | Atom | Angle [ ${ }^{\circ}$ ] | Atom | Atom | Atom | Angle [ ${ }^{\circ}$ ] |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| C1 | P1 | S1 | $115.06(5)$ | C8 | C9 | C10 | 99.23(11) |
| C10 | P1 | S1 | $120.94(5)$ | C9 | C8 | P1 | $89.43(9)$ |
| C10 | P1 | C1 | $106.73(6)$ | C9 | C10 | P1 | $89.18(8)$ |
| C8 | P1 | S1 | $120.30(5)$ | C8 | P1 | C10 | $81.12(7)$ |
| C8 | P1 | C1 | $107.58(7)$ |  |  |  |  |

## SPBnz\{( $\left.\left.\mathrm{CH}_{2}\right)_{4}\right\}\left(7^{\prime}\right)$



Fig. S48. Molecular structure of $7^{\prime}$ in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity.
Table S20. Selected bond lengths of 7'.

| Atom | Atom | Length $[\AA ̊]$ | Atom | Atom | Length $[\AA ̊]$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| P1 | S1 | $1.9557(16)$ | C10 |  | $1.514(8)$ |
| P1 | C8 | $1.831(5)$ | C11 | C10 | $1.521(9)$ |
| P1 | C11 | $1.818(7)$ | C8 | C9 | $1.540(8)$ |
| P1 | C1 | $1.826(5)$ |  |  |  |

Table S21. Selected angles of 7'.

| Atom | Atom | Atom | Angle [ ${ }^{\circ}$ ] | Atom | Atom | Atom | Angle [ ${ }^{\circ}$ ] |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| C8 | P1 | S1 | $116.16(17)$ | C9 | C8 | P1 | 104.8(4) |
| C11 | P1 | S1 | $115.39(19)$ | C10 | C11 | P1 | 105.6(4) |
| C11 | P1 | C8 | $95.4(3)$ | C9 | C10 | C11 | 107.9(5) |
| C11 | P1 | C1 | $107.9(3)$ | C10 | C9 | C8 | 106.6(4) |
| C1 | P1 | C8 | $105.3(2)$ |  |  |  |  |

SPBnz\{( $\left.\left.\mathrm{CH}_{2}\right)_{5}\right\}\left(8^{\prime}\right)$


Fig. S49. Molecular structure of $\mathbf{8}^{\prime}$ in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity.
Table S22. Selected bond lengths of 8'.

| Atom | Atom | Length $[\AA \AA]$ | Atom | Atom | Length $[\AA ̊]$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| P2 | C18 | $1.827(8)$ | C18 | C19 | $1.508(11)$ |
| P2 | C17 | $1.802(7)$ | C14 | C15 | $1.531(11)$ |
| P2 | C13 | $1.789(8)$ | C14 | C13 | $1.507(10)$ |
| P2 | S2 | $1.963(3)$ | C16 | C15 | $1.513(11)$ |
| C16 | C17 | $1.525(10)$ |  |  |  |

Table S23. Selected angles of $\mathbf{8}^{\prime}$.

| Atom | Atom | Atom | Angle [ ${ }^{\circ}$ ] | Atom | Atom | Atom | Angle [ $\left.{ }^{\circ}\right]$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| C18 | P2 | S2 | $114.2(2)$ | C 15 | C 16 | C 17 | $113.2(6)$ |
| C17 | P2 | C18 | $107.0(3)$ | C13 | C14 | C15 | $112.5(6)$ |
| C17 | P2 | S2 | $112.8(2)$ | C16 | C15 | C14 | $113.8(6)$ |
| C13 | P2 | C18 | $105.6(4)$ | C16 | C17 | P2 | $110.0(5)$ |
| C13 | P2 | C17 | $101.9(4)$ | C14 | C13 | P2 | $111.6(5)$ |
| C13 | P2 | S2 | $114.3(2)$ | C19 | C18 | P2 | $113.3(5)$ |

$\operatorname{SPBnz\{ (\mathrm {CH}_{2})_{6}\} (9^{\prime })}$


Fig. S50. Molecular structure of $9^{\prime}$ in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity.
Table S24. Selected bond lengths of 9'

| Atom | Atom | Length $[\AA ̊]$ | Atom | Atom | Length $[\AA ̊]$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| S4 | P4 | $1.9673(9)$ | C42 | C43 | $1.528(4)$ |
| P4 | C41 | $1.815(3)$ | C45 | C46 | $1.537(4)$ |
| P4 | C47 | $1.825(3)$ | C45 | C44 | $1.537(5)$ |
| P4 | C46 | $1.816(3)$ | C43 | C44 | $1.538(4)$ |
| C41 | C42 | $1.532(4)$ |  |  |  |

Table S25. Selected angles of ${ }^{\prime}$.

| Atom | Atom | Atom | Angle [ ${ }^{\circ}$ ] | Atom | Atom | Atom | Angle [ ${ }^{\circ}$ ] |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| C41 | P4 | S4 | $114.30(9)$ | C43 | C42 | C41 | $115.5(2)$ |
| C41 | P4 | C47 | $105.17(13)$ | C46 | C45 | C44 | $117.5(3)$ |
| C41 | P4 | C46 | $105.78(13)$ | C42 | C43 | C44 | $113.6(2)$ |
| C47 | P4 | S4 | $114.04(9)$ | C45 | C46 | P4 | $116.1(2)$ |
| C46 | P4 | S4 | $113.92(10)$ | C45 | C44 | C43 | $117.7(2)$ |
| C46 | P4 | C47 | $102.49(13)$ |  |  |  |  |

$\left[\left(\left\{\mathrm{C}_{4} \mathrm{H}_{8}\right\} \mathrm{PH}\right)_{2} \mathrm{PtCl}_{2}\right](11)$


Fig. S51. Molecular structure of 11 in the solid state with thermal ellipsoids at 50\% probability level. Hydrogen atoms are omitted for clarity.
Table S26. Selected bond lengths of 11.

| Atom | Atom | Length $[\AA ̊]$ | Atom | Atom | Length [Å] |
| :--- | :--- | :--- | :--- | :--- | :--- |
| Pt01 | P003 | $2.2263(14)$ | P003 | C 006 | $1.831(5)$ |
| Pt01 | $\mathrm{ClO2}$ | $2.3600(14)$ | C 005 | C 2 | $1.519(9)$ |
| P003 | CO 5 | $1.823(4)$ | C 006 | C 1 | $1.529(8)$ |
| C 1 | C 2 | $1.503(12)$ |  |  |  |

Table S27. Selected angles of 11.

| Atom | Atom | Atom | Angle [ ${ }^{\text {] }}$ ] | Atom | Atom | Atom | Angle [ ${ }^{\text {] }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ClO 2 | Pt01 | P003 | 87.30(4) | C005 | P003 | C006 | 95.5(2) |
| P003 | Pt01 | $\mathrm{ClO2}^{1}$ | 179.39(5) | C006 | P003 | Pt01 | 116.43(19) |
| C005 | P003 | Pt01 | 117.50(19) |  |  |  |  |

${ }^{1} 1-Y, 1-X, 1 / 2-Z$

## 4. Additional Information

## NMR Investigations



Fig. S52. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of the reaction of I with 1,5 -dibromopentane $\left(^{*}=\right.$ unidentified sideproduct).


Fig. S53. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of the reaction of I with 1,6 -dibromohexane $\left(^{*}=\right.$ unidentified sideproduct).


Fig. S54. Cutout: ${ }^{31} \mathrm{P}$ NMR (top) and ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}$ (button) ( $161.98 \mathrm{MHz}, \mathrm{THF}-\mathrm{d}_{8}$ ) spectrum of the reaction of 2 with $\mathrm{LiAlH}_{4}$ : Phosphetane $\mathrm{HP}\left\{\left(\mathrm{CH}_{2}\right)_{3}\right\}\left(\mathrm{PPh}_{3}\right.$ capillary in toluene- $\mathrm{d}_{8}, \mathrm{c}=0.2 \mathrm{~mol} / \mathrm{L}$, internal reference).


Fig. S55. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $161.98 \mathrm{MHz}, \mathrm{THF}-\mathrm{d}_{8}$ ) spectrum of the reaction of 3 with $\mathrm{LiAlH}_{4}$ and distillation of the phospholane $\left(\mathrm{HP}\left\{\left(\mathrm{CH}_{2}\right)_{4}\right\}, 10 \mathrm{~b}\right)\left(\mathrm{PPh}_{3}\right.$ capillary in toluene $-\mathrm{d}_{8}, \mathrm{c}=0.2 \mathrm{~mol} / \mathrm{L}$, internal reference).


Fig. S56. ${ }^{31} \mathrm{P}$ NMR (top) and ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}$ (button) ( 161.98 MHz , THF) spectrum of the reaction of 4 with $\mathrm{LiAlH}_{4}$ and distillation of the phosphinane $\mathrm{HP}\left\{\left(\mathrm{CH}_{2}\right)_{5}\right\}\left(\mathrm{PPh}_{3}\right.$ capillary in toluene- $\mathrm{d}_{8}, \mathrm{c}=0.2 \mathrm{~mol} / \mathrm{L}$, internal reference).


Fig. S57. Cutout: ${ }^{31} \mathrm{P}$ NMR (top) and ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}$ (button) ( $161.98 \mathrm{MHz}, \mathrm{THF}-\mathrm{d}_{8}$ ) spectrum of the reaction of 5 with $\mathrm{LiAlH}_{4}$ : Phosphepane $\mathrm{HP}\left\{\left(\mathrm{CH}_{2}\right)_{6}\right\}\left(\mathrm{PPh}_{3}\right.$ capillary in toluene- $\mathrm{d}_{8}, \mathrm{c}=0.2 \mathrm{~mol} / \mathrm{L}$, internal reference). (*, \# = unidentified sideproducts).



Fig. S58. Cutout: ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $161.98 \mathrm{MHz}, \mathrm{THF}-\mathrm{d}_{8}$ ) spectrum of the reaction of 2 with $\mathrm{LiAlH}_{4}$ and distillation.

## 5. References

[i] E. S. S. A, L. Lochmann and J. Trekoval, J. Organomet. Chem., 1987, 326, 1-7.
[ii] M. V. Butovskiy, G. Balázs, M. Bodensteiner, E. V. Peresypkina, A. V. Virovets, J. Sutter and M. Scheer, Angew. Chem. Int. Ed., 2013, 52, 2972-2976.
[iii] L. J. Bourhis, O. V Dolomanov, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Crystallogr., 2009, 42, 339-341.
[iv] G. M. Sheldrick, Acta Crystallogr. Sect. A, 2015, 71, 3-8.
[v] G. M. Sheldrick, Acta Crystallogr. Sect. C, 2015, 71, 3-8.

# 7 Controlled functionalization of one $P$ atom in $\left[C p^{*} F e\left(\eta^{5}-P_{5}\right)\right]$ by successive reactions with nucleophiles and electrophiles containing functional groups 

### 7.1 Preface

The following chapter is about to be submitted.
S. Reichl, F. Riedlberger, M. Piesch, G. Balázs, M. Seidl, M. Scheer, manuscript in preparation.

## Authors

Stephan Reichl, ${ }^{1}$ Felix Riedlberger, ${ }^{1}$ Martin Piesch, ${ }^{1}$ Gábor Balázs, ${ }^{1}$ Michael Seidl, ${ }^{1}$ Manfred Scheer ${ }^{1}$
${ }^{1}$ Institute of Inorganic Chemistry, University of Regensburg; Universitätsstraße 31, 93053 Regensburg, Germany.
*Corresponding author. Email: manfred.scheer@chemie.uni-regensburg.de

## Author Contribution

S.R., F.R. and M.P. conceived the experiments. S.R., M.P. and M. Sei. analysed and revised the X-ray data; S.R., G. B. and M.Sch. wrote the manuscript. M.Sch. directed and coordinated the research.

Controlled functionalization of one $P$ atom in [Cp*Fe( $\left.\left.\eta^{5}-P_{5}\right)\right]$ by successive reactions with nucleophiles and electrophiles

## containing functional groups





Functionalization

# Controlled functionalization of one $P$ atom in $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\boldsymbol{\eta}^{5}-\mathrm{P}_{5}\right)\right]$ by <br> successive reactions with nucleophiles and electrophiles 

containing functional groups


#### Abstract

In subsequent salt metathesis reactions, a variety of organo-polyphosphorus ligands can be obtained containing different functional groups such as halogen or nitrile, which can be accesed in further functionalization reactions. The reaction of anionic complexes of the type $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} R\right)\right]^{-}\left(R={ }^{\dagger} \mathrm{Bu}\right.$ (1a), Me (1b), $-\equiv-P h(1 c))$ with carbon-based electrophiles, containing functional groups (FG), leads to the formation of complexes of type $\left[C p^{*} F e\left(\eta^{4}-P_{5} R R^{F G}\right)\right]$ (2). The bromine in $2 a$ can be easily substituted by nucleophiles leading to 4, 5 or 6 . The reaction of the dianionic species $\left[K(d m e)_{2}\right]_{2}\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}\right)\right]$ (I') with bromo-nitriles leads to compond 7, allowing the introduction of two functional groups attached to one phosphorus atom. 7 reacts with Cul in a self assemble reactions to form the supramolecular structures 8 .


### 7.2 Introduction

Chela originates from the ancient Greek language and means claw or pincer and is related to the word chelos - crab. Chelate ligands, similar to a crab's prey, surround the metal center not with only one donor atom, but with two or more coordinating bonds separated from each other. The chelate effect ${ }^{1}$ can be explained using principles of thermodynamics and favors in principle the chelated complex, featuring a two, tri or multidentate ligand. Chemists took advantage of this phenomenon and synthesized, developed, and tuned a variety of different chelate or pincer ligands which are very important in coordination chemistry and catalysis. ${ }^{2-8}$ Prominent classes are e.g BINAP [2,2'-bis(diphenylphosphino)-1,1'-binaphthyl],9 DPPE (1,2-bis(diphenylphosphino)- ethane), ${ }^{10,11}$ DPPF (1,1'-bis(diphenylphosphino)ferrocene) ${ }^{12}$ or $[P, N]^{4,13}$ ligands (Scheme 1). These are used e.g., for asymmetric catalysis, ${ }^{4,14}$ hydrogenation, ${ }^{6,15,16}$ and coupling reactions ${ }^{17}$.

Although polydentate ligands are an important class of ligands for the stabilization of metal complexes and catalysis, their synthesis is not trivial. Specifically, polyphosphorus ligands ${ }^{9,18,19}$ are based on the use of $\mathrm{PCl}_{3}$, obtained from chlorination of white phosphorus. By doing this, in general, $\mathrm{PCl}_{3}$ is converted to the corresponding phosphine by stepwise salt metathesis with a suitable lithium-organyl / Grignard-reagent. The downsides of this route are the poor selectivity and the difficult separation of the reaction products. Furthermore, this route does,
in general, not tolerate functional groups in the "backbone", which becomes crucial when it comes to adaptation to the desired ligand properties. In principle, multidentate ligands are first synthesized according to electronic and steric requirements, then coordinated to a transition metal fragment, and later on tested for their use in subsequent reactions. ${ }^{20-22}$ Especially the synthesis of new and especially unsymmetrically substituted organophosphorus compounds is a challenge. ${ }^{15}$ There are only very few poly- or especially cyclic phosphines known, which carry functional groups and allow coordination and subsequent reactions. ${ }^{23-26}$ Therefore, the need for alternative synthetic routes is a hot topic in (organophosphorus) chemistry.

This prompted us to study whether it is possible to tune and functionalize a polyphosphorus ligand, already in the coordination-sphere of a transition metal, and then use it for subsequent reactions. Inter alia different coordination modes towards other Lewis acidic metals, synthetically modify or remove the prebuilt ligand from the transition metal complex (Scheme 1).


Scheme 1. Top: Selected bidentate phosphine ligands; ${ }^{9-11,25}$ Bottom: Functionalization of Pentaphosphaferrocene: introduction of functional groups and subsequent chemical reactions.

Pentaphosphaferrocene ( $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right]$ ( I$)$ ) as a P-atom carrier, ${ }^{27}$ seemed to be an ideal candidate for such an investigation as the compound is readily accessible with a wide range of $C p^{R}$ ligands and substituents as well as its capability to release functionalized phosphines by abstraction. ${ }^{27,28}$ Thus, the initial obtained anionic precursor $\left[C p^{*} F e\left(\eta^{4}-P_{5} R\right]^{-}\right.$(1a: $R={ }^{\dagger} B u$; 1b: $R=M e ; 1 c: R=-\equiv P h$ ), by nucleophilic modification, were reacted with the electrophiles, bearing function groups (FG) (Scheme 2).

### 7.3 Results

Herein we report the synthesis of a variety of neutral complexes of the type [Cp*Fe( $\left.\left.\eta^{4}-P_{5} R R^{\prime}\right)\right]$ (2a: $\mathrm{R}={ }^{\dagger} \mathrm{Bu}, \mathrm{R}^{\prime}=\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br} ; \mathbf{2 b}: \mathrm{R}=\mathrm{Me}, \mathrm{R}^{\prime}=\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br} ; \mathbf{2 c}: \mathrm{R}=-\equiv \mathrm{Ph}, \mathrm{R}^{\prime}=\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CN} ; \mathbf{2 d}: \mathrm{R}=\mathrm{Me}$, $\left.\mathrm{R}^{\prime}=\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CN} ; 2 \mathrm{e}: \mathrm{R}=\mathrm{Me}, \mathrm{R}^{\prime}=\left(\mathrm{CH}_{2}\right)_{4} \mathrm{Br}\right)$ featuring functional groups, with ethynyl, nitrile and/or bromine substituents. The obtained complexes, like 2a readily react with nucleophiles e.g., $\mathrm{KPPh}_{2}$ or KBnz resulting in the selective formation of complexes in which the Br substituent is replaced by a terminal $\mathrm{PPh}_{2}$ or Bnz unit, respectively. Furthermore, complex 7, containing two nitrile units, proved to be a versatile ligand towards $\mathrm{ZnBr}_{2}$ leading to the unprecedented coordination aggregate 8 in the solid state.

In a first step, the scope of anionic starting materials was extended by introducing an ethynyl group by synthesising the complex $[\mathrm{K}(18 \mathrm{c} 6)($ thf $)]\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}-\equiv \mathrm{Ph}\right)\right]$ (1c). When ethynylbenzene is deprotonated with benzyl potassium and added to a solution of $\left[C p^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right](\mathrm{I})$ in THF a colour change from green to brown is observed. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of the reaction solution show only one set of signals corresponding to an ABB'XX' spin system with resonances centered at 37.3, 27.9, and 58.4 ppm (Figure 1 and S16). Crystals of 1 c are obtained from a concentrated THF solution layered with $n$-hexane. Single crystal Xray structure analysis revealed the molecular structure of a of the resulting product 1 c in the solid-state (Figure 1 and S34). The main structural feature of 1 c is a $\eta^{4}$ coordinated cyclo- $\mathrm{P}_{5}$ ligand in an envelope conformation with a phenylethynyl substituent attached to the out-of-the-plane phosphorus atom.


Figure 1. Molecular structure of 1a in the solid state with thermal ellipsoids at $50 \%$ probability level: Cations and Hydrogen atoms are omitted for clarity; The $\mathrm{Cp}^{*}$ ligand is drawn in a wire frame model. Experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{THF}-\mathrm{d}_{8}\right)$ spectrum of the anion of 1 c .

All P-P bonds are in the expected range and reveal double bond character with a $\mathrm{P}-\mathrm{P}$ bond lengths of $2.127(4)-2.187(3) ~ \AA,{ }^{29,30}$ whereas the newly formed $P-C$ bond is with $1.782(7) \AA$ in the range of a single bond. ${ }^{29}$

Similarly to 1c, the anionic complexes $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} R\right]^{-}\left(R={ }^{\mathrm{t}} \mathrm{Bu}(1 a)\right.\right.$ and $\left.R=\mathrm{Me}(1 \mathrm{~b})\right)$ can be synthesised. ${ }^{27}$ Due to the nucleophilic character of the out-of-plane phosphorus atom in these complexes we reacted $1 \mathrm{a}-\mathrm{c}$ with carbon cantered electrophiles, containing in addition a functional group.

The reaction of $\mathbf{1 a}, \mathbf{b}$ with $\mathbf{1 , 3}$-dibromopropane results in the formation of a mixture of $\mathbf{2 a} \mathbf{a}, \mathbf{b}$ and 3a,b (Scheme 2), which can be separated by column chromatography under inert atmosphere. 2a,b can be obtained as brown needles in a moderate crystalline yield of $53 \%(2 a)$ and $50 \%$ (2b), respectively, while 3a,b in 32 \% (3a) and 33 \% (3b) yield. Single crystal X-ray structure analysis shows the expected structure of $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{RR}^{\prime}\right]\left(\mathbf{2 a}: \mathrm{R}={ }^{\mathrm{t}} \mathrm{Bu}, \mathrm{R}^{\prime}=\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br} ; \mathbf{2 b}: \mathrm{R}=\right.\right.$ $\left.\mathrm{Me}, \mathrm{R}^{\prime}=\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br}\right)$ containing a 1-bromopropane substituent attached the out-of-plane phosphorus atom (Scheme 2, Figure 2). This stated method can be extended to introduce a nitrile group (2d), by using 4-bromobutyronitrile or extend the alkyl chain length, by using 1,4dibromobutane (2e).


Scheme 2. Reaction of $\mathbf{1 a},{ }^{14} \mathbf{b},{ }^{14} \mathbf{c}$ with 1,3-dibromopropane / 1,4-dibromobutane / 4-bromobutyronitrile and Mel. (Yields are given in parenthesis; *complexes co-crystallize, so the yields are summed up, respectively)

In all of these complexes 2a-e, the phosphorus carbon distances are close to a single bond, ${ }^{29}$ whereas the P-P bond lengths lie within the range of a single and double bond (Table S2O-29). ${ }^{29,30}$


Figure 2. Molecular structures of 2a and 2d in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligands are drawn in a wire frame model.

The second fraction of the chromatographic workup was identified as $3 \mathbf{a}$ and $\mathbf{b}$, which reveals two [Cp*Fe( $\left.\left.\eta^{4}-P_{5}\right) R\right]$ (3a: $R={ }^{\text {t }} \mathrm{Bu}$; 3b: $R=M e$ ) moieties linked by a propane-1,3-diyl-group, respectively. In the major product 3 a , the $n$-propyl group is attached to the out-of-plane phosphorus atom P1 (Fig. S40). In addition to 3a, a minor product 3a' co-crystalizes in a ratio of 8:92. In 3a' the electrophile is attached to the $P$ atom next to the out-of-plain $P$ atom leading to a 1,2-substitution pattern, instead of the 1,1-substitution (Fig. S41). However, the separation of 3 a and 3 a ' via column chromatography or other methods failed. Therefore, ${ }^{31} \mathrm{P}$ NMR spectroscopy was investigated whether the temperature, order of addition of the starting materials or chain length (1,4-dibromobutane instead of 1,3-dibromopropane) have an influence on the reaction progress. Unfortunately, it was not possible to completely hamper the formation of $3 a^{\prime}$ as in compound $\mathbf{3 b}$. However, a minimum amount of $3 a^{\prime}$ is formed when adding slowly 1,3-dibromopropane to a $-80^{\circ} \mathrm{C}$ pre-cooled solution of 1 a (Fig. S55). On the other hand, within the same reaction conditions, the amount of 2a decreases thereby significantly (Fig. S55). Therefore, the formation of $3 a^{\prime}$ can be seen as the kinetic product whereas $3 a$ is the thermodynamic one. This assumption is in hand with the results of DFT calculations (B3LYP/def2-TZVP level of theory), which predict 3a to be with $29 \mathrm{~kJ} / \mathrm{mol}$ more stable than 3a' (Table S46). Since the migration is very little to none present when changing the starting material to $\left[\mathrm{Li}(\mathrm{dme})_{3}\right]\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Me}\right)\right]$ (1b) (Fig. S56), the formation of 3a' is probably also due to steric bulk of the tert-butyl group in contrast to the significantly smaller methyl group.

However, the formation of $\mathbf{2 a} / \mathbf{b}$ can be completely suppressed by using a ratio of 2:1 in the reaction between $1 \mathrm{a} / \mathrm{b}$ and 1,3 -dibromopropane at $-80^{\circ} \mathrm{C}$, respectively. Increasing the carbon chain length i.e., by using 1,4-dibromobutane does have a relevant influence on the ratio of the 1,1 and 1,2 -substitution products, according to ${ }^{31}$ P NMR spectroscopic investigations (Fig. S57), and favours the 1,2 -substituted product $3 \mathbf{c}$ ', although the $3 \mathbf{c}$ still remains the major isomer. The reaction of compound $\mathbf{1 b}$ with 1,4 -dibromobutane still leads to the formation of $\mathbf{2 e}$ (Scheme 2) and as described above, to the bridged compounds $3 \mathrm{c} / \mathrm{c}^{\prime}$ (Fig. S58). The 1,2 -substitution product $3 c^{\prime}$ is formed only in minor amounts, but a minor component of a migration of the $n$ -butyl-bromine substituent can be seen in the crystal structure of 2 e (Fig. S41). When the reaction is conducted at room temperature, 2 e can be isolated as spectroscopically pure compound (Fig. S6, S21).

In order to extend the scope of functional groups, we used 4-bromobutyronitrile to attach a terminal nitrile group (Scheme 2). ${ }^{31} \mathrm{P}$ NMR spectroscopic investigations of the reaction mixtures of 1a-c with 4-bromobutyronitrile show selective conversions. However, only by using 1b, it was possible to receive single crystals of 2d (Scheme 2). Compound 2d can be isolated as dark brown blocks in 72 \% yield. 2d co-crystalizes with traces of I (5 \%), which can be washed
with hexane to yield the spectroscopic pure compound 2d. It is interesting to see that a versatile nitrile group can easily be introduced (Figure 2).

To prove the accessibility of the bromine functionality in 2a for consecutive reactions, complex 2a was reacted with 1b, which serves as a nucleophile. Indeed, the reactions lead to the formation of the asymmetric organo-substituted polypnictogen ligand complex 4 as dark green blocks in 80 \% yield (Scheme 3). The molecular structure in solid-state is depicted in Figure 4 and exhibits two organo-substituted $\left[C p^{*} F e\left(\eta^{4}-P_{5} R\right)\right]\left(R={ }^{\dagger} B u, M e\right)$ moieties which are linked via a $n$-propyl group. The formation of different isomers by migration of the organic groups has not been observed.


Scheme 3. Consecutive reactions of 2a: a) Reaction with $1 \mathrm{~b} \rightarrow 4$; b) Functionalization with $\mathrm{KPPH}_{2} \rightarrow 5$; c) First Reaction with KBnz, then abstraction of the functionalized phosphine 6. (Yields are given in parenthesis)

The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of 4 reveals two different $A M M$ ' $X X$ ' spin systems, corresponding to the two inequivalent $\mathrm{P}_{5}$ units (Figure 3). Based on the presence of different P -H coupling in the ${ }^{31} \mathrm{P}$ NMR spectrum, an unambiguous assignment of the spin systems to the differently substituted $\mathrm{P}_{5}$ units could be made (Fig. S25, 26). Both spin systems show multiplets centered at $-120.3,41.0$, and 164.3 ppm as well as at $-129.9,29.8$, and 128.9 ppm , respectively.


Figure 3. Experimental (top) in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at 293 K and simulated (bottom) ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right] \mathrm{NMR}$ spectrum of 4.

Since compound 4 shows two different $\eta^{4}-P_{5} R R^{\prime}(R=M e, ~ ' B u ; ~ R '=n$-propyl) ligands, we measured a cyclovoltammogram to investigate the redox chemistry and check whether the two iron atoms are electrochemical inequivalent. Indeed, the CV (Fig. S63, in o-DFB, revered to $\left[\mathrm{Cp}_{2} \mathrm{Fe}\right] /\left[\mathrm{Cp}_{2} \mathrm{Fe}\right]^{+}$) shows three oxidation processes, one quasi reversible ( $\mathrm{E}_{\mathrm{rev}}=-210 \mathrm{mV}$ ) and two irreversible ( $\mathrm{E}_{1 \text { irev }}=900 \mathrm{mV}$; $\mathrm{E}_{2 \mathrm{irev}}=1.01 \mathrm{~V}$ ), as well as two irreversible reductions ( $\mathrm{E}_{1 \text { irev }}=2.70 \mathrm{~V}$; $\mathrm{E}_{2 \text { irev }}=2.57 \mathrm{~V}$ ).

Since complexes 2 can be rationalised as being formally bromo-alkanes, their reactivity towards charged nucleophiles was investigated. Thus, compound 2a was reacted with potassium diphenylphosphanide $\left(\mathrm{KPPh}_{2}\right)$ leading to the formation of complex 5 (Scheme 3, Figure 4). The ${ }^{31} P\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of the reaction solution shows an $A M M{ }^{\prime} X X$ ' spin system and an additional singlet located at $\delta=-17.9 \mathrm{ppm}$, which proofs the formation of the desired product 5, featuring a terminal phosphine unit. Crystallization from n-pentane at r.t. under reduced pressure leads to pure 5 in $75 \%$ yield. The molecular structure proves the identity of 5 (Figure 4). It has to be noted that the nature of the phosphanide can be varied. The use of LiPCy2 (Cy = cyclo-hexyl) does also lead to the desired product, according to ${ }^{31} \mathrm{P}$ NMR spectroscopic (Fig. S59) and mass spectrometric investigations.


4


5


Figure 3. Molecular structures of 4, 5 and 6 ' in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligands are drawn in a wire frame model.

Interestingly, the ${ }^{31} \mathrm{P}$ NMR spectrum of the reaction mixture does not show any signs of a phosphine abstraction or the formation of $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{4}\right)\right]^{-}$as reported for the for the reaction of $\left.\left[\mathrm{Cp}^{*} \mathrm{FeP}_{5} \mathrm{R}_{2}\right)\right]\left(\mathrm{R}=\mathrm{Me},{ }^{\mathrm{t}} \mathrm{Bu}\right)$ with $\mathrm{KBnz} .{ }^{27}$ Instead, KPPh 2 reacts selectively, under salt metathesis, with the bromine in 2a. Formally, one can state that the functional group acts a protecting group and shields the $\mathrm{P}_{5}$ ligand from the nucleophile. Inspired by this observation and the reported phosphine abstraction, ${ }^{27}$ compound 2 a was reacted with two equivalents (in portions) of benzyl potassium (KBnz). According to ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopic investigations (Fig. S60) the first equivalent of KBnz reacts with 2a via salt metathesis i.e. substitution of the bromine group, and the second equivalent leads to the elimination of the phosphine $\mathrm{P}^{\mathrm{t}} \mathrm{BuBnz}\left(\left(\mathrm{CH}_{2}\right)_{4} \mathrm{Ph}\right) 6$ (Scheme 3 and Fig. S60) and formation of $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{4}\right)\right]^{-}$. The identity of the phosphine 6 (Scheme 3) was proven by NMR spectroscopy $\left(\delta\left({ }^{(11} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}\right)=4.5 \mathrm{ppm}\right.$ which is in the typical range of phosphines $)^{31}$ and, after oxidation with sulphur to the corresponding phosphine sulphide 6', also by single-crystal X-ray diffraction analysis (Fig. S50). It has to be mentioned that 6 and 6 ' are obtained as racemates.

This result shows that is not only possible to selectively functionalize one phosphorus atom in [Cp*Fe( $\left.\left.\eta^{4}-\mathrm{P}_{5}\right)\right]$ (I) but also to introduce different substituents containing functional groups, which can be further converted to other functionalities and finally cleave off the corresponding phosphine or bis-phosphine. This route represents an easy and convenient way to synthesize in principle any desired phosphine.

To extent the number or functional groups attached to the $\mathrm{P}_{5}$-platform, and which, do not tolerate strong nucleophiles, the dianionic species $\left[\mathrm{K}(\mathrm{dme})_{2}\right]_{2}\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}\right)\right]$ ( $\left.\mathrm{I}^{\prime}\right)$ was reacted with two equivalents of 4-bromobutyronitrile (Scheme 4). This reaction results quantitatively in the formation of the desired product $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}\left(\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CN}\right)_{2}\right\}\right](7)$ in $67 \%$ isolated yield. The molecular structure in the solid state reveals an $\eta^{4}-P_{5}$ moiety, bearing two $n$-propyl substituents with terminal nitrile groups (Fig. S51).


[^0]The presence of the nitrile functionalities in 7, renders it as a suitable starting material for the synthesis of coordination compounds containing polyphosphorus units, with potentially uncommon structures. Based on our expertise in the supramolecular chemistry of polypnictogen ligand complexes, ${ }^{28}$ coordinating groups, such as nitriles, are feasible ligands in self-assembly reactions with transition metal halides. ${ }^{28}$ Therefore, compound 7 was reacted with zinc(II)bromide in THF. After three days, green/brownish plate shaped crystals of 8 were obtained in 81 \% yield, exhibiting a linear 1D structure in solid state (Figure 5). Within the strain, monomers of $\left[\left\{\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}\left(\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CN}\right)_{2}\right\}\right\}\right]$ are connected by zinc(II)bromide. Thereby, the endo(with respect to the envelope $P_{5}$ unit) nitrile group coordinates to the zinc atom ( $\left.d_{N-Z n}=2.053(6) A ̊\right)$ (Figure 5, Table S44), which is on the other side coordinated in a tetrahedral coordination environment towards the phosphorus atom ( $\mathrm{dp}-\mathrm{zn}=2.4296(18)$ Å) (Figure 5 , Table S44), next to the P atom out of the plane which bears the nitril linking units. The zincphosphorus/nitrogen distances and angles are in alignment with similar complexes. ${ }^{32,33}$ The sum of the covalent radii corresponds approximately to the bond distances in solid state, indicating a bonding interaction between phosphorus-zinc/nitrogen-zinc, respectively. ${ }^{32}$ To best of our knowledge, compound 8 represents the first complex featuring a $\mathrm{ZnBr}_{2}$ unit which is coordinated by a phosphorus atom and a nitrile group. Surprisingly, the exo nitril group does not coordinate (Figure 5). This opens the pathway for further coordination reactions, by using e.g., different stoichiometry or reactions with copper halides. However, this would go beyond the scope of this publication and will be topic of future work. Nevertheless, the reaction of 7 with zinc(ii)bromide show the versatility of the system and the possibility for consecutive reactions different than using $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right](\mathrm{I})$, which does not show any reactivity towards zinc(II)bromide.


Figure 4. Molecular structures of 8 in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligands are drawn in a wire frame model.

The composition of 8 was also proven by elemental analysis and NMR spectroscopy. The latter shows a AMM'XX' spin system in THF-d ${ }_{8}$ at room temperature (Fig. S31). The ${ }^{31} \mathrm{P}$ and ${ }^{1} \mathrm{H}$ NMR spectra are similar to complex 7 but slightly shifted (Fig. S61 and S62), indicating no phosphorus-zinc-interaction, but a nitrogen-zinc-coordination in solution which is in accordance with HSAB principle. ${ }^{34}$ Herein it has to be noted, that after crystallization complex 8 is completely insoluble in non-coordinating solvents like $\mathrm{CH}_{2} \mathrm{Cl}_{2}$.

### 7.4 Conclusion

To sum up, pentaphosphaferrocene (I) represents a very versatile platform for successful functionalization of the cyclo- $\mathrm{P}_{5}$ ligand. In consecutive reactions with electrophiles and nucleophiles, a variety of functional groups can be easily introduced to this polyphosphorus ligand complex, which was up to this date unachieved. This new modular system can even be further synthetically modified (4 and 5), or in a consecutive nucleophilic attack, the functionalized phosphine abstracted (6). In addition, it was possible to synthesize polyphosphorus ligand complexes, which bear two functional groups (7) and can be used for consecutive reactions in coordination chemistry.

## Conflicts of interest

There are no conflicts to declare.

## Author Contributions

Conceptualization: SR, FR, MP, GB, MS
Investigation: SR, FR, MP, GB, MS, MS
Visualization: SR, FR, GB, MS
Funding acquisition: MS
Project administration: GB, MS
Supervision: GB, MS
Writing - original draft: SR, FR, GB, MS
Writing - review \& editing: SR, GB, MS

## Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft within the project Sche 384/38-2. S.R. is grateful to the Studienstiftung des Deutschen Volkes and M.P. to the Fonds der Chemischen Industrie for PhD fellowships.

### 7.5 References

G. Schwarzenbach, Helv. Chim. Acta, 1952, 35, 2344-2359.
H. Guo, Y. C. Fan, Z. Sun, Y. Wu and O. Kwon, Chem. Rev., 2018, 118, 10049-10293.
S. Lühr, J. Holz and A. Börner, ChemCatChem, 2011, 3, 1708-1730.
M. P. Carroll and P. J. Guiry, Chem. Soc. Rev., 2014, 43, 819-833.
C. Redshaw and Y. Tang, Chem. Soc. Rev., 2012, 41, 4484.
H. Wang, J. Wen and X. Zhang, Chem. Rev., 2021, 121, 7530-7567.
H. Han and S. A. Johnson, Organometallics, 2006, 25, 5594-5602.
H. Han, M. Elsmaili and S. A. Johnson, Inorg. Chem., 2006, 45, 7435-7445.
A. Miyashita, A. Yasuda, H. Takaya, K. Toriumi, T. Ito, T. Souchi and R. Noyori, J. Am. Chem. Soc., 1980, 102, 7932-7934.
W. Hewertson and H. R. Watson, J. Chem. Soc., 1962, 1490.
J. Dogan, J. B. Schulte, G. F. Swiegers and S. B. Wild, J. Org. Chem., 2000, 65, 951-957.
G. Marr and T. Hunt, J. Chem. Soc. C Org., 1969, 1070.
D. Peng, X. Yan, C. Yu, S. Zhang and X. Li, Polym. Chem., 2016, 7, 2601-2634.
Q. Zhou, Ed., Privileged Chiral Ligands and Catalysts, Wiley, 2011.
W. Tang and X. Zhang, Chem. Rev., 2003, 103, 3029-3069.
H. Brunner, C. Zettler and M. Zabel, Monatshefte für Chemie, 2003, 134, 1253-1269.
A. L. Clevenger, R. M. Stolley, J. Aderibigbe and J. Louie, Chem. Rev., 2020, 120, 61246196.
H. Gali, S. R. Karra, V. S. Reddy and K. V Katti, Angew. Chem. Int. Ed., 1999, 38, 20202023.
M. M. Rauhut, I. Hechenbleikner, H. A. Currier, F. C. Schaefer and V. P. Wystrach, J. Am. Chem. Soc., 1959, 81, 1103-1107.
H. Li, B. Zheng and K.-W. Huang, Coord. Chem. Rev., 2015, 293-294, 116-138.
M. E. van der Boom and D. Milstein, Chem. Rev., 2003, 103, 1759-1792.
M. Sietzen, S. Batke, L. Merz, H. Wadepohl and J. Ballmann, Organometallics, 2015, 34, 1118-1128.
W. A. Henderson, M. Epstein and F. S. Seichter, J. Am. Chem. Soc., 1963, 85, 2462-2466.
L. S. Meriwether, M. F. Leto, E. C. Colthup and G. W. Kennerly, J. Org. Chem., 1962, 27, 3930-3941.
L. S. Meriwether and J. R. Leto, J. Am. Chem. Soc., 1961, 83, 3192-3196.
A. K. Adhikari, C. G. P. Ziegler, K. Schwedtmann, C. Taube, J. J. Weigand and R. Wolf, Angew. Chemie Int. Ed., 2019, 58, 18584-18590.
S. Reichl, E. Mädl, F. Riedlberger, M. Piesch, G. Balázs, M. Seidl and M. Scheer, Nat. Commun., 2021, 12, 5774.
E. Peresypkina, A. Virovets and M. Scheer, Coord. Chem. Rev., 2021, 446, 213995.
P. Pyykkö and M. Atsumi, Chem. - A Eur. J., 2009, 15, 186-197.
P. Pyykkö and M. Atsumi, Chem. - A Eur. J., 2009, 15, 12770-12779.
O. Kühl, Phosphorus-31 NMR Spectroscopy, Springer Berlin Heidelberg, Berlin, Heidelberg, 2009.
U. Siemeling, T. Klemann, C. Bruhn, J. Schulz and P. Tpnika, Dalt. Trans., 2011, 40, 47224740.
T. Tsukuda, C. Nishigata, K. Arai and T. Tsubomura, Polyhedron, 2009, 28, 7-12. R. G. Pearson, J. Chem. Educ., 1968, 45, 581.

### 7.6 Supplementary Information

# Controlled functionalization of one $P$ atom in [Cp*Fe( $\left.\eta^{5}-P_{5}\right)$ ] by successive reactions with nucleophiles and electrophiles containing functional groups 

Stephan Reichl, ${ }^{1}$ Felix Riedlberger, ${ }^{1}$ Martin Piesch, ${ }^{1}$ Gábor Balázs, ${ }^{1}$ Michael Seidl, ${ }^{1}$ Manfred Scheer ${ }^{1 *}$

${ }^{1}$ Institute of Inorganic Chemistry, University of Regensburg; Universitätsstraße 31, 93053 Regensburg, Germany.
*Corresponding author. Email: manfred.scheer@chemie.uni-regensburg.de

## Table of Content

1. Experimental details 236
2. NMR spectroscopic characterization243
3. Crystallographic details ..... 263
4. Additional Information ..... 282
5. Computational details ..... 286
6. References ..... 288

## 1. Experimental details

## General methods:

All manipulations were carried out under an inert atmosphere of dried argon using standard Schlenk and glove box techniques. 1,2-dimethoxyethane (DME) was dried and deoxygenated by distillation under argon atmosphere from sodium. All other solvents were dried using a MB SPS-800 device of the company MBRAUN and stored over molecular sieve. Ortho-diflourobenze (o-DFB) was dried and deoxygenated by distillation under argon atmosphere from $\mathrm{P}_{2} \mathrm{O}_{5}$. NMR spectra were recorded on a Bruker Avance III 400/600 MHz NMR spectrometer. Chemical shifts were measured at ambient temperature and are given in ppm; they are referenced to TMS for ${ }^{1} \mathrm{H}$ and $85 \% \mathrm{H}_{3} \mathrm{PO}_{4}$ for ${ }^{31} \mathrm{P}$ as external standard. Signal multiplicities are described using common abbreviations: $s$ (singlet), $d$ (doublet), $t$ (triplet), q (quartet), quint (quintet), $m$ (multiplet) and br (broad). LIFDI-/FD-/EI-MS spectra (LIFDI = liquid injection field desorption ionization, $F D=$ field desorption, EI = electron ionization) were measured on a JEOL AccuTOF GCX. ESI-MS spectra (ESI = Electrospray ionization) were measured on an Agilent Q-TOF 6540 UHD. Elemental analysis (CHN) was determined using a Vario micro cube instrument. A glass stirring bar was used in reactions with potassium benzyl. CV / SQV measurements were conducted via the following setup: glass carbon-, Pt- and Ag electrodes; 0.01 mmol analyte, $500 \mathrm{mg}\left[\mathrm{NBu}_{4}\right]\left[\mathrm{PF}_{6}\right]$ as conductive salt, 5 mL solvent (o-DFB), ferrocene for reference.

The compounds potassium benzyl (KBnz, $\mathrm{KC}_{7} \mathrm{H}_{7}$ ), $\left[\mathrm{K}(\mathrm{dme})_{2}\right]_{2}\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}\right)\right] \quad\left(\mathbf{I}^{\prime}\right)$, $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right] \quad(\mathrm{I})$, [Li(dme) $\left.)_{3}\right]$ $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Me}\right)\right]$ (1a) and $\left[\mathrm{Li}(12 \mathrm{c} 4)_{2}\right]\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\right)\right]$ (1b), were synthesized according to literature procedures. ${ }^{[i-i v]}$ Modified Synthesis of $\mathrm{KPPh}_{2}$ : Deprotonation of $\mathrm{PPh}_{2} \mathrm{H}$ with KH in DME and stored as a stock solution at 8 C .

Unless otherwise noted, all other materials were obtained from commercial suppliers and used without purification.
DFT calculations were carried out using the Gaussian 16 program. ${ }^{[v]}$ The geometries were optimised using the B3LYP ${ }^{[v i-i x]}$ functional together with the def2-TZVP basis set ${ }^{[x]}$.

Crystals suitable for single crystal X-ray diffraction analysis were obtained as described below. The diffraction data were collected either on a Gemini Ultra diffractometer equipped with an Atlas ${ }^{52}$ CCD detector and with a finefocus sealed Cu-K $\mathrm{K}_{a}$ X-ray tube, on a XtaLAB Synergy R, DW system diffractometer equipped with a HyPix-Arc 150 detector and a rotating-anode $\mathrm{Cu}-\mathrm{K}_{a} \mathrm{X}$-ray tube or a GV50 diffractometer equipped with a Titan ${ }^{52}$ CCD detector and a micro-focus $\mathrm{Cu}-\mathrm{K}_{a} \mathrm{X}$-ray tube. Data collection and reduction were performed with CrysAlisPro software package. The structures were solved with Olex2, ${ }^{[x i]}$ using ShelXT ${ }^{[x i i]}$ and a least-square refinement on $F^{2}$ was carried out with ShelXL ${ }^{[x i i i]}$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms at the carbon atoms were located in idealized positions and refined with isotropic displacement parameters according to the riding model. The images of the molecular structures were made using Olex2. ${ }^{[x]}$ All NMR simulations were conducted with the WinDaisy application within the NMR software Top Spin 4.1.1 by Bruker.

## Synthetic protocols:

## Synthesis of $[\mathrm{K}(18 \mathrm{c} 6)(\mathrm{THF})]\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}-\equiv-\mathrm{Ph}\right)\right](1 \mathrm{c})$ :

Benzyl potassium ( $0.29 \mathrm{mmol}, 37.8 \mathrm{mg}, 1 \mathrm{eq}$ ) was dissolved in THF and $0.29 \mathrm{mmol}(0.50 \mathrm{~mL}, 1 \mathrm{eq})$ of a 0.58 molar solution of ethynylbenzene in THF was added. Thereby the color changed from red to colorless. Afterwards this solution was added to a solution of $100 \mathrm{mg}(0.29 \mathrm{mmol}, 1 \mathrm{eq})\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right]$ (I) at $-80^{\circ} \mathrm{C}$ in THF. The solution was slowly warmed up to ambient temperatures and stirred overnight. All volatiles were removed in vacuum and the
brown residue was washed three times with 10 mL n-hexane. $38 \mathrm{mg}(0.145 \mathrm{mmol}, 1$ eq) 18 -crown- 6 was dissolved in THF 5 mL , added to the brown residue, layered with $20 \mathrm{~mL} n$-hexane and stored at $4^{\circ} \mathrm{C}$. After two weeks metallic dark green blocks of $[K(18 c 6)($ thf $\left.)]\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}\right)-\equiv-\mathrm{Ph}\right)\right]$ (1c) were formed.

Yield: $124.0 \mathrm{mg}\left(0.151 \mathrm{mmol}, 27\right.$ \%). ${ }^{1} \mathrm{H}$ NMR (THF- $\left.\mathrm{d}_{8}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=7.25(\mathrm{~m}, 3 \mathrm{H},-\mathrm{Ph}), 7.15(\mathrm{~m}, 2 \mathrm{H},-\mathrm{Ph}), 3.87$ (s, $33 \mathrm{H}, 18 \mathrm{c} 6$ ), 3.87 ( $33 \mathrm{H}, \mathrm{THF}$ ), 2.01 ( $\mathrm{m}, 3 \mathrm{H}, \mathrm{THF}$ ), 1.73 ( $\left.\mathrm{s}, 15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}$ (THF-d8, 293 K ): $\delta$ [ppm] $=35.5\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 26.1\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{B}, \mathrm{B}}\right),-60.3\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{X}, \mathrm{X}}\right) .{ }^{31} \mathrm{P}$ NMR (THF- $\left.\mathrm{d}_{8}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=35.5\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 26.1$ (m, 2 P, $\mathrm{P}_{\mathrm{B}, \mathrm{B}^{\prime}}$ ), -60.3 (m, 2 P, $\mathrm{P}_{\mathrm{x}, \mathrm{X}}$ ). (ESI-MS (DME): 446.96 (100 \%, [M] ${ }^{+}$), 478.95 ( $16 \%,\left[\mathrm{M}-\mathrm{O}_{2}\right]^{+}$); analysis (calcd., found for $\left.\mathrm{C}_{34} \mathrm{H}_{52} \mathrm{FeKO}_{7} \mathrm{P}_{5}\right)$ : $\mathrm{C}(49.64,49.66), \mathrm{H}(6.37,6.39)$.

Alternative route: Compound I ( $0.87 \mathrm{mmol}, 300.0 \mathrm{mg}, 1 \mathrm{eq}$ ) and Li-=-Ph ( $0.87 \mathrm{mmol}, 94.0 \mathrm{mg}, 1 \mathrm{eq}$ ) were dissolved together in THF at r.t. Within the next 30 minutes, the green color of the solution got darker. After letting the solution stir overnight, the solvent was removed under reduced pressure and a 0.8102 molar solution of 12 c 4 in DME ( $1.74 \mathrm{mmol}, 2.15 \mathrm{~mL}, 2 \mathrm{eq}$ ) was added. The solution was layered with 10 mL of n -Hexane and stored at r.t. Crystals suitable for XRD were obtained as green plates after one week. The analytical data matches the anion of 1c.

Yield: $497.0 \mathrm{mg}(0.69 \mathrm{mmol}, 79 \%) .{ }^{1} \mathrm{H}$ NMR (THF- $\left.\mathrm{d}_{8}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=7.31(\mathrm{~m}, 3 \mathrm{H},-\mathrm{Ph}), 7.17(\mathrm{~m}, 2 \mathrm{H},-\mathrm{Ph}), 4.06$ ( $\mathrm{s}, 16 \mathrm{H}, 12 \mathrm{c} 4$ ), 3.67 ( $6 \mathrm{H}, \mathrm{DME}$ ), 3.51 (m, $4 \mathrm{H}, \mathrm{DME}), 1.73\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}$ (THF-d $\left.8,293 \mathrm{~K}\right): \delta[\mathrm{ppm}]$ $=35.7\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 26.0\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{B}, \mathrm{B}^{\prime}}\right),-59.3\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\left.\mathrm{x}, \mathrm{X}^{\prime}\right)} .{ }^{31} \mathrm{P} \mathrm{NMR}\left(\mathrm{THF}-\mathrm{d}_{8}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=35.7\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 26.0\right.$ ( $m, 2$ P, $P_{B, B^{\prime}}$ ), $-59.3\left(m, 2\right.$ P, $P_{X, X^{\prime}}$ ). For coupling constants, see Table S1).

## Reaction of $\left[\mathrm{Li}(12 \mathrm{c} 4)_{2}\right]\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\right)\right]$ (1a) with 1,3-dibromopropane:

A solution of insitu generated $1 \mathrm{a}\left(\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right](\mathrm{I}): 2.9 \mathrm{mmol}, 1 \mathrm{~g}, 1 \mathrm{eq}\right.$; ${ }^{\mathrm{t}} \mathrm{BuLi}$ in $n$-pentane: $0.4 \mathrm{mmol}, \mathrm{v}=0.97 \mathrm{~mL}$, $\left.\mathrm{c}=1.028 \mathrm{~mol} \cdot \mathrm{~L}^{-1}, 1 \mathrm{eq}\right)$ in 20 mL THF was added to a 0.917 molar solution of 1,3-dibromopropane in DME ( 2 mmol , $2.18 \mathrm{~mL}, 2 \mathrm{eq}$ ) at room temperature. A colour change from brown to green occurred and a colourless solid was formed. The mixture was stirred for 18 hours. The solvent was removed under reduced pressure. The residue was dissolved in dichloromethane, silica is added, and the solvent was removed in vacuo. The preabsorbed reaction mixture was purified via column chromatography $\left(\mathrm{SiO}_{2}\right.$, hexane, $\left.15 \times 3 \mathrm{~cm}\right)$. Using a mixture of hexane/toluene (8:2), a first green fraction ([ $\left.\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br}\right)\right](2 \mathrm{a})$, followed by a brown one ([(Cp* $\left.\left.\left.{ }^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4: 4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\right\}\right]\right)$ (3a) can be eluted. The solvent of both fractions was removed under reduced pressure. [ $\left.\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br}\right)\right]$ (2a) can be isolated as dark green needles after one day in a concentrated $n$-hexane solution, stored at $-30^{\circ} \mathrm{C}$. $\left[\left(\mathrm{Cp}{ }^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4: 4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\right\}\right]$ (3a) can be obtained as brown needles after one week via layering a dichloromethane $(3 \mathrm{~mL})$ solution with acetonitrile $(10 \mathrm{~mL})$ and stored at $-30^{\circ} \mathrm{C}$.

## Data for $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br}\right)\right]$ (2a):

Yield: $917.0 \mathrm{mg}(1.69 \mathrm{mmol}, 58 \%) .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=3.62\left(\mathrm{t}, 2 \mathrm{H}, \mathrm{J}_{\mathrm{H}-\mathrm{H}}=6.34 \mathrm{~Hz},-\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{2}-\mathrm{Br}\right)$, $2.70\left(\mathrm{~m}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{3}\right), 2.56\left(\mathrm{~m}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{3}\right), 1.63\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 0.59\left(\mathrm{~d}, 9 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=14.54 \mathrm{~Hz},-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right)$. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=165.1\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 40.2\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}}\right)$, $-121.6\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{X}, \mathrm{K}}\right) .{ }^{31} \mathrm{P}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right.$, $293 \mathrm{~K}): \delta[\mathrm{ppm}]=165.1\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 40.2\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}\right),-121.6\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{X}, \mathrm{X}^{\prime}}\right)$. For coupling constants, see Table S2. LIFDI-MS (toluene): $m / z=523.90\left(100 \%,[M]^{+}\right)$. analysis (calcd., found for $\mathrm{C}_{17} \mathrm{H}_{30} \mathrm{FeBrP}_{5}$ ): $\mathrm{C}(47.26,47.61), \mathrm{H}(7.40$, 7.49).

## Data for $\left[\left(C p^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4: 4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{P}_{5}{ }^{t} \mathrm{Bu}\right\}\right]\left(3 \mathrm{a} / 3 \mathrm{a}^{\prime}\right):$

Yield: $390.0 \mathrm{mg}(0.46 \mathrm{mmol}, 32 \%) .3 \mathrm{a}:{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=2.92\left(\mathrm{~m}, 6 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{-}-\right), 1.69(\mathrm{~s}, 30 \mathrm{H}$, $\left.\mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 0.69\left(\mathrm{~d}, 18 \mathrm{H},{ }^{3} \mathrm{JP}_{\mathrm{P}-\mathrm{H}}=14.32 \mathrm{~Hz},-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right),{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=162.4\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 44.6$
( $\mathrm{m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}$ ), -120.1 (m, $\left.\left.2 \mathrm{P}, \mathrm{P}_{\mathrm{X}, \mathrm{X}}\right)^{31}{ }^{31} \mathrm{P} \mathrm{NMR} \mathrm{( } \mathrm{CD}_{2} \mathrm{Cl}_{2}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=162.4\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 44.6\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}\right),-120.1$ ( $m, 2$ P, $P_{x, x}$ ). For coupling constants, see Table S7.

3a': ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=2.75\left(\mathrm{~m}, 1 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{3}-{ }^{-}\right), 2.61\left(\mathrm{~m}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{3}-\right), 1.77\left(\mathrm{~s}, 8 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 1.69$ $\left(\mathrm{s}, 8 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 0.66\left(\mathrm{~d}, 5 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=13.83 \mathrm{~Hz},-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.64\left(\mathrm{~d}, 5 \mathrm{H}, \mathrm{J}_{\mathrm{P}-\mathrm{H}}=14.33 \mathrm{~Hz},-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}$ $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=162.4\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 44.6\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}\right),-120.1\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{x}, \mathrm{x}}\right) .{ }^{31} \mathrm{P}$ NMR ( $\left.\mathrm{CD}_{2} \mathrm{Cl}_{2}, 293 \mathrm{~K}\right): \delta$ [ppm] = $162.4\left(m, 1\right.$ P, $\left.P_{A}\right), 44.6\left(m, 2 P, P_{M, M^{\prime}}\right),-120.1\left(m, 2 P, P_{X, X}\right)$. LIFDI-MS (toluene): $m / z=847.93\left(100 \%,[M]^{+}\right)$. analysis (calcd., found for $\mathrm{C}_{31} \mathrm{H}_{54} \mathrm{Fe}_{2} \mathrm{P}_{10}$ ): $\mathrm{C}(43.87,43.61), \mathrm{H}(6.42,6.36)$. The given Proton NMR Spectrum (Fig. S7) and corresponding signals belong to an attempt to maximize 2b' (see Additional Information) and does not correspond to the ratio in of $\mathbf{3 a} / \mathbf{3 a}$ ' in the solid state (see Crystallographic details).

## Reaction of [Li(dme) $\left.{ }_{3}\right]\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Me}\right)\right]$ (1b) with 1,3-dibromopropane:

A solution of insitu generated $\mathbf{1 b}\left(\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right](\mathrm{I}): 0.4 \mathrm{mmol}, 138.4 \mathrm{mg}, 1 \mathrm{eq} ; \mathrm{MeLi}\right.$ in $\mathrm{Et}_{2} \mathrm{O}: 0.4 \mathrm{mmol}, \mathrm{v}=0.50 \mathrm{~mL}$, $\left.\mathrm{c}=0.802 \mathrm{~mol} \cdot \mathrm{~L}^{-1}, 1 \mathrm{eq}\right)$ in 15 mL THF was added to a 0.917 molar solution of 1,3 -dibromopropane in DME ( 0.8 mmol , $0.9 \mathrm{~mL}, 2$ eq). A colour change from brown to green occurred and a colourless solid was formed. The mixture was stirred for one hour. The solvent was removed under reduced pressure. The residue was dissolved in dichloromethane, silica is added and the solvent was removed in vacuo. The preabsorbed reaction mixture was purified via column chromatography $\left(\mathrm{SiO}_{2}\right.$, hexane, $\left.15 \times 2 \mathrm{~cm}\right)$. Using a mixture of hexane/dichloromethane (10:1), a first green fraction ([ $\left.\mathrm{Cp}{ }^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br}\right\}\right](2 b)$, followed by a brown one ([(Cp*Fe) $\left.\left.)_{2}\left\{\mu, \eta^{4: 4}-\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{P}_{5} \mathrm{Me}\right\}\right]\right)$ (3b) can be eluted. The solvent of both fractions was removed under reduced pressure. [ $\left.\mathrm{Cp}{ }^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br}\right\}\right]$ (2b) can be isolated as dark green needles after one day in a concentrated $n$-hexane solution, stored at $-30^{\circ} \mathrm{C}$. $\left[\left(\mathrm{Cp}{ }^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4: 4}-\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{P}_{5} \mathrm{Me}\right\}\right]$ (3b) can be obtained after one week as brown needles via layering a dichloromethane solution $(3 \mathrm{~mL})$ with acetonitrile $(10 \mathrm{~mL})$ and stored at $-30^{\circ} \mathrm{C}$.

