Reactivity of Tetrahedral E_4 Molecules ($E_4 = P_4, As_4, AsP_3$) and E_n Ligand Complexes

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Maria Haimerl

aus Brennberg

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Prüfungsausschuss: Prof. Dr. Manfred Scheer

Prof. Dr. Henri Brunner

Prof. Dr. Frank-Michael Matysik

Universität Regensburg

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Maria Haimerl

This thesis was elaborated within the period from December 2017 until November 2021 in the Institute of Inorganic Chemistry at the University of Regensburg, under the supervision of Prof. Dr. Manfred Scheer.

List of Publications:

- M. Haimerl, M. Piesch, G. Balázs, P. Mastrorilli, W. Kremer, M. Scheer*
  'Reactivity of Cu(I) Nacnac Complexes Toward Polypnictogen Compounds'
  Inorg. Chem. **2021**, *60*, 5840-5850; DOI: 10.1021/acs.inorgchem.1c00215.

- M. Haimerl, C. Graßl, M. Seidl, M. Piesch, M. Scheer*
  'Conversion of E_4 (E_4 = P_4, As_4, AsP_3) by Ni(0) and Ni(I) Synthon –
  A Comparative Study'
  Chem. Eur. J., **2021**, 27, 18129-18134; DOI: 10.1002/chem.202103372.

- M. Haimerl, M. Scheer*
  'Reactivity of Cu(I) Nacnac Complexes Towards [Cp*Ru(η^5-E_5)] (E = P, As)'
  Phosphorus, Sulfur, and Silicon and the Related Elements **2021**;
  DOI: 10.1080/10426507.2021.2011888.

dedicated to my parents

‘I have no special talent. I am only passionately curious.’

Albert Einstein

Preface

Some of the presented results have already been published during the preparation of this thesis (vide supra). The corresponding citations are given at the beginning of the respective chapters.

Each chapter includes a list of authors. At the beginning of each chapter the individual contribution of each author is described. Additionally, if some of the presented results have already been partly discussed in other thesis, it is stated at the beginning of the respective chapters.

To ensure uniform design of this work, all chapters are subdivided into ‘Introduction’, ‘Results and Discussion’, ‘Conclusion’, ‘References’, and ‘Supporting Information’. Furthermore, all chapters have the same text settings and the numeration of compounds starts for every chapter from the beginning. For more clarity the different nacnac ligands (L^0 to L^3) are named the same in every chapter, even if it is different in the publication. The depicted molecular structures may differ in their style. A general ‘Introduction’ and the ‘Research Objectives’ are given at the beginning of this thesis. In addition, a comprehensive ‘Conclusion’ of this work is presented at the end of this thesis.

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1. Introduction

1.1. Phosphorus and Arsenic

The element phosphorus was discovered by the German alchemist Henning Brand in 1669 on his quest for the philosopher's stone.[1] He evaporated urine and heated the residue in absence of air to obtain a luminescent material – phosphorus (Greek: phosphorus – light bearer). Phosphorus can be considered as an element of organic life. The human body contains phosphorus as components of the DNA, bones, teeth and as cellular energy carrier ATP in all organisms.[1] The most important phosphorus sources in the environment are apatite [$Ca_5(PO_4)_3(OH, F, Cl)$] and phosphorite [$Ca_3(PO_4)_2$]. Phosphorus containing compounds has a wide range of applications in industry as e.g. detergents, insecticides, fertilizer, flame retardants or food products but also in the chemical and pharmaceutical industry as organophosphorus derivatives.[2] There are numerous phosphorus allotropes known which can be divided into three main groups: white, black and red phosphorus (Scheme 1.1). The different structures lead to different chemical and physical properties of the allotropes. White phosphorus is the starting material for all of them – which makes it the most important allotrope. It is produced by an electrothermal process via the reduction of calcium phosphates with coke and silicone dioxide and subsequent distillation.

$$Ca_3(PO_4)_2 + 3\ SiO_2 + 5\ C + 1542\ kJ \rightarrow 3\ CaSiO_3 + 5\ CO + P_2$$

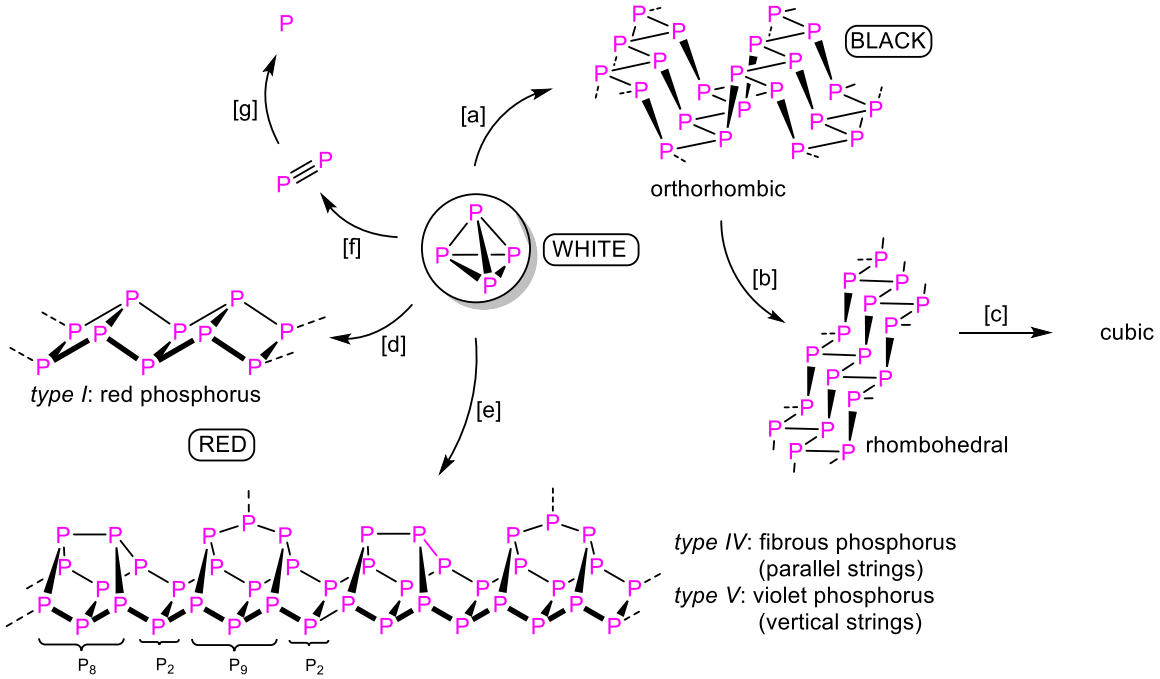
$$2\ P_2 \rightarrow P_4$$

White phosphorus is obtained as a waxy, air sensitive white solid, which can be stored under water. It is the most reactive allotrope of phosphorus and there are three different crystalline modifications (α, β and γ-P_4) known.[3] The phosphorus atoms in P_4 form a tetrahedron, with bond angles of 60° and P-P bond distances of approximately 2.21 Å (determined by electron diffraction: 2.1994(3) Å[4], Raman spectroscopy: 2.2228(5) Å[5] and DFT calculations: 2.1994(3) Å[4]), which is generally known as a phosphorus-phosphorus single bond. Furthermore, the good solubility of P_4 in organic solvents makes it an excellent starting material for chemical industry.

Black phosphorus was discovered by *P. W. Bridgman* in 1914,[6] when he investigated the effect of high pressure on the melting point of white phosphorus (Scheme 1.1, [a]). At ambient conditions black phosphorus is detected in an orthorhombic structure, which consist of corrugated bands of condensed P_6 rings in chair conformation.[7] By increasing the pressure to 80 kbar the structure changed to rhombohedral (arsenic type structure, Scheme 1.1 [b]) and by even higher pressure (110 kbar, Scheme 1.1 [c]) to the cubic structure.[8] Black phosphorus is the thermodynamically most stable modification of

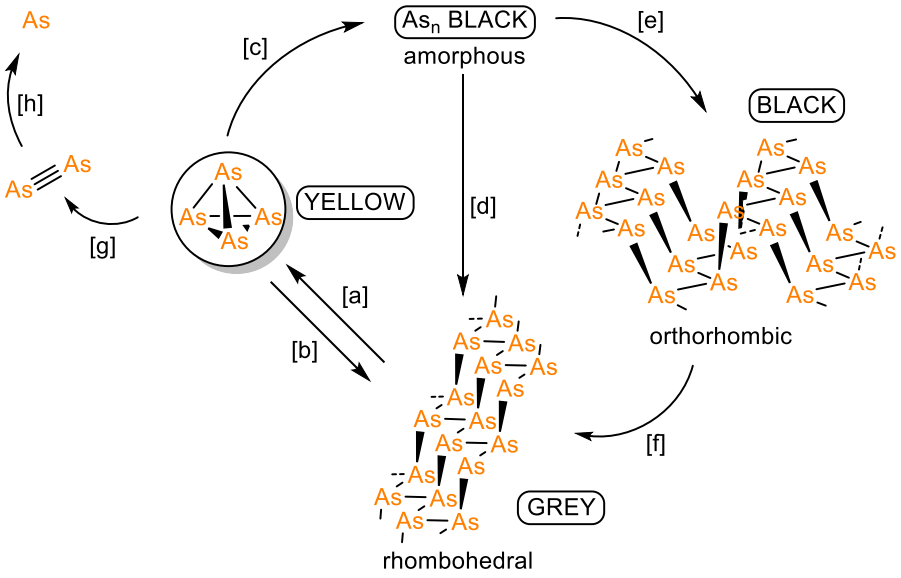
phosphorus at ambient conditions and due to its electric properties of a semiconductor it is also the most metallic modification.[9]

At temperatures over 200 °C and under exclusion of oxygen, white phosphorus transforms into *red phosphorus*. *Roth et al.* were able to classify five types of red phosphorus by successive annealing of P_4 based on X-ray powder diffraction, optical microscopy and differential thermal analysis (DTA).[10] The commercially available red phosphorus (*type I*) is mainly described as an amorphous solid[10] for which several structural proposals are available in the literature.[11] Recent studies imply a linear polymer with a zig-zag ladder structure for red phosphorus (Scheme 1.1, [d]).[12] Until now the molecular structures of *type II* and *type III* red phosphorus are unknown. Increasing the temperature to 500 °C leads to a reorganization of the phosphorus units and to more crystalline forms. The structure of *type IV* red phosphorus was clarified by X-ray diffraction in 2005 and is known as fibrous phosphorus.[13] *Type V* red phosphorus was already discovered in 1865 by *J. W. Hittorf*.[14] The temperature has to be increased to 550 °C for two weeks and due to its violet colour it is known as violet phosphorus or Hittorf's phosphorus. The structure of *type V* red phosphorus was clarified by *Thurn* and *Krebs*.[15] *Type IV* and *type V* red phosphorus consist of alternating P_8 and P_9 units that are connected by P_2 units and can be described as $^1_\infty\{[P_8]P_2[P_9]P_2\}$ strands (Scheme 1.1, [e]). In the case of *type IV* red phosphorus two strands are connected over the P_9 units to form parallel double tubes.[13] In contrast to that the structure of *type V* red phosphorus is linked crosswise, which leads to a 2D double layer.[15]



Scheme 1.1. Systematic summary of the main allotropes of phosphorus and selected formation conditions:[16] a) 12 kbar/200 °C or Hg(cat.)/380 °C, b) 80 kbar, c) 110 kbar, d) type I: 200 – 400 °C, e) type IV: fibrous phosphorus (parallel strings), slow vapor deposition, 500 – 600 °C; type V: violet phosphorus (vertical strings), two weeks/550 °C, f) above 800 °C, g) above 2000 °C.

The heavier analog of phosphorus is arsenic, which was already discovered around 1250 by Bishop *Albertus Magnus* in Regensburg who reduced arsenic trioxid (As_sO_3) with charcoal.[17] In the nature arsenic often occurs in sulfidic ores (e.g. realgar As_4S_4, orpiment As_2S_3) or metal arsenides (e.g. Fe[AsS], Co[AsS]).[17] Arsenic is a double-edged sword: On the one hand it has a very bad reputation due to the criminal poisoning over centuries,[18] the use as herbicides, pesticides and against pests. On the other hand arsenic has several technical applications, for instance in metal alloys, as semi-conductor in the electronic industry (GaAs or InAs) or in the glass industry. The thermodynamically most stable modification at ambient conditions is *grey arsenic* which is produced by heating metal arsenides under exclusion of air to 650 – 700 °C and sublime the arsenic (FeAsS → FeS + As).



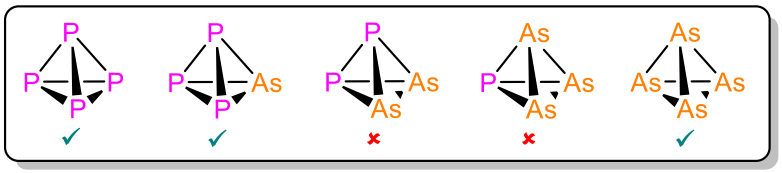
Scheme 1.2. Systematic summary of the main allotropes of arsenic and selected formation conditions:[19] a) sublimation at 616 °C and cool down, b) light or room temperature (slow), c) vapor deposition onto surfaces (100-200 °C), d) T > 270 °C, e) Hg/100-175 °C, f) 300 °C, g) T > 800 °C, h) T > 1700 °C.

Grey arsenic crystallizes in a rhombohedral structure, which consists of condensed As_6 rings in chair conformation, building densely packed arsenic layers (Scheme 1.2, phosphorus analogous: black, rhombohedral phosphorus). Each arsenic atom is surrounded by three arsenic atoms of the same layer (As-As bond lengths: 2.517 Å) and three arsenic atoms of the next layer (As-As distances: 3.120 Å).[20] This formation leads to a distorted octahedral environment which reminds a cubic packing and is in accordance with the metallic character of grey arsenic. The sublimation of grey arsenic occurs at 616 °C.[21] By injecting the arsenic vapor into a solvent and allowing it cool down, *yellow arsenic* can be obtained as very air, moisture and light-sensitive solid, which transform auto-catalytically back to grey arsenic by time or light. It is the most reactive modification of arsenic and the only allotrope which can be handled in solution. The As-As bond length of the As_4 tetrahedron (Scheme 1.2, phosphorus analogous: white phosphorus) amount to

2.435 Å (determined by gas electron diffraction on As_4 vapor: 2.435(4) Å[22] and DFT calculations: 2.437 Å[23]), which is generally known as an arsenic-arsenic single bond. The preparation of yellow arsenic in CS_2 was first described by *Bettendorff* in 1867.[24]

Condensing the arsenic vapor onto heated surfaces (100 – 200 °C) amorphous *black arsenic* can be obtained.[25] Heating amorphous black arsenic under presence of metallic mercury to 100 – 175 °C there is a formation to orthorhombic black arsenic which is isostructural to orthorhombic black phosphorus. Both modifications of black arsenic decompose to grey arsenic at temperatures above 300 K.

In 2009, *Cummins et al.* reported the synthesis of the interpnictogen compound AsP_3 (Scheme 1.3), which can be obtained from the reaction of [Na][(ODipp)$_3$Nb(η^3-P_3)] with $AsCl_3$.[26] In contrast to yellow arsenic, AsP_3 is stable and as easy to handle as P_4. This interpnictogen compound represent the first step to close the gap between white phosphorus and yellow arsenic. After this success, they were also interested in a synthesis of As_2P_2 and As_3P (Scheme 1.3). The reaction of AsP_3 with [(ODipp)$_3$NbCl_2] and a subsequent reduction with Na/Hg amalgam leads to the formation of a mixture of compounds of the formular [Na][(ODipp)$_3$Nb(η^3-E_3)] (E_3 = P_3, AsP_2, As_2P, As_3).[27,28] Treating the reaction solution with $AsCl_3$ under exclusion of light generates a mixture of AsP_3, As_2P_2, As_3P and As_4.[29] The presence of these compounds were confirmed by ^{31}P NMR spectroscopy and GC-MS,[27] but up to now, there is no synthesis known for pure As_2P_2 or As_3P.



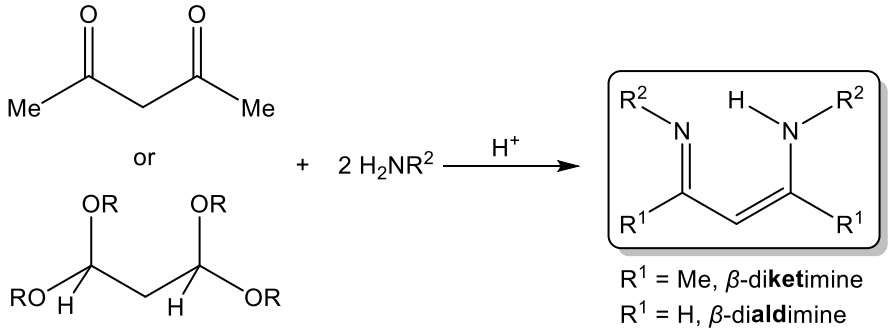
Scheme 1.3. Overview over the different E_4 tetrahedra (E = P, As). (Synthesis for pure E_4 compounds, known: ✓, unknown: ✗).

1.2. The *β*-diiminato ligand

While the chemistry of *β*-diketones was extensively studied over decades, the chemistry of *β*-diiminato ligands was quite unknown until easy synthesis were published in 1968 and their first application in coordination chemistry identify them as tunable and extensive steric spectator ligands with strong metal to ligand bonds.[30] Increased attention was paid to the *β*-diiminato ligands after the preparation of [{N($C_6H_3{}^iPr_2$-2,6)C(Me)}$_2$CH]$^-$ (L^3, Scheme 1.5) and its application in an ethylene polymerization process.[31] Up to now, the use of *β*-diiminato ligands reaches from the use as catalysis for polymerization,[32] the stabilization

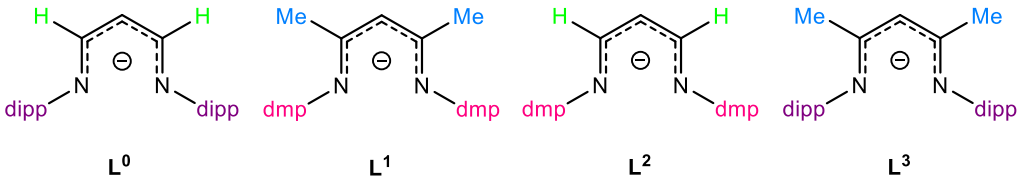
of metal(I) oxidation states[33] towards the activation of small molecules like H_2, N_2 or O_2[34] with such M(I) complexes.

There are various known routes for the synthesis of *β*-diiminato ligands.[35] One of the simplest methods is a condensation reaction of acetylacetone (acac) or 1,1,3,3-tetraalkoxypropane with two equivalents of a primary amine under acid conditions (Scheme 1.4). The family of *β*-diiminato ligands can be divided into two different classes depending on the substituent R^1. For R^1 = H the ligands are specified as *β*-di**ald**iminato ligands, for R^1 = Me as *β*-di**ket**iminato ligands also known as “nacnac” (in analogy to acac).



Scheme 1.4. Synthetic route of *β*-diiminato ligands (*β*-diketiminato ligands= nacnac).

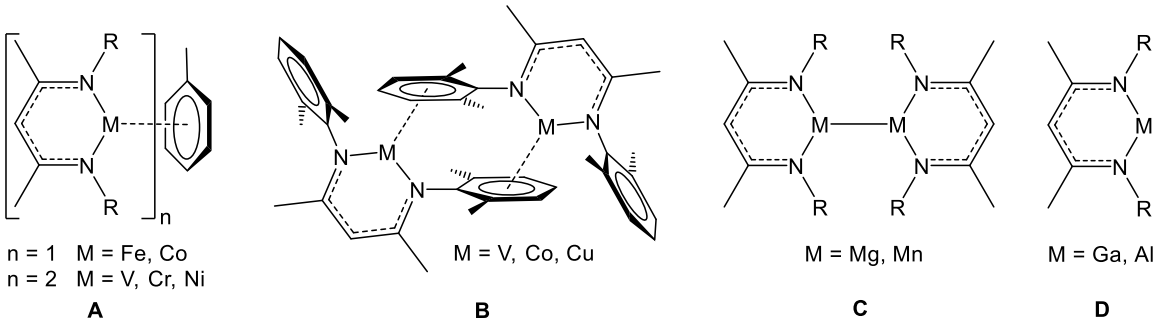
The use of *β*-diiminato ligands has various advantageous: the simple synthetic route, cheap starting materials, good yields and the possibility to scale up. Further, the electronical and steric properties can be fine-tuned by varying the substituents R^1 and R^2. Various combinations of *β*-diiminato ligands are existing with different backbone substituents (R^1 = H, Me, CF_3, ^{t}Bu) and imine substituents (R_2 = Et, various phenyl groups, fluorinated groups).[34b,36] The most common *β*-diiminato ligands used in this work are depicted in Scheme 1.5.



Scheme 1.5. Selected examples of *β*-diiminato ligands L^0-L^3 (dmp = 2,6-dimethylphenyl, dipp = 2,6-diisopropylphenyl).

By deprotonation (e.g. with ^{n}BuLi) and subsequent salt metathesis, numerous low valent main group or transition metals have been stabilized.[35] The metal center is stabilized by the sterically demanding aromatic flanking groups (e.g. dmp, dipp) and can attain additionally stabilization by various labile ligands (for selected examples see Scheme 1.6). There are complexes bearing solvent molecules as toluene or benzene as labile ligands. Such complexes are realized as mono- or dinuclear species (Scheme 1.6, **A**).[34d,37] Another possibility is an intramolecular saturation of the metal center by coordination of the aromatic flanking groups (Scheme 1.6, **B**).[38] Moreover, the metal center can also be

saturated by a M-M bond (Scheme 1.6, **C**)[34c,39] and with the group 13 metals aluminum and gallium no further saturation is observed (Scheme 1.6, **D**).[33]

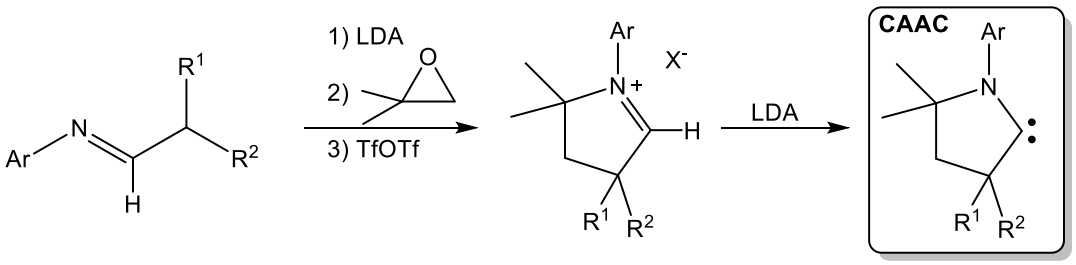


Scheme 1.6. Selected examples of low valent metal complexes stabilized by *β*-diiminato ligands (R = aromatic flanking group, e.g. dmp, dipp).

Due to the labile ligands of such low valent metal complexes, they are suitable precursors for the reductive activation of small molecules.

1.3. Cyclic Alkyl Amino Carbenes – CAACs

Since their discovery in 2005,[40] cyclic alkyl amino carbenes (CAACs) gained increased attention.[41] Formally, one electronegative amino substituent of a N-heterocyclic carbene (NHC) is replaced by a strong σ-donor alkyl group,[40] that make CAACs to the most nucleophilic and also electrophilic carbenes, that are still stable, up to now. This is due to the fact, that the HOMO (= highest occupied molecular orbital) of CAACs is energetically slightly higher than that of NHCs and the singlet-triplet gap is slightly smaller.[42] Various ligand combinations were created displaying different R^1 and R^2 substituents (Scheme 1.7) and different (but urgently required) aryl groups on the nitrogen center (e.g. dipp). One possible synthetic route and the general structure of CAACs is depicted in Scheme 1.7.

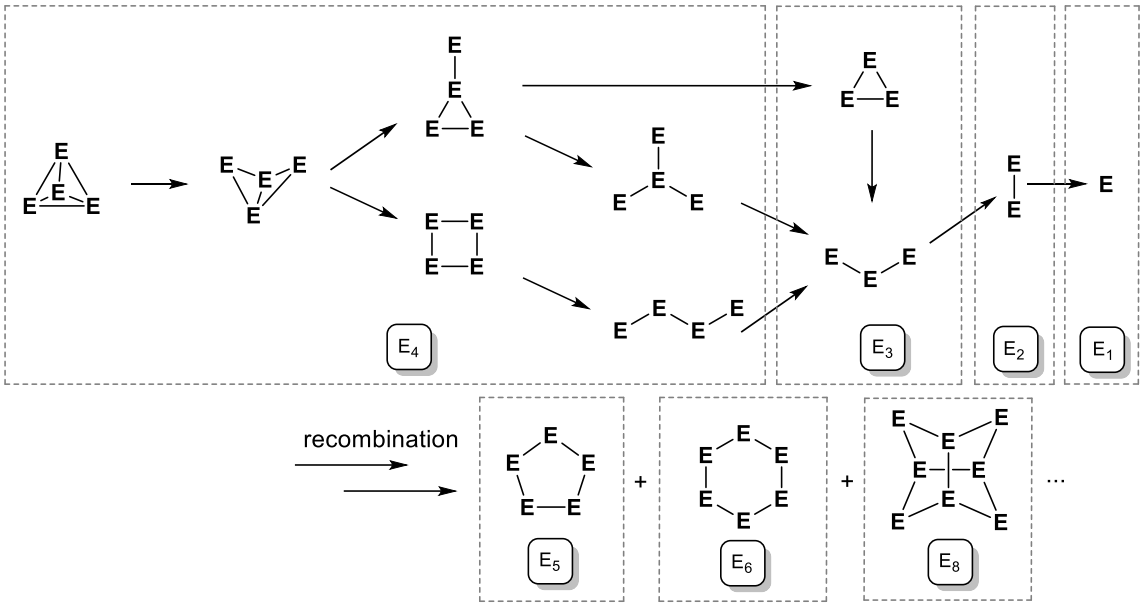


Scheme 1.7. Synthetic route of CAACs (LDA = lithiumdiisopropylamide, TfOTf = trifluoromethanesulfonic acid anhydride).

Its versatile applications in different research objectives range from the coordination chemistry, transition metal catalysis, stabilization of reactive intermediates to activation of small molecules like H_2 or N_2.[41h]

1.4. Reactivity of E_4 (E_4 = P_4, As_4, AsP_3)

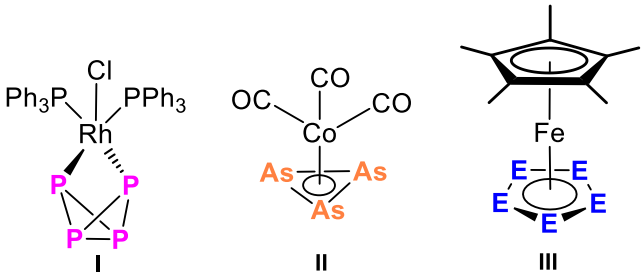
White phosphorus is an important starting material in industry for the synthesis of organophosphorus compounds like R_3P, R_5P or $(RO)_3P$, which is based on chlorination of white phosphorus and a subsequent reaction with alcohols or Grignard/organolithium reagents. These processes lead to stoichiometric amounts of waste (HCl, LiCl, MgClX), which is neither environmentally friendly nor sustainable.[2] Because of that a direct functionalization of white phosphorus is desirable, which can be feasible by the activation in the coordination sphere of transition metal or main group units. Such reactive fragments can be produced by thermolysis, photolysis or the release of labile ligands (e.g. toluol, acetonitrile). The activation of white phosphorus and also its heavier analogue yellow arsenic has become a central topic in the academic research over the last decades. Up to now, there are numerous research articles about the activation of E_4 with transition metal or main group compounds.[43] This gives a deeper insight into the stepwise degeneration by successive E-E bond cleavage of the E_4 tetrahedra or the recombination to higher E_n units (Scheme 1.8).



Scheme 1.8. Overview of the stepwise degeneration of an intact E_4 (E = P, As) tetrahedron in the coordination sphere of metal complexes and possible aggregation products. Bonding modes and charges are omitted for clarity.

The first polyphosphorus (P_n) ligand complexes were reported by *Ginsberg and Lindsell* in 1971.[44] These complexes $[L_2RhCl(\eta^{1:1}\text{-}P_4)]$ (**I**, L = PPh_3, $P(p\text{-}CH_3C_6H_4)_3$, $P(m\text{-}CH_3C_6H_4)_3$ or $As(C_6H_5)_3$, Scheme 1.9) contain a P_4 unit in an $\eta^{1:1}$ side-on coordination mode, which is also known as butterfly unit.[45] Already two years before *Dahl et al.* synthesized the first polyarsenide (As_n) compound $[(CO)_3Co(\eta^3\text{-}As_3)]$ (**II**, Scheme 1.9) by the reaction of $[Co_2(CO)_8]$ with $[AsCH_3]_5$.[46] Decades of extensive studies lead to a plethora of E_n ligand complexes with E_n units up to 24 phosphorus[47] and 18 arsenic atoms[48]. One of the most

prominent derivatives is [Cp*Fe(η^5-E_5)] (**III**; E = P, As, Scheme 1.9) which was synthesized by *Scherer et al*..[49] These compounds were the subject of numerous research topics: The reactivity of **III** towards electrophiles, nucleophiles and their redox behavior[48,50] and further its use as a building block for coordination polymers and spherical aggregates[51] was extensively studied.

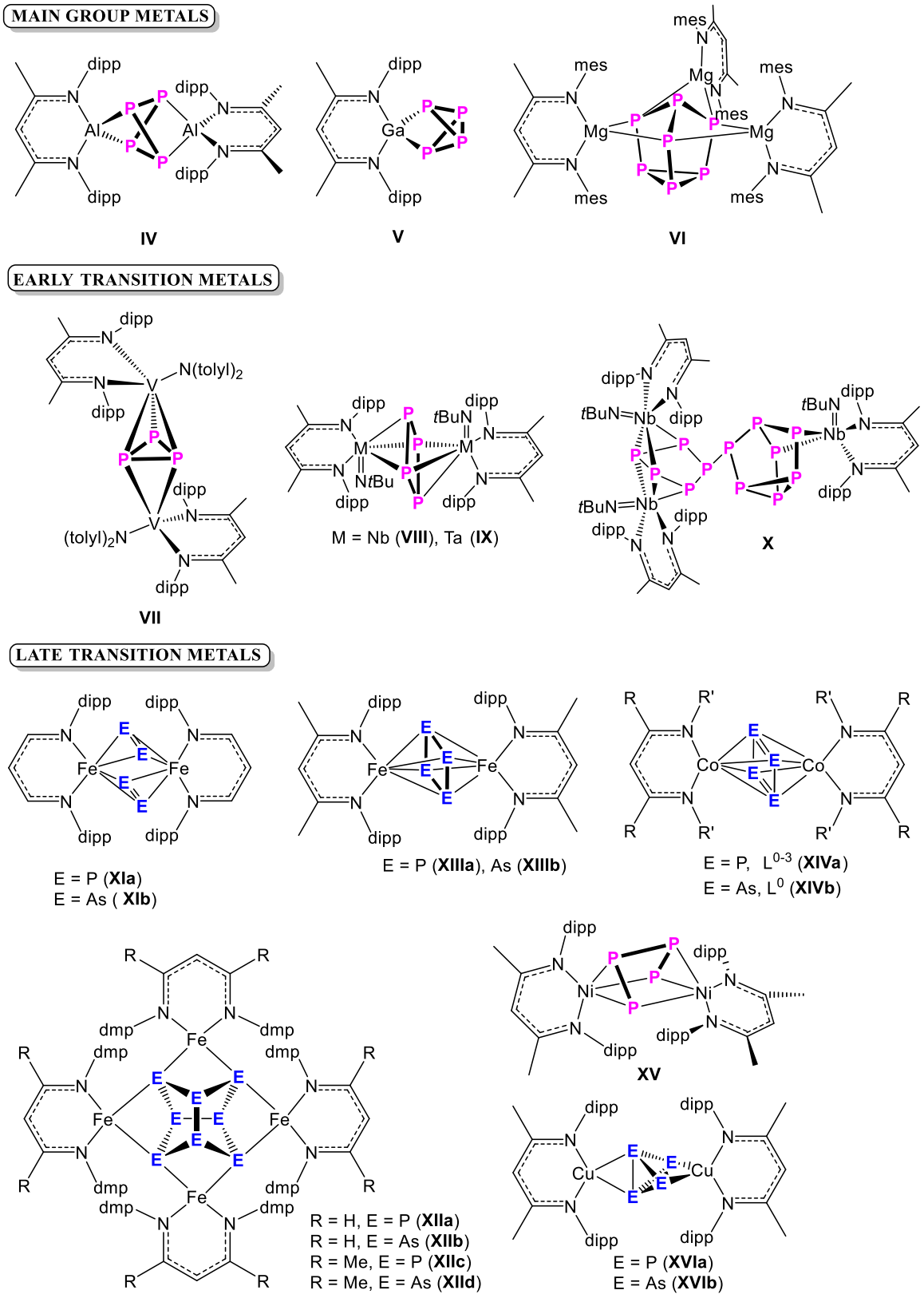


Scheme 1.9. Selected examples of E_n ligand complexes (E = P, As).

As already mentioned, low valent metal complexes stabilized by *β*-diiminato ligands are suitable precursors for the reductive activation of small molecules like P_4 and As_4. As illustrated in Scheme 1.10 several main group and transition metal complexes were used for the activation of E_4 in the last two decades. Started in 2004, *Roesky et al.* reported the reaction of the main group compound [L^3Al] (L^3 = [{N($C_6H_3{}^iPr_2$-2,6)C(Me)}$_2$CH]$^-$) with white phosphorus, this leads to the formation of the dinuclear aluminum complex [(L^3Al)$_2$(μ,$\eta^{1:1:1:1}$-P_4)] (**IV**) which contains a folded *cyclo*-[P_4]$^{4-}$ unit.[52] In comparison to that, the reaction of white phosphorus with the Al(I) species [Cp*Al]$_4$ leads to the formation of five Al_2P_2 rings which sharing the edges and form a P_4Al_6 framework.[53] The reaction with the corresponding gallium complex leads to the formation of [L^3Ga($\eta^{1:1}$-P_4)][54] (**V**) and other polyphosphanes stabilized by two {L^3Ga} fragments[55]. *Mahon et al.* synthesized the compound [($L^{Me,mes}$Mg)$_3$(μ,$\eta^{1:1:1:1:1:1}$-P_7)] (**VI**, $L^{Me,mes}$ = [{N($C_6H_2Me_3$-2,4,6)C(Me)}$_2$CH]$^-$) containing a nortricyclan like [P_7]$^{3-}$ unit.[56] There are also some examples of P_4 activation with early transition metal complexes known. The neutral, dinuclear vanadium complex [(L^3V(N(tolyl$_2$))$_2$(μ,$\eta^{3:2}$-P_3)][57] (**VII**, tolyl = 4-MeC_6H_4) containing a *cyclo*-[P_3]$^{3-}$ ligand was reported in 2015. With the heavier group 5 metals, the dinuclear complexes [(L^3(N^tBu)M)$_2$(μ,$\eta^{3:3}$-P_4)][58] (M = Nb (**VIII**), Ta (**IX**)) with a bridging *cyclo*-P_4 unit in an $\eta^{3:3}$ coordination mode and with niobium also the minor product of the reaction [(L^3NbN^{t}Bu)$_3$(μ$_3$,$\eta^{3:3:1:1}$-P_{12})][58] (**X**) could be isolated. Up to now, there are no known examples of the conversion of yellow arsenic with main group or early transition metals stabilized by *β*-diiminato ligands.

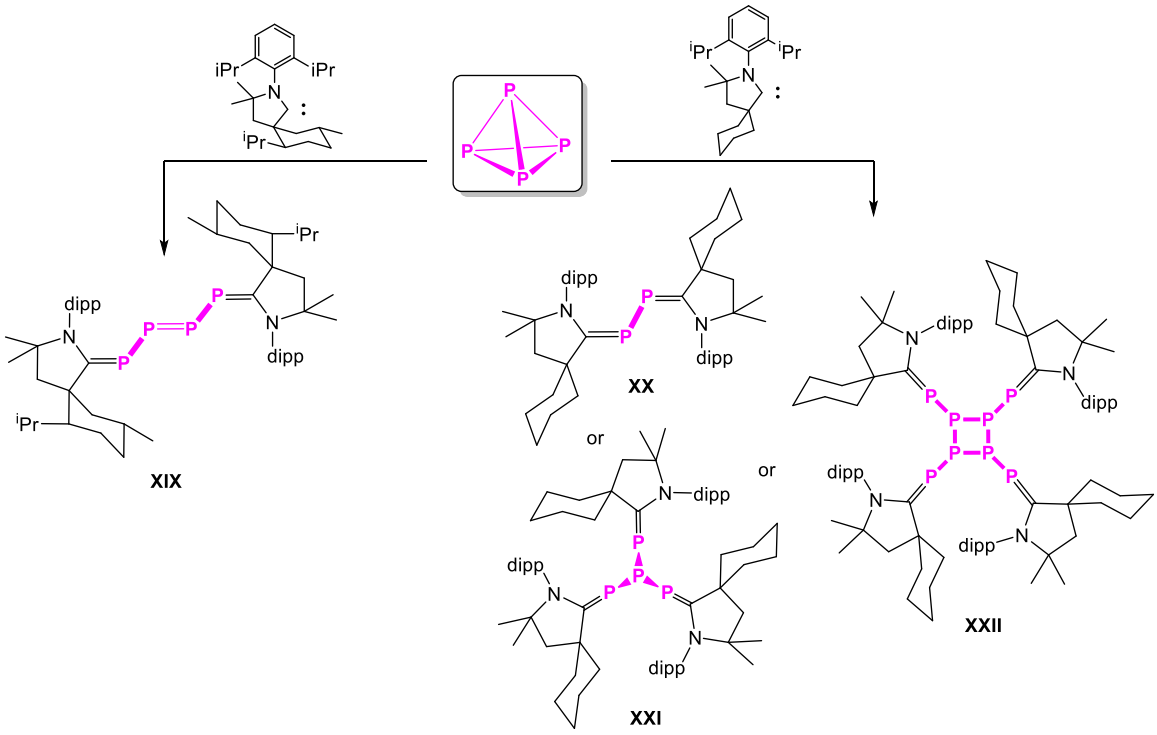
Quite different is the situation with late transition metal complexes stabilized by *β*-diiminato ligands. In the last few years there have been many efforts to activate E_4. In the case of iron and cobalt complexes a systematic study with different *β*-diiminato ligands was performed.[37d,37e,38c,59] The steric and electronic properties of the ligands can have a strong influence on the reactivity and the structure of the resulting E_n unit. *Driess et al.* reported

the synthesis of the dinuclear complex $[(L^0Fe)_2(\mu,\eta^{2:2}\text{-}P_2)_2]$ (**XIa**, L^0 = $[\{N(C_6H_3{}^iPr_2\text{-}2,6)C(H)\}_2CH]^-$) containing two $[P_2]^{2-}$ units, an analogues arsenic derivative has also been reported.[59a,59c] By replacing the aromatic flaking groups of the *β*-diiminato ligand from dipp (= 2,6-diisopropylphenyl) groups to the sterically less hindered dmp (= 2,6-dimethylphenyl) groups a realgar-type[60] E_8 unit stabilized by four iron(II) centers could be obtained (**XIIa-XIId**).[37d,59c] Further, using the bulkiest ligand in this line – L^3 – the same reaction conditions leads to the dinuclear iron complex $[(L^3Fe)_2(\mu,\eta^{4:4}\text{-}E_4)]$ (E = P (**XIIIa**), As (**XIIIb**))[37d,59c], which contains a planar *cyclo*-$[E_4]^{2-}$ unit. This study elucidates the effect of slightly different ligands on the structure of the obtained products. In the case of *β*-diiminato Co(I) complexes a similar study was performed, which indicates that the ligand system not always influence the E_n unit. While in the case of phosphorus with L^0-L^3 a rectangular-shaped $[P_4]^0$ moiety stabilized by two {LCo} fragments (**XIVa**) is formed,[37e,38c] the reactions with yellow arsenic lead to four different compounds, all with slightly different $[Co_2As_4]$ cores.[59b] Moreover, *Driess et al.* reported the nickel complex $[(L^3Ni)_2(\mu\text{-}\eta^2,\kappa^1\text{:}\eta^2\kappa^1\text{-}P_4)]$ (**XV**) containing a prism-like structure motif, from which a $\{L^3Ni\}$ fragment can be released in solution.[61] Recently, our group reported the first neutral and molecular complexes of copper containing an intact E_4 tetrahedra, which can be released in a controlled manner.[62] In solution there is an equilibrium between the mono- and dinuclear compound $[(L^3Cu)_2(\mu,\eta^{2:2}\text{-}P_4)]$ (**XVIa**) and $[L^3Cu(\eta^2\text{-}P_4)]$ (**XVII**).[62] Furthermore, there are efforts to investigate the reactivity of *β*-diiminato M(I) complexes towards E_n ligand complexes. Recently, *Roesky et al.* reported the reaction of $[L^3Al]$ with $[Cp^*Fe(\eta^5\text{-}P_5)]$ which leads to $[(Cp^*Fe)(\mu,\eta^{5:3}\text{-}P_5)(L^3Al)]$ (**XVIII**) containing an envelope-shaped P_5 ring.[63]



Scheme 1.10. Selected examples of E_n ligand complexes containing *β*-diiminato ligands with main group, early and late transition metals (dmp = 2,6-dimethylphenyl, dipp = 2,6-diisopropylphenyl, mes = 2,4,6-methylphenyl, tolyl = 4-MeC_6H_4).

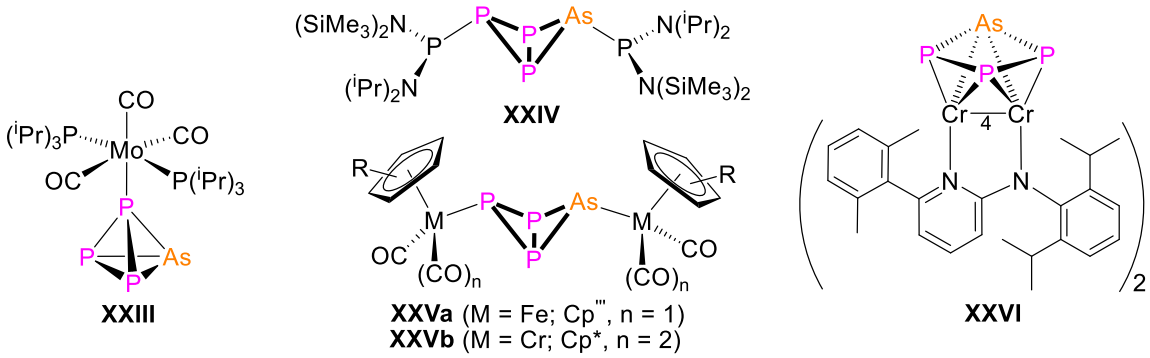
There are also some known examples of the conversion of white phosphorus with different CAACs, which are depicted in Scheme 1.11. *Bertrand et al.* reported a 2,3,4,5-tetraphosphatriene derivative which is stabilized by two menthyl substituted CAACs (**XIX**) in 2007.[64] The reaction with a less hindered cyclohexyl-substituted CAAC leads in dependence of the stoichiometry to three different products: A 1:3 stoichiometry (P_4:CAAC) leads to the formation of the P_2-dicarbene adduct [(CAAC)$_2$(μ,η$^{1:1}$-P_2)][65] (**XX**) and an isotetraphosphan adduct stabilized by three CAAC molecules [(CAAC)$_3$(μ$_3$,η$^{1:1:1}$-P_4)] (**XXI**).[66] The same reaction in a 2:1 stoichiometry (P_4:CAAC) leads to the formation of a P_8 tetracarbene (**XXII**).[67] To the best of our knowledge there are no reactions of yellow arsenic with CAACs known. But in the last years there have been efforts to find another way to synthesized arsenic containing compounds stabilized by CAACs. The reaction of ^{Et}CAAC with $AsCl_3$ and further reduction leads to the formation of [(^{Et}CAAC)$_2$(μ,η$^{1:1}$-As_2)].[68] An isostructural compound with antimony is also known.[69]



Scheme 1.11. Conversion of white phosphorus by different CAACs.

Due to the fact, that AsP_3 was first synthesized in its pure form in 2009,[26] there are only a few complexes known which contain AsP_3 as a ligand. Selected examples are depicted in Scheme 1.12. The first compound synthesized by the activation of AsP_3 was [(P^{i}Pr$_3$)$_2$Mo(CO)$_3$(η^1-AsP_3)] (**XXIII**)[26,27] which contains an intact η^1-coordinated AsP_3 tetrahedron. The reaction of the diphosphine [P{N(SiMe$_3$)$_2$}$_2${(N^{i}Pr$_2$)$_2$}]$_2$[70] (which reversibly dissociates in solution to the phosphinyl radical $^{\bullet}$[P{N(SiMe$_3$)}(N^{i}Pr$_2$)]) with AsP_3 leads to [{(^{i}Pr$_2$N)(SiMe$_3$)P}$_2$(μ,η$^{1:1}$-AsP_3)] (**XXIV**)[27] which contains an AsP_3 butterfly unit. Similar AsP_3 butterfly units could be obtained within the complexes [(Cp^{R}M(CO)$_n$)(μ,η$^{1:1}$-AsP_3)] (M = Fe, Cp^R = Cp‴, n = 2 (**XXVa**); M = Cr, Cp^R = Cp*, n = 3 (**XXVb**)).[71] Further, our group

reported the reactivity of E_4 (E_4 = P_4, As_4, AsP_3) towards a chromium complex, which lead to bimetallic complexes containing *cyclo*-E_4^{2-} ligands as terminal *cyclo*-E_4-enddecks (**XXVI**).[72] The X-ray structure of these compounds show a disorder over more than one position for the arsenic atom in the AsP_3 ligand.



Scheme 1.12. Selected examples of complexes containing AsP_3 ligands.

1.5. References

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2. Research Objectives

The conversion of white phosphorus and yellow arsenic by transition metal and main group complexes was extensively studied and leads to a plethora of E_n ligand complexes (E = P, As). Most of them containing well established ligand systems as Cp^R (= cyclopentadienyl derivatives) or multidentate phosphines. In the last two decades two more ligand systems gained increasing attention by activating small molecules: the *β*-diiminato ligands and cyclic alkyl amino carbenes (CAACs). Only a few examples for the conversion of white phosphorus with main group and early transition metal complexes stabilized by *β*-diiminato ligands has been reported. Examples of the conversion with yellow arsenic are unknown. *Bertrand et al.* have already reported some reactions of white phosphorus with different CAACs but reactions of yellow arsenic are still missing, too. A different situation is obtained with late transition metal complexes stabilized by *β*-diiminato ligands. With iron and cobalt complexes, a comparative study of the conversion of E_4 was performed with different *β*-diiminato ligand systems. Furthermore, molecular and neutral copper complexes could be obtained with neutral and intact E_4 tetrahedra. Nevertheless, there are still some late transition metal complexes (e.g. $[(L^3Ni)_2tol]$, $L^3 = [\{N(C_6H_3{}^iPr_2\text{-}2,6)C(Me)\}_2CH]^-$) which were not reacted with yellow arsenic. Another interesting topic is the reactivity of such *β*-diiminato ligand complexes towards E_n ligand compounds. First investigations of the reactivity of $[L^3Al]$ towards $[Cp^*Fe(\eta^5\text{-}P_5)]$ ($Cp^* = C_5(CH_3)_5$) have already been performed by the group of *Roesky et al.* in 2020. These lead to the question if the E-E bonds in *cyclo*-E_n units can be activated, opened up, or be still intact by nacnac metal fragments.

Therefore, the following research objectives arise:

- Reactivity of white phosphorus, yellow arsenic and the interpnictogen compound AsP_3 towards low valent transition metal (Ni, Cu) or main group (Al, Ga) compounds stabilized by *β*-diiminato ligands.
- Reactivity of white phosphorus, yellow arsenic and the interpnictogen compound AsP_3 towards cyclic alkyl amino carbenes (CAACs).
- Investigations on the reactivity of M(I) (M = Cu, Ga) nacnac complexes towards E_n ligand compounds.

Preface

"Reactivity of Cu(I) Nacnac Complexes Toward Polypnictogen Compounds"

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Authors

M. Haimerl, M. Piesch, G. Balázs, P. Mastrorilli, W. Kremer, M. Scheer*

Author contributions

The main part of the manuscript was done by the first author (M. Haimerl). The preparation and characterization (NMR, MS, EA, X-ray) of all compounds was done by the first author. G. Balázs and M. Piesch performed the DFT calculations and contributed the corresponding parts in the manuscript and the Supporting Information. P. Mastrorilli performed and analyzed the $^{31}P\{^{1}H\}$ EXSY spectra and contributed the corresponding part in the manuscript. W. Kremer recorded the $^{31}P\{^{1}H\}$ MAS spectra. M. Scheer supervised the research and revised the manuscript.

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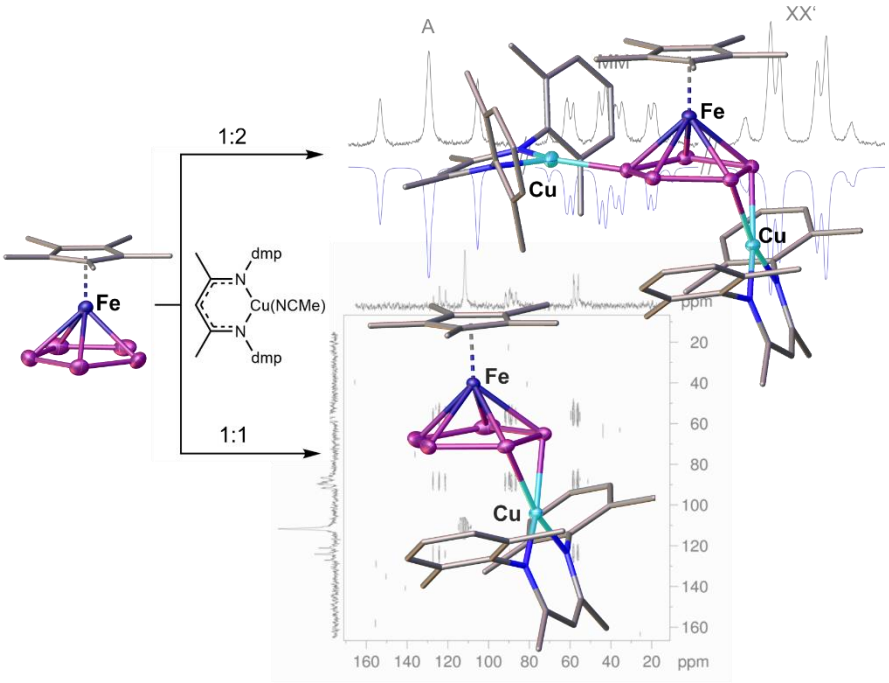
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Cu
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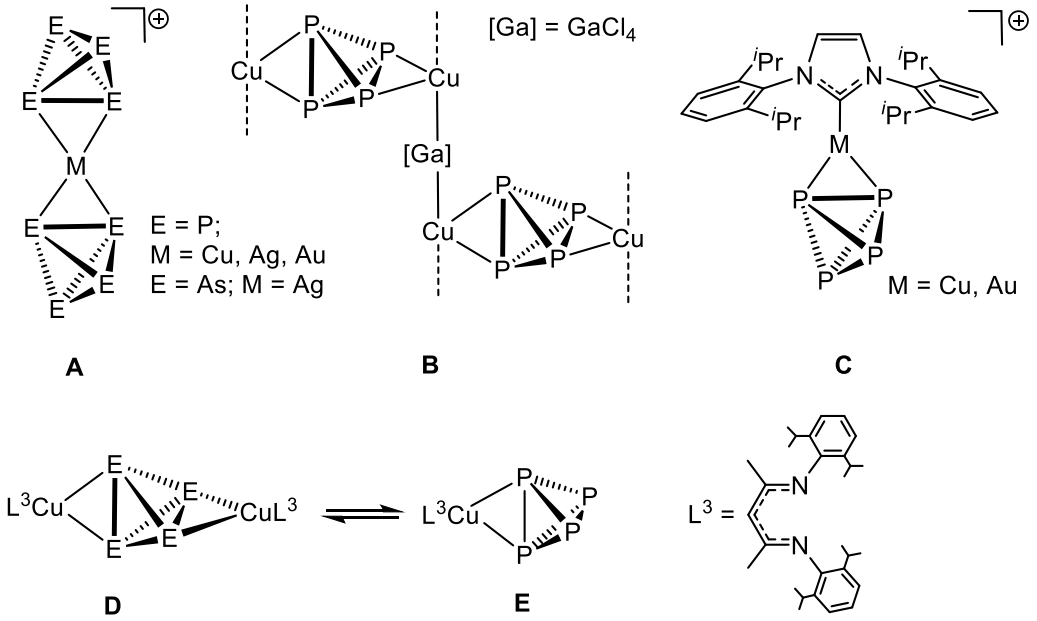
3. Reactivity of Cu(I) Nacnac Complexes Toward Polypnictogen Compounds

Abstract: *The nancnac Cu(I) compound [L^1Cu(MeCN)] (**2**) (L^1 = [{N($C_6H_3Me_2$-2,6)C(Me)}$_2$CH]$^-$) was reacted with complexes containing aromatic cyclo-E_5 ([Cp*Fe(η^5-E_5)], E = P (**1a**), As (**1b**), Cp* = η^5-C_5Me_5), cyclo-P_4 ([Cp'''Co(η^4-P_4)] (**3**), Cp''' = η^5-$C_5H_2{}^tBu_3$) and cyclo-E_3 ligands ([Cp'''Ni(η^3-E_3)], E = P (**4a**), As (**4b**)) yielding the heterometallic complexes [(Cp*Fe)(μ,$\eta^{5:2}$-E_5)(L^1Cu)] (E = P (**5a**), As (**5b**)), [(Cp*Fe)(μ_3,$\eta^{5:2:1}$-E_5)(L^1Cu)$_2$] (E = P (**6a**), As (**6b**)), [(Cp'''Co)(μ,$\eta^{4:2}$-P_4)(L^1Cu)] (**7**), [(Cp'''Co)(μ_3,$\eta^{4:2:1}$-P_4)(L^1Cu)$_2$] (**8**) and [(Cp'''Ni)(μ,$\eta^{3:2}$-E_3)(L^1Cu)] (E = P (**9a**), As (**9b**)). These complexes are rare examples for the coordination of a group 11 metal coordinating to aromatic cyclo-E_n (E = P, As; n = 3-5) ligand complexes. All products were comprehensively characterized by crystallographic and spectroscopic methods. The dynamic behavior in solution was studied by VT (variable temperature) NMR spectroscopy and their electronic structures were elucidated by DFT calculations.*

3.1. Introduction

Element-Element bond cleavage, activation or preservation after coordination to Lewis acidic moieties is a central question in coordination chemistry and catalysis. The conversion of white phosphorus and yellow arsenic, respectively, was studied extensively in the last decades yielding a plethora of polypnictogen (E_n) ligand complexes (E = P, As).[1] The first step of the E_4 transformation by transition metals moieties reveals complexes containing intact E_4 tetrahedra (E = P, As) as ligands.[1c-e,2] By using weakly coordinating anions (WCAs), even complexes of such weak ligands as E_4 (E = P, As) could be stabilized in the coordination sphere of coinage metal ions.[3] Selected examples are [Cu(η^2-P_4)$_2$][pftb] (pftb = [Al{OC(CF_3)$_3$}$_4$]) (**A**),[3b] the coordination polymer [P_4CuGaCl_4]$_n$ (**B**)[3c] or [IPrM(η^2-P_4)][Al(pftb)$_4$] (**C**; M = Cu, Ag) (Scheme 3.1).[3e] They contain intact P_4 tetrahedra, although an elongation of the coordinated P-P bond has occurred. Beside WCAs, also organometallic copper complexes containing a permanent coordinating ligand as for instance *β*-diketiminate (nacnac) can coordinate P_4 and As_4. Thus, it was possible to synthesize and characterize the complexes [(L^3Cu)$_2$(μ_2,$\eta^{2:2}$-E_4)] (L^3 = nacnac = [{N($C_6H_3{}^iPr_2$-2,6)C(Me)}$_2$CH]$^-$, **D1**: E = P; **D2**: E = As) and [L^3Cu(η^2-P_4)] (**E**) (Scheme 3.1).[4a] These were the first neutral molecular complexes containing an intact E_4 tetrahedron in a bridging, side-on coordination mode. These complexes are neither sensitive to light nor flammable. They can be stored for a long time and serve as sources of E_4 by releasing it in a controlled manner. In addition to E_4-containing complexes, there is a large number of polypnictogen ligand complexes that are formed by a stepwise degeneration of E_4 by successive E-E bond cleavages or the aggregation (n>4) of E_4 units. The most prominent derivative is [Cp*Fe(η^5-E_5)] (E = P (**1a**), As (**1b**), Cp* = η^5-C_5Me_5) which contains a *cyclo*-E_5 ligand that is isolobal to the well-known Cp (cyclopentadienyl) ligand.[5] Beside the investigation of the reactivity of **1** towards nucleophiles and its redox chemistry,[6] **1** was used as building block for coordination polymers and for spherical aggregates in the supramolecular chemistry.[7]



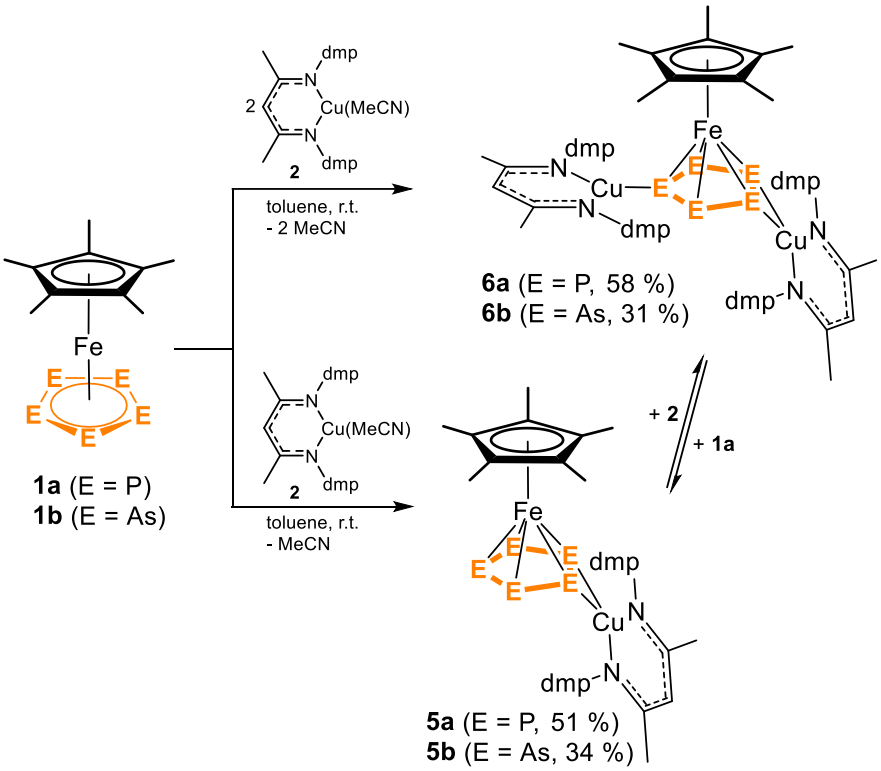
Scheme 3.1. Selected examples of compounds containing intact E_4 (E = P, As) ligands.

Based on the properties of {LCu} moieties to coordinate and to activate E-E bonds, the question arose as to what extent the E-E bonds in E_n ligands can be activated, opened up or be still intact by {LCu} fragments as well as what types of coordination modes are preferred. To increase the level of activation (from a simple single bond in E_4 to a more multiple bond), we focused especially on aromatic *cyclo*-E_n systems, which are known to be rather robust. Also the question of the reaction progress arose weather a mono or a disubstitution occurs. Herein, we report on the reactivity of [L^1Cu(MeCN)] (**2**)[8] (L^1 = [{N(C_6H_3Me-2,6)C(Me)}$_2$CH]$^-$) towards complexes containing aromatic *cyclo*-E_n ligands as end decks i.e. [Cp*Fe(η^5-E_5)] (E = P (**1a**), As (**1b**)), [Cp'''Co(η^4-P_4)] (Cp''' = η^5-$C_5H_2{}^tBu_3$) (**3**)[9] and [Cp'''Ni(η^3-E_3)] (E = P (**4a**), As (**4b**)).[10] This results in compounds in which, first, a side-on coordination occurs, revealing a closed E-E bond, whereas, afterwards, the second molecule {L^1Cu} tends to be end-on coordinated. These products represent neutral molecular complexes of group 11 metals containing the rare η^2-side-on coordination mode to the intact *cyclo*-E_n ligand complexes. All molecules show a highly dynamic behavior in solution, which could be clarified by detailed NMR studies.

3.2. Results and Discussion

The reaction of [L^1Cu(MeCN)] (**2**) with one equivalent of [Cp*Fe(η^5-E_5)] (E = P (**1a**), As (**1b**)) in toluene at room temperature leads to the quantitative formation of [(Cp*Fe)(μ,$\eta^{5:2}$-E_5)(L^1Cu)] (E = P (**5a**), As (**5b**)).[11] Crystals of **5** were obtained as brown air-sensitive solids in isolated crystalline yields of 51% (**5a**) and 34% (**5b**), respectively (Scheme 3.2). Performing the reaction in a 2:1 stoichiometry of the reactants leads to the formation of the

trinuclear heterobimetallic complex [(Cp*Fe)(μ$_3$,η$^{5:2:1}$-E$_5$)(L^{1}Cu)$_2$] (E = P (**6a**), As (**6b**)), which is obtained as a brown (**6a**) or orange (**6b**) air-sensitive solid in crystalline yields of 58% and 31%, respectively (Scheme 3.2).



Scheme 3.2. Reaction of [Cp*Fe(η^5-E$_5$)] with [L^{1}Cu(MeCN)]. (dmp = 2,6-dimethylphenyl).

Compound **6a** shows a dynamic behavior in solution, which was studied by variable temperature (VT) NMR spectroscopy (Figure 3.1). At room temperature, the ^{31}P{^{1}H} NMR spectrum of **6a** in toluene-d_8 shows a broad signal at 86.1 ppm ($\omega_{1/2}$ = 1578 Hz). Dissolving compound **6a** at -80 °C and recording its ^{31}P{^{1}H} NMR spectrum at this temperature, the broad signal splits into three sharp multiplets centered at δ = 122.9 ppm, 89.4 ppm and 54.8 ppm, respectively, with an integral ratio of 1:2:2 displaying an AMM'XX' spin system. With increasing temperature, the signals broaden and, at 333 K, only a broad singlet at 89.0 ppm ($\omega_{1/2}$ = 213 Hz) is observed. At this temperature, the dynamic process is fast on the NMR time scale and all phosphorus atoms become equivalent. The activation parameters, calculated by a line shape analysis, are: $\Delta H^{\ddagger}$ = 51.5±4 kJ/mol; $\Delta S^{\ddagger}$ = 18±8 J/mol·K; $\Delta G^{\ddagger}_{298}$ = 46±2 kJ/mol. The ^{31}P{^{1}H} VT NMR spectrum of **6a** in toluene-d$_8$ shows also a signal at δ = 116.1 ppm, which is attributable to an impurity of **5a**, presumably formed by minimal thermal decomposition of **6a** during warming.[12] The ^{31}P{^{1}H} NMR spectrum of **5a** in toluene-d_8 at room temperature shows a sharp singlet at 116.1 ppm and at 183 K a broad signal at 110.5 ppm ($\omega_{1/2}$ = 6050 Hz). The temperature of 183 K is not low enough to reach the coalescence of the NMR signals of **5a**. The coupling pattern observed in the ^{31}P{^{1}H} NMR spectrum of **6a** at -80 °C indicates that the geometry of **6a**, determined by single crystal X-ray diffractions, is retained in solution at that temperature

(vide infra). This is also confirmed by the solid state $^{31}P\{^{1}H\}$ MAS NMR spectrum of a crystalline sample of **6a** which exhibits also three multiplets at similar chemical shifts (Figure 3.2). Interestingly, only the coupling of the η^1-coordinating phosphorus atom to the obviously terminal coordinated Cu atom is observed.

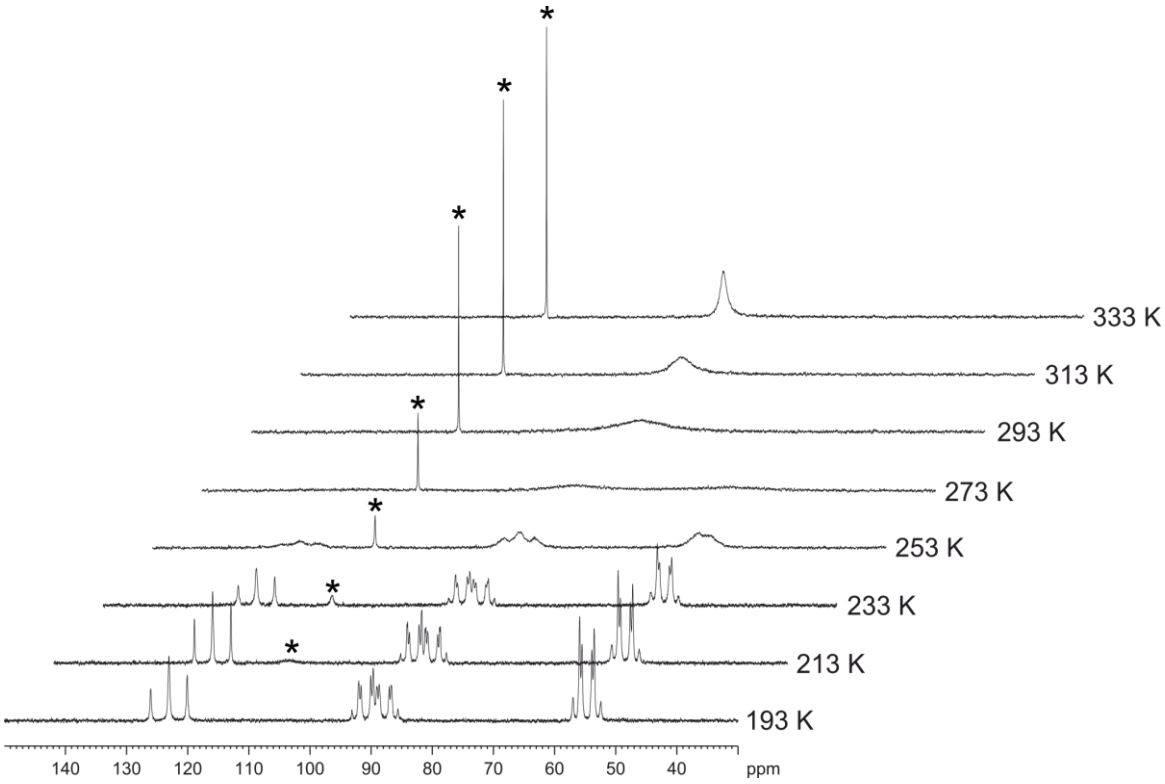


Figure 3.1. VT $^{31}P\{^{1}H\}$ NMR spectra of **6a** in toluene-d_8 at different temperatures between 193 K and 333 K (* = **5a**).

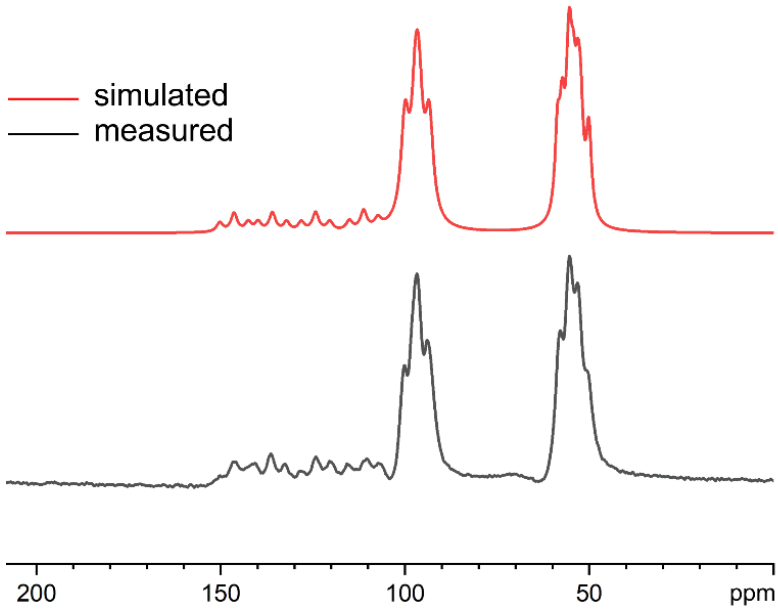
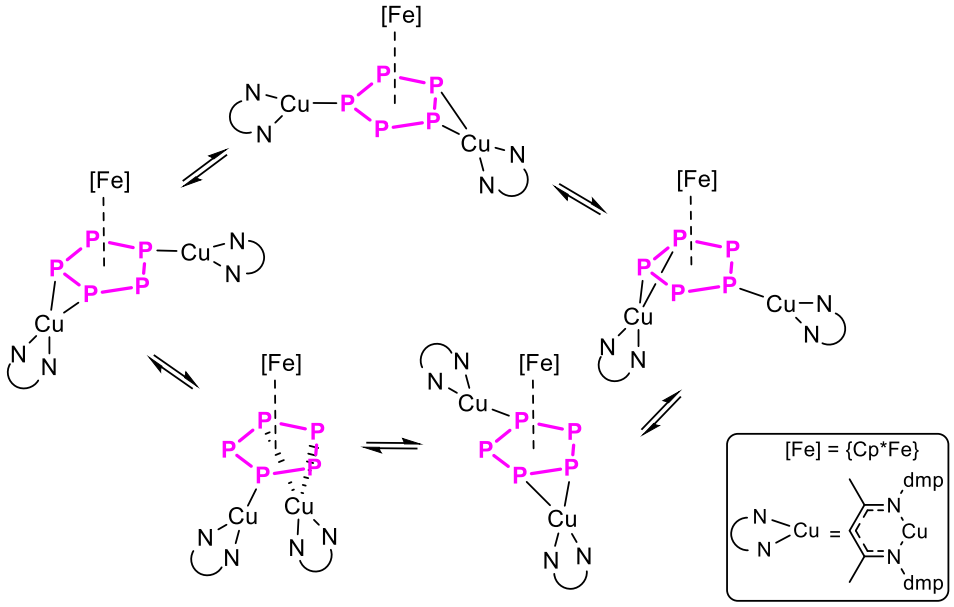


Figure 3.2. $^{31}P\{^{1}H\}$ MAS NMR spectrum of dried crystals of **6a**. Recorded at 25000 Hz MAS frequency (measured: bottom (black), fitted: top (red)).



Scheme 3.3. Molecular $\eta^1 \rightarrow \eta^2 \rightarrow \eta^1$ motion consisting of Cu(Nacnac) migration around the P_5 ring while remaining chemically connected to the P atoms.

The dynamic process responsible for the scrambling of the ^{31}P nuclei at temperatures higher than 273 K is either a fast dissociation-reassociation of the Cu(nacnac) moiety[13] or an $\eta^1 \rightarrow \eta^2 \rightarrow \eta^1$ walk of the two Cu atoms along the pentaphosphacyclopentadiene ring, as shown in Scheme 3.3. In order to shed light on the dynamic process, we recorded a $^{31}P\{^1H\}$ EXSY spectrum of a toluene-d_8 solution of **6a** at 233 K. The result is shown in Figure 3.3 which reveals that while there are exchange cross peaks between each couple of P atoms of **6a**, no exchange between **6a** and **5a** is detected.[12] The absence of cross peaks between the signal of **5a** (δ = 111 ppm) and any of the ^{31}P nuclei belonging to **6a** indicates that the dissociative process does not occur and that the dynamic motion consists of an $\eta^1 \rightarrow \eta^2 \rightarrow \eta^1$ walk of the two Cu atoms along the P_5 ring, as shown in Scheme 3.3. To check whether the dissociative process (consisting in the dissociation-reassociation of the Cu(nacnac) moiety) does occur at higher temperatures,[4a] we also carried out a $^{31}P\{^1H\}$ EXSY experiment on a toluene-d_8 solution of **6a** at 333 K. However, under these conditions, during the relatively long time needed to record the $^{31}P\{^1H\}$ EXSY spectrum (some hours), an irreversible conversion of **6a** to **5a** and, eventually, to **1a** occurred, with no clear off-diagonal peaks detectable in the $^{31}P\{^1H\}$ EXSY spectrum. The same behavior was observed when carrying out the $^{31}P\{^1H\}$ EXSY experiment at 313 K. It should be noted that the small value found for the activation entropy is consistent with a non-dissociative dynamic process, like that depicted in Scheme 3.3.

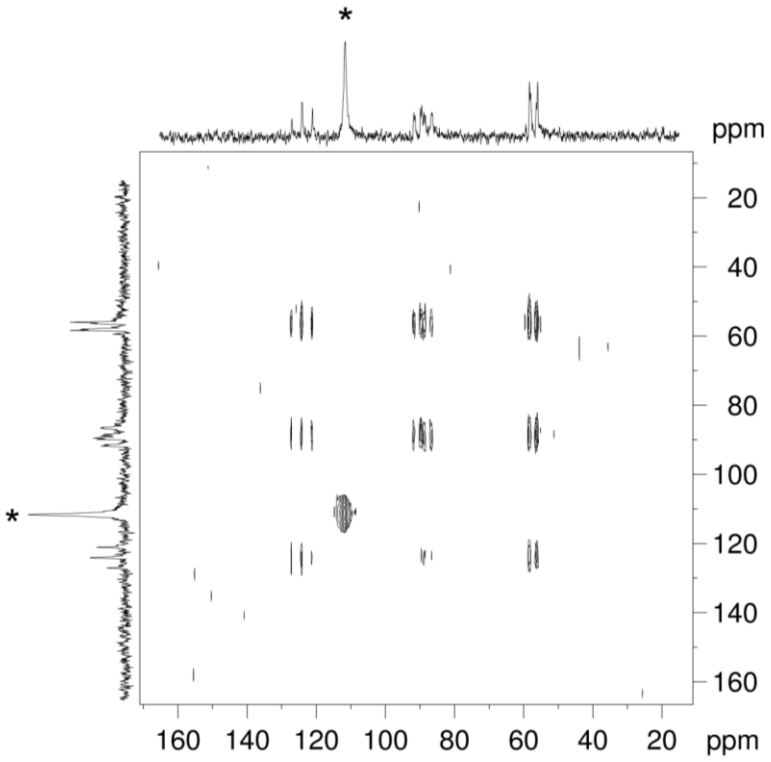


Figure 3.3. $^{31}P\{^{1}H\}$ EXSY spectrum of **6a** (T = 233 K, toluene-d_8) (* = **5a**).

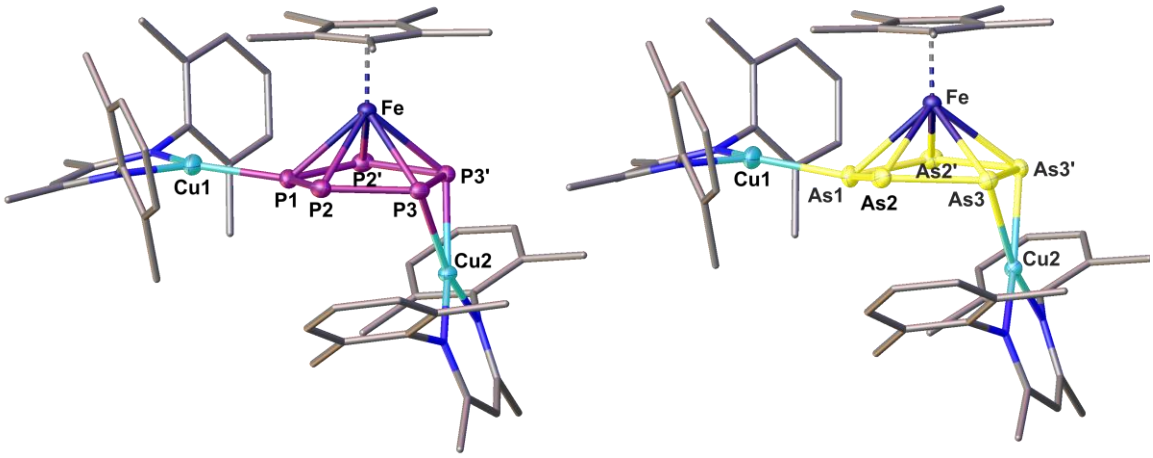


Figure 3.4. Molecular structure of **6a** (left) and **6b** (right) in the solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

The molecular structure of **6** reveals a trinuclear heterobimetallic complex in which the [Cp*Fe(η^5-E_5)] ligand coordinates in an η^1 fashion end-on to one {L^1Cu} fragment and in an η^2 fashion side-on to the second {L^1Cu} fragment (Figure 3.4). The η^1-coordinated {L^1Cu} fragment is nearly coplanar with the *cyclo*-E_5 ring, while the η^2-coordinated {L^1Cu} fragment is almost perpendicular to the *cyclo*-E_5 plane (dihedral angle of 80.62(2)° and 85.243(14)° for **6a** and **6b**, respectively). The molecular structure of **5** reveals a [Cp*Fe(η^5-E_5)] ligand coordinating in an η^2 fashion side-on to the {L^1Cu} fragment (Figure 3.5). The

η^1 coordination is theoretically possible but is energetically less favored by 20 kJ·mol^{-1} for **5a** and by 45 kJ·mol^{-1} for **5b** (cf. SI). The {L^{1}Cu} fragment is also coordinated almost perpendicularly to the *cyclo*-E_5 plane, with a dihedral angle of 83.43(2)° (**5a**) and 94.29(2)° (**5b**), respectively.

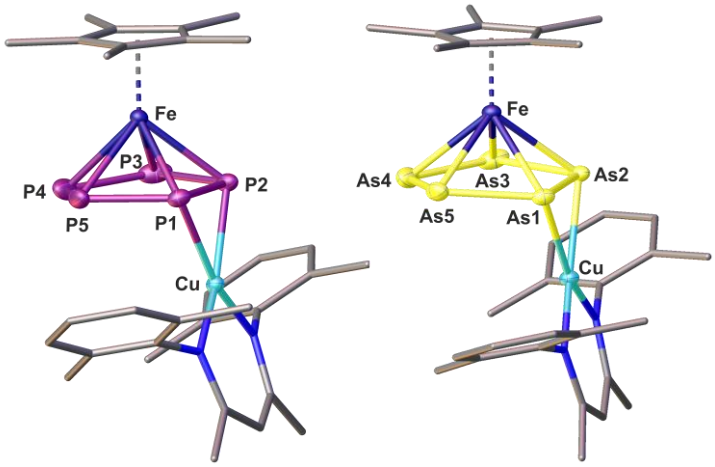


Figure 3.5. Molecular structure of **5a** (left) and **5b** (right) in the solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

Interestingly, the η^2-coordinated Cu-P distances in **5a** and **6a** (**5a**: Cu-P1/Cu-P2 2.2859(7)/2.2820(7) Å, **6a**: Cu2-P3/Cu2-P3' 2.2888(5)/2.2889(5) Å) are between the Cu-P distances found in **A** (2.336(2) – 2.345(2) Å), **B** (2.342(2) Å), **D1** (2.2592(6) – 2.2707(6) Å) and **E** (2.280(3) Å). In the case of Cu-As, the bond distances are in the same range (**5b**: Cu-As1/Cu-As2 2.4255(7)/2.4002(7) Å, **6b**: Cu2-As3/Cu2-As3' 2.3987(4) Å) as for **D2** (Cu-As 2.3761(9)/2.3877(9) Å). Four E-E bond distances are in the range between an E-E single[14] and double[15] bond, while the Cu-coordinated E-E bond is elongated but still intact (**5a**: P1-P2 2.2100(10) Å, **5b** As1-As2 2.4039(6) Å, **6a**: P3-P3' 2.2242(10) Å; **6b**: As3-As3' 2.4156(4) Å). The Wiberg Bond Indices underline this description (**5a**: P1-P2 1.04, **5b**: As1-As2 1.03; **6a**: P3-P3' 1.01, **6b**: As3-As3' 1.0). These values are slightly lower than the non-coordinated E-E bonds (between 1.06 and 1.22, more detailed information cf. SI). To the best of our knowledge, only few examples with an η^2-side-on coordination to the *cyclo*-P_5 ring of the pentaphosphaferrocene are known.[7e,16] Most akin to the compounds reported herein is [(Cp*Fe)(μ_3,$\eta^{5:2:2}$-P_5)(Cu(3,5-$(CF_3)_2$Pz))$_3$] (**F**, Pz = pyrazolate).[16a] Interestingly, a macrocycle such as copper pyrazolate Cu(3,5-$(CF_3)_2$Pz)$_3$ is able to coordinate two out of its three copper atoms in an η^2 side-on fashion at the *cyclo*-P_5 ring of **1a** because of the local proximity of the adjacent Cu atoms. In contrast, mononuclear Cu complexes such as **2** prefer first an η^2 coordination and, for the second molecule, an η^1 coordination that may be based on the steric bulk of the *β*-diketiminate ligand. The bond distances of the Cu-coordinated P-P bonds in the pyrazolate-containing complex are similarly elongated as in **6a** to 2.2085(14) and 2.2096(14) Å. The iridium complex [(Cp*Fe)(μ,$\eta^{5:2}$-P_5)(Cp*Ir(CO))] (**G**)[16b] was synthesized under rough conditions (4h, hν) and shows also an AMM'XX' spin system in the ^{31}P{^{1}H} NMR spectrum, which is

already observed at room temperature. However, the respective P-P bond is elongated to a much higher extent (P-P: 2.359(2) Å, WBI: 0.72, as compared to **6a**: P-P: 2.2242(10), WBI: 1.01). In the case of arsenic, there is only one molecular compound known with an η^2-side-on coordination to the *cyclo*-As_5 ligand of the pentaarsaferrocene. The rhodium complex [(Cp*Fe)(μ,$\eta^{5:2}$-As_5)(Cp*Rh(CO))] (**H**),[16b] synthesized by *Scherer et al.* exhibits an As-As bond distance of 2.502(2) Å (WBI: 0.78, compared to **6b**: 1.0), which is more widened. The η^2-side-on coordination is more characteristic of **1b** than of **1a**.[7c,17] Compound **5** and **6** are molecular and neutral examples of the rare η^2-side-on coordination to the *cyclo*-E_5 ligand of **1** by group 11 complex moieties. Furthermore, it is possible to change the Cp^R ligand from Cp* to Cp^{Benz} (Cp^{Benz} = η^5-$C_5(CH_2Ph)_5$) and obtain the same structural motif, which was verified by low temperature $^{31}P\{^1H\}$ NMR spectroscopy (spectra and simulation see SI, **S1** and **S2**). Exchanging the ligand L^1 with L^2 (L^2 = [{N(C_6H_3Me-2,6)C(H)}$_2$CH]$^-$) leads also to very similar compounds (synthesis and structures see SI, **S3**, **S4** and **S5**).

According to DFT calculations at the B3LYP/def2-TZVP level of theory, all reactions shown in Scheme 3.2 are exothermic with -86 kJ·mol^{-1} (**5a**) and -99 kJ·mol^{-1} (**5b**) for the 1:1 ratio and -173 kJ·mol^{-1} (**6a**) and -172 kJ·mol^{-1} (**6b**) for the 1:2 ratio reaction. To obtain a deeper insight into the nature of the bonding of the **1b** to the {L^1Cu} fragment, we investigated the bonding situation in **5b** by means of the interaction of the fragment orbitals [Cp*Fe(As_5)] and {L^1Cu}. The orbital interaction diagram (Figure 3.6) shows that there is a rather low orbital overlap between the two fragments. The highest occupied molecular orbital (HOMO) in **5b** represents basically a set of π orbitals of the nacnac ligand of the {L^1Cu} fragment, while the HOMO-1 represents the interaction of the HOMO of the {L^1Cu} fragment (mainly Cu d orbital character) with the HOMO-1 and the lowest unoccupied orbital (LUMO) (both As p orbitals) of the {Cp*Fe(As_5)} fragment. The HOMO-2 and HOMO-3 orbitals are mainly located on the {Cp*Fe(As_5)} fragment with only minor contributions from the {L^1Cu} fragment orbitals HOMO and HOMO-7. This rather low mixing of the fragment orbitals in **5b** explains the highly dynamic behaviour of this type of complexes in solutions and indicates the importance of charge transfer in the bonding. Indeed, in **5b**, a net charge transfer of 0.196e$^-$ occurs between the two fragments. The main part of the electron donation occurs via the As1 and As2 p orbitals (labelling according to Figure 3.5), while the copper s and p orbitals are the major acceptor orbitals. The bonding between the [Cp*FeAs_5] unit and the η^2-coordinated L^1Cu unit **6b** is basically identical to that of **5b**. Additionally, the η^1 coordination is realized over the overlap of HOMO-3 orbital of the {(Cp*Fe)(As_5)(L^1Cu)} fragment with the LUMO of the {L^1Cu} fragment, leading to the HOMO-5 orbital in **6b**. This interaction is, however, weak and the HOMO-5 orbital exhibits mainly As_5 character (see Supporting Information). Nevertheless, the charge transfer over the η^1 coordination is more pronounced (net charge transfer 0.420e$^-$) as compared to **5b** (η^2 coordination). We additionally investigated the topology of

the electron density of **5** and **6** by means of the Atoms In Molecules (AIM) theory. We were able to locate Bond Critical Points (BCPs) along all Cu-E axis (see SI).

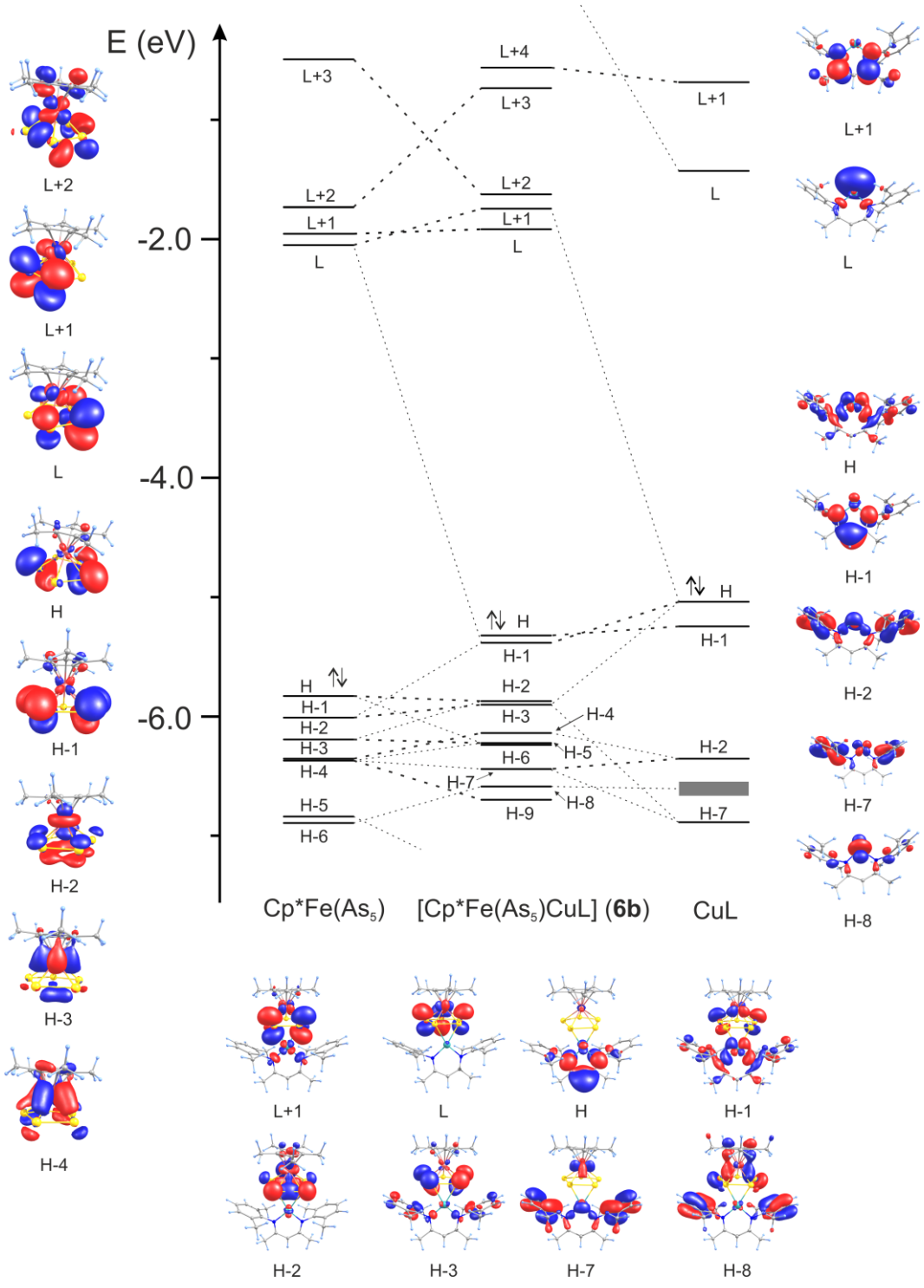
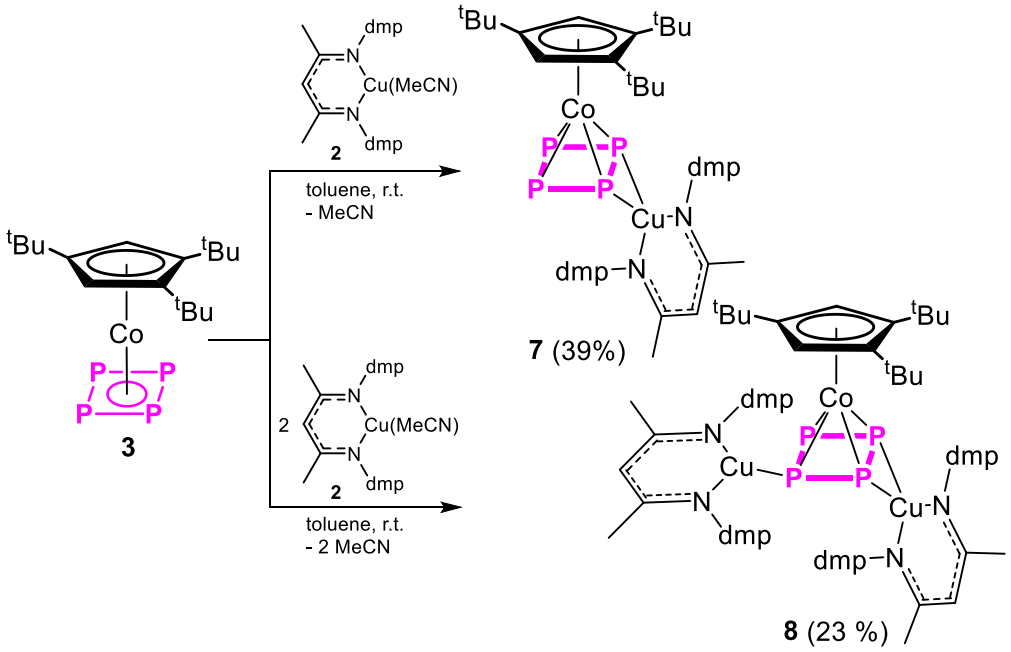


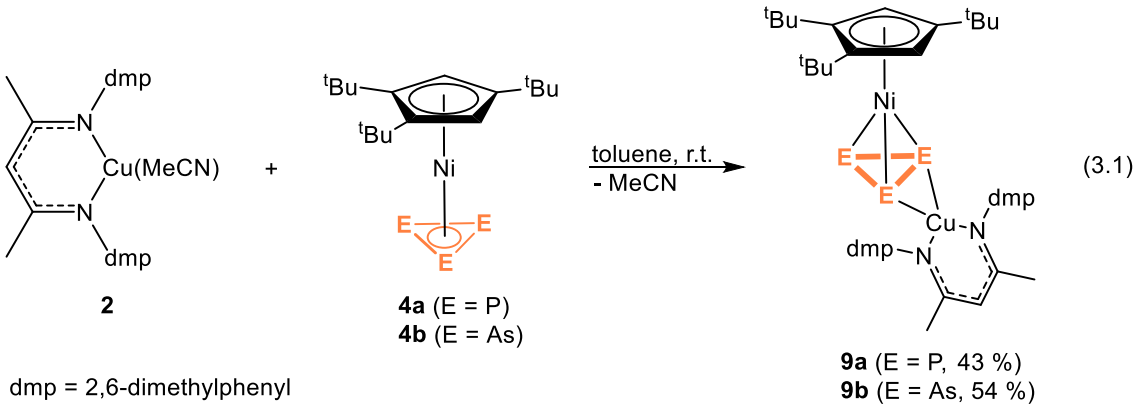
Figure 3.6. Molecular orbital interaction diagram of **5b**, calculated at the B3LYP/def2-TZVP level of theory. The MOs in grey are nonbonding. Only fragment contributions of more than 5% are depicted. The lines drawn in bold represent the main character of the corresponding molecular orbital.

The electron density at the BCPs corresponding to the η^1 coordination is slightly higher than for the η^2 coordination and generally higher for E = P compared to E = As (i.e. ρ = 0.076 and 0.061 e·bohr^{-3}, respectively, for **6b**; for details see SI). The positive sign of the Laplacian of the electron density and the ratio of the potential energy density (|V|) and the kinetic energy density (G) are indicative of an intermediate nature (between covalent and ionic) of the bonds. The eta index is characteristic of intermediate interactions between typical covalent and closed shell interactions. The properties of the BCPs corresponding to the η^2-coordinating E-E bonds in **5** and **6** clearly show that these bonds are slightly weakened but still intact, hence the coordination to the {L^{1}Cu} fragment does not critically affect the integrity of these bonds. A similar Cu-P bonding has been described for [(Cp*Fe)(μ$_3$,η$^{5:2:2}$-P$_5$)(Cu(3,5-(CF$_3$)$_2$Pz))$_3$] (Pz = pyrazolate).[16a]

In order to investigate if this reactivity of **2** can be extended to other *cyclo*-E$_n$ ligand complexes possessing aromatic multiple bond character, **2** was reacted with [Cp'''Co(η^4-P$_4$)] (**3**) and [Cp'''Ni(η^3-E$_3$)] (E = P (**4a**), As (**4b**)), respectively. The 1:1 reaction at room temperature in toluene leads to the quantitative formation of [(Cp'''Co)(μ,η$^{4:2}$-P$_4$)(L^{1}Cu)] (**7**, Scheme 3.4) and [(Cp'''Ni)(μ,η$^{3:2}$-E$_3$)(L^{1}Cu)] (E = P (**9a**), As (**9b**), Eq. 3.1), which are isolated as air-sensitive red solids in crystalline yields of 39% (**7**), 43% (**9a**) and 54% (**9b**).[11] The reaction of **3** with an excess of **2** leads to the formation of [(Cp'''Co)(μ$_3$,η$^{4:2:1}$-P$_4$)(L^{1}Cu)$_2$] (**8**, Scheme 3.4).



Scheme 3.4. Reaction of [Cp'''Co(η^4-P$_4$)] with [LCu(MeCN)]. (dmp = 2,6-dimethylphenyl)



2 (3.1)

4a (E = P)
4b (E = As)

9a (E = P, 43 %)
9b (E = As, 54 %)

dmp = 2,6-dimethylphenyl

The dynamic behavior of **7**, **8** and **9a** in solution was investigated by VT $^{31}P\{^1H\}$ NMR spectroscopy. At room temperature, the NMR spectra in C_6D_6 show broad singlets at δ = 129.6 ppm (**7**, $\omega_{1/2}$ = 7 Hz), δ = 108.1 ppm (**8**, $\omega_{1/2}$ = 234 Hz) and δ = -163.1 ppm (**9a**, $\omega_{1/2}$ = 8 Hz), respectively. Even when crystals of **7** and **9a**, respectively, were dissolved and measured at -80 °C (in toluene-d_8), it was not possible to freeze the dynamic process, and, hence, only one broad signal could be detected (**7**: 123.1 ppm ($\omega_{1/2}$ = 134 Hz); **9a**: δ = -161.75 ppm ($\omega_{1/2}$ = 44 Hz)). The $^{31}P\{^1H\}$ NMR spectrum of the reaction solution of **8** (-80°C, toluene-d_8) shows a splitting of the singlet into four broad signals at δ = 121.2, 114.7, 99.4 and 75.6 ppm with the integral ratio of 1:1:1:1. Compound **8** shows a highly dynamic behavior, even at -80 °C, there is no fine splitting visible. The MAS $^{31}P\{^1H\}$ NMR spectrum of **9a** shows just one broad singlet at -161.1 ppm ($\omega_{1/2}$ = 1850 Hz). This indicates that either the *cyclo*-P_3 ring is freely rotating in the solid state, too, so that, on the NMR time scale, all phosphorus atoms are equivalent, or that the difference in the magnetic shielding of the coordinating phosphorus atoms induced by the $\{L^1Cu\}$ fragment is low and the two signals overlap. In the LIFDI-MS spectra of **7**, **8**, **9a** and **9b**, respectively, the corresponding molecular ion peaks are detected.

In **7** and **9**, the $\{L^1Cu\}$ fragment is bonded in an η^2 fashion side-on to the $\{Cp'''Co(\eta^4\text{-}P_4)\}$ and $\{Cp'''Ni(\eta^3\text{-}E_3)\}$ ligands, respectively (Figure 3.7). A few complexes containing η^2-side-on coordinated Cu atoms to *cyclo*-P_3 ligands has already been reported.[18] The Cu coordinated P-P bonds of this ionic cobalt,[18a] molybdenum,[18b] or chromium[18b] complexes are all elongated but still intact. The *cyclo*-E_n-Cu unit is folded by 72.058(17)° (**7**), 59.90(2)° (**9a**) and 59.871(12)° (**9b**), respectively. The molecular structure of **8** reveals a trinuclear heterometallic complex in which the $\{Cp'''Co(\eta^4\text{-}P_4)\}$ ligand is coordinating in an η^2 fashion side-on to one $\{L^1Cu\}$ fragment and in an η^1 fashion end-on to the second $\{L^1Cu\}$ fragment. The η^2-coordinated $\{L^1Cu\}$ fragment is bent to the *cyclo*-P_4 plane (dihedral angle of 64.90(3)°), while the η^1-coordinated $\{L^1Cu\}$ fragment is twisted by 38° towards the P_4 ring.

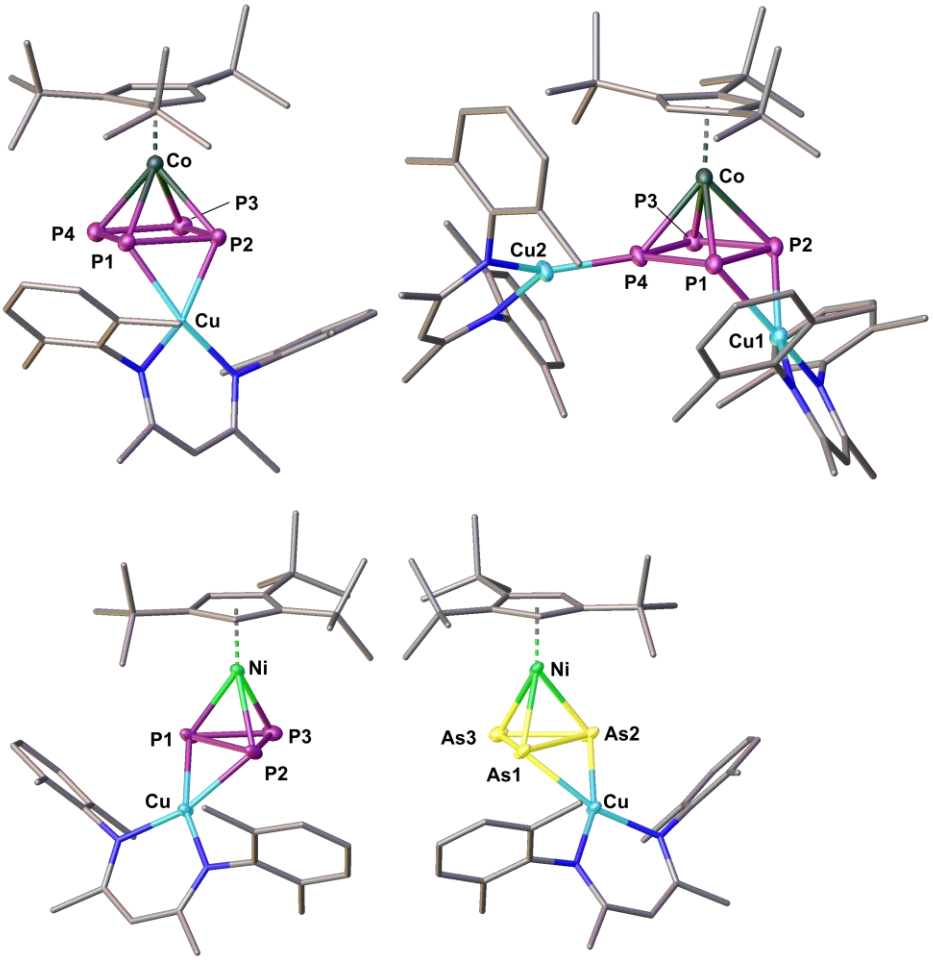


Figure 3.7. Molecular structure of **7** (top, left), **8** (top, right), **9a** (bottom, left) and **9b** (bottom, right) in the solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

The Cu-E bond lengths are similar to the distances in **5** and **6** (**7**: Cu-P1 2.2662(5), Cu-P2 2.2731(5), **8**: Cu1-P1 2.2995(7), Cu1-P2 2.2543(7), Cu2-P3 2.1382(7), **9a**: Cu-P1 2.2966(5), Cu-P2 2.2858(5), **9b**: Cu-As1 2.3857(4), Cu-As2 2.3980(4)). The Cu-coordinated E1-E2 bond is slightly elongated (**7**: 2.3278(6) Å, **8**: 2.3387(9), **9a**: 2.3143 Å, **9b**: 2.5625(3) Å) but the WBIs confirm the integrity of the bond (**7**: P1-P2 0.94, **8**: P1-P2 0.93, **9a**: P1-P2 0.91, **9b**: As1-As2 0.84, WBIs for other E-E bonds see SI). This is also confirmed by the AIM analysis which clearly shows that although the E1-E2 bonds are slightly elongated, they are still intact (c.f. SI). The other E-E bond lengths lie in the range between single[14] and double[15] bonds and are comparable to those in **3** and **4**. According to DFT calculations at the B3LYP/def2-TZVP level of theory, the reactions in Scheme 3.4 and Equation 3.1 are exothermic with -84 kJ·mol^{-1} (**7**), -155 kJ·mol^{-1} (**8**), -72 kJ·mol^{-1} (**9a**) and -85 kJ·mol^{-1} (**9b**). Compound **7**, **8** and **9** are rare molecular and neutral examples of group 11 element complexes coordinated to *cyclo*-P_4 and *cyclo*-E_3 ligands, respectively.

3.3. Conclusion

In summary, we reported the synthesis of the heterometallic complexes [(Cp*Fe)(μ,$\eta^{5:2}$-E_5)(L^1Cu)] (E = P (**5a**), As (**5b**), Scheme 3.2) and [(Cp*Fe)(μ_3,$\eta^{5:2:1}$-E_5)($L^1Cu)_2$] (E = P (**6a**), As (**6b**), Scheme 3.2) as neutral molecular complexes of group 11 metals containing the rare η^2-side-on coordination mode to the intact *cyclo*-E_5 ligand of [Cp*Fe(η^5-E_5)] (E = P (**1a**), As (**1b**)). We showed that the η^2-side-on coordination is preferred to the η^1-end-on coordination for phosphorus and arsenic by experimental proof and DFT calculations. Furthermore, the complexes [(Cp'''Co)(μ,$\eta^{4:2}$-P_4)(L^1Cu)] (**7**), [(Cp'''Co)(μ_3,$\eta^{4:2:1}$-P_4)($L^1Cu)_2$] (**8,** Scheme 3.4) and [(Cp'''Ni)(μ,$\eta^{3:2}$-E_3)(L^1Cu)] (E = P (**9a**), As (**9b**), Eq. 3.1) were synthesized, representing group 11 element complexes coordinated by the *cyclo*-E_n ligands (n = 3, 4). The dynamic behavior of **6a** was investigated by variable temperature $^{31}P\{^1H\}$ and $^{31}P\{^1H\}$ EXSY NMR spectroscopy, showing that the dynamic motion of **6a** consists of an $\eta^1 \rightarrow \eta^2 \rightarrow \eta^1$ walk of the two Cu atoms along the P_5 ring. Moreover, the WBIs as well as the AIMs of all copper-coordinated E-E (E = P, As) bond distances were calculated and show the integrity of the bonds.

3.4. References

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3.5. Supporting Information

3.5.1. Synthesis and Characterization

General Remarks

All manipulations were performed with rigorous exclusion of oxygen and moisture using standard Schlenk techniques on a dual manifold Schlenk line with Argon or N_2 inert gas or glove box filled with nitrogen containing a high-capacity recirculator (<0.1 ppm O_2). Traces of oxygen and moisture in the inert gas were removed by passing it through a drying column filled with Cu/$MgSO_4$ catalyst as well as, concentrated H_2SO_4 and orange gel, respectively. All solvents were degassed and purified by standard procedures. All NMR spectra have been recorded using deuterated benzene-d_6, toluene-d_8 or CD_2Cl_2 that were dried (over Na/K or CaH_2), refluxed for three hours and then distilled under inert atmosphere.

Characterization methods

Mass spectrometry was performed using a Jeol AccuTOF GCX LIFDI mass spectrometer by the MS department of the University of Regensburg. The compounds were dissolved in the corresponding solvent in a glove box under N_2 atmosphere. The observed fragments were assigned according to the mass/charge (m/z) ratio and the corresponding isotope pattern. Elemental analysis (CHN) were performed by the department of central analyses of the University of Regensburg on a Vario micro cube and a MT5 micro scale device. The compounds were filled in tin capsules in a glove box under N_2 atmosphere.

^1H and ^{31}P NMR spectra were recorded on a Bruker Avance III HD 400 (^1H: 400.130 MHz, ^{31}P: 161.976 MHz) spectrometer at the NMR department of the University of Regensburg. The chemical shifts are reported in ppm relative to external TMS (^1H) or 85 % H_3PO_4 (^{31}P). The chemical shifts δ are given in parts per million [ppm] and coupling constants J in [Hz]. $^{31}P\{^1H\}$ MAS NMR spectra were recorded on a Bruker Avance 300 spectrometer at room temperature by Prof. Dr. Werner Kremer. The chemical shifts are reported in ppm relative to external NaH_2PO_4 (^{31}P). The spectra were taken from dried crystals and were recorded at 25000 Hz MAS frequency. $^{31}P\{^1H\}$ EXSY spectra were recorded by using the library pulse program “noesyph” modified for ^1H decoupling by Prof. Dr. Piero Mastrorilli. Line shape analysis was performed by DNMR module of TopSpin BRUKER.

Starting Materials

The compounds [Cp*Fe(η^5-E_5)][1] (E = P (**1a**), As (**1b**)), [LCu(MeCN)][2] (L^1 = [{N($C_6H_3Me_2$-2,6)C(Me)}$_2$CH]$^-$) (**2**); L^2 = [{N($C_6H_3Me_2$-2,6)C(H)}$_2$CH]$^-$) (**2a**)), [Cp’’’Co(η^4-P_4)][3] (**3**) and [Cp’’’Ni(η^3-E_3)][4] (E = P (**4a**), As (**4b**)) were prepared according to literature procedures.

3.5.1.1. Synthesis of [(Cp*Fe)(μ,η$^{5:2}$-P$_5$)(L^{1}Cu)] (**5a**)

[L^{1}Cu(MeCN)] (**2**) (50.0 mg, 0.12 mmol, 1 eq) and [Cp*Fe(η^5-P$_5$)] (**1a**) (42.3 mg, 0.12 mmol, 1 eq) were dissolved in 10 mL Et$_2$O and stirred for 1 h at room temperature. The brown reaction mixture was filtered over diatomaceous earth and transferred into a double Schlenk (with 2 mL of toluene on the other side). The solvent was reduced by slow evaporation at -30 °C. Compound [(Cp*Fe)(μ,η$^{5:2}$-P$_5$)(L^{1}Cu)] (**5a**) crystallized as brown needles, suitable for X-ray analysis.

Crystalline yield: 45 mg (0.06 mmol, 51 %)

^{1}H NMR (400.13 MHz, C$_6$D$_6$, 300 K): δ [ppm] = 7.35 (d, 4H, *H$_{meta}$*, $^3J_{HH}$ = 8 Hz), 7.25 (t, 2H, *H$_{para}$*, $^3J_{HH}$ = 8 Hz), 4.67 (s, 1H, *H$_β$*), 2.02 (s, 12H, C$_{ortho}$*Me*), 1.50 (s, 6H, α-*Me*), 0.96 (s, 15H, Cp*).

^{31}P{^{1}H} NMR (161.98 MHz, toluene-d$_8$, 300 K): δ [ppm] 116.0 (s, 5P), 152.8 ppm (s, **1a**).

^{31}P{^{1}H} NMR (161.89 MHz, toluene-d$_8$, 183 K): δ [ppm] = 110.5 (b), 149.9 ppm (s, **1a**).

LIFDI-MS (toluene): m/z (%) = 1084.17 (100, [**6a**]$^+$), 714.08 (97.44, [M]$^+$).

3.5.1.2. Synthesis of [(Cp*Fe)(μ,η$^{5:2}$-As$_5$)(L^{1}Cu)] (**5b**)

[L^{1}Cu(MeCN)] (**2**) (54.2 mg, 0.13 mmol, 1 eq) and [Cp*Fe(η^5-As$_5$)] (**1b**) (75.0 mg, 0.13 mmol, 1 eq) were dissolved in 10 mL Et$_2$O and stirred for 2 h at room temperature. Work up see **5a**. Compound [(Cp*Fe)(μ,η$^{5:2}$-As$_5$)(L^{1}Cu)] (**5b**) crystallized as brown blocks, suitable for X-ray analysis.

Crystalline yield: 43 mg (0.04 mmol, 34 %)

^{1}H NMR (400.13 MHz, C$_6$D$_6$, 300 K): δ [ppm] = 7.37 (d, 4H, *H$_{meta}$*, ^{3}J$_{HH}$ = 7 Hz), 7.25 (t, 2H, *H$_{para}$*, ^{3}J$_{HH}$ = 7 Hz), 4.65 (s, 1H, *H$_β$*), 1.93 (s, 12H, C$_{ortho}$*Me*), 1.48 (s, 6H, α-*Me*), 0.96 (s, 15H, Cp*).

LIFDI-MS (toluene): m/z (%) = 933.81 (100, [M]$^+$).

EA calculated for C$_{31}$H$_{40}$N$_2$As$_5$FeCu: C: 39.84, H: 4.31, N: 3.00; found [%]: C: 40.24, H: 4.20, N: 2.92.

3.5.1.3. Synthesis of [(Cp*Fe)(μ$_3$,η$^{5:2:1}$-P$_5$)(L^{1}Cu)$_2$] (**6a**)

[L^{1}Cu(MeCN)] (**2**) (100.0 mg, 0.24 mmol, 2 eq) in 4 mL toluene was added to a stirred solution of [Cp*Fe(η^5-P$_5$)] (**1a**) (42.3 mg, 0.12 mmol, 1 eq) in 4 mL toluene at room temperature. The colour of the reaction mixtures turned immediately from green to brown. The reaction was stirred for 2 hours and then filtered over diatomaceous earth. The solvent was reduced to 3 mL. By storing the solution for four days at -30 °C, compound [(Cp*Fe)(μ$_3$,η$^{5:2:1}$-P$_5$)(L^{1}Cu)$_2$] (**6a**) crystallized as dark brown blocks, suitable for X-ray structure analysis.

Crystalline yield: 83 mg (0.07 mmol, 58 %)

^{1}H NMR (400.13 Hz, tol-d$_8$, 300 K): δ [ppm] = 7.25 (d, 8H, *H$_{meta}$*, $^3J_{HH}$ = 8 Hz), 7.13 (t, 4H, *H$_{para}$*, $^3J_{HH}$ = 8 Hz), 4.86 (s, 2H, *H$_β$*), 2.16 (s, 24H, C$_{ortho}$*Me*), 1.67 (s, 12H, α-*Me*), 0.79 (s, 15H, Cp*).

^{1}H NMR (400.13 MHz, tol-d$_8$, 193 K): δ [ppm] = 7.44 - 7.25 (m, 12H, *H$_{meta/para}$*), 5.16 (s, 1H, *H$_β$*), 4.79 (s, 1H, *H$_{β'}$*), 2.56 (br, 6H, C$_{ortho}$*Me*), 2.46 (s, 12H, C$_{ortho}$*Me'*), 1.91 (s, 6H, α-*Me*), 1.58 (s, 6H, α-*Me'*), 1.54 (br, 6H, C$_{ortho}$*Me*), 0.72 (s, 15H, Cp*).

^{31}P{^{1}H} NMR (161.98 MHz, tol-d$_8$, 300 K): δ [ppm] = 116.1 (s, **5a**), 86.1 (br).

^{31}P{^{1}H} NMR (161.98 MHz, tol-d$_8$, 193 K): δ [ppm] = 122.9 (m, 1P, P$_A$), 89.4 (m, 2P, P$_M$/P$_{M'}$), 54.8 (m, 2P, P$_X$/P$_{X'}$). Corresponding coupling constants are taken from the fitting of the experimental spectrum (Figure S3.7) and given in table S3.1.

^{31}P{^{1}H} MAS NMR: δ [ppm] = 129.6 ($J_{^{63/65}CuP}$ = 1424 Hz, J_{PP} = 469 Hz, D = 80 Hz), 96.9 (J_{PP} = 456 Hz, J_{PP} = 342 Hz), 55.7 (J_{PP} = 355 Hz, J_{PP} = 406 Hz), 53.9 (J_{PP} = 368 Hz, J_{PP} = 511 Hz)[5] (see Figure 3.2).

LIFDI-MS (toluene): m/z (%) = 1084.19 (100, [M$^+$]), 714.09 (19.43, [5a]$^+$).

EA calculated for $C_{59}H_{73}N_4P_5FeCu_2$: C: 60.26, H: 6.26, N: 4.76; found [%]: C: 60.17, H:6.06, N: 4.89.

3.5.1.4. Synthesis of [(Cp*Fe)(μ$_3$,η$^{5:2:1}$-As$_5$)(L^{1}Cu)$_2$] (**6b**)

[L^{1}Cu(MeCN)] (**2**) (75.0 mg, 0.18 mmol, 2 eq) in 4 mL toluene was added to a stirred solution of [Cp*Fe(η^5-As$_5$)] (51.8 mg, 0.09 mmol, 1 eq) in 4 mL toluene at room temperature. Work up see **6a**. By storing the solution for three weeks at -30 °C, compound **6b** crystallized as dark orange blocks, suitable for X-ray structure analysis.

Crystalline yield: 40 mg (0.03 mmol, 31 %)

^{1}H NMR (400.13 MHz, tol-d_8, 193 K): δ [ppm] = 7.51-7.36 (m, 12H, $H_{meta/para}$), 4.99 (s, 2H, H_{β}) 2.51 (s, 18H, $C_{ortho}Me$), 1.78 (s, 12H, α-Me), 0.76 (s, 15H, Cp*), there is also a set of signals for compound **5b** visible at -80 °C.

3.5.1.5. Synthesis of [($Cp^{Benz}Fe$)(μ,$\eta^{5:2}$-P_5)(L^1Cu)] (**S1**)

[$L^1Cu(MeCN)$] (14.1 mg, 0.03 mmol, 1 eq) and [$Cp^{Benz}Fe(\eta^5\text{-}P_5)$] (25.0 mg, 0.03 mmol, 1 eq) were dissolved in 5 mL of toluene and stirred for 10 minutes. The solvent was removed by vacuum and the crude product was dissolved in C_6D_6.

^{1}H NMR (C_6D_6, 300 K): δ [ppm] = 7.45 (d, 4H, H_d, $^3J_{HH}$ = *8 Hz*), 7.33 (t, 2H, H_e, $^3J_{HH}$ = 7 Hz), 6.66 (t, 5H, $C_5(CH_2C_6\underline{H_5})_5$, $^3J_{HH}$ = 7 Hz), 6.55 (t, 10H, $C_5(CH_2C_6\underline{H_5})_5$, $^3J_{HH}$ = 8 Hz), 6.05 (d, 10H, $C_5(CH_2C_6\underline{H_5})_5$, $^3J_{HH}$ = 8 Hz), 4.74 (s, 1H, H_a), 3.49 (s, 10H, $C_5(C\underline{H_2}C_6H_5)_5$), 2.12 (s, 12H, Me_c), 1.56 (s, 6H, Me_b).

^{31}P{^{1}H} NMR (C_6D_6, 300 K): δ [ppm] = 121.7 (s, 5P).

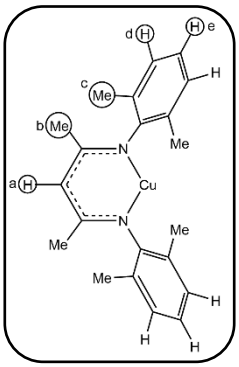


Figure S3.1. L^1Cu

3.5.1.6. Synthesis of [($Cp^{Benz}Fe$)(μ_3,$\eta^{5:2:1}$-P_5)($L^1Cu)_2$] (**S2**)

[$L^1Cu(MeCN)$] (28.2 mg, 0.06 mmol, 2 eq) and [$Cp^{Benz}Fe(\eta^5\text{-}P_5)$] (25.0 mg, 0.03 mmol, 1 eq) were dissolved in 5 mL of toluene and stirred for 30 minutes, the solvent was removed by vacuum and the crude product was dissolved in deuterated solvent.

^{1}H NMR (C_6D_6, 300 K): δ [ppm] = 7.32 (d, 8H, H_d, $^3J_{HH}$ =7 Hz), 7.21 (t, 4H, H_e, $^3J_{HH}$ =8 Hz), 6.57 (t, 10 H, $C_5(CH_2C_6\underline{H_5})_5$, $^3J_{HH}$ =8 Hz), 6.12 (d, 10H, $C_5(CH_2C_6\underline{H_5})_5$, $^3J_{HH}$ = 8 Hz), 4.95 (s, 1H, H_a), 3.28 (s, 10H, $C_5(C\underline{H_2}C_6H_5)_5$),), 2.24 (s, 24H, Me_c), 1.71 (s, 12H, Me_b), contaminated with **S1**.

^{31}P{^{1}H} NMR (toluene-d_8, 300 K): δ [ppm] = 121.7 (s, S1), 92.1 (br).

^{31}P{^{1}H} NMR (toluene-d_8, 193 K): δ [ppm] = 131.9 (m, 1P, P_A), 91.1 (m, 2P, $P_M/P_{M'}$), 67.3 (m, 2P, $P_X/P_{X'}$). Corresponding coupling constants are taken from simulation (Figure S3.11) and given in table S3.2.

3.5.1.7. Synthesis of [(Cp*Fe)(μ,η$^{5:2}$-P$_5$)(L^{2}Cu)] (**S3**)

[L^{2}Cu(MeCN)] (**2a**) (55.0 mg, 0.14 mmol, 1 eq) in 5 mL Et$_2$O was added to a stirred solution of [Cp*Fe(η^5-P$_5$)] (50.0 mg, 0.14 mmol, 1 eq) in 5 mL Et$_2$O at room temperature. The colour of the reaction mixtures turned immediately from green to redish-brown. The reaction was stirred overnight and the brown reaction mixture was filtered over diatomaceous earth and transferred into a double Schlenk (with 2 mL of toluene on the other side). The solvent was reduced by slow evaporation at -30 °C. Compound [(Cp*Fe)(μ,η$^{5:2}$-P$_5$)(L^{2}Cu)] (**S3**) crystallized as brown plate, suitable for X-ray analysis.

Crystalline yield: 24 mg (0.03 mmol, 24 %)

^{1}H NMR (C$_6$D$_6$, 300 K): δ [ppm] = 7.29 (d, 4H, *H$_d$*, $^3J_{HH}$ = 7 Hz), 7.20 (m, 2H, *H$_e$*), 6.89 (d, 2H, *H$_b$*, $^3J_{HH}$ = 6 Hz), 4.56 (t, 1H, *H$_a$*, $^3J_{HH}$ = 6 Hz), 2.10 (s, 12H, *Me$_c$*), 0.92 (s, 15H, *Cp**).

^{31}P{^{1}H} NMR (C$_6$D$_6$, 300 K): δ [ppm] = 115.3 (s).

LIFDI-MS (toluene): m/z (%) = 685.99 (34.05, [M$^+$]), 1028.08 (100, [S5]$^+$).

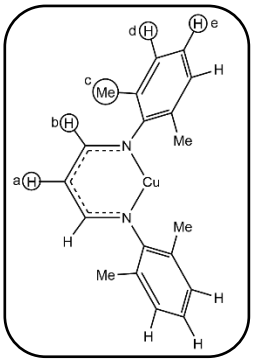


Figure S3.2. L^{2}Cu

EA calculated for C$_{29}$H$_{36}$N$_2$P$_5$FeCu: C: 50.71, H: 5.28, N: 4.08; found [%]: C: 50.20, H: 5.28, N: 4.05.

3.5.1.8. Synthesis of [(Cp*Fe)(μ,η$^{5:2}$-As$_5$)(L^{2}Cu)] (**S4**)

[L^{2}Cu(MeCN)] (**2a**) (54.0 mg, 0.14 mmol, 1 eq) in 5 mL Et$_2$O was added to a stirred solution of [Cp*Fe(η^5-As$_5$)] (80.0 mg, 0,14 mmol, 1 eq) in 10 mL Et$_2$O at room temperature. The colour of the reaction mixtures turned immediately from green to redish-brown. The reaction was stirred for 2 h and the brown reaction mixture was filtered over diatomaceous earth and transferred into a double Schlenk (with 2 mL of toluene on the other side). The solvent was reduced by slow evaporation at -30 °C. Compound [(Cp*Fe)(μ,η$^{5:2}$-As$_5$)(L^{2}Cu)] (**S4**) crystallized as brown plate, suitable for X-ray analysis.