## Data for $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br}\right\}\right]$ (2b):

Yield: $77.7 \mathrm{mg}(0.161 \mathrm{mmol}, 40 \%) .{ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=2.88\left(\mathrm{t}, 2 \mathrm{H}, \mathrm{J}_{\mathrm{H}-\mathrm{H}}=6.28 \mathrm{~Hz},-\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{2} \mathrm{Br}\right)$, $2.05\left(\mathrm{~m}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{2} \mathrm{Br}\right), 1.75\left(\mathrm{~m}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{2} \mathrm{Br}\right), 1.63\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 0.04\left(\mathrm{~d}, 3 \mathrm{H},-\mathrm{CH}_{3},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=10.57 \mathrm{~Hz}\right)$.
 $293 \mathrm{~K}): \delta[\mathrm{ppm}]=128.9\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 32.0\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}\right),-130.3\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{x}, \mathrm{X}}\right)$. For coupling constants, see Table S3. FD-MS (toluene): $m / z=481.91$ (100 \%, [M] ${ }^{+}$). analysis (calcd., found for $\mathrm{C}_{15} \mathrm{H}_{24} \mathrm{FeBrP}_{5}$ ): $\mathrm{C}(34.82,34.77), \mathrm{H}(5.01$, 4.90).

## Data for $\left[\left(\mathrm{Cp}^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4: 4}-\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{P}_{5} \mathrm{Me}\right\}\right]$ (3b):

Yield: $100.9 \mathrm{mg}(0.132 \mathrm{mmol}, 33 \%) .{ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=2.27\left(\mathrm{~m}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{3}-\right), 1.86\left(\mathrm{~m}, 1 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{3_{3}}\right)$, $1.67\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 0.19\left(\mathrm{~d}, 3 \mathrm{H},{ }^{2} \int_{\mathrm{P}-\mathrm{H}}=10.48 \mathrm{~Hz},-\mathrm{CH}_{3}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=127.4(\mathrm{~m}, 1 \mathrm{P}$, $\left.\mathrm{P}_{\mathrm{A}}\right), 32.6\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}\right),-129.5\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{X}, \mathrm{K}^{\prime}}\right) .{ }^{31} \mathrm{P}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=127.4\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 32.6\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}\right)$, $-129.5\left(m, 2 P, P_{x, x}\right)$. For coupling constants, see Table S8. LIFDI-MS (toluene): $m / z=763.94\left(100 \%,[M]^{+}\right)$. analysis (calcd., found for $\mathrm{C}_{25} \mathrm{H}_{42} \mathrm{Fe}_{2} \mathrm{P}_{10}$ ): $\mathrm{C}(39.30,39.05)$, $\mathrm{H}(5.54,5.55)$.

## Synthesis of [Cp*Fe\{n $\left.\left.\eta^{4}-\mathrm{P}_{5}(-\mathrm{C}=\mathrm{C}-\mathrm{Ph}) \mathrm{Me}\right\}\right](2 \mathrm{c})$ :

An insitu generated solution of $1 \mathrm{c}\left(\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\mathrm{n}^{5}-\mathrm{P}_{5}\right)\right](\mathrm{I}): 0.6 \mathrm{mmol}, 207.6 \mathrm{mg}, 1 \mathrm{eq} ; \mathrm{Li}-\mathrm{C} \equiv \mathrm{C}-\mathrm{Ph}: 0.6 \mathrm{mmol}, \mathrm{m}=64.8 \mathrm{mg}\right.$, 1 eq ) in 15 mL THF was cooled to $-80^{\circ} \mathrm{C}$ and a 1.116 molar solution of Mel in $\mathrm{Et}_{2} \mathrm{O}(0.6 \mathrm{mmol}, 0.54 \mathrm{~mL}, 1 \mathrm{eq})$ was added. The mixture was allowed to stir overnight and reach room temperature, thereby the solution turned brownish/red. The solvent was removed under reduced pressure. The residue was dissolved in dichloromethane, silica is added and the solvent was removed in vacuo. The preabsorbed reaction mixture was purified via column
chromatography $\left(\mathrm{SiO}_{2}\right.$, hexane, $\left.7 \times 1 \mathrm{~cm}\right)$. Using a mixture of hexane/dichloromethane (8:1), a first green fraction, can be eluted. A second red one showed decomposition within the workup and could not be further characterized. The solvent of the first fraction was removed under reduced pressure. of [ $\left.\mathrm{Cp}{ }^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}(-\mathrm{C} \equiv \mathrm{C}-\mathrm{Ph}) \mathrm{Me}\right\}\right]$ (2b) can be isolated as dark green plates after one week in a concentrated $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution, layered with $n$-hexane and stored at $-30^{\circ} \mathrm{C}$.

Yield: $180.0 \mathrm{mg}(0.389 \mathrm{mmol}, 65 \%) .{ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=6.89(\mathrm{~m}, 2 \mathrm{H},-\mathrm{Ph}), 6.79(\mathrm{~m}, 1 \mathrm{H},-\mathrm{Ph}), 6.68(\mathrm{~m}$, $1 \mathrm{H},-\mathrm{Ph}), 2.17\left(\mathrm{~m}, 3 \mathrm{H},-\mathrm{CH}_{3}\right), 1.56\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=76.2\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 39.6$ (m, 2 P, $\mathrm{P}_{\mathrm{M}, \mathrm{m}^{\prime}}$ ), $-83.2\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\left.\mathrm{x}, \mathrm{x}^{\prime}\right) .}{ }^{31} \mathrm{P}\right.$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=76.2\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 39.6\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{G}, \mathrm{G}^{\prime}}\right),-83.2(\mathrm{~m}$, $\left.2 P, P_{x, x^{\prime}}\right)$. For coupling constants, see Table S4. FD-MS (toluene): $m / z=461.04\left(100 \%,[M]^{+}\right)$. analysis (calcd., found for $\left.\mathrm{C}_{19} \mathrm{H}_{23} \mathrm{FeP}_{5}\right)$ : $\mathrm{C}(49.38,49.16), \mathrm{H}(5.02,5.02)$.

## Synthesis of $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CN}\right\}\right](2 \mathrm{~d})$ :

A solution of 1a ( $0.16 \mathrm{mmol}, 100 \mathrm{mg}, 1 \mathrm{eq}$ ) in 10 mL DME was cooled to $-50^{\circ} \mathrm{C}$ and a 0.1093 molar solution of 4-Bromobutyronitrile in DME ( $0.2 \mathrm{mmol}, 1.43 \mathrm{~mL}, 1 \mathrm{eq}$ ) was added. The mixture was allowed to stir overnight and reach room temperature, thereby a colourless solid is formed. The solvent was removed under reduced pressure and a brown solution was extracted with 10 mL toluene and filtered over diatomaceous earth. The solvent was reduced, layered with $n$-pentane and stored at $-30^{\circ} \mathrm{C}$. Compound $\mathbf{2 d}$ was isolated as dark blocks after one week.

Yield: $233 \mathrm{mg}(0.12 \mathrm{mmol}, 72 \%) .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=1.93\left(\mathrm{~m}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{2} \mathrm{CN}\right), 1.62(\mathrm{~s}, 15 \mathrm{H}$, $\left.\mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 1.43\left(\mathrm{t}, 2 \mathrm{H}, \mathrm{J}_{\mathrm{H}-\mathrm{H}}=6.66 \mathrm{~Hz},-\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{2} \mathrm{CN}\right), 1.28\left(\mathrm{~m}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{2} \mathrm{CN}\right),-0.01\left(\mathrm{~d}, 3 \mathrm{H},{ }^{2} J_{\mathrm{P}-\mathrm{H}}=10.41 \mathrm{~Hz}\right.$, $\left.-\mathrm{CH}_{3}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=127.3\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 32.0\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}}\right),-129.6\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P} 1_{\mathrm{x}, \mathrm{X}^{\prime}}\right) .{ }^{31} \mathrm{P}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=127.3\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 32.0\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}\right)$, $-129.6\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P} 1_{\mathrm{x}, \mathrm{X}}\right)$. For coupling constants, see Table S5. LIFDI-MS (toluene): $m / z=428.99\left(100 \%,[M]^{+}\right)$. analysis (calcd., found for $\mathrm{C}_{15} \mathrm{H}_{24} \mathrm{FeP}_{5} \mathrm{~N}$ ): $\mathrm{C}(41.99,42.25)$, H (5.64, 5.61), N (3.26, 3.09).

## Reaction of $\left[\mathrm{Li}(\mathrm{dme})_{3}\right]\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Me}\right)\right]$ (1b) with 1,4-dibromobutane:

A solution of insitu generated $\mathbf{1 b}$ ( $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right](\mathrm{I}): 0.58 \mathrm{mmol}, 200.6 \mathrm{mg}, 1 \mathrm{eq} ; \mathrm{MeLi}$ in Et ${ }_{2} \mathrm{O}: 0.58 \mathrm{mmol}, \mathrm{v}=0.72 \mathrm{~mL}$, $\mathrm{c}=0.802 \mathrm{~mol} \cdot \mathrm{~L}^{-1}, 1 \mathrm{eq}$ ) in 15 mL THF was added to a 0.0968 molar solution of 1,4 -dibromopropane in DME $(1.16 \mathrm{mmol}, 12.0 \mathrm{~mL}, 2 \mathrm{eq})$ at room temperature. The mixture was stirred for one hour. The solvent was removed under reduced pressure. The residue was dissolved in dichloromethane, silica is added and the solvent was removed in vacuo. The preabsorbed reaction mixture was purified via column chromatography ( $\mathrm{SiO}_{2}$, hexane, $10 \times 2 \mathrm{~cm}$ ). Using a mixture of hexane/dichloromethane (8:1), a first green fraction ([Cp*Fe( $\left.\left.\eta^{4}-\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{4} \mathrm{Br}\right)\right](2 e)$ can be eluted. Compound 2 e can be obtained as dark brown needles from a concentrated cyclo-hexane solution, stored at $8^{\circ} \mathrm{C}$.

Increasing the amount of dichloromethane up to a ratio of 1:1 (hexane), yields [(Cp*Fe) $\left.2\left\{\mu, \eta^{4: 4}-\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{4} \mathrm{P}_{5} \mathrm{Me}\right\}\right]$ (3c) as a green-brown fraction. Compound 3 c can be obtained after one week as green plates via layering a dichloromethane solution $(3 \mathrm{~mL})$ with hexane $(10 \mathrm{~mL})$ and stored at $-30^{\circ} \mathrm{C}$.

## Data for $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{4} \mathrm{Br}\right)\right](2 \mathrm{e})$ :

Yield: $124.2 \mathrm{mg}(0.250 \mathrm{mmol}, 43 \%) .{ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=2.88\left(\mathrm{t}, 2 \mathrm{H}, \mathrm{J}_{\mathrm{H}-\mathrm{H}}=6.06 \mathrm{~Hz},-\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{\underline{2}}-\mathrm{Br}\right)$, $1.87\left(\mathrm{~m}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{2}-\mathrm{Br}\right), 1.63\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 1.47\left(\mathrm{~m}, 4 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{2}-\mathrm{Br}\right), 0.11\left(\mathrm{~d}, 3 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{p}-\mathrm{H}}=\right.$ $\left.10.61 \mathrm{~Hz},-\mathrm{CH}_{3}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=130.8\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 32.0\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}\right),-130.8\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{x}, \mathrm{X}}\right)$. ${ }^{31} \mathrm{P}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=130.8\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 32.0\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}}\right),-130.8\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{x}, \mathrm{x}}\right)$. For coupling constants, see Table S6. LIFDI-MS (toluene): $m / z=496.00\left(100 \%,[M]^{+}\right)$. analysis (calcd., found for $\mathrm{C}_{15} \mathrm{H}_{26} \mathrm{FeBrP}$ ): C (36.25, $37.70), \mathrm{H}(5.27,5.08)$. elemental analysis failed after several attempts of the isolated crystals.

## Data for $\left[\left(\mathrm{Cp}^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4: 4}-\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{4} \mathrm{P}_{5} \mathrm{Me}\right\}\right](3 \mathrm{c})$ :

Yield: $106.7 \mathrm{mg}(0.137 \mathrm{mmol}, 24 \%) .{ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=2.10\left(\mathrm{~m}, 4 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{4}-\right), 1.68\left(\mathrm{~s}, 30 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right)$, $2.92\left(\mathrm{~m}, 4 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{4}-\right), 0.23\left(\mathrm{~d}, 6 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=10.55 \mathrm{~Hz},-\mathrm{CH}_{3}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=130.1\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right)$,
 $-130.1\left(m, 2 P, P_{x, x}\right)$. For coupling constants, see Table S9. LIFDI-MS (toluene): $m / z=777.92\left(100 \%,[M]^{+}\right)$. analysis (calcd., found for $\left.\mathrm{C}_{26} \mathrm{H}_{44} \mathrm{Fe}_{2} \mathrm{P}_{10}\right)$ : $\mathrm{C}(40.14,39.82)$, $\mathrm{H}(5.70,5.57)$.

## Synthesis of $\left[\left(\mathrm{Cp}^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4: 4}-\mathrm{P}_{5}{ }^{t} \mathrm{Bu}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{P}_{5} \mathrm{Me}\right\}\right]$ (4):

Compound 1 b ( $0.1 \mathrm{mmol}, 63.8 \mathrm{mg}, 1 \mathrm{eq}$ ) and $\mathbf{2 a}$ ( $0.1 \mathrm{mmol}, 52.5 \mathrm{mg}, 1 \mathrm{eq}$ ) were dissolved separately in 10 mL THF. The solution of $\mathbf{1 b}$ was added to $\mathbf{2 a}$. A colourless solid was formed and the suspension was allowed to stir for 1 hour. The solvent was removed under reduced pressure and a brown solution was extracted with 5 mL toluene and filtered over diatomaceous earth. The solvent was removed in vacou. The brown residue was dissolved in 2 mL THF, layered with $4 \mathrm{~mL} n$-pentane and stored at $-30^{\circ} \mathrm{C}$. $\left[\left(\mathrm{Cp}{ }^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4: 4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{P}_{5} \mathrm{Me}\right\}\right](4)$ was formed as dark green blocks after one day.

Yield: $64.5 \mathrm{mg}(0.08 \mathrm{mmol}, 80 \%) .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=2.79\left(\mathrm{~m}, 4 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{3}\right), 2.44(\mathrm{~m}, 2 \mathrm{H},-$ $\left.\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{3}\right), 1.67\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 1.66\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 0.79\left(\mathrm{~d}, 3 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=10.67 \mathrm{~Hz},-\mathrm{CH}_{3}\right), 0.64\left(\mathrm{~d}, 9 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}\right.$ $\left.=14.54 \mathrm{~Hz},-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right),{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=164.3\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P} 1_{\mathrm{A}}\right), 128.9\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P} 2_{\mathrm{A}}\right), 41.0(\mathrm{~m}, 2 \mathrm{P}$,
 $164.3\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P} 1_{\mathrm{A}}\right), 128.9\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P} 2_{\mathrm{A}}\right), 41.0\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P} 1_{\mathrm{M}, \mathrm{M}^{\prime}}\right) 29.8\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P} 2_{\mathrm{M}, \mathrm{M}^{\prime}}\right),-120.3\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P} 1_{\left.\mathrm{X}, \mathrm{X}^{\prime}\right)},-129.9(\mathrm{~m}\right.$, 2 P, P2 $2_{x, x}$ ). For coupling constants, see Table S10, S11. LIFDI-MS (toluene): $m / z=806.02$ ( $100 \%,[M]^{+}$). analysis (calcd., found for $\mathrm{C}_{28} \mathrm{H}_{48} \mathrm{Fe}_{2} \mathrm{P}_{10}$ ): C (41.72, 41.49), $\mathrm{H}(6.42,5.79)$.

## Synthesis of ([Cp* $\left.{ }^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}{ }^{t} \mathrm{Bu}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{PPh}_{2}\right\}\right]$ (5):

Complex 2a ( $0.5 \mathrm{mmol}, 262.5 \mathrm{mg}$, 1 eq ) was dissolved in 10 mL THF and cooled to $-80^{\circ} \mathrm{C}$ and a 0.233 molar solution of $\mathrm{KPPh}_{2}$ in DME ( $2.2 \mathrm{~mL}, 1 \mathrm{eq}$ ) was added dropwise. The mixture was allowed to stir overnight and reach room temperature, thereby a colour solid was formed. The solvent was removed in vacuu, the brown residue was solved in hexane and purified via column chromatography ( $\mathrm{SiO}_{2}$, hexane, $5 \times 2 \mathrm{~cm}$ ). Using a mixture of hexane/toluene (1:1) yields $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}{ }^{t} \mathrm{Bu}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{PPh}_{2}\right)\right]$ (8) as a brown greenish fraction. The solvent was removed under reduced pressure and the brown residue is dissolved in $15 \mathrm{~mL} n$-pentane. Compound 8 can be obtained spectroscopically pure as dark green crystals by slow removal of the solvent under reduced pressure at room temperature.

Yield: $237.1 \mathrm{mg}(0.375 \mathrm{mmol}, 75 \%) .{ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=7.48\left(\mathrm{~m}, 8 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{3} \mathrm{PPh}_{2}\right), 7.11(\mathrm{~m}, 8 \mathrm{H},-$ $\left.\left(\mathrm{CH}_{2}\right)_{3} \mathrm{PPh}_{2}\right), 2.50\left(\mathrm{~m}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{3} \mathrm{PPh}_{2}\right), 2.18\left(\mathrm{~m}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{3} \mathrm{PPh}_{2}\right), 2.10\left(\mathrm{~m}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{3} \mathrm{PPh}_{2}\right), 1.59(\mathrm{~s}, 15 \mathrm{H}$, $\left.\mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 0.29\left(\mathrm{~d}, 9 \mathrm{H}, \mathrm{J}_{\mathrm{P}-\mathrm{H}}=14.12 \mathrm{~Hz},-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=164.9\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 42.6(\mathrm{~m}$, $\left.2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}\right),-17.9\left(\mathrm{~s}, 1 \mathrm{P}, \mathrm{PPh}_{2}\right),-121.7\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{x}, \mathrm{x}}\right) .{ }^{31} \mathrm{P} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=164.9\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 42.6(\mathrm{~m}, 2$ P, $\mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}$ ), -17.9 ( $\mathrm{s}, 1 \mathrm{P}, \mathrm{PPh}_{2}$ ), -121.7 (m, $2 \mathrm{P}, \mathrm{P}_{\mathrm{x}, \mathrm{x}}$ ). For coupling constants, see Table S12. LIFDI-MS (toluene): $\mathrm{m} / \mathrm{z}=$ $630.05\left(100 \%,[\mathrm{M}]^{+}\right)$. analysis (calcd., found for $\left.\mathrm{C}_{29} \mathrm{H}_{40} \mathrm{FeP}_{6}\right)$ : $\mathrm{C}(55.23,55.71), \mathrm{H}(6.40,6.18)$.

## Synthesis of $\mathrm{P}^{t} \mathrm{BuBnz}\left(\left(\mathrm{CH}_{2}\right)_{4} \mathrm{Ph}\right)(6)$ :

Complex 2a ( $0.18 \mathrm{mmol}, 94.5 \mathrm{mg}, 1 \mathrm{eq}$ ) and $\mathrm{KBnz}(0.36 \mathrm{mmol}, 46.8 \mathrm{mg}, 2 \mathrm{eq})$ were dissolved separately in 10 mL THF and cooled to $-80^{\circ} \mathrm{C}$. One equivalent of the KBnz solution was added dropwise (a ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR was recorded of the reaction mixture) (see Fig. S60). The mixture was allowed to stir for one hour, thereby a colourless solid was formed (*). The solution was again cooled to $-80^{\circ} \mathrm{C}$. and the second equivalent of the KBnz solution was added. The reaction mixture was stirred for an additional hour. The solvent was removed under reduced pressure. The brownish
oily residue was extracted with $3 \times 10 \mathrm{~mL}$ of $n$-pentane and filtered over diatomaceous earth. The solvent was removed in vacuo. Compound 6 can be isolated as a slightly brownish oil.

Yield: $37.5 \mathrm{mg}(0.12 \mathrm{mmol}, 67 \%) .{ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=7.21(\mathrm{~m}, 3 \mathrm{H},-\mathrm{Ph}), 7.08(\mathrm{~m}, 7 \mathrm{H},-\mathrm{Ph}), 2.77$ (dd, $\left.1 \mathrm{H},{ }^{2} J_{\mathrm{P}-\mathrm{H}}=14.12 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=1.74 \mathrm{~Hz}, \mathrm{P}-\mathrm{CH}_{2}-\mathrm{Ph}\right), 2.45\left(\mathrm{dd}, 1 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=13.43 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=3.18 \mathrm{~Hz}, \mathrm{P}-\mathrm{CH}_{2}-\mathrm{Ph}\right), 2.37(\mathrm{t}$, $\left.2 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{H}-\mathrm{H}}=7.69 \mathrm{~Hz},{ }^{3} \int_{\mathrm{P}-\mathrm{H}}=1.74 \mathrm{~Hz},-\mathrm{CH}_{2}-\mathrm{Ph}\right), 1.51\left(\mathrm{~m}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{3}-\mathrm{Ph}\right), 1.30\left(\mathrm{~m}, 3 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{3}-\mathrm{Ph}\right), 1.20(\mathrm{~m}, 2 \mathrm{H},-$ $\left.\left(\mathrm{CH}_{2}\right)_{\underline{3}}-\mathrm{Ph}\right), 0.97\left(\mathrm{~d}, 9 \mathrm{H}, \mathrm{J}_{\mathrm{P}-\mathrm{H}}=14.12 \mathrm{~Hz},-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=4.5(\mathrm{~s}) .{ }^{31} \mathrm{P} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}\right.$, $293 \mathrm{~K}): \delta[\mathrm{ppm}]=4.5(\mathrm{~s}, \mathrm{br}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=142.4(\mathrm{~s}, \mathrm{Ph}), 139.7\left(\mathrm{~d},{ }^{2} \int_{\mathrm{p}-\mathrm{c}}=7.8 \mathrm{~Hz}, \mathrm{Ph}\right), 129.4$ ( $\mathrm{d},{ }^{3} J_{\mathrm{P}-\mathrm{C}}=6.8 \mathrm{~Hz}, \mathrm{Ph}$ ), $128.3\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=9.8 \mathrm{~Hz}, \mathrm{Ph}\right), 128.2\left(\mathrm{~d},{ }^{3} J_{\mathrm{P}-\mathrm{C}}=6.2 \mathrm{~Hz}, \mathrm{Ph}\right), 125.6(\mathrm{~s}, \mathrm{Ph}), 125.5\left(\mathrm{~d},{ }^{4} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=2.2 \mathrm{~Hz}\right.$, $\mathrm{Ph}), 35.6\left(\mathrm{~s},-\left(\mathrm{CH}_{2}\right)-\mathrm{Ph}\right), 33.0\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=12.0 \mathrm{~Hz}, \mathrm{P}-\left(\mathrm{CH}_{2}\right)-\mathrm{Ph}\right), 32.3\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=22.3 \mathrm{~Hz}, \mathrm{P}-(\mathrm{CH})-\left(\mathrm{CH}_{3}\right)_{2}-\mathrm{Ph}\right), 27.8\left(\mathrm{~d}, \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=\right.$ $14.7 \mathrm{~Hz}), 27.2\left(\mathrm{~d}, J_{P-C}=14.7 \mathrm{~Hz}\right), 27.2\left(\mathrm{~d}, J_{P-C}=19.1 \mathrm{~Hz}\right), 27.1\left(\mathrm{~d}, J_{\mathrm{P}-\mathrm{C}}=13.2 \mathrm{~Hz}\right), 23.9\left(\mathrm{~d},{ }^{2} J_{\mathrm{P}-\mathrm{C}}=20.5 \mathrm{~Hz}, \mathrm{P}-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right)^{3}$.

## Synthesis of SP'BuBnz((CH2)4Ph) (6'):

Compound 6 was synthesised insitu according to previous experimental details ( $0.18 \mathrm{mmol}, 1 \mathrm{eq}$ ) and dissolved in 5 mL of $n$-pentane. Sulfur ( $0.18 \mathrm{mmol}, 5.8 \mathrm{mg}, 1 \mathrm{eq}$ ) was dissolved in 2 mL of $n$-pentane and added to compound 6 at room temperature. The reaction mixture is stirred for one hour. The solvent is reduced in vacuo and stored at $-30^{\circ} \mathrm{C}$. Compound $6^{\prime}$ can be isolated as colourless blocks after three days.

Yield: $51.7 \mathrm{mg}\left(0.15 \mathrm{mmol}, 83\right.$ \%). ${ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right)$ : $\delta[\mathrm{ppm}]=7.35(\mathrm{~m}, 2 \mathrm{H},-\mathrm{Ph}), 7.05(\mathrm{~m}, 7 \mathrm{H},-\mathrm{Ph}), 2.86(\mathrm{~d}$, $\left.1 \mathrm{H},{ }^{2} J_{\mathrm{P}-\mathrm{H}}=6.37 \mathrm{~Hz}, \mathrm{P}-\mathrm{CH}_{2}-\mathrm{Ph}\right), 2.86\left(\mathrm{~d}, 1 \mathrm{H},{ }^{2} J_{\mathrm{P}-\mathrm{H}}=6.37 \mathrm{~Hz}, \mathrm{P}-\mathrm{CH}_{2}-\mathrm{Ph}\right), 2.83\left(\mathrm{~d}, 1 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{H}}=3.84 \mathrm{~Hz}, \mathrm{P}-\mathrm{CH}_{2}-\mathrm{Ph}\right)$, $2.28\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{CH}_{2}-\mathrm{Ph}\right), 1.59\left(\mathrm{~m}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{3}-\mathrm{Ph}\right), 1.35\left(\mathrm{~m}, 3 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{3}-\mathrm{Ph}\right), 1.11\left(\mathrm{~m}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{3}-\mathrm{Ph}\right), 0.98(\mathrm{~d}, 9 \mathrm{H}$, $\left.J_{\text {P-H }}=15.25 \mathrm{~Hz},-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=63.5(\mathrm{~s}) .{ }^{31} \mathrm{P} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=63.5(\mathrm{~s}$, br). ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=142.2(\mathrm{~s}, \mathrm{Ph}), 132.9\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{p}-\mathrm{c}}=7.5 \mathrm{~Hz}, \mathrm{Ph}\right), 130.2\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{\mathrm{p}-\mathrm{c}}=4.7 \mathrm{~Hz}, \mathrm{Ph}\right), 128.3$ ( $\mathrm{d},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=7.0 \mathrm{~Hz}, \mathrm{Ph}$ ), $126.8\left(\mathrm{~d},{ }^{4} \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=3.0 \mathrm{~Hz}, \mathrm{Ph}\right), 125.7(\mathrm{~s}, \mathrm{Ph}), 35.8\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{c}}=41.8 \mathrm{~Hz}, \mathrm{P}-\left(\mathrm{CH}_{2}\right)-\mathrm{Ph}\right), 35.4\left(\mathrm{~s},-\left(\mathrm{CH}_{2}\right)-\right.$ Ph), 33.9 (d, $\left.{ }^{1} J_{\mathrm{P}-\mathrm{C}}=47.8 \mathrm{~Hz}, \mathrm{P}-(\mathrm{CH})-\left(\mathrm{CH}_{3}\right)_{2}-\mathrm{Ph}\right), 32.9\left(\mathrm{~d}, J_{\mathrm{P}-\mathrm{c}=}=14.0 \mathrm{~Hz}\right), 25.6\left(\mathrm{~d},{ }^{2} J_{\mathrm{P}-\mathrm{C}}=20.5 \mathrm{~Hz}, \mathrm{P}-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 24.7(\mathrm{~d}$, $\left.J_{\mathrm{P}-\mathrm{C}}=0.2 \mathrm{~Hz}\right), 22.9\left(\mathrm{~d}, \mathrm{~J}_{\mathrm{P}-\mathrm{C}}=3.6 \mathrm{~Hz}\right) . \mathrm{GC}-\mathrm{MS}\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right): \mathrm{m} / \mathrm{z}=344.17\left(15 \%,[\mathrm{M}]^{+}\right)$, $91.06\left(100 \%,[\mathrm{Bnz}]^{+}\right), 57.07(15 \%$, $\left.\left[^{t} \mathrm{Bu}\right]^{+}\right), 312.20\left(5 \%,[\mathrm{M}-\mathrm{S}]^{+}\right)$. analysis (calcd., found for $\left.\mathrm{C}_{21} \mathrm{H}_{29} \mathrm{SP}\right)$ : $\mathrm{C}(73.22,70.23), \mathrm{H}(8.49,7.50), \mathrm{S}(9.31,12.01)$.

## Synthesis of $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}\left(\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CN}\right)_{2}\right\}\right](7)$ :

Complex I ( $0.15 \mathrm{mmol}, 90.7 \mathrm{mg}, 1 \mathrm{eq}$ ) was dissolved in DME, cooled to $-50^{\circ} \mathrm{C}$ and a 0.1093 molar solution of 4-Bromobutyronitrile in DME ( $0.3 \mathrm{mmol}, 2.75 \mathrm{~mL}, 2 \mathrm{eq}$ ) was added. Thereby the colour change to red/brown and a colourless solid formed. The solution was allowed to stir over night. The solvent was removed under reduced pressure and the brown residue was washed with $3 \times 10 \mathrm{~mL}$ of $n$-pentane. The residue was dissolved in 5 mL of toluene, filtered over diatomaceous earth, layered with 5 mL of $n$-pentane and stored at $-30^{\circ} \mathrm{C}$. Compound 7 can be isolated as dark green blocks after washing with 10 mL of $n$-hexane in order to remove residues of I .

Yield: $46.0 \mathrm{mg}(0.096 \mathrm{mmol}, 64 \%) .{ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=2.02\left(\mathrm{~m}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{2} \mathrm{CN}\right), 1.63(\mathrm{~s}, 15 \mathrm{H}$, $\left.\mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 1.48\left(\mathrm{t}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{2} \mathrm{CN}, \mathrm{J}_{\mathrm{H}-\mathrm{H}}=6.52 \mathrm{~Hz}\right), 1.32\left(\mathrm{~m}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{2} \mathrm{CN}\right), 1.05\left(\mathrm{t}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{2} \mathrm{CN}, \mathrm{J}_{\mathrm{H}-\mathrm{H}}\right.$ $=6.70 \mathrm{~Hz}), 0.59\left(\mathrm{~m}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{2} \mathrm{CN}\right), 0.25\left(\mathrm{~m}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{2} \mathrm{CN}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=133.7$ $\left(\mathrm{m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 37.0\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}\right),-129.2\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{X}, \mathrm{K}^{\prime}}\right) .{ }^{31} \mathrm{P} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=133.7\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 37.0(\mathrm{~m}$, 2 P, $\left.\mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}\right),-129.2\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{X}, \mathrm{X}^{\prime}}\right)$. For coupling constants, see Table S13. LIFDI-MS (toluene): $\mathrm{m} / \mathrm{z}=482.01(100 \%$, $\left.[\mathrm{M}]^{+}\right)$, $964.05\left(2 \%,[\mathrm{M}]_{2}{ }^{+}\right)$. analysis (calcd., found for $\left.\mathrm{C}_{18} \mathrm{H}_{27} \mathrm{FeP}_{5} \mathrm{~N}_{2}\right)$ : C (44.84, 45.34), $\mathrm{H}(5.64,5.23), \mathrm{N}(5.81,6.00)$.

## Synthesis of $\left[\left\{\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}\left(\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CN}\right)_{2}\right\}\right\} \mathrm{ZnBr}_{2}\right]$ (8):

Compound 7 ( $0.15 \mathrm{mmol}, 72.3 \mathrm{mg}, 1 \mathrm{eq}$ ) and $\mathrm{ZnBr}_{2}(0.15 \mathrm{mmol}, 72.3 \mathrm{mg}, 1 \mathrm{eq})$ were dissolved separately in 10 mL THF. The solution of 7 was added to $\mathrm{ZnBr}_{2}$. A colour change was not observed and the solution was allowed to stir
for 1 hour. The solvent was removed under reduced pressure and a brown oil was dissolved in $3 \mathrm{~mL} \mathrm{CH}_{2} \mathrm{Cl}_{2}$, layered with 10 mL toluene and stored at room temperature. $\left[\left\{\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}\left(\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CN}\right)_{2}\right\}\right\} \mathrm{ZnBr}_{2}\right]$ (8) was formed as dark green/brownish plates after three days.

Yield: $86.5 \mathrm{mg}(0.122 \mathrm{mmol}, 81 \%) .{ }^{1} \mathrm{H}$ NMR (THF-d $\left.{ }_{8}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=2.78\left(\mathrm{~m}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{2} \mathrm{CN}\right), 2.69(\mathrm{t}$, $\left.2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{2} \mathrm{CN}, \mathrm{J}_{\mathrm{H}-\mathrm{H}}=6.88 \mathrm{~Hz}\right), 2.21\left(\mathrm{t}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{2} \mathrm{CN}, \mathrm{J}_{\mathrm{H}-\mathrm{H}}=6.88 \mathrm{~Hz}\right), 2.17\left(\mathrm{~m}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{2} \mathrm{CN}\right), 1.63$ (s, $\left.15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 1.20\left(\mathrm{~m}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{2} \mathrm{CN}\right), 1.06\left(\mathrm{~m}, 2 \mathrm{H},-\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{2} \mathrm{CN}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]$ $=137.9\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 36.3\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}\right),-130.3\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{x}, \mathrm{X}^{\prime}}\right) .{ }^{31} \mathrm{P} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=137.9\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right)$, 36.3 ( $\mathrm{m}, 2$ P, $\mathrm{P}_{\mathrm{M}, \mathrm{M}}$ ), -130.3 ( $\mathrm{m}, 2$ P, $\mathrm{P}_{\mathrm{x}, \mathrm{X}}$ ). For coupling constants, see Table S14. LIFDI-MS (o-DFB): $\mathrm{m} / \mathrm{z}=482.01$ ( $100 \%$, [7] $]^{+}$). analysis (calcd., found for $\mathrm{C}_{18} \mathrm{H}_{27} \mathrm{FeP}_{5} \mathrm{~N}_{2} \mathrm{ZnBr} 2$ ): $\mathrm{C}(30.69,30.98), \mathrm{H}(3.87,3.91), \mathrm{N}(3.78,3.93)$.

## 2. NMR spectroscopic characterization

${ }^{1} \mathrm{H}$ NMR Spectra:
$[K(18 c 6)($ thf $)]\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}-\equiv-\mathrm{Ph}\right)\right](1 \mathrm{c})$


Fig. S1. Experimental ${ }^{1} \mathrm{H}$ NMR ( 400.13 MHz, THF- $\mathrm{d}_{8}$ ) spectrum of $1 \mathrm{c}\left({ }^{(\#}=\mathrm{THF},{ }^{\wedge}=\right.$ unidentified impurity, $\left.{ }^{*}=\mathrm{I}\right)$.
$\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br}\right)\right](2 \mathrm{a})$


Fig. S2. Experimental ${ }^{1} \mathrm{H}$ NMR $\left(400.13 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right)$ spectrum of $2 \mathrm{a}\left({ }^{*}=\mathrm{I}\right)$.
$\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br}\right)\right]$ (2b)


Fig. S3. Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of $\mathbf{2 b}$.

## $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left\{\mathrm{n}^{4}-\mathrm{P}_{5}(-\mathrm{C} \equiv \mathrm{C}-\mathrm{Ph}) \mathrm{Me}\right\}\right](2 \mathrm{c})$



Fig. S4. Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of $\mathbf{2 c}\left({ }^{*}=\mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$.

## $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\mathrm{n}^{4}-\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CN}\right\}\right](2 \mathrm{~d})$



Fig. S5. Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of $\mathbf{2 d}\left({ }^{*}=\mathrm{I}\right)$.
$\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left\{\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{4} \mathrm{Br}\right)\right\}\right](2 \mathrm{e})$


Fig. S6. Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of $\mathbf{2 e}$.


Fig. S7. Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) spectrum of 3 a ( ${ }^{*}=3 \mathrm{a}^{\prime}$ ).
$\left[\left(\mathrm{Cp}{ }^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4: 4}-\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{P}_{5} \mathrm{Me}\right\}\right]$ (3b)


Fig. S8. Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) spectrum of 3b.
$\left[\left(\mathrm{Cp}^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4: 4}-\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{4} \mathrm{P}_{5} \mathrm{Me}\right\}\right]$ (3c)


Fig. S9. Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) spectrum of $3 \mathrm{c}\left(^{*}=\mathrm{CH}_{2} \mathrm{Cl}_{2} ;{ }^{*}=3 \mathrm{c}^{\prime}\right)$.
$\left[\left(\mathrm{Cp}^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4: 4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{P}_{5} \mathrm{Me}\right\}\right](4)$


Fig. S10. Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) spectrum of 4 .
$\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left\{\mathrm{n}^{4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{PPh}_{2}\right\}\right](5)$


Fig. S11. Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of 5 .

## $\mathrm{P}^{\mathrm{t}} \mathrm{BuBnz}\left(\left(\mathrm{CH}_{2}\right)_{4} \mathrm{Ph}\right)$ (6)



Fig. S12. Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of 6 ( ${ }^{*}=$ unidentified sideproduct $)$.

## SPtBuBnz((CH2) $\left.{ }_{4} \mathrm{Ph}\right)\left(6^{\prime}\right)$



Fig. S13. Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of 6'.

## $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}\left(\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CN}\right)_{2}\right\}\right]$ (7)



Fig. S14. Experimental ${ }^{1} \mathrm{H}$ NMR $\left(400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 7 .
$\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}\left(\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CN}\right)_{2}\right\} \mathrm{ZnBr}_{2}\right]$ (8)


Fig. S15. Experimental ${ }^{1} \mathrm{H}$ NMR ( 400.13 MHz, THF- $\mathrm{d}_{8}$ ) spectrum of 8 ( ${ }^{*}=$ grease).

## ${ }^{31}$ P NMR Spectra:

## $[\mathrm{K}(18 \mathrm{c} 6)(\mathrm{thf})]\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}-\equiv-\mathrm{Ph}\right)\right](1 \mathrm{c})$



Fig. S16. Experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}\right.$, THF- $\mathrm{d}_{8}$ ) spectrum of the anion of 1c. (for a better resolution, I was reacted with $\mathrm{Li}-=-\mathrm{Ph}$ in $\mathrm{THF}-\mathrm{d}_{8}$ ).

Table S1. Chemical shifts and coupling constants obtained from the simulation ( R -factor $=2.43$ \%) in Figure S16.

| $J[\mathrm{~Hz}]$ |  |  |  | $\delta[\mathrm{ppm}]$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{1} \mathrm{~J}_{\mathrm{P}_{\mathrm{A}}, \mathrm{P}_{\mathrm{X}}}$ | 305.0 | ${ }^{1} \mathrm{P}_{\mathrm{P}_{\mathrm{B}}, \mathrm{P}_{\mathrm{X}}}$ | 377.5 | X, $\mathrm{X}^{\prime}$ | -59.3 |
| ${ }^{1} \mathrm{P}_{\mathrm{P}^{\prime}, \mathrm{P}^{\prime}}$ | 301.58 | ${ }^{1} \mathrm{P}_{\mathrm{P}^{\prime},} \cdot \mathrm{PX}^{\prime}$ | 377.5 |  |  |
| ${ }^{2} J_{P_{A}, P_{B}}$ | -48.37 | ${ }^{2} J_{\mathrm{P}_{\mathrm{B}}, \mathrm{P}_{\mathrm{X}}}$ | -21.25 | $B, B^{\prime}$ | 26.0 |
| ${ }^{2} J_{P_{A}, ~} P_{B}$, | -31.74 | ${ }^{2} \int_{\mathrm{P}_{\mathrm{B}}, \mathrm{P}_{\mathrm{X}}}$ | -2.30 |  |  |
| ${ }^{1} \mathrm{~J}_{\mathrm{P}_{\mathrm{B}}, \mathrm{P}_{\mathrm{B}}}$ | 418.99 | ${ }^{2} J_{P_{X}, P_{X}}$ | -48.37 | A | 35.7 |

## $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\mathrm{n}^{4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br}\right\}\right]$ (2a)




Fig. S17. Experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}$ NMR ( $161.98 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) spectrum of 2a.
Table S2. Chemical shifts and coupling constants obtained from the simulation ( R -factor $=0.27$ \%) in Figure S17.

| $J[\mathrm{~Hz}]$ |  |  |  | $\delta$ [ppm] |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{1} \mathrm{~J}_{\mathrm{P}_{\mathrm{A}}, \mathrm{P} \mathrm{X}}$ | 410.20 | ${ }^{1} J_{P_{A}, P_{X}}$ | 410.20 | ${ }^{1} J_{P_{A}, P_{X}}$ | 410.20 |
| ${ }^{1} J_{P_{A}, ~} P_{X}{ }^{\prime}$ | 410.36 | ${ }^{1} J_{P_{A}, P^{\prime}}{ }^{\prime}$ | 410.36 | ${ }^{1} J_{P_{A}, P^{\prime}}{ }^{\prime}$ | 410.36 |
| ${ }^{2} J_{P_{A}, ~} P_{M}$ | 14.77 | ${ }^{2} \mathrm{P}_{\mathrm{P}^{\prime}, P_{M}}{ }^{\prime}$ | 14.77 | ${ }^{2} \mathrm{P}_{\mathrm{P}_{\mathrm{A}}, \mathrm{P}{ }^{\prime}}$ | 14.77 |
| ${ }^{2} J_{P_{A}, P_{M}}{ }^{\prime}$ | 13.31 | ${ }^{2} J_{P_{A},} P_{M}$ | 13.31 | ${ }^{2} J_{P_{A}, ~} P_{M}$ | 13.31 |
| ${ }^{1} \mathrm{JP}_{\mathrm{P}^{\prime} \cdot \mathrm{P}_{\mathrm{M}}{ }^{\prime}}$ | 386.77 | ${ }^{1} J_{P_{M}, P_{M}}{ }^{\prime}$ | 386.77 | ${ }^{1} J_{P_{M}, P_{M}}{ }^{\prime}$ | 386.77 |

$\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P} 5 \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br}\right\}\right](2 b)$




Fig. S18. Experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of $\mathbf{2 b}$.
Table S3. Coupling constants obtained from the simulation ( R -factor $=2.02$ \%) in Figure S18.

| $J[\mathrm{~Hz}]$ |  |  |  | $\delta[\mathrm{ppm}]$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{1} \mathrm{~J}_{\mathrm{P}_{\mathrm{A}}, \mathrm{P} \mathrm{X}}$ | 387.09 | ${ }^{1} J_{P_{M, ~}, P_{X}}$ | 399.39 | $\mathrm{X}, \mathrm{X}^{\prime}$ | -130.3 |
| ${ }^{1} \mathrm{~J}_{\mathrm{P}_{\mathrm{A}}, \mathrm{P}^{\prime}}{ }^{\prime}$ | 387.32 | ${ }^{1} J_{P_{M^{\prime}}, P^{\prime}}$ | 398.72 |  |  |
| ${ }^{2} J_{P_{A}, P_{M}}$ | -10.20 | ${ }^{2} J_{\mathrm{P}_{\text {M }}} \cdot \mathrm{P}_{\mathrm{X}}$ | -38.00 | $\mathrm{M}, \mathrm{M}^{\prime}$ | 32.0 |
| ${ }^{2} J_{\mathrm{P}_{\text {A }}, P_{M}}{ }^{\prime}$ | -11.42 | ${ }^{2} J_{\mathrm{P}_{\mathrm{M}}, \mathrm{P}^{\prime}}$ | -37.62 |  |  |
| ${ }^{1} J_{\mathrm{P}_{\mathrm{M}}, \mathrm{P}_{\mathrm{M}}}$ | 379.54 | ${ }^{2} J_{P_{X}, P_{X}}$ | 2.56 | A | 128.9 |

## $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left\{\mathrm{\eta}^{4}-\mathrm{P}_{5}(-\mathrm{C} \equiv \mathrm{C}-\mathrm{Ph}) \mathrm{Me}\right\}\right](2 \mathrm{c})$



Fig. S19. Experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 2c.
Table S4. Coupling constants obtained from the simulation ( R -factor $=2.68 \%$ ) in Figure S19.


## $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CN}\right)\right](2 \mathrm{~d})$



Fig. S20. Experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 2d.
Table S5. Coupling constants obtained from the simulation ( R -factor $=0.85$ \%) in Figure S20.

| $J[\mathrm{~Hz}]$ |  |  |  | $\delta$ [ppm] |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{1} \mathrm{~J}_{\mathrm{P}}, \mathrm{P}_{\mathrm{X}}$ | 388.43 | ${ }^{1 / P_{\text {M }}}{ }^{\text {P }}$ P | 402.00 | X, $\mathrm{X}^{\prime}$ | -129.6 |
| ${ }^{1} J_{P_{A}, ~} P_{X}$, | 387.79 | ${ }^{1} J_{\mathrm{P}_{M^{\prime}}, P_{X}}$ | 396.52 |  |  |
| ${ }^{2} \mathrm{P}_{\mathrm{P}_{1}, \mathrm{P}_{\mathrm{M}}}$ | 10.38 | ${ }^{2} J_{P_{M}} / P_{X}$ | -41.41 | M, M ${ }^{\prime}$ | 32.0 |
| ${ }^{2} J_{P_{A}, P_{M}}{ }^{\prime}$ | 11.35 | ${ }^{2} J_{P_{M}}{ }^{\text {P }} \mathrm{P}^{\prime}$ | -35.78 |  |  |
| ${ }^{1} J_{\mathrm{P}_{\mathrm{M}}, \mathrm{P}^{\prime}}{ }^{\prime}$ | 381.21 | ${ }^{2} J_{P_{X}, P_{X}}$ | 2.56 | A | 127.3 |

## $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\left(\eta^{4}-\mathrm{P} 5 \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{4} \mathrm{Br}\right)\right\}\right](2 \mathrm{e})$




Fig. S21. Experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of $\mathbf{2 e}$.
Table S6. Coupling constants obtained from the simulation ( R -factor $=3.15 \%$ ) in Figure S21.

| $J[\mathrm{~Hz}]$ |  |  |  | $\delta$ [ppm] |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{1} \mathrm{~J}_{\mathrm{P}_{\mathrm{A}}, \mathrm{P}}$ | 385.4 | ${ }^{1} \mathrm{~J}_{\mathrm{P}_{\mathrm{M}}, \mathrm{P}}$ | 402.6 | X, X' | -130.8 |
| ${ }^{1} J_{P_{A}, ~} \cdot \mathrm{P}_{X}{ }^{\prime}$ | 385.7 | ${ }^{1} J_{\mathrm{P}_{\mathrm{M}^{\prime}} \mathrm{P}^{\prime}}$ | 395.4 |  |  |
| ${ }^{2} J_{P_{A}, ~} P_{M}$ | -10.4 | ${ }^{2} J_{P_{M}}{ }^{\prime} P_{X}$ | -41.0 | $\mathrm{M}, \mathrm{M}^{\prime}$ | 31.9, 32.0 |
| ${ }^{2} J_{P_{A}, P_{M}}{ }^{\prime}$ | -11.1 | ${ }^{2} J_{P_{M}, P_{X}}$ | -34.0 |  |  |
| ${ }^{1} J_{\mathrm{P}_{\mathrm{M}}, P_{M}{ }^{\text {P }}}$ | 380.3 | ${ }^{2} \mathrm{P}_{\mathrm{P}^{\prime}, \mathrm{P}_{X}}$ | -2.8 | A | 130.8 |

$\left[\left(\mathrm{Cp}^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4: 4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\right\}\right]\left(3 \mathrm{a} / 3 \mathrm{a}^{\prime}\right)$


3a


* 3a'


Fig. S22. Experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right.$ ) spectrum of $3 \mathbf{a}\left({ }^{*}=\mathbf{3 a}{ }^{\prime}\right)$.
Table S7. Chemical shifts and coupling constants obtained from the simulation (R-factor $=1.05 \%$ ) in Figure S22.

| $J[\mathrm{~Hz}]$ |  |  |  | $\delta[\mathrm{ppm}]$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{1} J_{P_{A}, P_{X}}$ | 403.07 | ${ }^{1} J_{P_{M}, P_{X}}$ | 404.00 | X, $\mathrm{X}^{\prime}$ | -120.14 |
| ${ }^{1} \mathrm{~J}_{\mathrm{P}^{\prime}, \mathrm{P}^{\prime}}{ }^{\prime}$ | 403.07 | ${ }^{1} \mathrm{P}_{\mathrm{P}^{\prime}} \cdot \mathrm{P}_{\mathrm{X}}{ }^{\prime}$ | 404.00 |  |  |
| ${ }^{2} J_{P_{A}, P_{M}}$ | 14.41 | ${ }^{2} J_{P_{M}} P^{\prime} P_{X}$ | -37.51 | $\mathrm{M}, \mathrm{M}^{\prime}$ | 44.64 |
| ${ }^{2} J_{P_{A}} \cdot{ }^{P_{M}}{ }^{\prime}$ | 14.41 | ${ }^{2} J_{P_{M}, P^{\prime}}{ }^{\prime}$ | -37.51 |  |  |
| ${ }^{1} \mathrm{P}_{\mathrm{P}^{\prime}, \mathrm{P}^{\prime}}{ }^{\prime}$ | 385.06 | ${ }^{2} J_{P_{X}, P_{X}}$ | 2.00 | A | 162.43 |

Three Signals of 3a' overlay with the Signals of 3a. Due to the low intensity of 3a' and the overlay, a simulation was not possible.

## $\left[\left(\mathrm{Cp}^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4: 4}-\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{P}_{5} \mathrm{Me}\right\}\right]$ (3b)



Fig. S23. Experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 3 b .
Table S8. Coupling constants obtained from the simulation ( R -factor $=0.43 \%$ ) in Figure S23.

| $J[\mathrm{~Hz}]$ |  |  |  | $\delta$ [ppm] |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{1} J_{P_{A}, P_{X}}$ | 386.34 | ${ }^{1} J_{P_{M}, P_{X}}$ | 401.41 | X, X | -129.6 |
| ${ }^{1} \mathrm{~J}_{\mathrm{P}_{\mathrm{A}}, \mathrm{P}^{\prime}{ }^{\prime}}$ | 387.07 | ${ }^{1} J_{P_{M^{\prime}}, P^{\prime}}$ | 396.75 |  |  |
| ${ }^{2} J_{P_{A}, P_{M}}$ | 10.32 | ${ }^{2} J_{P_{M}} \cdot P_{X}$ | -40.64 | $\mathrm{M}, \mathrm{M}^{\prime}$ | 32.6 |
| ${ }^{2} J_{P_{A}, ~} P_{M}{ }^{\prime}$ | 11.16 | ${ }^{2} J_{P_{M}, P^{\prime}}$ | -36.00 |  |  |
| ${ }^{1} J_{\mathrm{P}_{\mathrm{M},}, \mathrm{P}_{\mathrm{M}}}$ | 379.19 | ${ }^{2} J_{P_{X}, P_{X}}{ }^{\prime}$ | 3.21 | A | 127.4 |

$\left[\left(\mathrm{Cp}^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4: 4}-\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{4} \mathrm{P}_{5} \mathrm{Me}\right\}\right]\left(3 \mathrm{c} / 3 \mathrm{c}^{\prime}\right)$



Fig. S24. Experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of $\mathbf{3 c}\left({ }^{*}=\mathbf{3 c}\right.$ ).
Table S9. Coupling constants obtained from the simulation ( R -factor $=1.06$ \%) in Figure S24.

| $J[\mathrm{~Hz}]$ |  |  |  | $\delta[\mathrm{ppm}]$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{1} J_{\mathrm{P}_{\mathrm{A}}, \mathrm{P}_{\mathrm{X}}}$ | 386.37 | ${ }^{1} J_{\mathrm{P}_{\mathrm{M}}, \mathrm{P}}$ | 400.10 | $X, X^{\prime}$ | -130.1 |
| ${ }^{1} J_{P_{A}, P^{\prime}}{ }^{\prime}$ | 386.60 | ${ }^{1} J_{\mathrm{P}_{M^{\prime}} \mathrm{P} \mathrm{P}^{\prime}}$ | 398.96 |  |  |
| ${ }^{2} J_{P_{A},} P_{M}$ | 11.02 | ${ }^{2} J_{P_{M}}{ }^{\prime} P_{X}$ | -37.19 | $\mathrm{M}, \mathrm{M}^{\prime}$ | 32.9 |
| ${ }^{2} J_{P_{A},} \cdot P_{M}{ }^{\prime}$ | 11.27 | ${ }^{2} J_{P_{M}, P^{\prime}}$ | -38.77 |  |  |
| ${ }^{1} \mathrm{~J}_{\mathrm{P}_{\text {M }}} \mathrm{P}_{\mathrm{M}^{\prime}}$ | 378.84 | ${ }^{2} J_{P_{X}, P_{X}}{ }^{\prime}$ | 3.49 | A | 130.8 |

Three Signals of 3c' overlay with the Signals of 3c. Due to the low intensity of 3c' and the overlay, a simulation was not possible.
$\left[\left(\mathrm{Cp}^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \boldsymbol{\eta}^{4: 4}-\mathrm{P}_{5}{ }^{t} \mathrm{Bu}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{P}_{5} \mathrm{Me}\right\}\right](4)$



Fig. S25. Experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right)$ spectrum of 4.


Fig. S26. View frame of the essential part of the experimental ${ }^{31} \mathrm{P}$ NMR $\left(161.98 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right)$ spectrum of 4. $\mathrm{P}_{5}{ }^{t} \mathrm{Bu}-\mathrm{R}$ :
Table S10. Chemical shifts and coupling constants obtained from the simulation (R-factor $=3.79$ \%) in Figure S25.

| $J[\mathrm{~Hz}]$ |  |  |  | $\delta$ [ppm] |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{1} J_{\mathrm{P}_{A}, \mathrm{P}^{\prime}}$ | 411.79 | ${ }^{1} J_{\mathrm{P}_{\mathrm{M}}, \mathrm{P} \mathrm{X}}$ | 402.75 | $X, X^{\prime}$ | -120.3 |
| ${ }^{1} J_{P_{A}, P^{\prime}}{ }^{\prime}$ | 411.53 | ${ }^{1} \mathrm{~J}_{\mathrm{P}^{\prime}} \mathrm{P}^{\mathrm{P}^{\prime}}$ | 404.17 |  |  |
| ${ }^{2} J_{P_{A}, ~} P_{M}$ | 14.41 | ${ }^{2} J_{\mathrm{P}_{\mathrm{M}^{\prime}}, \mathrm{P}_{\mathrm{X}}}$ | -38.32 | M, M ${ }^{\prime}$ | 41.0 |
| ${ }^{2} \mathrm{~J}_{\mathrm{P}^{\prime}} \cdot \mathrm{P}_{\mathrm{P}^{\prime}}$ | 14.28 | ${ }^{2} J_{P_{M}, P_{X}}$, | -39.65 |  |  |
| ${ }^{1} J_{P_{M},} P_{M}{ }^{\prime}$ | 386.85 | ${ }^{2} J_{P_{X}, P_{X}}$ | -0.52 | A | 164.3 |

$\mathrm{P}_{5} \mathrm{Me}-\mathrm{R}$ :
Table S11. Coupling constants obtained from the simulation ( R -factor $=3.79$ \%) in Figure S25.

| $J[\mathrm{~Hz}]$ |  |  |  | $\delta[\mathrm{ppm}]$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{1} J_{\mathrm{P}_{\mathrm{A}}, \mathrm{P}_{\mathrm{X}}}$ | 384.39 | ${ }^{1} J_{P_{M}, P_{X}}$ | 396.00 | X, $\mathrm{X}^{\prime}$ | -129.9 |
| ${ }^{1} J_{P_{A}, P^{\prime}}{ }^{\prime}$ | 383.85 | ${ }^{1} J_{P_{M}}{ }^{\prime} P^{\prime}{ }^{\prime}$ | 400.37 |  |  |
| ${ }^{2} J_{P_{A}, P_{M}}$ | 10.69 | ${ }^{2} J_{P_{M}} \cdot P_{X}$ | -35.00 | $\mathrm{M}, \mathrm{M}^{\prime}$ | 29.8 |
| ${ }^{2} J_{P_{A},} \cdot P_{M}{ }^{\prime}$ | 10.95 | ${ }^{2} J_{P_{M}, P^{\prime}}$ | -39.00 |  |  |
| ${ }^{1} J_{\mathrm{P}_{\mathrm{M}},{ }^{\mathrm{P}_{M^{\prime}}} \text { }}$ | 385.85 | ${ }^{2} J_{P_{X}, P_{X}}$ | 3.03 | A | 128.9 |

## $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\mathrm{n}^{4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{PPh}_{2}\right\}\right](5)$




Fig. S27. Experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 5 .
Table S12. Coupling constants obtained from the simulation ( R -factor $=8.07 \%$ ) in Figure S27.

| $J[\mathrm{~Hz}]$ |  |  |  | $\delta$ [ppm] |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{1} \mathrm{~J}_{\mathrm{P}}, \mathrm{P} \mathrm{X}$ | 412.20 | ${ }^{1} J_{P_{M, ~}, P_{X}}$ | 400.99 | X, X | -121.65 |
| ${ }^{1} J_{\mathrm{P}_{\text {A }}, P_{X}}$ | 412.09 | ${ }^{1} J_{\mathrm{P}_{\mathrm{M}^{\prime}}, \mathrm{P}^{\prime}}$ | 403.85 |  |  |
| ${ }^{2} J_{P_{A}, P_{M}}$ | 14.25 | ${ }^{2} J_{P_{M}} \cdot P_{X}$ | -37.84 | $\mathrm{M}, \mathrm{M}^{\prime}$ | 42.57 |
| ${ }^{2} J_{P_{A}, P_{M}}{ }^{\prime}$ | 14.26 | ${ }^{2} J_{P_{M}, P^{\prime} X^{\prime}}$ | -40.90 |  |  |
| ${ }^{1} J_{\mathrm{P}_{M},{ }^{\mathrm{P}_{M}}{ }{ }^{\prime}}$ | 383.98 | ${ }^{2} J_{P_{X}, P_{X}}$ | -0.344 | A | 164.88 |
|  |  |  |  | $\mathrm{PPh}_{2}$ | -17.87 |

## PtBuBnz((CH2)4Ph) (6)

$$
\begin{aligned}
& \text { ®. } \\
& \stackrel{\rightharpoonup}{\zeta}
\end{aligned}
$$



Fig. S28. Experimental ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 6 .
SP ${ }^{t}{ }^{\text {BuBnz }}\left(\left(\mathrm{CH}_{2}\right)_{4} \mathrm{Ph}\right)\left(6^{\prime}\right)$



## $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left\{\mathrm{n}^{4}-\mathrm{P}_{5}\left(\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CN}\right)_{2}\right\}\right]$ (7)




125
/1
-90
[ppm]

Fig. S30. Experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 7 .
Table S13. Coupling constants obtained from the simulation ( R -factor $=2.41 \%$ ) in Figure S30.