Crystalline yield: 26 mg (0.03 mmol, 20 %)

^{1}H NMR (C$_6$D$_6$, 300 K): δ [ppm] = 7.30 (d, 4H, *H$_d$*, $^3J_{HH}$ = *7 Hz*), 7.21 (t, 2H, *H$_e$*, $^3J_{HH}$= 7 Hz), 6.78 (d, 2H, *H$_b$*, $^3J_{HH}$ = 6 Hz), 4.53 (t, 1H, *H$_a$*, $^3J_{HH}$ = 6 Hz), 3.25 (q, Et$_2$O), 2.00 (s, 12H, *Me$_c$*), 1.11 (t, Et$_2$O), 0.92 (s, 15H, *Cp**).

LIFDI-MS (toluene): m/z (%) = 905.70 (100, [M$^+$]), 1247.79 (2.11, [(Cp*Fe)(As$_5$)(L^{2}Cu)$_2$]$^+$).

EA calculated for C$_{29}$H$_{36}$N$_2$As$_5$FeCu + 0.5 x C$_4$H$_{10}$O: C: 39.46, H: 4.38, N: 2.97; found [%]: C: 39.54, H: 4.25, N: 2.94.

3.5.1.9. Synthesis of [(Cp*Fe)(μ$_3$,η$^{5:2:1}$-P$_5$)(L^{2}Cu)$_2$] (**S5**)

[L^{2}Cu(MeCN)] (**2a**) (110.4 mg, 0.29 mmol, 2 eq) and [Cp*Fe(η^5-P$_5$)] (50.0 mg, 0.14 mmol, 1 eq) were dissolved in toluene at room temperature. The colour of the reaction mixtures turned to redish-brown. The reaction mixture was stirred for 30 minutes and filtrated over diatomaceous earth.

^{1}H NMR (C$_6$D$_6$, 300 K): δ [ppm] =7.21 (d, 8H, *H$_d$*, $^3J_{HH}$ = 7 Hz), 7.12-7.15 (m, 8H, *H$_{b+e}$*), 4.78 (t, 2H, $^3J_{HH}$ = 6 Hz, *H$_a$*), 2.24 (s, 24H, *Me$_c$*), 0.75 (s, 15H, *Cp**), 0.59 (s, 6H, NC*Me*).

^{1}H NMR (tol-d$_8$, 193 K): δ [ppm] = 7.21-7.36 (m, 12H, *H$_{d+e}$*), 6.68 (m, 2H, *H$_b$*), 5.01 (m, 1H, *H$_a$*), 4.62 (m, 1H, *H$_{a'}$*), 2.51 (s, 18H, *Me$_c$*), 1.54 (s, 6H, *Me$_{c'}$*), 0.65 (s, 15H, Cp*), 0.29 (s, 6H, NC*Me*).

^{31}P{^{1}H}-NMR (C$_6$D$_6$, 300 K): δ [ppm] = 84.6 (br).

^{31}P{^{1}H}-NMR (tol-d$_8$, 193 K): δ [ppm] = 118.4 (m, 1P, P$_A$), 94.5 (m, 2P, P$_M$/P$_{m'}$), 49.0 (m, 2P, P$_X$/P$_{X'}$). Corresponding coupling constants are taken from simulation (Figure S3.17) and given in table S3.3.

$\Delta G_{Tc}^{\ddagger}$ is 48 kJ · mol^{-1} (calculation see chapter 3.5.2.3. and 3.5.2.9.).

3.5.1.10. Synthesis of [(Cp'''Co)(μ,η$^{4:2}$-P$_4$)(L^{1}Cu)] (**7**)

[L^{1}Cu(MeCN)] (**2**) (20.0 mg, 0.05 mmol, 1 eq) and [Cp'''Co(η^4-P$_4$)] (**3**) (20.3 mg, 0.05 mmol, 1 eq) were dissolved in toluene and stirred for 30 minutes at room temperature. The reaction mixture was filtered over diatomaceous earth and the solvent was reduced. Compound [(Cp'''Co)(μ,η$^{4:2}$-P$_4$)(L^{1}Cu)] (**7**) crystallized as red blocks, suitable for X-ray structure analysis.

Crystalline yield: 15 mg (0.019 mmol, 39 %)

^{1}H NMR (400.13 MHz, tol-d$_8$, 300 K): δ [ppm] = 7.02 (d, 4H, *H$_{meta}$*), 6.84 (t, 2H, *H$_{para}$*, $^3J_{HH}$ = 8 Hz), 5.39 (s, 2H, C$_5$(^{t}Bu$_3$*H$_2$*)), 5.09 (s, 1H, *H$_\beta$*), 2.33 (s, 12H, C$_{ortho}$*Me*), 1.79 (s, 6H, α-*Me*), 1.20 (s, 18H, C$_5$(*^{t}Bu$_2$*^{t}BuH$_2$)), 1.02 (s, 9H, C$_5$(^{t}Bu$_2$*^{t}Bu*H$_2$)), 0.68 (s, 3H, free *Me*CN).

^{31}P{^{1}H} NMR (161.98 MHz, tol-d$_8$, 193 K): δ [ppm] = 123.0 ppm (br).

^{31}P{^{1}H} NMR (161.98 MHz, tol-d$_8$, 300 K): δ [ppm] = 130.8 ppm (s).

LIFDI-MS (toluene): m/z (%) = 784.19 (100, [M$^+$]), 1154.36 (58.27, [8]$^+$).

3.5.1.11. Synthesis of [(Cp'''Co)(μ$_3$,η$^{4:2:1}$-P$_4$)(L^{1}Cu)$_2$] (**8**)

[L^{1}Cu(MeCN)] (**2**) (47.2 mg, 0.12 mmol, 4 eq) and [Cp'''Co(η^4-P$_4$)] (**3**) (12.0 mg, 0.03 mmol, 1 eq) were dissolved in pentane and stirred for 30 minutes at room temperature. The reaction mixture was filtered and stripped almost to dryness. Compound [(Cp'''Co)(μ$_3$,η$^{4:2:1}$-P$_4$)(L^{1}Cu)$_2$] (**8**) crystallized as brown plates, suitable for X-ray structure analysis.

Crystalline yield: 8 mg (0.007 mmol, 23 %)

^{1}H NMR (400.13 MHz, tol-d$_8$, 300 K): δ [ppm] = 7.04-6.88 (m, 12H, *H$_{meta/para}$*), 5.03 (s, 2H, C$_5$(^{t}Bu$_3$*H$_2$*)), 4.88 (br, *H$_β$*), 2.17 (br, 24H, C$_{ortho}$*Me*), 1.67 (br, 12, α-*Me*), 1.03 (s, 18H, C$_5$(*^{t}Bu$_2$*^{t}BuH$_2$)), 0.86 (s, 9H, C$_5$(^{t}Bu$_2$*^{t}Bu*H$_2$)), 0.65 (s, free *Me*CN).

^{31}P{^{1}H} NMR (161.98 MHz, C$_6$D$_6$, 300 K): δ [ppm] = 108.1 ppm (s).

^{31}P{^{1}H} NMR (161.98 MHz, tol-d$_8$, 193 K): δ [ppm] = 121.2 ppm (br, ω$_{1/2}$ = 1160 Hz), 114.7 ppm (br, ω$_{1/2}$ = 1922 Hz), 99.4 ppm (br, ω$_{1/2}$ = 2481 Hz), 75.6 ppm (br, ω$_{1/2}$ = 4954 Hz).

LIFDI-MS (toluene): m/z (%) = 1154.24 (100, [M]$^+$), 784.12 (64.35, [**7**]$^+$).

3.5.1.12. Synthesis of [(Cp'''Ni)(μ,η$^{3:2}$-P$_3$)(L^{1}Cu)] (**9a**).

[L^{1}Cu(MeCN)] (**2**) (50.1 mg, 0.12 mmol, 1 eq) in 5 mL toluene was added to a stirred solution of [Cp'''Ni(η^3-P$_3$)] (47.0 mg, 0,12 mmol, 1 eq) in 3 mL toluene at room temperature. The colour of the reaction mixtures turned immediately from orange to redish-orange. The reaction was stirred for 2 hours and then filtered over diatomaceous earth. The solvent was reduced to 3 mL and layered with 6 mL of acetonitrile (both layers were separated with 1 mL of toluene). By storing the solution at -30 °C, compound [(Cp'''Ni)(μ,η$^{3:2}$-P$_3$)(L^{1}Cu)] (**9a**) crystallized as red blocks, suitable for X-ray structure analysis.

Crystalline yield: 40 mg (0.05 mmol, 43 %)

^{1}H NMR (400.13 MHz, tol-d$_8$, 193 K): δ [ppm] = 7.19 (d, 4H, *H$_{meta}$, ^{3}J$_{HH}$ = 8 Hz*), 7.12 (t, 2H, *H$_{para}$*, ^{3}J$_{HH}$ = 8 Hz), 5.12 (s, 2H, C$_5$(^{t}Bu$_3$*H$_2$*)), 4.98 (s, 1H, *H$_β$*), 2.25 (s, 12H, C$_{ortho}$*Me*), 1.69 (s, 6H, α-*Me*), 1.13 (s, 18H, C$_5$(*^{t}Bu$_2$*^{t}BuH$_2$)), 0.97 (s, 9H, C$_5$(^{t}Bu$_2$*^{t}Bu*H$_2$)).

^{1}H NMR (400.13 MHz, CD$_2$Cl$_2$, 300 K): δ [ppm] = 7.08 (d, 4H, *H$_{meta}$*, ^{3}J$_{HH}$ = 8 Hz), 6.91 (t, 2H, *H$_{para}$*, ^{3}J$_{HH}$ = 8 Hz), 5.03 (s, 2H, C$_5$(^{t}Bu$_3$*H$_2$*)), 4.80 (s, 1H, *H$_β$*), 2.04 (s, 12H, C$_{ortho}$*Me*), 1.62 (s, 6H, α-*Me*), 1.13 (s, 18H, C$_5$(*^{t}Bu$_2$*^{t}BuH$_2$), 0.95 (s, 9H, C$_5$(^{t}Bu$_2$*^{t}Bu*H$_2$)).

^{31}P{^{1}H} NMR (161.98 MHz, tol-d$_8$, 193 K): δ [ppm] = -161.8 ppm (s).

^{31}P{^{1}H} NMR (tol-d$_8$, 300 K): δ [ppm] = -163.1 ppm (br).

$^{31}P\{^{1}H\}$ MAS NMR (solid state, r.t.): δ [ppm] = -161.1 ppm (s).

LIFDI-MS (toluene): m/z (%) = 752.21 (100, [M^+]), 1122.36 (21.81, [(Cp'''Ni)(P_3)($L^1Cu)_2$]$^+$).

EA calculated for: $C_{38}H_{54}CuN_2NiP_3$: C: 60.53, H: 7.22, N: 3.72; found [%]: C: 60.81, H: 7.07, N: 3.74.

3.5.1.13. Synthesis of [(Cp'''Ni)(μ,$\eta^{3:2}$-As_3)(L^1Cu)] (**9b**)

[L^1Cu(MeCN)] (**2**) (63.3 mg, 0.15 mmol, 1 eq) in 5 mL toluene was added to a stirred solution of [Cp'''Ni(η^3-As_3)] (80.0 mg, 0.15 mmol, 1 eq) in 3 mL toluene at room temperature. Work up see **9a**. By storing the solution at -30 °C, compound [(Cp'''Ni)(μ,$\eta^{3:2}$-As_3)(L^1Cu)] (**9b**) crystallized as red blocks, suitable for X-ray structure analysis.

Crystalline yield: 75 mg (0.08 mmol, 54 %)

^{1}H NMR (400.13 MHz, CD_2Cl_2, 300 K): δ [ppm] = 7.10 (d, 4H, H_{meta}, $^3J_{HH}$ = 8 Hz), 6.93 (t, 2H, H_{para}, $^3J_{HH}$ = 8 Hz), 5.15 (s, 2H, $C_5(^tBu_3H_2)$), 4.81 (s, 1H, H_β), 2.04 (s, 12H, $C_{ortho}Me$), 1.63 (s, 6H, α-*Me*), 1.12 (s, 18H, $C_5(^tBu_2{}^tBuH_2)$), 0.93 (s, 9H, $C_5(^tBu_2{}^tBuH_2)$).

LIFDI-MS (toluene): m/z (%) = 884.00 (100, [M^+]), 1254.12 (2.13, [(Cp'''Ni)(As_3)($L^1Cu)_2$]$^+$).

EA calculated for: $C_{38}H_{54}CuN_2NiP_3$: C: 51.52, H: 6.14, N: 3.16; found [%]: C: 52.01, H: 5.88, N: 2.99.

3.5.2. NMR studies

3.5.2.1. [(Cp*Fe)(μ,η$^{5:2}$-P$_5$)(L^{1}Cu)] (**5a**)

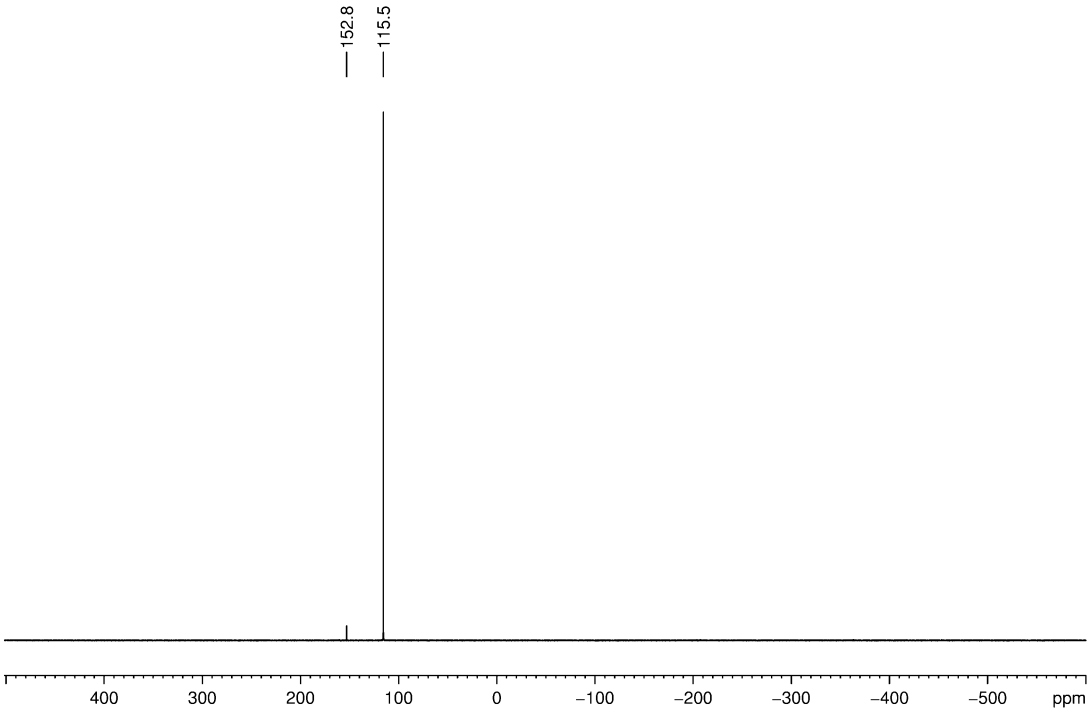


Figure S3.3. $^{31}P\{^1H\}$ NMR spectrum of **5a** in C_6D_6 at room temperature.

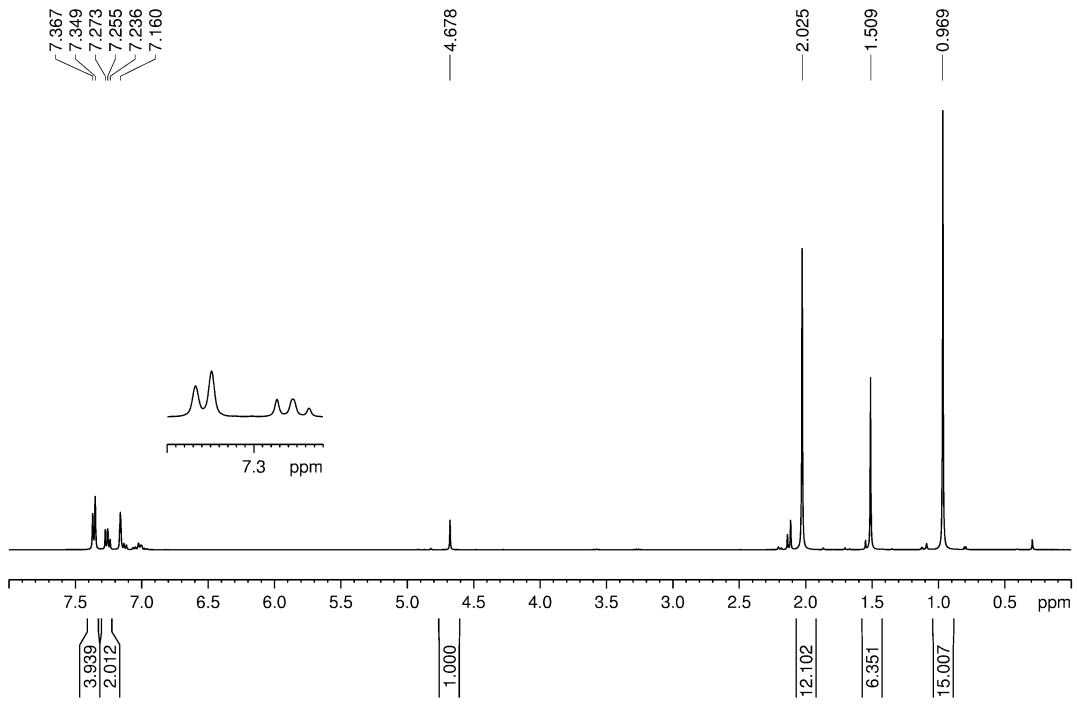


Figure S3.4. ^1H NMR spectrum of **5a** in C_6D_6 at room temperature.

3.5.2.2. [(Cp*Fe)(μ,η$^{5:2}$-As$_5$)(L^{1}Cu)] (**5b**)

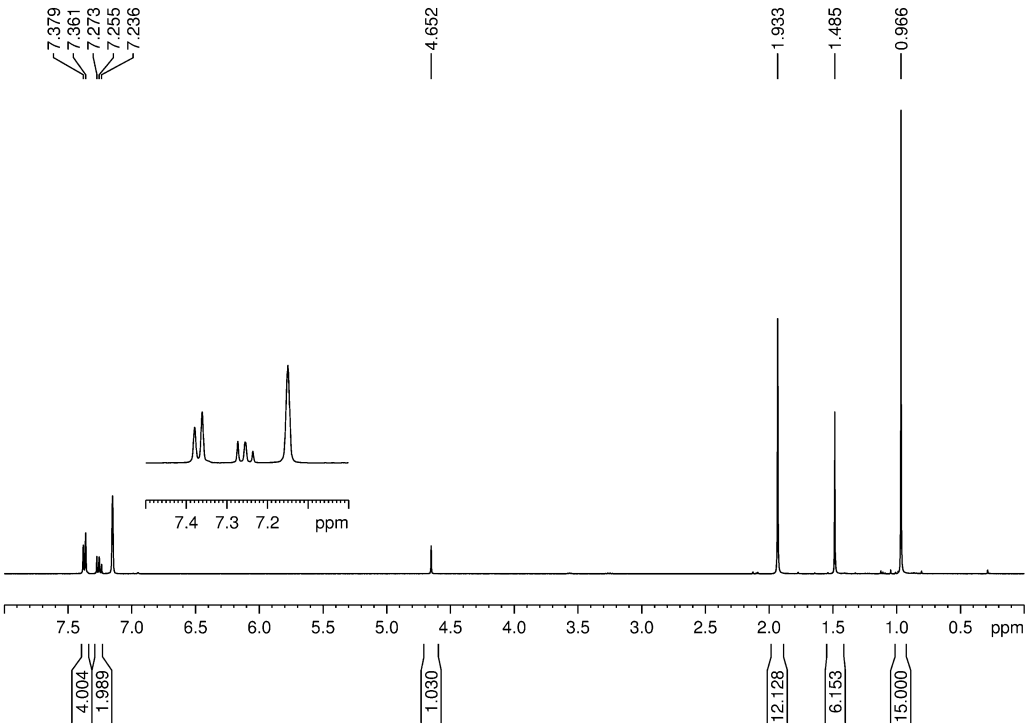


Figure S3.5. ^{1}H NMR spectrum of **5b** in C_6D_6 at room temperature.

3.5.2.3. [(Cp*Fe)(μ$_3$,η$^{5:2:1}$-P$_5$)(L^{1}Cu)$_2$] (**6a**)

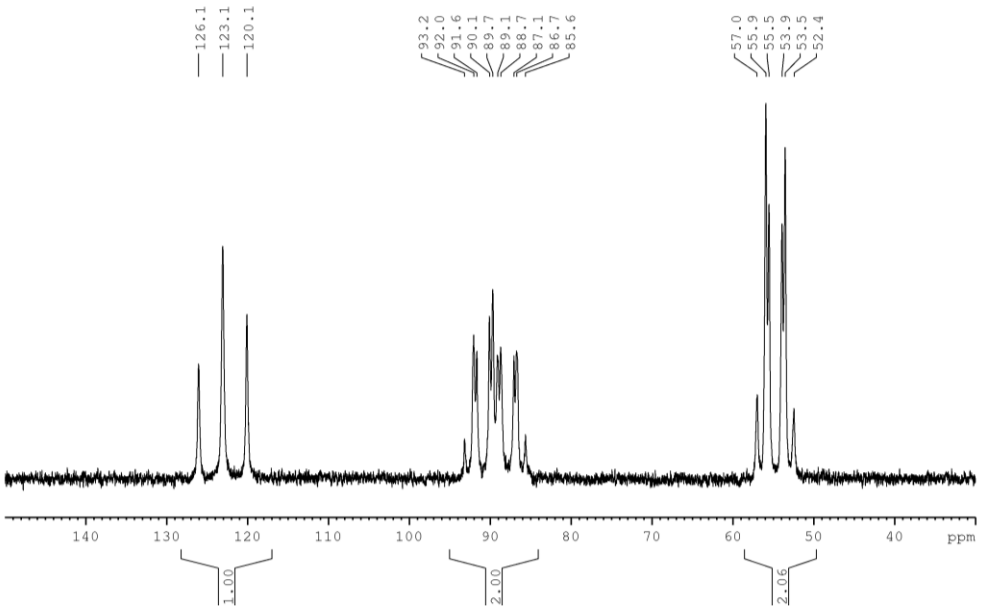


Figure S3.6. $^{31}P\{^1H\}$ NMR spectrum of **6a** in toluene-d$_8$ at 193 K.

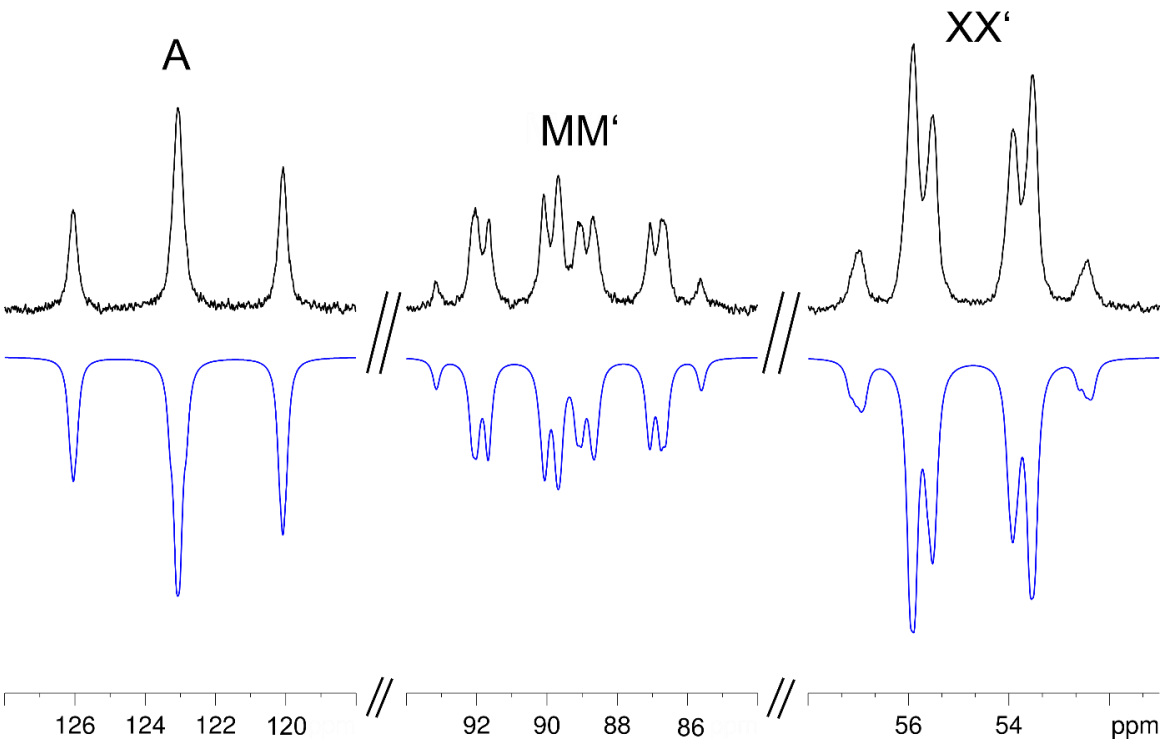


Figure S3.7. $^{31}P\{^1H\}$ NMR spectrum of **6a** in toluene-d$_8$ at 193 K (measured top (black) and simulated bottom (blue)).

Table S3.1. Coupling constants obtained from the simulation in Figure S3.7.

[(Cp*Fe)(μ$_3$,η$^{5:2:1}$-P$_5$)(L^{1}Cu)$_2$]		
$^1J_{PAPM}$ = $^1J_{PAPM'}$ = 484 Hz	$^1J_{PXPX'}$ = 240 Hz	$^2J_{PMPX'}$ = $^2J_{PM'PX}$ = -26 Hz
$^1J_{PMPX}$ = $^1J_{PM'PX'}$ = 414 Hz	$^2J_{PAPX}$ = $^2J_{PAPX'}$ = -17 Hz	$^2J_{PMPM'}$ = -2 Hz
δ = A = 122.9 ppm	MM' = 89.4 ppm	XX' = 54.8 ppm
R-factor [%] = 0.63		

Determination of activation barrier of the dynamic process (see Paper Figure 3.1)

The free activation enthalpy $\Delta G_{Tc}^{\ddagger}$ of this dynamic process can be determined with the Eyring equation. To calculate $\Delta G_{Tc}^{\ddagger}$ the coalescence temperature T_c (T_c = 285 K) and the rate constant k_c is needed. The rate constant k_c is determined from the distance $\Delta\nu$ of the signals at δ = 89.4 and 54.8 ppm and their coupling constant J ($^1J_{PMPX}$ = 414 Hz) at 193 K.[6]

$$k_c = 2.22\sqrt{\Delta\nu^2 + 6J^2}$$

$$k = \chi \frac{k_B T}{h} e^{-\frac{\Delta G_{Tc}^{\ddagger}}{RT}}$$

$$\Delta G_{Tc}^{\ddagger} = -RT_c ln \frac{hk_c}{\chi k_B T_c}$$

k_B = 1.3805 · 10^{-23} J K^{-1} (Boltzmann constant)

R = 8.3145 J K^{-1} mol^{-1} (universal gas constant)

h = 6.6261 · 10^{-34} J s

χ = transmission coefficient, generally equal to 1

$$\Delta\nu = 5604\ Hz$$

$$k_c = 12642.55\ s^{-1}$$

By entering all values into the Eyring equation the free activation enthalpy $\Delta G_{Tc}^{\ddagger}$ is $47\ kJ\ mol^{-1}$.

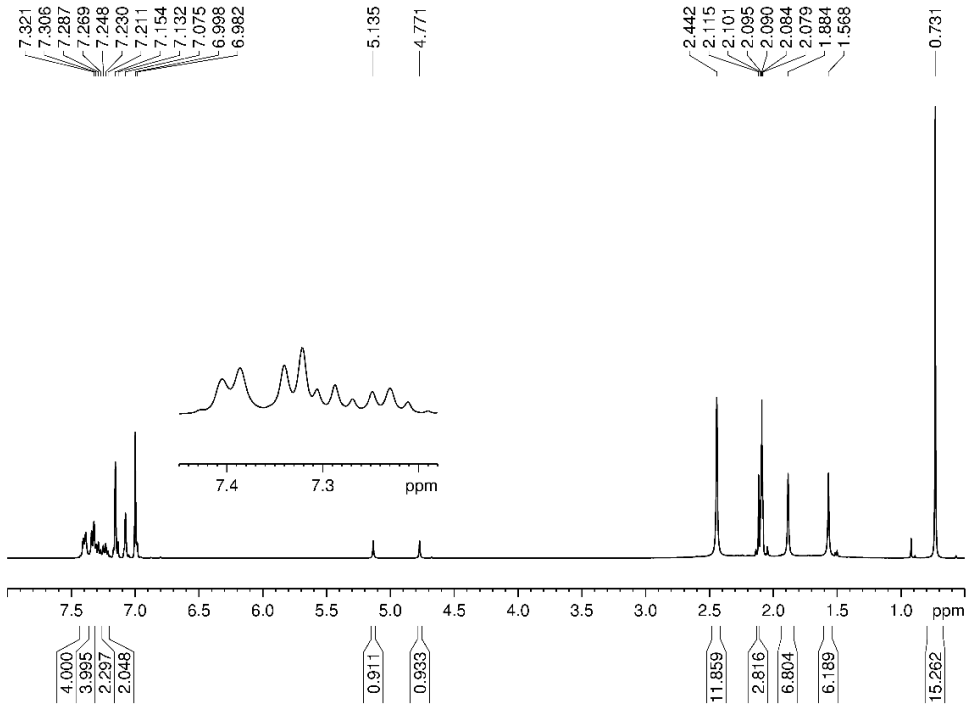


Figure S3.8. ^{1}H NMR spectrum of **6a** in toluene-d_8 at 213K.

3.5.2.4. [(Cp*Fe)(μ_3,$\eta^{5:2:1}$-As_5)($L^1Cu)_2$] (**6b**)

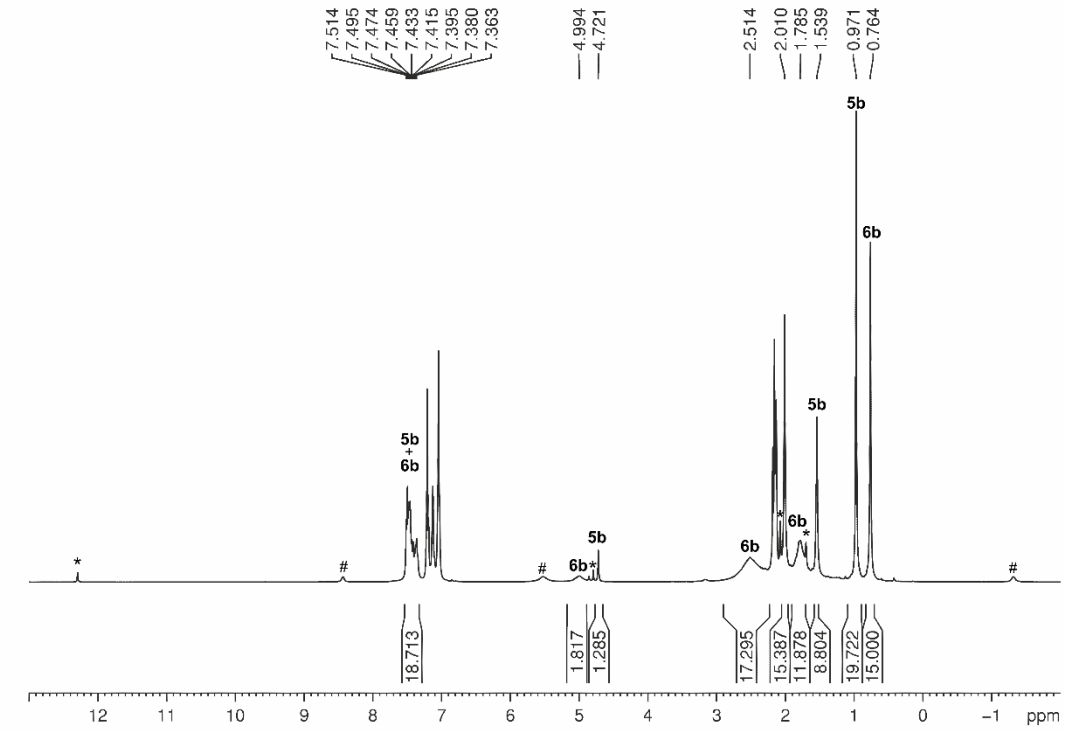


Figure S3.9. ^{1}H NMR spectrum of **1b** with 2 eq of **2** in toluene-d_8 at 193 K. Due to traces of moisture in the solvent, there is NacnacH (*) and $[(LCu)_2(OH)_2]$[2] (#) visible. There is also a set of signals for compound **5b** visible.

3.5.2.5. [(Cp^{Benz}Fe)(μ,η$^{5:2}$-P$_5$)(L^{1}Cu)] (**S1**)

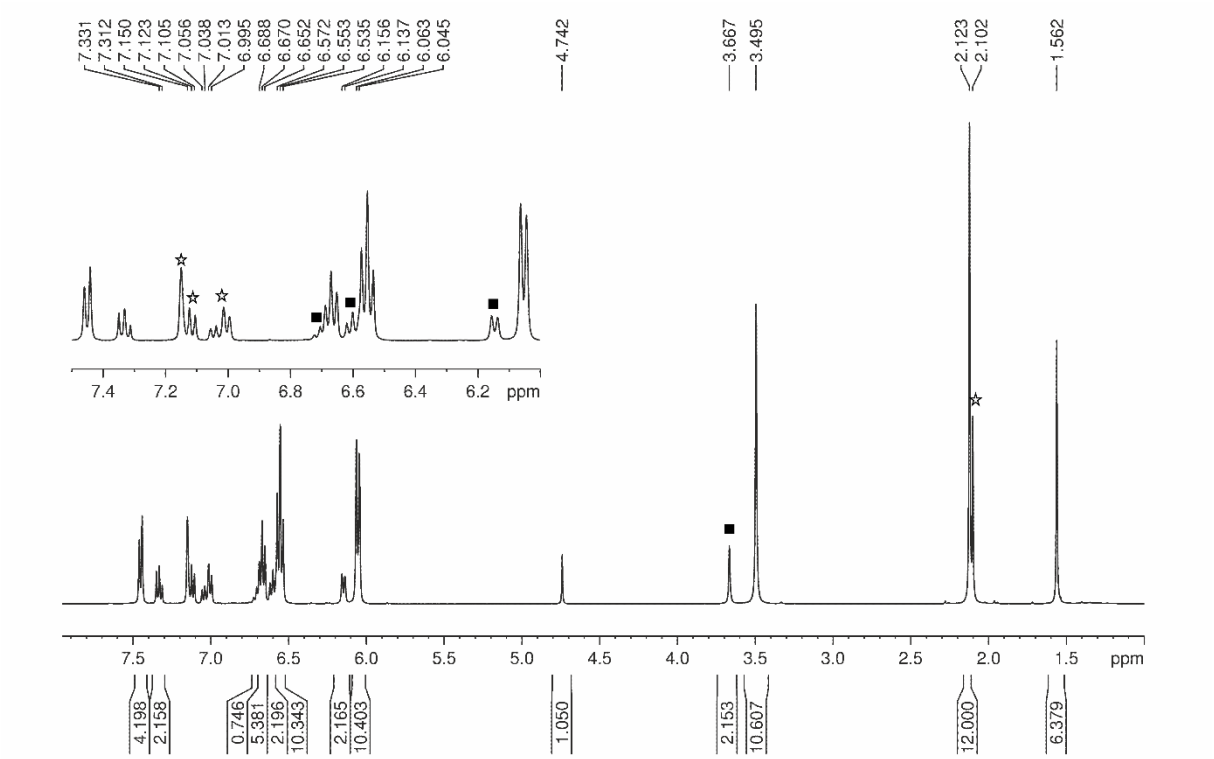


Figure S3.10. ^{1}H NMR spectrum of **S1** in C_6D_6 at room temperature. ☆ Solvent signals: toluene, ▪ starting material.

3.5.2.6. [(Cp^{Benz}Fe)(μ$_3$,η$^{5:2:1}$-P$_5$)(L^{1}Cu)$_2$] (**S2**)

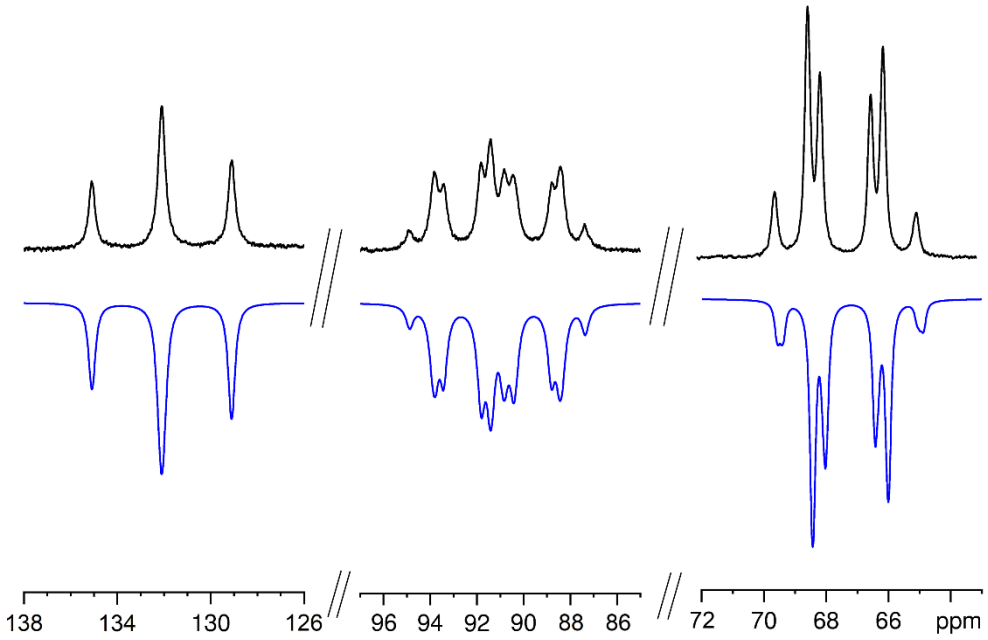


Figure S3.11. ^{31}P{^{1}H} NMR spectrum of **S2** in toluene-d$_8$ at 193 K (measured top (black) and simulated bottom (blue)).

Table S3.2. Coupling constants obtained from the simulation in Figure S3.11.

$[(Cp^{Benz}Fe)(\mu_3,\eta^{5:2:1}\text{-}P_5)(L^1Cu)_2]$		
$^1J_{PAPM} = {}^1J_{PAPM'} = 487$ Hz	$^1J_{PXPX'} = 238$ Hz	$^2J_{PMPX'} = {}^2J_{PM'PX} = -25$ Hz
$^1J_{PMPX} = {}^1J_{PM'PX'} = 417$ Hz	$^2J_{PAPX} = {}^2J_{PAPX'} = -11$ Hz	$^2J_{PMPM'} = 0$ Hz
A = 131.9 ppm	MM' = 91.1 ppm	XX' = 67.3 ppm
R-factor [%] = 0.62		

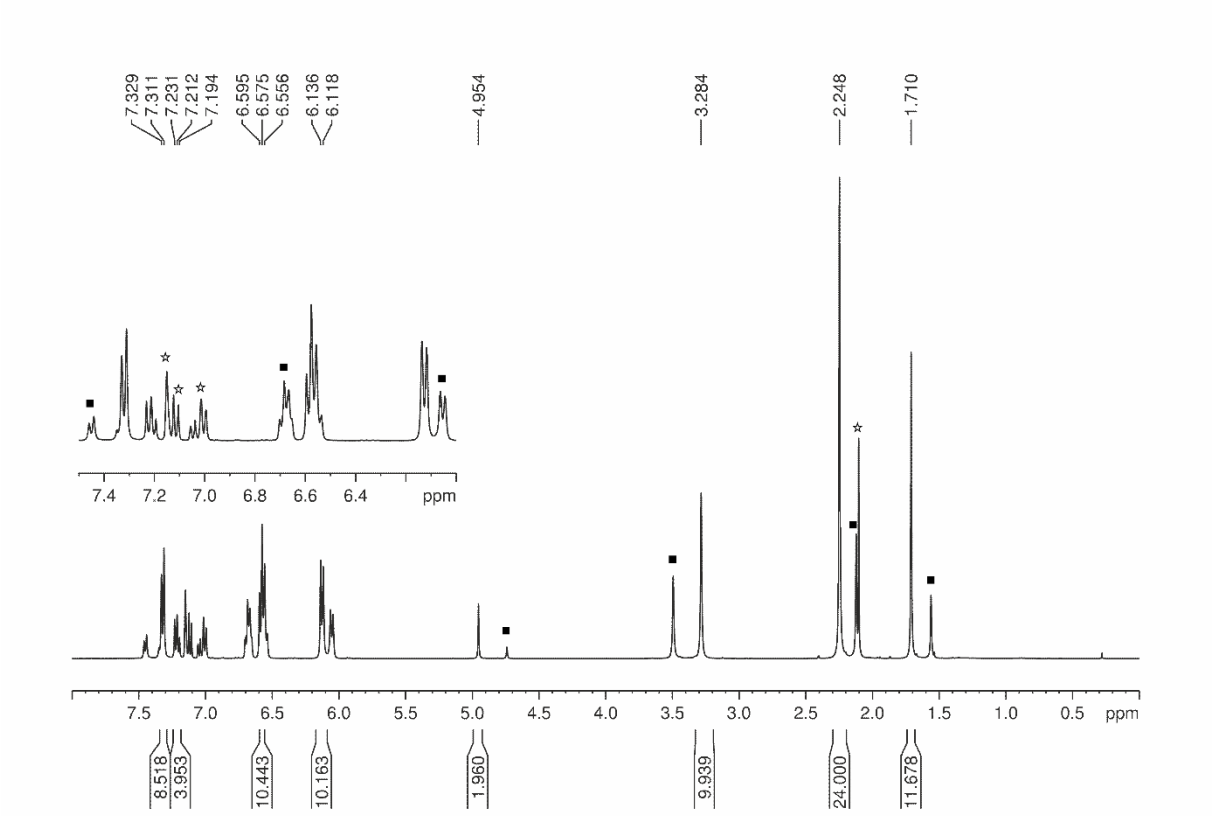


Figure S3.12. ^{1}H NMR spectrum of **S2** in C_6D_6 at room temperature. ☆ Solvent molecules ▪ **S1**.

3.5.2.7. [(Cp*Fe)(μ,η$^{5:2}$-P$_5$)(L^{2}Cu)] (**S3**)

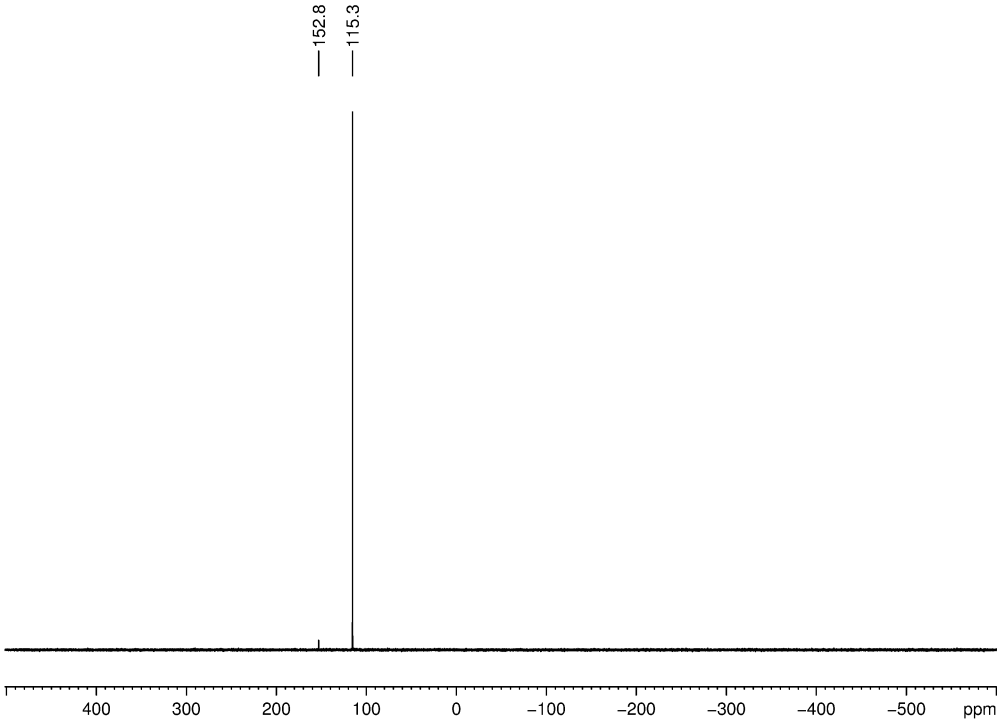


Figure S3.13. $^{31}P\{^1H\}$ NMR spectrum of **S3** in C_6D_6 at room temperature.

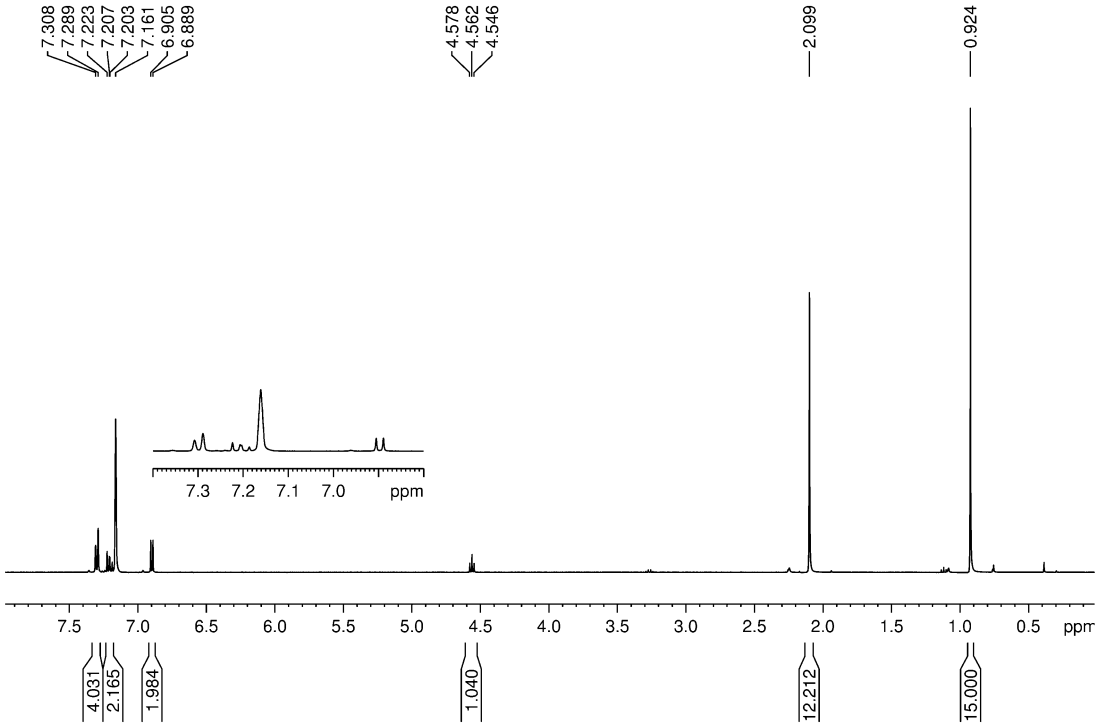


Figure S3.14. ^1H NMR spectrum of **S3** in C_6D_6 at room temperature.

3.5.2.8. [(Cp*Fe)(μ,η$^{5:2}$-As$_5$)(L^{2}Cu)] (**S4**)

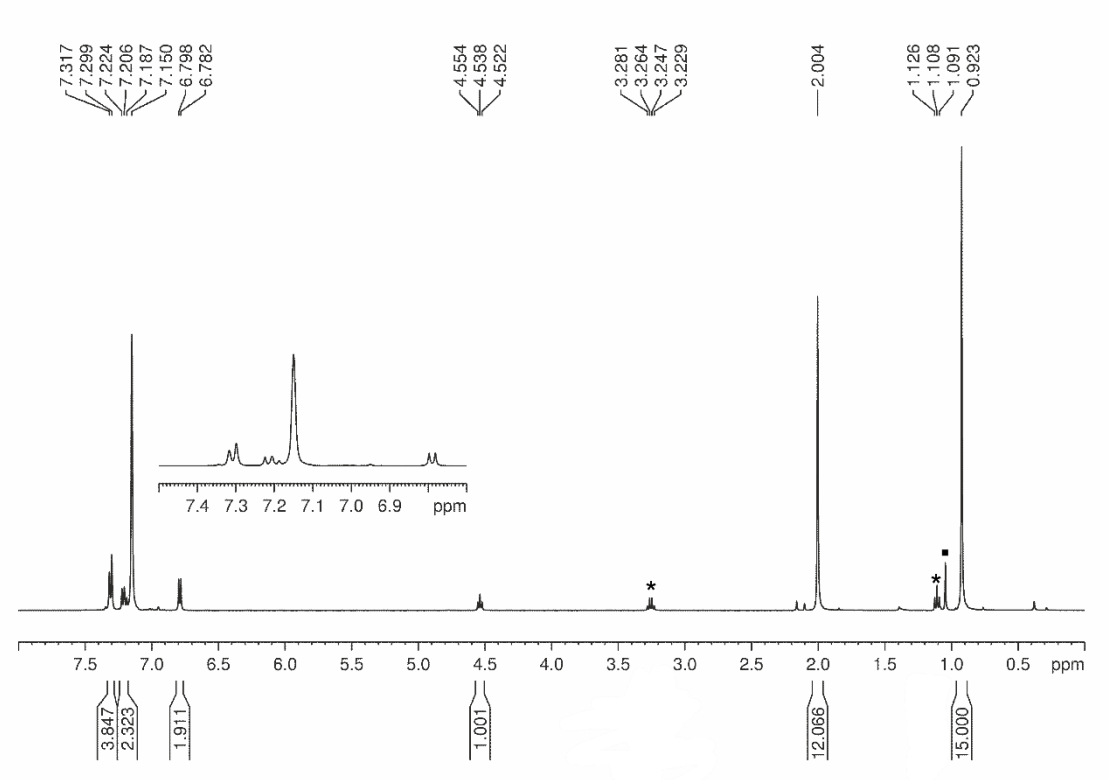


Figure S3.15. ^{1}H NMR spectrum of **S4** in C_6D_6 at room temperature (* Et_2O, ▪ **1a**).

3.5.2.9. [(Cp*Fe)(μ$_3$,η$^{5:2:1}$-P$_5$)(L^{2}Cu)$_2$] (**S5**)

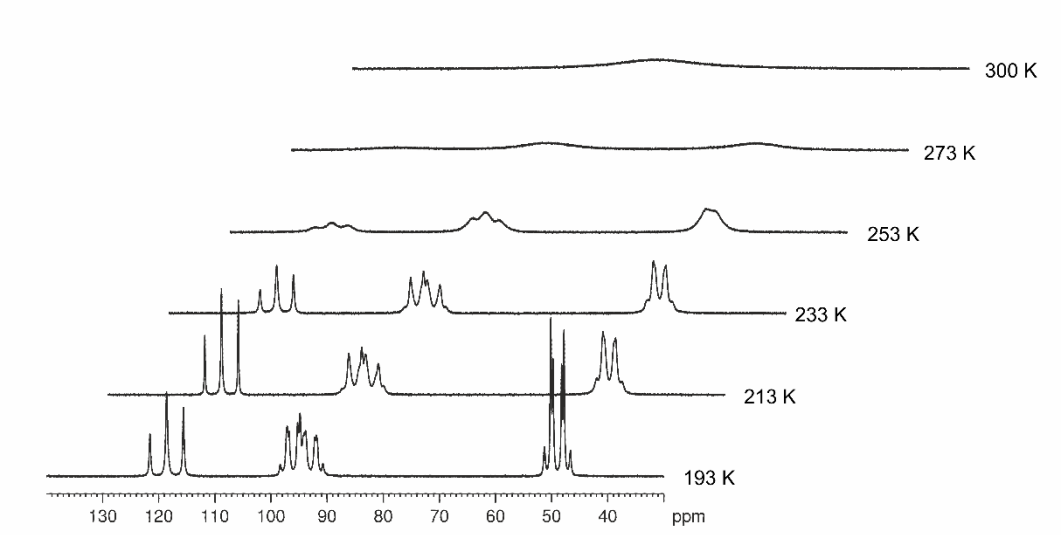


Figure S3.16. VT $^{31}P\{^1H\}$ NMR spectra of **S5** in toluene-d_8 at different temperatures between 193 K and 300 K.

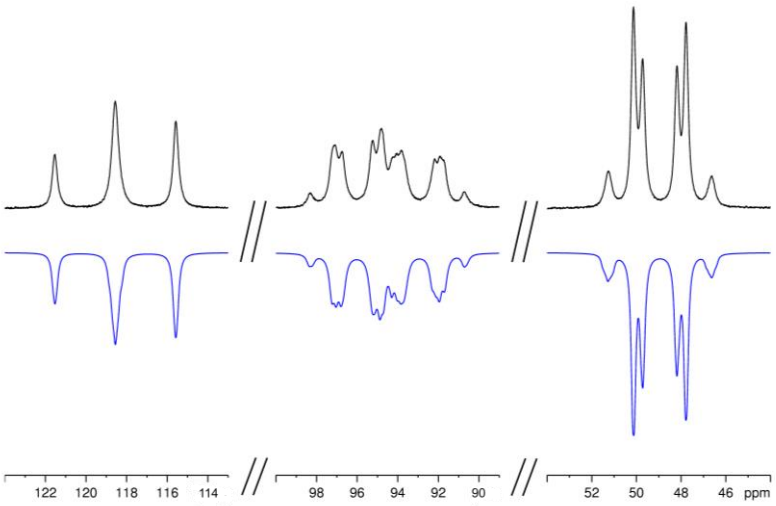


Figure S3.17. $^{31}P\{^{1}H\}$ NMR spectrum of **S5** in toluene-d_8 at 193 K (measured top (black) and simulated bottom (blue)).

Table S3.3. Coupling constants obtained from the simulation in Figure S3.17.

[(Cp*Fe)(μ3,η5:2:1-P5)(L2Cu)2]		
$^{1}J_{PAPM} = {}^{1}J_{PAPM'}$ = 484 Hz	$^{1}J_{PXPX'}$ = 253 Hz	$^{2}J_{PAPX'} = {}^{2}J_{PAPX}$ = -17 Hz
$^{1}J_{PMPX} = {}^{1}J_{PM'PX'}$ = 409 Hz	$^{2}J_{PMPM'}$ = 2 Hz	$^{2}J_{PMPX'} = {}^{2}J_{PM'PX}$ = -27 Hz
δ = A = 118.4 ppm	MM'= 94.5 ppm	XX' = 49.0 ppm
R-factor [%] = 0.72		

Determination of activation barrier of the dynamic process (Figure S3.16)

The free activation enthalpy $\Delta G_{Tc}^{\ddagger}$ of this dynamic process can be determined with the Eyring equation (see chapter 3.2.3.). To calculate $\Delta G_{Tc}^{\ddagger}$ the coalescence temperature T_c (T_c = 290 K) and the rate constant k_c (k_c = 16677.7 s^{-1}) is needed. The rate constant k_c is determined from the distance ($\Delta\nu$ = 7445 Hz) of the signals at δ = 94.5 and 49.0 ppm and their coupling constant J ($^{1}J_{PMPX}$ = 409 Hz) at 193 K.[6]

By entering all values into the Eyring equation the free activation enthalpy $\Delta G_{Tc}^{\ddagger}$ is $48\ kJ\ mol^{-1}$.

3.5.2.10. [(Cp'''Co)(μ,$\eta^{4:2}$-P_4)(L^1Cu)] (**7**)

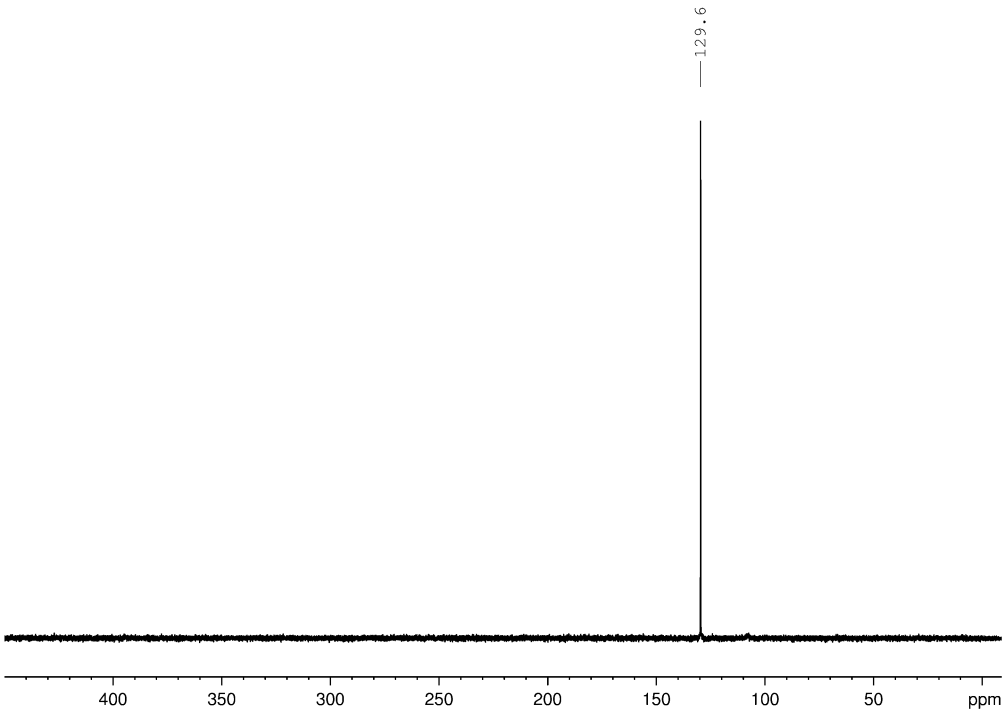


Figure S3.18. $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture of **7** in C_6D_6 at room temperature.

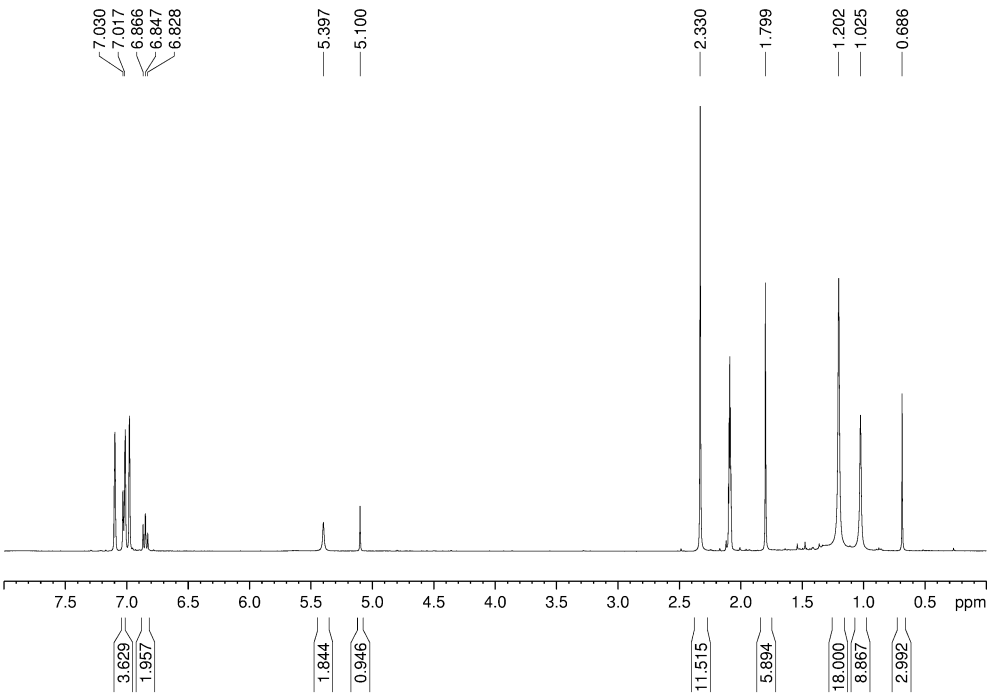


Figure S3.19. ^1H NMR spectrum of **7** in toluene-d_8 at room temperature.