## $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}\left(\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CN}\right)_{2}\right\} \mathrm{ZnBr}_{2}\right]$ (8)



Fig. S31. Experimental (top) and simulated (bottom) ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 161.98 MHz , THF-d8) spectrum of 8.
Table S14. Coupling constants obtained from the simulation ( R -factor $=0.39$ \%) in Figure S31.

| $J[\mathrm{~Hz}]$ |  |  |  | $\delta[\mathrm{ppm}]$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{1} \mathrm{~J}_{\mathrm{P}_{\mathrm{A}}, \mathrm{P} \mathrm{X}}$ | 398.68 | ${ }^{1} \mathrm{JP}_{\mathrm{M}, \mathrm{PX}}$ | 397.74 | X, $\mathrm{X}^{\prime}$ | -130.3 |
| ${ }^{1} J_{P_{A}, ~} P_{X}$, | 398.62 | ${ }^{1} J_{P_{M^{\prime}}, P^{\prime}}$ | 400.27 |  |  |
| ${ }^{2} J_{P_{A}, P_{M}}$ | 12.41 | ${ }^{2} \mathrm{P}_{\mathrm{P}_{\text {M }}}$ P $\mathrm{P}_{\mathrm{X}}$ | -37.83 | M, M ${ }^{\prime}$ | 36.3 |
| ${ }^{2} J_{P_{A}, P_{M}}{ }^{\prime}$ | 12.63 | ${ }^{2} \mathrm{~J}_{\mathrm{M}_{\mathrm{M}} \mathrm{P} \mathrm{P}^{\prime}}$ | -40.16 |  |  |
| ${ }^{1} \mathrm{~J}_{\mathrm{P}^{\prime}, \mathrm{P}^{\text {P }}}{ }^{\prime}$ | 378.88 | ${ }^{2} J_{P_{X}, P_{X}}$ | 2.26 | A | 137.9 |

## ${ }^{13} \mathrm{C}$ NMR Spectra:

## PtBuBnz(( $\left.\left.\mathrm{CH}_{2}\right)_{4} \mathrm{Ph}\right)(6)$



Fig. S32. Experimental ${ }^{13} \mathrm{C}_{\{ }\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(100.61 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 6 .

## SP'BuBnz(( $\left.\left.\mathrm{CH}_{2}\right)_{4} \mathrm{Ph}\right)\left(6^{\prime}\right)$



Fig. S33. Experimental ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(100.61 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 6'.

## 3. Crystallographic details

$[K(18 c 6)($ thf $)]\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}-\equiv-\mathrm{Ph}\right)\right]$ (1c): There are two molecules of 1 c , two by $18-\mathrm{c}-6$ coordinated K cations and two THF solvent molecules in the asymmetric unit. One of these THF molecule is disordered over two positions (50:50). Further are both $\mathrm{P}_{5}$ ligands disordered over two positions (94:6; 92:8). The restraints SADI and SIMU were applied to model these disorders. The structure in the solid state is given in Figure S34 and S35. Crystallographic and refinement data are summarized in Table S15.
$\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}{ }^{\text {t }} \mathrm{Bu}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br}\right)\right]$ (2a): The asymmetric unit contains one molecule of 2 a without any disorder. The structure in the solid state is given in Figure S36. Crystallographic and refinement data are summarized in Table S15.
$\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br}\right)\right]$ (2b): The asymmetric unit contains one molecule of $\mathbf{2 b}$. Compound $\mathbf{3 b}$ co crystallizes with another compound in the ratio (90:10). The second compound features a $\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br}$ ligand were one substituent migrated to a neighboring phosphorus atom. The SADI and SIMU restraints were applied to model this disorder. The structure in the solid state is given in Figure S37. Crystallographic and refinement data are summarized in Table S15. [Cp*Fe\{n $\left.\left.{ }^{4}-\mathrm{P}_{5}(-\mathrm{C} \equiv \mathrm{C}-\mathrm{Ph}) \mathrm{Me}\right\}\right](2 \mathrm{c})$ : The asymmetric unit contains one molecule of 2 c without any disorder. The structure in the solid state is given in Figure S38. Crystallographic and refinement data are summarized in Table S15. $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CN}\right)\right](2 \mathrm{~d})$ : The asymmetric unit contains one molecule of 3d. Furthermore, compound I cocrystalizes at the same position and can only be distinguished by the disordered middle deck, with a distribution of 5:95. The structure in the solid state is given in Figure S39 and S40. Crystallographic and refinement data are summarized in Table S15.
$\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{4} \mathrm{Br}\right)\right\}\right]$ (2e): The asymmetric unit contains one molecule of $\mathbf{2 e}$. Compound $\mathbf{3 b}$ co crystallizes with another compound in the ratio (90:10). The second compound features a $\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{4} \mathrm{Br}$ ligand were one substituent migrated to a neighboring phosphorus atom. The SADI and SIMU restraints were applied to model this disorder. The structure in the solid state is given in Figure S41. Crystallographic and refinement data are summarized in Table S15.
$\left[\left(\mathrm{Cp}{ }^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4: 4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\right\}\right]$ ( $3 \mathrm{a} / 3 \mathrm{a}^{\prime}$ ): The asymmetric unit contains one molecule of 3a and 3a' which cocrystalizes and a distribution of 92:8, respectively. The structures in the solid state are depicted in Figure S42, S43 and S44. The unit cell contains 2 uncoordinated molecules of dichloromethane and 3 molecules of $n$-hexane which were removed with the implemented tool SQUEEZE due to unresolvable disorder. Crystallographic and refinement data are summarized in Table S16.
$\left[\left(\mathrm{Cp}^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4: 4}-\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{P}_{5} \mathrm{Me}\right\}\right]$ (3b): The asymmetric unit contains one molecule of 3 b . One $\mathrm{Cp}^{*}$ ligand is disordered over two positions with a distribution of 58:42. To describe the disorders the SIMU restrain is applied. The structure in the solid state is given in Figure S45. Crystallographic and refinement data are summarized in Table S16.
$\left[\left(\mathrm{Cp}^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4: 4}-\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{4} \mathrm{P}_{5} \mathrm{Me}\right\}\right](3 \mathrm{c})$ : The asymmetric unit contains half a molecule of 3 c . The $\mathrm{Cp}^{*}$ ligand is disordered over two positions with a distribution of 60:40. The structure in the solid state is given in Figure S46. The unit cell contains 1.5 uncoordinated molecules of dichloromethane which were removed with the implemented tool SQUEEZE due to unresolvable disorder. Crystallographic and refinement data are summarized in Table S16.
$\left[\left(\mathrm{Cp}{ }^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4: 4}-\mathrm{P}_{5}{ }^{t} \mathrm{Bu}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{P}_{5} \mathrm{Me}\right\}\right]$ (4): The asymmetric unit contains one molecule of 4 without any disorder. The structure in the solid state is given in Figure S47. Crystallographic and refinement data are summarized in Table S16. $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{PPh}_{2}\right)\right]$ (5): The asymmetric unit contains two molecules of 5 . The $\mathrm{P}_{5}$ middle decks are disordered over two positions in both molecules with a distribution of 65:35/76:24, respectively. As well as the middle decks, both $\mathrm{Cp}^{*}$ ligands is disordered over two positions with a distribution of 85:15 in both molecules. In addition to this, the $n$-propyl-di-phenyl-phosphine residue is disorder over two positions. Thereby, the occupancy is 77:23 / 85:15, respectively. To describe the disorders the SADI and SIMU restrains are applied. Since the distribution, bond lengths, and bond angles are very similar, only one molecule in the solid state is depicted in Figure S48 and S49
and its bond lengths and angles are presented in Table S38 and S39. Crystallographic and refinement data are summarized in Table S17.
$S^{t} B u B n z\left(\left(\mathrm{CH}_{2}\right)_{4} \mathrm{Ph}\right)\left(6^{\prime}\right)$ : The asymmetric unit contains one molecule of 6' without any disorder. The structure in the solid state is given in Figure S50. Crystallographic and refinement data are summarized in Table S17.
$\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}\left(\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CN}\right)_{2}\right\}\right]$ (7): The asymmetric unit contains one molecule of 7. The $\mathrm{P}_{5}$ middle decks are disordered over two positions with a distribution of 97:3. Since the carbon atoms of part 2 cannot be resolved, due to the low occupation, only the bond lengths and angles of part 1 are presented in Table S42 and S43. The structure in the solid state is given in Figure S51 and S52. Crystallographic and refinement data are summarized in Table S17.
$\left[\left\{\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}\left(\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CN}\right)_{2}\right\}\right\} \mathrm{ZnBr}_{2}\right]$ (8): The asymmetric unit contains one molecule of 8 without any disorder, forming a linear polymer when grown. Since the measured crystal was twinned, a HKLF5 refinement was applied (BASF 0.368 ). The structure in the solid state is given in Figure S53. Crystallographic and refinement data are summarized in Table S17.

Table S15. Crystallographic details of 1c and 2a-d.

| Compound | 1c | 2a | 2b | 2c | 2d |
| :---: | :---: | :---: | :---: | :---: | :---: |
| CCDC | / | / | / | / | / |
| Formula | $\mathrm{C}_{34} \mathrm{H}_{52} \mathrm{FeKO}_{7} \mathrm{P}_{5}$ | $\mathrm{C}_{17} \mathrm{H}_{30} \mathrm{BrFeP}_{5}$ | $\mathrm{C}_{14} \mathrm{H}_{24} \mathrm{BrFeP}_{5}$ | $\mathrm{C}_{19} \mathrm{H}_{23} \mathrm{FeP}_{5}$ | $\mathrm{C}_{14.75} \mathrm{H}_{23.55} \mathrm{FeN} \mathrm{N}_{0.95} \mathrm{P}_{5}$ |
| $D_{\text {calc. }} / \mathrm{g} \mathrm{cm}^{-3}$ | 1.364 | 1.558 | 1.595 | 1.455 | 1.425 |
| $\mu / \mathrm{mm}^{-1}$ | 6.192 | 2.816 | 12.027 | 9.316 | 1.160 |
| Formula Weight | 1645.11 | 525.02 | 482.94 | 462.07 | 424.89 |
| Colour | Metallic dark green | dark brown | dark red | green | clear dark brown |
| Shape | Block | needle | plate | plate-shaped | block |
| Size/mm ${ }^{3}$ | $0.37 \times 0.15 \times 0.11$ | $0.27 \times 0.10 \times 0.07$ | $0.21 \times 0.12 \times 0.03$ | $0.39 \times 0.21 \times 0.06$ | $0.33 \times 0.20 \times 0.17$ |
| T/K | 123.00 | 123(1) | 122.9(2) | 123.00(10) | 123 |
| Crystal System | monoclinic | monoclinic | orthorhombic | monoclinic | monoclinic |
| Flack Parameter | / | / | -0.008(7) | / | / |
| Hooft Parameter | / | / | -0.003(5) | / | / |
| Space Group | P2 $1_{1} / \mathrm{c}$ | P2 $1_{1} / \mathrm{m}$ | P2 $1221^{2}{ }_{1}$ | P2 $1_{1}$ n | P2 ${ }_{1} / \mathrm{c}$ |
| $a / \AA$ | 20.3442(5) | 11.2089(5) | 8.1330(2) | 9.53044(5) | 14.2369(3) |
| b/Å | 26.2921(5) | 11.4407(4) | 9.6956(2) | 14.14435(7) | 9.0210(2) |
| $c / A$ | 15.0828(3) | 18.1308(8) | 25.5069(6) | 16.21683(8) | 16.3159(5) |
| $\alpha /{ }^{\circ}$ | 90 | 90 | 90 | 90 | 90 |
| $\beta 1^{\circ}$ | 96.721(2) | 105.764(4) | 90 | 105.2398(5) | 109.044(3) |
| $\gamma /{ }^{\circ}$ | 90 | 90 | 90 | 90 | 90 |
| $\mathrm{V} / \mathrm{A}^{3}$ | 8012.2(3) | 2237.60(17) | 2011.33(8) | 2109.183(19) | 1980.78(9) |
| Z | 4 | 4 | 4 | 4 | 4 |
| Z' | 2 | 1 | 1 | 1 | 1 |
| Wavelength/A | 1.54184 | 0.71073 | 1.54184 | 1.54184 | 0.71073 |
| Radiation type | $\mathrm{CuK}_{\alpha}$ | $\mathrm{MoK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ | $\mathrm{MoK}_{\alpha}$ |
| $\Theta_{\text {min }} /{ }^{\circ}$ | 3.362 | 3.499 | 3.466 | 4.213 | 3.231 |
| $\Theta_{\max } /^{\circ}$ | 66.600 | 32.281 | 74.916 | 74.357 | 32.255 |
| Measured Refl's. | 41460 | 13109 | 6543 | 51123 | 19036 |
| Ind't Refl's | 14019 | 7434 | 3431 | 4256 | 6439 |
| Refl's with I > 2(I) | 10664 | 6052 | 3190 | 4200 | 5702 |
| $R_{\text {int }}$ | 0.0652 | 0.0222 | 0.0322 | 0.0337 | 0.0189 |
| Parameters | 1010 | 255 | 259 | 232 | 214 |
| Restraints | 279 | 0 | 69 | 0 | 0 |
| Largest Peak | 0.659 | 1.046 | 0.888 | 0.858 | 1.173 |
| Deepest Hole | -0.535 | -0.440 | -1.150 | -0.435 | -0.490 |
| GooF | 1.085 | 1.064 | 1.071 | 1.074 | 1.051 |
| $w R_{2}$ (all data) | 0.1963 | 0.0807 | 0.1398 | 0.0801 | 0.0883 |
| $w R_{2}$ | 0.1829 | 0.0752 | 0.1361 | 0.0799 | 0.0851 |
| $R_{1}$ (all data) | 0.0981 | 0.0483 | 0.0551 | 0.0289 | 0.0385 |
| $R_{1}$ | 0.0754 | 0.0349 | 0.0510 | 0.0287 | 0.0328 |

Table S16. Crystallographic details of $2 \mathrm{e}, 3 \mathrm{a}-\mathrm{c}$ and 4.

| Compound | 3 a | 3 a | 3b | 3 c | 4 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| CCDC | / | / | / | / | / |
| Formula | $\mathrm{C}_{14} \mathrm{H}_{24} \mathrm{BrFeP}_{5}$ | $\mathrm{C}_{40.5} \mathrm{ClFe}_{2} \mathrm{H}_{76} \mathrm{P}_{10}$ | $\mathrm{C}_{25} \mathrm{H}_{42} \mathrm{Fe}_{2} \mathrm{P}_{10}$ | $\mathrm{C}_{27.5} \mathrm{Cl}_{3} \mathrm{Fe}_{2} \mathrm{H}_{47} \mathrm{P}_{10}$ | $\mathrm{C}_{28} \mathrm{H}_{48} \mathrm{Fe}_{2} \mathrm{P}_{10}$ |
| $D_{\text {calc. }} / \mathrm{g} \mathrm{cm}^{-3}$ | 1.595 | 1.432 | 1.470 | 1.460 | 1.443 |
| $\mu / \mathrm{mm}^{-1}$ | 12.027 | 1.037 | 11.252 | 11.265 | 10.494 |
| Formula Weight | 482.94 | 1019.86 | 763.98 | 905.40 | 806.06 |
| Colour | dark red | dark green | brownish green | green | dark green |
| Shape | plate | block | plate-shaped | plate-shaped | needle |
| Size/mm ${ }^{3}$ | $0.21 \times 0.12 \times 0.03$ | $0.57 \times 0.32 \times 0.29$ | $0.33 \times 0.05 \times 0.03$ | $0.23 \times 0.11 \times 0.03$ | $0.50 \times 0.12 \times 0.09$ |
| T/K | 122.9(2) | 123(1) | 123.01(10) | 123.00(10) | 123(1) |
| Crystal System | orthorhombic | monoclinic | monoclinic | monoclinic | triclinic |
| Flack Parameter | -0.008(7) | / | / | / | / |
| Hooft Parameter | -0.003(5) | / | / | / | / |
| Space Group | P2 $1_{21} 2_{1}$ | P2 $1_{1} / \mathrm{c}$ | P2 $1_{1} \mathrm{c}$ | P2 $1_{1}$ n | P-1 |
| a/Å | 8.1330(2) | 15.5101(3) | 14.3913(2) | 8.6991(2) | 8.8375(4) |
| b/Å | 9.6956(2) | 12.8109(2) | 8.09300(10) | 9.0109(2) | 14.5973(7) |
| $c / A ̊$ | 25.5069(6) | 24.2981(3) | 30.4026(3) | 26.6182(8) | 16.2499(8) |
| $\alpha /^{\circ}$ | 90 | 90 | 90 | 90 | 63.684(5) |
| $\beta{ }^{\circ}$ | 90 | 101.4490(10) | 102.9490(10) | 99.170(3) | 89.773(4) |
| $\gamma /{ }^{\circ}$ | 90 | 90 | 90 | 90 | 81.732(4) |
| $V /{ }^{3}$ | 2011.33(8) | 4731.92(13) | 3450.91(7) | 2059.85(9) | 1855.28(17) |
| Z | 4 | 4 | 4 | 2 | 2 |
| Z' | 1 | 1 | 1 | 0.5 | 1 |
| Wavelength/Å | 1.54184 | 0.71073 | 1.54184 | 1.54184 | 1.54184 |
| Radiation type | $\mathrm{CuK}_{\alpha}$ | $\mathrm{MoK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ |
| $\Theta_{\text {min }} /{ }^{\circ}$ | 3.466 | 3.370 | 2.983 | 5.157 | 5.069 |
| $\Theta_{\max } /{ }^{\circ}$ | 74.916 | 34.549 | 75.279 | 74.066 | 71.725 |
| Measured Refl's. | 6543 | 55081 | 36548 | 15304 | 12816 |
| Ind't Refl's | 3431 | 18675 | 6922 | 3980 | 7024 |
| Refl's with l > 2(I) | 3190 | 13489 | 6330 | 3136 | 6125 |
| $R_{\text {int }}$ | 0.0322 | 0.0309 | 0.0353 | 0.0622 | 0.0289 |
| Parameters | 259 | 525 | 441 | 273 | 375 |
| Restraints | 69 | 126 | 120 | 52 | 0 |
| Largest Peak | 0.888 | 1.098 | 0.851 | 0.827 | 0.555 |
| Deepest Hole | -1.150 | -0.448 | -0.571 | -0.371 | -0.543 |
| GooF | 1.071 | 1.026 | 1.044 | 1.082 | 1.030 |
| $w R_{2}$ (all data) | 0.1397 | 0.1252 | 0.1255 | 0.1626 | 0.0919 |
| $w R_{2}$ | 0.1360 | 0.1141 | 0.1226 | 0.1532 | 0.0870 |
| $R_{1}$ (all data) | 0.0551 | 0.0687 | 0.0509 | 0.0655 | 0.0434 |
| $R_{1}$ | 0.0510 | 0.0458 | 0.0471 | 0.0532 | 0.0356 |

Table S17. Crystallographic details of 5, 6', 7 and 8.

| Compound | 5 |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |

## $[\mathrm{K}(18 \mathrm{c} 6)(\mathrm{thf})]\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}-\equiv-\mathrm{Ph}\right)\right](1 \mathrm{c})$



Fig. S34. Molecular structure of $\mathbf{1 c}$ in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligands are drawn in a wire frame model.


Fig. S35. Side view of the molecular structure of $\mathbf{1 c}$ in the solid state with thermal ellipsoids at $50 \%$ probability level. The disorder is highlighted blue (Part 1) and green (Part 2). Hydrogen atoms are omitted for clarity. The Cp* ligand is drawn in a wire frame model.

Table S18. Selected bond lengths of 1c.

| Atom-Atom | Length [Å] |
| :---: | :---: |
| P1A-P2A | $2.142(5)$ |
| P1A-P5A | $2.162(3)$ |
| P2A-P3A | $2.187(3)$ |
| P3A-P4A | $2.127(4)$ |
| P4A-P5A | $2.142(3)$ |


| Atom-Atom | Length $[\AA ̊]$ |
| :---: | :---: |
| P1A-C11 | $1.782(7)$ |
| Fe1-P2A | $2.322(3)$ |
| Fe1-P3A | $2.312(2)$ |
| Fe1-P4A | $2.338(2)$ |
| Fe1-P5A | $2.317(2)$ |

Table S19. Selected angles of 1c.

| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| P5A-P1A-P2A | $93.56(16)$ |
| P3A-P2A-P1A | $107.09(16)$ |
| P4A-P3A-P2A | $103.14(13)$ |


| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| P3A-P4A-P5A | $103.82(11)$ |
| P4A-P5A-P1A | $107.18(14)$ |
|  |  |

## $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br}\right\}\right]$ (2a)



Fig. S36. Molecular structure of 2a in the solid state with thermal ellipsoids at 50\% probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}{ }^{*}$ ligand is drawn in a wire frame model.

Table S20. Selected bond lengths of 2a.

| Atom-Atom | Length [Å] |
| :---: | :---: |
| P1-P2 | $2.1580(7)$ |
| P2-P3 | $2.1461(8)$ |
| P3-P4 | $2.1594(11)$ |
| P4-P5 | $2.1461(8)$ |
| P1-P5 | $2.1580(7)$ |
| P1-C7 | $1.871(3)$ |
| $\mathrm{C} 12-\mathrm{Br} 1$ | $1.950(3)$ |


| Atom-Atom | Length $[A ̊]$ |
| :---: | :---: |
| Fe1-P2 | $2.3425(6)$ |
| Fe1-P3 | $2.3334(6)$ |
| Fe1-P4 | $2.3334(6)$ |
| Fe1-P5 | $2.3425(6)$ |
| Fe1-P1 | $3.1105(9)$ |
| P1-C10 | $1.838(3)$ |
|  |  |

Table S21. Selected angles of 2a.

| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| P1-P2-P3 | $99.57(3)$ |
| P2-P3-P4 | $104.662(19)$ |
| P4-P5-P1 | $99.57(3)$ |
| P5-P1-C10 | $120.16(5)$ |
| C10-P1-C12 | $103.94(14)$ |


| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| P3-P4-P5 | $104.662(19)$ |
| P5-P1-P2 | $97.53(4)$ |
| P5-P1-C7 | $120.16(5)$ |
| P2-P1-C7 | $120.16(5)$ |
| P2-P1-C10 | $107.04(7)$ |

## $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br}\right\}\right]$ (2b)



Fig. S37. Molecular structure of $\mathbf{2 b}$ (left part) and $\mathbf{2 b}$ ' (middle part) in the solid state with thermal ellipsoids at 50\% probability level. Hydrogen atoms are omitted for clarity. The disorder is highlighted blue (Part 1) and green (Part 2). The $\mathrm{Cp}{ }^{*}$ ligands are drawn in a wire frame model.

Table S22. Selected bond lengths of $\mathbf{2 b}$ and $\mathbf{2 b}$ '.

| Atom-Atom | Length [Å] |
| :---: | :---: |
| Part 1-2b |  |
| P1A-P2A | $2.129(3)$ |
| P1A-P5A | $2.142(3)$ |
| P2A-P3A | $2.147(4)$ |
| P3A-P4A | $2.143(11)$ |
| P4A-P5A | $2.119(9)$ |
| P1A-C11 | $1.817(8)$ |
| P1A-C12A | $1.842(9)$ |


| Atom-Atom | Length [Å] |
| :---: | :---: |
| Part 2-2b‘ |  |
| P1B-P2B | $2.07(4)$ |
| P1B-P5B | $2.11(3)$ |
| P2B-P3B | $2.34(8)$ |
| P3B-P4B | $2.33(8)$ |
| P4B-P5B | $2.18(3)$ |
| P1B-C12B | $1.84(3)$ |
|  |  |

Table S23. Selected angles of $\mathbf{2 b}$ and $\mathbf{2 b}$ '.

| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| Part 1-2b |  |
| P5A-P1A-P2A | $98.89(14)$ |
| P3A-P2A-P1A | $99.49(14)$ |
| P4A-P3A-P2A | $103.9(2)$ |
| P3A-P4A-P5A | $106.0(3)$ |
| P4A-P5A-P1A | $99.1(3)$ |


| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| Part 2-2b‘ |  |
| P7-P8B-P9B | $98.3(4)$ |
| P8B-P9B-P10B | $106.1(6)$ |
| P9B-P10B-P11B | $101.6(8)$ |
| P11B-P7-P8B | $91.9(8)$ |
| P8B-P7-C30 | $129.2(3)$ |

## $\left[C p^{*} F e\left\{\eta^{4}-P_{5}(-C \equiv C-P h) M e\right\}\right](2 c)$



Fig. S38. Molecular structure of $\mathbf{2 c}$ in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligand is drawn in a wire frame model.

Table S24. Selected bond lengths of 2c.

| Atom-Atom | Length [Å] |
| :---: | :---: |
| P1-P5 | $2.1405(6)$ |
| P1-P2 | $2.1425(6)$ |
| P1-C12 | $1.7582(18)$ |
| P1-C11 | $1.821(2)$ |


| Atom-Atom | Length [Å] |
| :---: | :---: |
| P2-P3 | $2.1419(7)$ |
| P4-P4 | $2.1538(7)$ |
| C13-C12 | $1.197(3)$ |
| P5-P4 | $2.1399(6)$ |

Table S25. Selected angles of 2c.

| Atom-Atom-Atom | Angle [$]$ |
| :---: | :---: |
| P5-P1-P2 | $93.56(16)$ |
| C12-P1-P5 | $107.09(16)$ |
| C12-P1-P2 | $103.14(13)$ |$\quad$|  | Atom-Atom-Atom |
| :---: | :---: |
| Angle [ ${ }^{\circ}$ ] |  |
|  | C12-P1-C11 |
| C11-P1-P5 | $103.82(11)$ |
| P1-C12-C13 | $175.18(14)$. |

## $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CN}\right\}\right](2 \mathrm{~d})$



Fig. S39. Molecular structure of 2d in the solid state with thermal ellipsoids at 50\% probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligand is drawn in a wire frame model.


Fig. S40. Side view of the mixed crystal of I and 2d in the solid state with thermal ellipsoids at 50\% probability level. The disordered $\mathrm{P}_{5}$ middle decks are highlighted green (I) and blue (3a). The Cp * ligand is drawn in a wire frame model.

Table S26. Selected bond lengths of 2d.

| Atom-Atom | Length [Å] |
| :---: | :---: |
| P1A-P2 | $2.1462(6)$ |
| P2-P3 | $2.1465(6)$ |
| P3-P4 | $2.1589(6)$ |
| P4-P5 | $2.1384(6)$ |
| P1A-P5 | $2.1499(5)$ |
| P1A-C11 | $1.8214(17)$ |
| N1-C15 | $1.142(2)$ |


| Atom-Atom | Length $[\AA \AA]$ |  |  |
| :---: | :---: | :---: | :---: |
| Fe1-P2 | $2.3340(4)$ |  |  |
| Fe1-P3 | $2.3355(4)$ |  |  |
| Fe1-P4 | $2.3422(4)$ |  |  |
| Fe1-P5 | $2.3199(5)$ |  |  |
| Fe1-P1A | $3.0591(5)$ |  |  |
| P1-C12 | $1.8284(16)$ |  |  |
|  |  |  |  |

Table S27. Selected angles of 2d.

| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| P1A-P2-P3 | $97.27(2)$ |
| P2-P3-P4 | $105.34(2)$ |
| P4-P5-P1 | $105.8(3)$ |
| P5-P1A-C11 | $118.98(6)$ |
| C10-P1A-C12 | $106.50(8)$ |


| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| P3-P4-P5 | $104.28(2)$ |
| P5-P1A-P2 | $98.48(2)$ |
| P5-P1A-C11 | $118.98(6)$ |
| P5-P1A-C12 | $106.70(6)$ |
| P2-P1A-C11 | $118.07(6)$ |

$\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{4} \mathrm{Br}\right\}\right](2 \mathrm{e})$


Fig. S41. Molecular structure of $\mathbf{2 e}$ (left part) and $2 e^{\prime}$ (middle part) in the solid state with thermal ellipsoids at 50\% probability level. Hydrogen atoms are omitted for clarity. The disorder is highlighted blue (Part 1) and green (Part 2). The $\mathrm{Cp}^{*}$ ligands are drawn in a wire frame model.

Table S28. Selected bond lengths of 2 e and $2 \mathrm{e}^{\prime}$.

| Atom-Atom | Length [Å] |
| :---: | :---: |
| Part 1-2e |  |
| P1A-P2A | $2.142(3)$ |
| P1A-P5A | $2.129(3)$ |
| P1A-C11 | $1.817(8)$ |
| P1A-C12A | $1.842(9)$ |
| P2A-P3A | $2.119(9)$ |
| P3A-P4A | $2.143(11)$ |
| P5A-P4A | $2.147(4)$ |


| Atom-Atom | Length $[A ̊]$ |
| :---: | :---: |
| Part 2-2 $\mathbf{e}^{\prime}$ |  |
| C11-P5B | $1.88(2)$ |
| C12A-C13A | $1.526(14)$ |
| P4B-P5B | $2.18(3)$ |
| P5B-P1B | $2.11(3)$ |
| P1B-P2B | $2.07(4)$ |
| P1B-C12B | $1.84(3)$ |
| C14-Br1 | $1.938(8)$ |

Table S29. Selected angles of $2 e$ and $2 e^{\prime}$.

| Atom-Atom-Atom | Angle [ ${ }^{\circ}$ ] | Atom-Atom-Atom | Angle [ ${ }^{\circ}$ ] |
| :---: | :---: | :---: | :---: |
| Part 1-2e |  | Part $2-2 e^{\text {d }}$ |  |
| P5A-P1A-P2A | 98.89(14) | P5B-P4B-P3B | 115(3) |


| C11-P1A-P2A | $120.0(3)$ |
| :---: | :---: |
| C11-P1A-P5A | $117.8(4)$ |
| C11-P1A-C12A | $107.5(4)$ |
| C12A-P1A-P2A | $106.6(3)$ |


| C11-P5B-P4B | $117.6(13)$ |
| :---: | :---: |
| C11-P5B-P1B | $100.2(12)$ |
| P1B-P5B-P4B | $84.8(11)$ |
| C13B-C12B-P1B | $103(3)$ |

## $\left[\left(\mathrm{Cp}{ }^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4: 4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\right\}\right]$ (3a)



Fig. S42. Molecular structure of 3a in the solid state with thermal ellipsoids at 50\% probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligands are drawn in a wire frame model.

## $\left[\left(\mathrm{Cp}{ }^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4: 4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\right\}\right]\left(3 \mathrm{a}^{\prime}\right)$



Fig. S43. Molecular structure of $3 a^{\prime}$ in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligands are drawn in a wire frame model.


Fig. S44. Molecular structure of 3a, highlighted blue (Part 1), and 3a', highlighted green (Part 2), in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

Table S30. Selected bond lengths of 3a and 3a'.

| Atom-Atom | Length [Å] |
| :---: | :---: |
| Part 1 - 3a |  |
| P1A-P2A | $2.1514(9)$ |
| P2A-P3A | $2.1422(15)$ |
| P3A-P4A | $2.1518(18)$ |
| P4A-P5A | $2.1422(11)$ |
| P1A-P5A | $2.1454(7)$ |
| P1A-C21A | $1.876(2)$ |
| P1A-C25A | $1.847(2)$ |
| Part 2 |  |
| P1B- 3a |  |
| P2B-P3B | $2.098(9)$ |
| P3B-P4B | $2.140(10)$ |
| P4B-P5B | $2.179(19)$ |
| P1B-P5B | $2.140(18)$ |
| P1B-C21B | $1.98(3)$ |
| P2B-C25B | $1.84(2)$ |


| Atom-Atom | Length [Å] |
| :---: | :---: |
| Part 1-3a |  |
| P6A-P7A | $2.1503(7)$ |
| P7A-P8A | $2.1419(8)$ |
| P8A-P9A | $2.1499(9)$ |
| P9A-P10A | $2.1361(8)$ |
| P6A-P10A | $2.1508(7)$ |
| P6A-C28 | $1.870(2)$ |
| P6A-C21 | $1.848(2)$ |
| Part 2 - 3a' |  |
| P6A-P7A | $2.1503(7)$ |
| P7A-P8A | $2.1419(8)$ |
| P8A-P9A | $2.1499(9)$ |
| P9A-P10A | $2.1361(8)$ |
| P6A-P10A | $2.1508(7)$ |
| P6A-C28 | $1.870(2)$ |
| P6A-C21 | $1.848(2)$ |

Table S31. Selected angles of 3a and 3a'.

| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| Part 1 - 3a |  |
| P1A-P2A-P3A | $100.49(5)$ |
| P2A-P3A-P4A |  |
| P1A-P5A-P2A | $104.81(4)$ |
| P2A-P1A-C21A | $120.58(3)$ |
| P2A-P1A-C25A | $104.01(8)$ |
| P5A-P1A-C21A | $118.92(7)$ |
| P6AA-P7A-P8A |  |
| P7A-P8A-P9A | $100.91(3)$ |
| P9A-P10A-P6A | $105.20(3)$ |
| P7A-P6A-C28 | $100.71(3)$ |
| C27-P6A-C28 | $119.33(7)$ |
| C21A- P1A-C25A | $106.91(10)$ |


| Atom-Atom-Atom |  |
| :---: | :---: |
| Part 1 - 3a |  |
| P6A-P7A-P8A |  |
| P8A-P9A-P10A | $100.91(3)$ |
| P9A-P10A-P6A | $105.20(3)$ |
| P7A-P6A-C28 | $100.71(3)$ |
| C27-P6A-C28 | $119.33(7)$ |
| C21A- P1A-C25A | $106.91(10)$ |
| P1B-P2B-P3B | $108.59(10)$ |
| P2B-P3B-P4B | $119.5(4)$ |
| P4B-P5B-P1B | $95.1(6)$ |
| P2B-P1B-C21B | $111.3(7)$ |
| P2B-P1B-C25B | $111.9(9)$ |
| P5B-P1B-C21B | $114.4(9)$ |

## $\left[\left(\mathrm{Cp}{ }^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4: 4}-\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{P}_{5} \mathrm{Me}\right\}\right]$ (3b)



Fig. S45. Molecular structure of 3b in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The Cp * ligands are drawn in a wire frame model.

Table S32. Selected bond lengths of 3b.

| Atom-Atom | Length [Å] |
| :---: | :---: |
| P1-P2 | $2.1407(12)$ |
| P2-P5 | $2.1417(11)$ |
| P2-P3 | $2.1394(13)$ |
| P1-C11 | $1.816(3)$ |
| P6-C14 | $1.829(3)$ |
| P6-C15 | $1.814(4)$ |
| P7-P8 | $2.1360(16)$ |


| Atom-Atom | Length $[\AA ̊]$ |
| :---: | :---: |
| P1-C12 | $1.824(3)$ |
| P4-P5 | $2.1358(14)$ |
| P6-P10 | $2.1488(14)$ |
| P6-P7 | $2.1290(15)$ |
| P9-P10 | $2.1361(14)$ |
| P3-P4 | $2.1488(16)$ |
| P9-P8 | $2.1434(19)$ |

Table S33. Selected angles of 3b.

| Atom-Atom-Atom | Angle [ ${ }^{\circ}$ ] |
| :---: | :---: |
| P2-P1-P5 | $98.46(4)$ |
| C12-P1-P2 | $105.49(11)$ |
| C12-P1-P5 | $105.89(11)$ |
| C11-P1-P2 | $119.77(14)$ |
| C11-P1-P5 | $119.09(12)$ |
| C14-P6-P7 | $106.83(12)$ |
| C15-P6-P7 | $118.38(16)$ |


| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| C11-P1-C12 | $106.74(15)$ |
| P1-P2-P3 | $99.61(5)$ |
| P5-P4-P1 | $99.46(5)$ |
| P6-P7-P10 | $100.00(6)$ |
| C14-P6-P10 | $103.83(12)$ |
| C15-P6-P10 | $121.22(16)$ |
| C15-P6-C14 | $105.10(18)$ |

## $\left[\left(\mathrm{Cp}^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4: 4}-\mathrm{P}_{5} \mathrm{Me}\left(\mathrm{CH}_{2}\right)_{4} \mathrm{P}_{5} \mathrm{Me}\right\}\right]$ (3c)



Fig. S46. Molecular structure of $3 \boldsymbol{c}$ in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligands are drawn in a wire frame model.

Table S34. Selected bond lengths of 3c.

| Atom-Atom | Length [Å] |
| :---: | :---: |
| P1-P2 | $2.1479(14)$ |
| P1-P5 | $2.1419(13)$ |
| P1-C3 | $1.812(4)$ |
| P1-C1 | $1.826(4)$ |


| Atom-Atom | Length $[\AA \AA]$ |
| :---: | :---: |
| P2-P3 | $2.1356(15)$ |
| P3-P4 | $2.1620(17)$ |
| P4-P5 | $2.1523(18)$ |
|  |  |

Table S35. Selected angles of 3c.

| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| P2-P1-P5 | $97.01(5)$ |
| C3-P1-P2 | $117.83(15)$ |
| C3-P1-P5 | $118.61(15)$ |
| C3-P1-C1 | $102.88(19)$ |
| P3-P2-P1 | $97.95(6)$ |


| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| P2-P3-P4 | $104.18(6)$ |
| P1-P5-P4 | $97.69(6)$ |
| P5-P4-P3 | $104.19(6)$ |
| C1-P1-P2 | $110.59(14)$ |
| C1-P1-P5 | $110.03(14)$ |

$\left[\left(\mathrm{Cp}^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4: 4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{P}_{5} \mathrm{Me}\right\}\right]$ (4)


Fig. S47. Molecular structure of 4 in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligands are drawn in a wire frame model.

Table S36. Selected bond lengths of 4.

| Atom-Atom | Length [Å] |
| :---: | :---: |
| P1-P2 | $2.1482(8)$ |
| P2-P3 | $2.1370(9)$ |
| P3-P4 | $2.1484(10)$ |
| P4-P5 | $2.1444(10)$ |
| P1-P5 | $2.1455(9)$ |
| P1-C11 | $1.874(3)$ |
| P1-C18 | $1.817(3)$ |


| Atom-Atom | Length [Å] |
| :---: | :---: |
| P6-P7 | $2.1451(9)$ |
| P7-P8 | $2.1491(11)$ |
| P8-P9 | $2.1639(12)$ |
| P9-P10 | $2.1450(10)$ |
| P6-P10 | $2.1514(9)$ |
| P6-C17 | $1.835(3)$ |
| P1-C15 | $1.849(3)$ |

Table S37. Selected angles of 4.

| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| P1-P2-P3 | $101.02(4)$ |
| P2-P3-P4 | $105.30(4)$ |
| P4-P5-P1 | $100.73(4)$ |
| P5-P1-C15 | $104.54(9)$ |
| P2-P1-C15 | $104.88(9)$ |
| C11-P1-C15 | $107.36(12)$ |
| P6-P7-P8 | $96.71(4)$ |
| P7-P8-P9 | $104.27(4)$ |
| P9-P10-P6 | $97.12(4)$ |
| P10-P6-C18 | $118.35(10)$ |
| C18-P6-C17 | $102.70(13)$ |


| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| P3-P4-P5 | $105.16(4)$ |
| P5-P1-P2 | $99.33(3)$ |
| P5-P1-C11 | $117.90(8)$ |
| P2-P1-C11 | $121.08(9)$ |
| P2-P1-C15 | $104.88(9)$ |
| P8-P9-P10 | $103.78(4)$ |
| P17-P6-P7 | $96.46(3)$ |
| P17-P6-C18 | $102.70(13)$ |
| P7-P6-C17 | $111.75(9)$ |
| P7-P6-C18 | $118.35(10)$ |
| $\mathrm{C} 17-\mathrm{P6}-\mathrm{P} 10$ | $111.57(9)$ |

## $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\mathrm{\eta}^{4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{PPh}_{2}\right)\right](5)$



Fig. S48. Molecular structure of 5 in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligand is drawn in a wire frame model.


Fig. S49. Molecular structure of 5 in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The disorder is highlighted blue (Part 1) and green (Part 2). The $\mathrm{Cp}^{*}$ ligand is drawn in a wire frame model.

Table S38. Selected bond lengths of 5 .

| Atom-Atom | Length [Å] | Atom-Atom | Length [Å] |
| :---: | :---: | :---: | :---: |
| Part 1 |  | Part 2 |  |
| P7-P8A | 2.147(3) | P7-P8B | 2.205(10) |
| P8A-P9A | 2.139(3) | P8B-P9B | 2.130(11) |
| P9A-P10A | $2.148(4)$ | P9B-P10B | 2.123(11) |
| P10A-P11A | 2.137(5) | P10B-P11B | 2.134(14) |
| P7-P11A | $2.140(4)$ | P7-P11B | 2.172(14) |
| P7-C30 | 1.867(6) | P7-C30 | 1.867(6) |
| P7-C44A | 1.829(5) | P7-C44B | 1.858(19) |
| P12A-C46A | $1.839(6)$ | P12B-C46B | 1.838(18) |
| P12A-C53A | 1.853(6) | P12B-C53B | 1.81(3) |
| P12A-C47A | 1.828(5) | P12B-C47B | 1.79(3) |

Table S39. Selected angles of 5.

| Atom-Atom-Atom |  |
| :---: | :---: |
| Part 1 |  |
| Angle [] |  |
| P7-P8A-P9A | $101.14(12)$ |
| P8A-P9A-P10A | $104.90(16)$ |


| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| 2 |  |
| P7-P8B-P9B | $98.3(4)$ |
| P8B-P9B-P10B | $106.1(6)$ |


| P9A-P10A-P11A | $106.0(2)$ |
| :---: | :---: |
| P11A-P7-P8A | $100.1(2)$ |
| P8A-P7-C30 | $118.15(19)$ |
| P11A-P7-C30 | $119.7(3)$ |
| C30-P7-C44A | $106.7(3)$ |
| C46A-P12A-C53A | $102.4(3)$ |
| C46A-P12A-C47A | $102.5(3)$ |
| C47A-P12A-C53A | $98.9(3)$ |


| P9B-P10B-P11B | $101.6(8)$ |
| :---: | :---: |
| P11B-P7-P8B | $91.9(8)$ |
| P8B-P7-C30 | $129.2(3)$ |
| P11B-P7-C30 | $122.8(9)$ |
| C30-P7-C44B | $117.9(15)$ |
| C46B-P12B-C53B | $102.3(15)$ |
| C46B-P12B-C47B | $100.5(14)$ |
| C47B-P12B-C53B | $102.3(15)$ |

SPtBuBnz( $\left.\mathrm{C}_{4} \mathrm{H}_{8} \mathrm{Ph}\right)\left(6^{\prime}\right)$


Fig. S50. Molecular structure of 6 ' in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity.

Table S40. Selected bond lengths of 6'.

| Atom-Atom | Length [Å] |
| :---: | :---: |
| P1-S1 | $1.9575(6)$ |
| P1-C1 | $1.8600(18)$ |


| Atom-Atom | Length $[\AA ̊]$ |
| :---: | :--- |
| P1-C12 | $1.8253(18)$ |
| P1-C5 | $1.8280(19)$ |

Table S41. Selected angles of 6'.

| Atom-Atom-Atom | Angle [ ${ }^{\circ}$ ] |
| :---: | :---: |
| C1-P1-S1 | $112.49(6)$ |
| C12-P1-S1 | $112.40(6)$ |
| C12-P1-C1 | $110.13(8)$ |


| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| C12-P1-C5 | $103.10(8)$ |
| C5-P1-S1 | $113.49(6)$ |
| C5-P1-C1 | $104.58(8)$ |

## $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\mathrm{n}^{4}-\mathrm{P}_{5}\left(\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CN}\right)_{2}\right\}\right](7)$



Fig. S51. Molecular structure of 7 in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligand is drawn in a wire frame model.


Fig. S52. Molecular structure of 7 in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The disorder is highlighted blue (Part 1) and green (Part 2). The $\mathrm{Cp}^{*}$ ligand is drawn in a wire frame model.

Table S42. Selected bond lengths of 7.

| Atom-Atom | Length [Å] |
| :---: | :---: |
| P002-P003 | $2.1478(5)$ |
| P002-P004 | $2.1482(5)$ |
| P003-PO05 | $2.1498(5)$ |
| P003-COOE | $1.8341(13)$ |


| Atom-Atom | Length [Å] |
| :---: | :---: |
| P003-C00G | $1.8360(13)$ |
| P004-P006 | $2.1614(5)$ |
| P005-P006 | $2.1446(5)$ |
|  |  |

Table S43. Selected angles of 7.

| Atom-Atom-Atom | Angle [ ${ }^{\circ}$ ] |
| :---: | :---: |
| P003-P002-P004 | $99.561(19)$ |
| P002-P003-P005 | $98.259(18)$ |
| COOE-P003-P002 | $117.94(5)$ |
| COOE-P003-PO05 | $122.24(5)$ |
| COOE-P003-COOG | $104.96(6)$ |


| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| C00G-P003-P002 | $105.14(4)$ |
| C00G-P003-P005 | $106.90(4)$ |
| P002-P004-P006 | $104.727(19)$ |
| P005-P006-P004 | $104.643(19)$ |
|  |  |

## $\left[\left\{\mathrm{Cp}^{*} \mathrm{Fe}\left\{\mathrm{n}^{4}-\mathrm{P}_{5}\left(\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CN}\right)_{2}\right\}\right\} \mathrm{ZnBr}_{2}\right]$ (8)



Fig. S53. Molecular structure of 8 in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligand is drawn in a wire frame model.

Table S44. Selected bond lengths of 8 .

| Atom-Atom | Length [Å] |
| :---: | :---: |
| P9-P7 | $2.141(2)$ |
| P7-P5 | $2.143(3)$ |
| P5-P8 | $2.140(3)$ |
| P8-P6 | $2.137(3)$ |
| P6-P9 | $2.168(2)$ |


| Atom-Atom | Length [Å] |
| :---: | :---: |
| $\mathrm{N} 1-\mathrm{Zn} 1$ | $2.053(6)$ |
| $\mathrm{Zn} 1-\mathrm{Br} 1$ | $2.3533(12)$ |
| $\mathrm{Zn} 1-\mathrm{Br} 2$ | $2.3653(12)$ |
| $\mathrm{P} 7-\mathrm{Zn} 2$ | $2.4296(18)$ |
|  |  |

Table S45. Selected angles of 8.

| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| $\mathrm{Br} 1-\mathrm{Zn} 1-\mathrm{Br} 2$ | $121.57(5)$ |
| $\mathrm{Br} 3-\mathrm{Zn} 2-\mathrm{P} 7$ | $106.06(6)$ |
| $\mathrm{Br} 4-\mathrm{Zn} 2-\mathrm{P} 7$ | $108.40(6)$ |$\quad$| Atom-Atom-Atom | Angle [] |
| :---: | :---: |
| $\mathrm{N} 1-\mathrm{Zn} 1-\mathrm{Br} 1$ | $109.88(18)$ |
| $\mathrm{N} 1-\mathrm{Zn} 1-\mathrm{Br} 2$ | $102.69(18)$ |
| $\mathrm{N} 1-\mathrm{Zn} 1-\mathrm{P} 7$ | $107.60(17)$ |



Fig. S54. Molecular structure of 8 as a grown structure in the solid state with thermal ellipsoids at $50 \%$ probability level. The $\mathrm{Cp}^{*}$ ligands are drawn in a wire frame model.

## 4. Additional Information

## NMR Investigations

${ }^{31}\left\{{ }^{1} \mathrm{H}\right\}\left(\mathrm{THF} / \mathrm{C}_{6} \mathrm{D}_{6}\right.$ cap); reaction in THF; starting at r.t; 1 eq $\mathrm{Br}_{2}\left(\mathrm{CH}_{2}\right)_{3}$

${ }^{31}\left\{{ }^{1} \mathrm{H}\right\}(\mathrm{THF}) / \mathrm{C}_{6} \mathrm{D}_{6}$ cap; reaction in THF; starting at r.t 10 eq $\mathrm{Br}_{2}\left(\mathrm{CH}_{2}\right)_{3}$

${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}\left(\mathrm{C}_{6} \mathrm{D}_{6}\right)$; reaction in THF; starting at $-80^{\circ} \mathrm{C}$; 1 eq $\mathrm{Br}_{2}\left(\mathrm{CH}_{2}\right)_{3}$


Fig. S55. ${ }^{31}$ P $\left\{{ }^{1} \mathrm{H}\right\}$ NMR Spectra ( 161.98 MHz )/ Cutout: Reaction of 1a with 1,3-dibromopropane at different reaction conditions (shifts are normalized for better overview) (+ = 2a; \# = 3a; ' = 3a').
${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}\left(\mathrm{C}_{6} \mathrm{D}_{6}\right)$; reaction in THF; starting at $-80^{\circ} \mathrm{C}$;

${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}(\mathrm{THF}) / \mathrm{C}_{6} \mathrm{D}_{6}$ cap; reaction in THF; starting at $\mathbf{- 8 0}{ }^{\circ} \mathrm{C}$;
10 eq $\mathrm{Br}_{2}\left(\mathrm{CH}_{2}\right)_{3}$

${ }^{31}{ }^{1}\left\{{ }^{1} \mathrm{H}\right\}\left(\mathrm{DME} / \mathrm{C}_{6} \mathrm{D}_{6}\right.$ cap); reaction in DME; starting at $\mathbf{- 5 0}{ }^{\circ} \mathrm{C}$;


Fig. S56. ${ }^{31}$ P $\left\{{ }^{1} \mathrm{H}\right\}$ NMR Spectra ( 161.98 MHz )/ Cutout: Reaction of $\mathbf{1 b}$ with 1,3-dibromopropane at different reaction conditions (shifts are normalized for better overview) (+ = 2b; \# = 3b).
${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}\left(\mathrm{C}_{6} \mathrm{D}_{6}\right)$; reaction in THF; starting at $-80^{\circ} \mathrm{C}$;
1 eq $\mathrm{Br}_{2}\left(\mathrm{CH}_{2}\right)_{3}$

${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}\left(\mathrm{C}_{6} \mathrm{D}_{6}\right)$; reaction in THF; starting at $-80^{\circ} \mathrm{C}$
1 eq $\mathrm{Br}_{2}\left(\mathrm{CH}_{2}\right)_{4}$


130


Fig. S57. ${ }^{31}$ P\{1 $\left.{ }^{1} \mathrm{H}\right\}$ NMR Spectra ( 161.98 MHz )/ Cutout: Reaction of 1b with 1,3-dibromopropane (top) and 1,4dibromobutane (button).


Fig. S58. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR Spectra ( 161.98 MHz )/ Cutout: Reaction of $\mathbf{1 b}$ with 1,4-dibromobutane.


Fig. S59. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}$ Spectra ( $161.98 \mathrm{MHz}, \mathrm{THF} / \mathrm{C}_{6} \mathrm{D}_{6}$ capillary): Reaction of 2 a with $\mathrm{LiPCy}_{2}$


Fig. S60. ${ }^{31}{ }^{\mathrm{P}}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}$ Spectra ( $161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ or $\mathrm{THF} / \mathrm{C}_{6} \mathrm{D}_{6}$ capillary (middle spectra)): Reaction of 2a with successive 2 eq KBnz (+ = 2a; \# = [Cp $\left.{ }^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{P}_{5}{ }^{\mathrm{t}} \mathrm{Bu}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Bnz}\right\}\right]$.


Fig. S61. ${ }^{1} \mathrm{H}$ NMR Spectra ( 400.13 MHz )/ Cutout: Complex 7 (top, $\mathrm{C}_{6} \mathrm{D}_{6}$ ) and Complex 8 (bottom, THF-d $\mathrm{d}_{8}$ ).


Fig. S62. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR Spectra ( 161.98 MHz ): Complex $\mathbf{7}\left(\right.$ top, $\mathrm{C}_{6} \mathrm{D}_{6}$ ) and Complex 8 (bottom, THF- $\mathrm{d}_{8}$ ).

## Cyclovoltammogram



Fig. S63. CV of compound $\left[\left(\mathrm{Cp}{ }^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4: 4}-\mathrm{P}_{5}{ }^{t} \mathrm{Bu}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{P}_{5} \mathrm{Me}\right\}\right]$ (4)

## 5. Computational details

DFT calculations were carried out using the Gaussian 16 program. ${ }^{[v]}$ The geometries were optimised using the B3LYP ${ }^{[v i-x i]}$ functional together with the def2-TZVP basis set. ${ }^{[x]}$

Table S46. Total energies for all optimized geometries (B3LYP/def2-TZVP level of theory).

|  | total energy [Hartree] |
| :--- | :--- |
| 3a | -7156.16341675 |
| 3a' | -7156.15244264 |



Table S47. Optimized geometries of 3a XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.

| P | 2.405613000 | -1.701726000 | -0.461266000 | H | 3.881847000 | 1.199068000 | 4.212157000 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| P | 4.093003000 | -2.023684000 | 0.836873000 | H | 4.037417000 | -0.460901000 | 3.637015000 |
| P | 3.018095000 | 0.120664000 | -1.427082000 | C | 2.992159000 | -3.772995000 | -2.171254000 |
| P | 5.039295000 | -0.352891000 | -1.990784000 | H | 3.676850000 | -4.187269000 | -1.432118000 |
| P | 5.742141000 | -1.742149000 | -0.512667000 | H | 3.544790000 | -3.060183000 | -2.782539000 |
| C | -4.309908000 | -2.214975000 | 0.058847000 | H | 2.648790000 | -4.584609000 | -2.816715000 |
| C | -5.452153000 | -1.794879000 | -0.679361000 | C | 5.022553000 | 3.190541000 | -0.860529000 |
| C | 5.855390000 | 0.747858000 | 1.876379000 | H | 5.217210000 | 4.214183000 | -0.526665000 |
| C | 4.011244000 | 1.956469000 | 1.189759000 | H | 4.039514000 | 3.180281000 | -1.331852000 |
| C | 1.084957000 | -1.193087000 | 0.716607000 | H | 5.758082000 | 2.942564000 | -1.624182000 |
| H | 0.810697000 | -2.060095000 | 1.318854000 | C | 1.057863000 | -4.133970000 | -0.613678000 |
| H | 1.583251000 | -0.487911000 | 1.381643000 | H | 0.806836000 | -5.017886000 | -1.204609000 |
| C | 6.225948000 | 1.493186000 | 0.715375000 | H | 0.129727000 | -3.736929000 | -0.203862000 |
| C | -4.552824000 | -1.941885000 | 1.444103000 | H | 1.692062000 | -4.457916000 | 0.213897000 |
| C | 4.485990000 | 1.040121000 | 2.168987000 | C | 7.581149000 | 1.526560000 | 0.090523000 |
| C | -6.405739000 | -1.259962000 | 0.241604000 | H | 7.521313000 | 1.737978000 | -0.976142000 |
| C | 5.084340000 | 2.237410000 | 0.286584000 | H | 8.096629000 | 0.574550000 | 0.210833000 |
| C | -5.849875000 | -1.352315000 | 1.552836000 | H | 8.199366000 | 2.302808000 | 0.551085000 |
| C | 1.773645000 | -3.118267000 | -1.508650000 | C | 0.838849000 | -2.577090000 | -2.596335000 |
| C | -5.652313000 | -1.971651000 | -2.147460000 | H | 0.536164000 | -3.403580000 | -3.243622000 |
| H | -6.313724000 | -1.209698000 | -2.555577000 | H | 1.340949000 | -1.831862000 | -3.214035000 |
| H | -6.098801000 | -2.949517000 | -2.353598000 | H | -0.063979000 | -2.127606000 | $-2.188661000$ |
| H | -4.707896000 | -1.916357000 | -2.687101000 | P | -2.520776000 | 1.524335000 | -1.532117000 |
| C | -3.123071000 | -2.914807000 | -0.517122000 | P | -2.606397000 | 0.722599000 | 0.441106000 |
| H | -2.818738000 | -2.474235000 | -1.465996000 | C | -1.868497000 | 3.294921000 | -1.583756000 |
| H | -3.353848000 | -3.968074000 | -0.702393000 | C | -2.096409000 | 3.777800000 | -3.021265000 |
| H | -2.272065000 | $-2.885313000$ | 0.160842000 | H | -1.587288000 | 3.138859000 | -3.745167000 |
| C | 2.656592000 | 2.582243000 | 1.147587000 | H | -1.708302000 | 4.793704000 | -3.134192000 |
| H | 2.335274000 | 2.764451000 | 0.124163000 | H | -3.159549000 | 3.796603000 | -3.269514000 |
| H | 2.658005000 | 3.540935000 | 1.675107000 | C | -0.368537000 | 3.213674000 | -1.277486000 |
| H | 1.908399000 | 1.950097000 | 1.622983000 | H | -0.190119000 | 2.888193000 | -0.251315000 |
| C | -3.656680000 | -2.291667000 | 2.586596000 | H | 0.086043000 | 4.201755000 | -1.391258000 |
| H | -2.623131000 | -2.408419000 | 2.263798000 | H | 0.149283000 | 2.526687000 | -1.949119000 |
| H | -3.962984000 | -3.237607000 | 3.042521000 | C | -2.559968000 | 4.228639000 | -0.595058000 |
| H | -3.680722000 | -1.527220000 | 3.362684000 | H | -3.631543000 | 4.284815000 | -0.783220000 |
| C | -6.526061000 | -0.945833000 | 2.819706000 | H | -2.141840000 | 5.235698000 | -0.687477000 |
| H | -5.801447000 | -0.693498000 | 3.592402000 | H | -2.419948000 | 3.894748000 | 0.432645000 |
| H | -7.152504000 | -1.757971000 | 3.200235000 | P | -4.717373000 | 1.352668000 | -1.448214000 |
| H | -7.164453000 | $-0.076466000$ | 2.666249000 | P | -5.492252000 | 1.996216000 | 0.477263000 |
| C | -7.769416000 | -0.765738000 | -0.110240000 | P | -3.946991000 | 1.564986000 | 1.882496000 |
| H | -8.143581000 | -0.065519000 | 0.634554000 | Fe | -4.613373000 | -0.172409000 | 0.364217000 |
| H | -8.475491000 | -1.599320000 | -0.172512000 | Fe | 4.672452000 | 0.193988000 | 0.252453000 |
| H | -7.772191000 | -0.258640000 | -1.074740000 | C | -0.150272000 | -0.546179000 | 0.095234000 |
| C | 6.745606000 | -0.131213000 | 2.691167000 | H | -0.734073000 | -1.287071000 | -0.446939000 |
| H | 6.200832000 | -0.989134000 | 3.085849000 | H | 0.149387000 | 0.204841000 | -0.635676000 |
| H | 7.159262000 | 0.417217000 | 3.542789000 | C | -1.027540000 | 0.111996000 | 1.159438000 |
| H | 7.578813000 | -0.510547000 | 2.101623000 | H | -0.504699000 | 0.947438000 | 1.626986000 |
| C | 3.723241000 | 0.541691000 | 3.351732000 | H | -1.288540000 | -0.594059000 | 1.948885000 |
| H | 2.651644000 | 0.512076000 | 3.158215000 |  |  |  |  |



Table S48. Optimized geometries of 3a' XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.

| Fe | -3.918028000 | -0.339979000 | -0.601396000 | C | -1.336293000 | 0.057862000 | -2.535396000 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Fe | 3.652665000 | -0.947561000 | 0.029413000 | H | -1.048899000 | 1.028213000 | -2.134130000 |
| P | 2.734647000 | 1.997369000 | -0.517432000 | H | -0.738466000 | -0.699477000 | -2.035018000 |
| P | -2.451532000 | 0.856663000 | 1.769223000 | H | -1.060294000 | 0.049593000 | -3.594110000 |
| P | -2.216047000 | -1.075223000 | 0.863633000 | C | -2.735598000 | -2.792248000 | -2.305686000 |
| P | -4.299066000 | 1.477379000 | 0.850639000 | H | -1.743400000 | -2.728698000 | -1.861917000 |
| P | 3.701349000 | 1.116100000 | 1.197913000 | H | -3.296170000 | -3.548420000 | -1.757485000 |
| P | 2.759314000 | 0.268209000 | -1.808364000 | H | -2.614936000 | -3.145223000 | -3.334219000 |
| P | -4.173565000 | -1.925258000 | 1.102024000 | C | -3.232520000 | 0.054137000 | 4.283849000 |
| P | -5.531366000 | -0.263800000 | 1.098938000 | H | -4.265865000 | 0.232013000 | 3.987219000 |
| P | 5.505625000 | 0.443173000 | 0.227082000 | H | -2.979118000 | -0.974062000 | 4.026766000 |
| P | 4.879754000 | -0.125880000 | -1.757048000 | H | -3.163205000 | 0.163313000 | 5.368503000 |
| C | -2.798812000 | -0.190742000 | -2.369233000 | C | 4.540710000 | -1.987568000 | 2.934365000 |
| C | -3.817711000 | 0.802922000 | -2.370061000 | H | 4.072631000 | -1.138315000 | 3.432534000 |
| C | 2.287966000 | -2.562360000 | -0.011143000 | H | 4.450496000 | -2.850723000 | 3.600713000 |
| C | 2.502218000 | -2.134724000 | 1.329557000 | H | 5.600677000 | -1.764127000 | 2.821575000 |
| C | -5.082072000 | 0.145307000 | -2.272395000 | C | -5.888368000 | $-2.325400000$ | -2.164796000 |
| C | -4.842465000 | -1.261843000 | -2.218641000 | H | -5.511366000 | -3.227374000 | -1.685322000 |
| C | 3.897310000 | -2.266902000 | 1.616941000 | H | -6.762403000 | -1.994019000 | -1.605423000 |
| C | 0.180711000 | 1.352260000 | 0.668812000 | H | -6.218466000 | -2.593888000 | -3.172696000 |
| H | 0.071856000 | 0.457081000 | 0.059912000 | C | 0.974000000 | $-2.679096000$ | -0.705820000 |
| H | 0.692507000 | 1.056091000 | 1.581822000 | H | 0.576973000 | -3.693613000 | -0.599270000 |
| C | -2.276541000 | 1.051214000 | 3.619906000 | H | 0.236149000 | -2.000092000 | -0.286083000 |
| C | 4.540255000 | -2.780804000 | 0.449825000 | H | 1.063235000 | -2.470633000 | -1.771370000 |
| C | -3.430958000 | -1.471813000 | -2.277146000 | C | -0.834648000 | 0.751502000 | 4.039357000 |
| C | 3.544789000 | -2.957409000 | -0.559208000 | H | -0.522533000 | -0.242084000 | 3.718161000 |
| C | 0.996442000 | 2.399723000 | -0.080588000 | H | -0.130455000 | 1.482553000 | 3.642405000 |
| H | 1.041757000 | 3.316351000 | 0.509643000 | H | -0.764963000 | 0.784783000 | 5.129201000 |
| H | 0.495481000 | 2.651628000 | -1.016525000 | C | 5.985278000 | -3.131640000 | 0.319952000 |
| C | -2.672134000 | 2.482354000 | 3.999306000 | H | 6.339683000 | -2.982593000 | -0.699398000 |
| H | -1.998098000 | 3.224923000 | 3.571436000 | H | 6.602820000 | -2.521762000 | 0.977325000 |
| H | -3.688322000 | 2.713477000 | 3.677447000 | H | 6.150265000 | -4.181206000 | 0.580927000 |
| H | -2.630756000 | 2.586164000 | 5.085969000 | C | 3.753040000 | -3.527332000 | -1.923325000 |
| C | 1.452622000 | $-1.737456000$ | 2.311694000 | H | 3.530327000 | $-4.598708000$ | -1.932914000 |
| H | 0.551234000 | -1.386475000 | 1.815295000 | H | 3.102385000 | -3.050300000 | $-2.656404000$ |
| H | 1.167030000 | -2.593387000 | 2.931600000 | H | 4.780729000 | -3.395302000 | -2.257114000 |
| H | 1.804712000 | -0.952351000 | 2.979714000 | C | 4.796710000 | 3.455163000 | -1.736493000 |
| C | -1.195984000 | 1.950211000 | 0.977789000 | H | 5.493795000 | 3.117659000 | -0.972252000 |
| H | -1.659452000 | 2.287889000 | 0.050669000 | H | 4.820844000 | 2.738395000 | -2.555502000 |
| H | -1.091186000 | 2.831844000 | 1.611919000 | H | 5.142238000 | 4.420073000 | $-2.114897000$ |
| C | -6.415270000 | 0.816558000 | -2.296433000 | C | 3.423192000 | 4.646730000 | -0.026839000 |
| H | -7.175612000 | 0.206679000 | -1.811293000 | H | 2.432427000 | 4.888147000 | 0.356336000 |
| H | -6.386684000 | 1.779236000 | $-1.785929000$ | H | 4.034155000 | 4.281001000 | 0.799692000 |
| H | -6.737794000 | 0.999194000 | -3.326021000 | H | 3.870027000 | 5.575376000 | -0.389052000 |
| C | 3.381756000 | 3.635350000 | -1.179113000 | C | 2.456890000 | 4.115224000 | -2.305729000 |
| C | -3.608674000 | 2.271505000 | -2.535449000 | H | 2.901106000 | 4.995918000 | -2.774709000 |
| H | -4.370511000 | 2.846771000 | -2.012105000 | H | 2.337657000 | 3.352926000 | -3.078168000 |
| H | -2.636142000 | 2.583233000 | -2.156480000 | H | 1.470651000 | 4.398546000 | -1.941401000 |
| H | -3.651103000 | 2.544718000 | -3.594296000 |  |  |  |  |

## 6. References

[i] E. S. S. A, L. Lochmann and J. Trekoval, J. Organomet. Chem., 1987, 326, 1-7.
[ii] O. J. Scherer and T. Brück, Angew. Chem. Int. Ed., 1987, 26, 11987.
[iii] M. V. Butovskiy, G. Balázs, M. Bodensteiner, E. V. Peresypkina, A. V. Virovets, J. Sutter and M. Scheer, Angew. Chem. Int. Ed., 2013, 52, 2972-2976.
[iv] S. Reichl, E. Mädl, F. Riedlberger, M. Piesch, G. Balázs, M. Seidl and M. Scheer, Nat. Commun., 2021, 12, 5774.
[v] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. a. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. a. Petersson, H. Nakatsuji, X. Li, M. Caricato, a. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, a. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. a. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. a. Keith, R. Kobayashi, J. Normand, K. Raghavachari, a. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, 2016, Gaussian 16, Revision D.09, Gaussian, Inc., Wallin.
[vi] A. D. Becke, J. Chem. Phys., 2005, 98, 5648-5652.
[vii] S. H. Vosko, L. Wilk and M. Nusair, Can. J. Phys., 1980, 58, 1200-1211.
[viii] C. Lee, W. Yang and R. G. Parr, Phys. Rev. B, 1988, 37, 785-789.
[ix] P. J. Stephen, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, J. Phys. Chem., 1994, 98, 1162311627.
[x] F. Weigend and R. Ahlrichs, Phys. Chem. Chem. Phys., 2005, 7, 3297-3305.
[xi] L. J. Bourhis, O. V Dolomanov, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Crystallogr., 2009, 42, 339-341.
[xii] G. M. Sheldrick, Acta Crystallogr. Sect. A, 2015, 71, 3-8.
[xiii] G. M. Sheldrick, Acta Crystallogr. Sect. C, 2015, 71, 3-8.

## 8 Synthesis of the Largest Molecular Anionic Arsenic Ligand Complex

### 8.1 Preface

The following chapter has not been submitted yet.
S. Reichl, C. Riesinger, M. Scheer, manuscript in preparation.

## Authors

Stephan Reichl, ${ }^{1}$ Christoph Riesinger, ${ }^{1}$ Gábor Balázs, ${ }^{1}$ Manfred Scheer ${ }^{1}$
${ }^{1}$ Institute of Inorganic Chemistry, University of Regensburg; Universitätsstraße 31, 93053 Regensburg, Germany.
*Corresponding author. Email: manfred.scheer@chemie.uni-regensburg.de

## Author Contribution

S.R. conceived the experiments. S.R. analysed and revised the X-ray data. C.R. performed the computational studies and measured NMR experiments of compound 1a. S.R. and M.Sch. wrote the manuscript. M.Sch. directed and coordinated the research.

## Synthesis of the Largest Molecular Anionic Arsenic Ligand

## Complex



# Synthesis of the Largest Molecular Anionic Arsenic Ligand 

## Complex


#### Abstract

Unique functionalized products with $\eta^{4}-A s_{n}(n=5,6,20)$ units are obtained by the reaction of $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{As} 5\right)\right](\mathrm{I})\left(\mathrm{Cp}^{*}=\mathrm{C}_{5} \mathrm{Me}_{5}\right)$ with main group nucleophiles. With carbon-based nucleophiles like MeLi or KBnz (Bnz $=\mathrm{CH}_{2} \mathrm{Ph}$ ), anionic organo-substituted polyarsenic complexes, [Li(2.2.2cryptand) $)\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{AssMe}\right)\right]$ (1a) and [K(2.2.2-cryptand) $]\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{Ass}_{5}\left(\mathrm{CH}_{2} \mathrm{Ph}\right)\right\}\right]$ (1b), are accessible. The usage of $K A s P h_{2}$ leads to a selective and controlled extension of the $\mathrm{As}_{5}$ unit and the formation of the monoanionic compound [K(2.2.2-cryptand][Cp*Fe( $\left.\left.\eta^{4}-\mathrm{As}_{6} \mathrm{Ph}_{2}\right)\right]$ (2). When I is reacted with $[\mathrm{M}] \operatorname{As}(S i M e 3)_{2}(\mathrm{M}=\mathrm{Li} \cdot \mathrm{THF} ; \mathrm{K})$ the formation of the biggest anionic polyarsenic unit in $\left[M^{\prime}(2.2 \cdot 2-c r y p t a n d)\right]_{2}\left[\left(C p^{*} F e\right)_{4}\left\{\mu 5-\eta^{4}: \eta^{4}: \eta^{3}: \eta^{3}: \eta^{1}: \eta^{1}-A s 20\right\}\right](3)$ is observed $\left(M^{\prime}=L i(3 a), K(3 b)\right)$.


### 8.2 Introduction

The generation and handling of yellow arsenic (As4) is barely possible due to its light and air sensitivity. One approach to handle the metastable As4 via its activation with carbonylcontaining complexes, which form polyarsenic transition metal complexes under harsh conditions (photolysis or thermolysis). ${ }^{[1]}$ The reaction of $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}(\mathrm{CO})_{2}\right]_{2}$ with a freshly prepared solution of As4 in decalin at $190^{\circ} \mathrm{C}$ for I .5 hours leads to $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{Ass}\right)\right]$ (I)..$^{11,2]}$ In contrast to yellow arsenic, complex I is stable towards light and oxygen. ${ }^{[2]}$ In addition to this, the starting materials for I are contrary to other $\mathrm{As}_{\mathrm{n}}$ ligand complexes easy accessible. ${ }^{[1,2]}$ The so-called pentaarsaferrocene (I) is isostructural to ferrocene and represents with its cyclo-Ass-ligand a true rarity as one of the very few end-on-polyarsenic ligand complexes (Scheme 1). ${ }^{[1]}$ DFT calculations show that the LUMO of I is mostly localized on the As atoms of the cyclo-Assligand, which suggests interesting reactivity as an electron acceptor. ${ }^{[3]}$ Our group reported about the reactivity of $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right]$ ( $\mathrm{I}^{\prime}$ ) towards main group nucleophiles and the isolation of up to that date unprecedented functionalized products. ${ }^{[4,5]}$ Over the years a variety of Asn ligand complexes has been reported, containing ligands up to 18 arsenic atoms. ${ }^{[6,7]}$ However, those arsenic-rich compounds are much less studied compared to the polyphosphorus ligand ones. Especially the synthesis of anionic organo-polyarsenic products is very challenging and highly interesting, e.g., for further functionalization. A look in the literature shows that the synthesis of novel polyarsenic ligand complexes is an actual topic, but due to bad yields and sensitivity, almost no consecutive reactions are published. With regards to its convincing features,
compound I represents a suitable starting material for further investigations in the chemistry of Asn ligand complexes.


Scheme 1. Complexes with a planar $\mathrm{As}_{\mathrm{n}}$ ligand.

In 2016, Roesky et. al presented the reactivity of $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{As} 5\right)\right](\mathrm{I})$ towards $\left[\mathrm{L}_{2} \mathrm{Sm}(\mathrm{thf})_{2}\right]^{[8]}(\mathrm{L}=$ (2,6-diisopropylphenyl-N $)_{2} \mathrm{CH}$ ), whereas our group investigated the versatile reduction chemistry of I. ${ }^{[6]}$ The latter shows the different reaction behavior of pentaarsaferrocene ${ }^{[6]}$ in comparison to its lighter homolog $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right]$ (I). ${ }^{[9]}$ Since the reduction of I is not very selective and several mono- and dianionic Asn ligand complexes were obtained ${ }^{[6]}$ we were interested in whether it is possible to get selective products by the reaction of I with nucleophiles, especially carbon- but also arsenic-based ones, whereby the latter offer the chance of ring expansion and rearrangement reactions. In doing so we have chosen different arsenic nucleophiles (KAsPh ${ }_{2},[\mathrm{M}] \mathrm{As}\left(\mathrm{SiMe}_{3}\right)_{2}(\mathrm{M}=\mathrm{Li} \cdot \mathrm{THF} ; \mathrm{K})$, KAsCO and $\left.\mathrm{KAsH}_{2}\right)$, bearing organo and/or labile substituents, to see if one can achieve a controlled extension of the polyarsenic ligand or induce a fragmentation/ rearrangement.

### 8.3 Results

Recently, we reported the controlled functionalization of one $P$ atom in $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right]\left(\mathrm{I}^{\prime}\right) .{ }^{[5]}$ Inspired by this work, the first step was the reaction between $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{Ass}\right)\right]$ (I) and organo nucleophiles. Thereby the reaction of I with MeLi and KBnz, respectively, as well as one equivalent of $2.2 \cdot 2$-cryptand at $-80^{\circ} \mathrm{C}$ leads to an immediate color change from green to brown. After workup the complexes [Li(2.2.2-cryptand)][Cp*Fe(n ${ }^{4}$-AssMe)] (1a) and $[K(2.2 .2-$ cryptand) $]\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As} 5 \mathrm{Bnz}\right)\right]$ (1b), respectively, can be isolated in crystalline yields of 80 and $75 \%$, respectively (Scheme 2, i). It has to be noted that the usage of cryptand at low
temperature is crucial. Otherwise, no crystals were obtained. This applies to all following reactions, indicating a more selective and controlled reaction when using cryptand and starting at $-80^{\circ} \mathrm{C}$. Single $X$-ray structure analysis of 1 a and 1 b reveals an $\eta^{4}$-As 5 R moiety, respectively (1a: $R=M e, 1 b: R=B n z$ ) (Figure 1). Compounds 1a and 1b represent the first anionic organo substituted polyarsenic ligand complexes without additional metal fragments needed to stabilize them. ${ }^{[8]}$ The $\eta^{4}$-As5R ligand exhibits an envelope geometry, featuring four arsenic atoms in the plane coordinating towards the $\mathrm{Cp}^{*} \mathrm{Fe}$ fragment, whereas the arsenic atom bearing the organo substituent is out of the plane. The As-As bond lengths of 2.306(8) - 2.401(4) $\AA$ are within the range of a single- and double bond, ${ }^{[10,11]}$ whereas the As-C distances (1.970(4) $\AA$ for 1a; $1.994(4) \AA$ Å for 1b) correlate with an arsenic carbon single bond. ${ }^{[10]}$ The corresponding angles (see Table S4 and S6) indicate a nearly square planar geometry of the arsenic atoms in the plane. Contrary to the analogue phosphorus anion $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Me}\right)\right]^{[5]}$ and all other anions of this type, ${ }^{[4,5,9]}$ the methyl group in 1 a is (disordered in the solid state structure and) located as well as in endo and exo position (with respect to the envelop of the $\eta^{4}$-As5 moiety) in a ratio of 86:14, respectively (Figure 1). The two methyl groups are chemical inequivalent and show different chemical shifts in the ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra (Figure S 1 and S 8 ). Thereby the endo position is favored, in contrast to the exo position, by (-)139.66 $\mathrm{kJ} \cdot \mathrm{mol}^{-1}$ according to DFT calculations (Table S15 and S16) and supports the occupation in the solid state. The ratio in solution does not change over a period of four days, storing the dissolved crystals of 1a at room temperature or heating the solution for three hours at $50^{\circ} \mathrm{C}$, indicating a thermodynamic controlled process during the formation of 1 a with regards to the endo/exo product, representing no equilibria. Therefore, the endo species can be seen as the thermodynamic-, whereas the exo represents the kinetic one.


Figure 1. Molecular structure of the anions of 1a (left) and 1b (right) in the solid state. $\mathrm{Cp}^{*}$ ligands are drawn in a wire model. Cations and H atoms are omitted for clarity.


Scheme 1. Reactivity of I towards i) MeLi or KBnz + 2.2.2-cryptand, $-80^{\circ} \mathrm{C}$ to r.t.; ii) 1,1'-dilithioferrocene +2.2 .2 cryptand, $-80^{\circ} \mathrm{C}$ to r.t.; iii) $\mathrm{KAsPh} 2+2.2 .2$-cryptand, $-80^{\circ} \mathrm{C}$ to r.t.; iv) $\mathrm{LiA} s S i M e 3+2.2 .2-c r y p t a n d, ~-80^{\circ} \mathrm{C}$ to r.t. for 3 a ; $\mathrm{KAsSiMe}_{3}$ or $\mathrm{KAsCO}+2.2 .2$-cryptand for $3 \mathrm{~b},-80^{\circ} \mathrm{C}$ to r.t. (Yields are given in parenthesis)

Mixing a green solution of I, 1, $1^{\prime}$-dilithioferrocene, and 2.2 .2-cryptand at $-80^{\circ} \mathrm{C}$ resulted in a dark green solution which turned brown-yellowish overnight. After workup (cf. SI) brown blocks of complex 1c ([Li(2.2.2-cryptand) $\left.\left.]_{2}\left[\left\{\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As5}\right)\right)_{2}\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{4}\right)_{2} \mathrm{Fe}\right)\right]\right)$ can be isolated after one day (Scheme 1, ii). XRD analysis revealed the formation of a dianionic species featuring two $\eta^{4}$-As $s_{5}$ moieties linked via a ferrocenyl unit (Figure 2). The As-As bond distances are similar to complex 1a/1b. The As-C bond lengths are 1.951(3) $\AA$ (As1-C11) / 1.942(3) $\AA$ (As6-C16), respectively, indicating an arsenic-carbon single bond. ${ }^{[10]}$

Due to two iron fragments and the bridging ferrocene unit, complex 1 c is expected to exhibit interesting electro-chemical properties. Hence, a cyclic- (CV) and square wave voltammogram (SQV) of 1c in THF was recorded. In alignment with initial expectations, the CV / SQV of 1c shows two oxidations at 878 mV and 1970 mV (Figure 2 and S23; vs. $\mathrm{fc} / \mathrm{fc}^{+}$), respectively, whereas the first oxidation is followed by an ECE (electron transfer - chemical reaction electron transfer) - type process, featuring the corresponding reduction at -814 mV (Figure 2). One should note that the second (irreversible) oxidation cannot be resolved properly by CV but detected by SQV (Figure S23).


Figure 2. Molecular structure of the anions of 1 c (top; $\mathrm{Cp}^{*}$ ligands are drawn in a wire model. Cations and H atoms are omitted for clarity) in the solid state and the corresponding cyclic voltammogram (bottom) of 1c.

In Recently, our group reported the manifold reduction chemistry of I. ${ }^{[6]}$ It has been shown that complex I tend to aggregate, forming arsenic-rich polyarsenides, stabilized by $\mathrm{Cp}^{*} \mathrm{Fe}$ fragments, in a rather unselective way under the formation of different products, e.g. $\left.\left[\mathrm{K}(\mathrm{dme})_{3}\right]_{2}\left[\left(\mathrm{Cp}{ }^{*} \mathrm{Fe}\right)_{4}\left\{\mu_{4}-\eta^{4}: \eta^{3}: \eta^{3}: \eta^{2}: \eta^{2}: \eta^{1}: \eta^{1}-\mathrm{As} 18\right\}\right]\right) .^{[6]}$ Since we were interested in whether it is possible to extend the polyarsenic unit of I in a more controlled manner, we reacted complex I with $\mathrm{KAsPh}_{2}$, as an arsenic nucleophile. Indeed, the reaction described above (cf. SI) yielded single crystals of pure $[\mathrm{K}(2.2 \cdot 2-c r y p t a n d)]\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As}_{6} \mathrm{Ph}_{2}\right)\right]$ (2) in $75 \%$ yield (Scheme 2, iii). The anion of complex 2 features an $\eta^{4}$-As $\mathrm{Ph}_{2}$ ligand (Figure S18) and proves that an extension of the polyarsenic ligand is possible in a selective manner. The newly formed As1-As2 bond distance of $2.4440(3) \AA$ is in agreement with an arsenic single bond. ${ }^{[10]}$ It was possible to selectively extend the polypnictogen unit, whereby the - $\mathrm{AsPh}_{2}$ group is exclusively located in exo position.

The logical consequence was the exchange of the rather strong bonded Phenyl substituents to labile ones to form bigger arsenic ligand complexes without any substituents. Therefore, we used $\mathrm{LiAs}\left(\mathrm{SiMe}_{3}\right)_{2}$ which tend to react as an As synthon by the release of the weakly bonded TMS (trimethylsilyl) groups. ${ }^{[12]}$ When mixing complex I, LiAs(SiMe3)2.THF and 2.2.2-cryptand at $-80^{\circ} \mathrm{C}$ a color change to brown was observed. After workup (c.f. SI) green/brownish blockshaped single crystals were obtained. XRD analysis revealed the formation of an unprecedented As 20 ligand complex, stabilized by four Cp*Fe fragments (Scheme 2, iv). Compound 3a ([Li(2.2.2-
cryptand $\left.)]_{2}\left[\left(\mathrm{Cp}{ }^{*} \mathrm{Fe}\right)_{4}\left\{\mu_{4}-\eta^{4}: \eta^{4}: \eta^{3}: \eta^{3}: \eta^{1}: \eta^{1}-\mathrm{As}_{20}\right\}\right]\right)$ can be synthesized in $50 \%$ yield and represents the largest molecular anionic $\mathrm{As}_{\mathrm{n}}(\mathrm{n}=20)$ ligand complex. The molecular structure of the anion of 3a comprises formally two norbornadiene-like As $7^{3-}$ moieties and one cyclo-hexane-like As 6 unit (Figure 3). The As-As bond distances (Table S11) are similar to other As ligand complexes. ${ }^{[6]}$ The alternating As-As bond length of 2.3903(7) - 2.5670(10) $\AA$ in the chair-like cyclo-As 6 moiety are within arsenic single-/ and a double bond. ${ }^{[10,11]} \mathrm{The}^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra of 3 a in THF-d8 at r.t. exhibits only one $\mathrm{Cp}^{*}$ related species (Figure S5 and S12). The analog potassium compound 3b ([K(2.2.2-cryptand) $\left.\left.]_{2}\left[\left(C p^{*} \mathrm{Fe}\right)\right)_{4}\left\{\mu_{4}-\eta^{4}: \eta^{4}: \eta^{3}: \eta^{3}: \eta^{1}: \eta^{1}-\mathrm{As} 20\right\}\right]\right)$ can be obtained when reacting I with $\mathrm{KAs}\left(\mathrm{SiMe}_{3}\right)_{3}\left(\mathrm{Scheme} 2 \text {, iv) under the formation of inter alia ( } \mathrm{As}\left\{\mathrm{SiMe}_{3}\right\}_{2}\right)_{2}{ }^{[13]}$ as a sideproduct according to NMR (Figure S24 and S25). LIFDI-MS of the washing solution (cf. SI) indicates the formation of $\left[\left\{\mathrm{Cp}^{*} \mathrm{Fe}\right\}_{2}(\mathrm{Ass})\right]^{+}$, traces of I and $\left[\mathrm{As}_{2} \mathrm{Si}_{4} \mathrm{C}_{10} \mathrm{H}_{33}\right]^{+}$, which can be can be assigned to a fragmentation product of $\left(\mathrm{As}\left\{\mathrm{SiMe}_{3}\right\}_{2}\right)_{2}$. This is in alignment with previous assumption and the tendency for polyarsenic ligand complexes to exhibit aggregation. Since the obtained crystals of $3 \mathrm{a} / \mathbf{3 b}$ also contain starting material ( $[\mathrm{M}] \mathrm{As}\left(\mathrm{SiMe}_{3}\right)_{2} ; \mathrm{M}=\mathrm{Li}(3 a), \mathrm{K}(3 b)$ ), we used 0.5 equivalents to see if a full conversion of $I$ can be achieved. Indeed, this led to the quantitative formation of complex 3a/3b in 50 / 42 \% yield, respectively. A better yield of $65 \%$ of $\mathbf{3} \mathbf{b}$ can be achieved when using 0.5 equivalents of KAsCO as a nucleophile. Thereby, the formation of grey arsenic (Asgr) can be observed as a side product. One must note that crystals of $3 \mathbf{a}$ are hardly soluble and crystals of $\mathbf{3 b}$ are not soluble at all in THF-d8. Using MeCN-d 3 , leads to slow decomposition of 3 which can be detected by the arise of additional peaks in the ${ }^{1} \mathrm{H}$ NMR, which cannot be assigned (Figure S6). Therefore, complex 3b was not investigated in solution, but its constitution was proven by elemental analysis (cf. SI).


Figure 3. Molecular structure of the anion of $3 a / 3 b$ in the solid state. $\mathrm{Cp}^{*}$ ligands are drawn in a wire model. The Cation and H atoms are omitted for clarity.

It is interesting to see, that the arsenic nucleophile seems in both reaction pathways not to be involved in the product but instead activates complex I which leads then to aggregation and release of $\left(\mathrm{As}\left\{\mathrm{SiMe}_{3}\right\}_{3}\right)_{2}{ }^{[13]}$ or As gr, respectively. To verify this assumption, we reacted I with $\mathrm{LiP}\left(\mathrm{SiMe}_{3}\right)_{2} \cdot 1.8 \mathrm{THF} / \mathrm{NaOCP}$ and 2.2.2-cryptand, respectively. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}$ spectrum of the reaction mixture of the latter shows exclusively traces of the starting material NaOCP . The obtained crystals from the reaction of I with $\mathrm{LiP}\left(\mathrm{SiMe}_{3}\right)_{2} \cdot 1.8 \mathrm{THF}$ correspond to complex 3a and its ${ }^{31} P\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum shows no signals, indicating an activation of the As5 unit of I , followed by a rearrangement and aggregation.

Surprisingly, when reacting complex I with $\mathrm{KAsH}_{2}+2.2$.2-cryptand, we observe the formation of two different anionic polyarsenic ligand complexes. Analogs to previous reactions, compound $\mathbf{3 b}$ can be identified via XRD analysis, alongside with ([K(2.2.2-cryptand) $\left.]_{2}\left[\left(C p^{*} \mathrm{Fe}\right) 2\left\{\mu, \eta^{2}: \eta^{2}: \eta^{2}: \eta^{2}-\mathrm{As} 14\right\}\right]\right)$. Unfortunately, the crystals of ([K(2.2.2cryptand $\left.)]_{2}\left[\left(\mathrm{Cp}{ }^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{2}: \eta^{2}: \eta^{2}: \eta^{2}-\mathrm{As} 14\right\}\right]\right)$ are highly twinned and the crystal structure cannot be discussed in detail. However, the connectivity and composition are clear (Figure S22) and the same anion has already been reported by our group (see CCDC 1535410). ${ }^{[6]}$ Since the latter complex can be also obtained by reducing with KH of I , one can propose that $\mathrm{KAsH}_{2}$ reacts as a nucleophile as well as a reducing agent in combination with complex $\mathbf{I}$.

The question arose if the formation of $3 \mathbf{a} / \mathbf{3 b}$ is caused by reduction and consecutive aggregation. Thus, we used $\mathrm{K}\left[\mathrm{CpFe}(\mathrm{CO})_{2}\right]$ as a molecular and soluble reducing agent. The reaction of I with $\mathrm{K}\left[\mathrm{CpFe}(\mathrm{CO})_{2}\right]$ and 2.2.2-cryptand did not yield complex $\mathbf{3 b}$, however, yellow crystals of $[K(2 \cdot 2.2-c r y p t a n d)]_{2}\left[\left(C p^{*} \mathrm{Fe}\right) 2\left\{\mu-\eta^{4}: \eta^{4}-\mathrm{As} 10\right\}\right]$ (4) were obtained after crystallization from acetonitrile and toluene at $-30^{\circ} \mathrm{C}$ (Equation 1). As an alternative route, complex 4 can be obtained spectroscopically pure in $63 \%$ yield when changing the reducing agent to potassium graphite ( $\mathrm{KC}_{8}$ ) (Equation 1). Contrary to previous observations in the reduction chemistry of I, ${ }^{[6]}$ the combination of $K C_{8}$ and 2.2.2-cryptand leads to a highly selective reduction of $I$.


Equation 1. Reaction of I with $\mathrm{K}\left[\mathrm{CpFe}(\mathrm{CO})_{2}\right]$ or $\mathrm{KC}_{8}+2 \cdot 2 \cdot 2$-cryptand starting at $-80^{\circ} \mathrm{C}$ to r.t. (Yields are given in parenthesis)

The anion of 4 was already published by our group, but alongside different side products which cannot be separated. ${ }^{[6]}$ Therefore, this route represents a selective synthesis of analytical pure
complex 4. It has to be noted that an excess of $\mathrm{KC}_{8}$ does not lead to the formation of, the phosphorus analog, ${ }^{[9]}$ dianion $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As} 5\right)\right]^{2-}$.

### 8.4 Conclusion

In conclusion, we presented a selective way to functionalize the polyarsenic ligand in I with organo nucleophiles, like Me (1a) and Bnz (1c), yielding unprecedented As5R moieties and extending the $\mathrm{As}_{5}$ unit in a controlled way by using $\mathrm{KAsPh}_{2}$ (2) (Scheme 2). Furthermore, it was possible to link two arsenic ligand complexes with a ferrocenyl unit (1c), featuring interesting electrochemical properties. Surprisingly, the reaction of I with arsenic nucleophiles, bearing labile substituents like TMS or CO groups, triggers aggregation of complex I and leads to the formation of the largest anionic molecular $\mathrm{As}_{n}$ ligand complexes (3a, 3b). Furthermore, a selective reduction of $I$ is possible when using $\mathrm{KC}_{8}$ and 2.2.2-cryptand. Under proper reaction conditions, complex I is a suitable starting material for the synthesis of polyarsenic complexes, which have had a shadowy existence so far due to their difficult handling and accessibility.

## Conflicts of interest

There are no conflicts to declare.

## Author Contributions

Conceptualization: SR, MS
Investigation: SR, CR, MS
Visualization: SR, MS
Funding acquisition: MS
Project administration: MS
Supervision: MS
Writing - original draft: SR, MS
Writing - review \& editing: SR, MS

## Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft within the project Sche 384/38-1. S.R and C.R are grateful to the Studienstiftung des Deutschen Volkes for PhD fellowships.

### 8.5 References

[1] M. Seidl, G. Balázs, M. Scheer, Chem. Rev. 2019, 119, 8406-8434.
[2] O. J. Scherer, C. Blath, G. Wolmershäuser, J. Organomet. Chem. 1990, 387, 21-24.
[3] H. Krauss, G. Balazs, M. Bodensteiner, M. Scheer, Chem. Sci. 2010, 1, 337-342.
[4] E. Mädl, M. V. Butovskii, G. Balázs, E. V. Peresypkina, A. V. Virovets, M. Seidl, M. Scheer, Angew. Chem. Int. Ed. Engl. 2014, 53, 7643-6.
[5] S. Reichl, E. Mädl, F. Riedlberger, M. Piesch, G. Balázs, M. Seidl, M. Scheer, Nat. Commun. 2021, 12, 5774.
[6] M. Schmidt, D. Konieczny, E. V. Peresypkina, A. V. Virovets, G. Balázs, M. Bodensteiner, F. Riedlberger, H. Krauss, M. Scheer, Angew. Chemie Int. Ed. 2017, 56, 7307-7311.
[7] M. Dietz, M. Arrowsmith, S. Reichl, L. I. Lugo-Fuentes, J. O. C. Jiménez-Halla,M. Scheer, H. Braunschweig, Angew. Chem. Int. Ed. 2022, DOI 10.1002/anie. 202206840.
[8] C. Schoo, S. Bestgen, M. Schmidt, S. N. Konchenko, M. Scheer, P. W. Roesky, Chem. Commun. 2016, 52, 13217-13220.
[9] M. V. Butovskiy, G. Balázs, M. Bodensteiner, E. V. Peresypkina, A. V. Virovets, J. Sutter, M. Scheer, Angew. Chem. Int. Ed. 2013, 52, 2972-2976.
[10] P. Pyykkö, M. Atsumi, Chem. - A Eur. J. 2009, 15, 186-197.
[11] P. Pyykkö, M. Atsumi, Chem. - A Eur. J. 2009, 15, 12770-12779.
[12] R. L. Wells, M. F. Self, J. D. Johansen, J. A. Laske, S. R. Aubuchon, L. J. Jones, A. H. Cowley, S. Kamepalli, Inorg. Synth. 1997, 31, 150-158.
[13] G. Becker, G. Gutekunst, H. J. Wessely, ZAAC 1980, 462, 113-129.
[14] N. Reinfandt, N. Michenfelder, C. Schoo, R. Yadav, S. Reichl, S. N. Konchenko, A. N. Unterreiner, M. Scheer, P. W. Roesky, Chem. - A Eur. J. 2021, 27, 7862-7871.

### 8.6 Supplementary Information

# Synthesis of the Largest Anionic Molecular Arsenic Ligand Complex 

Stephan Reichl, ${ }^{1}$ Christoph Riesinger, ${ }^{1}$ Manfred Scheer ${ }^{1 *}$<br>${ }^{1}$ Institute of Inorganic Chemistry, University of Regensburg; Universitätsstraße 31, 93053 Regensburg, Germany. *Corresponding author. Email: manfred.scheer@chemie.uni-regensburg.de

## Table of Content

1. Experimental details 301
2. NMR spectroscopic characterization 305
3. Crystallographic details 310
4. Additional Information 320
5. Computational details 32
6. References 322

## 1. Experimental details

## General methods:

All manipulations were carried out under an inert atmosphere of dried argon using standard Schlenk and glove box techniques. 1,2-dimethoxyethane (DME) was dried and deoxygenated by distillation under argon atmosphere from sodium. All other solvents were dried using a MB SPS-800 device of the company MBRAUN and stored over molecular sieve. NMR spectra were recorded on a Bruker Avance III $400 / 600 \mathrm{MHz}$ NMR spectrometer. Chemical shifts were measured at ambient temperature and are given in ppm; they are referenced to TMS for ${ }^{1} \mathrm{H}$ and $85 \%$ $\mathrm{H}_{3} \mathrm{PO}_{4}$ for ${ }^{31} \mathrm{P}$ as external standard. Signal multiplicities are described using common abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet) and br (broad). LIFDI-/FD-/EI-MS spectra (LIFDI = liquid injection field desorption ionization, FD = field desorption, EI = electron ionization) were measured on a JEOL AccuTOF GCX. ESI-MS spectra (ESI = Electrospray ionization) were measured on an Agilent Q-TOF 6540 UHD. Elemental analysis (CHN) was determined using a Vario micro cube instrument. A glass stirring bar was used in reactions with potassium benzyl. CV / SQV measurements were conducted via the following setup: glass carbon-, Pt- and Ag electrodes; 0.01 mmol analyte, $500 \mathrm{mg}\left[\mathrm{NBu}_{4}\right]\left[\mathrm{PF}_{6}\right]$ as conductive salt, 5 mL solvent (THF), ferrocene for reference.

The compounds $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{As} s_{5}\right)\right]$ ( I , ${ }^{[i]}$ potassium benzyl, ${ }^{[i]}$ and $\left[\mathrm{Li}_{2}(\mathrm{TMEDA})\right]\left[\mathrm{Cp}_{2} \mathrm{Fe}\right]$ (TMEDA =
 $\mathrm{KAsCO}{ }^{[\text {viii] }}$ and $\left[\mathrm{KCpFe}(\mathrm{CO})_{2}\right]^{[i x]}$ were synthesized according to literature procedures. Unless otherwise noted, all other materials were obtained from commercial suppliers and used without purification.

DFT calculations were carried out using the Gaussian 16 program ${ }^{[x]}$. The geometries were optimised using the B3LYP ${ }^{[x i-x i v]}$ functional together with the def2-TZVP basis set ${ }^{[x v]}$. Solvation effects were incorporated via the polarizable continuum model ${ }^{[x v i]}$ using the dielectric constant of THF.

Crystals suitable for single crystal X-ray diffraction analysis were obtained as described below. The diffraction data were collected either on a Gemini Ultra diffractometer equipped with an Atlas ${ }^{52}$ CCD detector and with a fine-focus sealed Cu-K X-ray tube, on a XtaLAB Synergy R, DW system diffractometer equipped with a HyPix-Arc 150 detector and a rotating-anode Cu- $\mathrm{K}_{\mathrm{a}} \mathrm{X}$-ray tube or a GV50 diffractometer equipped with a Titan ${ }^{52}$ CCD detector and a micro-focus $\mathrm{Cu}-\mathrm{K}_{\alpha} \mathrm{X}$-ray tube. Data collection and reduction were performed with CrysAlisPro software package. The structures were solved with Olex2, ${ }^{[\text {[xvii] }}$ using ShelXT ${ }^{[x v i i i]}$ and a least-square refinement on $F^{2}$ was carried out with ShelXLL. ${ }^{[i x]}$ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms at the carbon atoms were located in idealized positions and refined with isotropic displacement parameters according to the riding model. The images of the molecular structures were made using Olex2. [xvii] All NMR simulations were conducted with the WinDaisy application within the NMR software Top Spin 4.1.1 by Bruker.

## Synthetic protocols:

## Synthesis of [Li(2.2.2-cryptand)][Cp*Fe( $\left.\left.\eta^{4}-\mathrm{As}_{5} \mathrm{Me}\right)\right]$ (1a):

Compound I ( $0.15 \mathrm{mmol}, 84.9 \mathrm{mg}, 1 \mathrm{eq}$ ) and [2.2.2]-cryptand ( $0.15 \mathrm{mmol}, 56.5 \mathrm{mg}, 1 \mathrm{eq}$ ) are dissolved separately in 10 mL THF and cooled to $-80^{\circ} \mathrm{C}$. A 1.0312 molar solution of $\mathrm{MeLi}(0.15 \mathrm{mmol}, 0.15 \mathrm{~mL}, 1 \mathrm{eq})$ in $\mathrm{Et}_{2} \mathrm{O}$ is added to compound I dropwise. The dark green color of the solution intensifies and darkens. [2.2.2]-cryptand is added afterwards. The mixture is allowed to stir overnight and reach room temperature. The solvent is removed under reduced pressure. The green residue is washed with $3 \times 10 \mathrm{~mL}$-hexane, dissolved in 4 mL DME and layered with

4 mL n-hexane. The mixture is stored at room temperature. Compound 1a is isolated after one week in form of dark green blocks.
Yield: $116 \mathrm{mg}(0.12 \mathrm{mmol}, 80 \%) .{ }^{1} \mathrm{H}$ NMR (THF-d8, 300 K ): $\delta[\mathrm{ppm}]=3.75(\mathrm{~s}, 12 \mathrm{H},[2.2 .2]-\mathrm{cryptand}), 3.68\left(\mathrm{t},{ }^{3} \mathrm{~J}_{\mathrm{H}-\mathrm{H}}\right.$ $=5.0,12 \mathrm{H},[2.2 .2]$-cryptand), 2.76 ( $\mathrm{s}^{3}{ }^{3} \mathrm{H}_{\mathrm{H}-\mathrm{H}}=5.0,12 \mathrm{H},[2.2 .2]$-cryptand), 2.11 (s, $0.6 \mathrm{H},-\mathrm{CH}_{3}$, exo methyl group), 1.59 (s, $3 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}$, exo methyl group species), 1.54 ( $\mathrm{s}, 11 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}$, endo methyl group species), 0.33 (s, $2 \mathrm{H},-\mathrm{CH}_{3}$, endo methyl group). ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ (THF-d ${ }_{8}, 300 \mathrm{~K}$ ): 87.6 ( $\underline{\mathrm{C}}_{5} \mathrm{Me}_{5}$, exo methyl group species), 86.4 ( $\underline{\mathrm{C}}_{5} \mathrm{Me} \mathrm{Me}_{5}$, endo methyl group species), 70.2 (s, br, [2.2.2]-cryptand), 55.4 (s, br, [2.2.2]-cryptand), 25.2 (s, $-\mathrm{CH}_{3}$, endo methyl group), 13.6 ( $\mathrm{C}_{5} \mathrm{Me}_{5}$, endo methyl group species), 13.2 ( $\mathrm{C}_{5} \mathrm{Me}_{5}$, exo methyl group species), 9.6 ( $\mathrm{s},-\mathrm{CH}_{3}$, exo methyl group). ESI-MS (anion, DME): no corresponding signal detectable. Elemental analysis (calcd., found for $\mathrm{C}_{29} \mathrm{H}_{54} \mathrm{FeLiO}_{6} \mathrm{As}_{5} \mathrm{~N}_{2}$ ): C (36.13, 36.14), H (5.65, 5.75), N (2.91, 2.95).

## Synthesis of $[K(2.2 .2-c r y p t a n d)]\left[C p{ }^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{As}_{5}\left(\mathrm{CH}_{2} \mathrm{Ph}\right)\right\}\right]$ (1b):

A $-80^{\circ} \mathrm{C}$ cold solution of benzyl potassium ( $0.15 \mathrm{mmol}, 19.5 \mathrm{mg}, 1 \mathrm{eq}$ ) in THF is added to a $-80^{\circ} \mathrm{C}$ cold solution of compound I ( $0.15 \mathrm{mmol}, 84.9 \mathrm{mg}, 1 \mathrm{eq}$ ) in 5 mL THF. To the resulting dark green solution, a $-80^{\circ} \mathrm{C}$ cold solution of [2.2.2]-cryptand ( $0.15 \mathrm{mmol}, 56.5 \mathrm{mg}, 1 \mathrm{eq}$ ) in THF is added. The solution is stirred overnight and reach room temperature. The solvent is removed in vaccu and the dark green residue washed with $2 \times 10 \mathrm{~mL} n$-hexane. The residue is dissolved in 2 mL THF, layered with $4 \mathrm{~mL} n$-hexane and stored at room temperature. $[\mathrm{K}(2.2 .2-$ cryptand) $]\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{As}_{5}\left(\mathrm{CH}_{2} \mathrm{Ph}\right)\right\}\right](2 b)$ is isolated as dark green blocks.
Yield: 121 mg ( $0.11 \mathrm{mmol}, 75 \%$ ). ${ }^{1} \mathrm{H}$ NMR (THF-d, 300 K ): $\delta[\mathrm{ppm}]=6.89\left(\mathrm{~m}, 5 \mathrm{H},-\mathrm{CH}_{2}-\mathrm{Ph}\right), 3.61(\mathrm{~s}, 15 \mathrm{H},[2.2 .2]-$ cryptand), ${ }^{*} 3.57$ (s, $20 \mathrm{H},[2.2 .2]$-cryptand), 2.58 (s, $12 \mathrm{H},[2.2 .2]$-cryptand), 1.82 (s, $2 \mathrm{H},-\mathrm{CH}_{2}-\mathrm{Ph}$ ), 1.55 (s, 15 H , $\left.\mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}\left(\mathrm{THF}-\mathrm{d}_{8}, 300 \mathrm{~K}\right): 127.3\left(\mathrm{~s},-\mathrm{CH}_{2}-\mathrm{Ph}\right), 126.7\left(\mathrm{~s},-\mathrm{CH}_{2}-\mathrm{Ph}\right), 122.7\left(\mathrm{~s},-\mathrm{CH}_{2}-\mathrm{Ph}\right), 84.5\left(\underline{\mathrm{C}_{5}} \mathrm{Me}_{5}\right), 70.3(\mathrm{~s}$, $-\mathrm{CH}_{2}-\mathrm{Ph}$ ), 67.6 (s, [2.2.2]-cryptand), 53.9 (s, [2.2.2]-cryptand), 47.9 (s, [2.2.2]-cryptand), 11.8 ( $\mathrm{C}_{5} \mathrm{Me}_{5}$ ). ESI-MS (anion, DME): $m / z=656.72\left(100 \%,[M]^{-}\right)$. Elemental analysis (calcd., found for $\mathrm{C}_{35} \mathrm{H}_{58} \mathrm{FeKO}_{6} \mathrm{As}_{5} \mathrm{~N}_{2}$ ): $\mathrm{C}(39.20,38.66), \mathrm{H}$ (5.45, 5.56), N (2.61, 2.44).
*: wrong integrals due to overlap of [2.2.2]-cryptand and solvent signals.

## Synthesis of $[\mathrm{Li}(2.2 .2-\mathrm{cryptand})]_{2}\left[\left\{\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As}\right)\right)_{2}\left\{1,1-\left((\mathrm{Cp})_{2} \mathrm{Fe}\right)\right\}\right]$ (1c):

A $-80^{\circ} \mathrm{C}$ cold solution of $1,1^{\prime}$-dilithioferrocene-TMEDA ([Li ${ }_{2}($ TMEDA $\left.\left.)\right]\left[\mathrm{Cp}_{2} \mathrm{Fe}\right]\right)(0.075 \mathrm{mmol}, 24 \mathrm{mg}, 1 \mathrm{eq})$ in THF is added to a $-80^{\circ} \mathrm{C}$ cold solution of compound $\mathrm{I}(0.15 \mathrm{mmol}, 84.9 \mathrm{mg}, 2 \mathrm{eq})$ in 5 mL THF. To the resulting dark solution, a $-80^{\circ} \mathrm{C}$ cold solution of [2.2.2]-cryptand ( $0.15 \mathrm{mmol}, 56.5 \mathrm{mg}, 1 \mathrm{eq}$ ) in THF is added. The solution is stirred overnight and reach room temperature. The solvent was removed in vaccu and the brown-yellowish residue washed with $3 \times 10 \mathrm{~mL}$ n-hexane. The residue is dissolved in 4 mL THF, layered with $4 \mathrm{~mL} n$-hexane and stored at room temperature. $\left.[\mathrm{Li}(2.2 .2-\mathrm{cryptand})]_{2}\left[\left\{\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As} 5\right)\right\}_{2}\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{4}\right)_{2} \mathrm{Fe}\right)\right](1 \mathrm{c})$ is isolated as brown blocks after one day.
Yield: $110.0 \mathrm{mg}(0.053 \mathrm{mmol}, 71 \%) .{ }^{1} \mathrm{H}$ NMR (THF-d $\left.\mathrm{d}_{8}, 300 \mathrm{~K}\right): \delta[\mathrm{ppm}]=4.18\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.38\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right)$, $1.72\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right) .{ }^{* 13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}\left(\mathrm{THF}-\mathrm{d}_{8}, 300 \mathrm{~K}\right): \delta[\mathrm{ppm}]=84.3\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right), 70.4\left(\mathrm{C}_{5} \mathrm{H}_{4}\right), 68.6\left(\mathrm{C}_{5} \mathrm{H}_{4}\right), 11.8\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right) .{ }^{*}$ *Due to bad solubility (and decomposition in MeCN- $\mathrm{d}_{3}$ ), the NMR spectra were recorded from a reaction of I and 1,1'-dilithioferrocene-TMEDA in THF without cryptand. However, ${ }^{1} \mathrm{H}$ exhibits sideproducts (see Figure S3) and no clean reaction without cryptand. ESI-MS (anion, DME): $m / z=1316.33\left(12 \%,[M H]^{-}\right), 824.58\left(63 \%,\left[\mathrm{As}_{6} \mathrm{H}_{23} \mathrm{C}_{20} \mathrm{Fe}_{2}\right]^{-}\right)$. Elemental analysis (calcd., found for $\left.\mathrm{C}_{66} \mathrm{H}_{110} \mathrm{Fe}_{3} \mathrm{Li}_{2} \mathrm{O}_{12} \mathrm{As}_{10} \mathrm{~N}_{4}\right)$ : $\mathrm{C}(38.07,37.75), \mathrm{H}(5.32,5.44), \mathrm{N}(2.69,2.61)$. Synthesis of $[\mathrm{K}(2.2 .2-c r y p t a n d)]\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As}_{6} \mathrm{Ph}_{2}\right)\right]$ (2):
Compound I ( $0.15 \mathrm{mmol}, 84.9 \mathrm{mg}, 1 \mathrm{eq}$ ), $\mathrm{KAsPh}_{2} \cdot 1.4 \mathrm{C}_{4} \mathrm{H}_{8} \mathrm{O}_{2}(0.15 \mathrm{mmol}, 59 \mathrm{mg}, 1 \mathrm{eq})$ and [2.2.2]-cryptand ( $0.15 \mathrm{mmol}, 56 \mathrm{mg}, 1 \mathrm{eq}$ ) are dissolved in 5 mL THF and cooled to $-80^{\circ} \mathrm{C}$, respectively. $\mathrm{KAsPh}_{2}$ and [2.2.2]-cryptand are added to compound I one after each other. The solution is stirred overnight and allowed to reach room temperature. Thereby, the color changed from green to dark red. The solvent is removed under reduced pressure, the residue washed with $2 \times 10 \mathrm{~mL} n$-hexane and dissolved again in THF. The dark red solution is layered with
$n$-hexane and stored at room temperature. $[\mathrm{K}(2.2 .2-\mathrm{cryptand})]\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As}_{6} \mathrm{Ph}_{2}\right)\right](6)$ can be obtained as dark reddish blocks after five days.
Yield: $145 \mathrm{mg}\left(0.12 \mathrm{mmol}, 80 \%\right.$ ). ${ }^{1} \mathrm{H}$ NMR (THF- $\left.\mathrm{d}_{8}, 300 \mathrm{~K}\right): \delta[\mathrm{ppm}]=7.66\left(\mathrm{~m}, 4 \mathrm{H},-\mathrm{As}^{2}-\mathrm{Ph}_{2}\right), 7.66\left(\mathrm{~m}, 6 \mathrm{H},-\mathrm{As}-\mathrm{Ph}_{2}\right)$, 3.63 (s, $17 \mathrm{H},[2.2 .2]$-cryptand), ${ }^{*} 3.58$ (s, 17 H, [2.2.2]-cryptand), ${ }^{*} 2.60$ (s, 12 H, [2.2.2]-cryptand), 1.62 (s, 15 H , $\left.\mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}\left(\mathrm{THF}-\mathrm{d}_{8}, 300 \mathrm{~K}\right): \delta[\mathrm{ppm}]=147.0\left(\mathrm{~s},-\mathrm{As}-\mathrm{Ph}_{2}\right), 133.6\left(\mathrm{~s},-\mathrm{As}-\mathrm{Ph}_{2}\right), 127.3\left(\mathrm{~s},-\mathrm{As}-\mathrm{Ph}_{2}\right), 126.0(\mathrm{~s},-\mathrm{As}-$ $\mathrm{Ph}_{2}$ ), 86.2 ( $\mathrm{C}_{5} \mathrm{Me}_{5}$ ), 70.4 ( s, [2.2.2]-cryptand), 67.6 (s, [2.2.2]-cryptand), 54.0 (s, [2.2.2]-cryptand), 11.2 ( $\mathrm{C}_{5} \mathrm{Me}_{5}$ ). ESIMS (anion, DME): no corresponding signal detectable. Elemental analysis (calcd., found for $\mathrm{C}_{44} \mathrm{H}_{69} \mathrm{As}_{6} \mathrm{FeKN}_{2} \mathrm{O}_{7}$ ): C (41.21, 41.17), H (5.42, 5.39), N (2.18, 2.25).
*: wrong integrals due to overlap of [2.2.2]-cryptand and solvent signals.

## Synthesis of $[\mathrm{Li}(2.2 .2-c r y p t a n d)]_{2}\left[\left(\mathrm{Cp}^{*} \mathrm{Fe}\right)_{4}\left\{\mu_{4}-\eta^{4}: \eta^{4}: \eta^{3}: \eta^{3}: \eta^{1}: \eta^{1}-\mathrm{As}_{20}\right\}\right]$ (3a):

Compound I ( $0.2 \mathrm{mmol}, 113.1 \mathrm{mg}, 2 \mathrm{eq}$ ), LiAs $\left(\mathrm{SiMe}_{3}\right)_{2} \cdot \mathrm{THF}(0.1 \mathrm{mmol}, 37.6 \mathrm{mg}, 1 \mathrm{eq})$ and [2.2.2]-cryptand ( 0.1 mmol , $37.6 \mathrm{mg}, 1 \mathrm{eq}$ ) are dissolved in 5 mL THF and cooled to $-80^{\circ} \mathrm{C}$, respectively. LiAs $\left(\mathrm{SiMe}_{3}\right)_{2} \cdot$ THF and [2.2.2]-cryptand are added to compound I one after each other. The solution is stirred overnight and allowed to reach room temperature. Thereby, the color changed from green to brown. The solvent is removed in vacuo and the brown residue is washed with $3 \times 10 \mathrm{~mL} n$-hexane. The residue is dissolved in 3 mL THF, layered with 4 mL toluene and stored at room temperature. [Li(2.2.2-cryptand) $]_{2}\left[\left(C p^{*} F e\right)_{4}\left(\mu_{5}-\eta^{4}: \eta^{1}: \eta^{1}: \eta^{2}: \eta^{2}: \eta^{1}: \eta^{1}: \eta^{4}-\mathrm{As}_{20}\right]\right.$ (3a) can be isolated as green/brownish blocks after one week.
Yield: 75.4 mg ( $0.025 \mathrm{mmol}, 50 \%$ ). ${ }^{1} \mathrm{H}$ NMR (THF-d ${ }_{8}, 300 \mathrm{~K}$ ): $\delta$ [ppm] $=3.61$ (s, $80 \mathrm{H},[2.2 .2]$-cryptand), ${ }^{*} 3.55$ (s, $18 \mathrm{H},[2.2 .2]$-cryptand), 2.60 (s, $18 \mathrm{H},[2.2 .2]-c r y p t a n d),{ }^{*} 1.42\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ (THF-d $\left.8,300 \mathrm{~K}\right): \delta[p p m]$ $=89.1$ ( $\underline{C}_{5} \mathrm{Me}_{5}$ ), 72.7 (s, [2.2.2]-cryptand), 71.8 (s, [2.2.2]-cryptand), 58.6 (s, [2.2.2]-cryptand), 13.0 ( $\mathrm{C}_{5} \mathrm{Me}_{5}$ ). ESI-MS (anion, MeCN ): $m / z=1131.78$ ( $>1 \%,[\mathrm{M}]^{2-}$ ).
Elemental analysis (calcd., found for $\mathrm{C}_{76} \mathrm{H}_{132} \mathrm{As}_{20} \mathrm{Fe}_{4} \mathrm{Li}_{2} \mathrm{~N}_{4} \mathrm{O}_{12}$ ): $\mathrm{C}(30.13,30.62), \mathrm{H}(4.39,4.55), \mathrm{N}(1.85,2.04)$.