3.5.2.11. [(Cp'''Co)(μ$_3$,η$^{4:2:1}$-P$_4$)(L^{1}Cu)$_2$] (**8**)

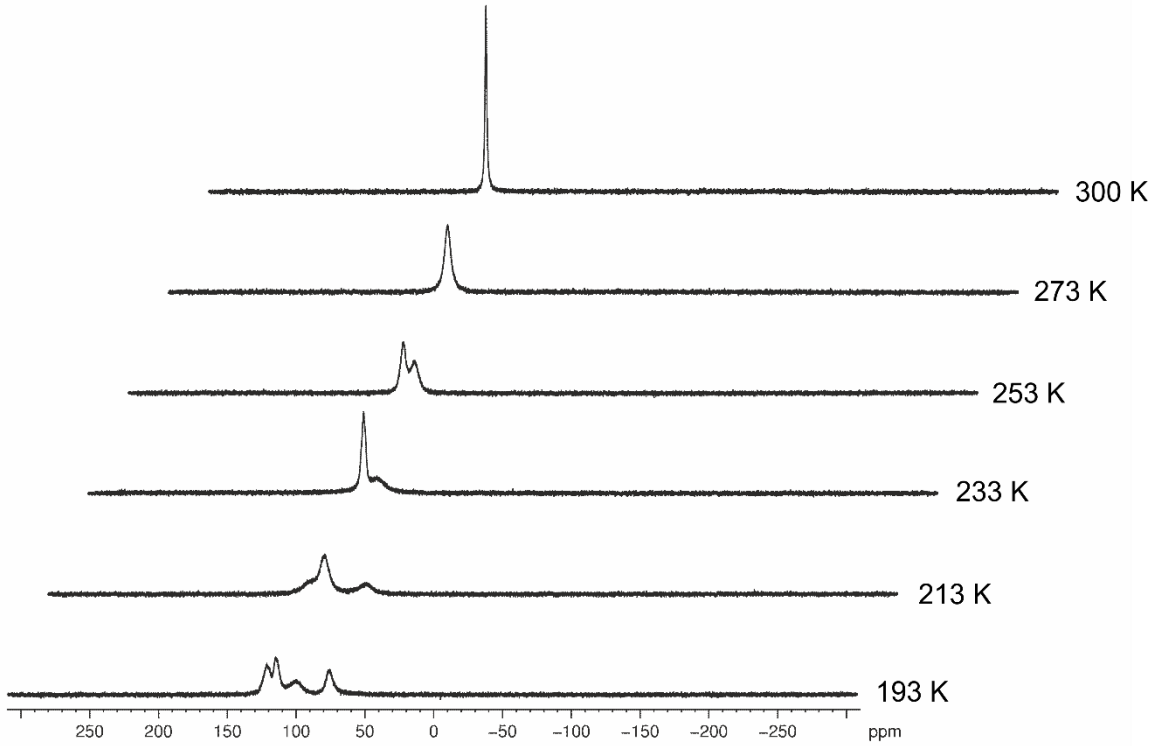


Figure S3.20. VT $^{31}P\{^1H\}$ NMR spectra of **8** in toluene-d$_8$ at different temperature between 193 K and 300 K.

3.5.2.12. [(Cp'''Ni)(μ,η$^{3:2}$-P$_3$)(L^{1}Cu)] (**9a**)

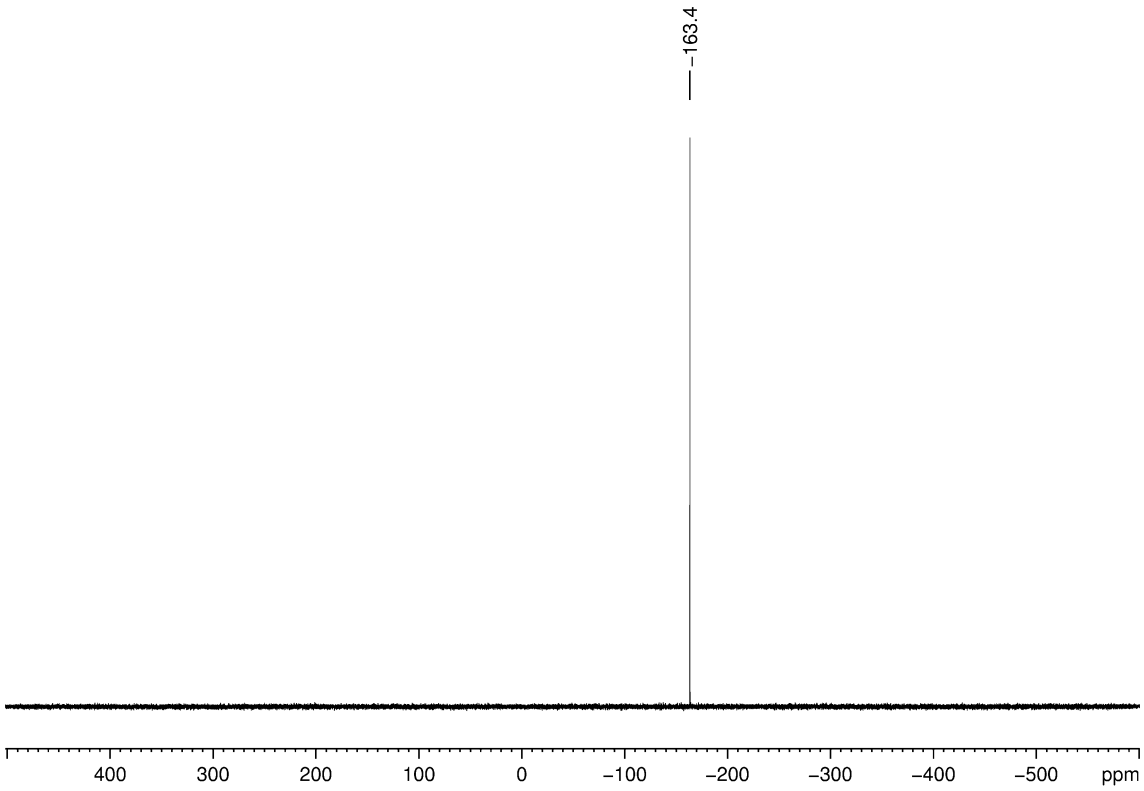


Figure S3.21. $^{31}P\{^1H\}$ NMR spectrum of **9a** in C_6D_6 at room temperature.

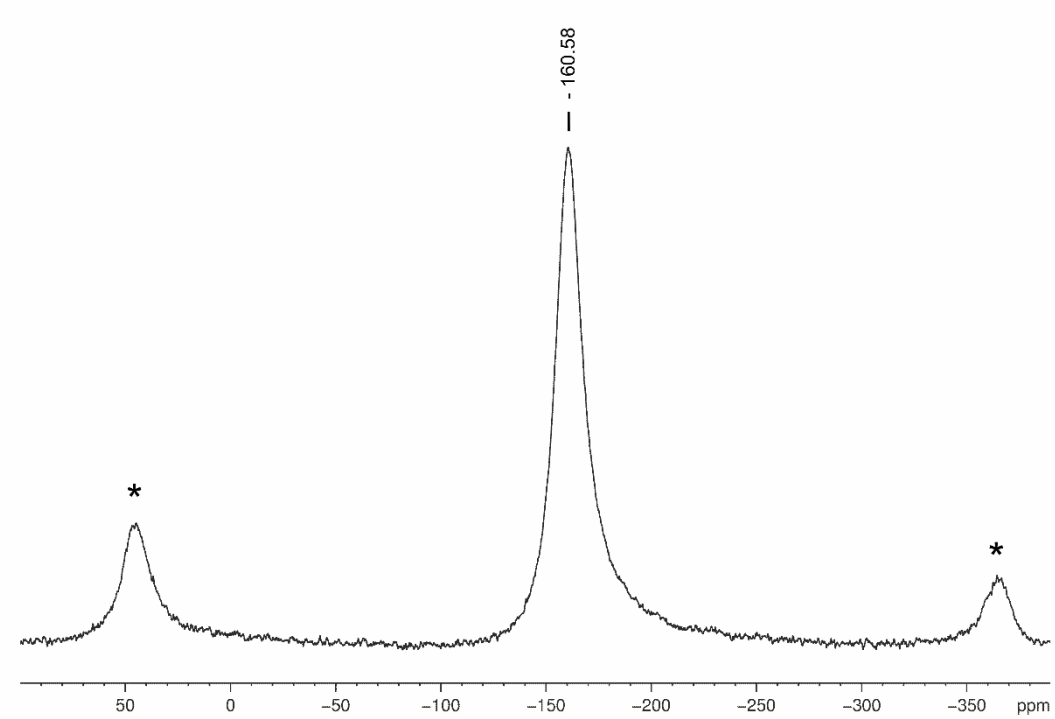


Figure S3.22. $^{31}P\{^{1}H\}$ MAS NMR spectrum of dried crystals of **9a**. Recorded at 25000 Hz MAS frequency. Rotational sidebands are marked with *.

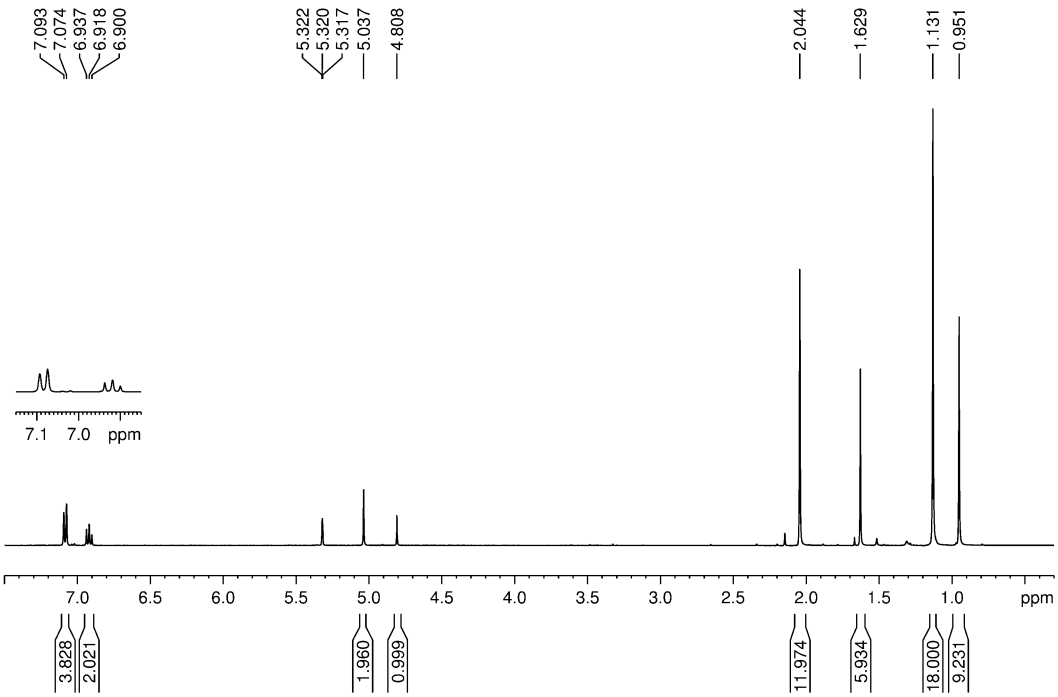


Figure S3.23. ^{1}H NMR spectrum of **9a** in CD_2Cl_2 at room temperature.

3.5.2.13. [(Cp'''Ni)(μ,η$^{3:2}$-As$_3$)(L^{1}Cu)] (**9b**)

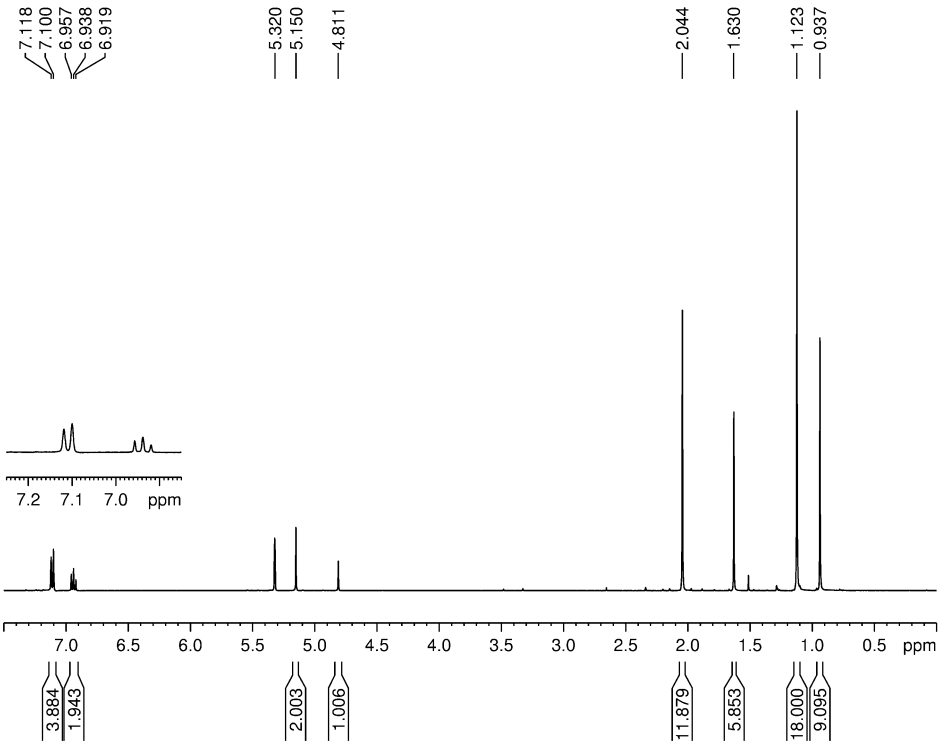


Figure S3.24. ^{1}H NMR spectrum of **9b** in CD_2Cl_2 at room temperature.

3.5.3. Details on single crystal X-ray structure analysis

The X-ray diffraction experiments were performed on either a Gemini Ultra diffractometer (Oxford diffraction) with an AtlasS2 detector Cu-K*α* radiation (λ = 1.54178 Å) (**6a**, **6b**, **S3**) or on a GV 50 diffractometer (Rigaku, formerly Agilent Technologies) with TitanS2 detector from applying Cu-K*α* radiation (λ = 1.54178 Å) (**5a**, **5b**, **8**, **9a**, **9b**, **S4**) or Cu-K*β* radiation (λ = 1.39222 Å) (**7**). All measurements were performed at 123 K. Data collection and reduction were performed with CrysAlisPro[7] (Version 171.38.41, 2015 (**5a**, **5b**, **6a**, **6b**, **S3**, **7**, **9b**), 171.41.21a, 2019 (**8**, **9a**), 171.41.76a, 2020 (**S4**)). For the compounds (**6a**, **6b**, **S3**) an analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid was applied.[8] For the compounds (**5a**, **5b**, **S4**, **7**, **8**, **9a**, **9b**) a gaussian absorption correction based on gaussian integration over a multifaceted crystal model was applied. All structures were solved by direct methods with ShelXT[9] and Olex2[10] and refined by full-matrix least-squares method against F^2 in anisotropic approximation using ShelXL[11]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined in calculated positions using riding on pivot atom model.

CCDC-2046249 (**5a**), CCDC-2046250 (**5b**), CCDC-2046251 (**6a**), CCDC-2046252 (**6b**), CCDC-2046253 (**7**), CCDC-2046254 (**8**), CCDC-2046255 (**9a**), CCDC-2046256 (**9b**), CCDC-2046257 (**S3**) and CCDC-2046258 (**S4**) 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).

3.5.3.1. [(Cp*Fe)(μ,η$^{5:2}$-P$_5$)(L^{1}Cu)] (**5a**)

Compound **5a** crystallized from a solution of Et_2O at -30 °C in the non-centrosymmetric orthorhombic space group $P2_12_12_1$. The asymmetric unit contains one molecule of **5a** and one molecule Et_2O. The structure in the solid state is shown in Figure S3.25.

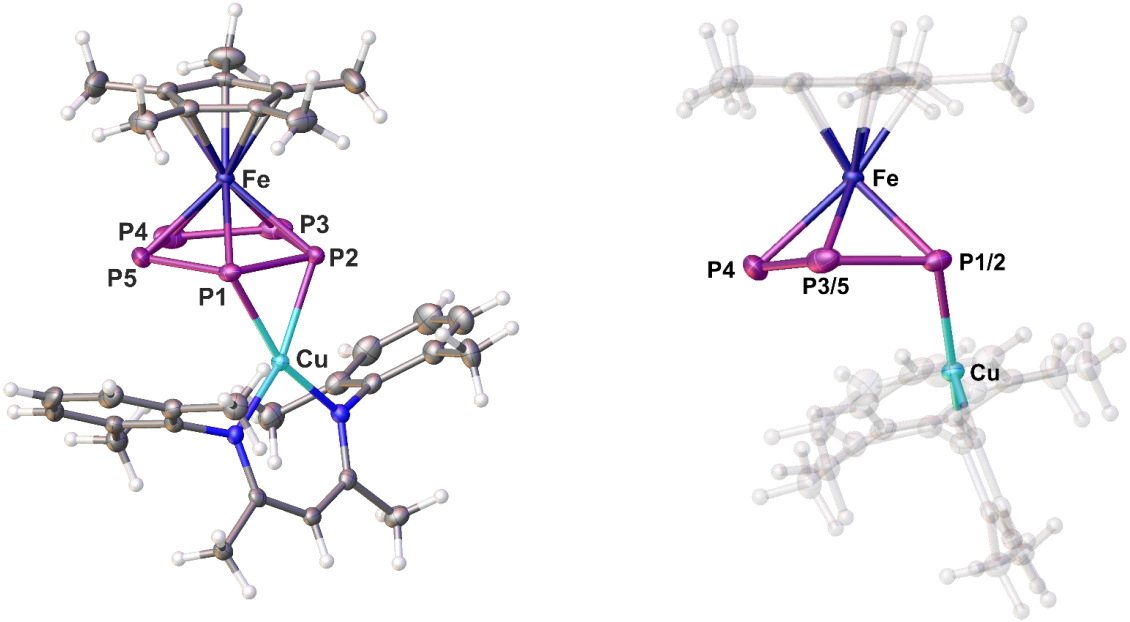


Figure S3.25. Molecular structure of **5a** in solid state (left: best view, right: side view). Solvent molecules are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Cu-P1 2.2859(7), Cu-P2 2.2820(7), Fe-P1 2.3778(7), 2.3732(7), Fe-P3 2.3323(9), Fe-P4 2.3685(9), Fe-P5 2.3376(8), P1-P2 2.200(10), P2-P3 2.1326(11), P3-P4 2.1184(13), P4-P5 2.1172(13), P5-P1 2.1252(11), P1-P2-P3 106.71(4), P2-P3-P4 107.87(5), P3-P4-P5 109.87(5), P4-P5-P1 107.51(5), P5-P1-P2 107.62(4).

3.5.3.2. [(Cp*Fe)(μ,$\eta^{5:2}$-As_5)(L^1Cu)] (**5b**)

Compound **5b** crystallized from a solution of Et_2O at -30 °C in the non-centrosymmetric orthorhombic space group $P2_12_12_1$. The asymmetric unit contains one molecule of **5b**. The structure in the solid state is shown in Figure S3.26.

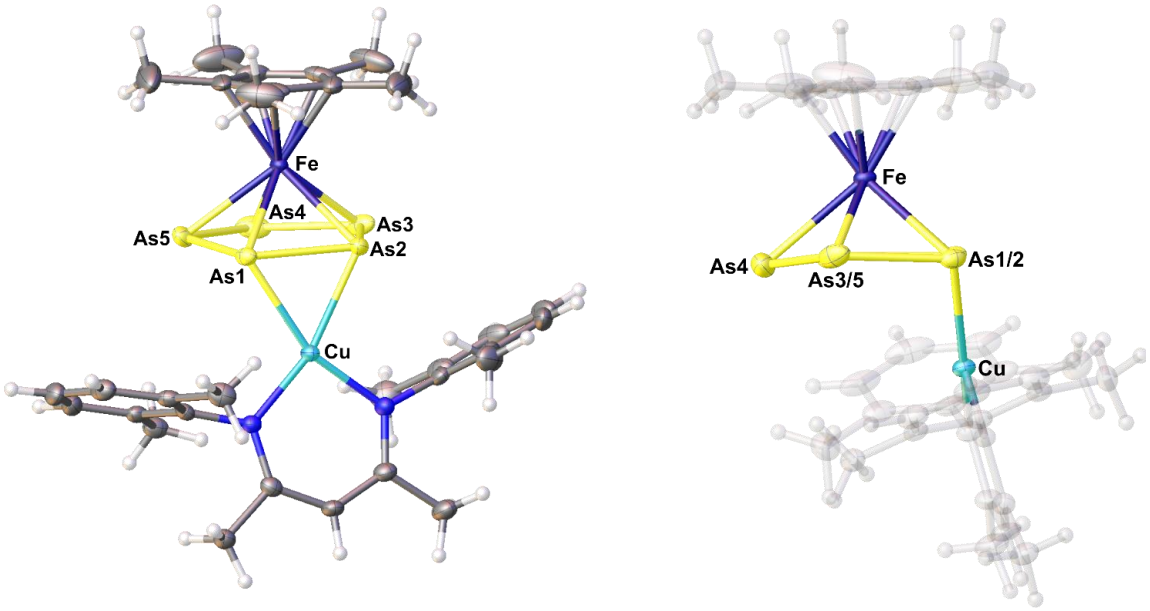


Figure S3.26. Molecular structure of **5b** in solid state (left: best view, right: side view). Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Cu-As1 2.4255(7), Cu-As2 2.4002(7), Fe-As1 2.5581(8), Fe-As2 2.5182(8), Fe-As3 2.4682(7), Fe-As4 2.5262(8), Fe-As5 2.4697(7), As1-As2 2.4039(6), As2-As3 2.3425(8), As3-As4 2.3251(9), As4-As5 2.3278(8), As5-As1 2.3416(7), As1-As2-As3 107.42(3), As2-As3-As4 107.84(3), As3-As4-As5 109.08(3), As4-As5-As1 107.99(3), As5-As1-As2 106.98(3).

3.5.3.3. $[(Cp^*Fe)(\mu_3,\eta^{5:2:1}\text{-}P_5)(L^1Cu)_2]$ (**6a**)

Compound **6a** crystallizes from a concentrated solution in toluene at -30 °C in the monoclinic space group $P2_1/m$ as brown plate. The asymmetric unit contains half a molecule of **6a** and a molecule of toluene. The structure in the solid state is given in Figure S3.27.

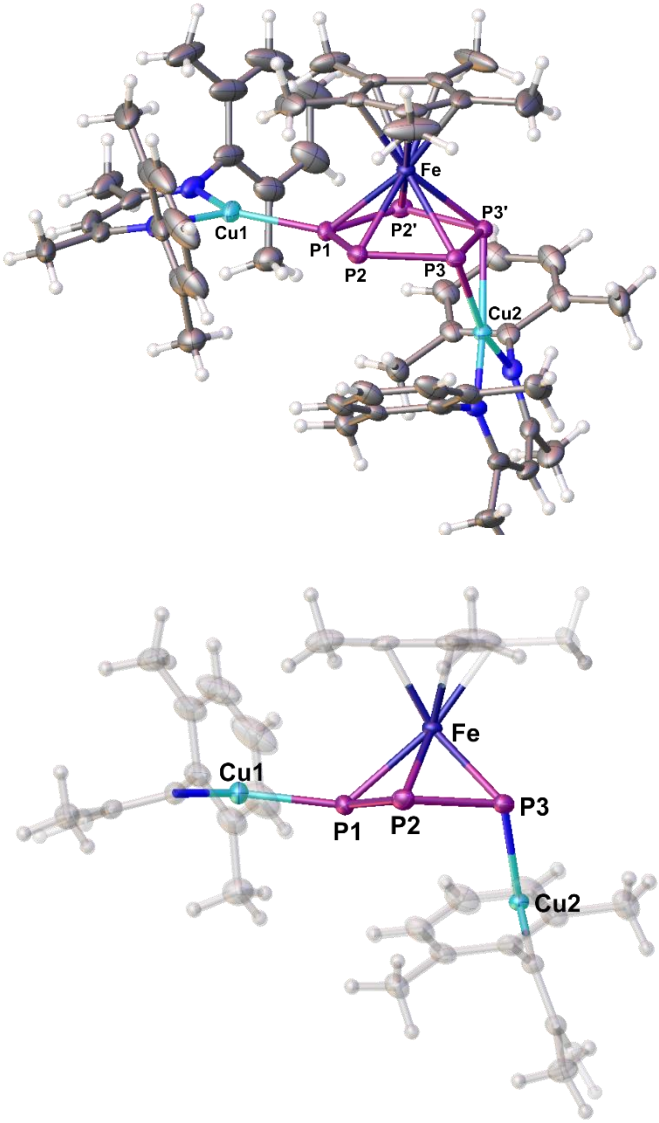


Figure S3.27: Molecular structure of **6a** in solid state (Top: best view, bottom side view). Solvent molecules are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Cu2-P3 2.2889(5), Cu2-P3' 2.2888(5), Fe-P1 2.3516(7), Fe-P2 2.3486(5), Fe-P3 2.3807(5), P1-P2 2.1248(6), P2-P3 2.1271(6), P3-P3' 2.2242(10), P3-Cu2-P3' 58.14(3), P1-P2-P3 106.02(3), P2-P3-P3' 107.740(1), P2-P1-P2' 111.87(4).

3.5.3.4. [(Cp*Fe)(μ_3,$\eta^{5:2:1}$-As_5)(L^1Cu)$_2$] (**6b**)

Compound **6b** crystallized from a concentrated solution in toluene at -30 °C in the monoclinic space group $P2_1/m$ as orange blocks. The asymmetric unit contains half a molecule of **6b** and a molecule of toluene. The structure in the solid state is given in Figure S3.28.

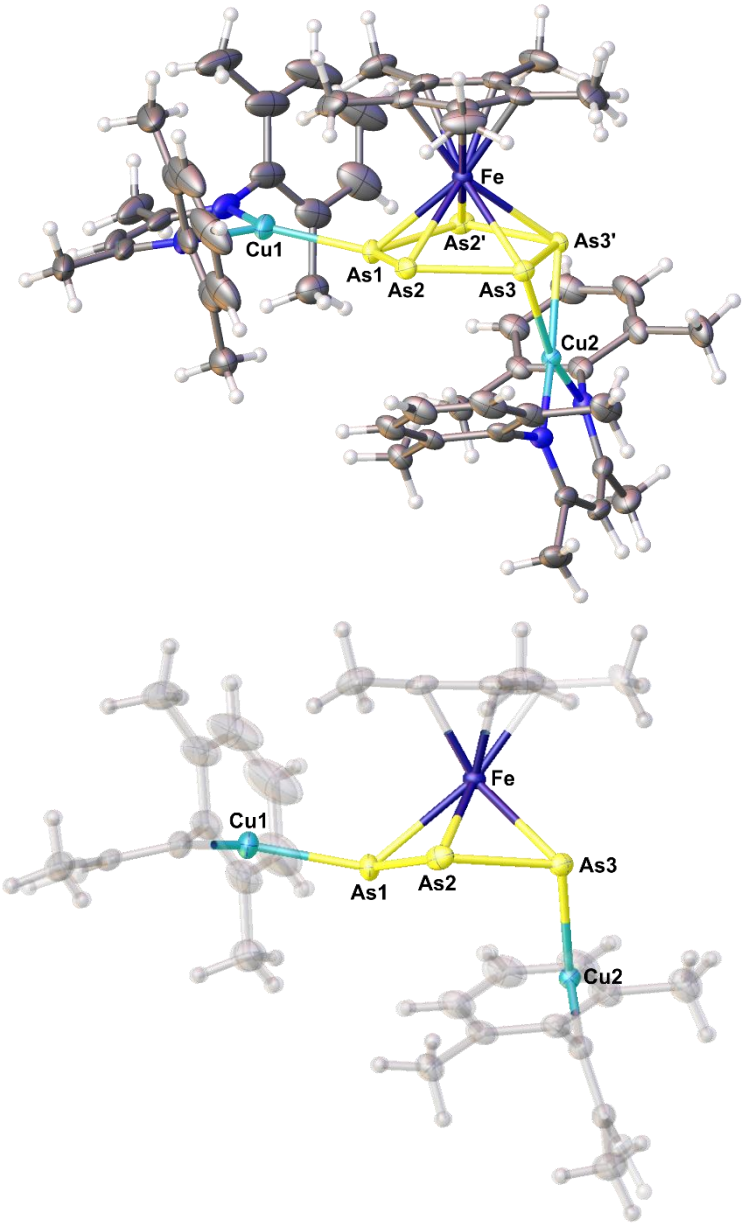


Figure S3.28. Molecular structure of **6b** in solid state (Top: best view, bottom side view). Solvent molecules are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Cu1-As1 2.2515(5), Cu2-As3 2.3987 (4), Fe-As1 2.5036(5), Fe-As2 2.4867(3), Fe-As3 2.5283(4), As1-As2 2.3260(3), As2-As3 2.3355(3), As3-As3' 2.4156(4), As3-Cu2-As3' 60.467(14), As1-As2-As3 105.207(1), As2-As1-As2' 112.290(1), As2-As3-As3' 108,054(8).

3.5.3.5. [(Cp*Fe)(μ,η$^{5:2}$-P$_5$)(L^{2}Cu)] (**S3**)

Compound **S3** crystallized from a solution of Et_2O at -30 °C in the monoclinic space group $P2_1/c$. The asymmetric unit contains one molecule of **S3**. The P3, P4 and P5 atoms are disordered over two positions in an occupancy of 62:38. The structure in the solid state is shown in Figure S3.29.

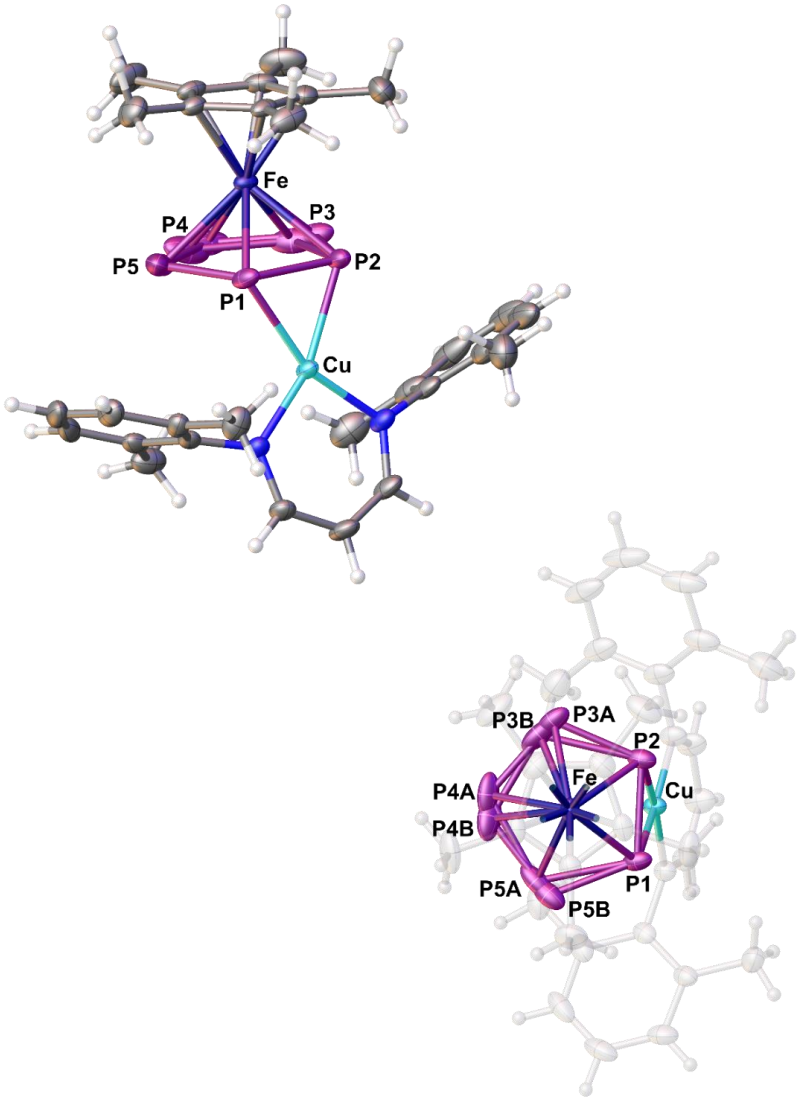


Figure S3.29. Molecular structure of **S3** in solid state (Top: best view, bottom: disorder of the P_5 ring). Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Cu-P1 2.2899(5), Cu-P2 2.2775(5), Fe-P1 2.3767(5), Fe-P2 2.3694(5), Fe-P3A 2.290(9), Fe-P4A 2.365(7), Fe-P3B 2.375(5), Fe-P4B 2.357(4), Fe-P5B 2.295(6), P1-P2 2.1972(6), P2-P3A 2.254(13), P3A-P4A 2.098(10), P4A-P5A 2.092(10), P5A-P1 2.023(10), P2-P3B 2.062(5), P3B-P4B 2.119(6), P4B-P5B 2.127(5), P5B-P1 2.198(7), P2-Cu-P1 57.509(17), P5A-P1-P2 113.7(3), P1-P2-P3A 100.7(4), P2-P3A-P4A 107.6(4), P3A-P4A-P5A 110.8(5), P4A-P5A-P1 106.6(4), P1-P2-P3B 110.82(17), P2-P3B-P4B 107.9(2), P3B-P4B-P5B 109.3(3), P4B-P5B-P1107.9(2), P2-P1-P5B 103.9(3).

3.5.3.6. [(Cp*Fe)(μ,η$^{5:2}$-As$_5$)(L^{2}Cu)] (**S4**)

Compound **S4** crystallized from a solution of Et_2O at -30 °C in the tetragonal space group $I4_1/a$. The asymmetric unit contains one molecule of **S4** and 0.5 molecules of Et_2O. The structure in the solid state is shown in Figure S3.30.

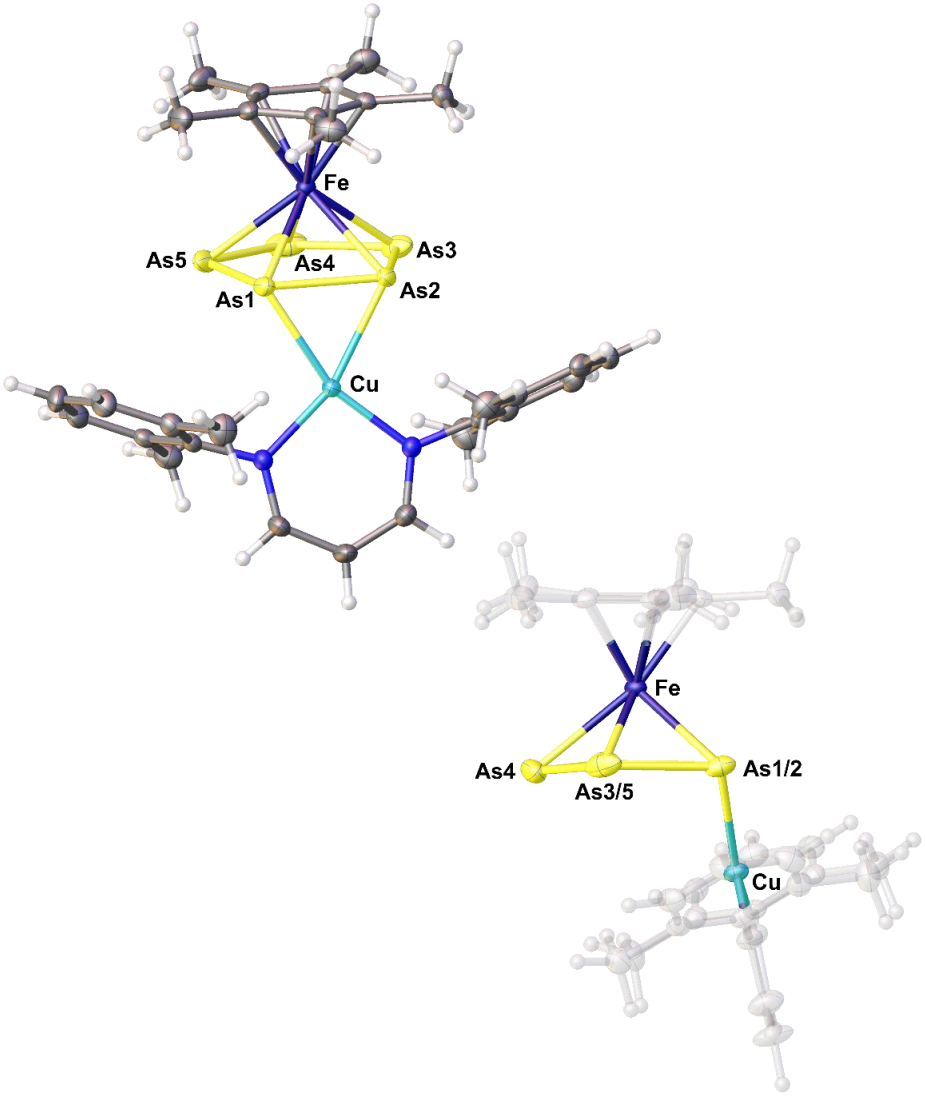


Figure S3.30. Molecular structure of structure of **S4** in solid state (Top: best view, bottom side view). Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Cu-As1 2.3860(4), Cu-As2 2.3897(4), Fe-As1 2.5092(4), Fe-As2 2.5241(5), Fe-As3 2.4795(5), Fe-As4 2.5266(5), Fe-As5 2.4826(5), As1-As2 2.4171(4), As2-As3 2.3432(5), As3-As4 2.3251(6), As4-As5 2.3263(6), As5-As1 2.3408(5), As1-As2-As3 106.661(17), As2-As3-As4 108.325(17), As3-As4-As5 109.310(18), As4-As5-As1 107.824(18), As5-As1-As2 107.533(16).

3.5.3.7. [(Cp'''Co)(μ,η$^{4:2}$-P$_4$)(L^{1}Cu)] (**7**)

Compound **7** crystallized from a very concentrated toluene solution at room temperature in the triclinic space group $P\bar{1}$. The asymmetric unit contains one molecule of **7**. The structure in the solid state is shown in Figure S3.31.

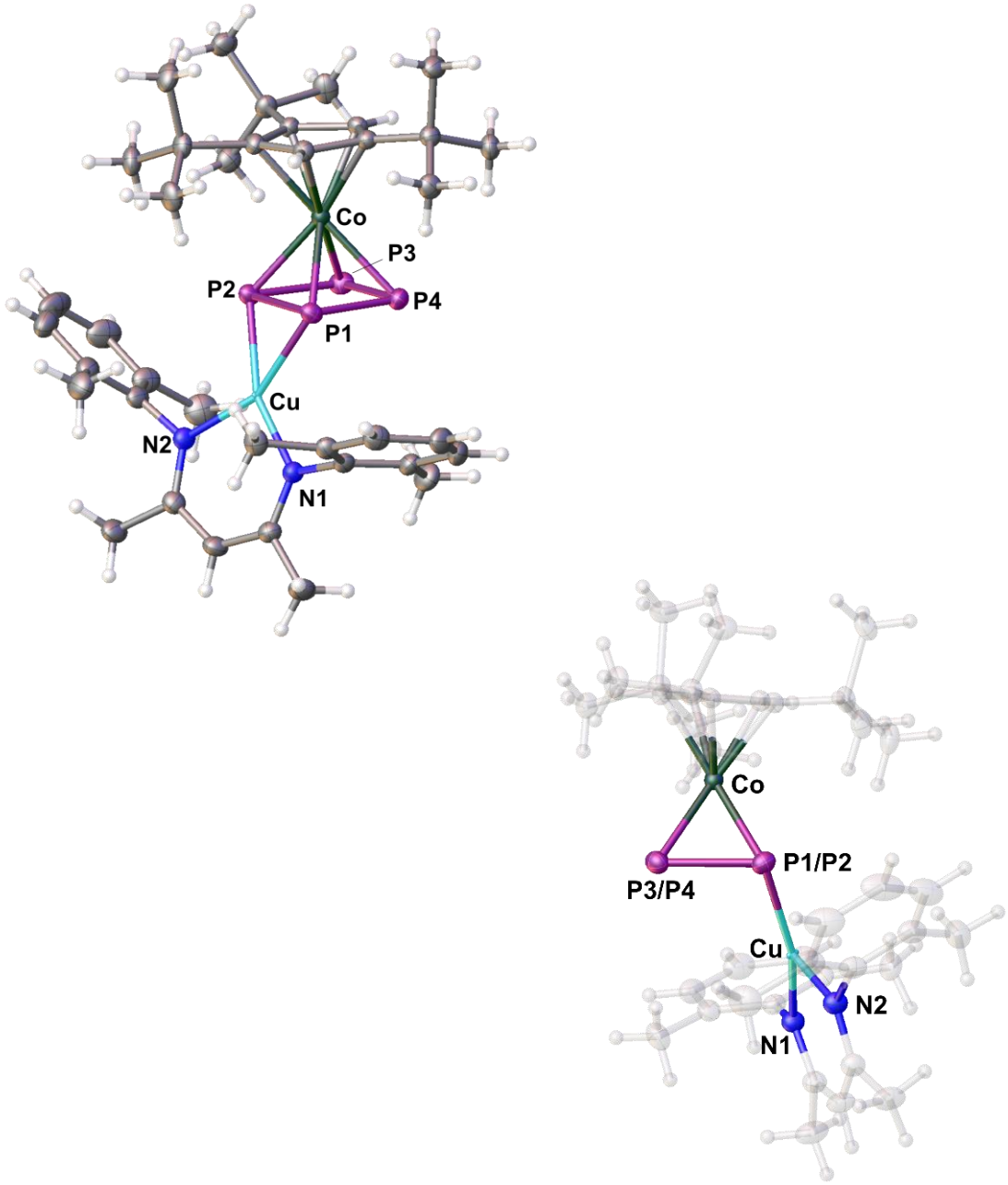


Figure S3.31. Molecular structure of **7** in solid state (Top: best view, bottom side view). Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Cu-P1 2.2662(5), Cu-P2 2.2731(5), Co-P1 2.2814(5), Co-P2 2.3029(4), Co-P3 2.3140(5), Co-P4 2.3017(5), P1-P2 2.3278(6), P2-P3 2.1618(6), P3-P4 2.1594(6), P4-P1 2.1795(6), Cu-N1 1.9362(14), Cu-N2 1.9240(13), P1-Cu-P2 61.701(16), P1-P2-P3 88.41(2), P2-P3-P4 92.00(2), P3-P4-P1 92.43(2), P4-P1-P2 87.14(2).

3.5.3.8. [(Cp'''Co)(μ$_3$,η$^{4:2:1}$-P$_4$)(L^{1}Cu)$_2$] (**8**)

Compound **8** crystallized from a pentane solution at room temperature in the triclinic space group P$\bar{1}$. The asymmetric unit contains one molecule of **8**. The structure in the solid state is shown in Figure S3.32.

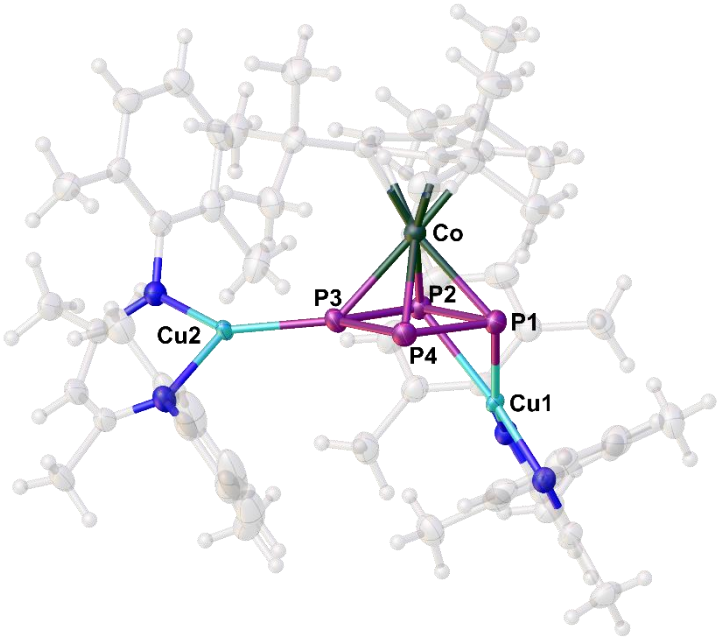


Figure S3.32. Molecular structure of **8** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Cu1-P1 2.2995(7), Cu1-P2 2.2543(7), Cu2-P3 2.1382(7), Co-P1 2.3113(7), Co-P2 2.2792(8), Co-P3 2.3279(8), Co-P4 2.2767(7), P1-P2 2.3387(9), P2-P3 2.1678(9), P3-P4 2.1536(9), P4-P1 2.1700(9), Cu1-N1 1.932(2), Cu1-N2 1.933(2), Cu2-N3 1.948(2), 1.942(2), P1-Cu1-P2 61.79(2), P1-P2-P3 85.51(3), P2-P3-P4 94.72(3), P3-P4-P1 90.17(3), P4-P1-P2 89.59(3).

3.5.3.9. [(Cp'''Ni)(μ,η$^{3:2}$-P$_3$)(L^{1}Cu)] (**9a**)

Compound **9a** crystallized from a concentrated solution in toluene layered with MeCN at -30 °C in the monoclinic space group P21/c. The asymmetric unit contains one molecule of **9a**. The structure in the solid state is shown in Figure S3.33.

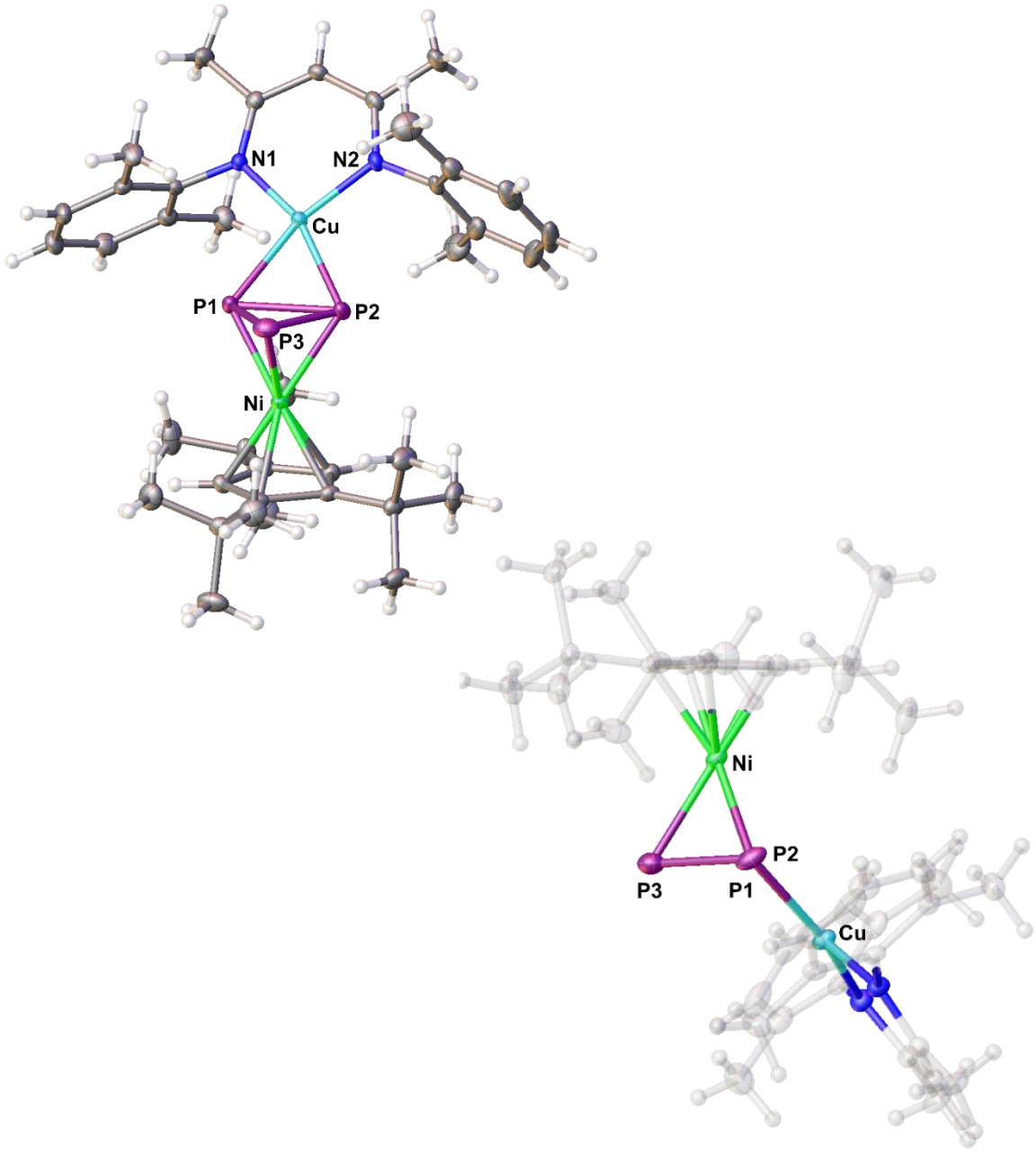


Figure S3.33: Molecular structure of **9a** in solid state (Top: best view, bottom: side view). Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Cu-P1 2.2966(5), Cu-P2 2.2858(5), Ni-P1 2.2466(5), Ni-P2 2.2375(5), Ni-P3 2.2466(6), P1-P2 2.3143(6), P1-P3 2.1569(7), P2-P3 2.1616(7), P1-Cu-P2 60.667(17), Ni-P1-Cu 114.51(2), Ni-P2-Cu 115.30(2), P1-P2-P3 57.50(2), P2-P3-P1 64.81(2), P3-P1-P2 57.69(2).

3.5.3.10. [(Cp'''Ni)(μ,η$^{3:2}$-As$_3$)(L^{1}Cu)] (**9b**)

Compound **9b** crystallized from a concentrated solution in toluene layered with MeCN at -30 °C in the monoclinic space group $P2_1/c$. The asymmetric unit contains one molecule of **9b**. The structure in the solid state is shown in Figure S3.34.

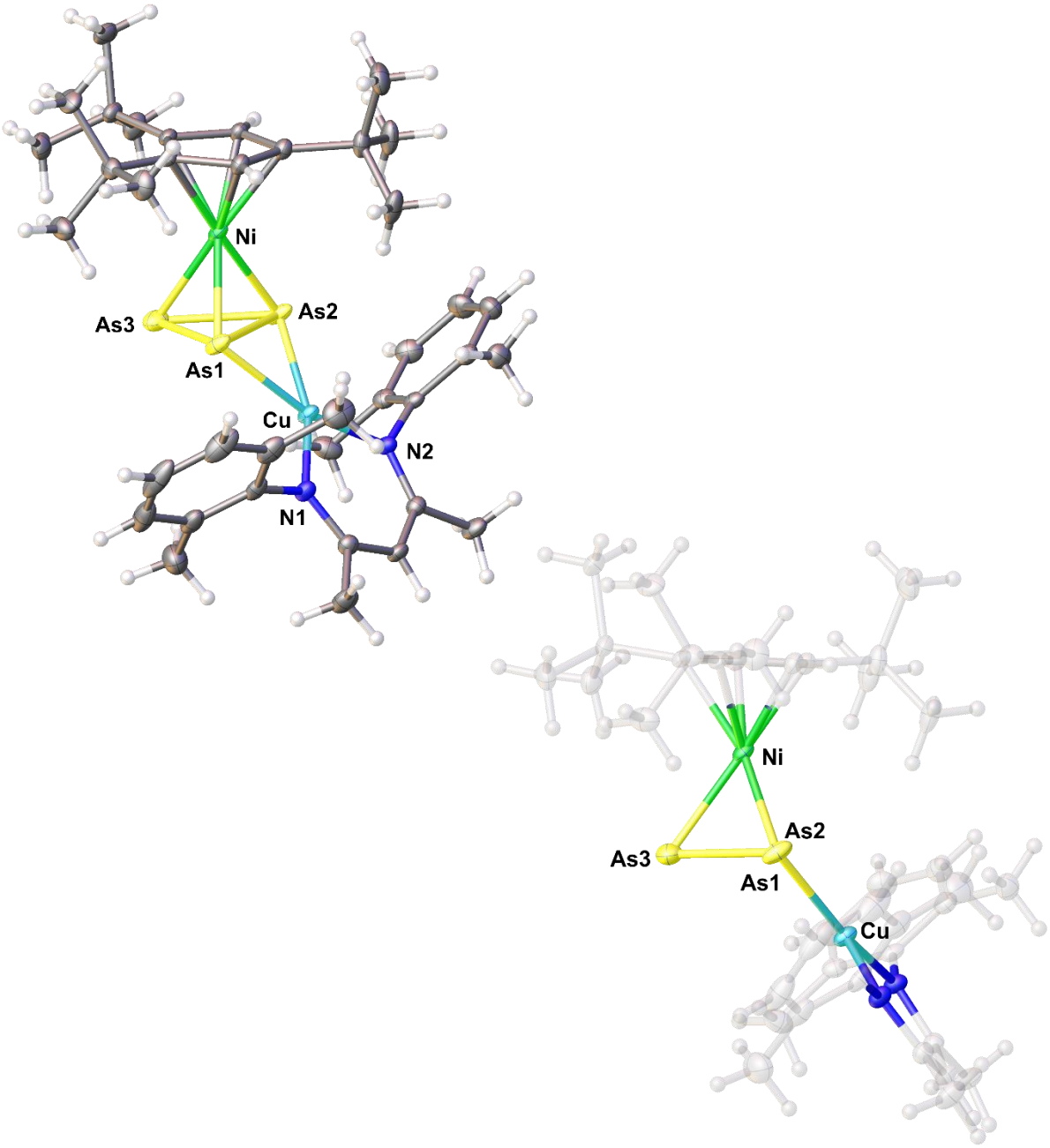


Figure S3.34: Molecular structure of **9b** in solid state (Top: best view, bottom: side view). Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Cu-As1 2.3857(4), Cu-As2 2.3980(4), Ni-As1 2.3476(4), Ni-As2 2.3607(4), Ni-As3 2.3563(4), As1-As2 2.5625(3), As2-As3 2.3877(4), As3-As1 2.3920(4), As1-Cu-As2 64.779(10), Ni As1-Cu 112.320(14), Ni-As2-Cu 111.410(13), As1-As2-As3 57.661(10), As2-As3-As1 64.840(10), As3-As1-As2 57.499(10).

3.5.3.11. Crystallographic information

Table S3.4. Crystallographic data and details of diffraction experiments for **5a**, **5b**, **6a** and **6b**.

Compound	**5a** · Et_2O	**5b**	**6a** · toluene	**6b** · toluene
CCDC	2046249	2046250	2046251	2046252
Formula	$C_{35}H_{50}CuFeN_2OP_5$	$C_{31}H_{40}As_5CuFeN_2$	$C_{59}H_{73}Cu_2FeN_4P_5$	$C_{59}H_{73}As_5Cu_2FeN_4$
$D_{calc.}$/ g cm^{-3}	1.375	1.793	1.365	1.580
μ/mm^{-1}	5.949	9.598	4.500	6.235
Formula Weight	789.01	934.64	1175.99	1395.74
Colour	brown	brown	brown	dark orange
Shape	needle	block	plate	block
Size/mm^3	0.74×0.10×0.07	0.23×0.12×0.10	0.40×0.19×0.04	0.19×0.11×0.09
T/K	123.00(10)	122.98(10)	123(1)	123(1)
Crystal System	orthorhombic	orthorhombic	monoclinic	monoclinic
Flack Parameter	-0.008(2)	-0.003(4)	-	-
Hooft Parameter	-0.0074(19)	-0.001(3)	-	-
Space Group	$P2_12_12_1$	$P2_12_12_1$	$P2_1/m$	$P2_1/m$
a/Å	8.7544(2)	14.5039(4)	11.1050(2)	11.2264(2)
b/Å	13.5679(3)	15.1604(3)	18.0201(3)	18.0999(3)
c/Å	32.0939(4)	15.7460(3)	14.7436(3)	14.9184(2)
α/°	90	90	90	90
β/°	90	90	104.096(2)	104.638(2)
γ/°	90	90	90	90
V/Å^3	3812.08(13)	3462.31(13)	2861.55(9)	2932.98(9)
Z	4	4	2	2
Z'	1	1	0.5	0.5
Wavelength/Å	1.54184	1.54184	1.54184	1.54184
Radiation type	Cu K$_\alpha$	Cu K$_\alpha$	Cu K$_\alpha$	CuK$_\alpha$
Θ_{min}/°	3.537	4.048	3.946	3.917
Θ_{max}/°	74.314	74.003	72.946	72.874
Measured Refl's.	12136	10988	16093	16672
Ind't Refl's	6756	6316	5707	5818
Refl's with I > 2(I)	6537	6055	5279	5331
R_{int}	0.0235	0.0249	0.0290	0.0229
Parameters	419	372	352	352
Restraints	0	0	0	0
Largest Peak	0.307	0.445	0.372	0.466
Deepest Hole	-0.211	-0.353	-0.465	-0.353
GooF	1.024	1.040	1.027	1.036
wR_2 (all data)	0.0608	0.0569	0.0815	0.0550
wR_2	0.0600	0.0559	0.0792	0.0536
R_1 (all data)	0.0254	0.0254	0.0347	0.0262
R_1	0.0242	0.0236	0.0318	0.0227

Table S3.5. Crystallographic data and details of diffraction experiments for **7**, **8**, **9a**, **9b**.

Compound	**7**	**8**	**9a**	**9b**
CCDC	2046253	2046254	2046255	2046256
Formula	$C_{38}H_{54}CoCuN_2P_4$	$C_{59}H_{79}CoCu_2N_4P_4$	$C_{38}H_{54}CuN_2NiP_3$	$C_{38}H_{54}As_3CuN_2Ni$
$D_{calc.}$/ g cm^{-3}	1.312	1.314	1.300	1.513
μ/mm^{-1}	4.275	4.380	2.665	4.309
Formula Weight	785.18	1154.15	753.99	885.84
Colour	red	brown	red	red
Shape	block	plate	block	block
Size/mm^3	0.22×0.08×0.06	0.37×0.13×0.04	0.16×0.07×0.05	0.56×0.27×0.20
T/K	122.98(10)	122.98(16)	122.97(10)	123.01(10)
Crystal System	triclinic	triclinic	monoclinic	monoclinic
Space Group	P-1	P-1	$P2_1/c$	$P2_1/c$
a/Å	8.5866(3)	12.5441(6)	16.2542(2)	16.3581(2)
b/Å	14.0745(6)	13.0610(6)	13.13990(10)	13.14580(10)
c/Å	16.9601(7)	19.7943(8)	18.0352(2)	18.0882(2)
α/°	99.236(4)	78.555(4)	90	90
β/°	90.090(3)	81.863(4)	90.4230(10)	90.5380(10)
γ/°	100.671(3)	66.970(4)	90	90
V/Å^3	1987.07(14)	2917.9(2)	3851.83(7)	3889.52(7)
Z	2	2	4	4
Z'	1	1	1	1
Wavelength/Å	1.39222	1.54184	1.54184	1.54184
Radiation type	Cu K$_\beta$	Cu K$_\alpha$	Cu K$_\alpha$	Cu K$_\alpha$
Θ_{min}/°	2.384	2.283	4.163	4.157
Θ_{max}/°	68.062	73.926	73.920	74.040
Measured Refl's.	21238	23631	21437	21867
Ind't Refl's	9487	11313	7469	7650
Refl's with I > 2(I)	8591	9879	6624	7169
R_{int}	0.0300	0.0553	0.0309	0.0259
Parameters	430	652	421	421
Restraints	0	0	0	0
Largest Peak	0.537	1.379	0.371	0.379
Deepest Hole	-0.335	-0.603	-0.462	-0.537
GooF	1.034	1.014	1.020	1.069
wR_2 (all data)	0.0873	0.1154	0.0788	0.0669
wR_2	0.0834	0.1096	0.0755	0.0656
R_1 (all data)	0.0371	0.0523	0.0357	0.0290
R_1	0.0328	0.0453	0.0298	0.0267

Table S3.6. Crystallographic data and details of diffraction experiments for **S3** and **S4**.