## Synthesis of $[K(2.2 .2-c r y p t a n d)]_{2}\left[\left(C p^{*} F e\right){ }_{4}\left\{\mu_{4}-\eta^{4}: \eta^{4}: \eta^{3}: \eta^{3}: \eta^{1}: \eta^{1}-A s_{20}\right\}\right]$ (3b):

Route A: Analogues to previous, compound I ( $0.15 \mathrm{mmol}, 84.9 \mathrm{mg}, 2 \mathrm{eq}$ ), $\mathrm{KAs}\left(\mathrm{SiMe}_{3}\right)_{2}(0.075 \mathrm{mmol}, 19.5 \mathrm{mg}, 1 \mathrm{eq})$ and [2.2.2]-cryptand ( $0.15 \mathrm{mmol}, 56.5 \mathrm{mg}, 1 \mathrm{eq}$ ) are dissolved in 5 mL THF and cooled to $-80^{\circ} \mathrm{C}$, respectively. $\mathrm{KAs}\left(\mathrm{SiMe}_{3}\right)_{2}$ and [2.2.2]-cryptand are added to compound I one after each other. An immediate color change from green to brown is observed. The solution is stirred overnight and allowed to reach room temperature. The solvent is removed in vacuo and the brown residue is washed with $3 \times 10 \mathrm{~mL} n$-hexane.* The residue is dissolved in 4 mL THF, layered with 4 mL toluene and stored at room temperature. $\left[\mathrm{K}(2.2 .2 \text {-cryptand })_{2}\left[\left(\mathrm{Cp}{ }^{*} \mathrm{Fe}\right)_{4}\left(\mu_{5}-\eta^{4}: \eta^{1}: \eta^{1}: \eta^{2}: \eta^{2}: \eta^{1}: \eta^{1}: \eta^{4}-\right.\right.\right.$ $\left.\mathrm{As}_{20}\right]$ (7) can be isolated as brown blocks after one week.
*The solvent of the washing solution was removed under reduced pressure. The greenish residue was investigated via ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ as well as LIDFI-MS, after dissolving in $\mathrm{C}_{6} \mathrm{D}_{6} /$ toluene, respectively. LIFDI-MS (toluene): $m / z=756.80\left(100 \%,\left[\left\{\mathrm{Cp}^{*} \mathrm{Fe}\right\}_{2}\left(\mathrm{As}_{5}\right)\right]^{+}\right), 415.26\left(17 \%,\left[\mathrm{As}_{2} \mathrm{Si}_{4} \mathrm{C}_{10} \mathrm{H}_{33}\right]^{+}\right), 565.73\left(3 \%,\left[I^{+}\right) .{ }^{1} \mathrm{H}\right.$ NMR and ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}\left(\mathrm{C}_{6} \mathrm{D}_{6}\right.$, 300 K) exhibit two $\mathrm{Cp}^{*}$-containing species (see Figure S24 and S25) which cannot be assignment with 100 \% reliability. However, signal at $\delta=3.5 \mathrm{ppm}$ in ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ can be assigned to $\left[\left(\mathrm{As}\left\{\mathrm{SiMe}_{3}\right\}_{3}\right)_{2}\right] .{ }^{[\mathrm{Kx}]}$

Data for 3b: Yield: 49.5 mg ( $0.016 \mathrm{mmol}, 42$ \%). ${ }^{1} \mathrm{H}$ NMR ( $\mathrm{MeCN}-\mathrm{d}_{3}, 300 \mathrm{~K}$ ): $\delta$ [ppm] = 3.57 ( $\mathrm{s}, 55 \mathrm{H},[2.2 .2]-$ cryptand), ${ }^{*} 3.53$ (m, $57 \mathrm{H},[2.2 .2]$-cryptand), ${ }^{*} 2.53(\mathrm{~m}, 57 \mathrm{H},[2.2 .2]-c r y p t a n d), 1.49\left(\mathrm{~s}, 30 \mathrm{H},-\mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 1.48$ (s, 15 H , $\left.-\mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right)$ ) \# $1.46\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right)_{\text {. }} .^{\# 13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}\left(\mathrm{MeCN}-\mathrm{d}_{3}, 300 \mathrm{~K}\right): \delta[\mathrm{ppm}]=82.4\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right), 70.3$ (s, [2.2.2]-cryptand), 67.5 (s, [2.2.2]-cryptand), 53.7 (s, [2.2.2]-cryptand), 10.5 ( $\mathrm{C}_{5} \mathrm{Me}_{5}$ ). ESI-MS (anion, MeCN): no corresponding signal detectable. Elemental analysis (calcd., found for $\mathrm{C}_{76} \mathrm{H}_{132} \mathrm{As}_{20} \mathrm{Fe}_{4} \mathrm{~K}_{2} \mathrm{~N}_{4} \mathrm{O}_{12} \cdot$ toluene and THF): C (32.07, 32.55), H (4.58, 4.74), N (1.72, 2.38).
*: wrong integrals due unknown reasons
\#: slowly decomposition in MeCN- $\mathrm{d}_{3}$ (see Figure S6); 3b not soluble in THF- $\mathrm{d}_{8}$, therefore no NMR data can be given in contrast to 3a.

Route B: Analogues to previous, compound I ( $0.2 \mathrm{mmol}, 113.1 \mathrm{mg}, 2 \mathrm{eq}$ ), KAsCO ( $0.1 \mathrm{mmol}, 14.2 \mathrm{mg}, 1 \mathrm{eq}$ ) and [2.2.2]-cryptand ( $0.1 \mathrm{mmol}, 37.6 \mathrm{mg}, 1 \mathrm{eq}$ ) are dissolved in 5 mL THF and cooled to $-80^{\circ} \mathrm{C}$, respectively. KAsCO and [2.2.2]-cryptand are added to compound I one after each other. An immediate color change from green to brown is observed. The solution is stirred overnight and allowed to reach room temperature. The solvent is removed in vacuo and the brown residue is washed with $3 \times 10 \mathrm{~mL} n$-hexane. The residue is dissolved in 4 mL THF , layered with 10 mL toluene and stored at room temperature. [K(2.2.2-cryptand) $]_{2}\left[\left(C p^{*} \mathrm{Fe}\right)_{4}\left\{\mu_{4}-\eta^{4}: \eta^{4}: \eta^{3}: \eta^{3}: \eta^{1}: \eta^{1}-\mathrm{As} 20\right\}\right]$ (3b) can be isolated as brown blocks after one week.

Yield: 102.1 mg ( $0.033 \mathrm{mmol}, 65$ \%). NMR spectra: See above.
Since the anion of $\mathbf{3 b}$ cannot be detected via route $A$, no mass spectrometry was performed of the crystals, obtained from route B . Elemental analysis (calcd., found for $\mathrm{C}_{76} \mathrm{H}_{132} \mathrm{As}_{20} \mathrm{Fe}_{4} \mathrm{~K}_{2} \mathrm{~N}_{4} \mathrm{O}_{12} \cdot 0.5$ toluene): $\mathrm{C}(30.41,30.51), \mathrm{H}(4.37$, $4.53), \mathrm{N}(1.78,1.98)$.

## Synthesis of $[K(2.2 .2-c r y p t a n d)]_{2}\left[\left(C p^{*} \mathrm{Fe}\right)_{2}\left\{\mu-\eta^{4}: \eta^{4}-\mathrm{As}_{10}\right\}\right]$ (4):

Route A: Compound I ( $0.15 \mathrm{mmol}, 84.9 \mathrm{mg}, 1 \mathrm{eq}$ ), $\mathrm{KC}_{8}(0.225 \mathrm{mmol}, 30.4 \mathrm{mg} 1.5 \mathrm{eq}$ ) and [2.2.2]-cryptand ( 0.15 mmol , $56.5 \mathrm{mg}, 1 \mathrm{eq}$ ) are dissolved in 5 mL THF and cooled to $-80^{\circ} \mathrm{C}$, respectively. $\mathrm{KC}_{8}$ and [2.2.2]-cryptand are added to compound I one after each other. Thereby, the color changed immediately from green to dark yellow/red. The solution is stirred overnight and allowed to reach room temperature. The solvent is removed under reduced pressure, the residue washed with $2 \times 10 \mathrm{~mL} n$-hexane and dissolved again in acetonitrile. The dark red solution is underlayered with toluene and stored at $-30^{\circ} \mathrm{C}$. Crystals of $[K(2 \cdot 2 \cdot 2-c r y p t a n d)]_{2}\left[\left(C p^{*} \mathrm{Fe}\right)_{2}\left\{\mu-\eta^{4}: \eta^{4}-\mathrm{As} s_{10}\right\}\right]$ (4) can be obtained as dark yellow plates after three days.
Yield: 92.2 mg ( $0.047 \mathrm{mmol}, 63$ \%). ${ }^{1} \mathrm{H}$ NMR ( $\mathrm{MeCN}-\mathrm{d}_{3}, 300 \mathrm{~K}$ ): $\delta$ [ppm] = 3.57 (s, $24 \mathrm{H},[2.2 .2]$-cryptand), 3.53 (s, 24 $\mathrm{H},[2.2 .2]$-cryptand), $2.53\left(\mathrm{~s}, 24 \mathrm{H},[2.2 .2]\right.$-cryptand), $1.40\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}\left(\mathrm{MeCN}-\mathrm{d}_{3}, 300 \mathrm{~K}\right): \delta[\mathrm{ppm}]=$ 86.9 ( $\mathrm{C}_{5} \mathrm{Me}_{5}$ ), 70.8 (s, [2.2.2]-cryptand), 68.0 (s, [2.2.2]-cryptand), 54.3 (s, [2.2.2]-cryptand), 11.4 ( $\mathrm{C}_{5} \mathrm{Me}_{5}$ ). ESI-MS (anion, DME): no corresponding signal detectable. Elemental analysis (calcd., found for $\mathrm{C}_{56} \mathrm{H}_{102} \mathrm{Fe}_{2} \mathrm{~K}_{2} \mathrm{O}_{12} \mathrm{As}_{10} \mathrm{~N}_{4}$ ): C (34.27, 34.88), H (5.24, 5.02), N (2.85, 2.67).

Route B: same procedure as described in route A ; using $\mathrm{K}\left[\mathrm{CpFe}(\mathrm{CO})_{2}\right](0.15 \mathrm{mmol}, 32.4 \mathrm{mg}, 1 \mathrm{eq})$ instead of $\mathrm{KC}_{8}$. According to XRD, compound 4 formed, no signs of 3 b .

## 2. NMR spectroscopic characterization

## ${ }^{1} \mathrm{H}$ NMR Spectra:

## [Li(2.2.2-cryptand) $]\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As}{ }_{5} \mathrm{Me}\right)\right]$ (1a)



Fig. S1. Experimental ${ }^{1} \mathrm{H}$ NMR ( 400.13 MHz, THF- $\mathrm{d}_{8}$ ) spectrum of 1 a .
$[\mathrm{K}(2.2 .2$-cryptand $)]\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{As}_{5}\left(\mathrm{CH}_{2} \mathrm{Ph}\right)\right\}\right]$ (1b)


Fig. S2. Experimental ${ }^{1} \mathrm{H}$ NMR ( 400.13 MHz , THF- $\mathrm{d}_{8}$ ) spectrum of $\mathbf{1 b}$ ( ${ }^{*}=$ wrong integrals due overlap of solvent and cryptand signals).
$\left[\mathrm{Li}(\text { thf })_{4}\right]_{2}\left[\left\{\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As} 5\right)\right\}_{2}\left\{1,1-\left((\mathrm{Cp})_{2} \mathrm{Fe}\right)\right\}\right]\left(1 \mathrm{c}^{\prime}\right)$


Fig. S3. Experimental ${ }^{1} \mathrm{H}$ NMR ( 400.13 MHz , THF- $\mathrm{d}_{8}$ ) spectrum of I with $1,1^{\prime}$-dilithioferrocene•TMEDA and without cryptand ( ${ }^{*}=$ THF, \# = unidentified sideproducts - cf. above).

## $\left[K(2.2 .2\right.$-cryptand) $]\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As}_{6} \mathrm{Ph}_{2}\right)\right]$ (2)



Fig. S4. Experimental ${ }^{1} \mathrm{H}$ NMR ( 400.13 MHz , THF-d8) spectrum of 2 (\# = wrong integrals due overlap of solvent and cryptand signals; * $=$ THF).
$[\text { Li(2.2.2-cryptand) }]_{2}\left[\left(\mathrm{Cp}^{*} \mathrm{Fe}\right)_{4}\left\{\mu_{4}-\eta^{4}: \eta^{4}: \eta^{3}: \eta^{3}: \eta^{1}: \eta^{1}-\mathrm{As} 20\right\}\right]$ (3a)


Fig. S5. Experimental ${ }^{1} \mathrm{H}$ NMR ( 400.13 MHz, THF- $\mathrm{d}_{8}$ ) spectrum of 3a.
$[K(2.2 .2-\text { cryptand })]_{2}\left[\left(C p^{*} F e\right) 4\left\{\mu_{4}-\eta^{4}: \eta^{4}: \eta^{3}: \eta^{3}: \eta^{1}: \eta^{1-A} s_{20}\right\}\right]$ (3b)
Obtained from route a - cf. above:


Fig. S6. Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{MeCN}-\mathrm{d}_{3}$ ) spectrum of 3 b (\# = decomposition products due to $\mathrm{MeCN}-\mathrm{d}_{3} ;{ }^{*}=$ toluene).

## $[K(2.2 .2-c r y p t a n d)]_{2}\left[\left(C p^{*} \mathrm{Fe}\right)_{2}\left\{\mu-\eta^{4}: \eta^{4}-\mathrm{As}_{10}\right\}\right]$ (4)



Fig. S7. Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{MeCN}-\mathrm{d}_{3}$ ) spectrum of 4 ( ${ }^{*}=$ toluene).

## ${ }^{13}$ C NMR Spectra:

[Li(2.2.2-cryptand) $]\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As}_{5} \mathrm{Me}\right)\right]$ (1a)


Fig. S8. Experimental ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 100.62 MHz , THF- $\mathrm{d}_{8}$ ) spectrum of 1a. $[K(2.2 .2-c r y p t a n d)]\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{As}_{5}\left(\mathrm{CH}_{2} \mathrm{Ph}\right)\right\}\right]$ (1b)


Fig. S9. Experimental ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 100.62 MHz, THF- $\mathrm{d}_{8}$ ) spectrum of $\mathbf{1 b}$.
$\left[\mathrm{Li}(\mathrm{thf})_{4}\right]_{2}\left[\left\{\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As} 5\right)\right\}_{2}\left\{1,1-\left((\mathrm{Cp})_{2} \mathrm{Fe}\right)\right\}\right]\left(1 \mathrm{c}^{\prime}\right)$


Fig. S10. Experimental $\left.{ }^{13} \mathrm{C}^{1}{ }^{1} \mathrm{H}\right\}$ NMR ( 100.62 MHz, THF- $\mathrm{d}_{8}$ ) spectrum of I with 1,1 '-dilithioferrocene•TMEDA and without cryptand - cf. above.
$\left[K(2.2 .2\right.$-cryptand) $]\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As}_{6} \mathrm{Ph}_{2}\right)\right]$ (2)


Fig. S11. Experimental ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 100.62 MHz, THF- $\mathrm{d}_{8}$ ) spectrum of 2.
$[L i(2.2 .2-c r y p t a n d)]_{2}\left[\left(\mathrm{Cp}^{*} \mathrm{Fe}\right)_{4}\left\{\mu_{4}-\eta^{4}: \eta^{4}: \eta^{3}: \eta^{3}: \eta^{1}: \eta^{1}-\mathrm{As} 20\right\}\right]$ (3a)


Fig. S12. Experimental ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 100.62 MHz , THF- $\mathrm{d}_{8}$ ) spectrum of 3a.

## $[K(2.2 .2 \text {-cryptand })]_{2}\left[\left(\mathrm{Cp}^{*} \mathrm{Fe}\right)_{4}\left\{\mu_{4}-\eta^{4}: \eta^{4}: \eta^{3}: \eta^{3}: \eta^{1}: \eta^{1}-\mathrm{As} 20\right\}\right]$ (3b)

Obtained from route a - cf. above:


Fig. S13. Experimental ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $100.62 \mathrm{MHz}, \mathrm{MeCN}-\mathrm{d}_{3}$ ) spectrum of $\mathbf{3 b}$ ( ${ }^{*}=$ toluene).
$[K(2.2 .2-c r y p t a n d)]_{2}\left[\left(C p^{*} \mathrm{Fe}\right)_{2}\left\{\mu-\eta^{4}: \eta^{4}-\mathrm{As}_{10}\right\}\right]$ (4)


Fig. S14. Experimental ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(100.62 \mathrm{MHz}, \mathrm{MeCN}-\mathrm{d}_{3}\right)$ spectrum of 4 (* = toluene).

## 3. Crystallographic details

[Li(2.2.2-cryptand)][Cp*Fe( $\left.\left.\eta^{4}-\mathrm{As}_{5} \mathrm{Me}\right)\right]$ (1a): The asymmetric unit contains one molecule of 1a. The anion of 1a cocrystallizes with another compound in the ratio (86:14). The second compound features a methyl group which is in exo-Position (with respect to the envelope of the $\mathrm{As}_{5}$ unit). The SADI and SIMU restraints were applied to model this disorder. The structure in the solid state is given in Figure S15. Crystallographic and refinement data are summarized in Table S1.
$[K(2.2 .2-c r y p t a n d)]\left[C p^{*} \operatorname{Fe}\left\{\eta^{4}-\mathrm{As}_{5}\left(\mathrm{CH}_{2} \mathrm{Ph}\right)\right\}\right]$ (1b): The asymmetric unit contains one molecule of 1 b . The $\mathrm{As}_{5}$ units of the anion of $\mathbf{1 b}$ are disordered over two positions with a distribution of 53 to 47 . The SIMU restraint was applied to model this disorder. The structure in the solid state is given in Figure S16. Crystallographic and refinement data are summarized in Table S1.
$\left[\mathrm{Li}(2.2 .2 \text {-cryptand) }]_{2}\left[\left\{\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As} 5\right)\right\}_{2}\left\{1,1-\left((\mathrm{Cp})_{2} \mathrm{Fe}\right)\right\}\right]\right.$ (1c): The asymmetric unit contains one molecule of 1 c without any disorder. The structure in the solid state is given in Figure S17. Crystallographic and refinement data are summarized in Table S1.
[K(2.2.2-cryptand)][Cp*Fe( $\left.\left.\eta^{4}-\mathrm{As}_{6} \mathrm{Ph}_{2}\right)\right]$ (2): The asymmetric unit contains one molecule of $\mathbf{2}$ without any disorder. The unit cell contains three THF molecules, one of them shows disorder (50:50). The SIMU restraint was applied to model this disorder. Since the measured crystal was twinned, a HKLF5 refinement was applied (BASF 0.045). The structure in the solid state is given in Figure S18. Crystallographic and refinement data are summarized in Table S1. [Li(2.2.2-cryptand) $]_{2}\left[\left(\mathrm{Cp}{ }^{*} \mathrm{Fe}\right)_{4}\left\{\mu_{5}-\eta^{4}: \eta^{4}: \eta^{3}: \eta^{3}: \eta^{1}: \eta^{1}-\mathrm{As} \mathbf{s}_{20}\right\}\right]$ (3a): The asymmetric unit contains half a molecule of 3a. One $\mathrm{Cp}^{*}$ ligand of the anion of 3 a is disordered over two positions with a distribution of 55 to 45 . The SIMU, SADI, DANG and DFIX restraints were applied to model this disorder. The cation of 1 b is disordered over two positions with a distribution of 56 to 44 . The SIMU restraint was applied to model this disorder. The structure in the solid state is given in Figure S19. Crystallographic and refinement data are summarized in Table S2.
$[K(2.2 .2-c r y p t a n d)]_{2}\left[\left(C p^{*} \mathrm{Fe}\right)_{4}\left\{\mu_{5}-\eta^{4}: \eta^{4}: \eta^{3}: \eta^{3}: \eta^{1}: \eta^{1}-\mathrm{As} s_{20}\right\}\right]$ (3b): The asymmetric unit contains half a molecule of $\mathbf{3 b}$. One $\mathrm{Cp}^{*}$ ligand of the anion of $\mathbf{3 b}$ is disordered over two positions with a distribution of 50 to 50 . The SIMU restraint was applied to model this disorder. The unit cell contains one THF molecule which is disordered over two positions (57:43). The SIMU and SADI restraints were applied to model this disorder. The structure in the solid state is given in Figure S20. Crystallographic and refinement data are summarized in Table S2.
$\left[K(2.2 .2 \text {-cryptand })_{2}\left[\left(C p^{*} \mathrm{Fe}\right)_{2}\left\{\mu-\eta^{4}: \eta^{4}-\mathrm{As}_{10}\right\}\right]\right.$ (4): The asymmetric unit contains half a molecule of 4 without any disorder. The structure in the solid state is given in Figure S21. Crystallographic and refinement data are summarized in Table S2.

Table S1. Crystallographic details of 1a-c and 2.

| Compound | 1a | 1b | 1c | 2 |
| :---: | :---: | :---: | :---: | :---: |
| CCDC | / | / | / | / |
| Formula | $\mathrm{C}_{29} \mathrm{H}_{54} \mathrm{Ass}_{5} \mathrm{FeLiN}_{2} \mathrm{O}_{6}$ | $\mathrm{C}_{35} \mathrm{H}_{58} \mathrm{As}_{5} \mathrm{FeKN}_{2} \mathrm{O}_{6}$ | $\mathrm{C}_{66} \mathrm{H}_{110} \mathrm{As}_{10} \mathrm{Fe}_{3} \mathrm{Li}_{2} \mathrm{~N}_{4} \mathrm{O}_{12}$ | $\mathrm{C}_{48} \mathrm{H}_{77} \mathrm{As}_{6} \mathrm{FeKN}_{2} \mathrm{O}_{8}$ |
| $D_{\text {calc. }} / \mathrm{g} \mathrm{cm}^{-3}$ | 1.729 | 1.638 | 1.731 | 1.583 |
| $\mu / \mathrm{mm}^{-1}$ | 4.880 | 4.260 | 9.376 | 3.854 |
| Formula Weight | 964.13 | 1072.38 | 2082.20 | 1354.58 |
| Colour | dark green | dark green | dark yellow | black |
| Shape | block-shaped | block-shaped | block-shaped | block-shaped |
| Size/mm ${ }^{3}$ | $0.66 \times 0.45 \times 0.35$ | $0.65 \times 0.25 \times 0.14$ | $0.34 \times 0.23 \times 0.14$ | $0.32 \times 0.19 \times 0.15$ |
| T/K | 123(1) | 123(1) | 122.98(10) | 123(1) |
| Crystal System | monoclinic | monoclinic | monoclinic | monoclinic |
| Flack Parameter | / | / | / | / |
| Hooft Parameter | / | / | / | / |
| Space Group | P2 $1^{\prime} \mathrm{C}$ | $\mathrm{P} 21 / \mathrm{n}$ | $P 2{ }_{1} / \mathrm{n}$ | $\mathrm{P} 21 / \mathrm{n}$ |
| a/Å | 13.6416(3) | 12.5401(4) | 19.8282(2) | 11.3492(2) |
| b/A | 15.0573(3) | 21.4431(6) | 20.4148(2) | 28.3189(4) |
| $c / \AA$ | 18.0679(3) | 16.1812(6) | 20.2258(2) | 17.8056(2) |
| $\alpha /{ }^{\circ}$ | 90 | 90 | 90 | 90 |
| $\beta 1^{\circ}$ | 93.504(2) | 91.820(3) | 102.6410(10) | 96.6620(10) |
| $\gamma /{ }^{\circ}$ | 90 | 90 | 90 | 90 |
| $\mathrm{V} / \mathrm{A}^{3}$ | 3704.31(13) | 4348.9(2) | 7988.72(14) | 5684.02(14) |
| Z | 4 | 4 | 4 | 4 |
| Z' | 1 | 1 | 1 | 1 |
| Wavelength/Å | 0.71073 | 0.71073 | 1.54184 | 0.71073 |
| Radiation type | MoK ${ }_{\alpha}$ | MoK ${ }_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ | MoK ${ }_{\alpha}$ |
| $\Theta_{\text {min }} /{ }^{\circ}$ | 3.323 | 3.387 | 3.532 | 3.398 |
| $\Theta_{\max } /{ }^{\circ}$ | 32.377 | 34.501 | 74.170 | 32.194 |
| Measured Refl's. | 37662 | 36501 | 47106 | 21619 |
| Ind't Refl's | 12216 | 16947 | 15922 | 21619 |
| Refl's with l > 2(I) | 9861 | 11240 | 14821 | 13162 |
| $R_{\text {int }}$ | 0.0227 | 0.0456 | 0.0345 | . |
| Parameters | 568 | 502 | 905 | 693 |
| Restraints | 127 | 144 | 48 | 192 |
| Largest Peak | 1.977 | 0.962 | 1.336 | 0.675 |
| Deepest Hole | -0.973 | -0.808 | -0.642 | -0.412 |
| GooF | 1.041 | 1.002 | 1.061 | 0.860 |
| $w R_{2}$ (all data) | 0.1020 | 0.1096 | 0.1004 | 0.0592 |
| wR2 | 0.0950 | 0.0933 | 0.0981 | 0.0572 |
| $R_{1}$ (all data) | 0.0566 | 0.0853 | 0.0404 | 0.0604 |
| $R_{1}$ | 0.0422 | 0.0466 | 0.0372 | 0.0302 |

Table S2. Crystallographic details of 3a,b and 4.

| Compound | 3 a | 3b | 4 |
| :---: | :---: | :---: | :---: |
| CCDC | / | / | / |
| Formula | $\mathrm{As}_{20} \mathrm{C}_{76} \mathrm{Fe}_{4} \mathrm{H}_{132} \mathrm{Li}_{2} \mathrm{~N}_{4} \mathrm{O}_{12}$ | $\mathrm{C}_{98} \mathrm{H}_{164} \mathrm{As}_{20} \mathrm{Fe}_{4} \mathrm{~K}_{2} \mathrm{~N}_{4} \mathrm{O}_{14}$ | $\mathrm{C}_{56} \mathrm{H}_{102} \mathrm{As}_{10} \mathrm{Fe}_{2} \mathrm{~K}_{2} \mathrm{~N}_{4} \mathrm{O}_{12}$ |
| $D_{\text {calc. }} / \mathrm{g} \mathrm{cm}^{-3}$ | 1.857 | 1.851 | 1.719 |
| $\mu / \mathrm{mm}^{-1}$ | 10.583 | 10.764 | 9.346 |
| Formula Weight | 3285.90 | 3422.32 | 1962.51 |
| Colour | dark green | brown | yellow |
| Shape | block-shaped | block-shaped | plate-shaped |
| Size/mm ${ }^{3}$ | $0.12 \times 0.11 \times 0.08$ | $0.20 \times 0.14 \times 0.09$ | $0.31 \times 0.06 \times 0.04$ |
| T/K | 123.01(10) | 100.01(10) | 122.97(11) |
| Crystal System | monoclinic | monoclinic | triclinic |
| Flack Parameter | / | / | / |
| Hooft Parameter | $/$ | 1 | / |
| Space Group | C2/c | C2/c | P-1 |
| $a / \AA$ | 25.9358(5) | 24.0468(2) | 12.5792(4) |
| b/Å | 17.0106(3) | 18.60340(10) | 13.3265(5) |
| $c / A$ | 28.2133(5) | 27.9001(2) | 14.3311(5) |
| $\alpha /{ }^{\circ}$ | 90 | 90 | 62.709(4) |
| $\beta /^{\circ}$ | 109.195(2) | 100.2900(10) | 69.567(3) |
| $\gamma /{ }^{\circ}$ | 90 | 90 | 64.742(4) |
| $\mathrm{V} / \AA^{3}$ | 11755.2(4) | 12280.43(15) | 1895.36(15) |
| Z | 4 | 4 | 1 |
| Z' | 0.5 | 0.5 | 0.5 |
| Wavelength/A | 1.54184 | 1.54184 | 1.54184 |
| Radiation type | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ |
| $\Theta_{\text {min }} /{ }^{\circ}$ | 3.317 | 3.022 | 3.535 |
| $\Theta_{\max } /{ }^{\circ}$ | 73.511 | 75.953 | 73.995 |
| Measured Refl's. | 23899 | 46289 | 21126 |
| Ind't Refl's | 11503 | 12418 | 7432 |
| Refl's with I > 2(I) | 10003 | 11342 | 7096 |
| Rint | 0.0229 | 0.0300 | 0.0307 |
| Parameters | 827 | 792 | 393 |
| Restraints | 824 | 180 | 0 |
| Largest Peak | 1.609 | 1.015 | 0.845 |
| Deepest Hole | -0.881 | -0.510 | -0.454 |
| GooF | 1.078 | 1.049 | 1.025 |
| $w R_{2}$ (all data) | 0.1190 | 0.1030 | 0.0651 |
| $w \mathrm{R}_{2}$ | 0.1149 | 0.1006 | 0.0641 |
| $R_{1}$ (all data) | 0.0484 | 0.0424 | 0.0256 |
| $R_{1}$ | 0.0430 | 0.0386 | 0.0244 |

[Li(2.2.2-cryptand) $]\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As}_{5} \mathrm{Me}\right)\right]$ (1a)


Fig. S15. Molecular structure of 1a (left: endo species; right: exo species) in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The Cp* ligands are drawn in a wire frame model.

Table S3. Selected bond lengths of 1a.

| Atom-Atom | Length $[\AA ̊]$ |
| :--- | :--- |
| As4A-As3A | $2.3533(14)$ |
| As4A-As5A | $2.3202(5)$ |
| As4B-As5B | $2.306(8)$ |
| As4A-As5A | $2.340(3)$ |
| As3A-As2A | $2.3645(9)$ |
| As1A-C1A | $1.970(4)$ |
| As5B-As1B | $2.740(3)$ |


| Atom-Atom | Length $[$ Å] |
| :--- | :--- |
| As5A-As1A | $2.3906(5)$ |
| As2A-As1A | $2.4058(6)$ |
| As1B-C1B | $1.959(17)$ |
| As4B-As3B | $2.310(6)$ |
| As3B-As2B | $2.298(5)$ |
| As2B-As1B | $2.401(4)$ |
|  |  |

Table S4. Selected angles of 1a.

| Atom-Atom-Atom | Angle [] |
| :--- | :--- |
| As5A-As4-As3A | $102.82(2)$ |
| As5A-As1A-As2A | $87.701(16)$ |
| As4-As3A-As2A | $101.06(4)$ |
| As3A-As2A-As1A | $106.32(3)$ |
| As4-As5A-As1A | $106.100(18)$ |
| C1A-As1A-As5A | $103.86(12)$ |


| Atom-Atom-Atom | Angle [] |
| :--- | :--- |
| C1A-As1A-As2A | $105.69(11)$ |
| As4B-As4-As1B | $92.58(16)$ |
| As4-As4B-As3B | $106.9(2)$ |
| As2B-As3B-As4B | $102.5(2)$ |
| As3B-As2B-As1B | $100.19(14)$ |
| C1B-As1B-As2B | $94.6(10)$ |

$[K(2.2 .2-c r y p t a n d)]\left[\mathrm{Cp}^{*} \mathrm{Fe}\left\{\eta^{4}-\mathrm{As}_{5}\left(\mathrm{CH}_{2} \mathrm{Ph}\right)\right\}\right]$ (1b)


Fig. S16. Molecular structure of 1b (left: Part 1; right: Part 2) in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligands are drawn in a wire frame model.

Table S5. Selected bond lengths of $\mathbf{1 b}$.

| Atom-Atom | Length $[\AA \AA]$ |
| :--- | :--- |
| As2A-As1A | $2.421(4)$ |
| As2A-As3A | $2.361(4)$ |
| As1A-As5A | $2.398(5)$ |
| As1A-C1 | $1.993(4)$ |
| As5A-As4A | $2.381(7)$ |
| As3A-As4 | $2.385(6)$ |


| Atom-Atom | Length [Å] |
| :--- | :--- |
| As2B-As3B | $2.357(5)$ |
| As2B-As1B | $2.392(5)$ |
| As3B-As4B | $2.329(8)$ |
| As4B-As5B | $2.327(8)$ |
| As5B-As1B | $2.393(5)$ |
| C1-As1B | $1.998(4)$ |

Table S6. Selected angles of 1 b .

| Atom-Atom-Atom | Angle [$\left.{ }^{\circ}\right]$ |
| :--- | :--- |
| As3A-As2A-As1A | $105.78(16)$ |
| As5A-As1A-As2A | $87.94(12)$ |
| C1-As1A-As2A | $106.08(17)$ |
| C1-As1A-As5A | $102.07(19)$ |
| As4A-As5A-As1A | $105.33(19)$ |
| C2-C1-As1A | $108.7(2)$ |
| C2-C1-As1B | $111.6(2)$ |
| As2A-As3A-As4A | $101.15(19)$ |


| Atom-Atom-Atom | Angle $\left.{ }^{\circ}{ }^{\circ}\right]$ |
| :--- | :--- |
| As5A-As4A-As3A | $102.2(2)$ |
| As3B-As2B-As1B | $104.05(18)$ |
| As4B-As3B-As2B | $101.8(2)$ |
| As5B-As4B-As3B | $102.4(3)$ |
| As4B-As5B-As1B | $104.7(2)$ |
| C1-As1B-As2B | $106.20(19)$ |
| C1-As1B-As5B | $103.21(19)$ |
| As2B-As1B-As5B | $87.53(12)$ |

$[\mathrm{Li}(2.2 .2-\mathrm{cryptand})]_{2}\left[\left\{\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As} 5\right)\right\}_{2}\left\{1,1-\left((\mathrm{Cp})_{2} \mathrm{Fe}\right)\right\}\right](1 \mathrm{c})$


Fig. S17. Molecular structure of 1 c in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligands are drawn in a wire frame model.

Table S7. Selected bond lengths of 1c.

| Atom-Atom | Length $[\AA ̊]$ |
| :--- | :--- |
| As10-As9 | $2.3662(5)$ |
| As10-As6 | $2.3958(4)$ |
| As2-As1 | $2.3903(5)$ |
| As2-As3 | $2.3701(5)$ |
| As9-As8 | $2.3625(5)$ |
| As7-As6 | $2.4142(5)$ |


| Atom-Atom | Length $[\AA ̊]$ |
| :--- | :--- |
| As7-As8 | $2.3564(5)$ |
| As5-As1 | $2.4242(5)$ |
| As5-As4 | $2.3610(5)$ |
| As1-C11 | $1.951(3)$ |
| As6-C16 | $1.942(3)$ |
| As3-As4 | $2.3530(6)$ |

Table S8. Selected angles of 1 c .

| Atom-Atom-Atom | Angle [$]$ |
| :--- | :--- |
| As9-As10-As6 | $108.605(17)$ |
| As3-As2-As1 | $108.238(17)$ |
| As8-As9-As10 | $102.244(17)$ |
| As8-As7-As6 | $108.548(17)$ |
| As4-As5-As1 | $107.550(18)$ |
| As2-As1-As5 | $87.428(15)$ |
| C11-As1-As2 | $106.92(9)$ |


| Atom-Atom-Atom | Angle [] |
| :--- | :--- |
| C11-As1-As5 | $110.55(9)$ |
| As10-As6-As7 | $88.126(16)$ |
| C16-As6-As10 | $108.19(9)$ |
| C16-As6-As7 | $108.28(9)$ |
| As7-As8-As9 | $101.769(17)$ |
| As4-As3-As2 | $101.738(18)$ |
| As3-As4-As5 | $102.025(17)$ |

## $[\mathrm{K}(2.2 .2-\mathrm{cryptand})]\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\mathrm{n}^{4}-\mathrm{As}_{6} \mathrm{Ph}_{2}\right)\right]$ (2)



Fig. S18. Molecular structure of $\mathbf{2}$ in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligands are drawn in a wire frame model.

Table S9. Selected bond lengths of 2.

| Atom-Atom | Length $[\AA ̊]$ |
| :--- | :--- |
| As2-As6 | $2.4379(3)$ |
| As2-As3 | $2.4413(3)$ |
| As6-As5 | $2.3760(3)$ |
| As1-C7 | $1.976(2)$ |


| Atom-Atom | Length $[\AA \AA]$ |
| :--- | :--- |
| As5-As4 | $2.3830(4)$ |
| As1-C1 | $1.977(2)$ |
| As3-As4 | $2.3744(3)$ |
| As2-As1 | $2.4440(3)$ |

Table S10. Selected angles of 2.

| Atom-Atom-Atom | Angle [${ }^{\circ}$ ] |
| :--- | :--- |
| As6-As2-As1 | $88.934(11)$ |
| As6-As2-As3 | $83.110(10)$ |
| As3-As2-As1 | $91.483(11)$ |
| As5-As6-As2 | $98.062(12)$ |
| C7-As1-As2 | $99.66(6)$ |


| Atom-Atom-Atom | Angle [ ${ }^{\circ}$ ] |
| :--- | :--- |
| As4-As3-As2 | $98.493(12)$ |
| As6-As5-As4 | $100.198(12)$ |
| As3-As4-As5 | $100.496(12)$ |
| C7-As1-C1 | $98.36(10)$ |
| C1-As1-As2 | $96.25(6)$ |

$[\text { Li(2.2.2-cryptand) }]_{2}\left[\left(\mathrm{Cp}^{*} \mathrm{Fe}\right) 4\left\{\mu_{5}-\eta^{4}: \eta^{4}: \eta^{3}: \eta^{3}: \eta^{1}: \eta^{1}-\mathrm{As} 20\right\}\right]$ (3a)


Fig. S19. Molecular structure of 3a (left: unit cell; right: grown molecule) in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}{ }^{*}$ ligands are drawn in a wire frame model.

Table S11. Selected bond lengths of 3a.

| Atom-Atom | Length $[\AA \AA]$ |
| :--- | :--- |
| As7-As1 | $2.4516(7)$ |
| As7-As8 | $2.4491(7)$ |
| As7-As4 | $2.4566(7)$ |
| As1-As2 | $2.4348(7)$ |
| As1-As6 | $2.4287(7)$ |
| As10-As9 | $2.3903(7)$ |
| As10-As10 ${ }^{1}$ | $2.5670(10)$ |


| Atom-Atom | Length $[\AA ̊]$ |
| :--- | :--- |
| As2-As3 | $2.3558(7)$ |
| As9-As8 | $2.4496(8)$ |
| As3-As4 | $2.4318(8)$ |
| As4-As5 | $2.4338(9)$ |
| As6-As5 | $2.3658(9)$ |
| As8-As8 ${ }^{1}$ | $2.4246(12)$ |
|  |  |

Table S12. Selected angles of 3a.

| Atom-Atom-Atom | Angle [] |
| :--- | :--- |
| As1-As7-As4 | $99.33(2)$ |
| As8-As7-As1 | $93.88(2)$ |
| As8-As7-As4 | $96.60(3)$ |
| As2-As1-As7 | $106.45(2)$ |
| As6-As1-As7 | $102.06(3)$ |
| As6-As1-As2 | $78.08(2)$ |
| As9-As101-As10 | $100.93(2)$ |
| As3-As2-As1 | $107.11(3)$ |
| As10-As9-As8 | $102.96(3)$ |


| Atom-Atom-Atom | Angle [] |
| :--- | :--- |
| As2-As3-As4 | $105.97(3)$ |
| As7-As8-As9 | $92.14(3)$ |
| As81-As8-As7 | $93.94(3)$ |
| As81-As8-As9 | $103.31(2)$ |
| As3-As4-As7 | $106.94(3)$ |
| As3-As4-As5 | $79.69(3)$ |
| As5-As4-As7 | $101.56(3)$ |
| As6-As5-As4 | $106.26(3)$ |
|  |  |

11-x,+y,3/2-z
$\left.[K(2.2 .2-c r y p t a n d)]_{2}\left[\left(C p^{*} \mathrm{Fe}\right)\right)_{4}\left\{\mu_{5}-\eta^{4}: \eta^{4}: \eta^{3}: \eta^{3}: \eta^{1}: \eta^{1}-\mathrm{As} 20\right\}\right]$ (3b)


Fig. S20. Molecular structure of 3b in the solid state with thermal ellipsoids at 50\% probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligands are drawn in a wire frame model.

The bond angles and lengths in the solid state of $\mathbf{3 b}$ are identical / very similar to $\mathbf{3 a}$. Therefore, a summary is not provided. For details, see corresponding CCDC entry.

## $[K(2.2 .2-c r y p t a n d)]_{2}\left[\left(C p^{*} \mathrm{Fe}\right)_{2}\left\{\mu-\eta^{4}: \eta^{4}-\mathrm{As}_{10}\right\}\right]$ (4)



Fig. S21. Molecular structure of 4 in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligands are drawn in a wire frame model

Table S13. Selected bond lengths of 4.

| Atom-Atom | Length $[\AA ̊]$ |
| :--- | :--- |
| As2-As3 | $2.3757(3)$ |
| As2-As1 | $2.4302(3)$ |
| As4-As5 | $2.3779(3)$ |

Table S14. Selected angles of 4.

| Atom-Atom-Atom | Angle [] |
| :--- | :--- |
| As3-As2-As1 | $100.091(12)$ |
| As4-As5-As1 | $100.933(12)$ |
| As4-As3-As2 | $99.900(12)$ |


| Atom-Atom-Atom | Angle $\left[^{\circ}{ }^{\circ}\right.$ |
| :--- | :--- |
| As2-As1-As5 | $82.051(11)$ |
| As2-As1-As1 ${ }^{1}$ | $90.951(15)$ |
| As5-As1-As1 ${ }^{1}$ | $91.472(15)$ |

[^1]| Atom-Atom | Length $[\AA ̊]$ |
| :--- | :--- |
| As4-As3 | $2.3737(4)$ |
| As5-As1 | $2.4441(3)$ |
| As1-As1 ${ }^{1}$ | $2.4557(5)$ |

## 4. Additional Information



Fig. S22. Preliminary molecular structure of the reaction of I with $\mathrm{KAsH}_{2}$ in the solid state with thermal ellipsoids at $50 \%$ probability level. The cation (K(2.2.2-cryptand)) and hydrogen atoms are omitted for clarity. The Cp* ligands are drawn in a wire frame model.


Fig. S23. Top: CV of 1c; Bottom: SQV of 1c; In THF at room temperature.


Fig. S24. Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of the washing solution - obtained by $n$-hexane from the reaction of I with $\mathrm{KAs}\left(\mathrm{SiMe}_{3}\right)_{2}$ - cf. above.


Fig. S25. Experimental ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $100.62 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of the washing solution - obtained by $n$-hexane from the reaction of I with $\mathrm{KAs}\left(\mathrm{SiMe}_{3}\right)_{2}$ - cf. above.

## 5. Computational details

Table S30. Cartesian coordinates of exo-[Cp*Fe(n $\left.\left.{ }^{4}-\mathrm{As}_{5} \mathrm{Me}\right)\right]$ (1a) optimized at the B3LYP/def2-TZVP level. Free energy = -12873.537934 Hartree.

| Atom | x | $y$ | z | Atom | x | y | z |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| As | -0.243070000 | 2.012731000 | 0.823510000 | H | 2.781506000 | 0.656676000 | -2.830222000 |  |
| As | -0.238775000 | 1.548333000 | -1.522262000 | C | 3.426411000 | 1.766381000 | -0.231634000 |  |
| As | -0.972934000 | -0.735858000 | -1.582076000 | H | 3.136632000 | 2.203913000 | -1.197925000 |  |
| As | -0.984331000 | -0.078248000 | 1.738610000 | H | 4.529117000 | 1.698767000 | -0.211849000 |  |
| Fe | 0.798311000 | -0.104817000 | 0.024975000 | H | 3.121290000 | 2.473890000 | 0.552713000 | 世 |
| As | -2.610086000 | -1.056334000 | 0.201934000 | C | 2.714106000 | 0.414769000 | 2.599846000 |  |
| C | -4.082354000 | 0.281949000 | -0.067613000 | H | 2.670533000 | 1.512668000 | 2.563654000 |  |
| H | -4.692148000 | 0.323802000 | 0.846514000 | H | 3.702849000 | 0.131069000 | 3.003754000 |  |
| H | -4.710871000 | -0.048417000 | -0.907342000 | H | 1.954847000 | 0.078363000 | 3.321693000 |  |
| H | -3.657872000 | 1.271253000 | -0.282800000 | C | 1.698843000 | -2.556415000 | 2.039547000 |  |
| C | 2.046450000 | -1.753235000 | -0.424918000 | H | 1.290859000 | -2.095035000 | 2.949595000 | + |
| C | 2.017969000 | -1.528129000 | 0.994913000 | H | 2.607560000 | -3.116824000 | 2.326155000 |  |
| C | 2.487332000 | -0.188822000 | 1.246025000 | H | 0.960696000 | -3.286479000 | 1.678671000 |  |
| C | 2.797150000 | 0.420075000 | -0.028386000 | C | 1.757366000 | -3.054998000 | -1.111888000 |  |
| C | 2.531792000 | -0.556050000 | -1.060656000 | H | 2.676807000 | -3.662395000 | -1.198133000 |  |
| C | 2.810521000 | -0.399194000 | -2.526070000 | H | 1.364640000 | -2.899311000 | -2.126483000 |  |
| H | 2.071768000 | -0.938622000 | -3.137494000 | H | 1.017383000 | -3.650265000 | -0.558568000 |  |
| H | 3.808226000 | -0.796390000 | -2.786926000 |  |  |  |  |  |

Table S31. Cartesian coordinates of endo-[Cp*Fe(n4-As5Me)] (1a) optimized at the B3LYP/def2-TZVP level. Free energy $=-12873.591128$ Hartree

| Atom | x | y | z | Atom | x | y | z |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| As | -0.243070000 | 2.012731000 | 0.823510000 | H | 2.781506000 | 0.656676000 | -2.830222000 |
| As | -0.238775000 | 1.548333000 | -1.522262000 | C | 3.426411000 | 1.766381000 | -0.231634000 |
| As | -0.972934000 | -0.735858000 | -1.582076000 | H | 3.136632000 | 2.203913000 | -1.197925000 |
| As | -0.984331000 | -0.078248000 | 1.738610000 | H | 4.529117000 | 1.698767000 | -0.211849000 |
| Fe | 0.798311000 | -0.104817000 | 0.024975000 | H | 3.121290000 | 2.473890000 | 0.552713000 |
| As | -2.610086000 | -1.056334000 | 0.201934000 | C | 2.714106000 | 0.414769000 | 2.599846000 |
| C | -4.082354000 | 0.281949000 | -0.067613000 | H | 2.670533000 | 1.512668000 | 2.563654000 |
| H | -4.692148000 | 0.323802000 | 0.846514000 | H | 3.702849000 | 0.131069000 | 3.003754000 |
| H | -4.710871000 | -0.048417000 | -0.907342000 | H | 1.954847000 | 0.078363000 | 3.321693000 |
| H | -3.657872000 | 1.271253000 | -0.282800000 | C | 1.698843000 | -2.556415000 | 2.039547000 |
| C | 2.046450000 | -1.753235000 | -0.424918000 | H | 1.290859000 | -2.095035000 | 2.949595000 |
| C | 2.017969000 | -1.528129000 | 0.994913000 | H | 2.607560000 | -3.116824000 | 2.326155000 |
| C | 2.487332000 | -0.188822000 | 1.246025000 | H | 0.960696000 | -3.286479000 | 1.678671000 |
| C | 2.797150000 | 0.420075000 | -0.028386000 | C | 1.757366000 | -3.054998000 | -1.111888000 |
| C | 2.531792000 | -0.556050000 | -1.060656000 | H | 2.676807000 | -3.662395000 | -1.198133000 |
| C | 2.810521000 | -0.399194000 | -2.526070000 | H | 1.364640000 | -2.899311000 | -2.126483000 |
| H | 2.071768000 | -0.938622000 | -3.137494000 | H | 1.017383000 | -3.650265000 | -0.558568000 |
| H | 3.808226000 | -0.796390000 | -2.786926000 |  |  |  |  |



## 6. References

[i] O. J. Scherer, C. Blath, G. Wolmershäuser, J. Organomet. Chem. 1990, 387, 21-24.
[ii] E. S. S. A, L. Lochmann, J. Trekoval, J. Organomet. Chem. 1987, 326, 1-7.
[iii] P. Licence, J. Wrench, G. LI, Synthesis (Stuttg). 1996, 5387.
[iv] A. Tzschach, W. Lange, Chem. Ber. 1962, 95, 1360-1366.
[v] R. L. Wells, M. F. Self, J. D. Johansen, J. A. Laske, S. R. Aubuchon, L. J. Jones, A. H. Cowley, S. Kamepalli, Inorg. Synth. 1997, 31, 150-158.
[vi] H. H. Karsch, F. Bienlein, T. Rupprich, F. Uhlig, E. Herrmann, M. Scheer, Synth. Methods Organometallic and Inorg. Chem. Vol. 3, Thieme, Stuttgart, 1996.
[vii] D. E. Bergbreiter, J. M. Killough, J. Am. Chem. Soc. 1978, 100, 2126-2134.
[viii] R. Magnall, G. Balázs, E. Lu, M. Kern, J. van Slageren, F. Tuna, A. J. Wooles, M. Scheer, S. T. Liddle, Chem. - A Eur. J. 2019, 25, 14246-14252.
[ix] J. S. Plotkin, S. G. Shore, Inorg. Chem. 1981, 20, 284-285.
[x] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. a. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. a. Petersson, H. Nakatsuji, X. Li, M. Caricato, a. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, a. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. a. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. a. Keith, R. Kobayashi, J. Normand, K. Raghavachari, a. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, 2016, Gaussian 16, Revision D.09, Gaussian, Inc., Wallin.
[xi] A. D. Becke, J. Chem. Phys. 2005, 98, 5648-5652.
[xii] S. H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 1980, 58, 1200-1211.
[xiii] C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 1988, 37, 785-789.
[xiv] P. J. Stephen, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, J. Phys. Chem. 1994, 98, 11623-11627.
[xv] F. Weigend, R. Ahlrichs, Phys. Chem. Chem. Phys. 2005, 7, 3297-3305.
[xvi] J. Tomasi, B. Mennucci, R. Cammi, Chem. Rev. 2005, 105, 2999-3093.
[xvii] L. J. Bourhis, O. V Dolomanov, R. J. Gildea, J. A. K. Howard, H. Puschmann, J. Appl. Crystallogr. 2009, 42, 339-341.
[xviii] G. M. Sheldrick, Acta Crystallogr. Sect. A 2015, 71, 3-8.
[xix] G. M. Sheldrick, Acta Crystallogr. Sect. C 2015, 71, 3-8.
[xx] V. G. Becker, G. Gutekunst, H. J. Wessely, Zeitschrift für Anorg. und Allg. Chemie 1980, 462, 113129.

## 9 Reactivity of $\left[C p^{*} F e\left(\eta^{5}-A s_{5}\right)\right]$ <br> towards <br> Carbenes <br> and <br> Analogues

### 9.1 Preface

The following chapter has not been submitted yet.
S. Reichl, R. Yadav, P. W. Roesky, M. Scheer, manuscript in preparation.

## Authors

Stephan Reichl, ${ }^{1}$ R. Yadav, ${ }^{2}$ P. W. Roesky, ${ }^{2}$ Manfred Scheer ${ }^{1}{ }^{*}$
${ }^{1}$ Institute of Inorganic Chemistry, University of Regensburg; Universitätsstraße 31, 93053 Regensburg, Germany.
${ }^{2}$ Institute of Inorganic Chemistry, Karlsruhe Institute of Technology (KIT), Engesserstraße 15, 76131 Karlsruhe, Germany
*Corresponding author. Email: manfred.scheer@chemie.uni-regensburg.de

## Author Contribution

S.R. conceived the experiments. S.R. analysed and revised the X-ray data. R.Y. synthesized [LE] ${ }_{2}$ $\left(L=P h C\left(N^{t} B u_{2}\right) ; E=S i, G e\right) . S . R$. and $M . S c h$. wrote the manuscript. M.Sch. and P.W.R. directed and coordinated the research.

## Reactivity of $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{As} 5\right)\right]$ towards Carbenes and Analogues



## Reactivity of $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{As} 5\right)\right]$ towards Carbenes and Analogues


#### Abstract

The reaction behavior of $\left[C p^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{As} 5\right)\right]$ (I) $\left(C p^{*}=\mathrm{C}_{5} \mathrm{Me}_{5}\right)$ towards carbenes and analogs was investigated. The reaction of I with NHCs (= N-heterocyclic carbenes) results in the first adducts of NHC polyarsenic ligand complexes (1a: IMe = 1,3,4,5-tetramethylimidazolin-2-ylidene, 1b: IMes $=1,3$-bis(2,4,6-trimethylphenyl)-imidazolin-2-ylidene). In contrast, the reaction of I with ${ }^{\text {Et }}$ CAAC (= cyclic alkyl amino carbenes) leads to a selective fragmentation and the formation of a unique Ass-sawhorse type structure (2). The reaction of $[L E]_{2}\left(L=P h C\left(N^{t} B u_{2}\right)(E=S i, G e)\right.$ with I resulted in a rearrangement and insertion of [LE] fragments, forming unique silicon (4: [Cp ${ }^{*} F e\left(\eta^{4}-\right.$ As $\left.\left.{ }_{4} \mathrm{SiL}\right)\right]$, 5a: [Cp*$\left.{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As}{ }_{6} \mathrm{SiL}\right)\right)$ - and germanium containing (5b: [Cp*Fe( $\left.\eta^{4}-A s_{6} G e L\right)$ - polyarsenic ligand complexes.


### 9.2 Introduction

In 1991 Arduengo synthesized the first crystallizable NHC. ${ }^{[1]}$ This breakthrough in chemistry opened the way for a multitude of further milestones, combining inorganic and organic chemistry interests as well as providing a diverse class of substances, for example, ligands in (a)symmetric catalysis. ${ }^{[2-4]}$ Bertrand continued to advance this research and synthesized in 2005 a novel type of carbene, the so-called CAAC (cyclic alkyl amino carbene). ${ }^{[5]}$ This further development influences the properties of the carbene since CAACs reveal a larger HOMO/LUMU gap in comparison to NHCs. ${ }^{[3]}$ Based on their electronic properties, these are stronger sigma-donors and pi-acceptors. ${ }^{[2,3]}$ Over the last three decades a plethora of different NHCs and CAACs arose, featuring different substituents in order to tune their stereo/electronic properties. ${ }^{[2,3]}$

In recent years, scientific interest has also focused on the heavier homologs of carbon. These are generally more difficult to stabilize (than carbon) and require special substituents, such as amidinate ligands, like $\mathrm{L}=\mathrm{PhC}\left(\mathrm{N}^{t} \mathrm{Bu}_{2}\right)$ ). One class of such low valent compounds of silicon and germanium are amidinate-stabilized chloro- or bis-silylenes / germylenes. ${ }^{[6,7]}$ In contrast to NHCs or CAACs, these compounds usually react as electrophiles (depending on the reactant). ${ }^{[8]}$ Since the activation of white phosphorus $\left(\mathrm{P}_{4}\right)$ by main group element compounds is a current topic in science, ${ }^{[9-12]}$ it was obvious to investigate the reactivity of $P_{4}$ towards carbenes and (chloro-)silylenes or germylenes. Interesting results were reported inter alia by Bertrand, ${ }^{[13-16]}$ Roesky, ${ }^{[17]}$ Driess, ${ }^{[18]}$ and West ${ }^{[19]}$.

Having a look at the heavier homolog, arsenic, the reactivity of yellow arsenic (As4) towards carbenes and analogs is little to no studied. Only a very few examples of arsenic-silicon or -germanium compounds, such as $\left[\mathrm{As} 10\left(\mathrm{SiN}(\mathrm{TMS})_{3} \mathrm{~L}_{3}\right]^{[20]}\left(\mathrm{TMS}=\mathrm{SiMe}_{3}\right),\left[\mathrm{As}_{2}(\mathrm{SiL})_{2}\right]^{[21]}\right.$ $\left[\mathrm{As}_{3}\left(\mathrm{SiL}_{3}\right)_{3}\right]^{[21]}\left(\mathrm{L}=\mathrm{PhC}\left(\mathrm{N}^{+} \mathrm{Bu}_{2}\right)\right)$ by our group, $\left[\mathrm{As}_{4}\left(\mathrm{SiL}^{\prime \prime}\right)_{4}\right]^{[19]}\left(\mathrm{L}^{\prime}=\mathrm{Mes}\right)$ by West as well as $\mathrm{As}_{2}\left(\mathrm{GeLL}^{\prime}\right)_{2}{ }^{[22]}\left(\mathrm{L}^{\prime \prime}=\mathrm{CH}[\mathrm{CMeNDipp}]_{2}\right)$ by Grützmacher and Driess could be found (Scheme 1). Especially concerning the activation of $\mathrm{As}_{4}$ by NHCs and CAACs as well as towards germylenes, there is a large scientific gap. With respect to the difficult handling of yellow arsenic, an interesting transition metal derivative is the so-called pentaarsaferrocene $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{As} 5\right)\right]$ (I), which has not been investigated towards low valent group 14 containing compounds. [ $\left.\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{As} 5\right)\right]$ (I) can be prepared with little effort and represents one of the very few enddeck $A s_{n}$ ligand complexes, featuring a versatile and sterically undemanding As5 moiety. Inspired by the reactivity of $\mathrm{Cp}^{*} \mathrm{FeP}_{5}$ towards $\mathrm{NHCs},{ }^{[23]}$ (chloro-/bis-)silylenes ${ }^{[24]}$ and (chloro-)germylenes ${ }^{[25]}$ these studies should be extended to $\mathrm{Cp}^{*} \mathrm{FeAs5}$ (I). Herein we report the reactivity of I towards IMe, IMes, EtCAAC as well as low valent (bis-)silylenes and germylenes leading to unprecedented polyarsenic-silicon/ and germanium complexes as well as a unique CAAC-stabilized As6 sawhorse type molecules.


Scheme 1. Reactivity of yellow arsenic (As4) (up) as well as [Cp*Fe(n $\left.\left.\eta^{5}-\mathrm{As} 5\right)\right]$ (I) (bottom) towards Carbenes and Analogs.

### 9.3 Results

By mixing an equimolar solution of I with ${ }^{\text {MeN }} \mathrm{NHC}$ (IMe) in THF at room temperature, an immediate change in color from green to red/brownish occurred. After workup (cf. SI) brown crystals of [ $\left.\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As} 5 \mathrm{IMe}\right)\right]$ (1a) can be obtained in 89 \% yield (Scheme 2).


Scheme 2. Reactivity of [Cp*Fe( $\left.\left.\eta^{5}-\mathrm{As}_{5}\right)\right]$ (I) towards IMe, IMes and ${ }^{\text {Et }} \mathrm{CAAC}$. (Yields are given in parenthesis)

Single X-ray structure analysis of 1a reveals an $\eta^{4}$-AssIMe moiety, featuring an envelope geometry with four arsenic atoms in the plane coordinating towards the $\mathrm{Cp}{ }^{*} \mathrm{Fe}$ fragment, where the arsenic atom bearing the NHC is out of the plane (Figure 1). The newly formed As-C Bond is with $1.982(3) \AA$ in accordance with an arsenic carbon single bond. ${ }^{[26]}$ The As-As bond lengths of $2.3623(6)-2.4376(3) \AA$ are within the range of a single- and double bond. ${ }^{[26,27]}$ In contrast to previous investigations on the reactivity of $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right]$ towards $\mathrm{IMe},{ }^{[23]}$ the equilibrium is highly shifted/exclusively towards $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As} 5 \mathrm{IMe}\right)\right]$ (1a), since no starting material I can be monitored in the ${ }^{1} \mathrm{H}$ NMR spectrum (Figure S1). The same applies when using the weaker donating IMes. The color of the reaction solution does not change drastically and crystals of [Cp*Fe( $n^{4}$-AssIMes)] (1b) can be obtained at $-80^{\circ} \mathrm{C}$, losing crystallinity at higher temperatures. XRD reveals an isostructural complex as the phosphorus analog ${ }^{[23]}$ with similar bond lengths as in 1a (Table S3 and S5). A minor difference in the solid state structure is given in the envelope structure of the As5 unit (Figure 1). Whereas in 1a, the arsenic atom bearing the NHC is bent out of the plane with an angle of $56.5^{\circ}$, the corresponding angle in 1 b is $41.6^{\circ}$.