Compound	**S3**	**S4** · 0.5 Et_2O
CCDC	2046257	2046258
Formula	$C_{29}H_{36}CuFeN_2P_5$	$C_{31}H_{41}As_5CuFeN_2O_{0.5}$
$D_{calc.}$/ g cm^{-3}	1.425	1.759
μ/mm^{-1}	6.976	9.343
Formula Weight	686.84	943.65
Colour	brown	brown
Shape	plate	needle
Size/mm^3	0.56×0.22×0.07	0.17×0.03×0.02
T/K	123(1)	122.96(11)
Crystal System	monoclinic	tetragonal
Space Group	$P2_1/c$	$I4_1/a$
a/Å	18.5050(2)	41.7083(6)
b/Å	8.74780(10)	41.7083(6)
c/Å	20.0339(3)	8.1936(2)
α/°	90	90
β/°	99.0770(10)	90
γ/°	90	90
V/Å^3	3202.44(7)	14253.4(5)
Z	4	16
Z'	1	1
Wavelength/Å	1.54184	1.54184
Radiation type	Cu K$_\alpha$	Cu K$_\alpha$
Θ_{min}/°	4.470	4.240
Θ_{max}/°	71.633	73.424
Measured Refl's.	18130	15215
Indep't Refl's	6124	6880
Refl's I≥2 σ(I)	5829	6328
R_{int}	0.0322	0.0230
Parameters	380	446
Restraints	0	60
Largest Peak	0.586	0.785
Deepest Hole	-0.409	-0.687
GooF	1.039	1.029
wR_2 (all data)	0.0814	0.0698
wR_2	0.0795	0.0681
R_1 (all data)	0.0325	0.0305
R_1	0.0308	0.0272

3.5.4. DFT Calculations

The geometry of the molecules has been optimized with Gaussian 09,[12] using the B3LYP functional[13] together with the def2-TZVP basis set for all atoms.[14] To account for long-range van der Waals forces the dispersion corrections proposed by Grimme et al. has been added (DFT-D3).[15] Solvents effects were accounted by using continuous polarizable continuum model (CPM).[16] The dielectric constant of thf (ε = 7.4257) has been used in the calculations. The Natural Bond Orbital (NBO) analysis has been performed with the NBO6 program.[17]

The topological analysis of the electron density obtained from the DFT calculations, according to the Atoms in Molecules theory[18] has been performed with the MultiWFN program (version 3.6).[19] The molecular orbital interaction diagram based on the interaction of fragment orbitals has been constructed using the results obtained from the AOMIX program.[20] The figures for the supporting information concerning the DFT calculations were created with Chemcraft.[21]

Table S3.7: Total energies for all optimized geometries (B3LYP/def2-TZVP level of theory).

	total energy [Ha]
1a [Cp*Fe(η^5-P_5)]	-3361.14387431
1b [Cp*Fe(η^5-As_5)]	-12833.8894849
2 [L^1Cu(MeCN)]	-2698.73585730
3 [Cp'''Co(η^4-P_4)]	-3414.10100308
4a [Cp'''Ni(η^3-P_3)]	-3198.25221381
4b [Cp'''Ni(η^3-As_3)]	-8881.90571328
5a [(Cp*Fe)(μ,$\eta^{5:2}$-P_5)(L^1Cu)]	-5927.09036526
I-5a [(Cp*Fe)(μ,$\eta^{5:1}$-P_5)(L^1Cu)]	-5927.08267667
5b [(Cp*Fe)(μ,$\eta^{5:2}$-As_5)(L^1Cu)]	-15399.8408647
I-5b [(Cp*Fe)(μ,$\eta^{5:1}$-As_5)(L^1Cu)]	-15399.8235716
6a [(Cp*Fe)(μ_3,$\eta^{5:2:1}$-P_5)(L^1Cu)$_2$]	-8493.03719635
6b [(Cp*Fe)(μ_3,$\eta^{5:2:1}$-As_5)(L^1Cu)$_2$]	-17965.7824510
7 [(Cp'''Co)(μ,$\eta^{4:2}$-P_4)(L^1Cu)]	-5980.04685390
8 [(Cp'''Co)(μ_3,$\eta^{4:2:1}$-P_4)(L^1Cu)$_2$]	-8545.98746652
9a [(Cp'''Ni)(μ,$\eta^{3:2}$-P_3)(L^1Cu)]	-5764.19342365
9b [(Cp'''Ni)(μ,$\eta^{3:2}$-As_3)(L^1Cu)]	-11447.8517436
MeCN	-132.822066436

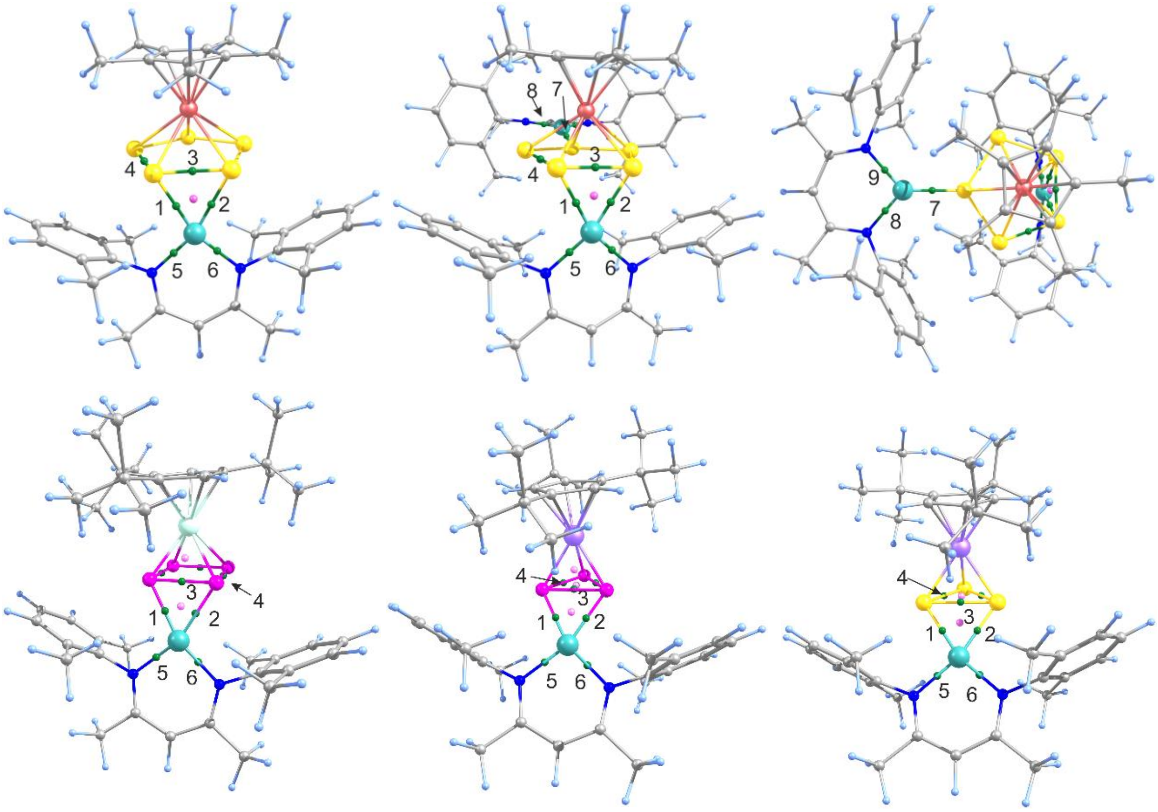


Figure S3.35. Locations an labelling of selected Bond Critical Points (BCP, green) and Ring Critical Points (RCP, violet) in the electron density of [(Cp*Fe)(μ,η$^{5:2}$-E$_5$)(L^{1}Cu)] (E = P (**5a**), As (**5b**)), [(Cp*Fe)(μ$_3$,η$^{5:2:1}$-E$_5$)(L^{1}Cu)$_2$] (E = P (**6a**), As (**6b**)), [(Cp'''Co)(μ,η$^{4:2}$-P$_4$)(L^{1}Cu)] (**7**) and [(Cp'''Ni)(μ,η$^{3:2}$-E$_3$)(L^{1}Cu)] (E = P (**9a**), As (**9b**)).

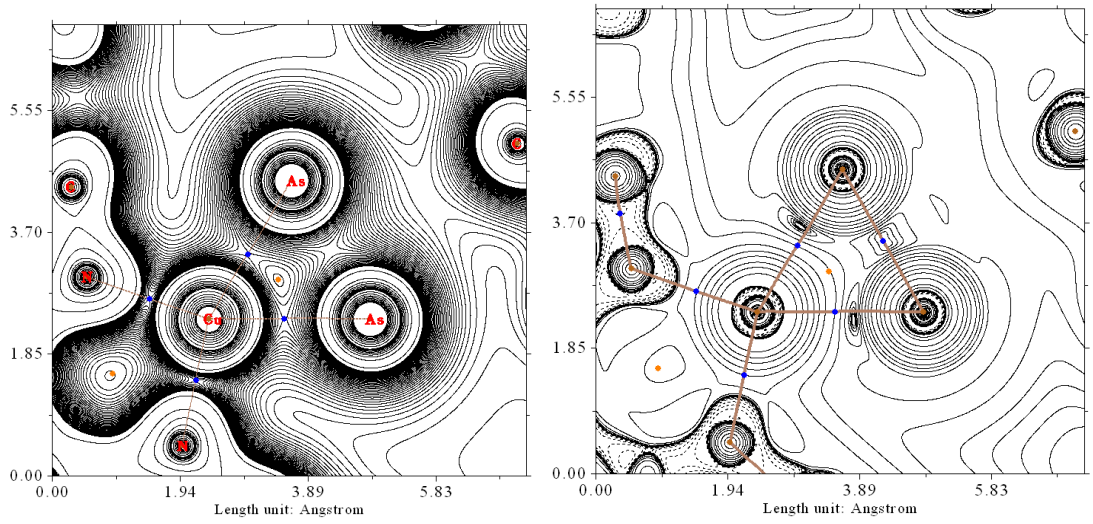


Figure S3.36. Electron density (left) and the Laplacian of the electron density in the CuAs$_2$ plane in [(Cp*Fe)(μ$_3$,η$^{5:2:1}$-As$_5$)(L^{1}Cu)$_2$] (**6b**).

Table S3.8. Properties of selected critical points in the electron density of **5a**, **5b**, **6a**, **6b**, **7**, **9a** and **9b**. ρ(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; ε(r) = ellipticity of electron density at CP (ε(r) = [$\lambda_1(r)/\lambda_2(r)$]-1; where λ_1 and λ_2 are the lowest and the second lowest eigenvalues of Hessian matrix of ρ, respectively); η(r) = eta index (η(r) = $|\lambda_1(r)|/\lambda_3(r)$, where λ_1 and λ_3 are the lowest and the highest eigenvalues of Hessian matrix of ρ, respectively); Bond degree, BD = H(r)/ρ(r).

	ρ(r)	**$\nabla^2\rho(r)$**	**H(r)**	**G(r)**	**V(r)**	**|V|/G**	**ε(r)**	**η(r)**	**BD**
[(Cp*Fe)(μ,$\eta^{5:2}$-P_5)(L^1Cu)] (**5a**)									
BCP 1	0.070	0.096	-0.021	0.045	-0.065	1.461	0.393	0.312	-0.294
BCP 2	0.070	0.096	-0.021	0.045	-0.065	1.461	0.393	0.312	-0.294
BCP 3	0.104	-0.066	-0.051	0.035	-0.086	2.471	0.655	1.048	-0.493
BCP 4	0.123	-0.139	-0.071	0.036	-0.107	2.966	0.273	1.441	-0.578
BCP 5	0.096	0.383	-0.031	0.126	-0.157	1.243	0.032	0.200	-0.320
BCP 6	0.096	0.383	-0.031	0.126	-0.157	1.243	0.032	0.200	-0.320
RCP	0.062	0.125	-0.013	0.044	-0.057	1.292	-2.343	0.372	-0.209
[(Cp*Fe)(μ,$\eta^{5:2}$-As_5)(L^1Cu)] (**5b**)									
BCP 1	0.061	0.076	-0.016	0.035	-0.051	1.457	0.261	0.307	-0.263
BCP 2	0.061	0.076	-0.016	0.035	-0.051	1.457	0.261	0.307	-0.263
BCP 3	0.080	0.001	-0.032	0.032	-0.064	1.993	0.553	0.603	-0.399
BCP 4	0.092	-0.031	-0.042	0.034	-0.076	2.229	0.280	0.703	-0.456
BCP 5	0.094	0.375	-0.030	0.123	-0.153	1.241	0.035	0.200	-0.314
BCP 6	0.094	0.375	-0.030	0.123	-0.153	1.241	0.035	0.200	-0.314
RCP	0.051	0.087	-0.009	0.031	-0.040	1.296	-2.113	0.429	-0.177
[(Cp*Fe)(μ$_3$,$\eta^{5:2:1}$-P_5)(L^1Cu)$_2$] (**6a**)									
BCP 1	0.071	0.094	-0.022	0.045	-0.067	1.478	0.352	0.317	-0.302
BCP 2	0.071	0.097	-0.021	0.045	-0.067	1.469	0.363	0.313	-0.299
BCP 3	0.102	-0.057	-0.049	0.034	-0.083	2.418	0.707	1.000	-0.479
BCP 4	0.124	-0.143	-0.072	0.036	-0.108	2.985	0.272	1.477	-0.582
BCP 5	0.097	0.385	-0.031	0.127	-0.158	1.244	0.030	0.200	-0.321
BCP 6	0.097	0.385	-0.031	0.128	-0.159	1.246	0.033	0.201	-0.323
BCP 7	0.091	0.167	-0.037	0.079	-0.116	1.473	0.070	0.260	-0.410
BCP 8	0.094	0.391	-0.029	0.127	-0.156	1.229	0.033	0.195	-0.309
BCP 9	0.125	-0.149	-0.075	0.037	-0.112	2.992	0.374	1.601	-0.595
RCP	0.062	0.124	-0.013	0.044	-0.057	1.298	-2.271	0.383	-0.211
[(Cp*Fe)(μ$_3$,$\eta^{5:2:1}$-As_5)(L^1Cu)$_2$] (**6b**)									
BCP 1	0.061	0.074	-0.016	0.035	-0.051	1.468	0.235	0.309	-0.267
BCP 2	0.061	0.074	-0.016	0.035	-0.051	1.464	0.247	0.309	-0.264
BCP 3	0.079	0.004	-0.030	0.031	-0.062	1.970	0.570	0.590	-0.388
BCP 4	0.094	-0.034	-0.043	0.035	-0.078	2.249	0.230	0.715	-0.461
BCP 5	0.094	0.372	-0.030	0.123	-0.152	1.242	0.038	0.202	-0.314
BCP 6	0.095	0.374	-0.030	0.123	-0.153	1.243	0.038	0.202	-0.316
BCP 7	0.076	0.147	-0.027	0.063	-0.090	1.422	0.077	0.244	-0.351
BCP 8	0.096	0.402	-0.030	0.131	-0.161	1.232	0.038	0.196	-0.316
BCP 9	0.096	0.401	-0.030	0.131	-0.161	1.232	0.038	0.196	-0.316

RCP	0.051	0.085	-0.009	0.030	-0.039	1.299	-2.069	0.440	-0.177
[(Cp'''Co)(μ,$\eta^{4:2}$-P_4)(L^1Cu)] (**7**)									
BCP 1	0.074	0.091	-0.024	0.046	-0.070	1.510	0.298	0.327	-0.318
BCP 2	0.072	0.093	-0.022	0.046	-0.068	1.487	0.346	0.320	-0.307
BCP 3	0.089	-0.030	-0.036	0.029	-0.065	2.259	1.232	0.900	-0.408
BCP 4	0.121	-0.140	-0.067	0.032	-0.099	3.096	0.312	1.436	-0.557
BCP 5	0.096	0.382	-0.031	0.126	-0.157	1.243	0.027	0.199	-0.319
BCP 6	0.098	0.389	-0.032	0.129	-0.161	1.245	0.026	0.200	-0.324
RCP	0.062	0.112	-0.013	0.041	-0.055	1.325	-2.181	0.435	-0.216
[(Cp'''Ni)(μ,$\eta^{3:2}$-P_3)(L^1Cu)] (**9a**)									
BCP 1	0.072	0.094	-0.021	0.045	-0.066	1.477	0.294	0.315	-0.300
BCP 2	0.071	0.093	-0.021	0.044	-0.066	1.477	0.298	0.316	-0.298
BCP 3	0.083	0.023	-0.032	0.038	-0.070	1.846	0.928	0.493	-0.383
BCP 4	0.116	-0.104	-0.064	0.038	-0.103	2.679	0.150	1.179	-0.555
BCP 5	0.094	0.372	-0.029	0.122	-0.152	1.239	0.030	0.199	-0.312
BCP 6	0.095	0.377	-0.030	0.124	-0.154	1.240	0.028	0.199	-0.315
RCP	0.060	0.102	-0.013	0.038	-0.050	1.330	-2.059	0.458	-0.207
[(Cp'''Ni)(μ,$\eta^{3:2}$-As_3)(L^1Cu)] (**9b**)									
BCP 1	0.063	0.071	-0.017	0.035	-0.053	1.493	0.163	0.315	-0.276
BCP 2	0.063	0.072	-0.018	0.036	-0.053	1.495	0.158	0.314	-0.278
BCP 3	0.059	0.042	-0.017	0.027	-0.044	1.613	1.282	0.357	-0.280
BCP 4	0.086	-0.017	-0.037	0.033	-0.069	2.127	0.200	0.631	-0.430
BCP 5	0.093	0.372	-0.029	0.122	-0.151	1.238	0.031	0.199	-0.311
BCP 6	0.093	0.367	-0.029	0.120	-0.149	1.237	0.032	0.199	-0.308
RCP	0.049	0.061	-0.009	0.024	-0.033	1.370	-1.798	0.667	-0.181

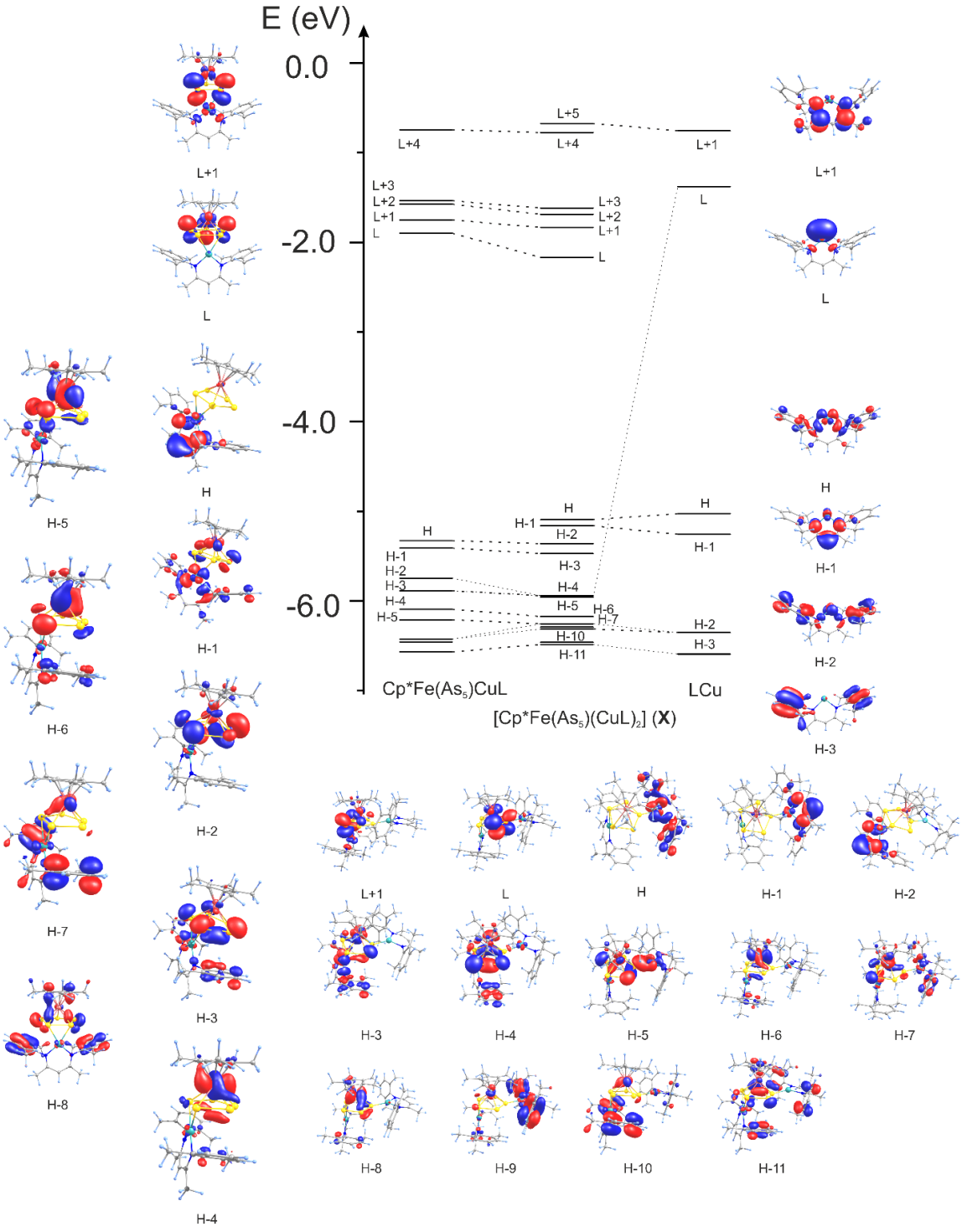


Figure S3.37. Molecular orbital interaction diagram of **6b**, calculated at the B3LYP/def2-TZVP level of theory. Only fragment contributions of more than 5% are depicted. The lines drawn in bold represent the main character of the corresponding molecular orbital.

Table S3.9. Wiberg Bond Indices for the E-E bonds of **5a**, **5b**, **6a**, **6b**, **7**, **8**, **9a**, **9b**.

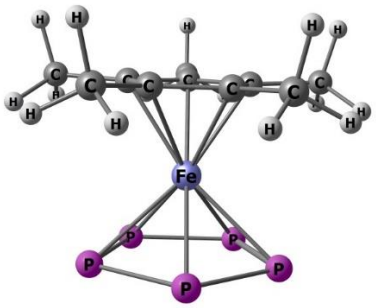
	E1-E2	E2-E3	E3-E4	E4-E5	E5-E1
5a	1.0380	1.0600	1.1097	1.1097	1.1236
5b	1.0279	1.0960	1.2234	1.2234	1.0960

	E3-E3'	E1-E2	E2-E3	E1-E2'	E2'-E3'
6a	1.0084	1.1614	1.1501	1.1635	1.1484
6b	0.9995	1.1430	1.1183	1.1428	1.1200

	E1-E2	E2-E3	E3-E4	E4-E1
7	0.9415	1.1256	1.1814	1.1168
8	0.9353	1.0841	1.0974	1.1106

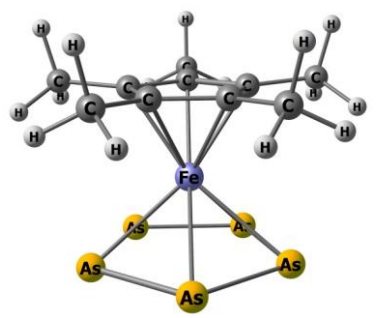
	E1-E2	E2-E3	E3-E1
9a	0.9163	1.1276	1.1212
9b	0.8444	1.1021	1.1083

Table S3.10. Optimized geometries of **1a**. XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.



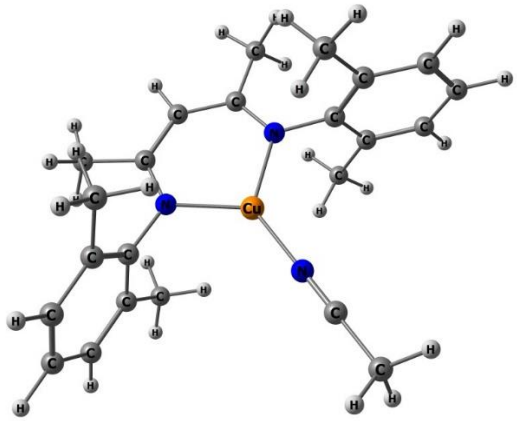
Fe	0.732426000	4.051805000	4.094817000	H	1.584077000	5.104255000	0.183258000
P	0.168422000	3.422946000	6.322538000	H	2.774978000	4.444900000	1.305178000
P	1.763504000	2.357178000	5.414240000	H	2.101729000	6.047976000	1.581205000
P	3.062413000	3.768861000	4.506488000	H	0.415811000	7.161628000	2.564155000
P	2.269464000	5.706945000	4.851992000	H	-1.075193000	6.971588000	3.480501000
P	0.481507000	5.493158000	5.975500000	H	-1.109470000	6.896411000	1.718470000
C	0.758496000	4.439021000	2.032102000	H	-2.428937000	5.468889000	4.446431000
C	-0.317153000	5.148444000	2.645654000	H	-2.683139000	3.749060000	4.721727000
C	-1.185265000	4.192897000	3.254285000	H	-3.293714000	4.504385000	3.248878000
C	-0.645625000	2.893120000	3.017365000	H	-1.932905000	1.234931000	2.648982000
C	0.555577000	3.045276000	2.261753000	H	-1.842792000	1.709940000	4.345366000
C	1.866723000	5.041816000	1.237874000	H	-0.505652000	0.836231000	3.605896000
C	-0.529857000	6.623512000	2.604750000	H	1.382735000	1.072987000	2.406755000
C	-2.462968000	4.495326000	3.960042000	H	2.453337000	2.252419000	1.657034000
C	-1.261587000	1.600088000	3.431242000	H	1.071022000	1.623765000	0.759808000
C	1.414334000	1.939939000	1.748812000				

Table S3.11. Optimized geometries of **1b**. XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.



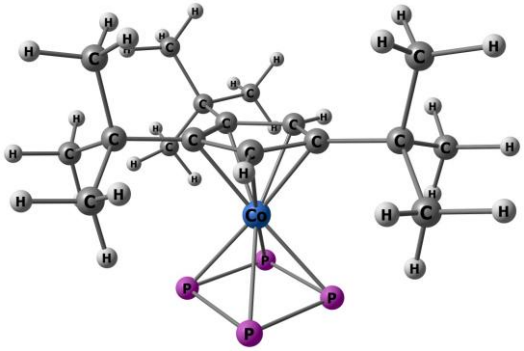
As	-1.152088000	9.144846000	4.006648000	As	1.911730000	10.710380000	2.417026000
As	-1.878328000	10.723736000	2.436237000	As	0.015113000	11.691484000	1.454263000
C	-1.157390000	7.698339000	0.807758000	Fe	0.007392000	9.170009000	1.748376000
C	-0.717238000	8.656150000	-0.153818000	C	-0.002573000	7.100910000	1.395435000
C	-2.573758000	7.323614000	1.085084000	C	1.151323000	7.689555000	0.796900000
C	-1.593336000	9.457365000	-1.056220000	C	0.709553000	8.650584000	-0.160744000
H	-0.007146000	5.026347000	1.883265000	C	-0.001589000	5.993582000	2.394029000
H	-0.878146000	6.036396000	3.038591000	C	2.567091000	7.303811000	1.061944000
H	0.881285000	6.030389000	3.030336000	C	1.582895000	9.444927000	-1.071535000
H	-2.886714000	6.515682000	0.417432000	H	2.866278000	6.489944000	0.395166000
H	-3.247207000	8.165134000	0.930047000	H	3.246412000	8.138591000	0.896322000
H	-2.702512000	6.979219000	2.110014000	H	2.702915000	6.962902000	2.087237000
H	-1.132100000	10.407762000	-1.320509000	H	1.127124000	10.399649000	-1.329457000
H	-2.555018000	9.671793000	-0.592502000	H	2.551089000	9.649928000	-0.617454000
H	-1.782457000	8.907039000	-1.982421000	H	1.757324000	8.894161000	-2.000350000
As	1.190176000	9.136471000	3.994600000				

Table S3.12. Optimized geometries of **2**. XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.



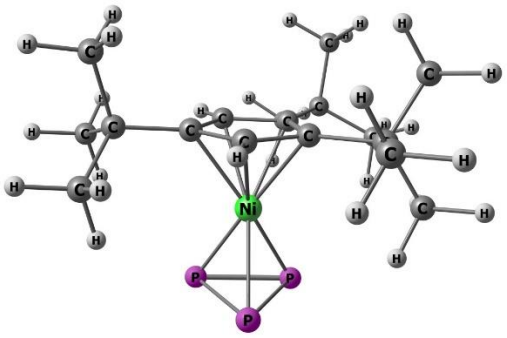
Cu	-0.000009000	0.474389000	-0.000073000	H	-5.171612000	0.820162000	2.141132000
N	1.480987000	-0.821835000	-0.000278000	C	-5.323409000	0.873144000	0.000728000
N	-1.481003000	-0.821824000	-0.000255000	H	-6.308617000	1.321871000	0.000983000
N	0.000030000	2.356480000	-0.000071000	C	-4.684848000	0.588789000	-1.200091000
C	2.465119000	-3.057923000	-0.000845000	H	-5.172154000	0.821409000	-2.139738000
H	3.092480000	-2.881453000	-0.876297000	C	-3.418108000	0.009510000	-1.219910000
H	2.151615000	-4.099035000	-0.001253000	C	0.000059000	3.505755000	0.000546000
H	3.092283000	-2.882087000	0.874875000	C	0.000090000	4.953534000	0.000509000
C	1.272739000	-2.126834000	-0.000646000	H	0.001302000	5.319563000	-1.026347000
C	-0.000016000	-2.726415000	-0.000859000	H	0.888267000	5.325509000	0.511592000
H	-0.000020000	-3.806070000	-0.001165000	H	-0.889253000	5.325563000	0.509520000
C	-1.272766000	-2.126826000	-0.000618000	C	2.713375000	-0.268387000	-2.517411000
C	-2.465155000	-3.057903000	-0.000839000	H	3.310164000	0.070857000	-3.363745000
H	-3.092393000	-2.881993000	0.874812000	H	2.508035000	-1.333005000	-2.649818000
H	-2.151661000	-4.099018000	-0.001145000	H	1.744364000	0.236331000	-2.547301000
H	-3.092439000	-2.881493000	-0.876361000	C	2.712850000	-0.270183000	2.517504000
C	2.791005000	-0.294536000	0.000044000	H	2.507545000	-1.334903000	2.649144000
C	3.417821000	0.008683000	1.220368000	H	3.309435000	0.068510000	3.364204000
C	4.684563000	0.587979000	1.201213000	H	1.743802000	0.234457000	2.547534000
H	5.171655000	0.819987000	2.141125000	C	-2.713443000	-0.268527000	-2.517389000
C	5.323408000	0.873097000	0.000721000	H	-1.744442000	0.236207000	-2.547351000
H	6.308621000	1.321815000	0.000982000	H	-2.508086000	-1.333152000	-2.649711000
C	4.684819000	0.588820000	-1.200102000	H	-3.310263000	0.070634000	-3.363734000
H	5.172107000	0.821495000	-2.139745000	C	-2.712805000	-0.269999000	2.517526000
C	3.418074000	0.009553000	-1.219929000	H	-2.507474000	-1.334708000	2.649217000
C	-2.791017000	-0.294513000	0.000068000	H	-1.743767000	0.234662000	2.547511000
C	-3.417807000	0.008782000	1.220388000	H	-3.309380000	0.068726000	3.364218000
C	-4.684542000	0.588091000	1.201224000				

Table S3.13. Optimized geometries of **3**. XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.



Co	-0.408168000	-0.538548000	-0.006352000	H	-1.830569000	3.780240000	-1.019023000
P	-2.337378000	-1.800349000	0.373220000	H	-2.866631000	1.660819000	-2.025729000
P	-0.515159000	-2.411411000	1.364220000	H	-4.308546000	1.998926000	-1.070805000
P	0.458583000	-2.616150000	-0.563909000	H	-3.524589000	0.420281000	-0.953829000
P	-1.365611000	-1.980855000	-1.552650000	H	-3.315380000	0.673196000	1.595764000
C	-1.101612000	1.425694000	0.083090000	H	-4.197913000	2.193414000	1.409184000
C	-0.283569000	1.113922000	1.197778000	H	-2.661426000	2.174353000	2.269712000
C	1.033189000	0.739625000	0.774553000	H	1.205984000	1.649677000	3.418163000
C	1.028261000	0.805613000	-0.680732000	H	2.388615000	0.453640000	3.941663000
C	-0.290189000	1.219185000	-1.058320000	H	0.790053000	-0.075578000	3.425336000
C	-2.490899000	2.020083000	0.098715000	H	2.041630000	-1.652962000	2.068765000
C	-2.310612000	3.544403000	-0.067908000	H	3.624138000	-0.953965000	2.410182000
C	-3.343569000	1.489434000	-1.060441000	H	3.098375000	-1.186949000	0.745907000
C	-3.203836000	1.744158000	1.426576000	H	3.756257000	1.496310000	0.689519000
C	2.142547000	0.494511000	1.802036000	H	3.951722000	1.502161000	2.437385000
C	1.585083000	0.644578000	3.229595000	H	2.773680000	2.576464000	1.675369000
C	2.765783000	-0.909093000	1.736643000	H	3.079863000	2.559768000	-1.072831000
C	3.221190000	1.582000000	1.630552000	H	1.811174000	2.826232000	-2.268773000
C	2.105387000	0.720238000	-1.766013000	H	3.374778000	2.169084000	-2.770360000
C	2.624371000	2.159883000	-1.977602000	H	3.951067000	-0.198253000	-2.351826000
C	3.289605000	-0.207269000	-1.484116000	H	2.953229000	-1.231731000	-1.330312000
C	1.493289000	0.234508000	-3.095075000	H	3.881020000	0.100563000	-0.628319000
H	-0.613701000	1.135784000	2.218566000	H	2.280255000	0.180624000	-3.848039000
H	-0.621335000	1.351208000	-2.070833000	H	0.726619000	0.904719000	-3.478844000
H	-1.696149000	3.954248000	0.735441000	H	1.058223000	-0.758702000	-2.986451000
H	-3.282951000	4.039851000	-0.042681000				

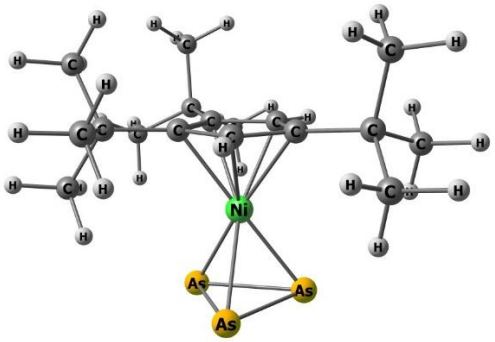
Table S3.14. Optimized geometries of **4a**. XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.



Ni	5.138888000	2.361795000	1.835133000	H	5.114653000	0.836688000	6.300875000
P	5.612827000	3.008615000	-0.265542000	H	3.601071000	2.438279000	4.216915000
P	6.544410000	4.058153000	1.374032000	H	1.375680000	2.262996000	3.691401000
P	4.437662000	4.321360000	0.976980000	H	0.327459000	2.205067000	2.277070000
C	5.541156000	1.471951000	3.709032000	H	1.798400000	3.185741000	2.242925000
C	6.311543000	2.018529000	4.913146000	H	2.537573000	0.183645000	0.076553000
C	5.688000000	3.349453000	5.379920000	H	2.448024000	1.946805000	0.091917000
C	7.795386000	2.314473000	4.670595000	H	0.971016000	0.978595000	0.221433000
C	6.167234000	1.001098000	6.065116000	H	0.461034000	-0.315848000	2.331557000
C	4.146861000	1.771285000	3.576948000	H	1.586337000	-0.274006000	3.696765000
C	3.586211000	1.077864000	2.473043000	H	2.027066000	-1.130424000	2.214619000
C	2.136312000	1.044383000	2.046071000	H	4.551508000	-0.307489000	1.047772000

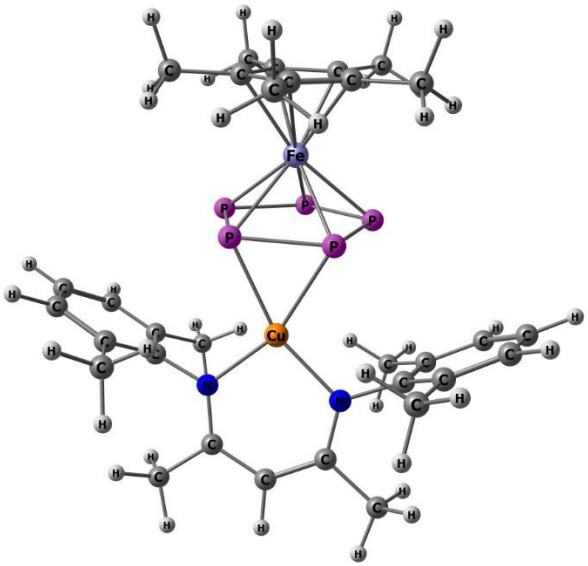
C	1.368661000	2.249311000	2.600545000	C	7.141066000	-0.221691000	2.261477000
C	2.020521000	1.037494000	0.515642000	C	8.244608000	0.704927000	1.721705000
C	1.515451000	-0.250466000	2.607891000	H	8.505835000	1.498161000	2.411694000
C	4.646609000	0.324118000	1.910827000	H	9.145068000	0.122391000	1.514168000
C	5.863384000	0.537421000	2.635675000	H	7.917633000	1.169367000	0.791019000
H	4.671351000	3.227444000	5.750338000	C	6.845713000	-1.234019000	1.138917000
H	5.676841000	4.080592000	4.570615000	H	7.763178000	-1.772727000	0.899151000
H	6.283037000	3.754356000	6.199310000	H	6.095950000	-1.966998000	1.439731000
H	8.376306000	1.430942000	4.429977000	H	6.506860000	-0.739713000	0.228012000
H	8.221821000	2.743650000	5.578717000	C	7.650059000	-1.041091000	3.460919000
H	7.918885000	3.039746000	3.866139000	H	6.863858000	-1.698438000	3.836657000
H	6.662483000	1.380303000	6.961572000	H	8.491286000	-1.663412000	3.149708000
H	6.609868000	0.039085000	5.813781000	H	7.988229000	-0.419585000	4.283767000

Table S3.15. Optimized geometries of **4b**. XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.



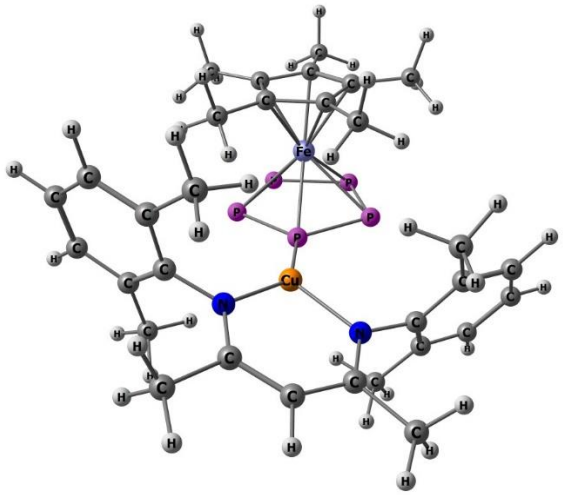
As	2.391359000	5.917088000	11.022536000	C	3.351766000	9.844652000	12.087043000
As	4.458449000	5.347027000	12.104730000	C	-0.581104000	7.001363000	14.460091000
As	2.382963000	4.470994000	12.942075000	H	-0.852535000	7.944475000	13.988659000
Ni	2.899751000	6.769463000	13.171071000	H	-1.470560000	6.626513000	14.968105000
C	1.739179000	8.444804000	13.622782000	H	-0.308464000	6.290253000	13.679439000
H	0.819788000	8.697040000	13.129410000	C	3.512737000	7.443916000	17.619368000
C	1.839547000	7.618450000	14.788364000	H	2.494190000	7.134288000	17.830805000
C	3.023540000	8.875702000	13.200061000	H	3.543536000	8.534912000	17.631367000
C	0.557644000	7.159015000	15.487477000	H	4.144218000	7.078473000	18.431384000
C	3.260204000	7.537604000	15.113000000	C	5.520962000	7.296176000	16.195768000
C	3.942317000	8.316592000	14.123567000	H	6.049964000	6.847358000	17.037315000
H	5.006494000	8.449542000	14.077624000	H	5.660522000	8.376624000	16.251320000
C	4.033446000	6.903653000	16.275053000	H	5.985753000	6.929577000	15.279825000
C	0.145984000	8.266088000	16.482021000	C	2.211988000	9.927018000	11.066058000
H	0.898251000	8.416600000	17.254264000	H	2.028942000	8.956595000	10.603175000
H	-0.794058000	7.999267000	16.969540000	H	2.471515000	10.637213000	10.279127000
H	0.003580000	9.214627000	15.961969000	H	1.283579000	10.268077000	11.526260000
C	0.648546000	5.818593000	16.222764000	C	3.551615000	11.233401000	12.728216000
H	0.933236000	5.019979000	15.537093000	H	2.647956000	11.554001000	13.249713000
H	-0.331967000	5.574671000	16.635131000	H	3.785683000	11.974586000	11.961198000
H	1.350657000	5.830566000	17.049022000	H	4.371210000	11.215302000	13.448396000
C	4.001279000	5.365720000	16.253588000	C	4.641891000	9.432011000	11.365773000
H	4.538586000	4.976444000	17.121379000	H	5.486552000	9.374095000	12.053004000
H	4.494260000	4.996446000	15.354184000	H	4.888532000	10.165092000	10.595473000
H	2.997189000	4.959777000	16.269103000	H	4.524627000	8.457473000	10.890915000

Table S3.16. Optimized geometries of **5a**. XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.



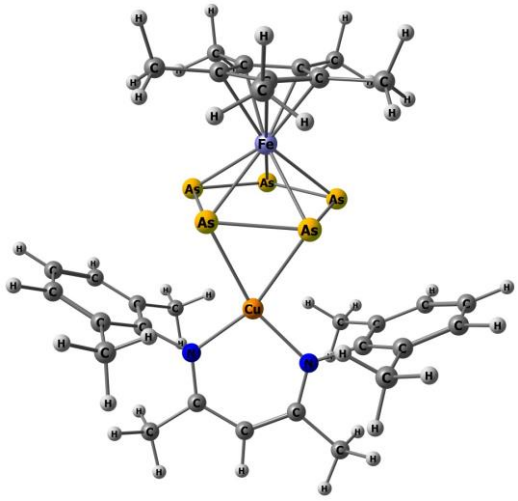
P	0.551508000	1.106224000	0.841219000	P	1.551579000	0.000086000	-2.257530000
P	1.246035000	1.738069000	-1.076687000	P	1.246398000	-1.737891000	-1.076587000
N	-2.726019000	-1.472454000	0.163947000	N	-2.726387000	1.471830000	0.163942000
C	4.411762000	0.713351000	-0.405645000	C	4.411903000	-0.712501000	-0.405579000
C	-1.867480000	-3.223691000	-1.284719000	C	-1.868417000	3.223363000	-1.284716000
C	-1.889059000	-3.546822000	1.134678000	C	-1.890086000	3.546463000	1.134687000
C	-2.192680000	-2.774204000	0.004271000	C	-2.193416000	2.773733000	0.004276000
C	-1.253916000	-4.466034000	-1.426056000	C	-1.255345000	4.465949000	-1.426049000
H	-0.994790000	-4.815679000	-2.418105000	H	-0.996371000	4.815705000	-2.418099000
C	-2.146850000	-2.356391000	-2.478797000	C	-2.147472000	2.355973000	-2.478803000
H	-3.214292000	-2.159948000	-2.600173000	H	-3.214838000	2.159105000	-2.600153000
H	-1.779164000	-2.824758000	-3.390945000	H	-1.779999000	2.824508000	-3.390951000
H	-1.661643000	-1.383800000	-2.370855000	H	-1.661870000	1.383575000	-2.370896000
C	-1.269871000	-4.782378000	0.954378000	C	-1.271388000	4.782265000	0.954390000
H	-1.030641000	-5.382688000	1.823970000	H	-1.032391000	5.382666000	1.823983000
C	-4.031037000	-1.267153000	0.105091000	C	-4.635806000	-0.000554000	0.131584000
C	3.957127000	1.155515000	0.874341000	H	-5.714532000	-0.000688000	0.101170000
C	-0.954497000	-5.245147000	-0.316259000	C	-4.031352000	1.266196000	0.105095000
H	-0.470014000	-6.205132000	-0.440670000	C	3.957354000	-1.154637000	0.874447000
C	-2.215213000	-3.037510000	2.509128000	C	-0.956210000	5.245167000	-0.316248000
H	-1.726642000	-2.078335000	2.695306000	H	-0.472100000	6.205339000	-0.440658000
H	-1.889310000	-3.744354000	3.271433000	C	-2.216060000	3.037027000	2.509133000
H	-3.287101000	-2.869450000	2.634300000	H	-1.727103000	2.078050000	2.695324000
C	-4.951352000	-2.459537000	-0.019800000	H	-1.890457000	3.744005000	3.271442000
H	-4.782078000	-2.977477000	-0.965659000	H	-3.287882000	2.868532000	2.634284000
H	-5.993863000	-2.154576000	0.025125000	C	3.677299000	0.000447000	1.663680000
H	-4.760319000	-3.183252000	0.773518000	C	-4.951963000	2.458356000	-0.019747000
C	4.863406000	1.587942000	-1.525315000	H	-4.782838000	2.976360000	-0.965597000
H	5.935206000	1.788249000	-1.440014000	H	-5.994398000	2.153139000	0.025195000
H	4.342613000	2.544098000	-1.519242000	H	-4.761088000	3.182098000	0.773585000
H	4.687772000	1.118667000	-2.492094000	C	4.863726000	-1.587109000	-1.525163000
C	3.855823000	2.572166000	1.329074000	H	5.935559000	-1.787220000	-1.439818000
H	3.631316000	3.241449000	0.500209000	H	4.343101000	-2.543356000	-1.519018000
H	4.800376000	2.895300000	1.775760000	H	4.688034000	-1.117952000	-2.491988000
H	3.074355000	2.695352000	2.077439000	C	3.856323000	-2.571268000	1.329306000
H	2.621085000	0.880287000	3.308538000	H	3.631942000	-3.240666000	0.500500000
H	2.621266000	-0.879452000	3.308623000	H	4.800937000	-2.894181000	1.776019000
Cu	-1.446729000	-0.000158000	0.378620000	H	3.074878000	-2.694535000	2.077681000
Fe	2.470196000	0.000249000	-0.055156000	C	3.221755000	0.000468000	3.083341000
P	0.551744000	-1.106073000	0.841280000	H	4.083161000	0.000590000	3.756948000

Table S3.17. Optimized geometries of **I-5a**. XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.



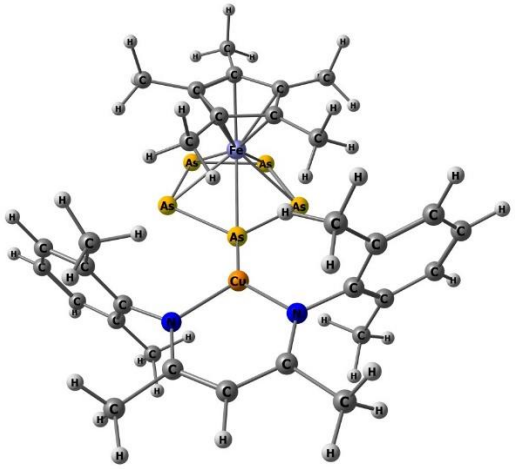
P	-3.584222000	-0.403316000	-2.231632000	N	2.659792000	1.660990000	-0.002414000
P	-1.660701000	-1.250306000	-1.967489000	C	-2.063144000	-0.222399000	1.943402000
N	2.910836000	-1.298636000	-0.066066000	C	-3.345992000	0.390492000	1.812086000
C	-2.144618000	-1.539830000	1.400113000	C	1.999423000	2.988192000	-2.446341000
C	-3.477809000	-1.740735000	0.931410000	H	3.078222000	2.845540000	-2.533784000
C	2.323937000	-2.585249000	-2.549238000	H	1.671042000	3.640190000	-3.255074000
H	3.346400000	-2.233360000	-2.700079000	H	1.545591000	2.004169000	-2.593182000
H	2.056689000	-3.237559000	-3.379980000	C	1.989366000	2.901628000	0.072494000
H	1.684215000	-1.699331000	-2.587524000	C	1.617550000	3.560392000	-1.111606000
C	2.498569000	-2.650948000	-0.036548000	C	-4.220020000	-0.547815000	1.185170000
C	2.169205000	-3.299761000	-1.237822000	C	3.971977000	1.566570000	0.099543000
C	4.191569000	-0.971217000	0.024327000	C	4.675877000	0.347099000	0.085298000
C	-1.037960000	-2.535191000	1.370997000	H	5.750000000	0.437732000	0.142230000
H	-0.998131000	-3.089765000	2.312242000	C	-0.863760000	0.385384000	2.585611000
H	-1.159227000	-3.254898000	0.564120000	H	-0.855456000	0.168625000	3.657303000
H	-0.073596000	-2.054237000	1.231265000	H	-0.848092000	1.466317000	2.461687000
C	2.320368000	-3.297360000	1.197960000	H	0.057414000	-0.009790000	2.159898000
C	5.224957000	-2.075272000	0.043564000	C	1.599508000	3.407109000	1.324175000
H	5.116972000	-2.712122000	-0.836523000	C	4.791292000	2.830758000	0.223953000
H	6.232966000	-1.668177000	0.059664000	H	4.578959000	3.506761000	-0.606068000
H	5.096926000	-2.719859000	0.914096000	H	5.856123000	2.610941000	0.233961000
C	1.679464000	-4.602352000	-1.185527000	H	4.539626000	3.367940000	1.139946000
H	1.422415000	-5.105072000	-2.110331000	C	0.874269000	4.734966000	-1.023329000
C	1.835560000	-4.603051000	1.209869000	H	0.586767000	5.244608000	-1.935177000
H	1.692046000	-5.102302000	2.160763000	C	0.850304000	4.580789000	1.371159000
C	2.596662000	-2.568793000	2.483080000	H	0.544111000	4.970589000	2.334871000
H	2.037373000	-1.631221000	2.526159000	C	1.986202000	2.691699000	2.588007000
H	2.315751000	-3.179220000	3.340633000	H	1.815326000	1.618701000	2.501922000
H	3.649843000	-2.300881000	2.588954000	H	1.418849000	3.071911000	3.437093000
C	1.516377000	-5.258332000	0.028189000	H	3.048364000	2.818161000	2.813813000
H	1.134512000	-6.270966000	0.052618000	C	0.490202000	5.248493000	0.208202000
C	-4.016152000	-2.997928000	0.337769000	H	-0.095706000	6.157130000	0.260930000
H	-3.236472000	-3.563421000	-0.169673000	C	-3.716649000	1.750429000	2.296598000
H	-4.434218000	-3.634757000	1.122391000	H	-2.866430000	2.429618000	2.259766000
H	-4.806518000	-2.794115000	-0.382760000	H	-4.061602000	1.700276000	3.333123000
Fe	-2.598027000	-0.127175000	-0.076670000	H	-4.517043000	2.183220000	1.698583000
Cu	1.540199000	0.069577000	-0.306159000	C	-5.668994000	-0.344109000	0.899714000
P	-3.570063000	1.570964000	-1.432571000	H	-5.981402000	-0.895342000	0.014064000
P	-0.493484000	0.247063000	-1.029694000	H	-5.899344000	0.707376000	0.738436000
P	-1.636062000	1.995023000	-0.682266000	H	-6.271966000	-0.694401000	1.742136000

Table S3.18. Optimized geometries of **5b**. XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.



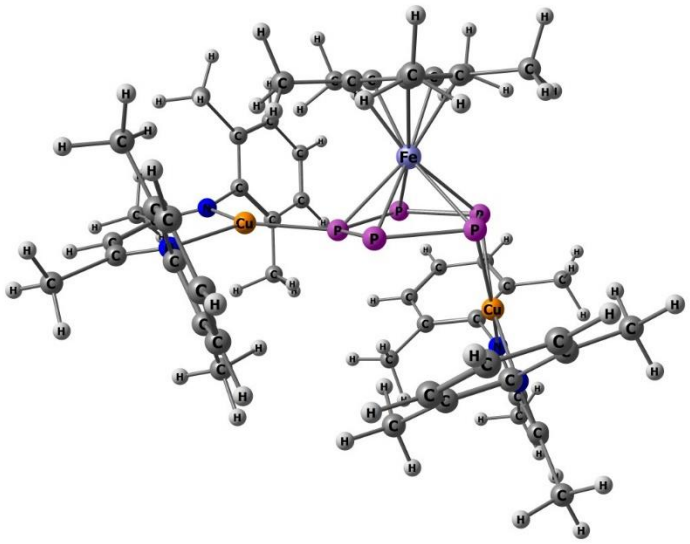
As	0.285051000	1.211421000	1.084103000	As	1.573164000	0.000048000	-2.268117000
As	1.167556000	1.915981000	-0.985459000	As	1.167638000	-1.915912000	-0.985474000
N	-3.006696000	-1.476009000	0.110313000	N	-3.006783000	1.475848000	0.110305000
C	4.286463000	0.712678000	-0.084002000	C	4.286501000	-0.712456000	-0.084026000
C	-2.062155000	-3.256027000	-1.247664000	C	-2.062320000	3.255906000	-1.247672000
C	-2.266883000	-3.544113000	1.167521000	C	-2.267179000	3.544036000	1.167497000
C	-2.476136000	-2.784172000	0.007255000	C	-2.476309000	2.784045000	0.007242000
C	-1.448546000	-4.504168000	-1.325300000	C	-1.448799000	4.504091000	-1.325310000
H	-1.119045000	-4.869908000	-2.290254000	H	-1.119290000	4.869836000	-2.290259000
C	-2.247115000	-2.404644000	-2.470934000	C	-2.247183000	2.404490000	-2.470935000
H	-3.301224000	-2.199939000	-2.670117000	H	-3.301270000	2.199704000	-2.670146000
H	-1.821355000	-2.890528000	-3.348075000	H	-1.821431000	2.890391000	-3.348071000
H	-1.759009000	-1.436041000	-2.342409000	H	-1.759010000	1.435924000	-2.342380000
C	-1.644747000	-4.786010000	1.051394000	C	-1.645131000	4.785978000	1.051368000
H	-1.476257000	-5.375527000	1.944628000	H	-1.476741000	5.375536000	1.944593000
C	-4.302814000	-1.267162000	-0.048684000	C	-4.905768000	-0.000136000	-0.074379000
C	3.763138000	1.154755000	1.169242000	H	-5.979099000	-0.000168000	-0.185865000
C	-1.237657000	-5.268627000	-0.185157000	C	-4.302887000	1.266924000	-0.048694000
H	-0.751750000	-6.233060000	-0.259373000	C	3.763202000	-1.154603000	1.169204000
C	-2.695953000	-3.014915000	2.505893000	C	-1.238015000	5.268591000	-0.185175000
H	-2.234038000	-2.045983000	2.709042000	H	-0.752184000	6.233062000	-0.259394000
H	-2.418190000	-3.704382000	3.302398000	C	-2.696321000	3.014864000	2.505857000
H	-3.775991000	-2.858217000	2.550323000	H	-2.234362000	2.045969000	2.709080000
C	-5.217204000	-2.456714000	-0.234841000	H	-2.418662000	3.704380000	3.302357000
H	-4.982470000	-2.980817000	-1.163136000	H	-3.776353000	2.858101000	2.550210000
H	-6.258594000	-2.146327000	-0.268438000	C	3.442628000	0.000054000	1.942944000
H	-5.090055000	-3.177412000	0.573947000	C	-5.217344000	2.456427000	-0.234834000
C	4.820374000	1.585981000	-1.168243000	H	-4.982646000	2.980549000	-1.163127000
H	5.888133000	1.767819000	-1.014841000	H	-6.258717000	2.145984000	-0.268422000
H	4.315954000	2.550667000	-1.188917000	H	-5.090224000	3.177125000	0.573960000
H	4.697266000	1.125800000	-2.147662000	C	4.820455000	-1.585694000	-1.168297000
C	3.660972000	2.570565000	1.627640000	H	5.888220000	-1.767495000	-1.014896000
H	3.483008000	3.248530000	0.794403000	H	4.316073000	-2.550400000	-1.189012000
H	4.589404000	2.877028000	2.118215000	H	4.697334000	-1.125480000	-2.147699000
H	2.848986000	2.702034000	2.341474000	C	3.661115000	-2.570433000	1.627556000
H	2.328265000	0.879415000	3.551771000	H	3.483190000	-3.248382000	0.794298000
H	2.328300000	-0.879417000	3.551734000	H	4.589564000	-2.876859000	2.118122000
Cu	-1.737140000	-0.000044000	0.410435000	H	2.849136000	-2.701970000	2.341386000
Fe	2.328886000	0.000054000	0.161139000	C	2.936599000	0.000015000	3.345758000
As	0.285110000	-1.211408000	1.084097000	H	3.774534000	0.000017000	4.048737000

Table S3.19. Optimized geometries of **I-5b**. XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.



As	3.649509000	1.309428000	-0.772837000	Fe	2.149689000	-0.308586000	0.472443000
As	1.441293000	1.989691000	-0.416947000	Cu	-2.071745000	0.105096000	-0.285901000
C	2.530924000	0.326569000	2.434173000	C	2.703288000	-1.873199000	1.755282000
N	-3.106544000	1.767115000	-0.095590000	N	-3.517365000	-1.191528000	-0.135472000
C	1.212422000	-0.212091000	2.342111000	C	1.318572000	-1.572038000	1.923768000
C	2.885783000	1.692870000	2.913907000	C	3.452591000	-0.700627000	2.071622000
H	3.800948000	2.056157000	2.448497000	C	3.270582000	-3.204011000	1.394211000
H	3.042663000	1.680657000	3.996303000	H	4.223950000	-3.104619000	0.877686000
H	2.094501000	2.409475000	2.699337000	H	3.437295000	-3.799050000	2.296646000
C	-2.132447000	3.013621000	-2.474191000	H	2.596459000	-3.762766000	0.746587000
H	-1.711632000	2.008966000	-2.570504000	C	-2.747446000	-2.594253000	-2.504577000
H	-1.701640000	3.640293000	-3.254347000	H	-2.053630000	-1.748957000	-2.505186000
H	-3.204003000	2.917063000	-2.658147000	H	-2.439607000	-3.290912000	-3.283687000
C	-0.049162000	0.496687000	2.694670000	H	-3.726141000	-2.188797000	-2.768377000
H	-0.894760000	0.096763000	2.136176000	C	0.181984000	-2.521127000	1.767235000
H	0.011749000	1.561035000	2.477016000	H	-0.710110000	-2.019990000	1.400600000
H	-0.267868000	0.380657000	3.759807000	H	0.413303000	-3.322710000	1.068672000
C	-1.848987000	3.583674000	-1.114662000	H	-0.067285000	-2.977382000	2.729063000
C	-4.426058000	1.738219000	-0.105828000	C	-2.767015000	-3.267536000	-1.162854000
H	5.400012000	-1.239310000	1.352844000	C	-5.189783000	0.555979000	-0.166915000
H	5.269864000	0.425787000	1.909409000	H	-6.258256000	0.705284000	-0.203979000
C	-2.379511000	2.970208000	0.033625000	C	-4.779111000	-0.789477000	-0.161300000
C	-1.042574000	4.709079000	-0.965324000	C	4.939436000	-0.594062000	2.099487000
H	-0.631068000	5.181786000	-1.849092000	H	5.319432000	-0.892551000	3.080767000
C	-2.093770000	3.479977000	1.311815000	C	-3.183131000	-2.559778000	-0.022990000
C	-5.187942000	3.043754000	-0.068892000	C	-2.355449000	-4.590319000	-1.019989000
H	-4.986631000	3.585919000	0.856405000	H	-2.034641000	-5.138934000	-1.897611000
H	-6.259669000	2.876398000	-0.144394000	C	-3.163618000	-3.168629000	1.243142000
H	-4.874997000	3.692925000	-0.888781000	C	-5.872814000	-1.832966000	-0.212827000
C	-1.274447000	4.601878000	1.420497000	H	-5.865898000	-2.457831000	0.681169000
H	-1.044919000	4.991014000	2.405570000	H	-6.852422000	-1.370028000	-0.302809000
C	-2.667177000	2.829028000	2.539214000	H	-5.719726000	-2.500103000	-1.063320000
H	-3.719194000	3.092961000	2.678256000	C	-2.752004000	-4.495412000	1.345353000
H	-2.128119000	3.143206000	3.432623000	H	-2.729819000	-4.965442000	2.321434000
H	-2.627301000	1.743008000	2.465693000	C	-3.528433000	-2.382149000	2.470826000
C	-0.750602000	5.219330000	0.292839000	H	-4.582978000	-2.098265000	2.482876000
H	-0.112229000	6.087622000	0.393701000	H	-3.326026000	-2.959532000	3.372358000
As	3.657331000	-0.935202000	-1.474088000	H	-2.960294000	-1.450559000	2.518646000
As	1.450070000	-1.704450000	-1.536759000	C	-2.350821000	-5.208817000	0.223968000
As	0.127390000	0.129271000	-0.941090000	H	-2.027485000	-6.237499000	0.319533000

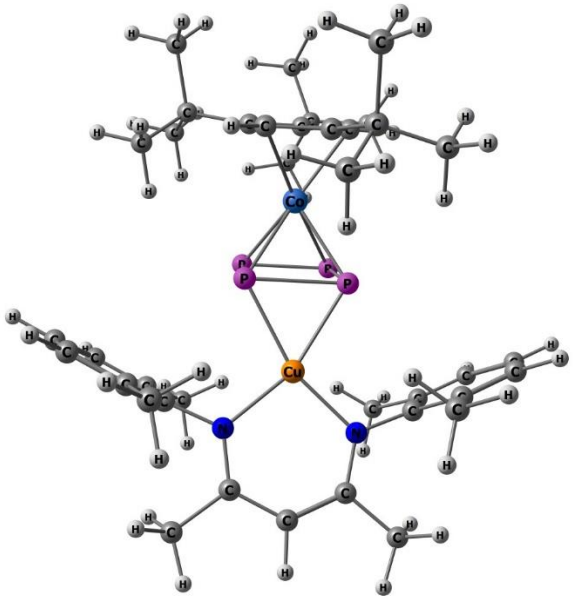
Table S3.20. Optimized geometries of **6a**. XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.