Figure 1. Molecular structures in the solid state of 1a and 1b. Hydrogen atoms are omitted for clarity. The Cp* ligands are drawn in a wire frame model.

Complexes $\mathbf{1 a}$ and $\mathbf{1 b}$ represent the first NHC functionalized poly arsenic ligand complexes.

Replacing the NHC with ${ }^{\text {Et }} \mathrm{CAAC}$ in the reaction setup leads to intensive bright green color at $-80^{\circ} \mathrm{C}$ in THF (Scheme 2). While warming the mixture to room temperature, the color changed from green to red. NMR spectroscopy and mass spectrometry of the reaction solution indicate the presence of starting material I and one additional $\mathrm{Cp}{ }^{*} \mathrm{Fe}$ - as well as one ${ }^{\text {Et }} \mathrm{CAAC}$ species, respectively. Using two equivalents of ${ }^{\text {Et C CAAC, leads to the disappearance of complex I. After }}$ consecutive workup and crystallization (cf. SI), the two complexes $\mathrm{As}_{6}\left({ }^{(\mathrm{Et}} \mathrm{CAAC}\right)_{4}$ (2) and $\left[\left(\mathrm{Cp}^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4: 4}-\mathrm{As} 4\right\}\right]$ (3) can be obtained in 40 and $37 \%$ yield, respectively. XRD of 2 reveals an ${ }^{\text {Et C CAAC }}$ stabilized unique As 6 sawhorse type molecule (Figure 2).


Figure 2. Molecular structure in the solid state of 3 (left: asymmetric unit; right: view along the As1-As2 bond). Hydrogen atoms are omitted for clarity. The EtCAAC molecules are drawn in a wire frame model and translucent is set to $20 \%$ for clarity.

All As-As bond distances in 2 of 2.4313(3) - 2.4404(3) Å are very close to an arsenic-arsenic single bond. ${ }^{[26]}$ The corresponding arsenic carbon distances of $1.865(2) / 1.869(2) \AA$ are within a single- and double bond. ${ }^{[26,28]}$ The wingtip arsenic atoms As4 and As3 / As5 and As6 are almost at right angles to each other at $96.8^{\circ} / 95.9^{\circ}$ and are linked via As1 / As 2, respectively. With a torsion angle of $57.5^{\circ}$ (As1-As3-As4 towards As2-As5-As6 plane) a gauche effect is present within the sawhorse type structure in the solid state.

Compound 2 can be obtained as yellows plates, is soluble in $n$-hexane, toluene, diethyl-ether as well as THF and shows decomposition to grey arsenic when exposed to light. ${ }^{1} \mathrm{H}$ NMR spectroscopic investigation of 2 exhibits signals for four ${ }^{E t} C A A C-s u b s t i t u e n t s ~(F i g u r e ~ S 3), ~$ suggesting a gauche effect of the CAAC groups in solution, making them chemical inequivalent and inhibiting a rotation. Mass spectrometry reveals a peak corresponding to $\left[\mathrm{As}_{3}{ }^{5 \mathrm{Et}} \mathrm{CAAC}_{2}\right]^{+}$, suggesting the formation of $\mathbf{2}$ via the dimerization of two $\left[\mathrm{As}_{3}{ }^{5 \mathrm{tt}} \mathrm{CAAC}_{2}\right]$ radicals, which might also give an explanation for the intense bright color when mixing I with ${ }^{\text {Et }} \mathrm{CAAC}$ at $-80^{\circ} \mathrm{C}$. The corresponding anionic species of the type $\left[\left(\mathrm{R}_{2} \mathrm{C}=\mathrm{P}\right)_{2} \mathrm{Pn}\right]^{-}\left(\mathrm{Pn}=\mathrm{N}, \mathrm{P}, \mathrm{As}, \mathrm{Sb} ; \mathrm{R}=\mathrm{H}, \mathrm{Me}, \mathrm{CF}_{3}, \mathrm{SiH}_{3}\right.$, $\mathrm{SiMe}_{3}, \mathrm{SiF}_{3}$ ) are known in literature ${ }^{[29]}$ and similar to $\left[\mathrm{As}_{3}{ }^{5 \mathrm{Et}} \mathrm{CAAC} \mathrm{C}_{2}\right]$ which would explain the
preceding formation of 2 by radical dimerization. However, EPR investigation of the reaction mixture at $-80^{\circ} \mathrm{C}$ shows no signals.

Compound 3 represents an As4-triple-decker-complex. Similar complexes with bulkier Cp ligands are known in literature. ${ }^{[30]}$ However, the described route offers a way to its $\mathrm{Cp}^{*}$ derivative, which was not accessible so far.

Unfortunately, crystals of 3 were of limited quality due to twinning and it was unable to get suitable crystals for successful measurement. Therefore, the bond features are not discussed in detail. However, the constitution of 3 was undoubtedly be detected (Figure S15).

In contrast, the reaction of the phosphorus complex $\left[C p^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right]\left(\mathrm{I}^{\prime}\right)$ with ${ }^{\text {Et }} \mathrm{CAAC}$ does not lead to fragmentation. Instead, the carbene adduct [ $\mathrm{Cp} \mathrm{F}^{*} \mathrm{Fe}\left(\mathrm{n}^{4}-\mathrm{P}_{5}{ }^{\mathrm{Et}} \mathrm{CAAC}\right)$ ] ( $\mathrm{I}^{\prime}$ ) (Figure S19) is formed. Similar to the previous publication, ${ }^{[23]}$ an equilibrium between $\left[C p^{*} \mathrm{Fe}\left(\mathrm{n}^{5}-\mathrm{P}_{5}\right)\right]$ ( $\mathrm{I}^{\prime}$ ) and ${ }^{\text {Et }}$ CAAC is present. $\mathrm{VT}{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR investigations in toluene $-\mathrm{d}_{8}$ show a ratio of I ' to $1^{\prime}$ of $1: 5$ (193 K) to 1:7 (313 K) (Figure S19) (decomposition above 313 K ). However, a phosphorus analog to 2 cannot be detected. Instead, a dynamic behavior like in the previous publication can be stated. ${ }^{[23]}$

Given the reactivity of $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right]$ ( $\mathrm{I}^{\prime}$ ) towards (chloro-) silylene ${ }^{[31]}$ and germylene ${ }^{[25]}$, the question arose what happens to the arsenic homolog $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{A} \mathbf{s}_{5}\right)\right]$ (I). Therefore we investigated the reactivity of $\mathbf{I}$ the towards [LSiCl] / [LE] $]_{2}$, respectively ( $\mathrm{L}=\mathrm{PhC}^{\mathrm{P}} \mathrm{N}^{\dagger} \mathrm{Bu}_{2}$ ); $E=S i, G e$ (see Scheme 3).

The reaction of $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\mathrm{n}^{5}-\mathrm{As} 5\right)\right]$ (I) with $[\mathrm{LSi}]_{2}$ (and [LSiCl]; cf. SI ) at $-80^{\circ} \mathrm{C}$ leads to an immediate change in color from green to red. After letting the mixture reach room temperature overnight and consecutive workup (cf. SI) the complexes [ $\left.\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As} 4 \mathrm{SiL}\right)\right]$ (4) and $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(n^{4}-\mathrm{As} \mathrm{s}_{6} \mathrm{SiL}\right)\right]$ (5a) were obtained (Scheme 3). The solid-state structure of 4 (Figure 3) shows the formation of envelope [As4SiL] moiety, coordinating in a $\eta^{4}$ fashion via four arsenic atoms to the $\left[\mathrm{Cp}^{*} \mathrm{Fe}\right.$ ] fragment (Figure 3). The silicon arsenic bond distances of 2.2855(7) Å (As1-Si1) to 2.2792(7) A (As4-Si1) are in between a single and double bond. ${ }^{[26,28]}$ The As-As bond lengths (2.3579(4) A to $2.3866(4) \AA$ A) exhibit double bond character. ${ }^{[28]}$ The molecular structure in the solid state of complex 5a (Figure S18) exhibits two arsenic dumbbells ( $\left({ }^{( } \mathrm{As}_{2}-\mathrm{As}_{3}\right)=2.3751(9) \mathrm{A}$ ), coordinating to the $\mathrm{Cp}^{*} \mathrm{Fe}$-moiety and bridged by an $\mathrm{As}{ }_{2} \mathrm{SiL}$-fragment (Figure S17). The arsenic-silicon distance of $2.3055(15) / 2.3047(17) \AA$ is like complex 4, representing a shortened single bond. ${ }^{[26]}$
$\left.{ }^{29} \mathrm{Si} i{ }^{1} \mathrm{H}\right\}$ NMR investigations of the reaction mixture show a selective reaction and solely two silicon-containing species, 4 and 5a (Figure S21). The singlet at $\delta=45.9 \mathrm{ppm}$ can be attributed
to complex 4 with a similar NMR shift to the analog phosphorus complex. ${ }^{[31]}$ Henceforth, the signal at $\delta=85.9 \mathrm{ppm}$ in the ${ }^{29} \mathrm{Si}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}$ spectrum (Figure S12) represents compound 5 a . The latter complex can be selectively isolated after crystallization from THF/n-pentane, storing at $8{ }^{\circ} \mathrm{C}$, as dark green plates in $36 \%$ yield. ${ }^{1} \mathrm{H}$ and ${ }^{29} \mathrm{Si}\left\{{ }^{1} \mathrm{H}\right\}$ NMR investigations of the isolated crystals confirms the previous assignment of complex 5a. After consecutive workup (cf. Si) 4 can be separated from complex 5 a . ${ }^{29} \mathrm{Si}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy of the obtained crystals of 4 exhibits solely one singlet at $\delta=46.1 \mathrm{ppm}$ (Figure S11). However, ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra indicates the presence of a second $\mathrm{Cp}^{*}$ containing species, which can be attributed to the starting material I, as a presumable decomposition product (Figure S 5 and S9). Due to similar solubility of 4 and I as well as the light sensitive of 4, the latter cannot be synthesized analytically pure.

Both complexes, 4a and 5a represent to the best of our knowledge the second mixed polyarsenic-silicon ligand complexes ${ }^{[32]}$, but the first five membered As 4 SiL- as well as the first norbornadiene-like As6SiL ligand complex.


Scheme 3. Reactivity of $\left[C p^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{As}_{5}\right)\right](\mathrm{I})$ towards $[\mathrm{LSiCL}] /[\mathrm{LSi}]_{2}$ or $[\mathrm{LGe}]_{2}\left(\mathrm{~L}=\mathrm{PhC}\left(\mathrm{N}^{t} \mathrm{Bu}_{2}\right)\right)$. (Yields are given in parenthesis)

When mixing I with chloro-germylene at $-80^{\circ} \mathrm{C}$, the formation of a germanium mirror can be observed after letting the reaction mixture stirred overnight and reach room temperature. No corresponding species were obtained via this route. The formation of elemental germanium can be avoided when using bis-germylene ( $[\mathrm{LGe}]_{2}$ ) $\left(\mathrm{L}=\mathrm{PhC}\left(\mathrm{N}^{t} \mathrm{Bu}_{2}\right)\right.$. However, the resulting red reaction mixture is highly air, light and moisture sensitive. ${ }^{1} \mathrm{H}$ NMR spectroscopy of the reaction mixture reveals the formation of several different species, bearing a Cp*- or tert-butyl unit (Figure S22). Utilizing the different solubilities of the given products (cf. SI, workup), single crystals of $\mathbf{5 b}$ were obtained from a solution of THF, layering with $n$-pentane, and storage at $8^{\circ} \mathrm{C}$ under the exclusion of light. Unfortunately, no other species were unambiguously identified. It has to be noted, that (LIFDI) mass spectrometry does not show any peaks, instead, the formation of a solid (presumably germanium or arsenic) can be observed blocking the canula.

Nevertheless, complex 5b was obtained as brown blocks in $17 \%$ yield, after consecutive workup (cf. SI) as the solely isolatable product. Single crystals X-Ray analysis of complex $\mathbf{5 b}$ reveals an isostructural motive like 5a, replacing silicon (5a) with germanium (5b) (Figure 3). The respective Ge -As bond distances of 2.38-2.39 $\AA$ indicate the presence of a single to double bond character. ${ }^{[26,28]}$ Thus, pentaarsaferrocene I can be used as polyarsenic source to form an unprecedented germylene-polyarsanide complex $\mathbf{5 b}$, representing the first literature known of its kind.


Figure 3. Molecular structure in the solid state of 4 and 5b. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligands are drawn in a frame model.

### 9.4 Conclusion

In summary, the polyarsenic complex $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{As} 5\right)\right]$ (I) can be used as a valuable platform for the synthesis of arsenic-carbene, -silylene, and -germylene ligand complexes. Thereby, novel neutral polyarsenic-NHC-adduct complexes were obtained (1a, 1b). Beyond, the reaction of I with EtCAAC leads to fragmentation and a unique CAAC stabilized Ass sawhorse molecule (2) can be obtained. Furthermore, the reaction I with bis-silylene/germylene $[L E]_{2}(E=S i, G e)$ leads to unique mixed polyarsenic-silicon (4, 5a)/ and first polyarsenic-germanium (5b) complexes.

## Conflicts of interest

There are no conflicts to declare.

## Author Contributions

Conceptualization: SR, YR, PWR, MS
Investigation: SR, MS
Visualization: SR, MS
Funding acquisition: PWR, MS
Project administration: PWR, MS

Supervision: PWR, MS
Writing - original draft: SR, MS
Writing - review \& editing: SR, PWR, MS

## Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft within the project Sche 384/45-1. S.R. is grateful to the Studienstiftung des Deutschen Volkes for his PhD fellowship.

### 9.5 References

[1] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361-363.
[2] M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, Nature 2014, 510, 485-496.
[3] V. Nesterov, D. Reiter, P. Bag, P. Frisch, R. Holzner, A. Porzelt, S. Inoue, Chem. Rev. 2018, 118, 9678-9842.
[4] D. Zhao, L. Candish, D. Paul, F. Glorius, ACS Catal. 2016, 6, 5978-5988.
[5] V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu, G. Bertrand, Angew. Chem. Int. Ed. 2005, 44, 5705-5709.
[6] S. Inoue, J. D. Epping, E. Irran, M. Driess, J. Am. Chem. Soc. 2011, 133, 8514-8517.
[7] S. Nagendran, S. S. Sen, H. W. Roesky, D. Koley, H. Grubmüller, A. Pal, R. Herbst-Irmer, Organometallics 2008, 27, 5459-5463.
[8] W. W. Schoeller, Phys. Chem. Chem. Phys. 2009, 11, 5273-5280.
[9] M. Scheer, G. Balázs, A. Seitz, Chem. Rev. 2010, 110, 4236-4256.
[10] D. J. Scott, J. Cammarata, M. Schimpf, R. Wolf, Nat. Chem. 2021, 13, 458-464.
[11] D. Sarkar, C. Weetman, D. Munz, S. Inoue, Angew. Chem. Int. Ed. 2021, 60, 3519-3523.
[12] M. M. D. Roy, A. Heilmann, M. A. Ellwanger, S. Aldridge, Angew. Chem. Int. Ed. 2021, 60, 2655026554.
[13] C. D. Martin, C. M. Weinstein, C. E. Moore, A. L. Rheingold, G. Bertrand, Chem. Commun. 2013, 49, 4486-4488.
[14] J. D. Masuda, W. W. Schoeller, B. Donnadieu, G. Bertrand, J. Am. Chem. Soc. 2007, 129, 1418014181.
[15] O. Back, G. Kuchenbeiser, B. Donnadieu, G. Bertrand, Angew. Chem. Int. Ed. 2009, 48, 55305533.
[16] J. D. Masuda, W. W. Schoeller, B. Donnadieu, G. Bertrand, Angew. Chem. Int. Ed. 2007, 46, 70527055.
[17] S. S. Sen, S. Khan, H. W. Roesky, D. Kratzert, K. Meindl, J. Henn, D. Stalke, J. P. Demers, A. Lange, Angew. Chem. Int. Ed. 2011, 50, 2322-2325.
[18] Y. Xiong, S. Yao, M. Brym, M. Driess, Angew. Chem. Int. Ed., 2007, 46, 4511-4513.
[19] R. P. Tan, N. M. Comerlato, D. R. Powell, R. West, Angew. Chem. Int. Ed. 1992, 31, 1217-1218.
[20] A. E. Seitz, M. Eckhardt, S. S. Sen, A. Erlebach, E. V. Peresypkina, H. W. Roesky, M. Sierka, M. Scheer, Angew. Chem. Int. Ed. 2017, 56, 6655-6659.
[21] A. E. Seitz, M. Eckhardt, A. Erlebach, E. V. Peresypkina, M. Sierka, M. Scheer, J. Am. Chem. Soc. 2016, 138, 10433-10436.
[22] S. Yao, Y. Grossheim, A. Kostenko, E. Ballestero-Martínez, S. Schutte, M. Bispinghoff, H. Grützmacher, M. Driess, Angew. Chem. Int. Ed. 2017, 56, 7465-7469.
[23] F. Riedlberger, S. Todisco, P. Mastrorilli, A. Y. Timoshkin, M. Seidl, M. Scheer, Chem. Eur. J. 2020, 26, 16251-16255.
[24] R. Yadav, T. Simler, S. Reichl, B. Goswami, C. Schoo, R. Köppe, M. Scheer, P. W. Roesky, J. Am. Chem. Soc. 2020, 142, DOI 10.1021/jacs.9b12151.
[25] R. Yadav, B. Goswami, T. Simler, C. Schoo, S. Reichl, M. Scheer, P. W. Roesky, Chem. Commun. 2020, 56, 10207-10210.
[26] P. Pyykkö, M. Atsumi, Chem. Eur. J. 2009, 15, 186-197.
[27] P. Pyykkö, M. Atsumi, Chem. Eur. J. 2009, 15, 12770-12779.
[28] P. Pyykkö, M. Atsumi, Chem. Eur. J. 2009, 15, 12770-12779.
[29] A. B. Rozhenko, A. Ruban, V. Thelen, M. Nieger, K. Airola, W. W. Schoeller, E. Niecke, Eur. J. Inorg. Chem. 2012, 2502-2507.
[30] M. Schmidt, A. E. Seitz, M. Eckhardt, G. Balázs, E. V. Peresypkina, A. V. Virovets, F. Riedlberger, M. Bodensteiner, E. M. Zolnhofer, K. Meyer, et al., J. Am. Chem. Soc. 2017, 139, 1398113984.
[31] R. Yadav, T. Simler, S. Reichl, B. Goswami, C. Schoo, R. Köppe, M. Scheer, P. W. Roesky, J. Am. Chem. Soc. 2020, 142, 1190-1195.
[32] M. Piesch, S. Reichl, M. Seidl, G. Balázs, M. Scheer, Angew. Chem. Int. Ed. 2021, 60, 15101-15108.

### 9.6 Supplementary Information

# Reactivity of [Cp*Fe(n²-Ass)] towards Carbenes and Analogs 

Stephan Reichl, ${ }^{1}$ Ravi Yadav, ${ }^{2}$ Peter W. Roesky, ${ }^{2}$ Manfred Scheer ${ }^{1 *}$<br>${ }^{1}$ Institute of Inorganic Chemistry, University of Regensburg; Universitätsstraße 31, 93053 Regensburg, Germany. ${ }^{2}$ Institute of Inorganic Chemistry, Karlsruhe Institute of Technology, Engesserstr. 15, 76131 Karlsruhe (Germany)<br>*Corresponding author. Email: manfred.scheer@chemie.uni-regensburg.de

## Table of Content

1. Experimental details ..... 336
2. NMR spectroscopic characterization ..... 339
3. Crystallographic details ..... 343
4. Additional Information ..... 353
5. References ..... 354

## 1. Experimental details

## General methods:

All manipulations were carried out under an inert atmosphere of dried argon using standard Schlenk and glove box techniques. 1,2-dimethoxyethane (DME) was dried and deoxygenated by distillation under argon atmosphere from sodium. Solvents were dried using a MB SPS-800 device of the company MBRAUN. NMR spectra were recorded on a Bruker Avance III 400 MHz or Bruker Avance III 600 MHz NMR spectrometer equipped with a 5 mm Prodigy BBOprobe ( $\mathrm{X},{ }^{1} \mathrm{H}$ ) with Z-gradient. The temperatures for measurements were controlled by a Bruker BVTE 3000 temperature control unit. Chemical shifts were measured at ambient temperature and are given in ppm; they are referenced to TMS for ${ }^{1} \mathrm{H}$ and $85 \% \mathrm{H}_{3} \mathrm{PO}_{4}$ for ${ }^{31} \mathrm{P}$ as external standard. LIFDI-MS spectra (LIFDI = liquid injection field desorption ionization) were measured on a JEOL AccuTOF GCX. ESI-MS spectra (ESI = Electrospray ionization) were measured on an Agilent Q-TOF 6540 UHD. Elemental analysis (CHN) was determined using a Vario micro cube instrument. The X-Band EPR measurements were carried out with a MiniScope MS400 device with a frequency of 9.44 GHz and a rectangular resonator TE102 of the company Magnettech GmbH.

The compounds $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{As} 5\right)\right]$ (I), ${ }^{[i]}\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right](\mathrm{I})$, ${ }^{[\mathrm{iri,iii]}]} \mathrm{NHCs}$ (IMe: ${ }^{[i v]} 1,3,4,5$-tetramethyl-imidazol-2-ylidene, IMes: ${ }^{[v]} 1,3$-bis(2,4,6-trimethylphenyl)-imidazolin-2-ylidene), $[\mathrm{LSiCl}]\left(\mathrm{L}=\mathrm{PhC}\left(\mathrm{N}^{t} \mathrm{Bu}\right)_{2}\right),{ }^{[\text {rvi] }}[\mathrm{LSi}]_{2},{ }^{[\text {vii] }}$ and $[\mathrm{LGel}]_{2}{ }^{[v i i i]}$ were synthesized according to literature procedures. Unless otherwise noted, all other materials were obtained from commercial suppliers and used without purification.

## Synthetic protocols:

## Synthesis of [Cp*Fe( ${ }^{4}$-AssIMe)] (1a):

Compound I ( $0.15 \mathrm{mmol}, 84.9 \mathrm{mg}, 1 \mathrm{eq}$ ) and $\mathrm{IMe}(0.15 \mathrm{mmol}, 19 \mathrm{mg}, 1 \mathrm{eq})$ are dissolved separately in 5 mL THF. IMe is added dropwise to compound I and an immediate colour change from green to red/brownish occurred. The mixture is allowed to stir overnight. The solvent is reduced in vacuo, layered with $n$-hexane and stored at $-30^{\circ} \mathrm{C}$. Compound 3 can be obtained as brown prisms after five days.

Yield: $92.0 \mathrm{mg}(0.134 \mathrm{mmol}, 89 \%) .{ }^{1} \mathrm{H}$ NMR (toluene $\left.-\mathrm{d}_{8}, 300 \mathrm{~K}\right): \delta[\mathrm{ppm}]=2.99\left(\mathrm{~s}, 6 \mathrm{H},-\mathrm{N}-\mathrm{CH}_{3}\right), 1.71(\mathrm{~s}, 15 \mathrm{H}$, $\left.\mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 1.12\left(\mathrm{~s}, 6 \mathrm{H},-\mathrm{C}-\mathrm{CH}_{3}\right)$. LIFDI-MS (DME): $\mathrm{m} / \mathrm{z}=125.1\left(100 \%,[\mathrm{Me}-\mathrm{H}]^{+}\right), 565.6\left(>1 \%\right.$, [I] ${ }^{+}$). Elemental analysis (calcd., found for $\mathrm{C}_{17} \mathrm{H}_{27} \mathrm{FeAs}_{5} \mathrm{~N}_{2}$ ): $\mathrm{C}(29.60,29.38), \mathrm{H}(3.95,3.86), \mathrm{N}(4.06,4.01)$.

## Synthesis of [Cp*Fe( $\left.\left.\eta^{4}-\mathrm{As}_{5} I \mathrm{Mes}\right)\right]$ (1b):

Compound I ( $0.15 \mathrm{mmol}, 84.9 \mathrm{mg}, 1 \mathrm{eq}$ ) and IMes ( $0.15 \mathrm{mmol}, 19 \mathrm{mg}, 1 \mathrm{eq}$ ) are dissolved in 5 mL THF. Thereby, the solution turned brownish green. The solution is stirred overnight, the volume is reduced in vacuo and stored at $-80^{\circ} \mathrm{C}$. Crystals of $\mathbf{1 b}$ formed after several days, but lose crystallinity above $-80^{\circ} \mathrm{C}$. Therefore, the synthetic route was repeated, after stirring overnight, the solvent is removed in vacuo, the brown/greenish residue was washed with 10 ml of $n$-hexane
${ }^{1} \mathrm{H}^{\mathrm{NMR}}{ }^{*}\left(\mathrm{THF}-\mathrm{d}_{8}, 300 \mathrm{~K}\right): \delta[\mathrm{ppm}]=7.16(\mathrm{~s}, 2 \mathrm{H},-\underline{\mathrm{H}}), 6.98(\mathrm{~s}, 4 \mathrm{H},-\mathrm{Ph}-\underline{\mathrm{H}}), 2.34\left(\mathrm{~s}, 6 \mathrm{H},-\mathrm{Ph}-\mathrm{CH}_{3}\right), 2.04(\mathrm{~s}, 12 \mathrm{H},-\mathrm{Ph}-$ $\left.\mathrm{CH}_{3}\right), 1.38$ (s, $\left.18 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right)$. Due to time restraints, no elemental analysis and mass spectrometry data are given. ${ }^{* 1} \mathrm{H}$ NMR was recorded in THF- $\mathrm{d}_{8}$ of the reaction of I ( $0.03 \mathrm{mmol}, 16.9 \mathrm{mg}, 1 \mathrm{eq}$ ) and IMes ( $0.03 \mathrm{mmol}, 9.1 \mathrm{mg}, 1 \mathrm{eq}$ ) at r.t.

## Reaction of [ $\left.\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{As} 5\right)\right]$ (I) with ${ }^{\text {Et }} \mathrm{CAAC}$ :

Compound I ( $0.30 \mathrm{mmol}, 169.7 \mathrm{mg}, 1 \mathrm{eq}$ ), ${ }^{\text {Et }}$ CAAC ( $0.60 \mathrm{mmol}, 188.1 \mathrm{mg}, 2 \mathrm{eq}$ ) are dissolved separately in 10 mL THF and cooled to $-80^{\circ} \mathrm{C}$. ${ }^{\text {Et }} \mathrm{CAAC}$ is added to compound I . Thereby, an immediate color change to dark-bright-
green is observed. The mixture is allowed to stir overnight and reach r.t. Thereby, the color changed to red. The solvent is removed in vacuo, the dark red residue is extracted with $3 \times 10 \mathrm{~mL}$ of $-80^{\circ} \mathrm{C}$ cold $n$-pentane, filtered over diatomaceous earth and the solvent is removed under reduced pressure. The residue is dissolved in 2 mL THF, layered with 6 mL Acetonitrile and stored at $-30^{\circ} \mathrm{C}$. Dark yellow plates of $\mathrm{As}_{6}\left({ }^{\mathrm{Et}} \mathrm{CAAC}\right)_{4}(2)$ can be obtained after one week. The red residue, before extraction, is dissolved in THF, layered with $6 \mathrm{~mL} n$-pentane and stored at $-30^{\circ} \mathrm{C}$. Dark red blocks of $\left[\left(\mathrm{Cp}^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4: 4}-\mathrm{As}_{4}\right\}\right]$ (3) can be obtained after four days.

## Data for $\mathrm{As}_{6}\left({ }^{\mathrm{Et}} \mathrm{CAAC}\right)_{4}(2)$ :

Yield: 104.3 mg ( $0.06 \mathrm{mmol}, 40 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 300 \mathrm{~K}\right)$ : $\delta[\mathrm{ppm}]=7.24(\mathrm{~m}, 4 \mathrm{H},-\mathrm{N}-\mathrm{Ph}), 7.02(\mathrm{~m}, 2 \mathrm{H},-\mathrm{N}-\mathrm{Ph}), 3.18$ $\left(\mathrm{m}, 1 \mathrm{H},-\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 3.06\left(\mathrm{~m}, 1 \mathrm{H},-\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 2.96\left(\mathrm{~m}, 1 \mathrm{H},-\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 2.85\left(\mathrm{~m}, 3 \mathrm{H},-\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right),{ }^{*} 2.73(\mathrm{~m}, 2 \mathrm{H},-$ $\left.\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right),{ }^{*} 2.19\left(\mathrm{~m}, 1 \mathrm{H}, \underline{-\mathrm{CH}_{2}}\right), 2.11\left(\mathrm{~m}, 1 \mathrm{H},-\mathrm{CH}_{2}\right), 1.91\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{CH}_{2}\right), 1.86\left(\mathrm{~m}, 1 \mathrm{H},-\mathrm{CH}_{2}\right), 1.81\left(\mathrm{~m}, 2 \mathrm{H},-\mathrm{CH}_{2}\right)$, $1.67\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{\mathrm{H}-\mathrm{H}}=6.5 \mathrm{~Hz}, 3 \mathrm{H},-\mathrm{CH}_{3}\right), 1.57\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{\mathrm{H}-\mathrm{H}}=6.4 \mathrm{~Hz}, 3 \mathrm{H},-\mathrm{CH}_{3}\right), 1.41\left(\mathrm{~m}, 8 \mathrm{H},-\mathrm{CH}_{3}\right),{ }^{*} 1.32\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{\mathrm{H}-\mathrm{H}}=6.7 \mathrm{~Hz}\right.$, $6 \mathrm{H},-\mathrm{CH}_{3}$ ), 1.29 (m, $\left.6 \mathrm{H},-\underline{\mathrm{Et}}\right), 1.17(\mathrm{~m}, 9 \mathrm{H},-\mathrm{Et}), 1.10(\mathrm{~s}, 3 \mathrm{H},-\mathrm{Et}), 1.07(\mathrm{~s}, 3 \mathrm{H},-\mathrm{Et}), 0.98$ (s, $\left.3 \mathrm{H},-\mathrm{Et}\right), 0.91$ (m, $6 \mathrm{H},-$ Et)

LIFDI-MS (toluene): $m / z=314.27\left(100 \%,\left[{ }^{[t} C A A C-H\right]^{+}\right), 851.30\left(9 \%,\left[\mathrm{As}_{3}\left({ }^{E t} \mathrm{CAAC}\right)_{2}\right]^{+}\right), 861.70\left(4 \%,[3]^{+}\right), 565.66$ ( $2 \%,[I]^{+}$). Elemental analysis failed after several attempts of the isolated crystals.
*Integrals wrong due to the overlap of signals.

## Data for $\left[\left(\mathrm{Cp}^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4: 4}-\mathrm{As} 4\right\}\right]$ (3):

Yield: $38.2 \mathrm{mg}(0.056 \mathrm{mmol}, 37 \%) .{ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 300 \mathrm{~K}\right): \delta[\mathrm{ppm}]=1.70\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 300 \mathrm{~K}\right)$ : $90.4\left(\underline{C}_{5} \mathrm{Me}_{5}\right), 13.6\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right)$. LIFDI-MS (toluene): $\mathrm{m} / \mathrm{z}=681.69\left(100 \%,[\mathrm{M}]^{+}\right), 314.25\left(20 \%\right.$, $\left.\left[{ }^{[\mathrm{tt}} \mathrm{CAAC}-\mathrm{H}\right]^{+}\right) .{ }^{*}$ Elemental analysis (calcd., found for $\left.\mathrm{C}_{20} \mathrm{H}_{30} \mathrm{Fe}_{2} \mathrm{As}_{4}\right)$ : $\mathrm{C}(35.23,35.95), \mathrm{H}(4.44,4.53)$.

## Reaction of $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{As} 5\right)\right]$ (I) with [LSi] $]_{2}$ :

Compound I ( $0.20 \mathrm{mmol}, 113.1 \mathrm{mg}, 2 \mathrm{eq}$ ), $[\mathrm{LSi}]_{2}(0.10 \mathrm{mmol}, 51.9 \mathrm{mg}, 1 \mathrm{eq})$ are dissolved separately in 5 mL THF and cooled to $-80^{\circ} \mathrm{C}$. [LSi $]_{2}$ is added to compound $\mathbf{I}$. Thereby, an immediate color change to red is observed. The mixture is allowed to stir overnight and reach r.t. Thereby, the color changed to green. The volume is reduced under reduced pressure, the reaction is layered with 5 mL of $n$-pentane and stored at $8^{\circ} \mathrm{C}$. [ $\left.\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As} \mathrm{s}_{6} \mathrm{SiL}\right)\right]$ (5a) can be obtained after one week as dark green blocks. The solvent of the supernatant solution is removed in vacuo and the browngreenish residue is dissolved in toluene, layered with equal amount of $n$-pentane and stored at $-30^{\circ} \mathrm{C}$. Complex 4 can be isolated as dark green plates alongside with unidentified sideproducts.

Data for [Cp*Fe( $\left.\left.\eta^{4}-\mathrm{As}_{5} \mathrm{SiL}\right)\right]$ (4):
Yield: 57.0 mg ( $0.076 \mathrm{mmol}, 38 \%$ ). ${ }^{1} \mathrm{H}$ NMR (THF- $\left.\mathrm{d}_{8}, 298 \mathrm{~K}\right)$ : The spectrum (see Figure S 5 ) exhibits different species which cannot be assigned properly. Therefore, no chemical shifts are given. ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR (THF- $\mathrm{d}_{8}, 298 \mathrm{~K}$ ): The spectrum (see Figure S9) exhibits different species which cannot be assigned properly. Therefore, no chemical shifts
 No elemental analysis was performed due to impurities within the ${ }^{1} \mathrm{H}$ NMR.
*Mass spectrometry of the isolated crystals showed no signal, therefore FD-MS of the crude reaction mixture was performed, which exhibits signals of the corresponding complexes 4 and 5 a.

## Data for [Cp*Fe( $\left.\left.\eta^{4}-\mathrm{As}_{6} \mathrm{SiL}\right)\right]$ (5a):

Yield: $65.0 \mathrm{mg}(0.072 \mathrm{mmol}, 36 \%) .{ }^{1} \mathrm{H}$ NMR (THF- $\left.\mathrm{d}_{8}, 300 \mathrm{~K}\right): \delta[\mathrm{ppm}]=7.56(\mathrm{~m}, 3 \mathrm{H},-\mathrm{Ph}), 7.49(\mathrm{~m}, 2 \mathrm{H},-\mathrm{Ph}), 1.57$ (s, $\left.15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 1.07\left(\mathrm{~s}, 18 \mathrm{H},-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}\left(\mathrm{THF}-\mathrm{d}_{8}, 300 \mathrm{~K}\right): 171.4(\mathrm{~s}, \mathrm{NCN}), 132.2(\mathrm{~s},-\mathrm{Ph}), 130.4(\mathrm{~s},-\mathrm{Ph})$, $129.2(\mathrm{~s},-\mathrm{Ph}), 128.9(\mathrm{~s},-\underline{\mathrm{Ph}}), 86.2\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right), 55.7\left(\mathrm{~s},-\underline{\mathrm{C}}\left(\mathrm{CH}_{3}\right)_{3}\right), 31.8\left(\mathrm{~s},-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 10.4\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right) .{ }^{29} \mathrm{Si}\left\{{ }^{1} \mathrm{H}\right\}\left(\mathrm{THF}-\mathrm{d}_{8}, 300 \mathrm{~K}\right):$
86.0 (s). LIFDI-MS (toluene): $m / z=899.70\left(11 \%,\left[\mathrm{M}^{+}\right), 749.86\left(100 \%,[4]^{+}\right) .{ }^{*}\right.$ Elemental analysis (calcd., found for $\left.\mathrm{C}_{25} \mathrm{H}_{38} \mathrm{FeAs}_{6} \mathrm{~N}_{2} \mathrm{Si}\right)$ : C (33.36, 34.41), H (4.26, 4.75), $\mathrm{N}(3.11,3.02)$.
*Mass spectrometry of the isolated crystals showed no signal, therefore LIFDI-MS of the crude reaction mixture was performed, which shows complex 4 and 5a.

Alternative route with $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{As}_{5}\right)\right](\mathrm{I})$ and $[\mathrm{LSiCl}]$ leads to the formation of 4, 5 a and additional $[\mathrm{LSiAs}]_{2}$ as well as [ $\left.\mathrm{LSiCl}_{3}\right]$ according to mass spectrometry. The latter two complexes cannot be separated from the others and therefore the primary setup, using $[\mathrm{LSi}]_{2}$, is preferred.

## Reaction of [Cp*Fe( $\left.\left.\eta^{5}-\mathrm{As}_{5}\right)\right]$ (I) with [LGeCl] / [LGe] ${ }_{2}$ :

Compound I ( $0.30 \mathrm{mmol}, 169.7 \mathrm{mg}, 2 \mathrm{eq}$ ), $[\mathrm{LGe}]_{2}(0.15 \mathrm{mmol}, 91.2 \mathrm{mg}, 1 \mathrm{eq})$ are dissolved separately in 10 mL THF and cooled to $-80^{\circ} \mathrm{C}$. $[\mathrm{LGe}]_{2}$ is added to compound I . Thereby, an immediate color change to red is observed. The mixture is allowed to stir overnight and reach r.t. Thereby, the color remained red. The solvent is removed under reduced pressure, the red residue* is washed with $n$-pentane and filtered over diatomaceous earth. The solvent of the filtrate is removed in vacuo, but no sideproduct can be clearly identified by means of NMR, mass spectrometry or (due to the lack of single crystals) XRD. The initial red residue* was dissolved in 2 mL of THF, layered with 7 mL of $n$-pentane and stored at $8{ }^{\circ} \mathrm{C}$, leading to the formation of $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As} \mathrm{s}_{6} \mathrm{GeL}\right)\right](5 \mathrm{~b})$ as brown blocks.

## Data for [Cp*Fe( $\left.\left.\eta^{4}-\mathrm{As}_{6} \mathrm{GeL}\right)\right]$ (5b):

Yield: $47.3 \mathrm{mg}(0.050 \mathrm{mmol}, 17 \%) .{ }^{1} \mathrm{H}$ NMR (THF-d $\left.{ }_{8}, 300 \mathrm{~K}\right): \delta[\mathrm{ppm}]=7.24(\mathrm{~m}, 5 \mathrm{H},-\mathrm{Ph}), 1.40\left(\mathrm{~s}, 18 \mathrm{H},-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right)$, 0.97 (s, $15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}$ ). LIFDI-MS (toluene): no signal; decomposition within the injection canular. Elemental analysis failed after several attempts of the isolated crystals.

Alternative route with $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{As} 5\right)\right]$ (I) and $[\mathrm{LGeCl}]$ leads to the formation of an arsenic/germanium mirror and does not yield complex $\mathbf{5 b}$ as crystals. Therefore, the primary setup, using $[\mathrm{LGe}]_{2}$, is preferred.

## 2. NMR spectroscopic characterization

## ${ }^{1}$ H NMR Spectra:

$\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As}_{5} \mathrm{IMe}\right)\right](1 \mathrm{a})$


Fig. S1. Experimental ${ }^{1} \mathrm{H}$ NMR ( 400.13 MHz , toluene- $\mathrm{d}_{8}$ ) spectrum of 1a.
[Cp*Fe( ${ }^{4}$-As ${ }_{5}$ IMes)] (1b)


Fig. S2. Experimental ${ }^{1} \mathrm{H}$ NMR ( 400.13 MHz , THF- $\mathrm{d}_{8}$ ) spectrum of the reaction of I + IMes.

## $\left.\mathrm{As}_{6}\left({ }^{\mathrm{Et}} \mathrm{CAAC}\right)\right)_{4}(2)$



Fig. S3. Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of 2 ( ${ }^{*}=$ THF; $\left.\#=\mathrm{MeCN}\right)$.
$\left[\left(\mathrm{Cp}^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4}-\mathrm{As}_{4}\right\}\right]$ (3)


Fig. S4. Experimental ${ }^{1} \mathrm{H}$ NMR ( $400.13 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) spectrum of 3 ( $^{*}=2$ ).

## $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As}_{5} \mathrm{SiL}\right)\right]$ (4)

See above.


Fig. S5. Experimental ${ }^{1} \mathrm{H}$ NMR ( 600.28 MHz , THF- $\mathrm{d}_{8}$ ) spectrum of 5 a ( $\left.{ }^{*}=\mathrm{THF}\right)$.
$\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As}_{6} \mathrm{SiL}\right)\right](5 \mathrm{a})$


Fig. S6. Experimental ${ }^{1} \mathrm{H}$ NMR ( 400.13 MHz, THF- $\mathrm{d}_{8}$ ) spectrum of 5 a ( ${ }^{*}=$ THF).
$\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As}_{6} \mathrm{GeL}\right)\right](5 \mathrm{~b})$


Fig. S7. Experimental ${ }^{1} \mathrm{H}$ NMR ( 400.13 MHz, THF- $\mathrm{d}_{8}$ ) spectrum of $5 \mathbf{b}$.

## ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR Spectra:

$\left[\left(\mathrm{Cp}^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4}-\mathrm{As}_{4}\right\}\right]$ (3)


Fig. S8. Experimental ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(100.62 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectrum of 3 .
[Cp*Fe( $\left.\left.\eta^{4}-\mathrm{As}_{4} \mathrm{SiL}\right)\right]$ (4)


Fig. S9. Experimental ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $100.62 \mathrm{MHz}, \mathrm{THF}-\mathrm{d}_{8}$ ) spectrum of 5 a .
$\left[C p^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As}_{6} \mathrm{SiL}\right)\right](5 \mathrm{a})$


Fig. S10. Experimental ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 100.62 MHz, THF- $\mathrm{d}_{8}$ ) spectrum of 5 a .

## ${ }^{29}{ }^{\text {Si }}$ [ $\left.{ }^{1} \mathrm{H}\right\}$ NMR Spectra:

$\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As} \mathbf{s}_{4} \mathrm{SiL}\right)\right](4)$


Fig. S11. Experimental $\left.{ }^{29} \mathrm{Si}{ }^{1}{ }^{1} \mathrm{H}\right\}$ NMR ( 119.25 MHz , THF- $\mathrm{d}_{8}$ ) spectrum of 4 .
[Cp*Fe( $\left.\left.\eta^{4}-\mathrm{As}_{6} \mathrm{SiL}\right)\right]$ (5a)


Fig. S12. Experimental $\left.{ }^{29} \mathrm{Si}{ }^{1} \mathrm{H}\right\}$ NMR (79.48 MHz, THF- $\mathrm{d}_{8}$ ) spectrum of 5 a .

## 3. Crystallographic details

[Cp*Fe( $\left.\left.\eta^{4}-\mathrm{As}_{5} \mathrm{IMe}\right)\right]$ (1a): The asymmetric unit contains half a molecule of 1 a without any disorder. The structure in the solid state is given in Figure S13. Crystallographic and refinement data are summarized in Table S1.
[Cp*Fe( $\eta^{4}$-As $\mathbf{S}_{5}$ IMes)] (1b): The asymmetric unit contains one molecule of 1 b without any disorder. The unit cell contains three non-coordinating THF molecules. The structure in the solid state is given in Figure S14. Crystallographic and refinement data are summarized in Table S1.
$\mathrm{As}_{6}\left({ }^{\mathrm{Et}} \mathrm{CAAC}\right)_{4}(2)$ : The asymmetric unit contains one molecule of 2 without any disorder. The unit cell contains two non-coordinating acetonitrile and THF molecules, respectively. One THF molecule is disorder over two positions (35:25). The SIMU and DFIX restraint was applied to model this disorder. The structure in the solid state is given in Figure S15. Crystallographic and refinement data are summarized in Table S1.
$\left[\left(\mathrm{Cp}^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4}-\mathrm{As}_{4}\right\}\right]$ (3): The asymmetric unit contains three molecules of 3 a. One As $\mathbf{s}_{4}$ ligand is disordered over two positions with a distribution of 80 to 20. The SIMU and DFIX restraints were applied to model this disorder. The structure in the solid state is given in Figure S16. Crystallographic and refinement data are summarized in Table S1. Due to the bad crystal habit and twinning, no complete measurement was able. Therefore, the bond lengths and angles will not be discussed in detail. A HKLF5 refinement was applied (BASF 0.1318).
[ $\left.\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As} \mathbf{s}_{5} \mathrm{SiL}\right)\right]$ (4): The asymmetric unit contains one molecule of 4 without any disorder. The structure in the solid state is given in Figure S17. Crystallographic and refinement data are summarized in Table S2.

Data for $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As}_{6} \mathrm{SiL}\right)\right]$ (5a): The asymmetric unit contains half a molecule of 5 b featuring a vertical mirror plane. The Cp * ligand is disordered over two positions with a distribution of 50 to 50 . One methyl group of the tert-butyl substituent is disordered over two positions with a distribution of 53 to 47 . The SIMU and SADI restraint was applied to model both disorders. The Phenyl substituent is disordered over two positions with a distribution of 50 to 25 . The SIMU and SADI restraint was applied to model this disorder. The structure in the solid state is given in Figure S18. Crystallographic and refinement data are summarized in Table S2.

Data for [ $\left.\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As} \mathbf{s}_{6} \mathrm{GeL}\right)\right]$ (5b): The asymmetric unit contains half a molecule of $5 \mathbf{b}$ featuring a vertical mirror plane. The $\mathrm{Cp}^{*}$ ligand is disordered over two positions with a distribution of 50 to 50 . The SIMU and ISOR restraint was applied to model this disorder. The Phenyl substituent is disordered over two positions with a distribution of 50 to 25 . The SIMU and SADI restraint was applied to model this disorder. The structure in the solid state is given in Figure S19. Crystallographic and refinement data are summarized in Table S2.

Table S1. Crystallographic details of 1a, 1b, 2 and 3.

| Compound | 1a | 1b | 2 | 3 |
| :---: | :---: | :---: | :---: | :---: |
| CCDC | / | / | / | / |
| Formula | $\mathrm{C}_{17} \mathrm{H}_{27} \mathrm{As}_{5} \mathrm{FeN}_{2}$ | $\mathrm{C}_{41} \mathrm{H}_{59} \mathrm{As}_{5} \mathrm{FeN}_{2} \mathrm{O}_{2.5}$ | $\mathrm{C}_{96.4} \mathrm{H}_{155.3} \mathrm{As}_{6} \mathrm{~N}_{5.5} \mathrm{O}_{1.35}$ | $\mathrm{C}_{20} \mathrm{H}_{30} \mathrm{As}_{4} \mathrm{Fe}_{2}$ |
| $D_{\text {calc. }} / \mathrm{g} \mathrm{cm}^{-3}$ | 2.092 | 1.611 | 1.236 | 1.988 |
| $\mu / \mathrm{mm}^{-1}$ | 13.941 | 7.322 | 2.633 | 16.677 |
| Formula Weight | 689.85 | 1050.35 | 1862.47 | 681.82 |
| Colour | brown | dark green | yellow | dark red |
| Shape | plate-shaped | block-shaped | plate-shaped | sphere-shaped |
| Size/mm ${ }^{3}$ | $0.34 \times 0.12 \times 0.07$ | $0.18 \times 0.14 \times 0.10$ | $0.34 \times 0.23 \times 0.09$ | $0.55 \times 0.42 \times 0.22$ |
| T/K | 123(1) | 123.01(10) | 123.00(10) | 293(2) |
| Crystal System | orthorhombic | monoclinic | monoclinic | monoclinic |
| Flack Parameter | / | / | / | / |
| Hooft Parameter | / | / | / | / |
| Space Group | Pnma | $\mathrm{P} 21 / \mathrm{c}$ | $P 21 / n$ | $\mathrm{P} 21 / \mathrm{c}$ |
| $a / A$ | 8.82190(10) | 11.5424(3) | 20.49710(10) | 27.7449(7) |
| b/Å | 14.1102(2) | 23.0099(6) | 22.45760(10) | 14.5724(3) |
| $c / A$ | 17.5966(3) | 16.5323(5) | 21.74130(10) | 17.4455(5) |
| $\alpha /{ }^{\circ}$ | 90 | 90 | 90 | 90 |
| $\beta /^{\circ}$ | 90 | 99.456(3) | 90.27 | 104.327(3) |
| $\gamma /{ }^{\circ}$ | 90 | 90 | 90 | 90 |
| $\mathrm{V} / \AA^{3}$ | 2190.40(5) | 4331.1(2) | 10007.75(8) | 6834.0(3) |
| Z | 4 | 4 | 4 | 12 |
| Z' | 0.5 | 1 | 1 | 3 |
| Wavelength/Å | 1.54184 | 1.54184 | 1.54184 | 1.54184 |
| Radiation type | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ |
| $\Theta_{\text {min }} /{ }^{\circ}$ | 4.016 | 3.322 | 3.552 | 3.288 |
| $\Theta_{\max } /{ }^{\circ}$ | 72.897 | 65.835 | 74.322 | 73.025 |
| Measured Refl's. | 7712 | 15407 | 109938 | 15388 |
| Ind't Refl's | 2242 | 7324 | 20089 | 15388 |
| Refl's with I > 2(I) | 2156 | 6555 | 18369 | 8103 |
| Rint | 0.0252 | 0.0408 | 0.0261 |  |
| Parameters | 126 | 498 | 1106 | 770 |
| Restraints | 0 | 39 | 183 | 85 |
| Largest Peak | 0.343 | 1.131 | 1.139 | 4.455 |
| Deepest Hole | -0.361 | -0.880 | -0.453 | -3.048 |
| GooF | 1.107 | 1.038 | 1.041 | 1.515 |
| $w R_{2}$ (all data) | 0.0452 | 0.1405 | 0.0888 | 0.4400 |
| $w R_{2}$ | 0.0443 | 0.1363 | 0.0857 | 0.4190 |
| $R_{1}$ (all data) | 0.0211 | 0.0583 | 0.0353 | 0.1917 |
| $R_{1}$ | 0.0196 | 0.0514 | 0.0316 | 0.1574 |

Table S2. Crystallographic details of 4, 5a and 5b.

| Compound | 4 | 5a | 5b |
| :---: | :---: | :---: | :---: |
| CCDC | $/$ | / | $/$ |
| Formula | $\mathrm{C}_{25} \mathrm{H}_{38} \mathrm{As}_{4} \mathrm{FeN} \mathrm{N}_{2} \mathrm{Si}$ | $\mathrm{As}_{6} \mathrm{C}_{35} \mathrm{FeH}_{38} \mathrm{~N}_{2} \mathrm{Si}$ | $\mathrm{As}_{6} \mathrm{C}_{25} \mathrm{FeGeH}_{38} \mathrm{~N}_{2}$ |
| $D_{\text {calc. }} / \mathrm{g} \mathrm{cm}^{-3}$ | 1.697 | 1.886 | 1.842 |
| $\mu / \mathrm{mm}^{-1}$ | 9.640 | 9.813 | 10.369 |
| Formula Weight | 750.19 | 1044.32 | 1016.68 |
| Colour | dark green | dark green | clear brown |
| Shape | block-shaped | plate-shaped | block-shaped |
| Size/mm ${ }^{3}$ | $0.35 \times 0.14 \times 0.09$ | $0.62 \times 0.10 \times 0.08$ | $0.26 \times 0.04 \times 0.03$ |
| T/K | 123(1) | 123(1) | 123.01(10) |
| Crystal System | monoclinic | tetragonal | tetragonal |
| Flack Parameter | / | / | / |
| Hooft Parameter | / | / | / |
| Space Group | P21/n | P42/mbc | P42/mbc |
| a/A | 13.0388(2) | 20.6072(2) | 20.62950(10) |
| b/Å | 16.8894(2) | 20.6072(2) | 20.62950(10) |
| $c / A$ | 14.1010(2) | 17.3250(3) | 17.22420(10) |
| $\alpha /{ }^{\circ}$ | 90 | 90 | 90 |
| $\beta /^{\circ}$ | 109.028(2) | 90 | 90 |
| $\gamma /{ }^{\circ}$ | 90 | 90 | 90 |
| $\mathrm{V} / \mathrm{A}^{3}$ | 2935.61(8) | 7357.18(19) | 7330.21(8) |
| Z | 4 | 8 | 8 |
| Z' | 1 | 0.5 | 0.5 |
| Wavelength/Å | 1.54184 | 1.54184 | 1.54184 |
| Radiation type | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ | $\mathrm{CuK}_{\alpha}$ |
| $\Theta_{\text {min }} /{ }^{\circ}$ | 4.013 | 4.291 | 3.029 |
| $\Theta_{\max } /{ }^{\circ}$ | 72.898 | 73.753 | 75.332 |
| Measured Refl's. | 16607 | 13579 | 109564 |
| Ind't Refl's | 5740 | 3786 | 3923 |
| Refl's with I > 2(I) | 5619 | 3505 | 3667 |
| Rint | 0.0226 | 0.0191 | 0.0415 |
| Parameters | 309 | 293 | 255 |
| Restraints | 0 | 412 | 171 |
| Largest Peak | 0.981 | 1.210 | 1.368 |
| Deepest Hole | -0.478 | -0.788 | -1.067 |
| GooF | 1.096 | 1.062 | 1.040 |
| $w R_{2}$ (all data) | 0.0682 | 0.1225 | 0.0990 |
| $w R_{2}$ | 0.0678 | 0.1205 | 0.0974 |
| $R_{1}$ (all data) | 0.0280 | 0.0482 | 0.0403 |
| $R_{1}$ | 0.0272 | 0.0453 | 0.0378 |

## $\left[C p^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As}_{5} \mathrm{IMe}\right)\right](1 \mathrm{a})$



Fig. S13. Molecular structure of 1a in the solid state with thermal ellipsoids at 50\% probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligands are drawn in a wire frame model.

Table S3. Selected bond lengths of 1 a.

| Atom-Atom | Length $[\AA \AA]$ |
| :--- | :--- |
| As1-As2 | $2.4376(3)$ |
| As1-As21 | $2.4376(3)$ |
| As1-C1 | $1.982(3)$ |


| Atom-Atom | Length $[\AA ̊]$ |
| :--- | :--- |
| As2-As3 | $2.3631(4)$ |
| As3-As31 | $2.3623(6)$ |
| C1-N1 | $1.345(3)$ |

11-x,+y,3/2-z
Table S4. Selected angles of 1a.

| Atom-Atom-Atom | Angle [] |
| :--- | :--- |
| As21-As1-As2 | $85.427(14)$ |
| C7-As1-As2 | $107.75(6)$ |
| C7-As1-As21 | $107.75(6)$ |


| Atom-Atom-Atom | Angle [] |
| :--- | :--- |
| As3-As2-As1 | $105.113(13)$ |
| As31-As3-As2 | $101.529(9)$ |
|  |  |

$11-x,+y, 3 / 2-z$
$\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As}{ }_{5} \mathrm{IMes}\right)\right]$ (1b)


Fig. S14. Molecular structure of 1b (left: Part 1; right: Part 2) in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligands and mesityl groups are drawn in a wire frame model.

Table S5. Selected bond lengths of $\mathbf{1 b}$.

| Atom-Atom | Length [Å] |
| :--- | :--- |
| As5-As1 | $2.3887(7)$ |
| As5-As4 | $2.3564(8)$ |
| As1-As2 | $2.3793(7)$ |


| Atom-Atom | Length [Å] |
| :--- | :--- |
| As1-C11 | $1.991(4)$ |
| As4-As3 | $2.3601(9)$ |
| C11-N2 | $1.354(6)$ |

Table S6. Selected angles of $\mathbf{1 b}$.

| Atom-Atom-Atom | Angle [] |
| :--- | :--- |
| As4-As5-As1 | $109.77(3)$ |
| As2-As1-As5 | $92.26(2)$ |
| C11-As1-As5 | $112.09(13)$ |
| C11-As1-As2 | $109.49(13)$ |


| Atom-Atom-Atom | Angle [${ }^{\circ}$ ] |
| :--- | :--- |
| As3-As2-As1 | $109.48(3)$ |
| As3-As4-As5 | $103.54(3)$ |
| As4-As3-As2 | $103.42(3)$ |
|  |  |

## $\mathrm{As}_{6}\left(\mathrm{Et}^{(\mathrm{CAAC}}\right)_{4}(2)$



Fig. S15. Molecular structure of $\mathbf{2}$ in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms and solvent molecules are omitted for clarity. The ${ }^{\text {Et CIAC molecules are drawn in a wire frame model and translucent }}$ is set to $20 \%$.

Table S7. Selected bond lengths of 2.

| Atom-Atom | Length $[\AA ̊]$ |
| :--- | :--- |
| As1-As2 | $2.4418(3)$ |
| As1-As4 | $2.4404(3)$ |
| As1-As3 | $2.4368(3)$ |
| As2-As6 | $2.4496(3)$ |
| As2-As5 | $2.4313(3)$ |


| Atom-Atom | Length $[\AA ̊]$ |
| :--- | :--- |
| As4-C23 | $1.871(2)$ |
| As3-C1 | $1.866(2)$ |
| As5-C45 | $1.865(2)$ |
| As6-C67 | $1.869(2)$ |
|  |  |

Table S8. Selected angles of 2.

| Atom-Atom-Atom | Angle [] |
| :--- | :--- |
| As4-As1-As2 | $99.274(11)$ |
| As3-As1-As2 | $100.937(11)$ |
| As3-As1-As4 | $96.761(11)$ |
| As1-As2-As6 | $99.085(11)$ |
| As5-As2-As1 | $99.983(11)$ |
| As5-As2-As6 | $95.928(11)$ |


| Atom-Atom-Atom | Angle [] |
| :--- | :--- |
| C67-As6-As2 | $103.50(6)$ |
| C23-As4-As1 | $102.83(6)$ |
| C1-As3-As1 | $102.37(6)$ |
| C45-As5-As2 | $102.83(6)$ |
| As5-As2-As5 | $95.928(11)$ |
|  |  |

## $\left[\left(\mathrm{Cp}^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4}-\mathrm{As}_{4}\right\}\right]$ (3)



Fig. S16. Molecular structure of 3 in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The Cp * ligands are drawn in a wire frame model.

Due to the bad crystal habit and twinning, no complete measurement was able. Therefore, the bond lengths and angles will not be discussed in detail. A HKLF5 refinement was applied (BASF 0.1318).

## $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As}_{5} \mathrm{SiL}\right)\right](4)$



Fig. S17. Molecular structure of 4 (left: unit cell; right: grown molecule) in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligands are drawn in a wire frame model.

Table S9. Selected bond lengths of 4.

| Atom-Atom | Length $[\AA ̊]$ |
| :--- | :--- |
| As4-As3 | $2.3579(4)$ |
| As4-Si1 | $2.2792(7)$ |
| As1-As2 | $2.3630(4)$ |
| As1-Si1 | $2.2855(7)$ |


| Atom-Atom | Length $[\AA ̊]$ |
| :--- | :--- |
| As3-As2 | $2.3866(4)$ |
| Si1-N1 | $1.836(2)$ |
| Si1-N2 | $1.837(2)$ |
|  |  |

Table S10. Selected angles of 4.

| Atom-Atom-Atom | Angle $\left[^{\circ}{ }^{\circ}\right]$ |
| :--- | :--- |
| Si1-As4-As3 | $95.47(2)$ |
| Si1-As1-As2 | $95.93(2)$ |
| As4-As3-As2 | $105.085(15)$ |
| As1-As2-As3 | $104.775(14)$ |
| As4-Si1-As1 | $104.26(3)$ |
| N1-Si1-As4 | $112.89(7)$ |


| Atom-Atom-Atom | Angle $\left[{ }^{\circ}\right]$ |
| :--- | :--- |
| N1-Si1-As1 | $115.55(8)$ |
| N1-Si1-N2 | $71.32(10)$ |
| N2-Si1-As4 | $122.15(8)$ |
| N2-Si1-As1 | $126.49(8)$ |
| C1-N1-Si1 | $90.99(16)$ |
| C1-N2-Si1 | $135.35(19)$ |

## Data for $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As}_{6} \mathrm{SiL}\right)\right]$ (5a)



Fig. S18. Molecular structure of 5a in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms and disorders are omitted for clarity. The $\mathrm{Cp}^{*}$ ligand is drawn in a wire frame model.

Table S11. Selected bond lengths of 5a.

| Atom-Atom | Length $[\AA ̊]$ |
| :--- | :--- |
| As1-As2 | $2.4524(8)$ |
| As1-As21 | $2.4524(8)$ |
| As1-Si1 | $2.3055(17)$ |
| As4-Si1 | $2.3047(17)$ |
| As2-As3 | $2.3751(9)$ |


| Atom-Atom | Length [Å] |
| :--- | :--- |
| As4-As3 | $2.4472(8)$ |
| As4-As31 | $2.4472(8)$ |
| N1-C1 | $1.333(5)$ |
| Si1-N11 | $1.825(4)$ |
| Si1-N1 | $1.825(4)$ |

${ }^{1} 1-x, 2-y, 2-z$
Table S12. Selected angles of 5a.

| Atom-Atom-Atom | Angle [ ${ }^{\circ}$ ] |
| :--- | :--- |
| As21-As1-As2 | $78.17(3)$ |
| Si1-As1-As21 | $95.65(4)$ |
| Si1-As1-As2 | $95.64(4)$ |
| As3-As4-As31 | $80.10(3)$ |
| Si1-As4-As3 | $96.02(4)$ |
| Si1-As4-As31 | $96.02(4)$ |
| As3-As2-As1 | $108.84(3)$ |


| Atom-Atom-Atom | Angle [${ }^{\circ}$ ] |
| :--- | :--- |
| As2-As3-As4 | $107.93(3)$ |
| As4-Si1-As1 | $116.53(7)$ |
| N1-Si1-As1 | $118.35(14)$ |
| N11-Si1-As1 | $118.35(14)$ |
| N11-Si1-As4 | $112.02(14)$ |
| N1-Si1-As4 | $112.02(14)$ |
| N1-Si1-N11 | $71.8(2)$ |

${ }^{11} 1-x, 2-y, 2-z$

## Data for [Cp*Fe( $\left.\left.\eta^{4}-\mathrm{As}_{6} \mathrm{GeL}\right)\right]$ (5b)



Fig. S19. Molecular structure of 5 b in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms and disorders are omitted for clarity. The $\mathrm{Cp}^{*}$ ligand is drawn in a wire frame model.

Table S13. Selected bond lengths of 5 b.

| Atom-Atom | Length $[\AA ̊]$ |
| :--- | :--- |
| As1-As2 | $2.4394(7)$ |
| As1-As21 | $2.4394(7)$ |
| As1-Ge1 | $2.3775(8)$ |
| As4-Ge1 | $2.3876(8)$ |
| As2-As3 | $2.3796(8)$ |


| Atom-Atom | Length $[\AA \AA]$ |
| :--- | :--- |
| As4-As3 | $2.4454(7)$ |
| As4-As31 | $2.4454(7)$ |
| Ge1-N1 | $1.945(3)$ |
| Ge1-N11 | $1.945(3)$ |
| N1-C1 | $1.326(4)$ |

${ }^{1} 1-x, 2-y, 2-z$

Table S14. Selected angles of 5b.

| Atom-Atom-Atom | Angle [$]$ |
| :--- | :--- |
| As21-As1-As2 | $80.25(3)$ |
| Ge1-As1-As21 | $95.88(2)$ |
| Ge1-As1-As2 | $95.88(2)$ |
| As3-As4-As31 | $78.07(3)$ |
| Ge1-As4-As3 | $95.36(2)$ |
| Ge1-As4-As31 | $95.36(2)$ |
| As3-As2-As1 | $108.87(2)$ |


| Atom-Atom-Atom | Angle [$]$ |
| :--- | :--- |
| As2-As3-As4 | $109.93(2)$ |
| As4-Ge1-As1 | $114.30(3)$ |
| N1-Ge1-As1 | $113.06(10)$ |
| N11-Ge1-As1 | $113.06(10)$ |
| N11-Ge1-As4 | $120.59(10)$ |
| N1-Ge1-As4 | $120.59(10)$ |
| N1-Ge1-N11 | $67.20(18)$ |

${ }^{1} 1-x, 2-y, 2-z$

## 4. Additional Information

## Reaction of $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right]$ ( $\mathrm{I}^{\prime}$ ) with ${ }^{\text {Et }} \mathrm{CAAC}$ :

Dissolving an equimolar amount of $\left[C p^{*} F e\left(\eta^{5}-P_{5}\right)\right]$ ( $I^{\prime}$ ) ( $\left.0.20 \mathrm{mmol}, 69.2 \mathrm{mg}, 1 \mathrm{eq}.\right)$ and ${ }^{\mathrm{Et}} \mathrm{CAAC}(0.21 \mathrm{mmol}, 69.0 \mathrm{mg}$, 1.1 eq.) in toluene at r.t, stirring the mixture for two hours, reducing the volume under reduced pressure, layering with acetonitrile and storing at $-30^{\circ} \mathrm{C}$, leads to the formation of [ $\left.\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}{ }^{\mathrm{Et}} \mathrm{CAAC}\right)\right]$ ( $1^{\prime}$ ). Complex ( $1^{\prime}$ ) crystalizes as dark green/brown blocks alongside with $I^{\prime}$ and ${ }^{\text {Et }} \mathrm{CAAC}$.

Due to the equilibrium of $\mathrm{I}^{\prime}, \mathbf{1}^{\prime}$ and ${ }^{\text {Et }} \mathrm{CAAC}$, all species are present which make an unambiguously spectroscopical analysis impossible.


Fig. S20. Left: Molecular structure of $\mathbf{1}^{\prime}$ in the solid state with thermal ellipsoids at $50 \%$ probability level. Hydrogen atoms and disorders are omitted for clarity. The $\mathrm{Cp}^{*}$ ligand and ${ }^{\mathrm{Et}} \mathrm{CAAC}$ part are drawn in a wire frame model; Right; Various temperature ${ }^{31}{ }^{2}\left\{{ }^{1} \mathrm{H}\right\}$ NMR (193 K (bottom) heated to 313 K (top); toluene- $\mathrm{d}_{8} ; 162.0 \mathrm{~Hz}$ ) with the corresponding ratio of $\mathbf{I}^{\prime}$ and $\mathbf{1}^{\prime}$.

Reaction of I with [SiL] $]_{2}-{ }^{29} \mathrm{Si}\left\{{ }^{1} \mathrm{H}\right\}$ NMR of the reaction mixture:


Fig. S21. Experimental $\left.{ }^{29} \mathrm{Si}^{1}{ }^{1} \mathrm{H}\right\}$ NMR $\left(79.48 \mathrm{MHz}\right.$, THF- $\left.\mathrm{d}_{8}\right)$ spectrum of the reaction of I with $[\mathrm{SiL}]_{2}$.

Reaction of I with [GeL] ${ }_{2}-{ }^{1} \mathrm{H}$ NMR of the reaction mixture:


Fig. S22. Experimental ${ }^{1} \mathrm{H}$ NMR ( 400.13 MHz , toluene $-\mathrm{d}_{8}$ ) spectrum of the reaction of I with $[\mathrm{GeL}]_{2}\left({ }^{*}=\mathrm{THF}\right)$.

## 5. References

[i] O. J. Scherer, C. Blath, G. Wolmershäuser, J. Organomet. Chem. 1990, 387, 21-24.
[ii] O. J. Scherer, T. Brück, Angew. Chem. Int. Ed. 1987, 26, 11987.
[iii] S. Reichl, E. Mädl, F. Riedlberger, M. Piesch, G. Balázs, M. Seidl, M. Scheer, Nat. Commun. 2021, 12, 5774.
[iv] T. K. N. Kuhn, Synthesis (Stuttg). 1993, 6, 561-562.
[v] A. J. Arduengo, J. R. Goerlich, W. J. Marshall, J. Am. Chem. Soc. 1995, 117, 11027-11028.
[vi] S. S. Sen, H. W. Roesky, D. Stern, J. Henn, D. Stalke, J. Am. Chem. Soc. 2010, 132, 1123-1126.
[vii] S. S. Sen, A. Jana, H. W. Roesky, C. Schulzke, Angew. Chem. Int. Ed. 2009, 48, 8536-8538.
[viii] S. Nagendran, S. S. Sen, H. W. Roesky, D. Koley, H. Grubmüller, A. Pal, R. Herbst-Irmer, Organometallics 2008, 27, 5459-5463.

## 10 Additional Findings

The chapter below contains preliminary, unpublished results, some of which stand on their own and cannot be meaningfully assigned to a stand-alone or existing chapter. In addition, some of the following compounds could not be fully characterized or analyzed spectroscopically clean. Nevertheless, the results are intended to provide the basis for future work and publications and are discussed as best as possible.

### 10.1 Quenching of $\left[K(\mathrm{dme})_{2}\right]_{2}\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\mathrm{n}^{4}-\mathrm{P}_{5}\right)\right]$ (1)

### 10.1.1 Reactivity of $\left[\mathrm{K}(\mathrm{dme})_{2}\right]_{2}\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}\right)\right](1)$ towards $\left[\mathrm{Cp}_{2} \mathrm{ZrCl}_{2}\right]$

The reaction of $\left[\mathrm{K}(\mathrm{dme})_{2}\right]_{2}\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\mathrm{n}^{4}-\mathrm{P}_{5}\right)\right]$ (1) with $\left[\mathrm{Cp}_{2} \mathrm{ZrCl}_{2}\right]$ leads to the formation of the anionic monomeric compound $\left[\mathrm{K}(\mathrm{dme})_{3}\right]\left[\left\{\mathrm{Cp}^{*} \mathrm{Fe}\left(\mathrm{n}^{4}-\mathrm{P}_{5}\right)\right\}_{2}\left(\mathrm{Cp}_{2} \mathrm{ZrCl}_{2}\right)\right]$ (T1) (Scheme 1).


Scheme 1. Reaction of 1 with $\left[\mathrm{Cp}_{2} \mathrm{ZrCl}_{2}\right]$.

The molecular structure in the solid state exhibits two $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}\right)\right]$-moieties bridged, by two [ $\mathrm{Cp}_{2} \mathrm{Zr}$ ] fragments, via one phosphorus atom (respectively) which is bent out of the plane. The corresponding P-Zr distances of 2.68-2.69 Å correspond to a slightly shortened single bond. ${ }^{1}$ The zirconium atom exhibit a tetrahedral coordination mode with a nearly square planar surrounding of $94.4^{\circ}$ (P-Zr-P). The complex exhibits an isotropic signal at $g_{\text {iso }}=2.0091$ in the EPR spectra in acetonitrile at 77 K , which shows hyperfine couplings to two phosphorus atoms at r.t. Besides, another broad isotropic signal at $g_{\text {iso }}=2.2480$ is present in solution at r.t. which cannot be assigned. The EPR spectrum of the isolated crystals of T1 in the solid state exhibits only one anisotropic signal at 77 K ( $g_{\text {aniso }}=2.0130$ ) as well as at room temperature (ganiso $=2.0132$ ). According to ${ }^{1} \mathrm{H}$ and ${ }^{31} \mathrm{P}$ NMR spectroscopy in MeCN- $\mathrm{d}_{3}$, the obtained crystals of T1 show impurities, inter alia [ $\left.\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right]\left(1^{\prime}\right)$. However, a broad signal in the ${ }^{1} \mathrm{H}$ NMR at $\delta=0.38 \mathrm{ppm}\left(\omega_{1 / 2}=225 \mathrm{~Hz}\right)$ is present which can be assigned to the $\mathrm{Cp}^{*}$ ligand of T1. Comparing the EPR and NMR spectra in solution, and its impurities, versus the EPR spectrum in the solid state, one can state that acetonitrile leads to a fragmentation of complex T1.

However, the crystals of T1 are insoluble in less polar solvents like THF or DME. Regarding the EPR, NMR, and XRD, one can state that compound (T1) consists of two (formal) [Cp*Fe( $\left.\left.\eta^{4}-\mathrm{P}_{5}\right)\right]$ ] units. Unfortunately, it is not possible to make a reliable statement about the reaction mechanism or side products.


Figure 1. Molecular structure in the solid state of T1. Cation and hydron atoms are omitted for clarity. The Cp and $\mathrm{Cp}{ }^{*}$ ligands are drawn in wire frame model. Thermal ellipsoids are drawn at $50 \%$ probability level.

### 10.1.2 Synthesis of $\left[\left(C p^{\prime \prime \prime} \mathrm{Ta}\right)\left(\mathrm{Cp}{ }^{*} \mathrm{Fe}\right)\left(\mu, \eta^{5}: \eta^{4}-\mathrm{P}_{5}\right)\right]$ (T2)

The salt metathesis reaction of $\left[\mathrm{K}(\mathrm{dme})_{2}\right]_{2}\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\mathrm{n}^{4}-\mathrm{P}_{5}\right)\right]$ (1) 0.5 equivalents of $\left[\mathrm{Cp}^{\prime \prime \prime} \mathrm{TaCl}_{4}\right]$ yields the triple-decker complex $\left[\left(C p^{\prime \prime \prime} T a\right)\left(C p^{*} F e\right)\left(\mu, \eta^{5}: \eta^{4}-P_{5}\right)\right]$ (T2) in $80 \%$ yield (Scheme 2). An isostructural complex $\left[\left(C p^{\prime \prime} T a\right)\left(C p^{*} \mathrm{Fe}\right)\left(\mu, \eta^{5}: n^{4}-\mathrm{P}_{5}\right)\right]$ can be obtained via thermolysis of $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right]$ and $\left[\mathrm{Cp}{ }^{\prime \prime} \mathrm{Ta}(\mathrm{CO})_{4}\right] .^{2}$ The advantage of the given method is the avoidance of the harsh reaction conditions and the usage of $\left[\mathrm{Cp}{ }^{\prime \prime} \mathrm{Ta}(\mathrm{CO}) 4\right],{ }^{3}$ which is only accessible via high pressure ( 400 bar ) CO reaction and an increase in yield from $52 \%$ to $80 \%$.


Scheme 2. Reaction of 1 with [ $\mathrm{Cp}^{\prime \prime \prime} \mathrm{TaCl}_{4}$ ].

The molecular structure in the solid state is depicted in Figure 2 and exhibits, as mentioned above, an isostructural complex like $\left[\left(C p^{\prime \prime} \mathrm{Ta}\right)\left(\mathrm{Cp}^{*} \mathrm{Fe}\right)\left(\mu, \eta^{5}: \eta^{4}-\mathrm{P}_{5}\right)\right]$. Therefore, the structure, as well as its bond lengths and angels, will not be discussed. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ spectrum of T2 reveals an $\mathrm{AM}_{2} \mathrm{X}_{2}$ spin system and is in accordance with the molecular structure in the solid state.


Figure 2. Middle: Molecular structure in the solid state of T2. Hydron atoms are omitted for clarity. The Cp'" and Cp* ligands are drawn in wire frame model. Thermal ellipsoids are drawn at $50 \%$ probability level; Surrounding: ${ }^{31}{ }^{1}\left\{{ }^{1} \mathrm{H}\right\}$ spectrum ( $161.98 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ).

### 10.1.3 Reactivity of $\left[K(d m e)_{2}\right]_{2}\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}\right)\right]$ (1) towards $\left[\mathrm{Cp}{ }^{\prime \prime \prime} \mathrm{Mn}(\mathrm{thf}) I\right]_{2}$

When mixing an equimolar solution of 1 with $\left[\mathrm{Cp}{ }^{\prime \prime \prime} \mathrm{Mn}(\text { (thf })\right]_{2}$, a few crystals of the triple-decker complex $\left[\left(C p^{\prime \prime \prime} \mathrm{Mn}\right)\left(C p^{*} F e\right)\left(\mu, \eta^{5}: \eta^{5}-\mathrm{P}_{5}\right)\right]$ (T3) (see Scheme 3) can be obtained after workup (cf. SI).


Scheme 2. Reaction of 1 with $[C p \text { '" } M n(\text { thf })]_{2}$.

XRD reveals the formation of the first heterometallic manganese containing $P_{n}$ ligand complex. One phosphorus atom of the $\mathrm{P}_{5}$ middle-deck is slightly bent out of the plane $\left(3.65^{\circ}\right)$. The $\mathrm{P}_{5}$ ligand coordinates in a $\eta^{5}$-fashion towards the $\mathrm{Cp}{ }^{*} \mathrm{Fe}-/ \mathrm{Cp}^{\prime \prime \prime} \mathrm{Mn}$-fragment, respectively (Figure 3).


Figure 3. Molecular structure in the solid state of T3. Hydrogen atoms are omitted for clarity. The Cp "' and $\mathrm{Cp}^{*}$ ligands are drawn in wire frame model. Thermal ellipsoids are drawn at $50 \%$ probability level.
${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ of the reaction mixture shows, alongside with $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\mathrm{n}^{5}-\mathrm{P}_{5}\right)\right]\left(1^{1}\right)$, minor sideproduct and one singlet at $\delta=-38.9 \mathrm{ppm}$, which can be attributed to complex T3. Chromatographic workup was not possible due to decomposition. In addition, complex T3 is highly sensitive towards air, cannot been detected via (LIFDI) mass spectrometry and the isolated yield is too low for NMR spectroscopy.

### 10.1.4 Synthesis of $\left[K(\mathrm{dme})_{2}\right]_{2}\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{SSe}\right)\right]$ (T4)

When adding consecutive equimolar solutions of sulfur and red selenium, respectively, in DME to a solution of $\left[\mathrm{K}(\mathrm{dme})_{2}\right]_{2}\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}\right)\right]$ (1), the mixed chalcogen substituted dianionic complex $\left[\mathrm{K}(\mathrm{dme})_{2}\right]_{2}\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{SSe}\right)\right]$ (T4) can be obtained (Scheme 3).


Scheme 3. Consecutive reaction of 1 with first yellow sulfur and second red selenium.

Single crystal X-ray analysis of T4 reveals an [ $\eta^{4}$ - $\mathrm{P}_{5} \mathrm{SSe}$ ]-ligand, featuring sulfur exclusively in the endo position (regarding the envelope of the $\mathrm{P}_{5}$ unit) and selenium in the exo position, respectively (Figure 4). ${ }^{31} \mathrm{P}$ NMR spectroscopy supports the presence of only one species present in solution (besides of tiny amounts of $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right]$ ( $1^{\prime}$ ) as a decomposition product), revealing an AMM'XX' spin system (see Figure 4). The phosphorus sulfur distance (dp-s = 2.05 Å)
is in between a P-S single/ and a double bond. ${ }^{1,4}$ The corresponding phosphorus selenium distance ( dP -Se $=2.19 \AA$ A ) correlates to a P-Se double bond. ${ }^{4}$


Figure 4. Middle: Molecular structure in the solid state of T4. Cation and hydron atoms are omitted for clarity. The Cp * ligand is drawn in wire frame model. Thermal ellipsoids are drawn at $50 \%$ probability level; Surrounding: ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ spectrum ( 161.98 MHz , THF- $\mathrm{d}_{8}$, \# = $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right]$ ).

However, if the order of addition is changed and selenium is added first and afterward sulfur, this leads to an exchange of the chalcogen atoms. This corresponds to a mixed occupation in the solid state. In addition, the ${ }^{31} \mathrm{P}$ NMR shows the presence of four different species (Figure S5): $\quad\left[\mathrm{K}(\mathrm{dme})_{2}\right]_{2}\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\mathrm{n}^{4}-\mathrm{P}_{5} \mathrm{SSe}\right)\right] \quad$ (T4), $\quad\left[\mathrm{K}(\mathrm{dme})_{2}\right]_{2}\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{SeS}\right)\right] \quad$ (T4'), $\left[K(d m e)_{2}\right]_{2}\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{~S}_{2}\right)\right](\#)^{5}\left[\mathrm{~K}(\mathrm{dme})_{2}\right]_{2}\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Se}_{2}\right)\right]\left({ }^{*}\right)^{5}$ (see Figure S 5$)$.


Figure 5. ${ }^{31}{ }^{1}\left\{{ }^{1} \mathrm{H}\right\}$ NMR Spectra ( $161.98 \mathrm{MHz}, \mathrm{DME} / \mathrm{C}_{6} \mathrm{D}_{6}$ capillary); Top: Reaction of 1 with 1. sulfur and 2 . selenium; Bottom: Reaction of 1 with 1. selenium and 2. sulfur.

Unfortunately, the scrambling cannot be avoided using different solvents and/or temperatures and the desired species $\left[\mathrm{K}(\mathrm{dme})_{2}\right]_{2}\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{SeS}\right)\right]$ ( $\mathrm{T} 4^{\prime}$ ) cannot be synthesized spectroscopically pure, nor selective.

In addition, the dianionic complex T4 is highly sensitive toward air and no satisficing elemental analysis could be obtained, even after several attempts of the isolated crystals. Furthermore, compound T4 cannot be detected in (ESI) mass spectrometry.

### 10.1.5 Synthesis of $[K(18 c 6)]_{2}\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{O}_{2}\right)\right]$ (T5)

The reaction of 1 with two equivalents of trimethyl-aminoxide $\left(\mathrm{Me}_{3} \mathrm{NO}\right)$ and 18-crown-6 (18c6) leads to the formation of the dianionic complex $[\mathrm{K}(18 \mathrm{c} 6)]_{2}\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{O}_{2}\right)\right]$ (T5) (Scheme 5)


Scheme 5. Reaction of 1 with $\mathrm{Me}_{3} \mathrm{NO}$ and 18 c 6 .

Single crystal analysis reveals the formation of a di-oxygen substituted $\eta^{4}$ - $\mathrm{P}_{5}$-moiety, coordinating to a Cp*Fe-fragment. The phosphorus-oxygen distances of 1.51 Å correspond to a P-O double bond. ${ }^{4}$ The unit cell contains half a molecule of water, which is not reproducible.


Figure 77. Molecular structure in the solid state of T5. Cation and hydron atoms are omitted for clarity. The Cp* ligand is drawn in wire frame model. Thermal ellipsoids are drawn at $50 \%$ probability level.

Like complex T4, compound T5 cannot be synthesized spectroscopically pure, nor in good yields. The presence of the anionic sideproduct [ $\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{OH}\right)$ ] impedes the selective isolation of T5.

### 10.1.6 Reactivity of $\left[K(d m e)_{2}\right]_{2}\left[C p^{*} F e\left(\eta^{4}-P_{5}\right)\right](1)$ towards yellow arsenic $\left(\mathrm{As}_{4}\right)$

The reaction of in situ generated complex 1 with solid yellow arsenic, under the exclusion of light, leads to the formation of the dianionic polypnictogen complex T6 (Scheme 6). Single crystals suitable for XRD analysis can be obtained from a mixture of DME and $n$-hexane, stored at room temperature.


Scheme 6. Reaction of 1 with yellow arsenic (As4).

As depicted in Figure 7, the molecular structure in the solid state of $[K(d m e)]_{2}\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\mathrm{n}^{4}-\mathrm{P}_{5} \mathrm{As} 2\right)\right]$ (T6) features a formal $\mathrm{E}_{7}{ }^{3-}$ ligand ( $\mathrm{E}=\mathrm{P}, \mathrm{As}$ ). For phosphorus, an isostructural complex is already known. XRD analysis reveals permutations of all atomic positions, occupied by arsenic/phosphorus, respectively (Figure 7). According to ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy and (ESI) mass spectrometry, this phenomenon also occurs in solution.


|  | Ratio |
| :--- | :--- |
| As1/P1 | $0.5: 0.5$ |
| As2/P2 | $0.15 / 0.85$ |
| As3/P3 | $0.12 / 0.88$ |
| As4/P4 | $0.4 / 0.6$ |
| As5/P5 | $0.2 / 0.8$ |
| As6/P6 | $0.3 / 0.7$ |
| As7/P7 | $0.35 / 0.65$ |

Figure 8. Left: Molecular structure in the solid state of T6. Cation and hydron atoms are omitted for clarity. The $\mathrm{Cp}^{*}$ ligand is drawn in wire frame model. Thermal ellipsoids are drawn at $50 \%$ probability level; Right: Occupation / ratio of arsenic to phosphorus in the solid state.

### 10.2 Synthesis of $\left[\left\{\mathrm{Na}(15 \mathrm{c} 5) \mathrm{thf} \mathrm{o}_{0.9}\right\}\{\mathrm{Na}(15 \mathrm{c} 5)\}\right]\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Te}_{2}\right)\right]$ (T7)

The reaction of $\left[\mathrm{K}(\mathrm{dme})_{2}\right]_{2}\left[\mathrm{Cp} \mathrm{p}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}\right)\right]$ (1) with grey tellurium does, according to previous investigations not lead to tellurium functionalized $\mathrm{P}_{\mathrm{n}}$ ligand complex. Therefore, $\mathrm{Na}_{2} \mathrm{Te}$ was used as a tellurium source. Mixing one equivalent of $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right]\left(1^{\prime}\right)$ with two equivalents of $\mathrm{Na}_{2} \mathrm{Te}$ and four equivalents of 15 -crown-5 in DME at room temperature leads to the formation of a white unidentified sideproduct solid and a change in color from green to red. Workup of the highly air-sensitive reaction mixture, leads to single crystals of $[\{\mathrm{Na}(15 \mathrm{c} 5)$ thfo. 9$\}\{\mathrm{Na}(15 \mathrm{c} 5)\}]\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Te}_{2}\right)\right]$ (T7) (Scheme 7). NMR spectroscopy of the isolated crystals exhibits the presence of at least two sideproduct, inter alia a paramagnetic one. The consecutive reaction of T 7 with $\mathrm{Ph}_{3} \mathrm{PO}$ leads to the better soluble complex T 7 , which can be obtained, according to NMR spectroscopy, pure.


Scheme 7. Reaction of 1 ' with $\mathrm{Na}_{2} \mathrm{Te}$ and 15 c 4 .

Single-crystal X-ray analysis of T7 reveals the formation of a di-tellurium substituted $\eta^{4}-P_{5}$ moiety, coordinating to a $\mathrm{Cp}^{*} \mathrm{Fe}$-fragment (Figure 8). The phosphorus-oxygen distances of 2.35 - $2.48 \AA$ are in between a P-Te single- and a double bond. ${ }^{1,4}$ XRD analysis of T7' $\left(\left[\{\mathrm{Na}(15 \mathrm{c} 5)\}\left\{\mathrm{Na}\left(\mathrm{Ph}_{3} \mathrm{PO}\right)(15 \mathrm{c} 5)\right\}\right]\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Te}_{2}\right)\right]\right)$ exhibits no substitution of Tellurium with oxygen on the $\mathrm{P}_{5}$ moiety, but the coordination of $\mathrm{Ph}_{3} \mathrm{PO}$ to sodium.


Figure 8. Molecular structure in the solid state of T7. Cation and hydron atoms are omitted for clarity. The Cp* ligand is drawn in wire frame model. Thermal ellipsoids are drawn at $50 \%$ probability level.

Unfortunately, it is not possible to make a reliable statement about the reaction mechanism or side products. Furthermore, both complexes T7 and T7' cannot be detected in (ESI) mass spectrometry, nor its constitution can be proven by elemental analysis, presumably due to their high sensitivity.

### 10.3Reactivity of $P_{n}$ ligand Complexes towards ${ }^{\text {Et }}$ CAAC

### 10.3.1 Reactivity of [Cp'"Ni( $\left.\left.\eta^{3}-\mathrm{P}_{3}\right)\right]$ (2) towards ${ }^{\text {Et }} \mathrm{CAAC}$

The reaction of $\left[\mathrm{Cp}^{\prime \prime \prime} \mathrm{Ni}\left(\eta^{3}-\mathrm{P}_{3}\right)\right]$ (2) with ${ }^{\text {Et }} \mathrm{CAAC}$ resulted in the formation of two, not separatable complexes, $\left[\left(\mathrm{Cp}{ }^{\prime \prime \prime} \mathrm{Ni}\right)_{2}\left\{\mu, \eta^{3}: \eta^{3}-\mathrm{P}_{6}\left({ }^{(\mathrm{Et}} \mathrm{CAAC}\right)_{2}\right\}\right]$ (T8) and $\left[\mathrm{Cp}^{\prime \prime \prime} \mathrm{Ni}\left\{\eta^{2}-\mathrm{P}_{3}\left({ }^{(\mathrm{Et}} \mathrm{CAAC}\right)_{2}\right\}\right]$ (T9) (Scheme 8). According to ${ }^{31} P\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy, the amount of ${ }^{\text {Et }} \mathrm{CAAC}$ (one or two equivalents) has an impact on the ratio of T8:T9, but cannot suppress one or the other, respectively. Both complexes can be detected via (LIFDI) mass spectrometry. Fractionalized crystallization is not possible due to a similar solubility. However, crystals suitable for XRD analysis can be obtained from toluene/acetonitrile.


Scheme 8. Reaction of 2 with ${ }^{\text {Et CAAC. }}$

Single crystal X-ray analysis of complex T8 reveals the formation of ${ }^{\mathrm{Et}} \mathrm{CAAC}-\mathrm{P}_{6}-\mathrm{Et} \mathrm{CAAC}$ chainlike ligand, coordinating to two [Cp'"Ni] fragments (see Figure 9). The newly formed carbon phosphorus bonds ( $\mathrm{d}_{\mathrm{c}-\mathrm{p}}=1.73-1.74 \AA$ ) are in between a C-P single-/double bond. ${ }^{1,4}$ The phosphorus chain features bond lengths of $2.21 \AA$ (P1-P2/P5-P6) and $2.16 \AA$ (P2-P3/P4-P5), respectively. The distance between P 3 and P 4 is $2.40 \AA$ and can therefore not be considered as a bond, but at most as an interaction. This gives a hint about a possible mechanism, whereas one ${ }^{\text {Et }} \mathrm{CAAC}$ molecule activates $\left[\mathrm{Cp}^{\prime \prime \prime} \mathrm{Ni}\left(\eta^{3}-\mathrm{P}_{3}\right)\right]$ (2), followed by a ring-opening and consecutive aggregation of two [Cp'"Ni\{n $\left.\left.{ }^{2}-\mathrm{P}_{3}\left({ }^{\text {Et }} \mathrm{CAAC}\right)\right\}\right]$ fragments. This assumption is supported by the molecular structure in the solid state of complex T9, which features ${ }^{\text {Et }} C A A C-\mathrm{P}_{3}-\mathrm{Et}^{\mathrm{Et}} \mathrm{CAAC}$ chainlike ligand, coordinating in a $\eta^{2}$-fashion to one [Cp'"Ni] moiety (Figure 9). The corresponding bond distances are similar to complex T8, comprising P-P lengths of 2.15 (P1-P2) - 2.22 (P2-P3) Å. The formation of complex T8 can be considered as the competing reaction to T9, depending on whether aggregation of the preliminary [Cp'"Ni\{n2-
$\left.\left.\mathrm{P}_{3}\left({ }^{\text {Et }} \mathrm{CAAC}\right)\right\}\right]$ fragment reacts with $\left[\mathrm{Cp}{ }^{\prime \prime \prime} \mathrm{Ni}\left(n^{3}-\mathrm{P}_{3}\right)\right]$ (2) (leading to T 8 ) or ${ }^{\text {Et }} \mathrm{CAAC}$ (leading to T9).
This is in alignment with the previously stated impact on the used amount of ${ }^{\mathrm{Et}} \mathrm{CAAC}$. To prove this assumption further investigations e.g., calculations must be made. In addition, according to ${ }^{1} \mathrm{H}$ NMR, another (paramagnetic) sideproduct is present.


T8


T9

Figure 9. Molecular structure in the solid state of T8 and T9. Hydron atoms are omitted for clarity. The Cp'" ligands


### 10.3.2 Synthesis of $\left[\mathrm{Cp}{ }^{\prime \prime \prime} \mathrm{Ta}(\mathrm{CO})_{2}\left\{\eta^{3}-\mathrm{P}_{4}\left(\mathrm{Et}^{\mathrm{t}} \mathrm{CAAC}\right)_{2}\right\}\right]$ (T10)

When mixing $\left[\mathrm{Cp}^{\prime \prime \prime} \mathrm{Ta}(\mathrm{CO})_{2}\left(\eta^{4}-\mathrm{P}_{4}\right)\right]$ (3) with Et CAAC complex T 10 can be obtained (Scheme 9).


3
$+$

${ }^{E t} C A A C$


T10

Scheme 9. Reaction of 3 with EtCAAC.

Single crystals $X$-ray analysis reveals the formation of a ${ }^{\text {Et }} C A A C-P_{4}-{ }^{\text {Et }} C A A C$ chain-like ligand, coordinating in a $\eta^{3}$-fashion to one $\left[\mathrm{Cp}{ }^{\prime \prime \prime} \mathrm{Ta}(\mathrm{CO})_{2}\right]$ fragment (Figure 10), comprising similar bond lengths like complex T9. ${ }^{31}$ P\{ $\left.{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy exhibits four signals with integrals of 1 each, respectively (see Figure 10). The assignment of the corresponding phosphorus atoms (Figure 10) was done in accordance to similar findings. ${ }^{6}$


Figure 10. Molecular structure in the solid state of T10. Hydron atoms are omitted for clarity. The Cp'" ligands and ${ }^{E t} C A A C$ substituents are drawn in wire frame model. Thermal ellipsoids are drawn at $50 \%$ probability level; Surrounding: ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ spectrum ( $161.98 \mathrm{MHz}, \mathrm{THF}-\mathrm{d}_{8}$ ).

In contrast to the previously discussed reaction, no aggregation nor the formation of a T8 like complex can be observed via XRD analysis, mass spectrometry or ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy.

### 10.4Reactivity of $\left[\left\{\mathrm{CpMo}(\mathrm{CO})_{2}\right\}_{2}\left(\mu, \eta^{2}: \eta^{2}-\mathrm{P}_{2}\right)\right]$ (4) towards IMe and ${ }^{\text {Et }} \mathrm{CAAC}$

### 10.4.1 Synthesis of $\left[(\mathrm{IMe})_{2} \mathrm{P}\right]\left[\left\{\mathrm{CpMo}(\mathrm{CO})_{2}\right\}_{2}\left(\mu, \eta^{1}: \eta^{1-P-I M e}\right)\right]$ (T11)

The reaction of $\left[\left\{\mathrm{CpMo}(\mathrm{CO})_{2}\right\}_{2}\left(\mu, \eta^{2}: \eta^{2}-\mathrm{P}_{2}\right)\right]$ (4) with three equivalents of $1,3,4,5-$ tetramethylimidazol-2-ylidene ( IMe ) yields the selective formation of the anionic complex T11 (Scheme 10). Dark purple single crystals can be obtained from an acetonitrile/toluene solution, stored at $-30^{\circ} \mathrm{C}$.


Scheme 10. Reaction of 4 with IMe.

Under NHC induced phosphorus abstraction, and the formation of the [(IMe) $\left.{ }_{2} \mathrm{P}\right]$ cation, the anion $\left[\left\{\mathrm{CpMo}(\mathrm{CO})_{2}\right\}_{2}\left(\mu, \eta^{1}: n^{1}-\mathrm{P}-\mathrm{IMe}\right)\right]$ is formed. According to XRD analysis and ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}$ spectroscopy, T11 features an NHC stabilized phosphinidenide type phosphorus atom (P2) (Figure 11). Its corresponding signal in the phosphorus at $\delta=587.5 \mathrm{ppm}$ is shifted to high ppm values. The phosphorus molybdenum distances of $2.34 \AA$ are in between a single and double bond, ${ }^{1,4}$ whereas the P-C distance of $1.86 \AA$ A corresponds to a single bound. ${ }^{1}$


Figure 11. Molecular structure in the solid state of T11. Hydron atoms are omitted for clarity. The Cp ligands, CO and IMe-substituents are drawn in wire frame model. Thermal ellipsoids are drawn at 50 \% probability level; Surrounding: ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ spectrum ( $161.98 \mathrm{MHz}, \mathrm{MeCN}-\mathrm{d}_{3}$ ).

### 10.4.2 Reaction of $\left[\left\{\mathrm{CpMo}(\mathrm{CO})_{2}\right\}_{2}\left(\mu, \eta^{2}: \eta^{2}-\mathrm{P}_{2}\right)\right]$ (4) with ${ }^{\text {Et }} \mathrm{CAAC}$

When mixing an equimolar solution of $\left[\left\{\mathrm{CpMo}(\mathrm{CO})_{2}\right\}_{2}\left(\mu, \eta^{2}: \eta^{2}-\mathrm{P}_{2}\right)\right]$ (4) and ${ }^{\text {Et }} \mathrm{CAAC}$, compound $\left[\left\{\mathrm{CpMo}(\mathrm{CO})_{2}\right\}_{2}\left(\mu, \eta^{2}: \eta^{1}-\mathrm{P}_{2}-{ }^{\text {Et }} \mathrm{CAAC}\right)\right]$ (T12) is formed, which is in equilibrium with 4 and ${ }^{\mathrm{Et}} \mathrm{CAAC}$ (Scheme 11). Single crystals of T12 show a decomposition below 150 K and ${ }^{31}{ }^{1}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy reveals the presence of 4 and T12.


Scheme 11. Reaction of 4 with EtCAAC.

Complex T12 co-crystalizes with compound 4 and ${ }^{\text {Et }}$ CAAC. As depicted in Figure 12, ${ }^{\text {Et C CAAC }}$ reacts with the $\mathrm{P}_{2}$ unit, leading to a $\mathrm{P}-\mathrm{C}$ single bond ${ }^{1}$ ( $\mathrm{d}_{\mathrm{P} 2-\mathrm{C} 1}=1.88 \AA$ ), whereas the initial Mo1P2 bond is broken. The usage of two equivalents of ${ }^{\text {Et }}$ CAAC does not lead to a consecutive reaction, instead the ratio of 4:T12 is shifted towards the latter (according to ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}$ spectroscopy). Due to the given equilibrium, complex T12 cannot be synthesized spectroscopically pure.


Figure 9. Molecular structure in the solid state of T12. Hydron atoms are omitted for clarity. The Cp ligands, COand IMe substituents are drawn in wire frame model. Thermal ellipsoids are drawn at $50 \%$ probability level.

### 10.5Supporting Information

### 10.5.1 General Remarks

All manipulations were carried out under an inert atmosphere of dried argon using standard Schlenk and glove box techniques. 1,2-dimethoxyethane (DME) was dried and deoxygenated by distillation under argon atmosphere from sodium. All other solvents were dried using a MB SPS-800 device of the company MBRAUN and stored over molecular sieve. NMR spectra were recorded on a Bruker Avance III $400 / 600 \mathrm{MHz}$ NMR spectrometer. Chemical shifts were measured at ambient temperature and are given in ppm; they are referenced to TMS for ${ }^{1} \mathrm{H}, 85 \% \mathrm{H}_{3} \mathrm{PO}_{4}$ for ${ }^{31} \mathrm{P}$ and $\mathrm{SeMe}_{2}$ for ${ }^{77} \mathrm{Se}$ as external standard. Signal multiplicities are described using common abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet) and br (broad). LIFDI-/FD-/EI-MS spectra (LIFDI = liquid injection field desorption ionization) were measured on a JEOL AccuTOF GCX. ESI-MS spectra (ESI = Electrospray ionization) were measured on an Agilent Q-TOF 6540 UHD. Elemental analysis (CHN) was determined using a Vario micro cube instrument. The X-band EPR measurements were carried out with a MiniScope MS400 device equipped with a Magnettech GmbH rectangular TE102 resonator at a frequency of 9.5 GHz .

Crystals suitable for single crystal X-ray diffraction analysis were obtained as described in the corresponding synthetic protocols below. The diffraction data were collected either on a Gemini Ultra diffractometer equipped with an Atlas ${ }^{52}$ CCD detector and with a fine-focus sealed Cu-K ${ }_{\alpha}$ X-ray tube, on a XtaLAB Synergy R, DW system diffractometer equipped with a HyPix-Arc 150 detector and a rotating-anode $\mathrm{Cu}-\mathrm{K}_{\mathrm{a}} \mathrm{X}$-ray tube or a GV50 diffractometer equipped with a Titan ${ }^{52}$ CCD detector and a micro-focus $\mathrm{Cu}-\mathrm{K}_{\alpha} \mathrm{X}$-ray tube. Data collection and reduction were performed with CrysAlisPro software package. The structures were solved with Olex2 ${ }^{48}$, using SheIXT ${ }^{49}$ and a least-square refinement on $F^{2}$ was carried out with SheIXL ${ }^{50}$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms at the carbon atoms were located in idealized positions and refined with isotropic displacement parameters according to the riding model. The images of the molecular structures were made using Olex2 ${ }^{48}$.

### 10.5.2 Experimental Details and Analytical Data

Synthesis of $\left[\mathrm{K}(\mathrm{dme})_{3}\right]\left[\left\{\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}\right)\right\}_{2}\left(\mathrm{Cp}_{2} \mathrm{ZrCl}_{2}\right)\right]$ (T1):
A $-50^{\circ} \mathrm{C}$ cold solution of $\left[\mathrm{Cp}_{2} \mathrm{ZrCl}_{2}\right]$ ( $0.299 \mathrm{mmol}, 87.4 \mathrm{mg}, 1$ eq.) in DME was added to an in situ generated $-50^{\circ} \mathrm{C}$ cold solution of 1 ([Cp*Fe( $\left.\left.\eta^{5}-P_{5}\right)\right]\left(1^{\prime}\right): 0.299 \mathrm{mmol}, 103.4 \mathrm{mg}, 1$ eq.; $\mathrm{KC} \mathrm{C}_{8}: 0.748 \mathrm{mmol}, 101.1 \mathrm{mg}, 2.5 \mathrm{eq}$.) in DME. A colour change from green to red occurred and a colourless solid was formed. The mixture was stirred for overnight and allowed to reach room temperature. The solvent was removed under reduced pressure. The residue was washed with $n$-hexane ( $3 \times 5 \mathrm{~mL}$ ), extracted with DME and filtered over diatomaceous earth. The volume was reduced under reduced pressure, layered with toluene and stored at room temperature. $\left[\mathrm{K}(\mathrm{dme})_{3}\right]\left[\left\{\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}\right)\right\}_{2}\left(\mathrm{Cp}_{2} \mathrm{ZrCl}\right)\right]$ (T1) can be obtained as dark blocks. Yield: $153.4 \mathrm{mg}(0.10 \mathrm{mmol}, 67 \%) .{ }^{1} \mathrm{H}$ NMR ( $\mathrm{MeCN}_{3}, 293 \mathrm{~K}$ ): $\delta$ [ppm] = 6.71 ( $\mathrm{m}, 5 \mathrm{H}$, toluene), 3.46 ( $\mathrm{s}, 12 \mathrm{H}, \mathrm{DME}$ ), 3.29 (s, $18 \mathrm{H}, \mathrm{DME}$ ), 2.98 ( $\mathrm{m}, 1 \mathrm{H}$, unidentified sideproduct), 2.14 ( $\mathrm{s}, \mathrm{br}, 3 \mathrm{H}$, unidentified sideproduct), 1.48 ( $\mathrm{s}, 1 \mathrm{H}$, unidentified sideproduct), $1.43(\mathrm{~s}, 4 \mathrm{H}$, unidentified sideproduct), $1.22(t, 1 \mathrm{H}, J=6.92 \mathrm{~Hz}$, unidentified sideproduct), $0.40\left(\mathrm{~s}, \mathrm{br}, \omega 1 / 2=225 \mathrm{~Hz}, 14 \mathrm{H}, \mathrm{Cp}^{*}\right.$ ), no signals for the corresponding Cp ligand are present in the range from +20 to $-40 \mathrm{ppm} .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{MeCN}_{3}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=151.8$ (s, ([Cp*Fe( $\left.\left.\eta^{5}-\mathrm{P}_{5}\right)\right]\left(1^{\prime}\right)$ as decomposition product)*. ${ }^{31} \mathrm{P} \mathrm{NMR}\left(\mathrm{MeCN}_{3}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=151.8\left(\mathrm{~s},{ }^{*}\right)$. EPR (MeCN, 77 K$): g_{\text {iso }}=2.0091 . \operatorname{EPR}(\mathrm{MeCN}, 293 \mathrm{~K}): g_{\text {iso }}=2.2480$ (impurity or decomposition); $g_{\text {iso }}=2.0080$. EPR (solid state, 77 K ): $g_{\text {aniso }}=2.0130$. EPR (solid state, 293 K ): $g_{\text {aniso }}=2.0132$. ESI-MS (DME): $m / z=1133.81\left(100 \%,[M]^{+}\right), 346.93\left(5 \%,\left[1^{\prime}\right]^{+}\right)$. No satisfying elemental analysis could be obtained after several attempts of the isolated crystals.

## Synthesis of $\left[\left(C p^{\prime \prime \prime} T a\right)\left(C p^{*} F e\right)\left(\mu, \eta^{5}: \eta^{4}-P_{5}\right)\right]$ (T2):

A $-50^{\circ} \mathrm{C}$ cold suspension of [ $\left.\mathrm{Cp}^{\prime \prime \prime} \mathrm{TaCl}_{4}\right]$ ( $1.49 \mathrm{mmol}, 829 \mathrm{mg}, 1 \mathrm{eq}$.) in DME was added to an in situ generated $-50^{\circ} \mathrm{C}$ cold solution of 1 ([Cp*Fe(n $\left.\left.{ }^{5}-\mathrm{P}_{5}\right)\right]\left(1^{\prime}\right): 2.89 \mathrm{mmol}, 999.8 \mathrm{mg}, 2$ eq.; $\left.\mathrm{KC}_{8}: 7.23 \mathrm{mmol}, 997.4 \mathrm{mg}, 5 \mathrm{eq}.\right)$ in DME. The green colour darkened and a colourless solid was formed. The mixture was stirred for three hours and allowed to reach room temperature. The solvent was removed under reduced pressure. The residue was dissolved in dichloromethane, silica is added, and the solvent was removed in vacuo. The preabsorbed reaction mixture was purified via column chromatography $\left(\mathrm{SiO}_{2}\right.$, hexane, $\left.25 \times 3 \mathrm{~cm}\right)$. Using $n$-hexane, a first green fraction of ( $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right]\left(1^{\prime}\right)$ can be eluted. Adding toluene (hexane/toluene ( $\left.9: 1\right)$ ) yields $\left[\left(\mathrm{Cp}{ }^{\prime \prime \prime} \mathrm{Ta}^{2}\right)\left(\mathrm{Cp}^{*} \mathrm{Fe}\right)\left(\mu, \eta^{5}: \eta^{4}-\mathrm{P}_{5}\right)\right]$ (T2) as a second green fraction. The solvent of both fractions was removed under reduced pressure. $\left[\left(C p{ }^{\prime \prime \prime} T a\right)\left(C p^{*} \mathrm{Fe}\right)\left(\mu, \eta^{5}: \eta^{4}-\mathrm{P}_{5}\right)\right]$ (T2) can be isolated as dark green plates after one day from a toluene $/ n$-hexane solution, and stored at $-30^{\circ} \mathrm{C}$. Yield: $904.7 \mathrm{mg}(1.19 \mathrm{mmol}, 80 \%) .{ }^{1} \mathrm{H} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=6.08(\mathrm{~s}, 2 \mathrm{H}$, $\left.\mathrm{C}_{5} \mathrm{H}_{2}\left({ }^{(t \mathrm{Bu}}\right)_{3}\right), 1.63\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right), 1.29\left(\mathrm{~s}, 18 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{2}\left({ }^{(\mathrm{Bu}}\right)_{3}\right), 1.13\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{2}\left({ }^{(t \mathrm{Bu}}\right)_{3}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right):$ $\delta[\mathrm{ppm}]=217.5\left(\mathrm{t},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{P}}=199.6 \mathrm{~Hz}, 1 \mathrm{P}, \mathrm{P}_{1}\right), 171.9\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{P}}=400.7 \mathrm{~Hz}, 2 \mathrm{P}, \mathrm{P}_{3,5}\right),-287.1\left(\mathrm{dd},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{P}}=199.6 \mathrm{~Hz},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{P}}=\right.$ $\left.400.7 \mathrm{~Hz}, 2 \mathrm{P} \mathrm{P}_{2,4}\right) .{ }^{31} \mathrm{P}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=217.5\left(\mathrm{t},{ }^{1} \mathrm{~J}_{\mathrm{p}-\mathrm{p}}=199.6 \mathrm{~Hz}, 1 \mathrm{P}, \mathrm{P}_{1}\right), 171.9\left(\mathrm{~d},{ }^{1}{ }_{\mathrm{Jp}-\mathrm{p}}=400.7 \mathrm{~Hz}\right.$, $2 \mathrm{P}, \mathrm{P}_{3,5}$ ), -287.1 (dd, $\left.{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{P}}=199.6 \mathrm{~Hz},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{p}}=400.7 \mathrm{~Hz}, 2 \mathrm{P} \mathrm{P} \mathrm{P}_{2,4}\right)$. LIFDI-MS (toluene): $\mathrm{m} / \mathrm{z}=760.05\left(100 \%,[\mathrm{M}]^{+}\right)$. Analysis (calcd., found for $\mathrm{C}_{27} \mathrm{H}_{44} \mathrm{FeTaP} 5$ ): $\mathrm{C}(42.65,43.11), \mathrm{H}(5.83,5.73)$.

## Synthesis of $\left[\left(C p^{\prime \prime \prime} \mathrm{Mn}\right)\left(\mathrm{Cp}{ }^{*} \mathrm{Fe}\right)\left(\mu, \eta^{5}: \eta^{5}-\mathrm{P}_{5}\right)\right]$ (T3):

A $-80^{\circ} \mathrm{C}$ cold solution of $\left[\mathrm{Cp}^{\prime \prime \prime} \mathrm{Mn}(\mathrm{thf}) \mathrm{I}_{2}\right]_{2}(0.299 \mathrm{mmol}, 292.4 \mathrm{mg}, 1 \mathrm{eq}$.) in THF was added to an in situ generated $-80^{\circ} \mathrm{C}$ cold solution of 1 ([ $\left.\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right]\left(1^{\prime}\right): 0.299 \mathrm{mmol}, 103.4 \mathrm{mg}, 1 \mathrm{eq} . ; \mathrm{KC}$ : $0.748 \mathrm{mmol}, 101.1 \mathrm{mg}, 2.5 \mathrm{eq}$.) in THF. The mixture was stirred for overnight and allowed to reach room temperature. A colour change from green to brown occurred and a colourless solid was formed. The solvent was removed under reduced pressure. The residue was extracted with $n$-pentane and filtered over diatomaceous earth. The volume was reduced under reduced pressure and stored at $8^{\circ} \mathrm{C}$. Complex T 3 can be obtained as brown-greenish plates. Yield: few crystals. ${ }^{1} \mathrm{H}$ NMR
 0.88 (s, $\left.12 \mathrm{H}, \mathrm{C}_{5}\left(\mathrm{CH}_{3}\right)_{5}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=152.8\left(\mathrm{~s}, 1 \mathrm{P}, 1^{\prime}\right),-38.4(\mathrm{~s}, 103 \mathrm{P}, \mathrm{T} 3) .{ }^{31} \mathrm{P}$ NMR ( $\mathrm{C}_{6} \mathrm{D}_{6}$, 293 K ): $\delta[\mathrm{ppm}]=152.8$ (s, 1 P, 1'), -38.4 ( $\mathrm{s}, 103 \mathrm{P}, \mathrm{T} 3$ ). LIFDI-MS (toluene): $m / z=345.91$ (100 \%, [Cp*Fe( $\left.\left.\eta^{5}-\mathrm{P}_{5}\right)\right]^{+}$). Due to the small amount of T3 no elemental analysis could be performed.

## Synthesis of $\left[K(\mathrm{dme})_{2}\right]_{2}\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{SSe}\right)\right]$ (T4):

-Preliminary Preparation of $\left[K(\mathrm{dme})_{2}\right]_{2}\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\mathrm{n}^{4}-\mathrm{P}_{5} \mathrm{~S}\right)\right]$ (TS4) according to literature-.${ }^{5}$ Red selenium ( 0.2 mmol , 15.8 mg , 1 eq.) was dissolved in DME and added to an equimolar solution of [K(dme) $\left.)_{2}\right]_{2}\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\mathrm{n}^{4}-\mathrm{P}_{5} \mathrm{~S}\right)\right]$ (TS4) ( 0.20 mmol, $127 \mathrm{mg}, 1 \mathrm{eq}$.) in DME at room temperature. The solution was allowed to stir overnight. The volume was reduced in vacuo, the reaction mixture layered with $n$-hexane and stored at r.t. Complex (T4) can be obtained as dark green
plates.
Yield: $100.2 \mathrm{mg}(0.14 \mathrm{mmol}, 69 \%) .{ }^{1} \mathrm{H}$ NMR (THF- $\left.\mathrm{d}_{8}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=3.43(\mathrm{~s}, 7 \mathrm{H}, \mathrm{DME}), 1.63(\mathrm{~s}, 10 \mathrm{H}, \mathrm{DME}), 1.61$ ( $\mathrm{s}, 15 \mathrm{H}, \mathrm{Cp}^{*}$ ). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{THF}-\mathrm{d}_{8}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=152.1\left(\mathrm{~s}, 2 \mathrm{P}, 1^{\prime}\right), 143.4\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 23.1\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}}\right),-0.5$ ( $\mathrm{m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{X}, \mathrm{x})}$. ${ }^{31} \mathrm{P}$ NMR (THF- $\left.\mathrm{d}_{8}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=152.1\left(\mathrm{~s}, 2 \mathrm{P}, 1^{\prime}\right), 143.4\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 23.1\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}}\right),-0.5(\mathrm{~m}$, $2 \mathrm{P}, \mathrm{P}_{\mathrm{X}, \mathrm{x}}$ ). ${ }^{77} \mathrm{Se}\left(\mathrm{THF}-\mathrm{d}_{8}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=-83.6\left(\mathrm{~m},{ }^{1} \mathrm{~J}_{\mathrm{se}-\mathrm{P}}=480.6 \mathrm{~Hz}\right)$. ESI-MS (DME): $\mathrm{m} / \mathrm{z}=458.92\left(55 \%,[\mathrm{MH}]^{+}\right)$, $378.9\left(100 \%,\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{O}_{2}\right)-\mathrm{H}\right]^{+}\right)$. No satisfying elemental analysis could be obtained after several attempts of the isolated crystals.

## Synthesis of $[K(18 c 6)]_{2}\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\mathrm{n}^{4}-\mathrm{P}_{5} \mathrm{O}_{2}\right)\right]$ (T5):

An in situ generated solution of 1 ([ $\left.\mathrm{Cp}^{*} \mathrm{Fe}\left(\mathrm{r}^{5}-\mathrm{P}_{5}\right)\right]\left(1^{\prime}\right): 0.20 \mathrm{mmol}, 69.2 \mathrm{mg}, 1 \mathrm{eq} . ; \mathrm{KC}_{8}: 0.50 \mathrm{mmol}, 67.6 \mathrm{mg}, 2.5 \mathrm{eq}$.) in DME was added to a suspension of $\mathrm{Me}_{3} \mathrm{NO}(0.40 \mathrm{mmol}, 30.0 \mathrm{mg}$, 2 eq .) in DME at r.t. In Addition, a cold solution of 18 c 6 ( $0.40 \mathrm{mmol}, 105.7 \mathrm{mg}$, 2 eq .) in DME was added to the reaction mixture and was stirred for overnight. The volume was reduced in vacuo, the reaction mixture layered with toluene and stored at $-30^{\circ} \mathrm{C}$. Complex (T5) can be obtained as dark blocks.
Yield: $25.0 \mathrm{mg}(0.027 \mathrm{mmol}, 14 \%) .{ }^{1} \mathrm{H}$ NMR (THF-d $\mathrm{d}_{8}, 293 \mathrm{~K}$ ): $\delta[\mathrm{ppm}]=3.66$ (s, $53 \mathrm{H}, 18 \mathrm{c} 6$ ), 2.73 (s, br, unidentified sideproduct), 1.65 (s, $\left.15 \mathrm{H}, \mathrm{Cp}^{*}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{THF}-\mathrm{d}_{8}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=144.8\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 2.4\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}}\right),-64.8$ ( $\mathrm{m}, 2 \mathrm{P}, \mathrm{P}_{\left.\mathrm{X}, \mathrm{X}^{\prime}\right)} .{ }^{31} \mathrm{P}$ NMR (THF- $\mathrm{d}_{8}, 293 \mathrm{~K}$ ): $\delta[\mathrm{ppm}]=144.8\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 2.4\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}^{\prime}}\right),-64.8\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{X}, \mathrm{X}}\right)$. ESI-MS (DME): $m / z=378.91\left(100 \%,[M H]^{+}\right), 362.96\left(88 \%,\left[C p^{*} F e\left(n^{4}-\mathrm{P}_{5} \mathrm{OH}\right)\right]^{+}\right)$. No satisfying elemental analysis could be obtained after several attempts of the isolated crystals.