P	-1.866521000	-1.476266000	1.491701000	N	3.483083000	2.075015000	-1.461442000
P	0.049604000	-1.865690000	0.654411000	C	1.521469000	0.765549000	3.271395000
N	-4.342153000	0.788659000	-1.029279000	C	-1.528474000	-3.181075000	-2.060551000
N	4.322700000	-0.749669000	-1.156710000	C	-2.991012000	-4.186008000	-0.384078000
C	1.573879000	-0.655589000	3.372937000	C	-2.707319000	-3.161637000	-1.299018000
C	-3.297673000	2.966205000	-1.294587000	C	-0.653740000	-4.254683000	-1.912130000
C	-4.890820000	2.592762000	0.516298000	H	0.257801000	-4.273652000	-2.493611000
C	-4.207312000	2.137952000	-0.620596000	C	-1.204298000	-2.040398000	-2.982360000
C	-3.094172000	4.260712000	-0.823217000	H	-1.998974000	-1.859485000	-3.707985000
H	-2.388237000	4.903334000	-1.333585000	H	-0.280134000	-2.231424000	-3.525280000
C	-2.537867000	2.443349000	-2.479328000	H	-1.082089000	-1.112904000	-2.416347000
H	-3.203538000	2.094107000	-3.270708000	C	-2.083714000	-5.236380000	-0.253067000
H	-1.891024000	3.213914000	-2.892535000	H	-2.294103000	-6.027531000	0.456596000
H	-1.915850000	1.590474000	-2.197938000	C	-5.323211000	-0.842303000	-2.508338000
C	-4.661207000	3.893956000	0.959515000	H	-6.093508000	-0.965349000	-3.253929000
H	-5.184513000	4.250433000	1.838625000	C	-4.520393000	-1.970832000	-2.279659000
C	-5.210419000	0.447819000	-1.965974000	C	0.282192000	1.204323000	3.830402000
C	0.365301000	-1.098924000	3.990717000	C	-0.923226000	-5.277778000	-1.013597000
C	-3.770292000	4.727288000	0.296633000	H	-0.225457000	-6.097184000	-0.898406000
H	-3.596741000	5.733714000	0.655447000	C	1.230300000	2.545707000	-3.142018000
C	2.726881000	-2.635818000	-2.565269000	H	2.077234000	2.414999000	-3.817231000
H	3.370564000	-2.131367000	-3.286726000	H	0.386978000	2.927961000	-3.714548000
H	2.294208000	-3.512937000	-3.043798000	H	0.970006000	1.548720000	-2.775463000
H	1.916963000	-1.939776000	-2.330427000	C	-4.247183000	-4.140882000	0.437989000
C	-5.829518000	1.678457000	1.248806000	H	-4.325944000	-3.196207000	0.979210000
H	-5.302970000	0.791568000	1.610624000	H	-4.266753000	-4.957469000	1.158903000
H	-6.277138000	2.185467000	2.102871000	H	-5.140193000	-4.217503000	-0.187036000
H	-6.632983000	1.319071000	0.602616000	C	2.707616000	3.230394000	-1.219149000
C	4.292073000	-2.078102000	-0.675372000	C	1.563386000	3.464261000	-2.001474000
C	3.476110000	-3.020684000	-1.322826000	C	-0.430562000	0.051338000	4.274884000
C	5.307543000	-0.317938000	-1.927613000	C	4.592468000	2.113787000	-2.176556000
C	-6.138000000	1.504387000	-2.520955000	C	5.423288000	1.000438000	-2.402996000
H	-5.571153000	2.273377000	-3.049149000	H	6.279490000	1.187259000	-3.033367000
H	-6.856015000	1.069477000	-3.211815000	C	-4.779172000	-3.178378000	-3.150891000
H	-6.679162000	2.007495000	-1.718601000	H	-3.924895000	-3.366162000	-3.804362000
C	2.712342000	-1.511015000	2.939070000	H	-5.660653000	-3.031274000	-3.770011000
H	3.507346000	-1.500093000	3.689573000	H	-4.916246000	-4.075457000	-2.546342000
H	2.407705000	-2.543520000	2.785589000	C	2.590817000	1.641260000	2.718405000
H	3.135165000	-1.156349000	2.003026000	H	3.264332000	1.974376000	3.512725000
C	4.985714000	-2.417413000	0.497703000	H	2.175605000	2.523285000	2.235424000
C	6.374931000	-1.295998000	-2.364637000	H	3.186773000	1.111692000	1.977153000
H	5.924062000	-2.135305000	-2.898085000	C	3.016968000	4.071391000	-0.137021000
H	7.102327000	-0.818480000	-3.016584000	C	5.006211000	3.417841000	-2.819988000
H	6.900187000	-1.715711000	-1.506202000	H	4.194097000	3.818776000	-3.428922000
C	3.358879000	-4.296774000	-0.779942000	H	5.883661000	3.285205000	-3.448427000
H	2.723650000	-5.023292000	-1.272189000	H	5.233976000	4.170110000	-2.063400000
C	4.846978000	-3.705930000	1.009379000	C	0.742712000	4.543409000	-1.687714000
H	5.369964000	-3.968327000	1.921487000	H	-0.134278000	4.729714000	-2.294298000
C	5.834353000	-1.397440000	1.204155000	C	2.157904000	5.128343000	0.158582000
H	5.307962000	-0.446256000	1.298541000	H	2.384939000	5.768798000	1.002845000

H	6.108588000	-1.745985000	2.199371000	C	4.256568000	3.842916000	0.681685000
H	6.757572000	-1.185148000	0.659153000	H	4.440764000	2.780621000	0.833446000
C	4.038829000	-4.643856000	0.381128000	H	4.176781000	4.330729000	1.652953000
H	3.934282000	-5.637935000	0.796716000	H	5.142305000	4.246462000	0.183394000
C	0.027454000	-2.509042000	4.338597000	C	1.026558000	5.370046000	-0.608639000
H	0.456915000	-3.209288000	3.623504000	H	0.367170000	6.193061000	-0.364902000
H	0.420378000	-2.758023000	5.328312000	C	-0.168697000	2.618772000	3.973191000
H	-1.049083000	-2.669125000	4.357183000	H	0.301844000	3.261784000	3.231530000
Cu	-3.148449000	-0.524058000	-0.194457000	H	0.089298000	3.000980000	4.964713000
Fe	-0.065704000	-0.077969000	2.206786000	H	-1.247952000	2.706146000	3.851836000
Cu	2.784786000	0.387501000	-0.722644000	C	-1.751115000	0.053873000	4.967157000
P	-2.188063000	0.727572000	1.508322000	H	-2.314023000	-0.854845000	4.759132000
P	0.771746000	0.016322000	0.004133000	H	-2.360099000	0.902562000	4.660335000
P	-0.478951000	1.622157000	0.598453000	H	-1.608129000	0.118018000	6.049475000
N	-3.554160000	-2.030344000	-1.378329000				

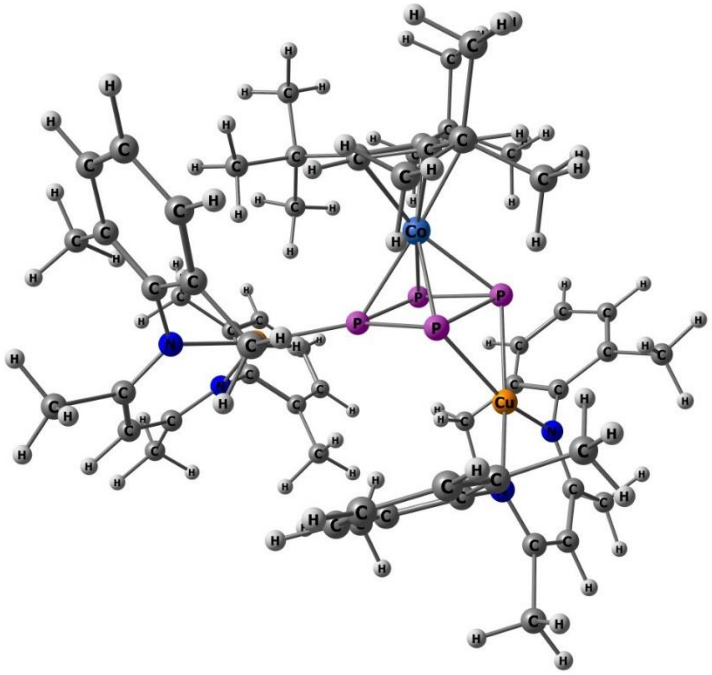
Table S3.21. Optimized geometries of **7**. XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.



Co	-1.912229000	-0.434345000	0.317656000	C	1.992952000	3.365674000	1.472090000
Cu	1.949669000	0.135693000	-0.193814000	C	3.172524000	-2.337873000	2.300452000
P	-0.165304000	1.013750000	0.052019000	H	2.525941000	-1.457564000	2.339943000
P	0.105833000	-1.243949000	-0.455919000	H	4.199171000	-1.971815000	2.367041000
P	-0.437439000	-1.693349000	1.596280000	H	2.970143000	-2.951250000	3.177627000
P	-0.672771000	0.402774000	2.081834000	C	2.512262000	-4.443282000	1.082274000
N	3.441141000	-1.128291000	-0.264255000	H	2.373397000	-4.920024000	2.045083000
N	3.015235000	1.779451000	-0.062994000	C	-2.599770000	2.581703000	-2.256706000
C	-3.557819000	-1.693936000	0.052114000	H	-2.475032000	3.003032000	-3.255591000
C	-3.153732000	-1.114336000	-1.171226000	H	-1.649076000	2.676159000	-1.734096000
H	-2.828495000	-1.670836000	-2.029775000	H	-3.343530000	3.183664000	-1.745830000
C	-3.861599000	-0.606067000	0.910602000	C	5.792265000	-1.779201000	-0.345367000
H	-4.161772000	-0.707292000	1.935842000	H	5.650676000	-2.446198000	-1.196869000
C	-3.690551000	0.644231000	0.229475000	H	5.767547000	-2.403174000	0.549937000
C	3.108246000	-2.503926000	-0.211750000	H	6.774063000	-1.318153000	-0.419626000
C	-3.224766000	0.318719000	-1.108012000	C	-4.343212000	1.036710000	-3.176093000
C	-3.766081000	-3.165865000	0.322223000	H	-5.155494000	1.501272000	-2.617880000
C	-3.821811000	-3.454772000	1.826021000	H	-4.619302000	0.000118000	-3.374463000
H	-2.893268000	-3.160539000	2.315344000	H	-4.246867000	1.554246000	-4.132532000
H	-3.972993000	-4.522955000	1.989504000	C	1.775848000	3.686180000	-0.936888000
H	-4.648019000	-2.926674000	2.304310000	C	-4.589890000	1.698703000	2.331691000
C	-2.960625000	2.990099000	1.021223000	H	-3.809753000	1.246494000	2.944726000
H	-2.443598000	3.180780000	0.091217000	H	-5.470683000	1.055703000	2.351015000
H	-2.223174000	2.647890000	1.747202000	H	-4.863110000	2.650024000	2.789623000
H	-3.368876000	3.935933000	1.383541000	C	2.255619000	-5.149595000	-0.085806000
C	2.834515000	-3.199396000	-1.398641000	H	1.922679000	-6.178509000	-0.037253000
C	2.935680000	-3.117141000	1.038535000	C	-1.915002000	0.452897000	-3.264752000
C	4.335060000	1.771257000	-0.131518000	H	-1.791984000	1.030077000	-4.181863000
C	4.702565000	-0.733408000	-0.294207000	H	-2.160612000	-0.566523000	-3.555201000

C	-2.664149000	-4.017222000	-0.321635000	H	-0.958261000	0.439524000	-2.743060000
H	-2.574805000	-3.824396000	-1.391016000	C	2.413955000	-4.525297000	-1.315972000
H	-2.894328000	-5.076236000	-0.192811000	H	2.199955000	-5.067804000	-2.229174000
H	-1.696690000	-3.822062000	0.140104000	C	2.034648000	3.206275000	-2.335181000
C	2.298433000	2.981230000	0.157526000	H	1.600297000	2.213482000	-2.485043000
C	-4.097702000	1.961846000	0.896874000	H	3.101446000	3.111837000	-2.545542000
C	5.112385000	0.609717000	-0.269107000	H	1.596976000	3.885273000	-3.066240000
H	6.178523000	0.769161000	-0.319019000	C	1.177198000	4.477603000	1.673222000
C	-5.123742000	-3.536829000	-0.311846000	H	0.931698000	4.773803000	2.685962000
H	-5.928865000	-2.934432000	0.112404000	C	5.077194000	3.084937000	-0.047178000
H	-5.348265000	-4.588988000	-0.126704000	H	4.905096000	3.562805000	0.919069000
H	-5.108776000	-3.374073000	-1.390717000	H	4.721645000	3.779799000	-0.809529000
C	-3.008611000	1.112659000	-2.401286000	H	6.146938000	2.939312000	-0.175697000
C	2.962062000	-2.507688000	-2.724895000	C	0.969606000	4.796179000	-0.697650000
H	3.973122000	-2.131357000	-2.893409000	H	0.559881000	5.340782000	-1.539878000
H	2.296211000	-1.642135000	-2.772745000	C	0.669780000	5.195221000	0.598348000
H	2.707933000	-3.183862000	-3.540495000	H	0.033037000	6.053721000	0.769666000
C	-5.291226000	2.553578000	0.121035000	C	2.506598000	2.562071000	2.632065000
H	-5.668592000	3.433917000	0.644319000	H	2.174658000	1.523684000	2.559958000
H	-6.101591000	1.825553000	0.052609000	H	2.149505000	2.972114000	3.575967000
H	-5.027019000	2.854490000	-0.888470000	H	3.598031000	2.537971000	2.659616000

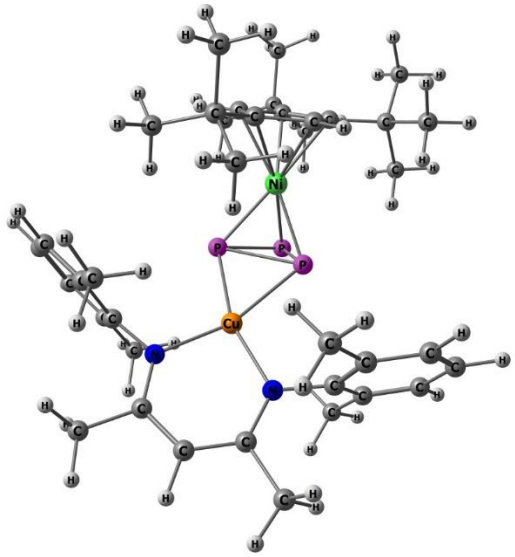
Table S3.22. Optimized geometries of **8**. XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.



Cu	2.893855000	-0.963954000	0.399615000	H	7.121427000	-0.867342000	-1.521246000
Cu	-2.254182000	-0.922657000	-0.856425000	C	1.073520000	-3.913486000	3.801348000
Co	0.146445000	1.807846000	0.967606000	H	1.136909000	-3.851099000	4.891164000
P	0.901486000	-0.350391000	1.459131000	C	-3.231853000	4.600861000	0.012220000
P	-0.360181000	-0.020151000	-0.278772000	H	-3.471717000	4.863705000	1.054351000
P	2.326180000	1.271290000	0.522668000	H	-4.162999000	4.646855000	-0.573699000
P	0.958512000	1.456513000	-1.189150000	H	-2.552770000	5.366397000	-0.380773000
N	4.478103000	-0.822318000	-0.755165000	C	4.932227000	2.998528000	-2.464734000
N	-3.819063000	-1.787312000	-0.025130000	H	5.016339000	4.001368000	-2.890325000
N	3.028076000	-2.867154000	0.820841000	C	-3.739852000	2.201822000	0.379185000
N	-2.641518000	-1.473153000	-2.720077000	H	-3.380854000	1.163938000	0.375410000
C	-4.357122000	-1.247506000	1.163419000	H	-4.582696000	2.260163000	-0.323905000
C	5.272591000	-1.860243000	-0.990146000	H	-4.127479000	2.425634000	1.382648000
C	2.009272000	-3.441112000	1.621130000	C	0.756403000	-3.994370000	-0.497139000
C	-1.505080000	2.257183000	2.075090000	H	0.930376000	-2.974564000	-0.871998000
H	-2.293520000	1.546024000	2.294312000	H	-0.243237000	-4.317110000	-0.820801000
C	-1.449018000	3.095037000	0.903206000	H	1.503976000	-4.636295000	-0.992436000
C	4.037236000	-3.615568000	0.383420000	C	5.553552000	2.698157000	-1.250736000
C	-5.537268000	-0.465844000	1.098711000	H	6.123802000	3.467872000	-0.723602000
C	4.705345000	0.434396000	-1.366920000	C	0.076152000	5.108279000	-1.289581000
C	0.882235000	-4.021717000	1.001228000	H	0.400089000	4.206983000	-1.827882000

C	-0.192049000	3.845819000	0.985599000	H	0.608177000	5.968830000	-1.722521000
C	5.078302000	-3.147440000	-0.446225000	H	-0.991722000	5.264296000	-1.471331000
H	5.829253000	-3.888244000	-0.717014000	C	6.065018000	1.102056000	0.651091000
C	-0.346247000	2.452561000	2.878058000	H	5.288138000	0.797315000	1.372460000
C	-6.011789000	0.143872000	2.266548000	H	6.598275000	1.971191000	1.061480000
H	-6.916745000	0.755663000	2.213958000	H	6.773647000	0.260796000	0.585748000
C	-3.661871000	-1.388064000	2.385394000	C	-0.756377000	-0.910026000	-4.175334000
C	-2.636924000	3.177782000	-0.065767000	C	-6.234754000	-0.251128000	-0.218739000
C	-0.063390000	1.890686000	4.258470000	H	-5.506524000	-0.023945000	-1.010646000
C	0.446239000	3.420701000	2.197070000	H	-6.957880000	0.574199000	-0.152285000
H	1.409802000	3.776504000	2.543971000	H	-6.781942000	-1.147220000	-0.555479000
C	-4.401996000	-2.817868000	-0.638626000	C	-0.035956000	6.305504000	0.917570000
C	0.428639000	5.014409000	0.201142000	H	-1.129941000	6.408617000	0.894610000
C	4.067964000	0.727386000	-2.591626000	H	0.402327000	7.189030000	0.427092000
C	5.446813000	1.421526000	-0.682311000	H	0.280647000	6.305650000	1.971748000
C	2.096335000	-3.351249000	3.026454000	C	-5.402210000	-3.649277000	0.140996000
C	-4.159237000	-3.198002000	-1.975915000	H	-4.971570000	-3.954087000	1.107480000
H	-4.700366000	-4.079716000	-2.318225000	H	-5.698623000	-4.546539000	-0.417142000
C	-4.170383000	-0.764200000	3.532352000	H	-6.309220000	-3.071103000	0.372103000
H	-3.640651000	-0.889505000	4.479870000	C	-0.016272000	-4.546086000	3.200371000
C	-0.113137000	-4.585760000	1.808566000	H	-0.805110000	-4.983267000	3.816838000
H	-0.982863000	-5.046412000	1.333130000	C	-0.475744000	2.993869000	5.260903000
C	-2.077630000	-0.672270000	-3.736482000	H	0.116890000	3.909570000	5.110794000
C	-5.339898000	-0.002824000	3.481753000	H	-0.317926000	2.646974000	6.294358000
H	-5.722735000	0.478962000	4.384699000	H	-1.539475000	3.252611000	5.143183000
C	1.971152000	4.950582000	0.269139000	C	3.234823000	-0.325608000	-3.266589000
H	2.358823000	5.009997000	1.294678000	H	3.834766000	-1.201289000	-3.563936000
H	2.391964000	5.802953000	-0.284738000	H	2.739651000	0.074616000	-4.160747000
H	2.356891000	4.028144000	-0.189531000	H	2.458253000	-0.702667000	-2.582566000
C	4.093438000	-5.072062000	0.796644000	C	-2.810631000	0.434425000	-4.224517000
H	4.104295000	-5.161839000	1.893855000	C	-2.397321000	-2.192079000	2.431665000
H	4.983311000	-5.569473000	0.391555000	H	-2.540443000	-3.196924000	2.010566000
H	3.198701000	-5.611480000	0.450440000	H	-2.014433000	-2.295946000	3.455113000
C	1.430552000	1.573814000	4.441775000	H	-1.606659000	-1.725533000	1.819846000
H	1.748229000	0.766444000	3.765871000	C	-3.626302000	-2.941166000	-4.411810000
H	1.619686000	1.246196000	5.475617000	H	-4.163639000	-2.167381000	-4.983369000
H	2.065663000	2.451040000	4.248471000	H	-4.197915000	-3.875908000	-4.474621000
C	-0.896786000	0.630621000	4.526235000	H	-2.655051000	-3.079493000	-4.910273000
H	-1.973877000	0.840265000	4.464417000	C	-4.208089000	0.684490000	-3.723922000
H	-0.687483000	0.249339000	5.537540000	H	-4.901270000	-0.121951000	-4.014611000
H	-0.659283000	-0.163526000	3.805157000	H	-4.606823000	1.632629000	-4.111587000
C	4.191939000	2.016297000	-3.126072000	H	-4.225383000	0.720502000	-2.624234000
H	3.688274000	2.250820000	-4.067521000	C	-0.186133000	-0.032041000	-5.106479000
C	-2.296684000	2.798255000	-1.519254000	H	0.833613000	-0.216899000	-5.453104000
H	-1.429234000	3.323369000	-1.919641000	C	-2.203948000	1.292619000	-5.150071000
H	-3.158523000	3.013564000	-2.168291000	H	-2.765580000	2.153640000	-5.522998000
H	-2.095122000	1.720301000	-1.592009000	C	0.015363000	-2.072004000	-3.616261000
C	-3.440194000	-2.496520000	-2.975998000	H	0.158350000	-1.948235000	-2.531468000
C	3.255761000	-2.629346000	3.657411000	H	1.003140000	-2.163156000	-4.087327000
H	4.222378000	-3.083255000	3.385670000	H	-0.522104000	-3.024661000	-3.744748000
H	3.172309000	-2.621175000	4.753333000	C	-0.898934000	1.065426000	-5.593217000
H	3.296765000	-1.584521000	3.303661000	H	-0.437152000	1.744035000	-6.314420000
C	6.467472000	-1.667455000	-1.900501000	H	7.054446000	-2.589518000	-1.994484000
H	6.141687000	-1.353061000	-2.904092000				

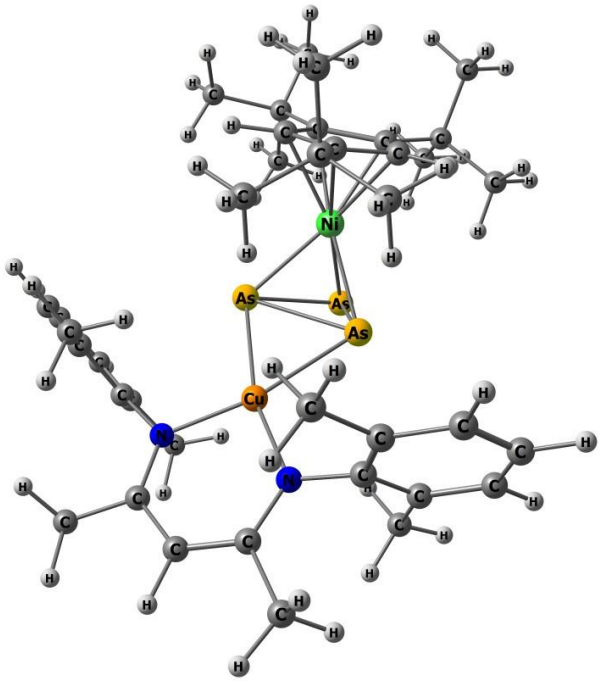
Table S3.23. Optimized geometries of **9a**. XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.



Cu	-1.907417000	0.117553000	0.301285000	H	2.974550000	3.196937000	-1.305167000
Ni	1.904316000	-0.095811000	0.163315000	C	-2.582178000	-2.650285000	-2.220713000
P	0.132179000	1.240369000	0.411144000	H	-3.635036000	-2.460609000	-2.441495000
P	0.021080000	-1.037835000	0.899783000	H	-2.172541000	-3.266329000	-3.019922000
P	1.026058000	0.385285000	2.183411000	H	-2.082602000	-1.680554000	-2.240650000
N	-3.253636000	-1.322700000	0.214062000	C	-1.654577000	-5.196975000	0.442292000
N	-3.153527000	1.613718000	0.005940000	H	-1.219542000	-6.186501000	0.501186000
C	2.956515000	0.488319000	-1.560676000	C	4.136545000	-2.482397000	1.908485000
H	2.643476000	1.274350000	-2.221610000	H	3.112139000	-2.298984000	2.234922000
C	3.798606000	0.670098000	-0.420971000	H	4.713322000	-2.826193000	2.767870000
C	3.189762000	-1.555884000	-0.613893000	H	4.127595000	-3.292910000	1.181494000
H	3.084080000	-2.606471000	-0.420270000	C	-5.338580000	2.659232000	-0.306548000
C	-2.774244000	-2.652795000	0.290727000	H	-5.203487000	3.372730000	0.507867000
C	-2.567410000	-3.244740000	1.545622000	H	-6.387834000	2.378829000	-0.355327000
C	-4.546382000	-1.082247000	0.074348000	H	-5.073992000	3.180463000	-1.228257000
C	-4.459775000	1.445560000	-0.108141000	C	4.940439000	-0.255151000	2.550873000
C	-5.103903000	0.199072000	-0.060778000	H	5.487689000	0.650731000	2.313928000
H	-6.178444000	0.228867000	-0.155782000	H	5.495992000	-0.772065000	3.335171000
C	-2.582287000	2.906131000	-0.082620000	H	3.967155000	0.023056000	2.955305000
C	-2.402368000	-3.317559000	-0.887385000	C	5.938990000	1.958413000	-0.067777000
C	3.942558000	-0.647832000	0.195514000	H	6.305624000	1.353849000	0.755496000
C	2.560951000	-0.869187000	-1.684275000	H	6.359519000	2.959457000	0.044715000
C	4.403039000	2.043798000	-0.107834000	H	6.322635000	1.531340000	-0.996100000
C	-2.010260000	-4.520720000	1.601855000	C	1.166920000	-2.829241000	-2.401100000
H	-1.848213000	-4.982131000	2.568676000	H	1.961952000	-3.543706000	-2.182729000
C	4.780865000	-1.196299000	1.352545000	H	0.570193000	-3.237167000	-3.218299000
C	-2.141250000	3.380854000	-1.326450000	H	0.527463000	-2.752101000	-1.522108000
C	-1.847031000	-4.591573000	-0.792661000	C	-1.284555000	5.363665000	-0.233434000
H	-1.554616000	-5.106831000	-1.699693000	H	-0.782455000	6.320891000	-0.292381000
C	-2.345773000	3.637362000	1.090829000	C	3.852348000	2.654142000	1.193196000
C	1.733305000	-1.462720000	-2.801395000	H	2.783926000	2.845762000	1.090371000
C	-2.913700000	-2.494749000	2.799628000	H	4.350036000	3.606291000	1.391317000
H	-2.345177000	-1.563086000	2.862874000	H	3.991673000	2.013209000	2.055108000
H	-2.692667000	-3.093017000	3.682832000	C	2.654921000	-1.635653000	-4.025347000
H	-3.968745000	-2.215117000	2.828563000	H	3.062503000	-0.675381000	-4.345703000
C	-5.508038000	-2.248713000	0.053338000	H	2.097991000	-2.066817000	-4.859934000
H	-5.280041000	-2.922880000	-0.773670000	H	3.490141000	-2.298533000	-3.792253000
H	-6.535213000	-1.907404000	-0.048513000	C	-1.700848000	4.868643000	0.995515000
H	-5.421944000	-2.835039000	0.969620000	H	-1.517093000	5.438178000	1.898649000
C	0.574578000	-0.527077000	-3.172330000	C	-2.323987000	2.544001000	-2.560252000
H	-0.093750000	-0.387426000	-2.323488000	H	-1.828605000	1.576384000	-2.447077000
H	0.000514000	-0.952080000	-3.997282000	H	-1.907511000	3.044592000	-3.433715000
H	0.932107000	0.454585000	-3.484311000	H	-3.376470000	2.329930000	-2.757060000
C	6.169990000	-1.570200000	0.793793000	C	-1.499556000	4.616380000	-1.384120000
H	6.072515000	-2.298025000	-0.013287000	H	-1.158245000	4.988559000	-2.342745000
H	6.783163000	-2.013786000	1.581207000	C	-2.745949000	3.073923000	2.424223000
H	6.696346000	-0.702258000	0.401272000	H	-3.814606000	2.856151000	2.471572000
C	4.051073000	3.042199000	-1.226868000	H	-2.500391000	3.767491000	3.227700000
H	4.430106000	2.715805000	-2.196279000	H	-2.229184000	2.129165000	2.615045000

H	4.506092000	4.006306000	-0.996113000

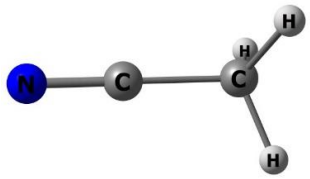
Table S3.24. Optimized geometries of **9b**. XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.



As	-0.039451000	-1.226288000	-0.749644000	H	2.871126000	2.779335000	-1.036541000
As	0.098880000	1.339675000	-0.309665000	H	4.136442000	1.918525000	-1.896637000
As	1.131801000	0.288597000	-2.211179000	C	1.647892000	-1.407372000	3.001387000
Cu	-2.000567000	0.102435000	-0.189352000	C	4.195949000	-2.566379000	-1.611715000
Ni	1.905385000	-0.132413000	-0.012828000	H	4.132323000	-3.357575000	-0.866525000
N	-3.363081000	-1.329311000	-0.092387000	H	4.812895000	-2.941971000	-2.428963000
N	-3.241625000	1.609132000	0.107461000	H	3.194497000	-2.374404000	-1.998529000
C	3.156338000	-1.567858000	0.852759000	C	-2.634339000	-2.656157000	2.324339000
H	3.059590000	-2.624865000	0.691553000	H	-2.128929000	-1.689109000	2.330701000
C	-4.651416000	-1.080200000	0.068884000	H	-2.210118000	-3.273109000	3.115050000
C	3.940994000	-0.686110000	0.043147000	H	-3.680659000	-2.459299000	2.568388000
C	2.494203000	-0.847781000	1.880661000	C	5.940707000	1.913514000	0.347229000
C	-5.619881000	-2.240468000	0.116581000	H	6.352742000	1.276580000	-0.429013000
H	-5.554612000	-2.836810000	-0.794824000	H	6.260931000	1.516972000	1.312436000
H	-6.642877000	-1.891478000	0.233446000	H	6.377259000	2.906769000	0.226506000
H	-5.381592000	-2.907560000	0.946611000	C	3.992740000	3.047901000	1.348748000
C	4.829989000	-1.276234000	-1.053637000	H	4.461585000	4.003269000	1.109695000
C	-5.199005000	0.204557000	0.207958000	H	4.316018000	2.757165000	2.349084000
H	-6.271520000	0.241091000	0.321230000	H	2.913572000	3.204486000	1.360949000
C	3.776368000	0.650079000	0.610836000	C	-5.417787000	2.665289000	0.448101000
C	-4.547018000	1.446998000	0.240610000	H	-5.137237000	3.188331000	1.363995000
C	-2.897679000	-2.663647000	-0.179596000	H	-6.467268000	2.389222000	0.513671000
C	2.892816000	0.504963000	1.725707000	H	-5.292515000	3.375653000	-0.370571000
H	2.561988000	1.310929000	2.353183000	C	1.097502000	-2.791331000	2.641515000
C	-2.491441000	-3.326666000	0.988379000	H	0.471682000	-2.748196000	1.750567000
C	-2.732510000	-3.260053000	-1.438789000	H	0.491098000	-3.174954000	3.463317000
C	-2.670551000	2.902381000	0.186348000	H	1.900781000	-3.506788000	2.459944000
C	-1.938384000	-4.600599000	0.879529000	C	-1.807527000	4.865793000	-0.905478000
H	-1.618581000	-5.113877000	1.778423000	H	-1.637505000	5.435013000	-1.811467000
C	4.405544000	2.010236000	0.287614000	C	-1.570022000	4.614789000	1.470920000
C	-1.784268000	-5.208931000	-0.359531000	H	-1.214257000	4.987340000	2.424085000
H	-1.350330000	-6.198182000	-0.429580000	C	2.550274000	-1.532859000	4.245855000
C	-3.116947000	-2.512735000	-2.683302000	H	3.394128000	-2.196274000	4.048001000
H	-4.176718000	-2.249630000	-2.688571000	H	1.982946000	-1.941167000	5.084925000
H	-2.906654000	-3.106099000	-3.572350000	H	2.945169000	-0.559327000	4.540985000
H	-2.565116000	-1.572051000	-2.756154000	C	0.478210000	-0.466853000	3.321543000
C	-2.453445000	3.634233000	-0.990816000	H	0.826124000	0.525917000	3.608529000
C	-2.177807000	-4.536565000	-1.508947000	H	-0.108769000	-0.867932000	4.149543000
H	-2.046324000	-5.000584000	-2.479110000	H	-0.175274000	-0.357004000	2.456922000
C	6.180967000	-1.654653000	-0.409878000	C	-1.372499000	5.361333000	0.316692000

H	6.696456000	-0.783141000	-0.010376000	H	-0.869601000	6.318584000	0.367438000
H	6.830110000	-2.124862000	-1.151629000	C	-2.375486000	2.542198000	2.659906000
H	6.029711000	-2.360220000	0.408522000	H	-3.425044000	2.331456000	2.875100000
C	-2.211916000	3.378927000	1.423507000	H	-1.941809000	3.040664000	3.526154000
C	5.074234000	-0.370328000	-2.264274000	H	-1.885545000	1.573147000	2.536331000
H	4.130713000	-0.088698000	-2.732076000	C	-2.873651000	3.069745000	-2.317473000
H	5.666369000	-0.916584000	-3.000497000	H	-2.366245000	2.120402000	-2.510451000
H	5.621646000	0.533195000	-2.018431000	H	-2.632714000	3.759078000	-3.125955000
C	3.943218000	2.582994000	-1.063580000	H	-3.944499000	2.859997000	-2.351053000
H	4.456225000	3.528408000	-1.255409000				

Table S3.25. Optimized geometries of MeCN. XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.



N	13.859512000	6.673873000	14.237419000	H	11.709410000	7.623884000	16.328320000
C	12.936652000	7.189663000	14.690289000	H	10.866224000	7.480028000	14.773630000
C	11.770920000	7.841166000	15.262206000	H	11.842583000	8.919687000	15.123536000

3.5.5. References

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Preface

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'Conversion of E_4 (E_4 = P_4, As_4, AsP_3) by Ni(0) and Ni(I) Synthons – A Comparative Study'

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Authors

M. Haimerl, C. Graßl, M. Seidl, M. Piesch, and M. Scheer*

Author contribution

The main part of the manuscript was done by the first author (M. Haimerl). C. Graßl described the synthesis and partly characterization of compound **2b**, **3a**, **3b**, **4**, **5a**, **5b**, **6** and **7a** already in his PhD thesis. The synthesis and characterization of compound **2c** and **7b** were done by M. Haimerl also the main parts of the characterization of the other compounds were done by M. Haimerl. D. Preitschaft (research student) helped by the reproduction of compound **1**, **3a** and **3b**. The single crystal X-ray diffraction measurements of compound **3a**, **3b**, **4** and **6** were done by C. Graßl, of compound **2b**, **2c**, **5a**, **5b**, **7a** and **7b** were done by M. Haimerl. The refinement of the structures **2c**, **3a**, **3b**, **4**, **6** and **7b** were done by M. Seidl, he also checked all crystallographic files and data. M. Piesch performed the DFT calculations and contributed the corresponding part in the Supporting Information. The EPR samples were prepared by the first author and measured with help of S. Dinauer. Samples for CV were prepared by the first author and measured with help of M. Weber. M. Scheer supervised the research and revised the manuscript.

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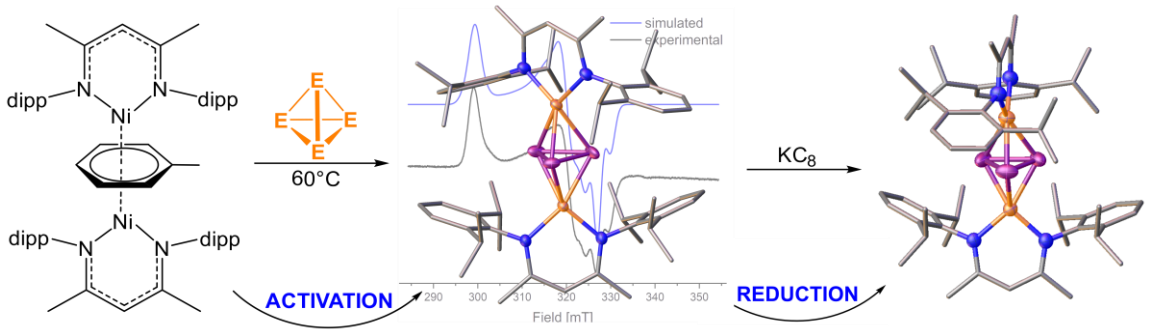
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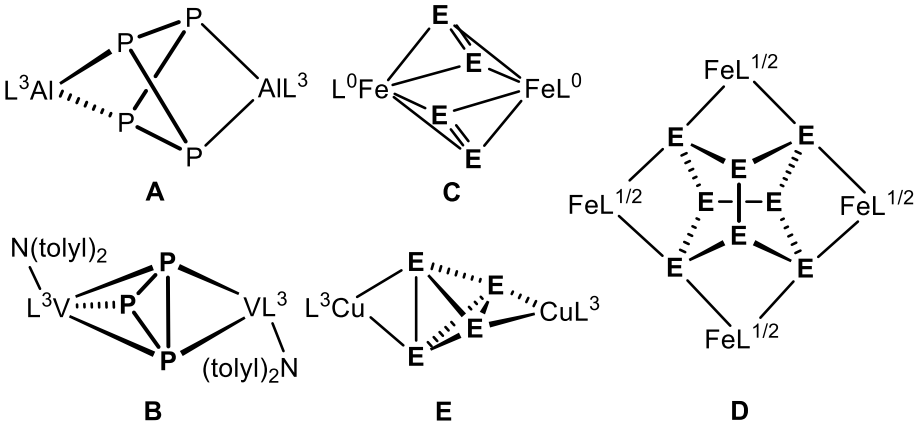
4. Conversion of E_4 (E_4 = P_4, As_4, AsP_3) by Ni(0) and Ni(I) Synthons – A Comparative Study

Abstract: *The reactivity of white phosphorus and yellow arsenic towards two different nickel nacnac complexes is investigated. The nickel complexes [(L^3Ni)$_2$tol] (**1**, L^3 = [{N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(Me)}$_2$CH]$^-$) and [K$_2$][(L^3Ni)$_2$(μ,η$^{1:1}$-N$_2$)] (**6**) were reacted with P_4, As_4 and the interpnictogen compound AsP_3, respectively, yielding the homobimetallic complexes [(L^3Ni)$_2$(μ-η^2,κ^1:η^2,κ^1-E$_4$)] (E = P (**2a**), As (**2b**), AsP_3 (**2c**)), [(L^3Ni)$_2$(μ,η$^{3:3}$-E$_3$)] (E = P (**3a**), As (**3b**)) and [K@18-c-6(thf)$_2$][L^3Ni(η$^{1:1}$-E$_4$)] (E = P (**7a**), As (**7b**)), respectively. Heating of **2a**, **2b** or **2c** also leads to the formation of **3a** or **3b**. Furthermore, the reactivity of these compounds towards reduction agents was investigated, leading to [K$_2$][(L^3Ni)$_2$(μ,η$^{2:2}$-P$_4$)] (**4**) and [K@18-c-6(thf)$_3$][(L^3Ni)$_2$(μ,η$^{3:3}$-E$_3$)] (E = P (**5a**), As (**5b**)), respectively. Compound **4** shows an unusual planarization of the initial Ni$_2$P$_4$-prism. All products were comprehensively characterized by crystallographic and spectroscopic methods.*

4.1. Introduction

The activation of small molecules under mild conditions is an important topic in current research, because it can contribute to future energy conversions.[1] Besides Cp^R coordinating transition metal complexes, also low valent metal complexes stabilized by *β*-diiminato ligands[2] are adequate precursors for the reductive activation of small molecules such as N_2, O_2 or S_8[3], but also for P_4 and As_4.[4] For the latter, by different reaction conditions such as photolysis or thermolysis, a broad variety of metal complexes with different polypnictogen moieties could be synthesized. With main group metal complexes of group 13, *Roesky et al.* reported the dinuclear aluminum complex [(L^3Al)$_2$(μ,η$^{1:1:1:1}$-P$_4$)] (**A**, L^3 = [{N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(Me)}$_2$CH]$^-$, Scheme 4.1) which contains a P_4^{4-} unit.[4a] The reaction of the corresponding Ga(I) complex [L^3Ga] with P_4 leads to [L^3Ga(η$^{1:1}$-P$_4$)] and other polyphosphine-containing complexes.[4b,4k] In the area of transition metal complexes, only few examples of the early transition metals of Group 5 are known, e.g. the neutral vanadium complex [(L^3V(Ntolyl$_2$))$_2$(μ,η$^{3:2}$-P$_3$)] (**B**, Scheme 4.1)[4d] containing a *cyclo*-[P$_3$]$^{3-}$ ligand or the dinuclear complexes [(L^3(N^{t}Bu)M)$_2$(μ,η$^{3:3}$-P$_4$)] (M = Nb, Ta)[4e] with a bridging *cyclo*-P_4 unit in an η$^{3:3}$ coordination mode. In contrast, during the last decade, for late Group 8-11 transition metals, numerous examples were reported. For cobalt and iron complexes, systematic studies with different nacnac ligands were performed leading to various E_n units (n = 3, 4 and 8) depending on the steric and electronic influence of the nacnac ligand.[4j,4l-n] *Driess et al.* first synthesized the dinuclear iron complex [(L^0Fe)$_2$(μ,η$^{2:2}$-P$_2$)$_2$] (**C**; L^0 = [{N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(H)}$_2$CH]$^-$)), which contains two anionic P_2 ligands. An analogues arsenic derivative has also been reported.[4n] By using nacnac systems with less steric flanking groups, the tetranuclear complexes [($L^{1/2}$Fe)$_4$(μ,η$^{2:2:2:2}$-E$_8$)] (**D1-D4**; E = P, As; L^1 = [{N(C$_6$H$_3$Me-2,6)C(Me)}$_2$CH]$^-$ or L^2 = [{N(C$_6$H$_3$Me-2,6)C(H)}$_2$CH]$^-$)[4j,4n] could be synthesized. These E_8 units display a realgar-type geometry.[5] Interestingly, the activation of white phosphorus by [LCo(tol)] (L = L^0, L^1, L^2, L^3) leads to the sole formation of [(LCo)$_2$(μ,η$^{4:4}$-P$_4$)],[4l,6] however, the reaction with yellow arsenic yields complexes containing different {Co$_2$As$_4$} cores.[4m] Recently, we were able to synthesize and

characterize the first neutral and molecular complex containing an intact E_4 tetrahedron i.e. $[(L^3Cu)_2(\mu,\eta^{2:2}\text{-}E_4)]$[4h] (E = P (**E1**), As (**E2**)) (Scheme 4.1), which is easy to handle (neither flammable nor light-sensitive) and can release E_4 in a controlled manner.



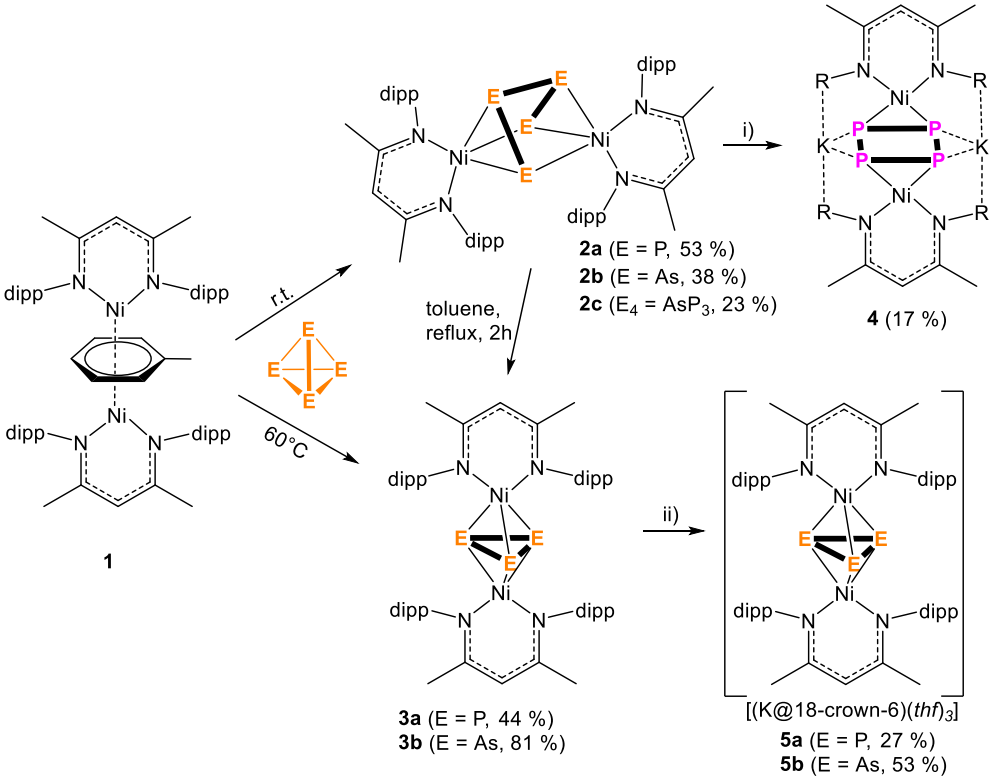
Scheme 4.1. Examples of known motifs of E_n ligand complexes stabilized by *β*-diiminato ligands (L^0 = $[\{N(C_6H_3{}^iPr_2\text{-}2,6)C(H)\}_2CH]^-$, L^1 = $[\{N(C_6H_3Me\text{-}2,6)C(Me)\}_2CH]^-$, L^2 = $[\{N(C_6H_3Me\text{-}2,6)C(H)\}_2CH]^-$ and L^3 = $[\{N(C_6H_3{}^iPr_2\text{-}2,6)C(Me)\}_2CH]^-$; D1 = L^1, P; D2 = L^1, As; D3 = L^2, P; D4 = L^2, As)

For *β*-diiminato complexes of Ni, the *Driess* group used the Ni(I) synthon $[(L^3Ni)_2tol]$ (**1**) to activate small molecules such as H_2, N_2[7] and chalcogens (O_2, S_8, Se and Te).[3e,8] The reaction of **1** with white phosphorus leads only to $[(L^3Ni)_2(\mu\text{-}\eta^2,\kappa^1{:}\eta^2,\kappa^1\text{-}P_4)]$ containing a Ni_2P_4 prism, from which an $\{L^3Ni\}$ fragment can be released in solution.[4c] Inspired by the different reaction outcome, in the case of Fe(I) and Co(I) nacnac complexes and the coordination of the intact E_4 moiety in the case of Cu(I) nacnac complexes, the question arose as to what would happen in the case of nickel nacnac compounds. Would a different reaction behavior occur between phosphorus and arsenic? Moreover, the reactivity of an already reduced nickel species as a formal Ni(0) synthon towards white phosphorus and yellow arsenic was of interest to explore if there are similarities or differences towards the reaction of the respective Ni(I) nacnac species with E_4. Furthermore, since only a few reactions of the interpnictogen compound AsP_3 are reported, we targeted to include this species in this research.

Herein we report on the reactivity of $[(L^3Ni)_2tol]$ (L^3 = $[\{N(C_6H_3{}^iPr_2\text{-}2,6)C(Me)\}_2CH]^-$) towards white phosphorus, yellow arsenic and AsP_3. The reaction of **1** with E_4 leads to two different species depending on the used temperature, $[(L^3Ni)_2(\mu\text{-}\eta^2,\kappa^1{:}\eta^2,\kappa^1\text{-}E_4)]$ and $[(L^3Ni)_2(\mu,\eta^{3:3}\text{-}E_3)]$. Further reduction of these products leads to novel anionic dinuclear species with an $\eta^{2:2}$ *cyclo*-P_4 unit or $\eta^{3:3}$ *cyclo*-E_3 units. Moreover, reactions of the formally Ni(0) species $[K_2][(L^3Ni)_2(\mu,\eta^{1:1}\text{-}N_2)]$ with white phosphorus and yellow arsenic give unique anionic mononuclear compounds bearing an E_4 butterfly ligand.

4.2. Result and Discussion

The reaction of $[(L^3Ni)_2tol]$ (**1**) with P_4 at -78 °C leads to the sole formation of the already reported $[(L^3Ni)_2(\mu\text{-}\eta^2,\kappa^1\text{:}\eta^2,\kappa^1\text{-}P_4)]$ (**2a**).[4c] Performing the reaction of **1** with E_4 in toluene at room temperature (to allow a high content of As_4) leads to the formation of $[(L^3Ni)_2(\mu\text{-}\eta^2,\kappa^1\text{:}\eta^2,\kappa^1\text{-}E_4)]$ (E_4 = As_4 (**2b**), AsP_3 (**2c**); Scheme 4.2). In contrast, the reaction of **1** with E_4 at + 60 °C yields $[(L^3Ni)_2(\mu,\eta^{3:3}\text{-}E_3)]$ (E = P (**3a**), E = As (**3b**)) (Scheme 4.2).



Scheme 4.2. Reaction of **1** with E_4 (E = P, As) and further reduction (R = dipp = 2,6-diisopropylphenyl). i) KC_8, toluene; ii) KC_8 + 18-crown-6, thf.

2b, **2c**, **3a** and **3b** are obtained as greenish-brown (**2b**, **3b**) or green (**2c**, **3a**) air-sensitive solids in isolated yields of 38 % (**2b**), 23 % (**2c**), 44 % (**3a**) and 81 % (**3b**). Obviously, the slightly higher temperature triggers a release of an E atom of the otherwise formed prismane-like structure. This can also be observed by refluxing a toluene solution of **2a**, **2b** or **2c** for 2h leading to the complete conversion to **3a** (for **2a** and **2c**) and **3b**, which was monitored by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. By further reduction of **2a**, **2b**,[9] **3a** and **3b** with KC_8, the compounds $[K_2][(L^3Ni)_2(\mu,\eta^{2:2}\text{-}P_4)]$ (**4**) and $[(K@18\text{-}c\text{-}6)thf)_3][(L^3Ni)_2(\mu,\eta^{3:3}\text{-}E_3)]$ (E = P (**5a**), As (**5b**)), respectively, were obtained in crystalline yields of 17 % (**4**), 27 % (**5a**) and 53 % (**5b**) (Scheme 4.2). **4** shows an interesting planarization to a *cyclo*-P_4^{2-} moiety, whereas the pseudo-triple decker compounds **3a** and **3b** retain their structures.

The ^{1}H NMR spectrum of **2a** shows a paramagnetic behavior in solution but is diamagnetic in the solid state and, accordingly, the $^{31}P\{^1H\}$ NMR spectrum is silent.[4c] In contrast, the ^{1}H NMR spectra of **2b** and **2c** at room temperature display one set of signals for the equivalent nacnac ligands. The $^{31}P\{^1H\}$ NMR spectrum of the reaction solution of **2c** in toluene-d_8 exhibits two broad signals at δ = 226.2 and 125.0 ppm, with an integral ratio of 1:2. Compounds **3a** and **3b** are paramagnetic. Their ^{1}H NMR spectra show broad and very shifted signals between 12.67 and -25.13 ppm for **3a** and between 12.01 and -23.31 ppm for **3b**. The $^{31}P\{^1H\}$ NMR spectrum of **3a** is silent because of an excessive line broadening. The effective magnetic moment (μ_{eff}) was determined by the Evans method to be 2.12 μ_B (**3a**) and 2.13 μ_B (**3b**), respectively, roughly corresponding to one unpaired electron. The X-band EPR spectra confirm the paramagnetic nature of **3a** and **3b** (frozen toluene solution, 77K: **3a**: g_1 = 2.254, g_2 = 2.108 and g_3 = 2.063; **3b**: g_1 = 2.2705, g_2 = 2.135, g_3 = 2.055). At 77 K, the EPR spectrum of **3a** displays a hyperfine coupling to two phosphorus nuclei (Figure 4.1). DFT calculations (B3LYP/def2-SVP level) show that the spin density is delocalized over both nickel atoms and two phosphorus atoms (Figure 4.1) being in agreement with the observed hyperfine coupling. The $^{31}P\{^1H\}$ NMR spectrum of **4** in C_6D_6 shows one singlet at δ = 80.3 ppm. Due to a dynamic behavior, **5a** reveals no signal at room temperature but a singlet at δ = -268.9 ppm in thf-d_8 at 193 K. In the LIFDI-MS spectra of **2b, 2c**, **3a** and **3b** and in the ESI spectrum of **5a**, corresponding molecular ion peaks are detected.

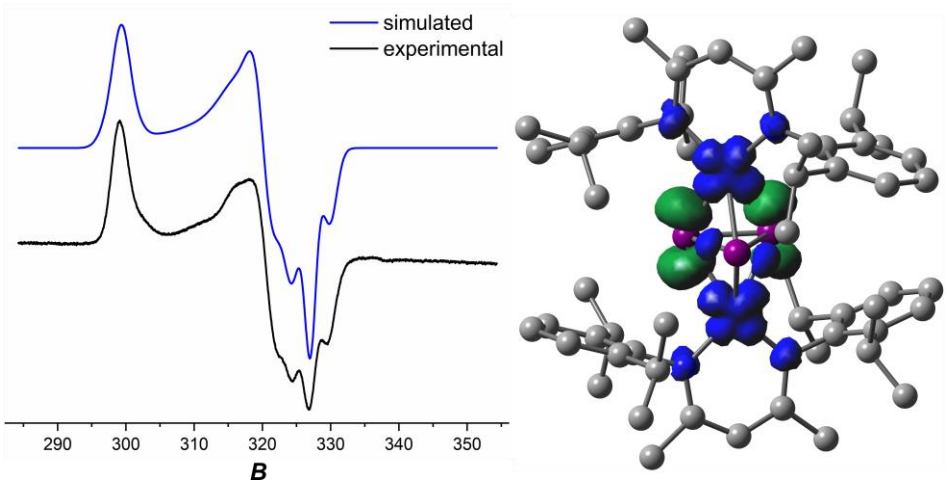


Figure 4.1. left: X-band EPR spectrum of **3a** (B in [mT], frozen toluene solution; 77K (black), simulation (blue)); right: Spin density distribution in **3a**, calculated at the B3LYP/def2-SVP level.

The molecular structures of **2b** and **2c**[10] (Figure 4.2) reveal dinuclear complexes bearing an E_4 unit, coordinating in an η^2,κ^1 fashion to both {L^3Ni} fragments, which are twisted by 37.46(12)° (**2b**) and 37.9882(6)° (**2c**) to each other. In the case of **2c** (use of AsP_3), the arsenic atom is disordered over all four positions, the major isomer, with the arsenic atom at the end of the E_4 chain and the minor isomer with the arsenic atom in the middle of the E_4 chain, is in a ratio of 68:12 (20 % are **2a**)[11] in the solid state. The minor isomer is

energetically less favored by 13 kJ·mol^{-1} to the major isomer (calculated at the BP86/def2-SVP level of theory, see SI). For **2b**, the As1-As2 and As3-As4 bond distances are 2.4115(5) and 2.4141(5) Å. The As1-As4 distance is slightly shortened (2.3917(5) Å) compared to As1-As2 and As3-As4, while the As2···As3 distance amounts to 2.7192(5) Å and is therefore in a non-bonding area. Compound **2c** shows E-E bond distances between 2.153(8) and 2.422(2) Å. Interestingly, compound [(Cp^{4}Ni)$_2$(μ-η^2,κ^1:η^2,κ^1-As$_4$)] (**F**, Cp^4 = C$_5$H^{i}Pr$_4$)[12] contains a similar As$_4$ core and shows longer As-As bond distances between 2.374(3) and 2.435(3) Å. The Ni-E bonds are in the range between 2.3111(7) and 2.4606(6) Å for **2b** and 2.21(3) and 2.378(3) Å for **2c**, which is comparable to **F** (Ni-As$_{av}$ 2.34 Å).

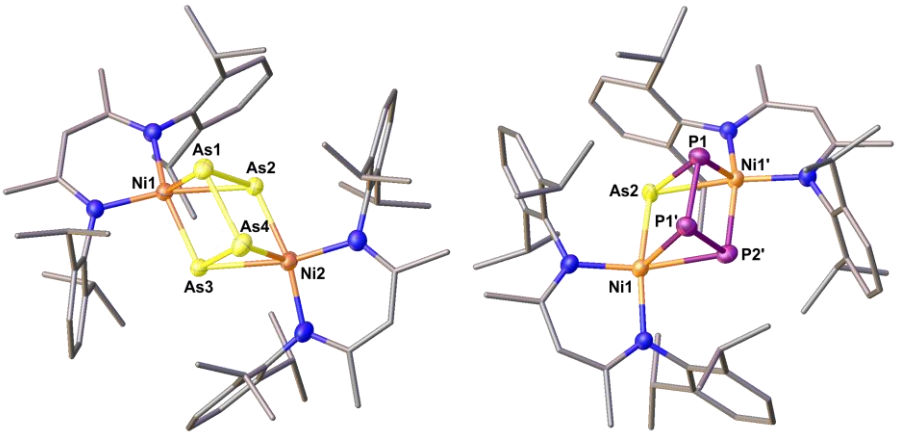


Figure 4.2. Molecular structures of **2b** (left) and one of the major products of **2c** (right) in the solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms are omitted for clarity.

The crystal structure analysis of **3a** and **3b** (Figure 4.3) reveals dinuclear complexes bearing a *cyclo*-E$_3$ (E = P, As) ligand as 'middle deck', which is disordered over two positions for **3a** (59:41) and three positions for **3b** (50:25:25) (cf. supporting information). The E-E bond distances (Table 4.1) are in the range between 2.158(10) and 2.206(14) Å (**3a**) or 2.373(7) and 2.599(14) Å (**3b**), respectively. The E-E-E bond angles are in the range of 60°. Both {L^{3}Ni} fragments are twisted to each other by 39.8° (**3a**) and 39.4° (**3b**), respectively. The Ni-E bond lengths are between 2.220(8) and 2.347(8) Å for **3a** and 2.277(8) and 2.521(9) Å for **3b**. The bond distances are comparable to the 33 valence electron complexes [{(triphos)Ni}$_2$(μ,η$^{3:3}$-E$_3$)][BPh$_4$]$_2$[13] (P-P 2.151(8) to 2.171(7) Å) or [(L^{3}Co)$_2$(μ,η$^{3:3}$-E$_3$)][4l,4m] (As-As 2.349(3) to 2.563(3) Å). Also, a few other metal complexes are known containing a *cyclo*-E$_3$ unit which is η^3-coordinated. [4g,14]

In order to evaluate the redox reactivity of **3a** and **3b**, we performed cyclic voltammetry measurements of **3a** (Figure 4.4) and **3b** (cf. supporting information). In thf, a reversible reduction at -1.77 V (**3a**) and -1.91 V (**3b**) and also an irreversible oxidation at 0.61 V (**3a**) and -0.42 V (**3b**), respectively, take place (against [Cp$_2$Fe]/[Cp$_2$Fe]$^+$). The chemical reduction of **3a** and **3b** was performed with potassium graphite, which was chosen as a

suitable reduction agent (redox potential: -2.93 V vs. the standard hydrogen electrode), which leads to the formation of $[(K@18\text{-}c\text{-}6)(thf)_3][(L^3Ni)_2(\mu,\eta^{3:3}\text{-}E_3)]$ (E = P (**5a**), As (**5b**)).

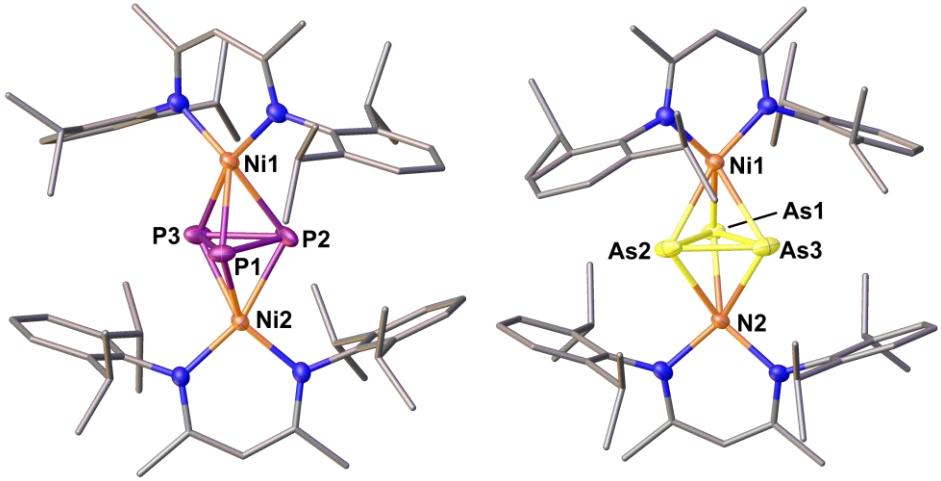


Figure 4.3. Molecular structures of **3a** (left) and **3b** (right) in the solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms are omitted for clarity.

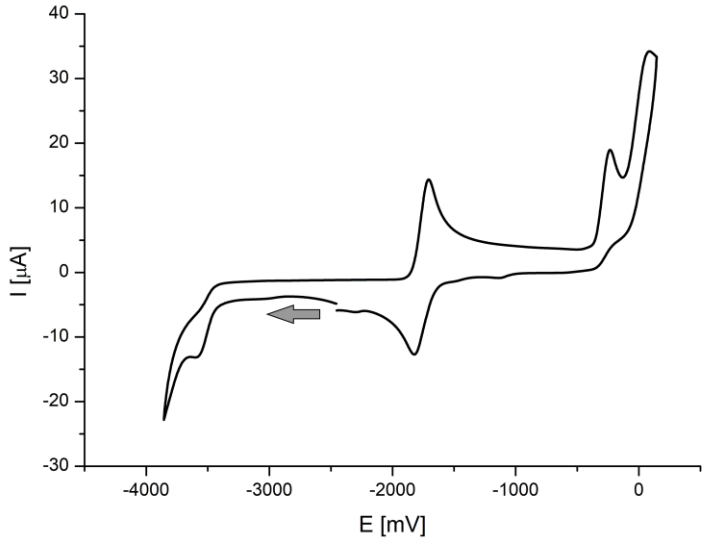


Figure 4.4. Cyclic voltammogram of **3a** in thf vs. $[Cp_2Fe]/[Cp_2Fe]^+$ (electrolyte: $[^nBu_4N][PF_6]$, scan rate: 100 mVs^{-1}, room temperature).

The solid-state structures of **5a** and **5b** (Figure 4.5) are very similar to that of **3a** and **3b** possessing a *cyclo*-E_3 ring which is η^3-coordinated by two $\{L^3Ni\}$ fragments (Table 4.1). The *cyclo*-E_3 units are disordered over two positions (ratio 90:10 (**5a**), 61:39 (**5b**)). The E-E bond distances are between 2.130(9) and 2.2065(10) Å (**5a**) and 2.397(5) to 2.423(3) Å (**5b**), respectively, and still intact. The Wiberg Bond Indices (WBIs) underlie this description (WBIs for E-E: **5a** between 0.87 to 1.03; **5b** between 0.93 and 0.98). The E-E-E bond angles are around 60° as also found in compound **3a** and **3b**. However, the structural difference lie in the orientation of the ligands in **3a**, **3b**, **5a** and **5b**. In **3a** and **3b**, the two

{L^3Ni} fragments are twisted by 39.8° (**3a**) and 39.4° (**3b**) to each other, respectively, in a kind of eclipsed orientation, whereas in **5a** and **5b**, the twist is, with 80.11(5)° (**5a**) and 73.6132(11)° (**5b**), much larger and a more staggered arrangement is present.

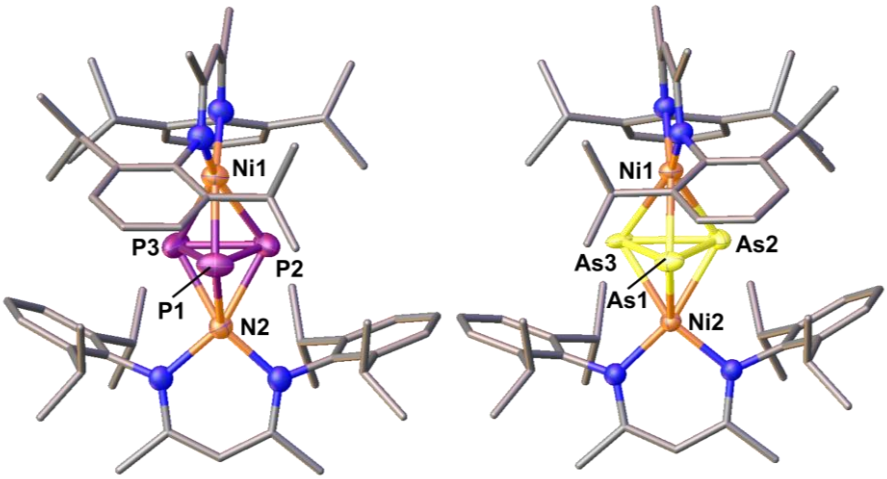


Figure 4.5. Molecular structures of the anions of **5a** (left) and **5b** (right) in the solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms, counter ions and solvent molecules are omitted for clarity.

Table 4.1. Comparison of selected atomic distances and angles in **3a**, **3b**, **5a** and **5b** (E = P, As).

Compound	**3a**	**3b**	**5a**	**5b**
d (E-E) [Å]	2.158(10) 2.202(11) 2.206(14)	2.365(6) 2.373(7) 2.385(6)	2.1760(10) 2.1848(10) 2.2065(10)	2.397(5) 2.417(4) 2.423(3)
∢ (E-E-E) [°]	58.7(4) 60.6(4) 60.8(4)	59.6(2) 59.9(2) 60.4(2)	59.14(4) 59.80(3) 60.79(4)	59.37(12) 60.19(11) 60.44(13)
d (Ni ⋯ Ni)	3.8456(6)	3.9398(6)	3.8169(4)	3.93112(4)
Θ [°]	39.8	39.4	80.11(5)	73.6132(11)

The chemical reduction of **2a** was also performed with potassium graphite. By using two equivalents of KC_8, the dinuclear complex [(L^3Ni)$_2$(μ,$\eta^{2:2}$-P_4)][K_2] (**4**) could be obtained as brown blocks (Scheme 4.2). Thus, a conversion and rearrangement to a novel planar *cyclo*-P_4 unit occur. The molecular structure of **4** reveals an anionic dinuclear complex bearing a *cyclo*-P_4 unit, coordinating in an $\eta^{2:2}$ fashion to two {L^3Ni} fragments (Figure 4.6). The two {L^3Ni} fragments are coplanar to each other and two potassium atoms are stabilized by two opposite dipp groups by C_{aryl}⋯K interactions. The Ni-P-P angle (cf. Figure 4.6, angle α) is 101.78(4)°. In the *cyclo*-P_4 unit, there are two different P-P bond lengths. The η^2-coordinated P-P bond length amounts to 2.1360(10) Å (WBI: 1.21), the other P-P bond length is 2.2611(10) Å (WBI: 0.90). In the literature, a few complexes

containing a planar *cyclo*-P_4 unit are known which are $\eta^{2:2}$ coordinated.[15] The bonding situation can be considered as being similar to the valence isomer derivative of a tetraphosphabenzene [{(^{i}Pr)$_2$NCP$_2$}$_2$] (**G**)[15a] with two single and two P-P double bonds, which was synthesized by *Bertrand et al*.. *Driess et al.* reported the reaction of **1** with sulfur, which leads to a complex containing a related core of sulfur, [(L^{3}Ni)$_2$(μ,$\eta^{2:2}$-S$_4$)].[8b]

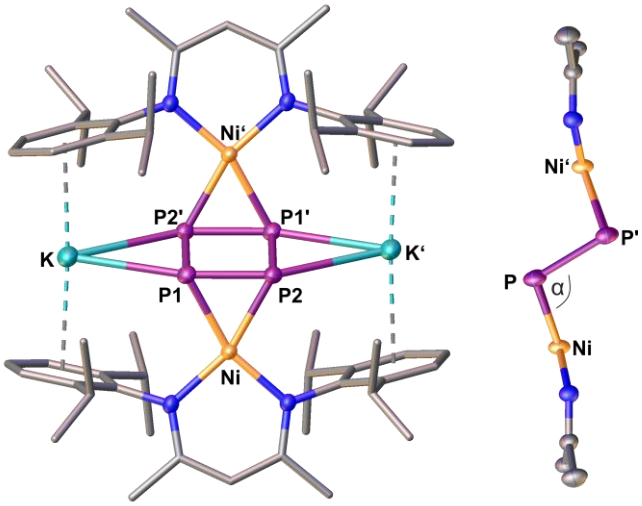


Figure 4.6. Molecular structure of **4** (left) in the solid state and side view (right) Isopropyl groups (for right), solvent molecules and hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50 % probability level.

Furthermore, the question arose whether the same reactivity could also be observed starting from a reduced Ni_2N_2 nacnac compound. In order to investigate the reactivity of an Ni(0) synthon towards E_4, the formally Ni(0) precursor [K$_2$][(L^{3}Ni)$_2$(μ,$\eta^{1:1}$-N$_2$)] (**6**) was synthesized and crystallized as purple needles in crystalline yields of 47 %.

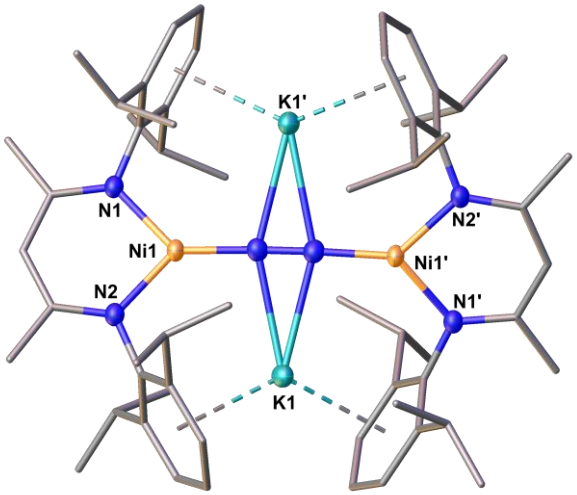
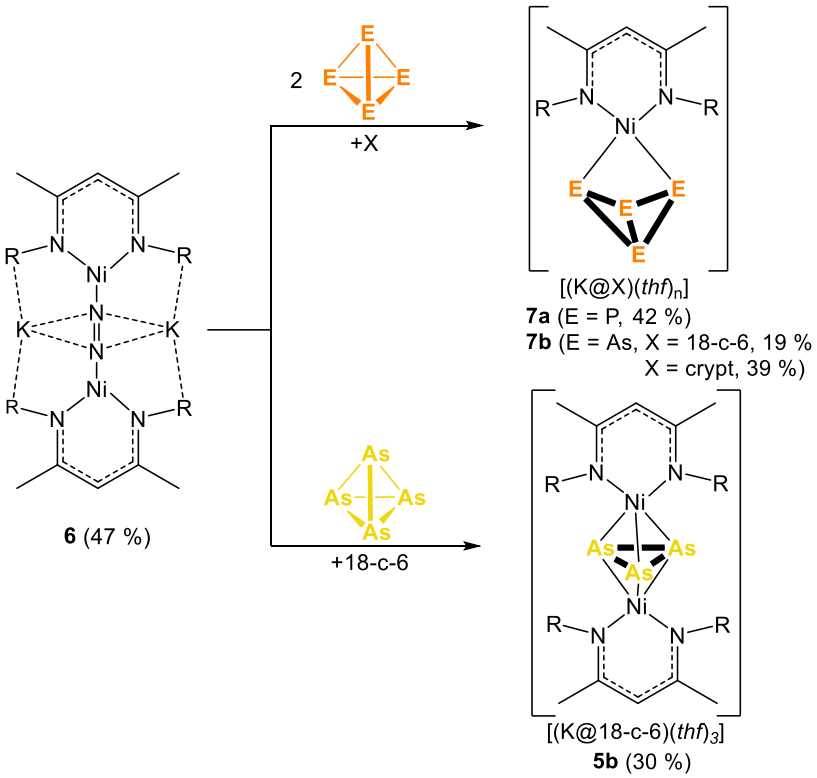


Figure 4.7. Molecular structure of **6** in the solid state. Thermal ellipsoids are shown in 50 % probability level. Hydrogen atoms are omitted for clarity.

In the ^{1}H-NMR spectrum of **6**, the typical signals for the *β*-diketiminato ligand can be observed. The X-ray structure of **6** (Figure 4.7) consists of two {L^{3}Ni} fragments bridged by a N_2 unit, which additionally coordinate to two potassium ions. The potassium ions are coordinated by the aromatic π system of the dipp substituent. The N-N bond distance with 1.195(5) Å corresponds to an N-N double bond (N_2H_2: 1.230 Å[16]) and the N-N stretching band in the Raman spectrum is detected at 1572 cm^{-1}. Complexes similar to **6** are known in the literature and the N-N bond distances and stretching bands show that the N_2 unit in **6** can be regarded as a N_2^{2-} unit.[3a,3b,17]

In order to investigate if this formally Ni(0) synthon leads in reactions with E_4 (E = P, As) to similar products or not as its Ni(I) derivative, **6** was reacted with white phosphorus and yellow arsenic at room temperature in the presence of 18-crown-6 (18-c-6) or cryptant (crypt). Adding 18-c-6 or crypt to **6** before E_4 leads to the formation of [(K@X)(thf)$_2$][L^{3}Ni(η$^{1:1}$-E_4)] (E = P, X = 18-c-6 (**7a**), E = As, X = 18-c-6 or crypt (**7b**)), which are isolated as air-sensitive orange (**7a**) or reddish-brown (**7b**) needles in crystalline yields of 42 % (**7a**) and 39 % (**7b**, X = crypt), respectively (Scheme 4.3). If **6** is reacted with yellow arsenic and 18-c-6 is added afterwards, the formation of [(K@18-c-6)(thf)$_3$][(L^{3}Ni)$_2$(μ,η$^{3:3}$-As_3)] (**5b**) in crystalline yields of 30 % occurs (Scheme 4.3), which, for phosphorus, could not be observed (formation of **7a**). Thus, the formation of **7a** and **7b** shows the difference between the use of a Ni(0) or Ni(I) synthon.



Scheme 4.3. Reaction of **6** with E_4 (E = P, As). R = dipp = 2,6-diisopropylphenyl, X = 18-c-6, crypt.

The $^{31}P\{^1H\}$ NMR spectrum of **7a** in thf-d_8 shows two triplets at -378.3 and -212.9 ppm ($^1J_{PP}$ = 133 Hz). The ^1H NMR spectrum of **7b** in thf-d_8 is very similar to the one of **7a**.

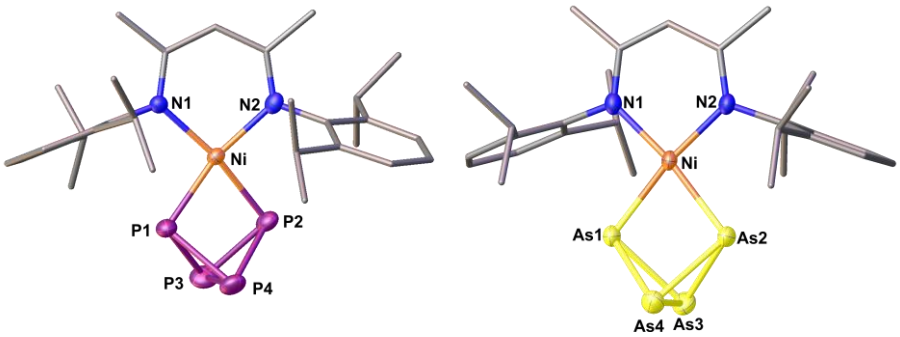


Figure 4.8. Molecular structure of the anions of **7a** (left) and **7b** (right) in the solid state. Thermal ellipsoids are shown in 50 % probability level. Hydrogen atoms and counter ions are omitted for clarity.

The molecular structures of **7a** and **7b** (Figure 4.8) reveal anionic mononuclear complexes bearing an E_4 butterfly ligand, coordinating in an $\eta^{1:1}$ fashion to the {L^3Ni} fragment. The six-membered NiN_2C_3 ring is twisted by 14.88470(5)° for **7a** and 0.78(4)° for **7b** to the E1-Ni-E2 plane. With 2.6759(15) (**7a**) and 2.8963(3) Å (**7b**), the E1···E2 distances lie in a non-bonding area. The E-E bond lengths are between 2.2115(16) and 2.2282(17) Å for **7a** and 2.4506(4) and 2.4687(3) Å for **7b**, except for the E3-E4 bond length which is shortened to 2.1567(18) (**7a**) and 2.3908(4) Å (**7b**). This is in accordance with other butterfly complexes. Interestingly, the *Driess* group proposed the occurrence of a neutral compound [L^3Ni(η^2-P_4)] with an η^2 side on coordinated P_4 tetrahedra by high-resolution ESI MS data.[4c] With compounds **7a** and **7b**, anionic species are formed and completely characterized.

4.3. Conclusion

In summary, we have shown the different reactivities of *β*-diketiminato Ni(I) and Ni(0) complexes towards white phosphorus, yellow arsenic and the interpnictogen compound AsP_3. The reactions of [(L^3Ni)$_2$tol] (**1**) with white phosphorus and yellow arsenic as well as AsP_3 are temperature-dependent. Thus, the homobimetallic complexes [(L^3Ni)$_2$(μ-η^2,κ^1:η^2,κ^1-E_4)] (E = As (**2b**), AsP_3 (**2c**)) and [(L^3Ni)$_2$(μ,$\eta^{3:3}$-E_3)] (E = P (**3a**), As (**3b**)) are formed, of which **3a** and **3b** are paramagnetic. DFT calculations exhibit that the spin density is delocalized over both nickel atoms and two pnictogen atoms. To investigate the redox reactivity of **3a** and **3b**, cyclic voltammetry measurements were performed and [(K@18-c-6)(thf)$_3$][(L^3Ni)$_2$(μ,$\eta^{3:3}$-E_3)] (E = P (**5a**), As (**5b**)) was isolated after experimental reduction. In contrast, the chemical reduction of **2a** leads to an unusual planarization of the initial Ni_2P_4-prism. Furthermore, the reaction of E_4 (E = P, As) with a formally Ni(0) synthon leads to the formation of the novel monoanionic compounds [(K@X)thf)$_2$][L^3Ni($\eta^{1:1}$-E_4)] (E = P, X = 18-c-6 (**7a**), As, X = crypt (**7b**)), which shows the differences between the use of an Ni(I) or Ni(0) synthon. Additionally, an alternative

synthetic approach for **5b** was found, using **6** as starting material, but by adding 18-c-6 after the reaction with As_4. The results show the broad variety of different E_n-structural motifs formed with nickel nacnac complexes in the conversion of E_4 and underline the great potential of the use of Ni(0) synthons in synthesis.

4.4. References

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4.5. Supporting Information

4.5.1. Synthesis and Characterization

General Remarks

All manipulations were performed with rigorous exclusion of oxygen and moisture using standard Schlenk techniques on a dual manifold Schlenk line with Argon or N_2 inert gas or glove box filled with nitrogen containing a high-capacity recirculator (<0.1 ppm O_2). Traces of oxygen and moisture in the inert gas were removed by passing it through a drying column filled with Cu/$MgSO_4$ catalyst as well as, concentrated H_2SO_4 and orange gel, respectively. All solvents were degassed and purified by standard procedures. All NMR spectra have been recorded using deuterated d_6-benzene, d_3-acetonitrile, toluene-d_8 and thf-d_8 that were dried (over Na/K or CaH_2), refluxed for three hours and then distilled under inert atmosphere.

Characterization methods

Mass spectrometry was performed using a Jeol AccuTOF GCX LIFDI mass spectrometer or an Agilent Q-TOF 6540 UHD ES mass spectrometer by the MS department of the University of Regensburg. The compounds were dissolved in the corresponding solvent in a glove box under N_2 atmosphere. The observed fragments were assigned according to the mass/charge (m/z) ratio and the corresponding isotope pattern. Elemental analysis (CHN) were performed by the department of central analyses of the University of Regensburg on a Vario micro cube and a MT5 micro scale device. The compounds were filled in tin capsules in a glove box under N_2 atmosphere. 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. The compounds were dissolved in a glovebox under N_2 inert gas atmosphere, placed in tip-sealed pasteur pipettes, and were rubber plugged. The measurements were conducted at room temperature and 77 K, respectively (see chapter 4.5.3.2). ^{1}H and ^{31}P NMR spectra were recorded on a Bruker Avance III HD 400 (^{1}H: 400.130 MHz, ^{31}P: 161.976 MHz) spectrometer at the NMR department of the University of Regensburg. The chemical shifts are reported in ppm relative to external TMS (^{1}H) or 85 % H_3PO_4 (^{31}P). The chemical shifts δ are given in parts per million [ppm] and coupling constants J in [Hz].

Starting materials

The compounds [$(L^3Ni)_2$tol] (**1**)[1], potassium graphite[2], P_4, AsP_3[3] and As_4[4] were prepared according to literature procedures (L^3 = [{N($C_6H_3{}^iPr_2$-2,6)C(Me)}$_2$CH]$^-$) or bought from chemical supplies and used as delivered or purified by sublimation (18-crown-6, cryptand).

4.5.1.1. Synthesis of $[(L^3Ni)_2(\mu\text{-}\eta^2,\kappa^1\text{:}\eta^2,\kappa^1\text{-}As_4)]$ (**2b**)

All preparations were performed under exclusion of light. 520 mg $[(L^3Ni)_2tol]$ (0.5 mmol) were dissolved in 50 mL of toluene and added to a freshly prepared toluene solution saturated with As_4. The mixture was stirred at room temperature for 2 hours and the colour changed from red to greenish-brown. The solvent was removed in vacuum and the brown solid was extracted with Et_2O and filtered over diatomaceous earth to remove the insoluble As_{grey}. By storing the greenish-brown solution at -30 °C, compound $[(L^3Ni)_2(\mu\text{-}\eta^2,\kappa^1\text{:}\eta^2,\kappa^1\text{-}As_4)]$ (**2b**) crystallized as dark greenish-brown blocks, suitable for X-Ray analysis.
Crystalline yield: 240 mg (0.19 mmol, 38 %)

^{1}H NMR (C_6D_6, 300 K): δ [ppm] = 7.49 (d, 8H, $^3J_{HH}$ = 8 Hz, *m*-C_6H_3), 6.10 (t, 4H, $^3J_{HH}$ = 8 Hz, *p*-C_6H_3), 3.94 (s, 2H, $C(CH_3)C\underline{H}C(CH_3)$), 3.45 (sept, 8H, $^3J_{HH}$ = 7 Hz, $C\underline{H}(CH_3)_2$), 1.30 (d, 24H, $^3J_{HH}$ = 6 Hz, $CH(C\underline{H}_3)_2$), 1.16 (d, 24H, $^3J_{HH}$ = 6 Hz, $CH(C\underline{H}_3)_2$), 0.92 (s, 12H, $C(C\underline{H}_3)CHC(C\underline{H}_3)$).

LIFDI MS (toluene): m/z (%) = 1252.30 (68.33, $[M]^+$), 1177.38 (100, $[(L^3Ni)_2(As_3)]^+$).

EA: calculated for: $C_{58}H_{82}N_4Ni_2As_4$: C: 55.63, H: 6.6, N: 4.47, found [%]: C: 56.01, H: 6.10, N: 4.49.

4.5.1.2. Synthesis of $[(L^3Ni)_2(\mu\text{-}\eta^2,\kappa^1\text{:}\eta^2,\kappa^1\text{-}AsP_3)]$ (**2c**)

All preparations were performed under exclusion of light. 50 mg $[(L^3Ni)_2tol]$ (0.05 mmol, 1 eq) and 8 mg AsP_3 (0.05 mmol, 1 eq) were dissolved in 5 mL of toluene. The mixture was stirred at room temperature for 2 hours and the colour changed from red to green. The solvent was removed in vacuum and the green solid was extracted with Et_2O and filtered over diatomaceous earth. By storing the green solution in a double Schlenk (with 1 mL of toluene at the other side) at -30 °C, compound $[(L^3Ni)_2(\mu\text{-}\eta^2,\kappa^1\text{:}\eta^2,\kappa^1\text{-}AsP_3)]$ (**2c**) crystallized as dark green needles, suitable for X-Ray analysis.

Yield: 30 mg (0.03 mmol, 23 %)

^{1}H NMR (C_6D_6, 300 K): δ [ppm] = 7.21 (d, 8H, $^3J_{HH}$ = 8 Hz, *m*-C_6H_3), 6.72 (t, 4H, $^3J_{HH}$ = 8 Hz, *p*-C_6H_3), 4.52 (s, 2H, $C(CH_3)C\underline{H}C(CH_3)$), 3.24 (sept, 8H, $^3J_{HH}$ = 7 Hz, $C\underline{H}(CH_3)_2$), 1.36 (s, 12H, $C(C\underline{H}_3)CHC(C\underline{H}_3)$), 1.26 (d, 24H, $^3J_{HH}$ = 7 Hz, $CH(C\underline{H}_3)_2$), 1.12 (d, 24H, $^3J_{HH}$ = 7 Hz, $CH(C\underline{H}_3)_2$), contaminated with NacnacH.

^{31}P{^{1}H} NMR (tol-d_8, 300 K): δ [ppm] = 226.2 (br, 1P), 125.0 (br, 2P).

LIFDI MS (toluene): m/z (%) = 1120.3 ($[M]^+$, 16.28).

4.5.1.3. Synthesis of $[(L^3Ni)_2(\mu,\eta^{3:3}\text{-}P_3)]$ (**3a**)

Route 1: 0.34 g (0.3 mmol) $[(L^3Ni)_2tol]$ (**1**) were dissolved in 100 mL hexane. To this boiling solution a solution of 50 mL hexane with P_4 (40 mg, 0.3 mmol) were added. The mixture was refluxed for three hours and the colour changed from red to green. The solvent was removed in vacuum and the compound was purified by column chromatography (SiO_2, 18 cm, Ø 4 cm, T = 25 °C). Using a mixture of hexan/toluene (4:1) as an eluent **3a** can be obtained as a green fraction. After removing the solvent in vacuum, the residue was dissolved in hexane and concentrated. After storage at + 8 °C, **3a** can be obtained as green chopsticks.

Route 2: 15 mg $[(L^3Ni)_2(\mu,\eta^{3:3}\text{-}P_4)]$ (**2a**) were refluxed in toluene for 2 hours. The conversion of **2a** to **3a** was tracked by NMR spectroscopy. (Stirring the solution at 60 °C for one hour do not lead to a conversion of **2a** to **3a**.)

Crystalline Yield: 150 mg (0.14 mmol, 44 %)

^{1}H NMR (C_6D_6, 300 K): δ [ppm] = 12.67 (b, 8H, *m*-C_6H_3), 7.97 (b, 4H, *p*-C_6H_3), 2.31 (b, 24H, $CH(C\underline{H_3})_2$), 1.79 (b, 24H, $CH(C\underline{H_3})_2$), -3.17 (b, 4H, $C\underline{H}(CH_3)_2$), -13.32 (b, 12H, $C(C\underline{H_3})CHC(C\underline{H_3})$), -25.13 (b, $C(CH_3)C\underline{H}C(CH_3)$).
^{1}H NMR (Evans-method, C_6D_6, 300 K): $\Delta\nu$ = 18.9 Hz, μ_{eff} = 2.12 μ_B, n = 1.35.

^{31}P{^{1}H} NMR (C_6D_6, 300 K): no signal detected in the range of: 600 ppm to -600 ppm.

LIFDI-MS (toluene): m/z (%) = 1043.4 (100, $[M]^+$).

4.5.1.4. Synthesis of $[(L^3Ni)_2(\mu,\eta^{3:3}\text{-}As_3)]$ (**3b**)

Route 1: All preparations were performed under exclusion of light. 490 mg $[(L^3Ni)_2tol]$ (0.47 mmol) were dissolved in 50 mL of toluene and added to a freshly prepared toluene solution saturated with As_4 at + 60 °C. The mixture was cooled to room temperature and the colour changed from red to brown. The solvent was removed in vacuum and the brown compound was purified by column chromatography (SiO2, hexane, 17 cm, Ø 4 cm). Using a mixture of hexane:toluene (4:1) as an eluent **3b** can be obtained as brown fraction. By storing the concentrated brown solution at + 8 °C, compound $[(L^3Ni)_2(\mu,\eta^{3:3}\text{-}As_3)]$ (**3b**) crystallized as brown blocks, suitable for X-Ray analysis.

Route 2: 10 mg $[(L^3Ni)_2(\mu,\eta^{3:3}\text{-}As_4)]$ (**2b**) were refluxed in toluene for 2 hours. The conversion of **2b** to **3b** was tracked by NMR spectroscopy. (Stirring the solution at 60 °C for one hour do not lead to a conversion of **2b** to **3b**.)

Crystalline Yield: 0.45 g (0.38 mmol, 81 %)

^{1}H NMR (C_6D_6, 300 K): δ [ppm] = 12.01 (b, 8H, *m*-C_6H_3), 8-6 (b, 4H, *p*-C_6H_3), 2.19 (b, 24H, CH(C$\underline{H_3}$)$_2$), 1.77 (b, 24H, CH(C$\underline{H_3}$)$_2$), -2.18 (b, 4H, C$\underline{H}$(CH$_3$)$_2$), -12.46 (b, 12H, C(C$\underline{H_3}$)CHC(C$\underline{H_3}$)), -23.31 (b, 2H, C(CH$_3$)C$\underline{H}$C(CH$_3$)).
^{1}H NMR (Evans-method, C_6D_6, 300 K): Δv = 18.8 Hz, μ_{eff} = 2.13 μ_B, n = 1.35.

LIFDI-MS (toluene): m/z (%) = 1175.2 (100, $[M]^+$).

EA: calculated for: $C_{58}H_{82}N_4Ni_2As_3$ (+ 7 % L^{3}H see NMR): C: 59.72, H: 7.09, N: 4.80, found [%]: C: 59.92, H: 7.08, N: 4.49.

4.5.1.5. Synthesis of $[K_2][(L^3Ni)_2(\mu,\eta^{2:2}\text{-}P_4)]$ (**4**)

100 mg of **1** (0.1 mmol) and 12.4 mg P_4 (0.1 mmol) were dissolved in 10 mL toluene. To this green solution was added 28.4 mg (0.21 mmol) potassium graphite. The colour changed within minutes to red and the solution was stirred for three hours. The solution was filtrated over diatomaceous earth and concentrated to 5 mL volume. By storing the solution at -30 °C, compound $[K_2][(L^3Ni)_2(\mu,\eta^{2:2}\text{-}P_4)]$ (**4**) crystallized as brown blocks, suitable for X-Ray analysis.

Crystalline Yield: 20 mg (17 %)

^{1}H NMR (C_6D_6, 300 K): δ [ppm] = 6.9 (d, 4H, $^3J_{HH}$ = 7 Hz, *m*-C_6H_3), 6.67 (d, 4H, $^3J_{HH}$ = 7 Hz, *m*-C_6H_3), 6.43 (t, 4H, $^3J_{HH}$ = 7.5 Hz, *p*-C_6H_3), 5.31 (sept, 4H, $^3J_{HH}$ = 7 Hz, C$\underline{H}$(CH$_3$)$_2$), 5.07 (s, 2H, C(CH$_3$)C$\underline{H}$C(CH$_3$)), 3.84 (sept, 4H, $^3J_{HH}$ = 7 Hz, C$\underline{H}$(CH$_3$)$_2$), 1.97 (d, 12H, $^3J_{HH}$ = 7 Hz, CH(C$\underline{H_3}$)$_2$), 1.46 (s, 12H, C(C$\underline{H_3}$)CHC(C$\underline{H_3}$)), 1.43 (d, 12H, $^3J_{HH}$ = 7 Hz, CH(C$\underline{H_3}$)$_2$), 1.05 (d, 12H, $^3J_{HH}$ = 7 Hz, CH(C$\underline{H_3}$)$_2$), 1.01 (d, 12H, $^3J_{HH}$ = 7 Hz, CH(C$\underline{H_3}$)$_2$).

^{31}P{^{1}H} NMR (C_6D_6, 300 K): δ [ppm] = 80.3 (s).

EA calculated for: $C_{58}H_{82}N_4Ni_2K_2P_4 \cdot C_7H_8$: C: 62.61, H: 7.28; N: 4.49, found [%]: C: 62.34, H: 7.27, N: 4.22.

4.5.1.6. Synthesis of $[(K@18\text{-crown-6})(thf)_3][(L^3Ni)_2(\mu,\eta^{3:3}\text{-}P_3)]$ (**5a**)

50 mg of $[(L^3Ni)_2(\mu,\eta^{3:3}\text{-}P_3)]$ (**3a**, 0.05 mmol, 1 eq) and 7 mg (0.05 mmol, 1.1 eq) potassium graphite were dissolved in 5 mL of toluene, the solution turned greenish-brown. The solution was stirred for 3 hours and then filtered over diatomaceous earth and 13 mg (0.05 mmol, 1 eq) 18-crown-6 were added. The solvent was removed in vacuum and the brown residue was taken up in 3 mL thf. The solution was layered under 10 mL hexane and stored at -30 °C. Compound $[(K@18\text{-crown-6})(thf)_3][(L^3Ni)_2(\mu,\eta^{3:3}\text{-}P_3)]$ (**5a**) crystallized as brown plates, suitable for X-Ray analysis.

Crystalline Yield: 20 mg (0.01 mmol, 27 %)

^{1}H NMR (thf-d_8, 300 K): δ [ppm] = 7.12 (br, 7H), 6.24 (br, 3H), 3.60 (br, thf-coordinated (8H) + 18-c-6 (24H)), 1.77 (thf-coordinated, 8H), 1.22 (br, 24H, CH*Me*Me), 0.98 (br, 24H, CHMe*Me*), 0.59 (br, 8H, C*H*MeMe).

Compound **5a** show broad signals in the ^{1}H NMR spectrum at room temperature and also at 193 K, this is due to dynamic behavior of **5a**, a paramagnetic nature was excluded by Evans-NMR and EPR spectroscopy.

^{1}H NMR (Evans-method, thf-d_8, 300 K): no signal shift detected.

EPR: silent at room temperature and 77 K.

^{31}P{^{1}H} NMR (thf-d_8, 300 K): no signal detected in the range of: 500 ppm to -600 ppm.

^{31}P{^{1}H} NMR (thf-d_8, 193 K): -268.4 ppm (s).

ESI-MS (CH_3CN): m/z = 1045.6 (88, $[M]^-$), 555.2 (100, $[C_{33}H_{47}N_4Ni]^-$), 535.2 (46, $[C_{29}H_{41}N_2NiP_2]^-$), 507.2 (16, $[C_{29}H_{41}N_2NiP]^-$), 303.0 (100, $[K@18\text{-crown-6}]^+$).

4.5.1.7. Synthesis of $[(K@18\text{-crown-6})(thf)_3][(L^3Ni)_2(\mu,\eta^{3:3}\text{-}As_3)]$ (**5b**)

All manipulations were performed under exclusion of light.

Route 1: 50 mg $[(L^3Ni)_2(\mu,\eta^{3:3}\text{-}As_3)]$ (**3b**, 0.04 mmol, 1 eq) and 6 mg (0.04 mmol, 1 eq) potassium graphite were dissolved in 5 mL of toluene. The brown solution was stirred for 3 hours and then filtered over diatomaceous earth and 11.3 mg (0.04 mmol, 1 eq) 18-crown-6 were added. The solvent was removed in vacuum and the brown residue was taken up in thf. The solution was layered under 10 mL hexane and stored at -30 °C. Compound $[(K@18\text{-crown-6})(thf)_3][(L^3Ni)_2(\mu,\eta^{3:3}\text{-}As_3)]$ (**5b**) crystallized as brown needles, suitable for X-Ray analysis.

Crystalline Yields: 53 mg (0.02 mmol, 53 %)

Route 2: 350 mg $[K_2][(L^3Ni)_2(\mu,\eta^{1:1}\text{-}N_2)]$ (**6**, 0.3 mmol) was dissolved in 25 mL of toluene and added to a freshly prepared solution of yellow arsenic in toluene. The reaction mixture was stirred at room temperature for 1 hour. The solvent was removed in vacuum and the brown residue was taken up in thf. The solution was filtered over diatomaceous earth to remove the insoluble As_{grey}. 180 mg (0.6 mmol) 18-crown-6 were added. By storing the brown solution at -30 °C, compound $[(K@18\text{-crown-6})(thf)_3][(L^3Ni)_2(\mu,\eta^{3:3}\text{-}As_3)]$ (**5b**) crystallized as brown blocks, suitable for X-Ray analysis.

Crystalline Yields: 150 mg (0.09 mmol, 30 %)

^{1}H NMR (thf-d_8, 300 K): δ [ppm] = 6.84 (d, 8H, $^3J_{HH}$ = 8 Hz, *m*-C_6H_3), 6.73 (t, 4H, $^3J_{HH}$ = 8 Hz, *p*-C_6H_3), 4.31 (s, 2H, $C(CH_3)C\underline{H}C(CH_3)$), 3.63 (s, 18-crown-6), 3.47 (sept, 8H,

C*H*$(CH_3)_2$), 1.77 (thf), 1.28 (s, 12H, C(C*H*$_3$)CHC(C*H*$_3$)), 1.25 (d, 24H, CH(C*H*$_3$)$_2$), 0.94 (d, 24H, CH(C*H*$_3$)$_2$).

EA calculated for: $[C_{58}H_{82}N_4Ni_2As_3][K@(C_{12}H_{24}O_6)(C_4H_8O)_{3.5}]$: C: 58.21, H: 7.79; N: 3.23, found [%]: C: 58.24, H: 7.68, N: 3.38.

4.5.1.8. Synthesis of $[K_2][(L^3Ni)_2(\mu,\eta^{1:1}\text{-}N_2)]$ (**6**)

All preparations were performed under N_2 gas atmosphere. In a 250 mL round flask 3.0 g L^3H (7.2 mmol, 1 eq) in toluene (30 mL) were cooled to 0 °C and 4.5 mL ^{n}BuLi (7.17 mmol, 1 eq, 1.6 M in ^{n}hexane) were added. The solution was stirred at r.t. over night. The solution was added to a suspension of $NiBr_2 \cdot$ DME (2.21 g, 7.17 mmol, 1 eq.) in toluene (20 mL) under stirring and heated to reflux for 24 h. This solution was added to a suspension of KC_8 (4.36 g, 32.3 mmol, 4.5 eq.) in toluene. At room temperature gaseous N_2 was bubbled trough the reaction mixture for 20 minutes. The colour changed to deep purple and the reaction mixture was stirred over night. After filtration over diatomaceous earth the solvent was removed in vacuum and redissolved in hexane for crystallization. By storing the solution at -30 °C, compound $[K_2][(L^3Ni)_2(\mu,\eta^{1:1}\text{-}N_2)]$ (**6**) crystallized as dark purple needles, suitable for X-Ray analysis.

Crystalline Yield: 1.8 g (3.6 mmol, 47 %)

^{1}H NMR (C_6D_6, 300 K): δ = 6.83 (m, 12H, C_6H_3), 4.69 (s, 2H, C(CH_3)C*H*C(CH_3)), 3.67 (sept, 8H, $^3J_{HH}$ = 7 Hz, C*H*$(CH_3)_2$), 1.51 (s, 12H, C(C*H*$_3$)CHC(C*H*$_3$)), 1.33 (d, 24H, $^3J_{HH}$ = 7 Hz, CH(C*H*$_3$)$_2$), 1.15 (d, 24H, $^3J_{HH}$ = 7 Hz, CH(C*H*$_3$)$_2$).

EA calculated for: $C_{58}H_{82}N_6Ni_2K_2$: C: 65.79, H: 7.81, N: 7.94, found [%]: C: 65.48, H: 8.19, N: 7.53.

Raman: ν(NN) = 1572 cm^{-1}.

4.5.1.9. Synthesis of $[(K@18\text{-crown-6})(thf)_2][L^3Ni(\eta^{1:1}\text{-}P_4)]$ (**7a**)

A solution of 25 mg (0.09 mmol) 18-crown-6 in thf was added to a stirred solution of **6** (50 mg, 0.05 mmol). To the red solution was added 12 mg (0.09 mmol) white phosphorus and the colour changed from red to yellow-red. The solution was filtrated over diatomaceous earth and was reduced in vacuum. The concentrated solution was layered under hexane. Compound $[(K@18\text{-crown-6})(thf)_2][L^3Ni(\eta^{1:1}\text{-}P_4)]$ (**7a**) crystallized as orange blocks, suitable for X-Ray analysis at -30 °C.

Crystalline Yield: 42 mg (0.04 mmol, 42 %)

^{1}H NMR (thf-d_8, 300 K): δ [ppm] = 6.93 (d, 4H, $^3J_{HH}$ = 8 Hz, *p*-C_6H_3), 6.70 (t, 2H, $^3J_{HH}$ = 8 Hz, *m*-C_6H_3), 4.44 (s, 1H, C(CH_3)C*H*C(CH_3)), 3.82 (sept, 4H, $^3J_{HH}$ = 7 Hz, C*H*(CH_3)$_2$), 3.62 (thf), 3.56 (s, 24H, 18-crown-6), 1.78 (thf), 1.55 (d, 12H, $^3J_{HH}$ = 7 Hz, CH(C*H*$_3$)$_2$), 1.39 (s, 6H, C(C*H*$_3$)CHC(C*H*$_3$)), 1.12 (d, 12H, $^3J_{HH}$ = 7 Hz, CH(C*H*$_3$)$_2$).

^{31}P{^{1}H} NMR (thf-d_8, 300 K): δ [ppm] = -212.9 (t, 2P, $^1J_{PP}$ = 132 Hz), -378,3 (t, 2P, $^1J_{PP}$ = 132 Hz).

EA calculated for: $C_{49}H_{81}N_2NiKO_8P_4$: C: 56.16, H: 7.79, N: 2.67; found [%]: C: 55.75, H: 7.65, N: 2.47.

4.5.1.10. Synthesis of [(K@X)(thf)$_2$][L^{3}Ni(η$^{1:1}$-As_4)] (**7b**) (X = 18-crown-6, cryptand)

All manipulations were performed under exclusion of light. A solution of 200 mg (0.2 mmol) **6** and 71.1 mg cryptand/ 100 mg 18-crown-6 in toluene were added to a freshly prepared solution of As_4 in toluene. The solution was stirred for 2 hours at room temperature and the colour changed to reddish-brown. The solvent was evaporated by vacuum and the crude product was taken up in thf, filtrated over diatomaceous earth and concentrated to 7 mL. The concentrated solution was layered under hexane. Compound [(K@X)(thf)$_2$][L^{3}Ni(η$^{1:1}$-As_4)] (**7b**) crystallized as red-brownish plates/ needles, suitable for X-Ray analysis at -30 °C.

Crystallin yield: 185 mg (X = cryptand, 0.16 mmol, 39 %)

^{1}H NMR (thf-d_8, 300 K): δ [ppm] = 6.95 (d, 4H, $^3J_{HH}$ = 8 Hz, *p*-C_6H_3), 6.67 (t, 2H, $^3J_{HH}$ = 8 Hz, *m*-C_6H_3), 4.43 (s, 1H, C(CH_3)C*H*C(CH_3)), 3.94 (sept, 4H, $^3J_{HH}$ = 7 Hz, C*H*(CH_3)$_2$), 3.61 (thf, 3H), 3.55 (s, 12H, cryptand), 3.50 (m, 12H, cryptand), 2.51 (m, 12H, cryptand), 1.77 (thf, 3H), 1.58 (d, 12H, $^3J_{HH}$ = 7 Hz, CH(C*H*$_3$)$_2$), 1.35 (s, 6H, C(C*H*$_3$)CHC(C*H*$_3$)), 1.11 (d, 12H, $^3J_{HH}$ = 7 Hz, CH(C*H*$_3$)$_2$).

EA calculated for: $C_{51}H_{85}N_4NiKO_7As_4$ (X = cryptand): C: 48.47, H: 6.78, N: 4.43; found [%]: C: 48.57, H: 6.72, N: 4.30.

Crystallin yield: 90 mg (X = 18-crown-6, 0.08 mmol, 19 %)

^{1}H NMR (thf-d_8, 300 K): δ [ppm] = 6.96 (d, 4H, $^3J_{HH}$ = 8 Hz, *p*-C_6H_3), 6.66 (t, 2H, $^3J_{HH}$ = 8 Hz, *m*-C_6H_3), 4.43 (s, 1H, C(CH_3)C*H*C(CH_3)), 3.94 (sept, 4H, $^3J_{HH}$ = 7 Hz, C*H*(CH_3)$_2$), 3.62 (thf), 3.58 (s, 24H, 18-crown-6 + thf), 1.78 (thf), 1.55 (d, 12H, $^3J_{HH}$ = 7 Hz, CH(C*H*$_3$)$_2$), 1.39 (s, 6H, C(C*H*$_3$)CHC(C*H*$_3$)), 1.12 (d, 12H, $^3J_{HH}$ = 7 Hz, CH(C*H*$_3$)$_2$).

4.5.2. NMR studies

4.5.2.1. [$(L^3Ni)_2(\mu\text{-}\eta^2,\kappa^1\text{:}\eta^2,\kappa^1\text{-}As_4)$] (**2b**)

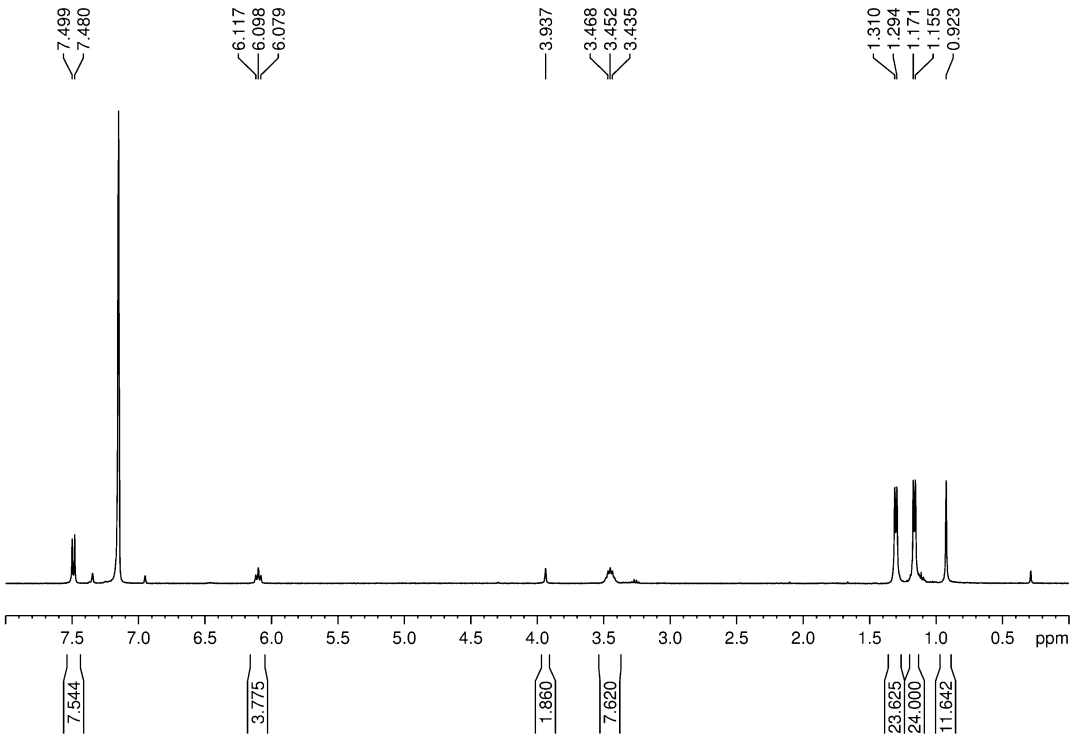


Figure S4.1. ^1H NMR spectrum of **2b** in C_6D_6 at room temperature.

4.5.2.2. [$(L^3Ni)_2(\mu\text{-}\eta^2,\kappa^1\text{:}\eta^2,\kappa^1\text{-}AsP_3)$] (**2c**)

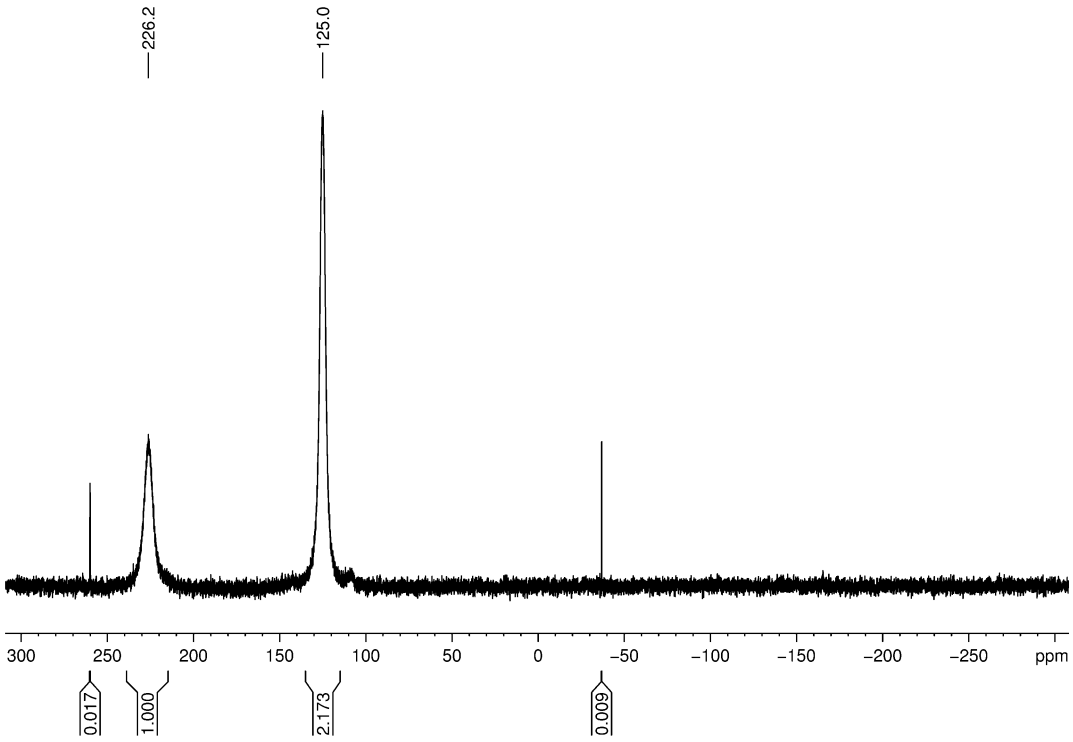


Figure S4.2. $^{31}P\{^1H\}$ NMR of the reaction solution of **2c** in toluene-d_8 at room temperature.

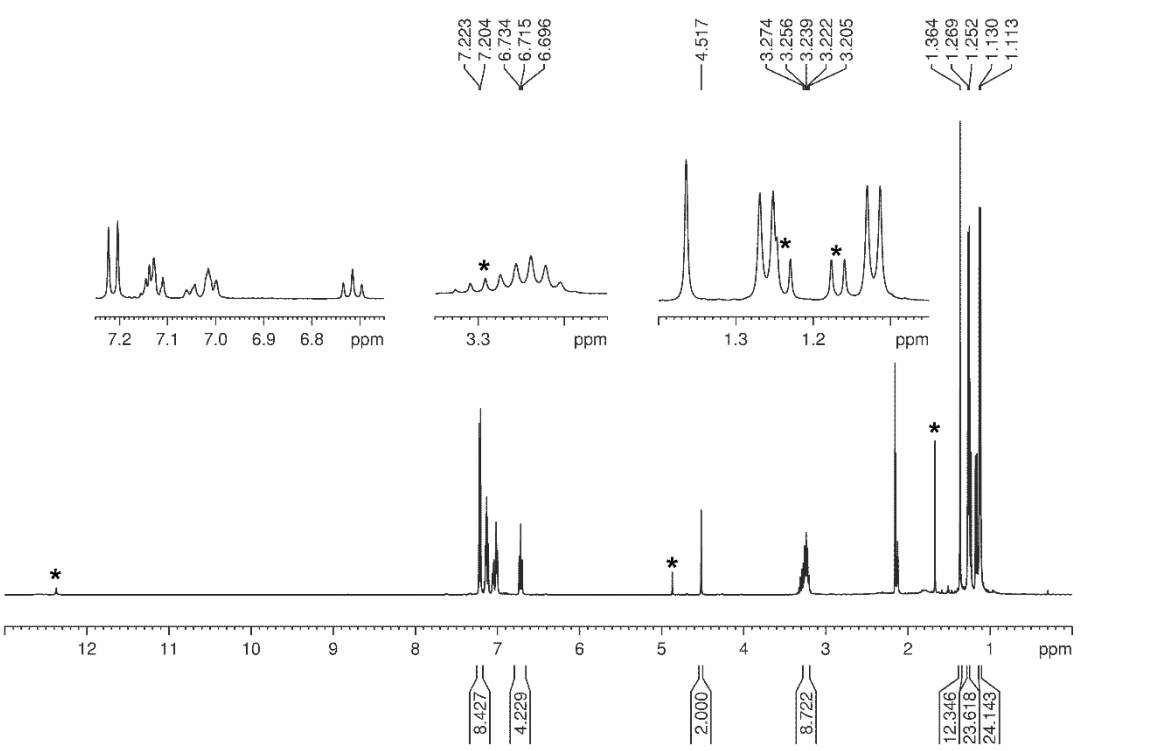


Figure S4.3. ^{1}H NMR of the reaction solution of **2c** in toluene-d_8 at room temperature (* = L^3H).

4.5.2.3. [(L^3Ni)$_2$(μ,η$^{3:3}$-P_3)] (**3a**)

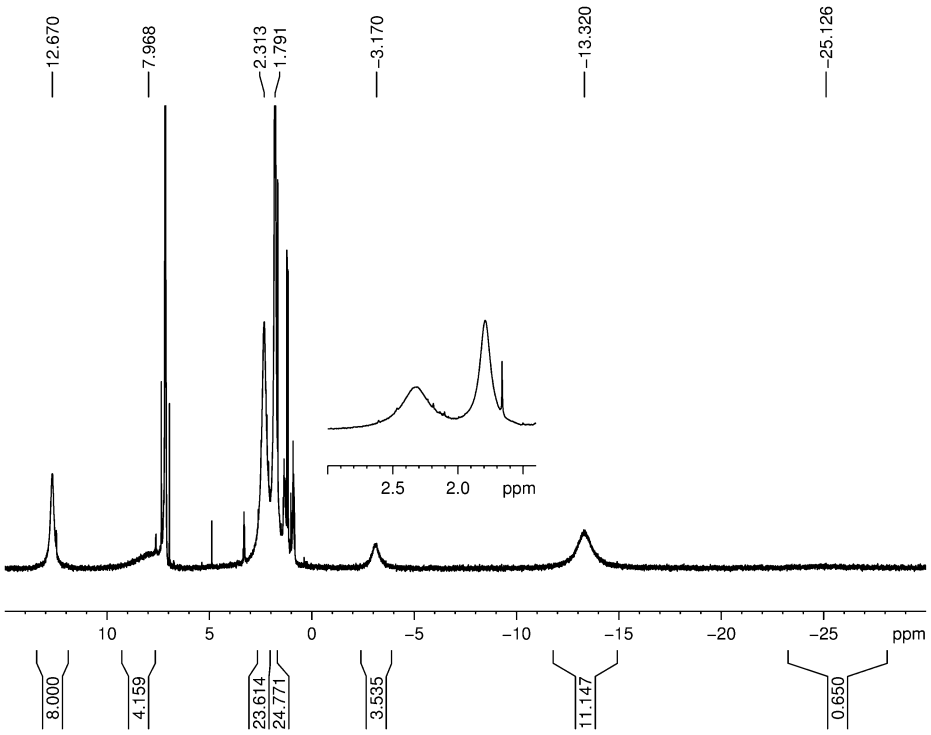


Figure S4.4. ^{1}H NMR spectrum of **3a** in C_6D_6 at room temperature.

4.5.2.4. $[(L^3Ni)_2(\mu,\eta^{3:3}\text{-}As_3)]$ (**3b**)

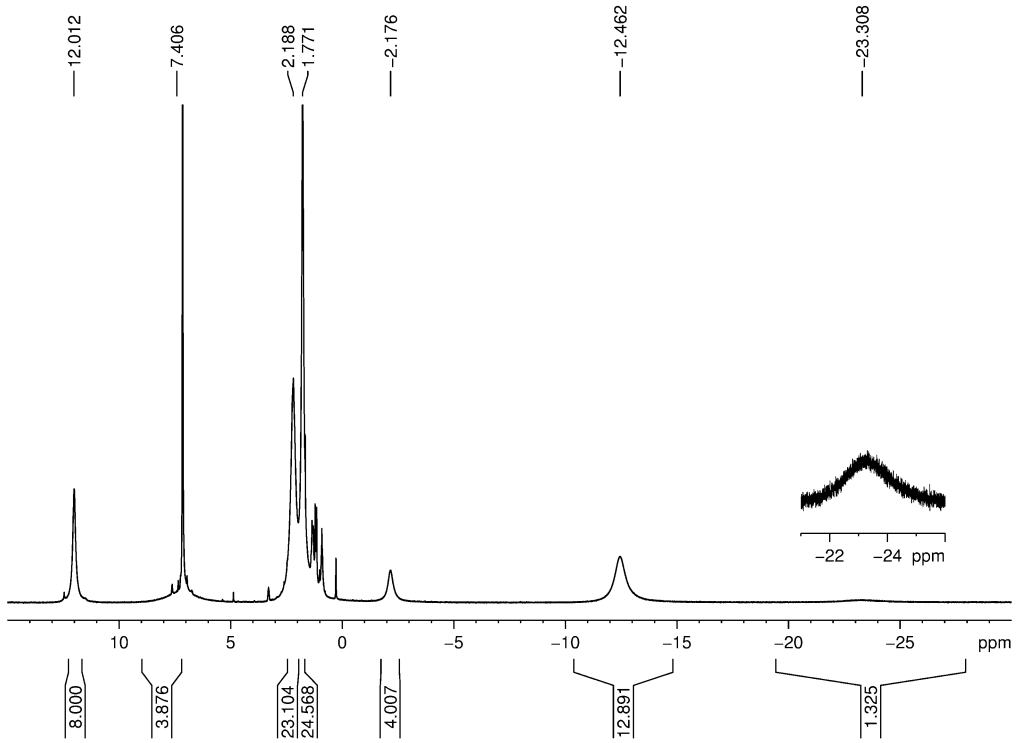


Figure S4.5. ^{1}H NMR spectrum of **3b** in C_6D_6 at room temperature (* = L^3H).

4.5.2.5. $[K_2][(L^3Ni)_2(\mu,\eta^{2:2}\text{-}P_4)]$ (**4**)

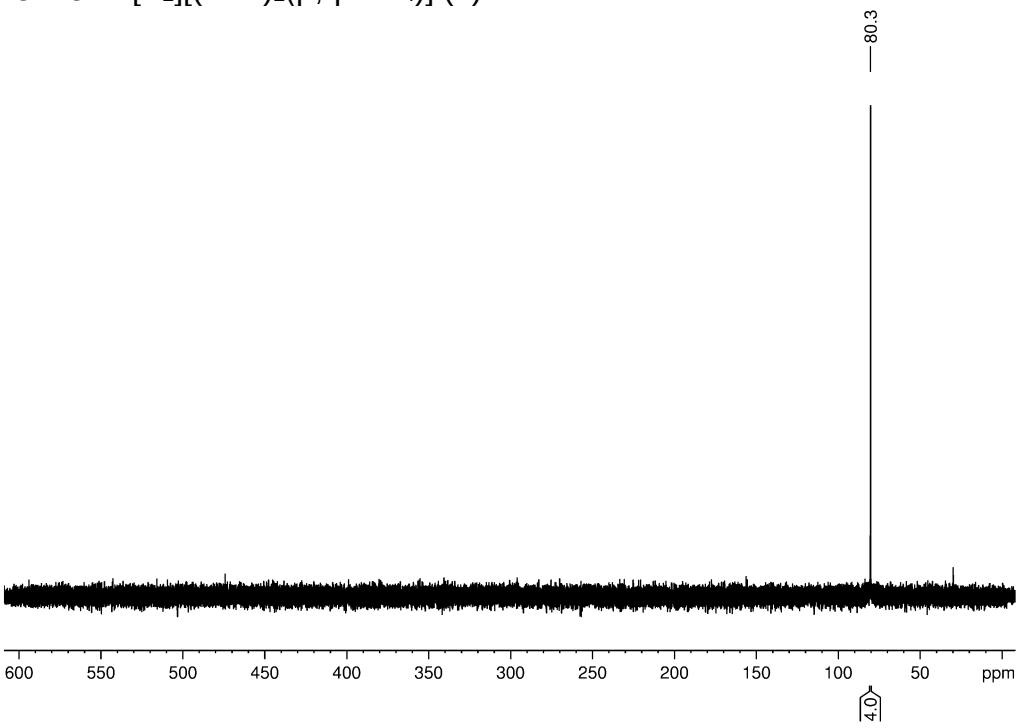


Figure S4.6. ^{31}P{^{1}H} NMR spectrum of **4** in C_6D_6 at room temperature.