## Synthesis of $[K(\mathrm{dme})]_{2}\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\mathbf{\eta}^{4}-\mathrm{P}_{5} \mathrm{~A} \mathrm{~s}_{2}\right)\right]$ (T6):

The solvent of a freshly prepared solution of yellow arsenic ${ }^{9}$ in $\mathrm{CS}_{2}$ was removed in vacuo and an in situ generated solution of 1 ( $\left[C p^{*} F e\left(\eta^{5}-P_{5}\right)\right]\left(1^{\prime}\right): 0.30 \mathrm{mmol}, 103.8 \mathrm{mg}, 1$ eq.; $\mathrm{KC}_{8}: 0.75 \mathrm{mmol}, 101.4 \mathrm{mg}, 2.5 \mathrm{eq}$. ) in DME was added. The mixture was stirred for two hours under the exclusion of light and grey arsenic is formed. The solvent was removed under reduced pressure. The residue was extracted with DME and filtered over diatomaceous earth, the volume of the filtrate was lowered under reduced pressure, layered with $n$-hexane and stored at r.t. Complex (T5) can be obtained as dark plates. Yield: 180.0 mg ( $0.24 \mathrm{mmol}, 80 \%$ ). ${ }^{1} \mathrm{H}$ NMR (THF-d ${ }_{8}, 293 \mathrm{~K}$ ): $\delta$ [ppm] = 3.42 (s, $8 \mathrm{H}, \mathrm{DME}$ ), 3.27 (s, $12 \mathrm{H}, \mathrm{DME}$ ), 2.73 ( s , br, unidentified sideproduct), a variety of signals in the region $1.37-1.60 \mathrm{ppm}$, assuming $\mathrm{Cp}^{*}$-signals, overlaying each other. ${ }^{31}$ P $\left\{{ }^{1} \mathrm{H}\right\}$ NMR (THF-d $8,293 \mathrm{~K}$ ): plethora of different signals, featuring multiplets and can be due to their complexity not assigned (see Figure SXX). ${ }^{31}$ P NMR (THF-d ${ }_{8}, 293 \mathrm{~K}$ ): see above. ESI-MS (DME): $m / z=408.88$ ( $100 \%$,

 $\left.\left[C p^{*} \mathrm{Fe}\left(n^{4}-\mathrm{PAs}_{6} \mathrm{H}\right)\right]^{+}\right), 716.51\left(<1 \%,\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{As}_{7} \mathrm{H}\right)\right]^{+}\right)$. No satisfying elemental analysis could be obtained after several attempts of the isolated crystals.

## Synthesis of $\left[\left\{\mathrm{Na}(15 \mathrm{c} 5)\right.\right.$ thf $\left.\left.\mathrm{o}_{0.9}\right\}\{\mathrm{Na}(15 \mathrm{c} 5)\}\right]\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Te}_{2}\right)\right](\mathrm{T} 7)$ :

( $\left[C p^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right]$ ( $1^{\prime}$ ) ( $\left.0.30 \mathrm{mmol}, 103.8 \mathrm{mg}, 1 \mathrm{eq}.\right)$ and $\mathrm{Na}_{2} \mathrm{Te}(0.30 \mathrm{mmol}, 51.1 \mathrm{mg}, 1 \mathrm{eq}$.$) were dissolved in DME. To$ the resulting suspension, a 0.667 molar solution of 15 c 5 in DME ( $0.80 \mathrm{mmol}, 1.2 \mathrm{~mL}, 2.67 \mathrm{eq}$.) was added. The mixture was stirred overnight. Thereby, the color changed to red/brown and a colorless solid is formed. The volume was reduced in vacuo and filtered over a glass frit. The solvent removed under reduced pressure, the residue dissolved in THF, layered with $n$-hexane and stored at r.t. Complex (T7) can be obtained as dark green plates.

Yield: 77.5 mg ( $0.067 \mathrm{mmol}, 22 \%$ ). ${ }^{1} \mathrm{H}$ NMR (THF- $\mathrm{d}_{8}, 293 \mathrm{~K}$ ): $\delta[\mathrm{ppm}]=3.75(\mathrm{~s}, 68 \mathrm{H}, 15 \mathrm{c} 5), 3.61(\mathrm{~m}, 8 \mathrm{H}, \mathrm{THF}), 1.77$ ( $\mathrm{m}, 8 \mathrm{H}, \mathrm{THF}$ ), $1.58\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{Cp}^{*}\right), 1.52\left(\mathrm{~s}, 12 \mathrm{H}\right.$, unidentified sideproduct). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}$ (THF- $\left.\mathrm{d}_{8}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=$ $80.9\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 26.6\left(\mathrm{~m}, 3 \mathrm{P}, \mathrm{P}_{\left.\mathrm{M}, \mathrm{M}^{\prime}\right)^{*},} 4.5\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\left.\mathrm{X}, \mathrm{X}^{\prime}\right)}{ }^{31}{ }^{31} \mathrm{P}\right.\right.$ NMR (THF- $\left.\mathrm{d}_{8}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=80.9\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 26.6$
 (100 \%, [Cp*Fe(n $\left.\left.{ }^{4}-\mathrm{P}_{5} \mathrm{OH}\right)\right]^{+}$). Elemental analysis not performed due to impurities in ${ }^{1} \mathrm{H}$ and ${ }^{31} \mathrm{P}$ NMR (see above).

## Synthesis of $\left[\{\mathrm{Na}(15 \mathrm{c} 5)\}\left\{\mathrm{Na}\left(\mathrm{Ph}_{3} \mathrm{PO}\right)(15 \mathrm{c} 5)\right\}\right]\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5} \mathrm{Te}_{2}\right)\right]\left(\mathrm{T} 7^{\prime}\right):$

Complex T7 ( $0.09 \mathrm{mmol}, 100.0 \mathrm{mg}, 1 \mathrm{eq}$.$) and \mathrm{Ph}_{3} \mathrm{PO}(0.111 \mathrm{mmol}, 30.9 \mathrm{mg}, 1.22$ eq.) were dissolved separately in THF. $\mathrm{Ph}_{3} \mathrm{PO}$ was added to T7. The reaction mixture was stirred for 30 minutes. The color remains red, but grey tellurium is formed. The solvent was removed under reduced pressure. The residue was washed with toluene, extracted with THF and filtered over diatomaceous earth, the volume of the filtrate was lowered under reduced pressure, layered with $n$-hexane and stored at r.t. Complex (T7') can be obtained as dark green blocks. Yield: $89.8 \mathrm{mg}(0.066 \mathrm{mmol}, 73 \%) .{ }^{1} \mathrm{H}$ NMR (THF- $\left.\mathrm{d}_{8}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=7.56\left(\mathrm{~m}, 15 \mathrm{H}, \mathrm{Ph}_{3} \mathrm{PO}\right), 3.75(\mathrm{~s}, 92 \mathrm{H}, 15 \mathrm{c} 5)$, 3.61 (m, $4 \mathrm{H}, \mathrm{THF}$ ), 1.77 ( $\mathrm{m}, 4 \mathrm{H}, \mathrm{THF}$ ), 1.58 ( $\mathrm{m}, 25 \mathrm{H}$, unidentified side product), 1.53 ( $\mathrm{m}, 15 \mathrm{H}, \mathrm{Cp}^{*}$ ). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR (THF-d $\mathrm{d}_{8}, 293 \mathrm{~K}$ ): $\delta[\mathrm{ppm}]=81.0\left(\mathrm{~m}, 1 \mathrm{P}, \mathrm{P}_{\mathrm{A}}\right), 26.2\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{M}, \mathrm{M}}\right), 24.9\left(\mathrm{~s}, 1 \mathrm{P}, \mathrm{Ph}_{3} \mathrm{PO}\right), 5.0\left(\mathrm{~m}, 2 \mathrm{P}, \mathrm{P}_{\mathrm{x}}, \mathrm{x}^{\prime}\right) .{ }^{31} \mathrm{P}$ NMR
 analysis not performed due to impurities in ${ }^{1} \mathrm{H}$ NMR (see above).

## Reaction of [ $\left.\mathrm{Cp}^{\prime \prime \prime} \mathrm{Ni}\left(\eta^{3}-\mathrm{P}_{3}\right)\right]$ (2) with ${ }^{\text {Et }} \mathrm{CAAC}$ :

Complex 2 ( $0.15 \mathrm{mmol}, 57.6 \mathrm{mg}, 1 \mathrm{eq}$. ) and ${ }^{\mathrm{Et}} \mathrm{CAAC}(0.16 \mathrm{mmol}, 50.2 \mathrm{mg}, 1.07 \mathrm{eq}$.) were dissolved in THF at r.t. The red cooler of 2 intensified and the reaction mixture was stirred overnight. The solvent was removed under reduced pressure. The residue was dissolved in toluene, layered with acetonitrile and stored at $-30^{\circ} \mathrm{C}$. [(Cp'" Ni$)_{2}\left\{\mu, \eta^{3}: \eta^{3}-\right.$ $\left.\left.\mathrm{P}_{6}\left({ }^{\mathrm{Et}} \mathrm{CAAC}\right)_{2}\right\}\right]$ (T8) and $\left[\mathrm{Cp}{ }^{\prime \prime} \mathrm{Ni}\left\{\eta^{2}-\mathrm{P}_{3}\left({ }^{(\mathrm{Et}} \mathrm{CAAC}\right)_{2}\right\}\right]$ (T9) crystalize at dark red blocks, respectively.

Yield: No yield given. ${ }^{1}$ H NMR (THF- $d_{8}, 293 \mathrm{~K}$ ): $\delta$ [ppm] = a variety of signals in the overlaying each other corresponding to T 8 and T9 which makes an assignment impossible. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}^{*}$ (toluene- $\mathrm{d}_{8}, 293 \mathrm{~K}$ ): $\delta[\mathrm{ppm}]=$ 115.4 (m, 1 P, T9), 98.1 (m, 10 P, T8), 90.3 (m, 5 P, T9)", 81.3 (m, 10 P, T9)\#, 79.9 (m, 10 P, T8)\#, 54.5 (m, 7 P, T8), 50.5 (m, 7 P, T8), 11.7 (m, 7 P, T9). LIFDI-MS (toluene): $m / z=1010.71$ ( $100 \%,[\text { T9 }]^{+}$), 314.31 ( $91 \%,\left[{ }^{[t} \mathrm{CAAC}-\mathrm{H}\right]^{+}$), $1396.83\left(11 \%,[\mathrm{~T} 8]^{+}\right), 719.53\left(11 \%,\left[{ }^{\mathrm{Et}} \mathrm{CAAC}_{2} \mathrm{P}_{3}\right]^{+}\right)$. Elemental analysis not performed due to mixture of T8 and T9.
\#due to the presence of T8 and T9 a unambiguously determination of the yield is impossible.
*The NMR is performed using two equivalents of ${ }^{\mathrm{Et}} \mathrm{CAAC}$; using one equivalent yield also T8 and T9 as well as starting material 2. \#Wrong integral due to overlay of two signals.

## Synthesis of $\left[\mathrm{Cp}{ }^{\prime \prime \prime} \mathrm{Ta}(\mathrm{CO})_{2}\left\{\eta^{3}-\mathrm{P}_{4}\left({ }^{(\mathrm{Et}} \mathrm{CAAC}\right)_{2}\right\}\right](\mathrm{T} 10)$ :

$\left[\mathrm{Cp}{ }^{\prime \prime \prime} \mathrm{Ta}(\mathrm{CO})_{2}\left(\mathrm{n}^{4}-\mathrm{P}_{4}\right)\right]$ (3) ( $\left.0.10 \mathrm{mmol}, 53.8 \mathrm{mg}, 1 \mathrm{eq}.\right)$ and ${ }^{\mathrm{Et}} \mathrm{CAAC}(0.10 \mathrm{mmol}, 31.4 \mathrm{mg}, 1 \mathrm{eq}$.$) were dissolved separately$ in THF and cooled to $-80^{\circ} \mathrm{C}$, respectively. ${ }^{\text {Et }} \mathrm{CAAC}$ was added to 3 , the color changed immediately from yellow to red and the mixture was stirred for two hours. The solvent was removed under reduced pressure, the residue was dissolved in $n$-hexane and stored at $-30^{\circ} \mathrm{C}$. $\left[\mathrm{Cp}{ }^{\prime \prime \prime} \mathrm{Ta}(\mathrm{CO})_{2}\left\{\eta^{3}-\mathrm{P}_{4}\left({ }^{\mathrm{Et}} \mathrm{CAAC}\right)_{2}\right\}\right](\mathrm{T} 10)$ can be obtained as red plates.

Yield: 57.8 mg ( $0.049 \mathrm{mmol}, 49 \%$ ). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{THF}-\mathrm{d}_{8}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=89.6\left(\mathrm{dd},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{p}}=250.6 \mathrm{~Hz},{ }^{2} \mathrm{~J}_{\mathrm{P}-\mathrm{p}}=78.8 \mathrm{~Hz}\right.$, $\left.1 \mathrm{P}, \mathrm{P}_{4}\right),-71.1\left(\mathrm{dt},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{P}}=301.3 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{P}-\mathrm{p}}=16.6 \mathrm{~Hz}, 1 \mathrm{P}, \mathrm{P}_{1}\right),-144.4\left(\mathrm{dt},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{P}}=301.3 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{P}-\mathrm{p}}=78.8 \mathrm{~Hz}, 1 \mathrm{P}, \mathrm{P}_{2}\right)$, -153.1 (dd, $\left.{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{P}}=301.3 \mathrm{~Hz},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{P}}=250.6 \mathrm{~Hz}, 1 \mathrm{P}, \mathrm{P}_{3}\right)$. LIFDI-MS (toluene): $\mathrm{m} / \mathrm{z}=1220.73\left(100 \%,[\mathrm{M}]^{+}\right), 314.31$ ( $98 \%$, $\left.{ }^{[\mathrm{Et}} \mathrm{CAAC}-\mathrm{H}\right]^{+}$), 594.12 ( $32 \%,[3]^{+}$). Analysis (calcd., found for $\mathrm{C}_{27} \mathrm{H}_{44} \mathrm{FeTaP} 5$ ): $\mathrm{C}(61.96,60.45), \mathrm{H}(8.17,8.13)$, N (2.29, 2.12).

## Synthesis of $\left[(\mathrm{Me})_{2} \mathrm{P}\right]\left[\left\{\mathrm{CpMo}(\mathrm{CO})_{2}\right\}_{2}\left(\mu, \eta^{1}: \eta^{1}-\mathrm{P}-\mathrm{IMe}\right)\right]$ (T11):

A solution of $\mathrm{IMe}(0.45 \mathrm{mmol}, 55.9 \mathrm{mg}, 3 \mathrm{eq}$.$) in THF is added to a solution of \left[\left\{\mathrm{CpMo}(\mathrm{CO})_{2}\right\}_{2}\left(\mu, \eta^{2}: \eta^{2}-\mathrm{P}_{2}\right)\right](4)$ $(0.15 \mathrm{mmol}, 74.4 \mathrm{mg}, 1 \mathrm{eq}$.) in THF at r.t. The resulting purple solution was stirred for 10 minutes and $n$-hexane was added. Thereby, a purple solid was formed, the upper solution was decanted off and the solid dried in vacuo. Singlecrystals of $\left[(I M e)_{2} \mathrm{P}\right]\left[\left\{\mathrm{CpMo}(\mathrm{CO})_{2}\right\}_{2}\left(\mu, \eta^{1}: \eta^{1}-\mathrm{P}-\mathrm{IMe}\right)\right](\mathrm{T} 11)$ can be obtained from a $\mathrm{MeCN} /$ toluene solution, stored at
$-30^{\circ} \mathrm{C}$ as purple needles. Yield: 96.0 mg ( $0.111 \mathrm{mmol}, 74 \%$ ). ${ }^{1} \mathrm{H}$ NMR (THF- $\mathrm{d}_{8}, 293 \mathrm{~K}$ ): $\delta[\mathrm{ppm}]=5.12(\mathrm{~s}, 9 \mathrm{H}, \mathrm{Cp})$, 3.65 (m, 5 H, THF), 3.58 ( $\mathrm{s}, 6 \mathrm{H},-\mathrm{NCH}_{3}$ ), $3.35\left(\mathrm{~s}, 12 \mathrm{H},-\mathrm{P}\left(-\mathrm{C}-\mathrm{NCH}_{3}\right)_{2}\right), 2.18\left(\mathrm{~s}, 6 \mathrm{H},-\mathrm{NCCH}_{3}\right), 2.16(\mathrm{~s}, 12 \mathrm{H},-$ $\left.\mathrm{P}\left(-\mathrm{NCCH}_{3}\right)_{2}\right), 1.81(\mathrm{~m}, 5 \mathrm{H}, \mathrm{THF}) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{MeCN}-\mathrm{d}_{3}, 293 \mathrm{~K}\right): \delta[\mathrm{ppm}]=587.5(\mathrm{~s}, 1 \mathrm{P},-\mathrm{P}-\mathrm{IMe}),-112.9(\mathrm{~s}, 1 \mathrm{P}$, $\left.(\mathrm{IMe})_{2} \mathrm{P}\right) .{ }^{31} \mathrm{P}$ NMR ( $\mathrm{MeCN}-\mathrm{d}_{3}, 293 \mathrm{~K}$ ): $\delta[\mathrm{ppm}]=587.5$ (s, $\left.1 \mathrm{P},-\mathrm{P}-\mathrm{IMe}\right),-112.9$ (s, $\left.1 \mathrm{P},(\mathrm{IMe})_{2} \mathrm{P}\right)$. No satisfying elemental analysis could be obtained after several attempts of the isolated crystals.

## Synthesis of $\left[\left\{\mathrm{CpMo}(\mathrm{CO})_{2}\right\}_{2}\left(\mu, \eta^{2}: \eta^{1}-\mathrm{P}_{2}-{ }^{\text {Et }} \mathrm{CAAC}\right)\right]$ (T12):

Dissolving an equimolar amount of $\left[\left\{\mathrm{CpMo}(\mathrm{CO})_{2}\right\}_{2}\left(\mu, \eta^{2}: \eta^{2}-\mathrm{P}_{2}\right)\right](4)(0.20 \mathrm{mmol}, 99.2 \mathrm{mg}, 1 \mathrm{eq}$.) and EtCAAC ( 0.20 $\mathrm{mmol}, 62.7 \mathrm{mg}, 1 \mathrm{eq}$.) in DME at $-50^{\circ} \mathrm{C}$, leads to an immediate change in color from red to green. The mixture was stirred overnight and allowed to reach r.t. Thereby, the color changed to orange. The solvent was removed in vacuo, the residue washed with $n$-hexane, dissolved in 1,2-difluorobenzene, layered with $n$-hexane and stored at $-30^{\circ} \mathrm{C}$.
 (toluene- $\mathrm{d}_{8}, 273 \mathrm{~K}$ ): No proper assignment possible due to a variety of signals overlaying each other*. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR (toluene- $\mathrm{d}_{8}, 273 \mathrm{~K}$ ): $\delta[\mathrm{ppm}]=277.0\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{p}}=440.3 \mathrm{~Hz}, 1 \mathrm{P},-\mathrm{P}-\mathrm{P}^{-E t} \mathrm{CAAC}\right.$ ), $9.9\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{P}-\mathrm{p}}=438.5 \mathrm{~Hz}, 1 \mathrm{P},-\mathrm{P}^{\mathrm{P}} \mathrm{P}-\mathrm{Et} \mathrm{CAAC}\right.$ ), -42.7 (s, 17 H, 4). Elemental analysis not performed*
*due to the equilibrium of T12, 4 and ${ }^{E t} \mathrm{CAAC}$, all species are present which makes a unambiguously spectroscopical analysis or the determination of the yield impossible.

### 10.5.3 Crystallographic Data

Table S1. Crystallographic details of T1, T2, T3, T4 and T5

| Compound | T1 | T2 | T3 | T4 | T5 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Internal Naming <br> Formula | $\begin{gathered} \mathrm{Res} 676 \\ \mathrm{C}_{56} \mathrm{H}_{90} \mathrm{Fe}_{2} \mathrm{KO}_{8} \mathrm{P}_{10} \mathrm{Zr}_{2} \end{gathered}$ | $\begin{gathered} \text { Res482 } \\ \mathrm{C}_{27} \mathrm{H}_{44} \mathrm{FeP}_{5} \mathrm{Ta} \end{gathered}$ | $\begin{gathered} \mathrm{Res} 716 \\ \mathrm{C}_{27} \mathrm{H}_{44} \mathrm{FeMnP}_{5} \end{gathered}$ | $\begin{gathered} \mathrm{Res} 356 \\ \mathrm{C}_{18} \mathrm{H}_{35} \mathrm{FeK}_{2} \mathrm{O}_{4} \mathrm{P}_{5} \mathrm{SSe} \end{gathered}$ | Res441 <br> $\mathrm{C}_{34} \mathrm{H}_{64} \mathrm{FeK}_{2} \mathrm{O}_{14.5} \mathrm{P}_{5}$ |
| $D_{\text {calc. }} / \mathrm{g} \mathrm{cm}^{-3}$ | 1.476 | 1.661 | 1.405 | 1.528 | 1.409 |
| $\mu / \mathrm{mm}^{-1}$ | 8.823 | 9.748 | 9.935 | 8.062 | 4.642 |
| Formula Weight | 1534.21 | 760.27 | 634.26 | 715.38 | 993.75 |
| Colour | dark red | dark green | brownish green | dark green | green |
| Shape | block-shaped | plate-shaped | plate-shaped | plate-shaped | block-shaped |
| Size/mm ${ }^{3}$ | $0.51 \times 0.16 \times 0.11$ | $0.28 \times 0.22 \times 0.05$ | $0.26 \times 0.23 \times 0.12$ | $0.19 \times 0.08 \times 0.06$ | $0.17 \times 0.12 \times 0.07$ |
| T/K | 123.01(10) | 123.01(10) | 100.00(10) | 122.99(11) | 123.00(10) |
| Crystal System | monoclinic | triclinic | monoclinic | triclinic | monoclinic |
| Flack Parameter | 1 | 1 | 1 | 1 | 1 |
| Hooft Parameter | 1 | 1 | 1 | 1 | 1 |
| Space Group | $P 21 / n$ | P-1 | $P 21 / n$ | P-1 | P21/c |
| $a / \AA$ | 16.47870(10) | 8.2697(3) | 12.14780(10) | 14.9993(6) | 13.3998(2) |
| $b / \AA$ | 24.2741(2) | 12.5312(7) | 13.55300(10) | 18.4360(6) | 13.9227(2) |
| $c / A ̊$ | 18.2055(2) | 15.5684(7) | 18.5913(2) | 18.5689(5) | 25.9090(4) |
| $\alpha 1^{\circ}$ | 90 | 72.230(4) | 90 | 77.442(3) | 90 |
| $\beta 1^{\circ}$ | 108.5070(10) | 86.063(3) | 101.6500(10) | 71.969(3) | 104.266(2) |
| $\gamma /{ }^{\circ}$ | 90 | 81.874(4) | 90 | 75.097(3) | 90 |
| $\mathrm{V} / \mathrm{A}^{3}$ | 6905.69(11) | 1520.39(13) | 2997.80(5) | 4665.0(3) | 4684.56(13) |
| Z | 4 | 2 | 4 | 6 | 4 |
| $Z^{\prime}$ | 1 | 1 | 1 | 3 | 1 |
| Wavelength/A | 1.54184 | 1.39222 | 1.54184 | 1.39222 | 1.39222 |
| Radiation type | CuKa | $\mathrm{CuK}_{b}$ | CuKa | $\mathrm{CuK}_{b}$ | CuKb |
| $\theta_{\text {min }} /{ }^{\circ}$ | 3.364 | 2.692 | 4.007 | 2.858 | 3.073 |
| $\theta_{\text {max }} /{ }^{\circ}$ | 72.635 | 73.983 | 75.220 | 72.434 | 67.871 |
| Measured Refl's. | 50641 | 17864 | 59246 | 41797 | 23326 |
| Ind't Refl's | 13568 | 8177 | 6140 | 23842 | 11184 |
| Refl's with I > $2 \sigma$ ( l$)$ | 11322 | 7851 | 5702 | 22026 | 9466 |
| Rint | 0.0371 | 0.0340 | 0.0573 | 0.0227 | 0.0236 |
| Parameters | 1082 | 321 | 321 | 892 | 522 |
| Restraints | 1334 | 0 | 0 | 0 | 0 |
| Largest Peak | 0.947 | 1.470 | 0.558 | 1.113 | 0.813 |
| Deepest Hole | -0.884 | -2.195 | -0.471 | -0.649 | -0.358 |
| GooF | 0.974 | 1.025 | 1.056 | 1.024 | 1.028 |
| wR2 (all data) | 0.0831 | 0.0652 | 0.0962 | 0.0725 | 0.1343 |
| wR2 | 0.0811 | 0.0643 | 0.0939 | 0.0705 | 0.1262 |
| $R_{1}$ (all data) | 0.0384 | 0.0281 | 0.0376 | 0.0294 | 0.0571 |
| $R_{1}$ | 0.0320 | 0.0268 | 0.0345 | 0.0266 | 0.0477 |

Table S2. Crystallographic details of T6, T7, T7‘, T8 and T9.

| Compound | T6 | T7 | T7' | T8 | T9 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Internal Naming <br> Formula | Res543 $\mathrm{C}_{18} \mathrm{H}_{35} \mathrm{As}_{2.02} \mathrm{FeK}_{2} \mathrm{O}_{4} \mathrm{P}_{4.98}$ | Res284 $\mathrm{C}_{36.4} \mathrm{H}_{67.8} \mathrm{FeNa}_{2} \mathrm{O}_{11.6} \mathrm{P}_{5} \mathrm{Te}_{2}$ | $\mathrm{Res440}^{\mathrm{C}_{56.63} \mathrm{H}_{83.47} \mathrm{FeNa}_{2} \mathrm{O}_{12.05} \mathrm{P}_{6} \mathrm{Te}_{2}}$ | $\begin{gathered} \text { Res287 } \\ \mathrm{C}_{78} \mathrm{H}_{127} \mathrm{~N}_{2} \mathrm{Ni}_{2} \mathrm{P}_{6} \end{gathered}$ | Res343 <br> $\mathrm{C}_{67.53} \mathrm{H}_{107.47} \mathrm{~N}_{3.4} \mathrm{NiP}_{3}$ |
| $D_{\text {calc. }} / \mathrm{g} \mathrm{cm}^{-3}$ | 1.664 | 1.495 | 1.358 | 1.172 | 1.084 |
| $\mu / \mathrm{mm}^{-1}$ | 11.645 | 1.567 | 9.563 | 2.034 | 1.350 |
| Formula Weight | 755.08 | 1202.98 | 1499.96 | 1396.05 | 1118.67 |
| Colour | dark red | dark green | dark green | red | dark green |
| Shape | plate-shaped | plate-shaped | block-shaped | block-shaped | block-shaped |
| Size/mm ${ }^{3}$ | $0.35 \times 0.24 \times 0.15$ | $0.27 \times 0.17 \times 0.05$ | $0.27 \times 0.20 \times 0.10$ | $0.16 \times 0.11 \times 0.08$ | $0.31 \times 0.18 \times 0.15$ |
| T/K | 123.00(10) | 293(2) | 293(2) | 123.00(10) | 293(2) |
| Crystal System | monoclinic | monoclinic | triclinic | monoclinic | triclinic |
| Flack Parameter | 1 | -0.030(5) | 1 | 1 | 1 |
| Hooft Parameter | 1 | -0.009(5) | 1 | 1 | 1 |
| Space Group | $\mathrm{P} 2_{1} / \mathrm{c}$ | $P 2{ }_{1}$ | P-1 | P2 $1_{1 / c}$ | P-1 |
| $a / \AA$ | 13.2843(4) | 13.5604(3) | 12.8122(3) | 12.95330(10) | 13.8624(4) |
| b/Å | 8.3518(3) | 12.6495(2) | 15.5393(4) | 20.4723(2) | 14.4370(3) |
| c/Å | 27.8624(10) | 15.7331(4) | 19.0865(4) | 30.3842(3) | 18.4661(5) |
| $\alpha 1^{\circ}$ | 90 | 90 | 80.520(2) | 90 | 85.977(2) |
| $\beta{ }^{\circ}$ | 102.838(3) | 98.128(2) | 78.115(2) | 100.8000(10) | 78.017(2) |
| $\gamma /{ }^{\circ}$ | 90 | 90 | 87.576(2) | 90 | 71.394(2) |
| $V / A^{3}$ | 3014.00(18) | 2671.62(10) | 3667.60(15) | 7914.68(13) | 3426.14(16) |
| Z | 4 | 2 | 2 | 4 | 2 |
| Z' | 1 | 1 | 1 | 1 | 1 |
| Wavelength/A | 1.54184 | 0.71073 | 1.54184 | 1.54184 | 1.54184 |
| Radiation type | CuKa | $\mathrm{MoKa}_{a}$ | CuKa | CuKa | CuKa |
| $\theta_{\text {min }}{ }^{\circ}$ | 4.160 | 3.436 | 3.525 | 3.474 | 3.431 |
| $\theta_{\text {max }} /{ }^{\circ}$ | 73.671 | 32.243 | 72.942 | 73.874 | 73.068 |
| Measured Refl's. | 11877 | 29024 | 40883 | 37822 | 38016 |
| Ind't Refl's | 5869 | 16484 | 14221 | 15737 | 13304 |
| Refl's with l > $2 \sigma$ (I) | 5559 | 13811 | 13305 | 14146 | 12198 |
| $R_{\text {int }}$ | 0.0301 | 0.0196 | 0.0319 | 0.0223 | 0.0198 |
| Parameters | 512 | 749 | 1008 | 857 | 813 |
| Restraints | 664 | 709 | 1110 | 12 | 304 |
| Largest Peak | 0.657 | 0.717 | 1.027 | 0.747 | 0.926 |
| Deepest Hole | -0.674 | -0.837 | -0.539 | -0.313 | -0.255 |
| GooF | 0.994 | 1.053 | 1.038 | 1.030 | 1.045 |
| $w R_{2}$ (all data) | 0.1106 | 0.1129 | 0.0997 | 0.0865 | 0.1212 |
| wR2 | 0.1090 | 0.1039 | 0.0976 | 0.0837 | 0.1183 |
| $R_{1}$ (all data) | 0.0431 | 0.0572 | 0.0373 | 0.0378 | 0.0427 |
| $R_{1}$ | 0.0412 | 0.0438 | 0.0351 | 0.0331 | 0.0393 |

Table S3. Crystallographic details of T10, T11 and T12.

| Compound | T10 | T11 | T12 |
| :---: | :---: | :---: | :---: |
| Internal Naming <br> Formula | Res327 | Res420 | Res408 |
| $D_{\text {calc. }} / \mathrm{g} \mathrm{cm}{ }^{-3}$ | 1.160 | 1.572 | 1.520 |
| $\mu / \mathrm{mm}^{-1}$ | 2.715 | 6.800 | 6.692 |
| Formula Weight | 1264.35 | 868.60 | 850.82 |
| Colour | red | dark violet | dark green |
| Shape | plate-shaped | needle-shaped | block-shaped |
| Size/mm ${ }^{3}$ | $0.19 \times 0.08 \times 0.02$ | $0.45 \times 0.04 \times 0.03$ | $0.48 \times 0.32 \times 0.17$ |
| T/K | 123.00(10) | 293(2) | 293(2) |
| Crystal System | monoclinic | triclinic | monoclinic |
| Flack Parameter | 1 | 1 | 1 |
| Hooft Parameter | 1 | 1 | 1 |
| Space Group | $\mathrm{P} 2_{1} / \mathrm{c}$ | P-1 | $\mathrm{P} 21 / \mathrm{n}$ |
| $a / \AA$ | 26.1534(2) | 8.3829(3) | 11.62850(10) |
| b/Å | 14.15680(10) | 11.8922(4) | 15.3001(2) |
| c/Å | 19.7579(2) | 18.9179(6) | 21.1512(3) |
| $\alpha 1^{\circ}$ | 90 | 103.071(3) | 90 |
| $\beta 1^{\circ}$ | 98.3940(10) | 90.453(3) | 98.9340(10) |
| $\gamma /{ }^{\circ}$ | 90 | 92.503(3) | 90 |
| $V / A^{3}$ | 7236.97(11) | 1835.02(11) | 3717.51(8) |
| Z | 4 | 2 | 4 |
| Z' | 1 | 1 | 1 |
| Wavelength/A | 1.39222 | 1.54184 | 1.54184 |
| Radiation type | $\mathrm{CuK}_{\text {b }}$ | CuKa | CuKa |
| $\theta_{\text {min }}{ }^{\circ}$ | 3.213 | 3.820 | 4.094 |
| $\theta_{\text {max }} /{ }^{\circ}$ | 67.820 | 71.813 | 71.779 |
| Measured Refl's. | 32647 | 13251 | 13118 |
| Ind't Refl's | 17092 | 6980 | 7069 |
| Refl's with I > $2 \sigma$ (I) | 14581 | 6257 | 6288 |
| $R_{\text {int }}$ | 0.0184 | 0.0356 | 0.0276 |
| Parameters | 702 | 452 | 468 |
| Restraints | 0 | 0 | 0 |
| Largest Peak | 0.910 | 2.351 | 2.964 |
| Deepest Hole | -0.504 | -1.666 | -1.088 |
| GooF | 1.017 | 1.106 | 1.042 |
| $w R_{2}$ (all data) | 0.0781 | 0.1376 | 0.1207 |
| wR2 | 0.0743 | 0.1328 | 0.1180 |
| $R_{1}$ (all data) | 0.0361 | 0.0523 | 0.0493 |
| $R_{1}$ | 0.0298 | 0.0472 | 0.444 |

### 10.6 References

1 P. Pyykkö and M. Atsumi, Chem. Eur. J., 2009, 15, 186-197.
2 M. Detzel, T. Mohr, O. J. Scherer and G. Wolmershaeuser, Angew. Chem. Int. Ed., 1994, 33, 1110-12.

3 O. J. Scherer, R. Winter and G. Wolmershäuser, ZAAC, 1993, 619, 827-835.
4 P. Pyykkö and M. Atsumi, Chem. Eur. J., 2009, 15, 12770-12779.
5 E. Mädl, PhD Thesis, Regensburg, 2016.
6 J. D. Masuda, W. W. Schoeller, B. Donnadieu and G. Bertrand, Angew. Chem. Int. Ed., 2007, 46, 7052-7055.

7 L. J. Bourhis, O. V Dolomanov, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Crystallogr., 2009, 42, 339-341.

8 G. M. Sheldrick, Acta Crystallogr. Sect. A, 2015, 71, 3-8.
9 M. Seidl, G. Balázs and M. Scheer, Chem. Rev., 2019, 119, 8406-8434.

## 11 Epilogue

This work deals extensively with the functionalization of polyphosphorus-, as well as polyarsenic ligand complexes. The main goal is the more selective and direct synthesis of organo-phosphines based on white phosphorus, utilizing transition metal complexes. A conceptually new and unique synthetic approach for the preparation of symmetric and asymmetric organo-phosphines was found, by consecutive reactions of pentaphosphaferrocene with nucleophiles-electrophiles-nucleophiles under the abstraction of the desired phosphine. Furthermore, the reactivity of the heavier analog, pentaarsaferrocene, towards nucleophiles, carbenes, and analogues was investigated.

### 11.1 Reactivity of Polypnictogen Ligand Complexes towards NHCs

As stated throughout the whole thesis, there has been a great interest in polyphosphorus ligand complexes, their synthesis and reactivity for several decades. Carbenes represent an equally historical topic, which was initially researched and used mostly in organic chemistry. Carbon as a basic building block of our ecological and physiological system has always been ubiquitous in the industrial and academic world. Accordingly, an almost uncountable amount of reactivities and reactions developed. Arduengo set a milestone with one of these in 1991: The synthesis of the first isolatable NHC. ${ }^{1}$ This class of substances, featuring a singlet-carbene, has become an established topic of research over the last 30 years and is also of great industrial interest, for example in heterogeneous ligand synthesis for catalysts. ${ }^{2,3}$ Put simply, NHCs are neutral carbon nucleophiles that exhibit broad reactivity, also with respect to phosphorus. ${ }^{4,5}$ At the present stage of research or publication, reactivity towards polyphosphorus and especially polyarsenic complexes has hardly been investigated. ${ }^{6}$ A logical consequence was to combine both topics and to examine the reactivity of $E_{n}(E=P, A s)$ ligand complexes towards NHCs.

An overview of the performed reactions and their different outcome, depending on the used polypnictogen ligand complex, is given in Scheme 1. Reacting the $\mathrm{P}_{4}$ end deck complex [Cp"'Co( $\left.\left.\eta^{4}-P_{4}\right)\right](S 1)$ with 1,3,4,5-tetramethylimidazol-2-ylidene (IMe), results in a selective ring contraction and the formation of $\left[(\mathrm{IMe})_{2} \mathrm{P}\right]\left[\mathrm{Cp}{ }^{\prime \prime \prime} \mathrm{Co}\left(\eta^{4}-\mathrm{P}_{3}\right)\right]$ (S1-1), under an NHC induced phosphorus atom abstraction. Ring contraction reactions are primarily used in organic synthesis and provide access to unique products. ${ }^{7-9}$ This concept can be extended to organometallic as well, and yields in the reaction of $\left[\left\{\mathrm{Cp}^{*} \mathrm{Mo}\right\}_{2}\left(\mu, \eta^{6: 6}-\mathrm{As} 6\right)\right](\mathrm{S} 3 \mathrm{~b})$, the second known As(I) cation (S3b-1) in literature ${ }^{10}$ and the first structurally characterized example of a doubly NHCsubstituted one. The reactivity of the triple-decker complex $\left[\left\{\mathrm{Cp}^{*} \mathrm{~V}\right\}_{2}\left(\mu, \eta^{6: 6}-\mathrm{P}_{6}\right)\right]$ (S2) towards IMe exhibits the versatility of the used NHC and resulted inter alia in the formation of a rare

NHC-phosphinidenide like ligand, bridging two $\mathrm{Cp}{ }^{*} \mathrm{~V}$ fragments ( $\mathbf{S} 2-3$ ). In all the preceding reactions, the formation of a $\left[(\mathrm{NHC})_{2} \mathrm{E}\right]^{+}(\mathrm{E}=\mathrm{P}, \mathrm{As})$ cation was observed. This circumstance changes when using the polyarsenic end-deck complex, pentaarsaferrocene (S4). Thereby, polyarsenic-NHC adducts, the first of their class, are formed in the reaction with IMe (S4-2) and IMes (S4-2). Even an excess of NHC did not lead to an arsenic abstraction. A similar observation was made by our group in the reactivity of the lighter homolog pentaphosphaferrocene ${ }^{11}$ and might be explained due to the stability of the $\mathrm{E}_{5}$ ligand. In contrast, no equilibrium seems to be present when reacting $\mathbf{S} 4$ with NHCs.


S2 S2-1 S2-2 $\quad$ S2-3


Scheme 1. Overview of performed Reactions of $E_{n}(E=P, A s)$ ligand complexes S1, S2, S3a, S3b and S4 towards 1,3,4,5-tetramethylimidaozol-2-ylidene (IMe) and 1,3-dimesitylimidaozol-2-ylidene (IMes)

As described in the previous paragraph and illustrated by the presented results (Scheme 1), the formation of the $\left[(\mathrm{NHC})_{2} \mathrm{P}\right]^{+}$cation is a common outcome in the reaction of $\mathrm{P}_{\mathrm{n}}$ ligand complexes with NHCs. ${ }^{12}$ This phenomenon continues when so-called $\mathrm{P}_{4}$ butterfly complexes of iron (S5) and chromium ( $\mathbf{S 6}$ ) are reacted with IMe. These highly reactive polyphosphorus complexes ( $\mathbf{S 5}$, S6) give different products depending on the transition metal and the amount of NHC (Scheme 2). In the case of iron, compounds S5-1 (2 eq. IMe) and S5-2 (4 eq. IMe) are formed selectively in high yields. The even more reactive (compared to iron) chromium butterfly complex (S6) tends to undergo uncontrolled fragmentation and phosphorus splitting, which however leads to the interesting compound S6-1, which contains a novel metal-bridged $\mathrm{P}_{2}$ dumbbell.


Scheme 2. Reactivity of $P_{n}$ butterfly complexes $\mathbf{S 5}$ and $\mathbf{S 6}$ towards IMe.

### 11.2 Functionalization of Pentaphosphaferrocene - Novel Synthetic Route for the Synthesize of (Asymmetric) Organo Phosphines

As presented in the introduction, an important challenge is the functionalization of white phosphorus as well as the synthesis of (asymmetric) organophosphorus compounds. Due to a huge amount of side products and the usage of hazardous chemicals, a more selective way is desired. To do so, white phosphorus was activated in the coordination sphere of a transition metal to form the so-called pentaphosphaferrocene 1 , which is a very useful complex for controlled consecutive reactions as stated in the introduction of this thesis.

The polyphosphorus compound $\left[\mathrm{Cp}{ }^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{P}_{5}\right)\right]$ (1) can be used as a recyclable platform for the targeted synthesis of symmetric or asymmetric phosphines, via a sequence of nucleophilic(2a-f)-electrophilic(3a-f)-nucleophilic reactions (Scheme 3), directly from white phosphorus and benefits voiding the use of intermediates such as $\mathrm{PCl}_{3}$ or $\mathrm{PH}_{3}$. With this new modular system, asymmetric phosphines (4a-c) are obtained in high yields as racemates in remarkable preparative scales and 1 can be regenerated and reused in a semi-'catalytic' cyclic process, which can be also run for several cycles in a one-pot reaction. The presented results pave the way for an unprecedented, selective, and easy synthetic route to asymmetric and (in future work potential) chiral phosphines based on white phosphorus. This conceptual new approach avoids radicals and is not limited to aryl or alkyl substituents, but phosphines with a variety of different substitution patterns are also accessible by a very simple synthetic route. In Addition to this, one can use the dianionic species $1^{\prime}$ in combination with (different) carbonbased electrophiles like ${ }^{\text {tBul }}$ or Mel to form the neutral precursors compounds 3a-f and surpass contingent limitation in the desired nucleophile.


Scheme 3. Synthesis of asymmetric phosphines 4, via successive nucleophilic-electrophilic-nucleophilic attack. Synthesis of the anionic precursor complexes 2 by nucleophilic attack; Electrophilic quenching of 2 (synthesis of 3); asymmetric phosphine abstraction by nucleophiles (synthesis of 4,5); Regeneration of 1 by thermolysis with $\mathrm{P}_{4}$; Alternative synthesis of 3 by electrophilic quenching of $\mathbf{1}^{\prime}$.

The question arose whether it is possible to introduce functional groups to the $P_{n}$ unit. The reactions of the anionic complexes 2c, 2d, and $2 f$ with 1,3-dibromopropane, 1,4dibromobutane, and 4-bromobutyronitrile lead to different complexes (Scheme 4), inter alia compounds bearing functional groups ( $3 \mathrm{~g}-\mathrm{k}$ ). The terminal bromine group in complex 3d enables a variety of consecutive reactions (Scheme 4; e.g., additional functionalization of the polyphosphorus unit (7) or linking of two complexes (8)). As a matter of principle and to demonstrate the versatility of this new conceptual method for the generation of phosphines, complex 3d was reacted with two equivalents of KBnz, yielding the corresponding phosphine 9 . Furthermore, it is possible to introduce two nitrile groups via alkyl substituents to the $\mathrm{P}_{5}$ moiety (see chapter 7). This functionality can be used for consecutive reactions, e.g., the reaction to $\mathrm{ZnBr}_{2}$, and pave the way for a variety of different coordination chemistry in future works.


Scheme 4. Overview of the functionalization of pentaphosphaferrocene (top) and consecutive reactions of 3d (bottom).

Heterocycles are an ever-present topic of research, have their "own journal" with the "Journal of Heterocyclic Chemistry", and are a daily companion of life as well as an essential part of the physiological- and ecosystem. Based on the previous findings of phosphine abstraction, a novel synthetic route was explored as part of this thesis to gain access to phosphorus-containing saturated heterocycles featuring ring sizes from $n=4$ to 7 (11a-d). This otherwise difficult or hardly accessible class of compounds can be obtained by quenching the dianionic complex ( $1^{\prime}$ ), followed by subsequent reaction of the obtained precursor compounds (10a-d) with a suitable nucleophile (Scheme 5). If, for example, $\mathrm{LiAlH}_{4}$ is used as a hydride source, parent cyclic phosphines (12a-d) can also be prepared by this novel route.


Scheme 5. Quenching of the dianionic complex 1' with di-bromoalkanes and consecutive phosphine abstraction.

### 11.3 Reactivity of Pentaarsaferrocene towards anionic Nucleophiles, Carbenes and Analogues

As described before, the handling of metastable yellow arsenic is very difficult due to its extreme sensitivity to light and air. One possibility for indirect conversion is the fixation/activation by transition metal fragments and the controlled conversion of the arsenic ligand in their coordination sphere, such as the utilized starting material pentaarsaferrocene $\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{5}-\mathrm{As} 5\right)\right]$ (1).

The reactivity of this polyarsenic end deck complex (1) towards anionic main group nucleophile shows, interestingly to see, (in contrast to pentaphosphaferrocene) functionalization-, extension- or rearrangement of the polyarsenic ligand, depending on the used nucleophile. For example, the usage of MeLi and KBnz leads to a selective functionalization and the formation of the anionic complexes $\mathbf{2 a}$ and $\mathbf{2 b}$ in very high yields (Scheme 6). Additional functionalization of $\mathbf{1}$ can be obtained when using $1,1^{\prime}$-dilithioferrocene. In doing so, the dianionic complex $\mathbf{2 c}$ is formed, featuring two [ $\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}\right.$-Ass) ] moieties, bridged by a ferrocenyl unit and exhibits interesting redox chemistry (chapter 8). Besides, it is possible to extend the Ass unit of $\mathbf{1}$ in the reaction with $\mathrm{KAsPh}_{2}$, forming a $\eta^{4}-\mathrm{As}_{6} \mathrm{Ph}_{2}$ ligand (3) (Scheme 6). The most interesting outcome was observed when reacting 1 with $\mathrm{MAsSiMe}_{3}(\mathrm{M}=\mathrm{Li}, \mathrm{K})$ or KAsCO. Thereby, a rearrangement and the formation of the biggest polyarsenic ligand complexes 4a, b takes place (Scheme 6). This outcome can be rationalized due to the labile substituent, like trimethylsilyl ( $-\mathrm{SiMe}_{3}$ ) or CO , of the arsenic nucleophile which is abstracted after the initial activation of the Ass unit in 1.


Scheme 6. Functionalization of pentaarsaferrocene (1) with anionic main group nucleophiles: i) MeLi or KBnz + 2.2.2cryptand; ii) 1,1'-dilithioferrocene + 2.2.2-cryptand; iii) $\mathrm{KAsPh}_{2}+2.2 .2$-cryptand; iv) $\mathrm{LiAsSiMe}_{3}+2.2 .2$-cryptand, for 3a; $\mathrm{KAsSiMe}_{3}$ or KAsCO + 2.2.2-cryptand for 3b.

As already published in cooperation projects, pentaphosphaferrocene shows an interesting reactivity towards chlorosilylenes and/or bis-silylenes/germylenes. ${ }^{13,14}$ This concept was attempted to be transferred to the heavier homolog pentaarsaferrocene 1. In addition to silylenes and germylenes, the reactivity towards ${ }^{E t}$ CAAC was also investigated. This cyclic(alkyl)(amino)carbene represents an extraordinary substance class of singlet carbenes, ${ }^{6,15}$ and in contrast to the reaction of 1 with IMe (described above), exhibits a considerably different reactivity. ${ }^{6}$ Thereby, a rearrangement and fragmentation of the polyarsenic ligand take place and the triple-decker complex $\left[\left(C p^{*} \mathrm{Fe}\right)_{2}\left\{\mu, \eta^{4}-\mathrm{As} 4\right\}\right]$ ( 6 ) as well as a, unique CAAC stabilized, As6 sawhorse type structure (5) are formed (Scheme 7).

Interesting to see is the different reaction outcome when reacting 1 with chlorosilylenes and/or bis-silylenes. $\left.{ }^{29} \mathrm{Si}^{1}{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy exhibits the selective formation of two novel mixed polyarsenic-silicon ligand complexes $\mathbf{7}$ and $\mathbf{8 a}$. Compound $\mathbf{7}$ is isostructural to the reaction outcome when using pentaphosphaferrocene, ${ }^{13}$ yet compound 8 a features a unique $\mathrm{As}_{6} \mathrm{SiL}$ ( $\mathrm{L}=\mathrm{PhC}\left(\mathrm{N}^{\mathrm{t}} \mathrm{Bu}_{2}\right.$ ) moiety (Scheme 7). The formation of the analog germanium complex $\mathbf{8 b}$ is observed when using bis-germylene. Unfortunately, no other (side)products can be identified due to the very high sensitivity of the reaction mixture. Nevertheless, complex 8 b features an unprecedented mixed polyarsenic-germanium ligand.


Scheme 7. Reactivity of I towards ${ }^{\text {Et }}$ CAAC, chlorosilylenes and bis-silylene/germylene

### 11.4 Closing Remarks

In summary, this dissertation deals with the synthesis and functionalization of polypnictogen ligand complexes. Besides the successful realization of the latter with organic nucleophiles and electrophiles, a conceptually new way for the preparation of phosphines could be found. For the first time, a functionalized phosphorus atom could be removed from the coordination sphere of a transition metal (Scheme 8). This finding was transferred to other substituents and the versatility of this method was demonstrated.


Scheme 8. Overview: Pentaphosphaferrocene mediated functionalization of white phosphorus, functionalization, extension, and abstraction - Synthesis of (a)symmetric as well es secondary phosphines.

In addition, the reactivity of pentaarsaferrocene, a rare representative of an end-deck polyarsenic ligand complex, towards nucleophiles was investigated.

### 11.5 References

1 A. J. Arduengo, R. L. Harlow and M. Kline, J. Am. Chem. Soc., 1991, 113, 361-363.
2 D. Zhao, L. Candish, D. Paul and F. Glorius, ACS Catal., 2016, 6, 5978-5988.
3 J. A. Osborn, G. Wilkinson and J. J. Mrowca, in Inorganic Syntheses, John Wiley \& Sons, Ltd, 1967, pp. 67-71.

4

5
M. N. Hopkinson, C. Richter, M. Schedler and F. Glorius, Nature, 2014, 510, 485-496.

5 C. D. Martin, C. M. Weinstein, C. E. Moore, A. L. Rheingold and G. Bertrand, Chem. Commun., 2013, 49, 4486-4488.

6 V. Nesterov, D. Reiter, P. Bag, P. Frisch, R. Holzner, A. Porzelt and S. Inoue, Chem. Rev., 2018, 118, 9678-9842.

7 S. A. Snyder and E. J. Corey, J. Am. Chem. Soc., 2006, 128, 740-742.
8 L. F. Silva, Synlett, 2014, 25, 466-476.
9 D. Redmore and C. D. Gutsche, eds. H. HART and G. J. B. T.-A. in A. C. KARABATSOS, Elsevier, 1971, vol. 3, pp. 1-138.

10 G. Märkl and F. Lieb, Tetrahedron Lett., 1967, 8, 3489-3493.
11 F. Riedlberger, S. Todisco, P. Mastrorilli, A. Y. Timoshkin, M. Seidl and M. Scheer, Chem. Eur. J., 2020, 26, 16251-16255.

12 C. L. B. Macdonald, J. F. Binder, A. Swidan, J. H. Nguyen, S. C. Kosnik and B. D. Ellis, Inorg. Chem., 2016, 55, 7152-7166.

13 R. Yadav, T. Simler, S. Reichl, B. Goswami, C. Schoo, R. Köppe, M. Scheer and P. W. Roesky, J. Am. Chem. Soc., 2020, 142, 1190-1195.

14 R. Yadav, B. Goswami, T. Simler, C. Schoo, S. Reichl, M. Scheer and P. W. Roesky, Chem. Commun., 2020, 56, 10207-10210.

15 V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu and G. Bertrand, Angew. Chem. Int. Ed., 2005, 44, 5705-5709.

## 12 Appendix

### 12.1 Thematic List of Abbreviations

| NMR spectroscopy |  | Solvents |  |
| :---: | :---: | :---: | :---: |
| NMR $\delta$ ppm Hz $J$ $\omega_{1 / 2}$ s $d$ d q $m$ $b r$ | nuclear magnetic resonance chemical shift <br> parts per milion <br> Hertz [ $\mathrm{s}^{-1}$ ] <br> coupling constant <br> full width at half maximum <br> singlet <br> doublet <br> triplet <br> quartet <br> multiplet <br> broad | THF <br> DME <br> Tol <br> $\mathrm{Et}_{2} \mathrm{O}$ <br> o-DFB <br> MeCN | tetrahydrofurane, $\mathrm{C}_{4} \mathrm{H}_{8} \mathrm{O}$ <br> 1,2-dimethoxyethane, $\mathrm{C}_{4} \mathrm{H}_{10} \mathrm{O}_{2}$ <br> toluene, $\mathrm{C}_{7} \mathrm{H}_{8}$ <br> diethylether, $\mathrm{C}_{4} \mathrm{H}_{10} \mathrm{O}$ <br> 1,2-fluorobenzene $\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{~F}_{2}$ <br> Acetonitrile, $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{~N}$ |


| Mass spectrometry |  | IR spectroscopy |  |
| :---: | :---: | :---: | :---: |
| MS | mass spectrometry | IR | infrared spectroscopy |
| $\mathrm{m} / \mathrm{z}$ | mass to charge ratio | ATR | attenuated total reflection |
| ESI | electron spray ionization | $v$ | wavenumber [ $\mathrm{cm}^{-1}$ ] |
| FD | field desorption | s | strong |
| LIFDI | liquid injection field desorption | vs | very strong |
|  |  | m | medium |
|  |  | w | weak |

Theoretical computations

| DFT | density functional theory |
| :--- | :--- |
| ESP | negative electrostatic potential |
| WBI | Wiberg Bond Indices |
| NBO | Natural Bond Orbital |
| NAO | Natural Atomic Orbitals |
| HOMO | highest occupied molecular orbital |


| LUMO | lowest occupied molecular orbital |
| :--- | :--- |
| SCF | Self-consistent field |
| a.u | atomic units |
| AIM | Atoms In Molecules |
| BCP | Bond Critical Points |
| RCP | Ring Critical Points |


| Physical Quantities \& Units |  | Others |  |
| :---: | :---: | :---: | :---: |
| Å | angstroem ( $1 \AA=10^{-10} \mathrm{~m}$ ) | r.t. | room temperature |
| T | temperature | cf. | confer |
| - | degree | e. g. | exempli gratia |
| ${ }^{\circ} \mathrm{C}$ | degree Celcius | eq. | equivalent |
| K | kelvin | M | metal |
| J | joule | R | organic substituent |
| g | gram | L | ligand |
| L | liter | LA | Lewis acid |
| M | molar mass | SI | supporting Information |
| m | mole | nat. | natural |
| \% | percent | ie. | id est |
| min | minute | E | pnictogen atom |
| cm | centimeter | En | polypnictogen units |
| p | pressure | EPR | electron paramagnetic |
| k | kilo (factor $10^{3}$ ) |  | resonance |
| $\mu$ | micro (factor $10^{-6}$ ) |  |  |
| m | milli (factor $10^{-6}$ ) |  |  |

Ligands / Substituents / Ions

| 18-crown-6 | 1,4,710,13,16-hexaoxacyclooctadecane |
| :--- | :--- |
| 15-crown-5 | 1,4,7,10,13-Pentaoxacyclopentadecane |
| 12-crown-4 | 1,4,7,10-Tetraoxacyclododecane |
| 2.2.2-crypt(and) | 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane |
| CAAC | cyclic-alkyl-amino-carbene |
| COD | 1,5-cyclo-octadiene $\left(\mathrm{C}_{8} \mathrm{H}_{12}\right)$ |
| Cp | cyclopentadienyl $\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)$ |


| Cp'' | 1,2,4-tri-tertbutyl-cyclopentadienyl ( $\left.\mathrm{C}_{5} \mathrm{H}_{2}{ }^{2} \mathrm{Bu}_{3}\right)$ |
| :---: | :---: |
| Cp* | 1,2,3,4,5-pentamethylcyclopentadienyl ( $\mathrm{C}_{5} \mathrm{Me}_{5}$ ) |
| ${ }^{\text {Me }} \mathrm{NHC} / \mathrm{IMe}$ | 1,3,4,5-tetramethylimidazol-2-ylidene |
| IMes | 1,3-dimesitylimidazol-2-ylidene |
| Et | ethyl |
| Me | methyl |
| Mes | Mesityl (2,4,6-trimethylphenyl) |
| NHC | N -heterocyclic carbene |
| Ph | phenyl |
| ${ }^{\text {tBu }}$ | tert-butyl |

### 12.2 Acknowledgement

It has been a long way and this work would not be possible without the help and support of many persons. Therefore, I want to thank:

- Prof. Dr. Manfred Scheer for providing extraordinary and excellent working conditions in combination with this interesting research topic. Furthermore, I want to thank you for enabling the possibility to join international conferences and research stays.
- Dr. Gábor Balázs for help and motivation in any kind of topic. You know more than all (organometallic) textbooks combined.
- Dr. Felix Riedlberger and Dr. Martin Piesch for teaching me how to work properly under inert gas. Without you, OH species would have been always present.
- My former lab mates Dr. Veronika Heinl and Dr. Martin Piesch for all the laugher, (bad) music, proofreading, ideas, and gossip.
- Dr. Michael Seidl for supervision/calculation of difficult Xray Structures.
- Studienstiftung des deutschen Volkes.
- All present and former members of the research group.
- Boy aka Matthias Ackermann for all the hate and rant about everything.
- Christoph Riesinger for assisting the CO-station
- The analytic department of University Regensburg
- The staff of glass blowing, without you this thesis would have been a lot more difficult and expensive.
- Former and present technical assistants, especially Petra Lugauer and Matthias Hautmann
- Christina for motivation and help especially in the early and stressful stages of the PhD.
- Niko and Grasi for Gin/Tonic and boardgame sessions as well as all the fun, parties, discussions and simply heaving a good time
... and especially my family for their enduring support! This work is dedicated to you!


[^0]:    Scheme 4. Reaction of $\left[\mathrm{K}(\mathrm{dme})_{2}\right]_{2}\left[\mathrm{Cp}^{*} \mathrm{Fe}\left(\eta^{4}-\mathrm{P}_{5}\right)\right]$ (I) with 4-bromobutyronitrile leading to complex 7 and consecutive reaction of 7 with zinc(II)bromide. (Yields are given in parenthesis)

[^1]:    ${ }^{1} 1-x, 2-y, 2-z$