4.5.2.6. [K@18-crown-6(thf)$_3$][(L^3Ni)$_2$($\eta^{3:3}$-P_3)] (**5a**)

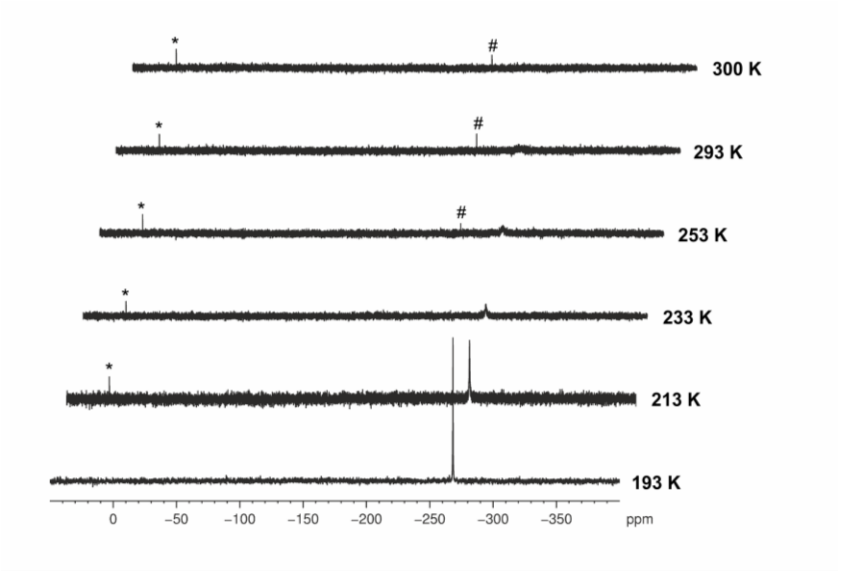


Figure S4.7. VT $^{31}P\{^1H\}$ NMR spectra of crystals of **5a** at different temperatures in thf-d_8. Crystals were disolved at -80 °C and the NMR spectra are measured from 193 K to room temperature. Afterwards also another spectrum at 193 K was recorded. * decomposition of **5a** during warming.

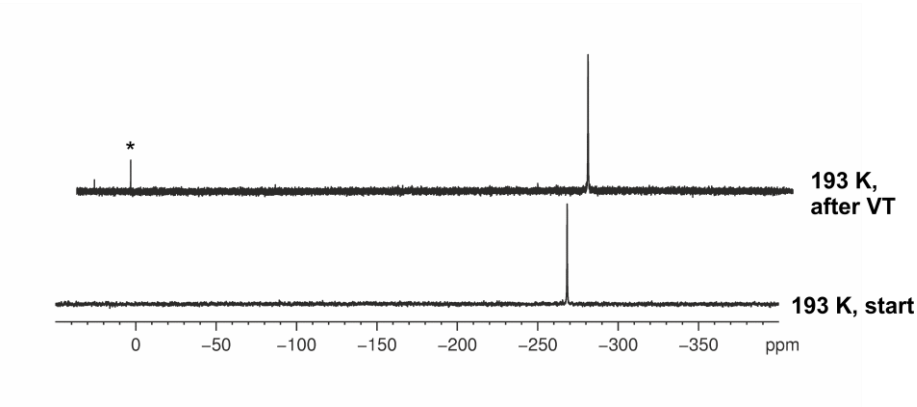


Figure S4.8. $^{31}P\{^1H\}$ NMR spectra of **5a** in thf-d_8 at 193 K before and after the VT NMR measurment.
* irreversible decomposition of **5a** during warming.

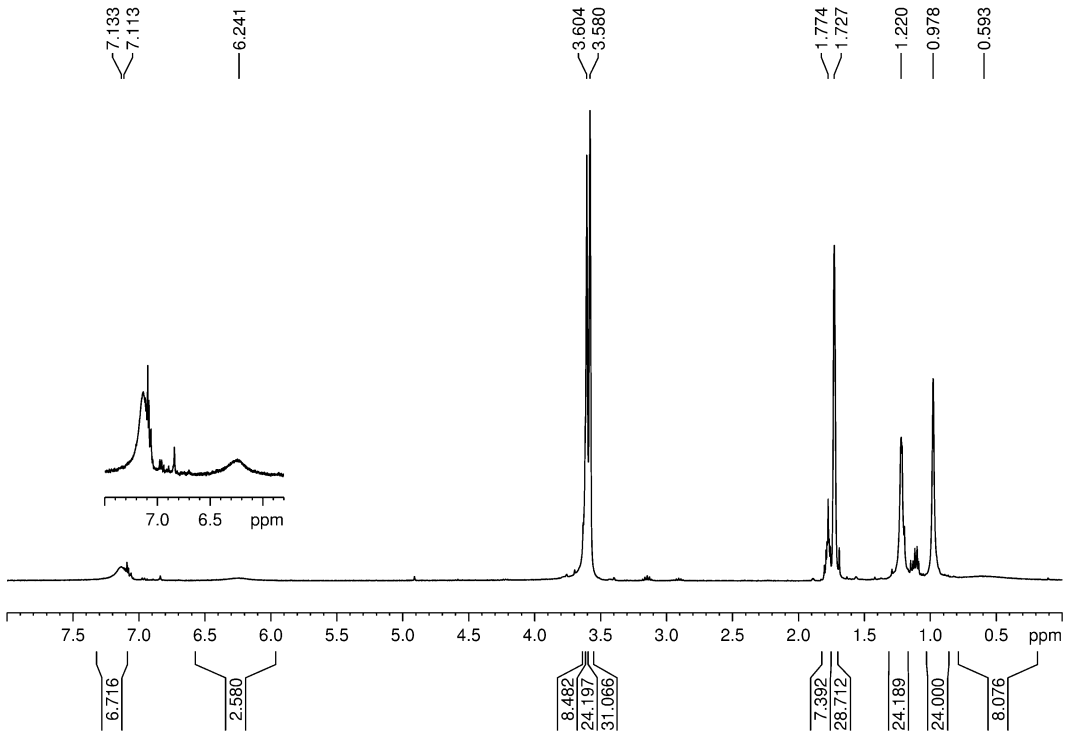


Figure S4.9. ^{1}H NMR spectrum of **5a** in thf-d_8 at room temperature.

4.5.2.7. [K@18-crown-6(thf)$_3$][(L^{3}Ni)$_2$($\eta^{3:3}$-As$_3$)] (**5b**)

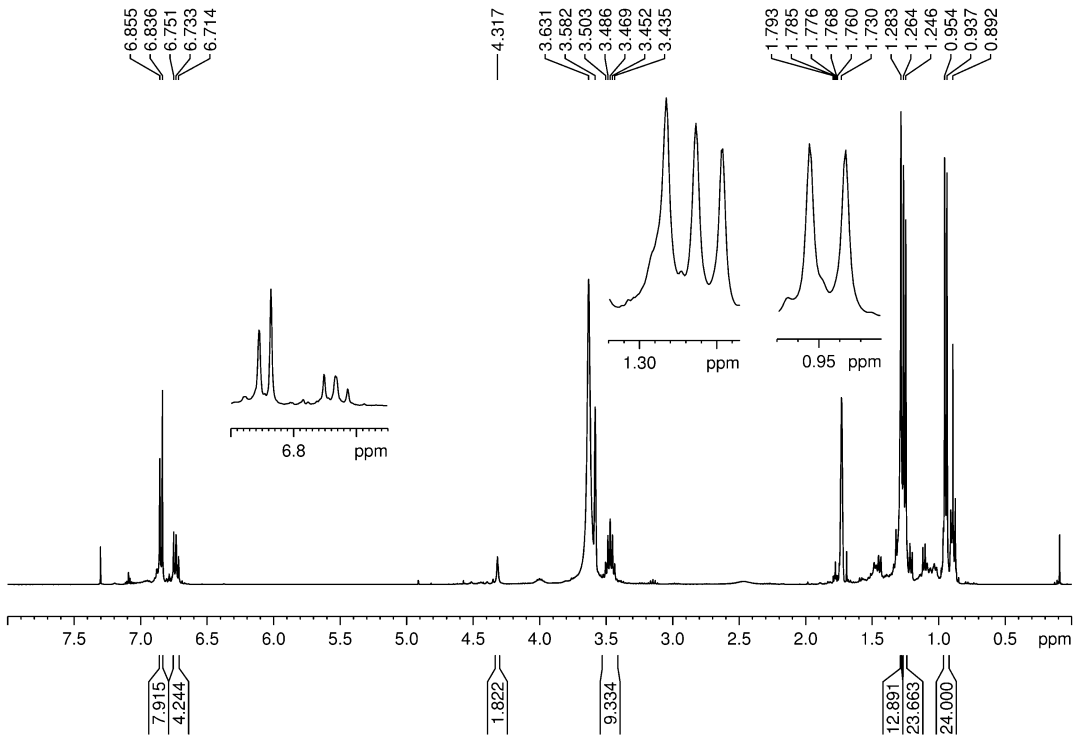


Figure S4.10. ^{1}H NMR spectrum of **5b** in thf-d_8 at room temperature.

4.5.2.8. $[K_2][(L^3Ni)_2(\mu,\eta^{1:1}\text{-}N_2)]$ (**6**)

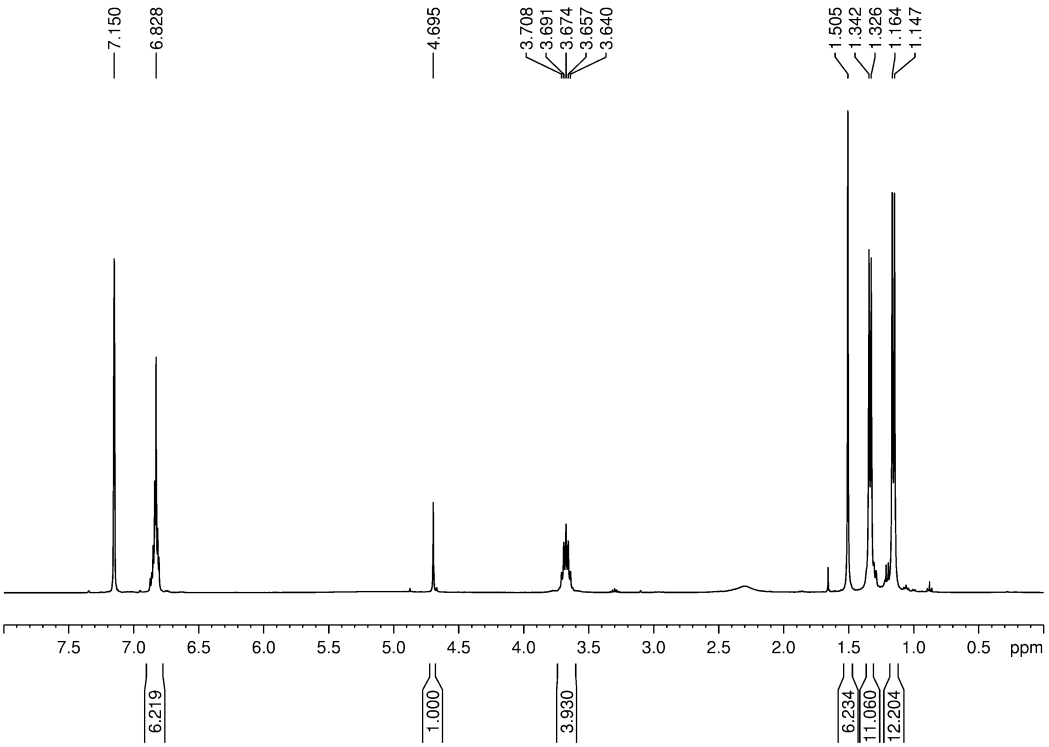


Figure S4.11. ^{1}H NMR spectrum of **6** in C_6D_6 at room temperature.

4.5.2.9. $[(K@18\text{-crown-6})(thf)_2)][L^3Ni(\eta^{1:1}\text{-}P_4)]$ (**7a**)

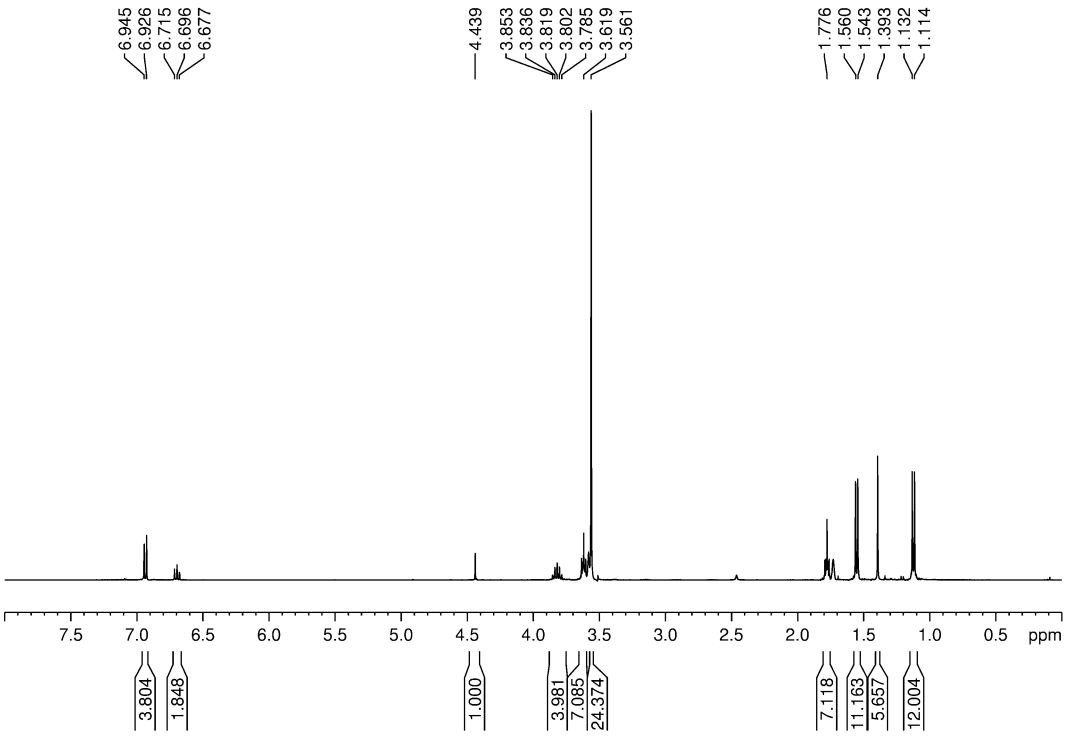


Figure S4.12. ^{1}H NMR spectrum of **7a** in thf-d_8 at room temperature.

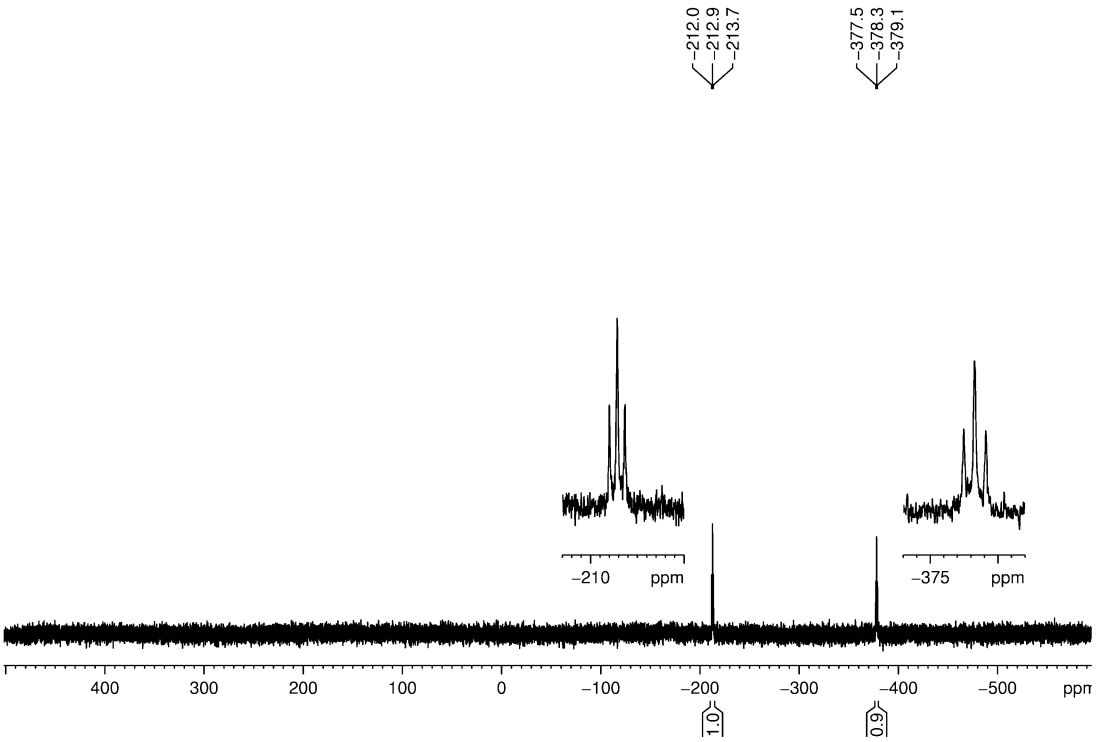


Figure S4.13. $^{31}P\{^1H\}$ NMR spectrum of **7a** in thf-d_8 at room temperature.

4.5.2.10. [(K@cryptand)(thf)][$L^3Ni(\eta^{1:1}$-$As_4)$] (**7b**)

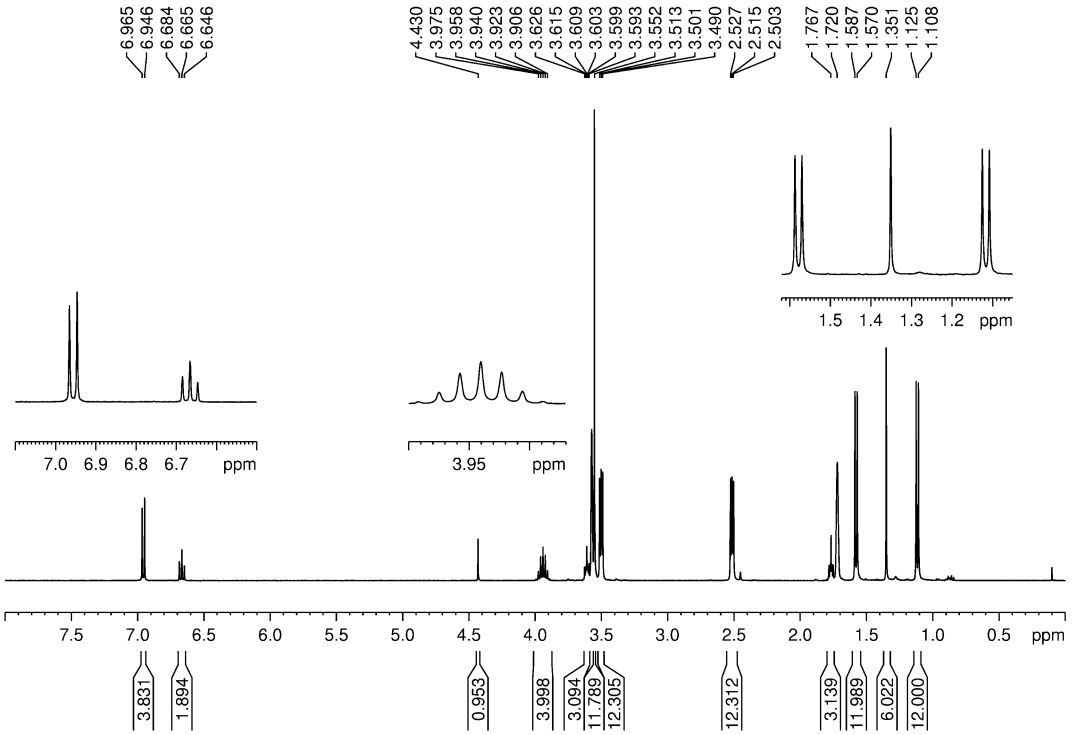


Figure S4.14. ^1H NMR spectrum of **7b** (cryptand) in thf-d_8 at room temperature.

4.5.2.11. [(K@18-crown-6)(thf)$_2$)][L^{3}Ni($\eta^{1:1}$-As$_4$)] (**7b**)

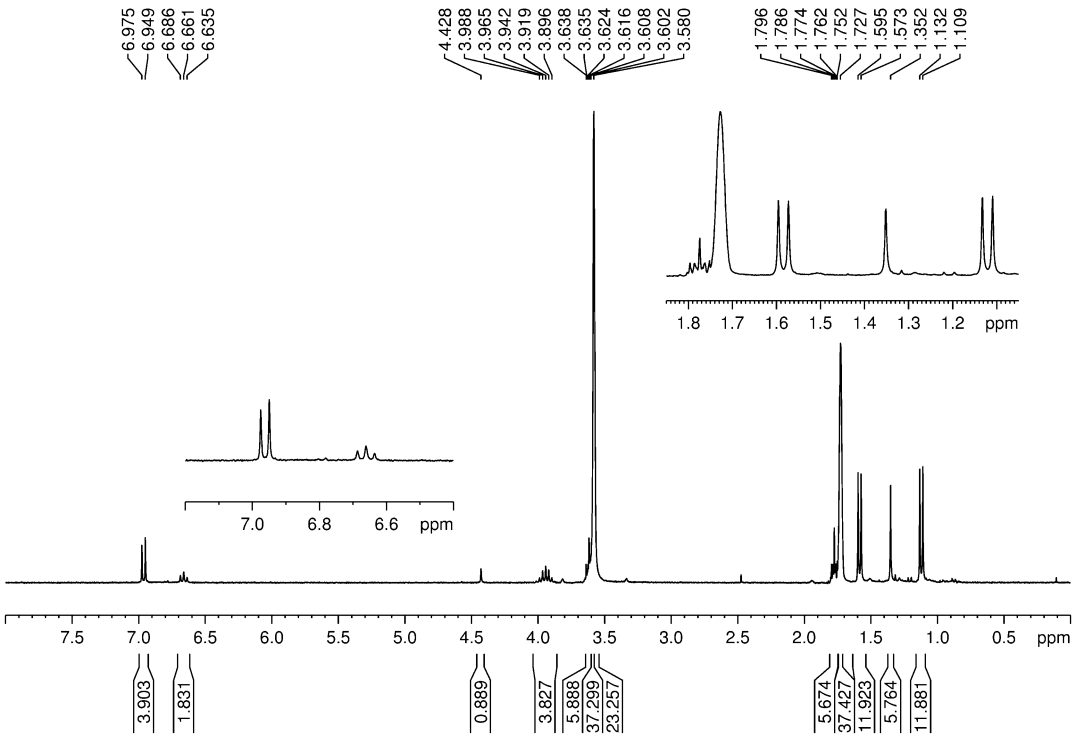


Figure S4.15. ^{1}H NMR spectrum of **7b** (18-crown-6) in thf-d_8 at room temperature.

4.5.3. Magnetic Measurements in Solution

4.5.3.1. Evans Methode

The effective magnetic moment (μ_{eff}) of paramagnetic compounds were determined by the Evans method.[5] The Evans method is based on the chemical shift difference of the residual solvent peak between the inner tube containing a solution of the paramagnetic species and the outer tube, which contains the pure deuterated solvent. The ^{1}H NMR spectra are recorded at room temperature[6] on a Bruker Avance III HD 400 (^{1}H: 400.13 MHz) spectrometer.

The molar paramagnetic susceptibility χ_P was obtained from the measured molar magnetic susceptibility χ_M after the correction for diamagnetic contribution χ_D according to equation (*1*).[7] The magnetic susceptibility χ_M and the effective magnetic moment μ_{eff} of the paramagnetic compounds was determined according, to equation (*2*)[6] and (*3*)[7].

$$\boldsymbol{\chi_P = \chi_M - \chi_D} \qquad (1)$$

$$\boldsymbol{\chi_M = \frac{3000 * \Delta\nu}{4\pi * \nu_0 * c}} \qquad (2)$$

$$\boldsymbol{\mu_{eff} = \sqrt{8 \cdot T \cdot \chi_p}} \qquad (3)$$

Finally, the number of unpaired electrons is calculated by the 'spin-only' formula[8] (equation 4):

$$\mathbf{n = -1 + \sqrt{\mu_{eff}^2 + 1}} \qquad (4)$$

Where

χ_M is the measured susceptibility of the sample in emu · mol^{-1},

χ_P is the molar paramagnetic susceptibility of the sample in emu · mol^{-1},

χ_D is the molar diamagnetic susceptibility of the sample in emu · mol^{-1},

$\Delta\nu$ is the chemical shift difference between the solvent in presence of paramagnetic solute and pure solvent in [Hz],

ν_0 is the measuring frequency of the NMR spectrometer [Hz],

c is the concentration of paramagnetic sample in mol · L^{-1},

T is the absolute temperature in K,

μ_{eff} is the effective magnetic moment in μ_B, and

n is the number of unpaired electrons.

4.5.3.2. EPR (Electrone Paramagnetic Resonance) measurements

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. The compounds were dissolved in a glovebox under N_2 inert gas atmosphere, placed in tip-sealed pasteur pipettes, and were rubber plugged. The measurements were conducted at room temperature and 77 K, respectively. With EPR, a magnetic field is applied to the sample, which interacts with the unpaired electrons. The simulation has been performed using the EasySpin[9] program.

Table S4.1. Experimental and fitted parameters used for the simulation of the X-band EPR spectrum of **3a**, see Figure 4.1 (Paper).

SysP.g = [2.254 2.108 2.063]	*Exp.Range = [284.2615 354.3425]*
SysP.lw = [0.5]	*Exp.nPoints 4096*
SysP.A = [27 88 80; 59.8 55 80]	*Exp.mwFreq = 9.440920*
SysP.HStrain = [70 80 55]	*Exp.Temperature= 77*
SysP.Astrain [150 250 78]	*Exp.ModAmp = 0.05*

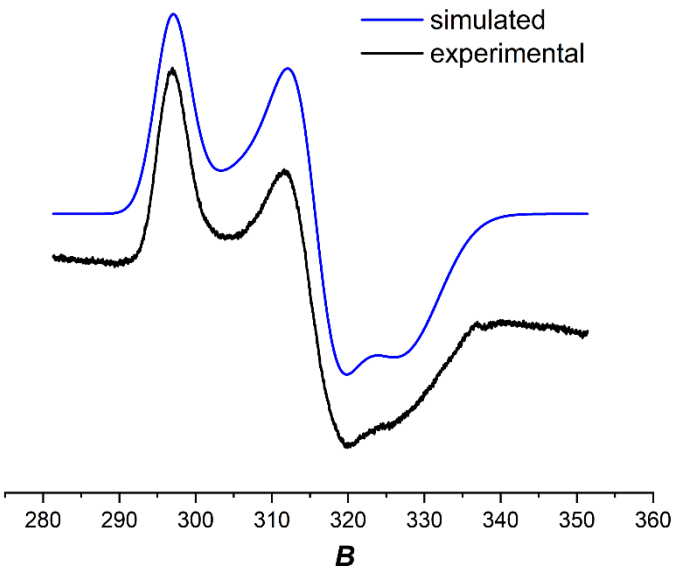


Figure S4.16. EPR spectrum of **3b** in toluol solution (liquid nitrogen (black), simulation (blue)).

Table S4.2. Experimental and fitted parameters used for the simulation of the X-band EPR spectrum of **3b**.

Sys.g = [2.2705 2.135 2.055]	*Exp.Range = [281.3095 351.3905]*
Sys.lw = [2.5]	*Exp.nPoints 4096*
Sys.HStrain = [150 180 300]	*Exp.mwFreq = 9.440920*
	Exp.Temperature= 77
	Exp.ModAmp = 0.05

4.5.4. Cyclic voltammetry (CV)

All cyclic voltammetry measurements were performed in thf at 300 K in a three electrode setup, with a glassy carbon electrode (working electrode), an Ag-wire (pseudo-reference electrode) an a Pt (auxiliary electrode), in combination with a Methrom Autolab PGSTAT101 potentiostat. Bu_4NPF_6 was used as supporting electrolyte and all cyclic voltammograms are referenced against Cp_2Fe/Cp_2Fe^+ redox couple.

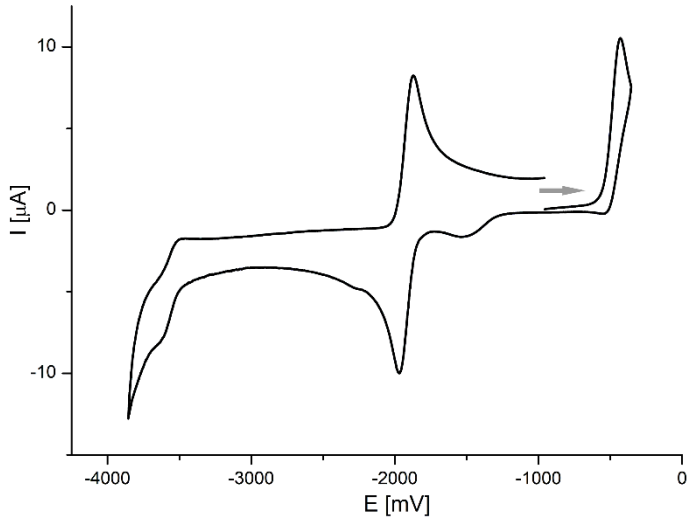


Figure S4.17. Cyclic voltammogram of **3b** in THF at 100 mV/s scan rate.

4.5.5. Details on single crystal X-ray structure analysis

The X-ray diffraction experiments were performed on either a Gemini Ultra diffractometer (Oxford diffraction) equipped with a Ruby CCD detector (**4**), on a SuperNova diffractometer (Agilent Technologies) equipped with an Atlas CCD detector (**3a**, **3b**, **6**), on a SuperNova Dualflex diffractometer (Rigaku) equipped with a TitanS2 CCD detector (**2b**, **7a**), or a XtaLAB Synergy R, DW system (Rigaku) equipped with a HyPix Arc 150° detector (**2c**, **5a**, **5b**, **7b**). All measurements were performed at 123 K or 100 K, respectively. Data collection and reduction were performed with CrysAlisPro[10] (Version 171.37.33, 2014 (**3a**, **3b**, **4**, **6**), 171.41.88a, 2020 (**2b**, **5a**, **5b**, **7a**, **7b**), 171.41.90a, 2020 (**2c**)). For all compounds a gaussian absorption correction based on gaussian integration over a multifaceted crystal model was applied. Using Olex2,[11] were the structures solved by direct methods with ShelXT[12] and refined by full-matrix least-squares method against F^2 in anisotropic approximation using ShelXL[13]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined in calculated positions using riding on pivot atom model.

Figures were created with Olex2.[11]

CCDC-2109927 (**2b**), CCDC-2109928 (**2c**), CCDC-2109929 (**3a**), CCDC-2109930 (**3b**), CCDC-2109931 (**4**), CCDC-2109932 (**5a**), CCDC-2109933 (**5b**), CCDC-2109934(**6**), CCDC-2109935 (**7a**), CCDC-2109936 (**7b**) 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).

4.5.5.1. $[(L^3Ni)_2(\mu\text{-}\eta^2,\kappa^1\text{:}\eta^2,\kappa^1\text{-}As_4)]$ (**2b**)

Compound **2b** crystallized from a concentrated solution in Et_2O at -30 °C in the monoclinic space group *P2₁/c*. The asymmetric unit contains one molecule of **2b** and 0.5 molecules of Et_2O. The structure in the solid state is given in Figure S4.18.

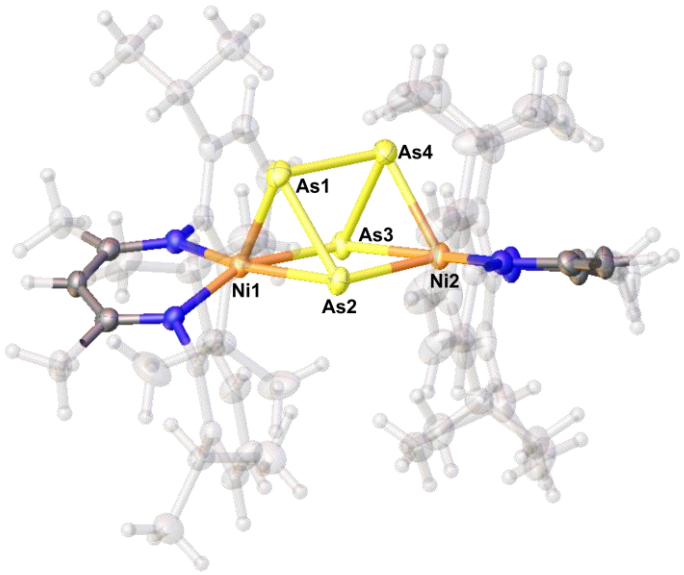


Figure S4.18. Molecular structure of **2b** in solid state. Solvent molecules are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Ni1-As1 2.3111(7), Ni1-As2 2.4606(6), Ni1-As3 2.3244(6), Ni2-As2 2.3308(6), Ni2-As3 2.4565(6), Ni2-As4 2.3169(6), As1-As2 2.4115(5), As1-As4 2.3917(5), As3-As4 2.4141(5), As2···As3 2.7192(5), Ni1···Ni2 3.93952(3), Ni1-As2-Ni2 110.58(2), Ni1-As3-Ni2 110.95(2), As2-Ni2-As3 69.166(18), As2-Ni1-As3 69.193(18), Ni1-As1-As4 101.90(2), As1-As4-As376.930(17), As4-As3-Ni1 100.83(2), As3-Ni1-As1 80.32(2), As1-As2-Ni2 56.622(17), As2-Ni2-As4 81.73(2), Ni2-As4-As1 100.33(2), As4-As1-As2 78.554(16).

4.5.5.2. $[(L^3Ni)_2(\mu\text{-}\eta^2,\kappa^1\text{:}\eta^2,\kappa^1\text{-}AsP_3)]$ (**2c**)

Compound **2c** crystallized from a concentrated solution in Et_2O at -30 °C in the monoclinic space group *C*2/*c*. The asymmetric unit contains three times 0.5 molecule of **2c** and two molecules of Et_2O. All three independent half molecules of **2c** show a disorder of the AsP_3 unit were the As atom is distributed over all positions (molecule 1: 35:5; molecule 2: 34:6; molecule 3: 33:0). Further, co-crystalizes **2c** with the compound $[(L^3Ni)_2(\mu\text{-}\eta^2,\kappa^1\text{:}\eta^2,\kappa^1\text{-}P_4)]$ (molecule 1+2: 80:20; molecule 3: 66:34). Additionally, is one Et_2O solvent molecule disordered over two positions (68:32). The second Et_2O molecule was heavily disordered. Therefore, was a solvent mask calculated. 352 electrons were detected in a volume of 2104 Å^3 in 4 voids per unit cell. This is consistent with the presence of one Et_2O molecule per asymmetric unit, which accounts for 336 electrons per unit cell. The structure in the solid state is given in Figure S4.19-S4.21.

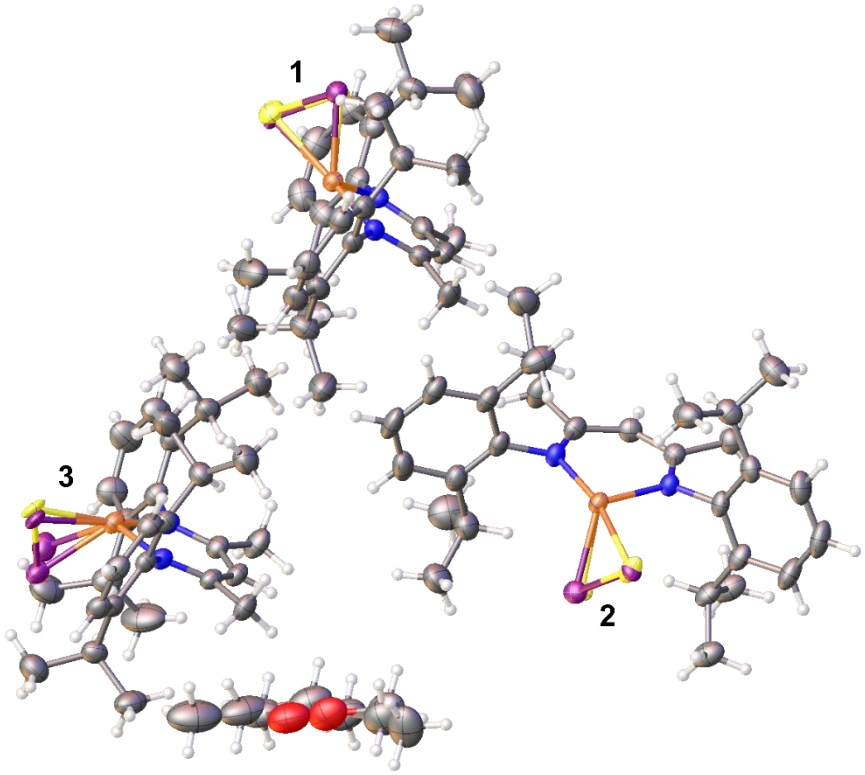


Figure S4.19. Asymmetric unit of **2c** in solid state.

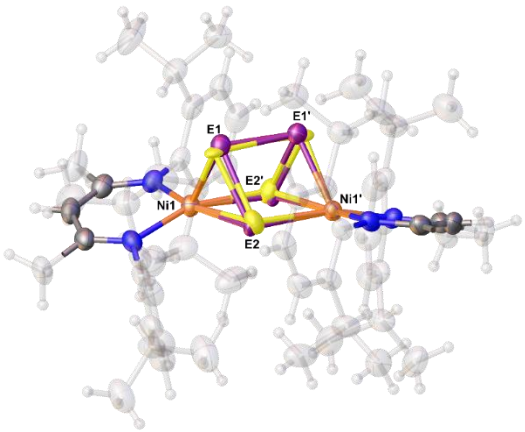


Figure S4.20. Molecular structure of **2c** in solid state. Molecule 1: **2c** (ratio of the arsenic atom: As1 0.35, As2 0,05). Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Ni1-N1 1.965(2), Ni1-N2 1.938(2), Ni1···Ni1' 3.8407(9), Ni1-P1 2.238(4), Ni1-P2 2.385(6), Ni1-P2' 2.330(8), Ni1-As1 2.16(3), Ni1-As2 2.445(6), Ni1-As2' 2.251(7), P1-P1' 2.157(7), P1-P2 2.316(9), P1-As2 2.215(5), P1-As1' 2.37(3), As1-P2 2.198(15), P1-Ni1-As2 56.25(17), P1-Ni1-As2' 77.02(17), P1-Ni1-P2' 79.7(2), P2'-Ni1-P2 70.7(3), As1-Ni1-P2 57.6(5), Ni1'-As2-Ni1 109.7(3), P1-As2-Ni1' 100.6(3), P1-As2-Ni1 57.17(16), P1'-P1-As2' 51.16(13), P1'-P1-As2 79.5(2), Ni1'-P2-Ni1 109.1(3), As1-P2-Ni1 56.1(8), Ni1-As1-P2 66.3(6), Ni1-P2-As1' 51.70(12), As1-P2-Ni1 66.6(2), P2'-P2-Ni1 102.81(12).

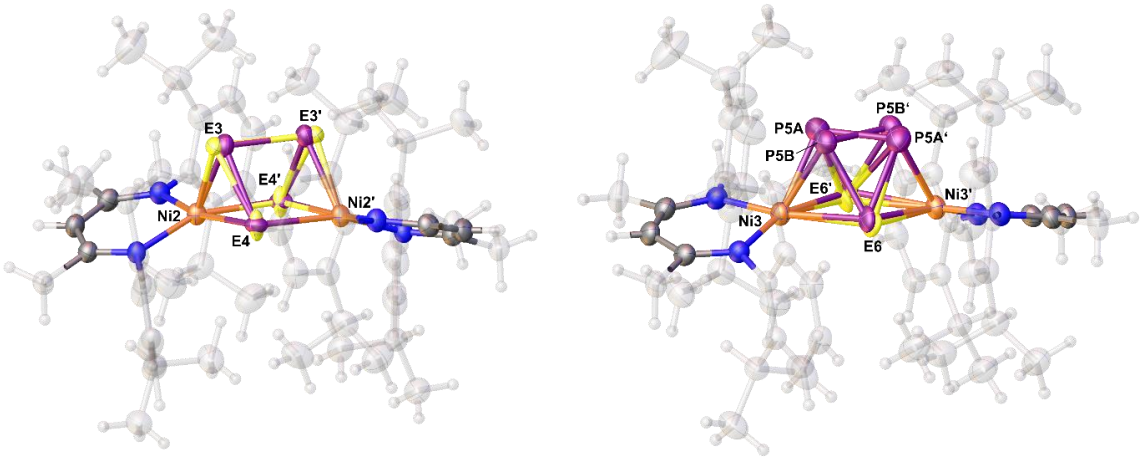


Figure S4.21. Molecule structure of **2c** in solid state. Molecule 2 (left, ratio of the arsenic atom: As3 0.34, As4 0,06) and molecule 3 (right, ratio of the arsenic atom: As6 0.33) of **2c**. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: *Molecule 2:* N3-Ni2 1.942(2), N4-Ni2 1.966(2), Ni2···Ni2' 3.7918(9), Ni2-P3 2.252(5), Ni2-P4 2.393(5), Ni2-As3 2.21(3), Ni2-As4 2.378(3), Ni2-As4' 2.275(4), Ni2-P4' 2.29646(3), As3-P4 2.32(3), P3-As4 2.245(6), P3-As3' 2.41963(3), P3-P4 2.24190(2), P3-P3' 2.153(8), As4'-Ni2-As4 70.82(16), P3-Ni2-As4 57.93(15), P3-Ni1-As4' 77.58(14), As3-Ni1-P4 60.5(8), Ni2'-As4-Ni2 109.14(16), P3-As4-Ni2' 99.23(17), P3-As4-Ni2 58.22(15), As4-P3-Ni2 63.85(18), P3'-P3-Ni2 102.8(2), P3'-P3-As4 80.28(16), Ni2'-P4-Ni2 107.89(19), Ni2'-P4-As3 105.0(7), As3-P4-Ni1 55.8(8); *Molecule 3:* N5-Ni3 1.940(2), N6-Ni3 1.965(2), Ni3···Ni3' 3.8345(9), Ni3-P5A 2.2383(10), Ni3-P5B 2.248(16), Ni3-P6 2.374(7), Ni3-P6' 2.421(7), Ni3-As6 2.437(7), Ni3-As6' 2.220(6), P5A-P5A' 2.1968(15), P5A-P6 2.322(7), P5B-P5B' 2.172(17), P5B-P6 2.155(13), P5B-As6 2.208(17), As6'-Ni3-P5A 79.70(17), P5A-Ni3-As6 59.39(16), P5A-Ni3-

P6' 75.8(2), P5B-Ni3-P6 75.9(3), Ni3'-As1-P5A 99.3(2), P5A-As6-Ni3 56.05(15), Ni3-P5A-As6 64.56(16), P5A'-P5A-Ni3 102.63(3), P5A'-P5A-As6 78.37(15), Ni3-P6-Ni3' 106.2(3), P5B'-P6-Ni3 99.1(4), P6'-P5B-Ni3 66.7(5), P5B'-P5B-Ni3 102.6(5).

4.5.5.3. $[(L^3Ni)_2(\mu,\eta^{3:3}\text{-}P_3)]$ (**3a**)

Compound **3a** crystallized from a concentrated solution of hexane at + 8 °C in the orthorhombic space group *Pbca*. The asymmetric unit contains one molecule of **3a**. The *cyclo*-P_3 ring is disordered over two positions in a ratio of 59:41. The structure in solid state is shown in Figure S4.22.

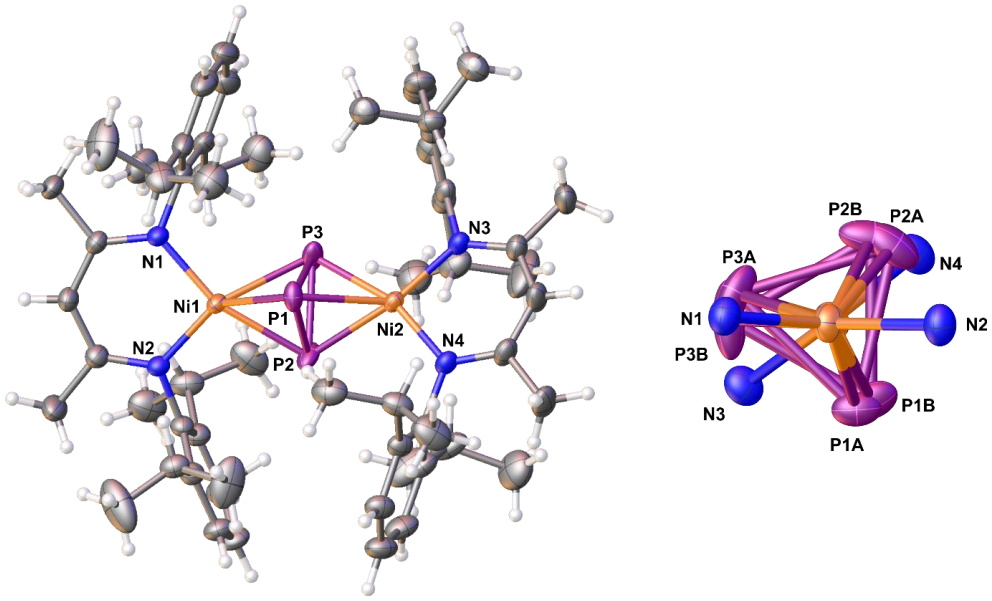


Figure S4.22. Molecular structure of **3a** in solid state (Left: best view; right: disorder of the P_3 ring). Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Ni1-P1A 2.312(9), Ni1-P2A 2.356(6), Ni1-P3A 2.300(11), Ni2-P1A 2.220(8), Ni2-P2A 2.279(6), Ni2-P3A 2.344(11), Ni1-P1B 2.190(13), Ni1-P2B 2.347(8), Ni1-P3B 2.252(15), Ni2-P1B 2.317(13), Ni2-P2B 2.330(9), Ni2-P3B 2.326(15), P1A-P2A 2.202(11), P2A-P3A 2.158(10), P3A-P1A 2.206(14), P1B-P2B 2.164(17), P2B-P3B 2.168(16), P3B-P1B 2.16(2), Ni1-N1 1.9173(16), Ni1-N2 1.9175(16), Ni2-N3 1.9131(15), Ni2-N4 1.9157(15), P1A-P2A-P3A 60.8(4), P2A-P3A-P1A 60.6(4), P3A-P1A-P2A 58.7(4), P1B-P2B-P3B 59.7(6), P2B-P3B-P1B 60.0(6), P3B-P1B-P2B 60.2(5).

4.5.5.4. $[(L^3Ni)_2(\mu,\eta^{3:3}\text{-}As_3)]$ (**3b**)

Compound **3b** crystallized from a concentrated solution of hexane at + 8 °C in the orthorhombic space group *Pbca*. The asymmetric unit contains one molecule of **3b**. The *cyclo*-As_3 ring is disordered over three positions in a ratio of 50:25:25. The structure in solid state is shown in Figure S4.23.

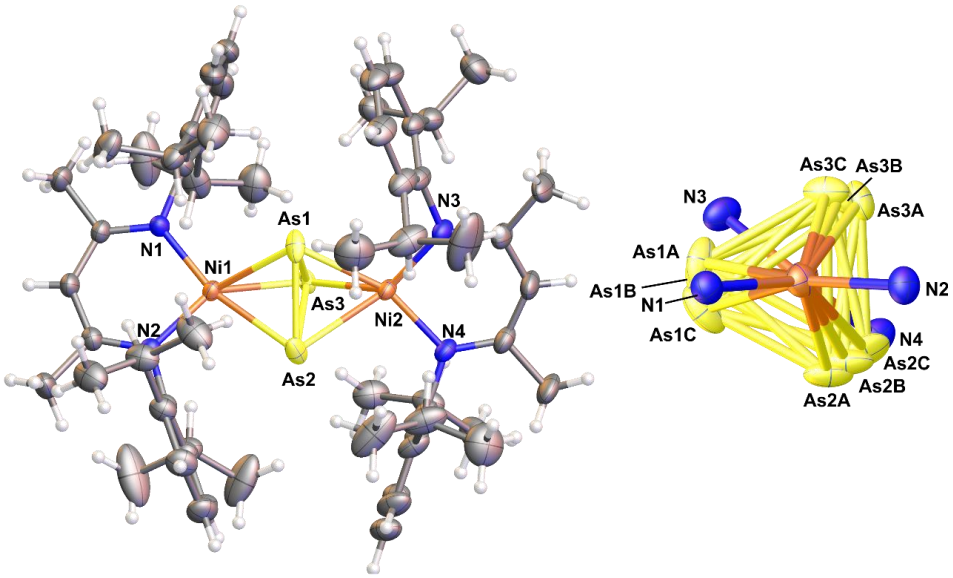


Figure S4.23. Molecular structure of **3b** in solid state (left: best view, right: disorder of the As3 ring). Solvent molecules are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Ni1-As1A 2.353(5), Ni1-As2A 2.381(4), Ni1-As3A 2.460(4), Ni2-As1A 2.385(6), Ni2-As2A 2.418(4), Ni2-As3A 2.421(4), As1A-As2A 2.390(7), As2A-As3A 2.376(6), As3A-As1A 2.375(7), Ni1-As1B 2.469(8), Ni1-As2B 2.327(6), Ni1-As3B 2.476(9), Ni2-As1B 2.277(9), Ni2-As2B 2.508(8), Ni2-As3B 2.443(9), As1B-As2B 2.389(13), As2B-As3B 2.429(12), As3B-As1B 2.458(14), Ni1-As1C 2.387(11), Ni1-As2C 2.440(10), Ni1-As3C 2.519(9), Ni2-As1C 2.478(11), Ni2-As2C 2.453(11), Ni2-As3C 2.397(6), As1C-As2C 2.574(14), As2C-As3C 2.480(13), As3C-As1C 2.474(12), As1A-As2A-As3A 59.8(2), As2A-As3A-As1A 60.4(2), As3A-As1A-As2A 59.8(2), As1B-As2B-As3B 61.3(4), As2B-As3B-As1B 58.5(4), As3B-As1B-As2B 60.1(4), As1C-As2C-As3C 58.6(4), As2C-As3C-As1C 62.6(4), As3C-As1C-As2C 58.8(4).

4.5.5.5. $[K_2][(L^3Ni)_2(\mu,\eta^{2:2}\text{-}P_4)]$ (**4**)

Compound **4** crystallized from a concentrated solution of toluene at - 30 °C in the monoclinic space group *P2₁/n*. The asymmetric unit contains half a molecule of **4** and two toluene molecules. The P_4 unit is disordered over two positions (93:7). Further, is one of the toluene molecules disordered over two positions (75:25). The structure in solid state is shown in Figure S4.24.

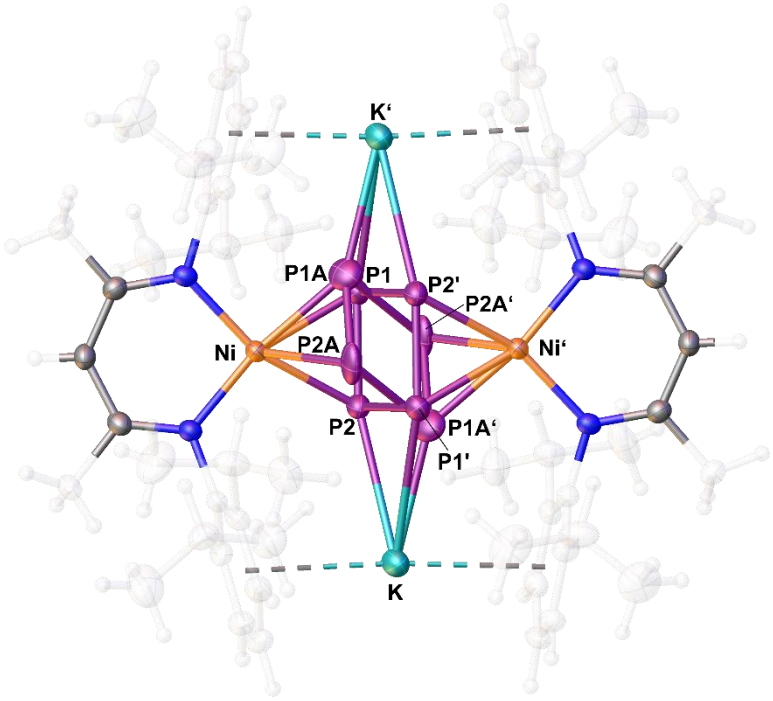


Figure S4.24. Molecular structure of **4** in solid state. Solvent molecules are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Ni-P1 2.2467(7), Ni-P2 2.2471(8), Ni-P1A 2.232(12), Ni-P2A 2.405(11), P1-P2 2.2611(10), P1-P2' 2.1360(10), P1A-P2A 2.053(17), P1A-P2A' 2.213(15). P1-P2-P1' 89.80(3), P2'-P1-P2 90.21(3), P1A-P2A-P1A' 82.2(6).

4.5.5.6. [K@18-crown-6(thf)$_2$][(L^{3}Ni)$_2$($\eta^{3:3}$-P$_3$)] (**5a**)

Compound **5a** crystallized from a concentrated solution in thf layered with hexane at -30 °C in the triclinic space group $P\bar{1}$ as brown plates. The asymmetric unit contains one molecule of **5a**, two times half the unit [K(18-c-6)(thf)$_2$] and a further thf molecule. The P_3 ring is disordered over two positions (ratio: 90:10). Additionally, are the thf molecules disordered over two positions (65:35; 54:46). The structure in solid state is shown in Figure S4.25.

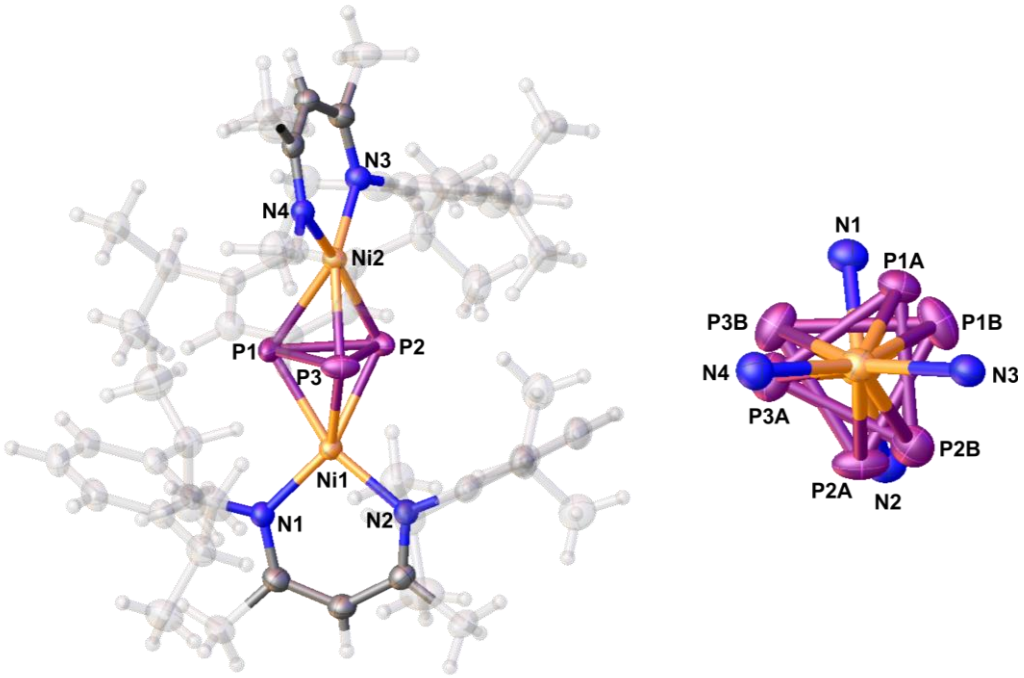


Figure S4.25. Molecular structure of **5a** in solid state (left: best view, right: disorder of the P_3 ring). Counterion and solvent molecules are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Ni1-P1A 2.2490(7), Ni1-P2A 2.2694(7), Ni1-P3A 2.3574(6), Ni2-P1A 2.2872(6), Ni2-P2A 2.3051(7), Ni2-P3A 2.2683(6), Ni1-P1B 2.207(5), Ni1-P2B 2.237(7), Ni1-P3B 2.335(6), Ni2-P1B 2.328(5), Ni2-P2B 2.275(7), Ni2-P3B 2.267(6), P1A-P2A 2.2065(10), P2A-P3A 2.1848(10), P3A-P1A 2.1760(10), P1B-P2B 2.130(9), P2B-P3B 2.133(9), P3B-P1B 2.171(8), P1A-P2A-P3A 59.41(4), P2A-P3A-P1A 60.79(4), P3A-P1A-P2A 59.80(3), P1B-P2B-P3B 61.2(3), P2B-P3B-P1B 59.3(3), P3B-P1B-P2B 59.4(3).

4.5.5.7. [K@18-crown-6(thf)$_2$][(L^{3}Ni)$_2$($\eta^{3:3}$-As$_3$)] (**5b**)

Compound **5b** crystallized from a concentrated solution in thf layered with hexane at -30 °C in the monoclinic space group *I*2/a as brown needle. The asymmetric unit contains one molecule of **5b**, one potassium ion chelated by one molecule of 18-crown-6 with 2 molecules of thf and a further 1.5 thf molecules. The As_3 ring is disordered over two positions (ratio: 61:39). Additionally, is one of the thf molecules disordered over two positions (58:42). The other half occupied thf molecule was heavily disordered and therefore, a solvent mask was calculated. In its volume of 1060 Å^3 were 168 electrons found in two voids per unit cell. This is consistent with the presence of half a thf molecule per asymmetric unit, which accounts for 160 electrons per unit cell. The structure in solid state is shown in Figure S4.26.

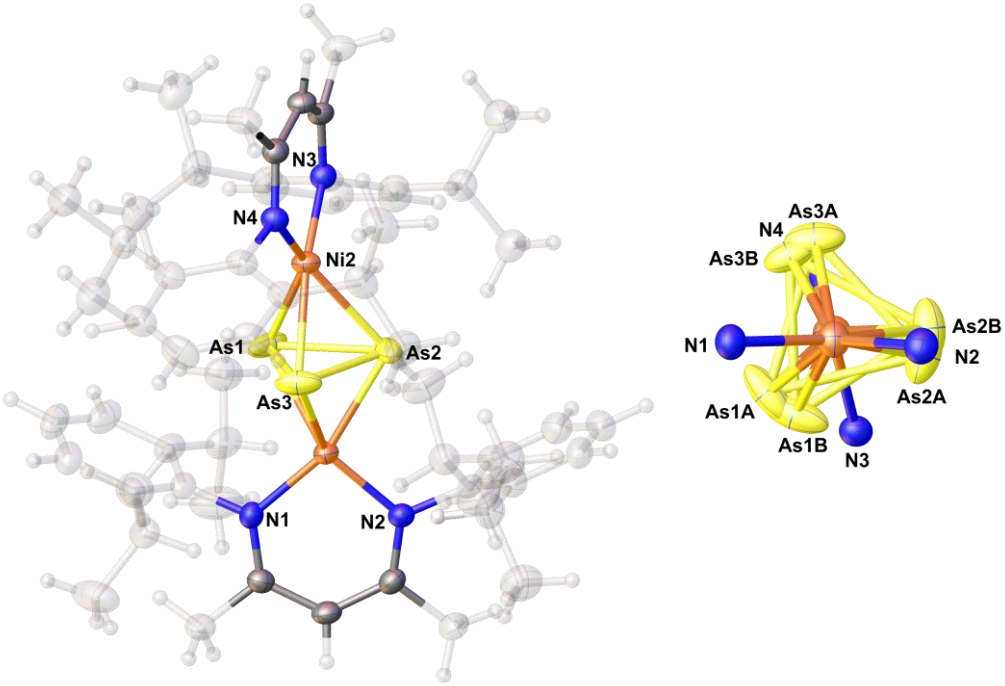


Figure S4.26. Molecular structure of **5b** in solid state (left: best view, right: disorder of the As_3 ring). Counterion and solvent molecules are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Ni1-As1A 2.516(3), Ni1-As2A 2.357(4), Ni1-As3A 2.362(2), Ni2-As1A 2.404(3), Ni2-As2A 2.472(4), Ni2-As3A 2.353(3), Ni1-As1B 2.437(4), Ni1-As2B 2.408(7), Ni1-As3B 2.370(4), Ni2-As1B 2.354(4), Ni2-As2B 2.470(7), Ni2-As3B 2.351(4), As1A-As2A-As3A 60.44(13), As2A-As3A-As1A 59.37(12), As3A-As1A-As2A 60.19(11), As1B-As2B-As3B 60.5(2), As2B-As3B-As1B 59.5(2), As3B-As1B-As2B 60.05(17).

4.5.5.8. $[K_2][(L^3Ni)_2(\mu,\eta^{1:1}\text{-}N_2)]$ (**6**)

Compound **6** crystallized from a concentrated solution of hexane at + 8 °C in the orthorhombic space group *Pbcn*. The asymmetric unit contains half a molecule of **6**. The structure in solid state is shown in Figure S4.27.

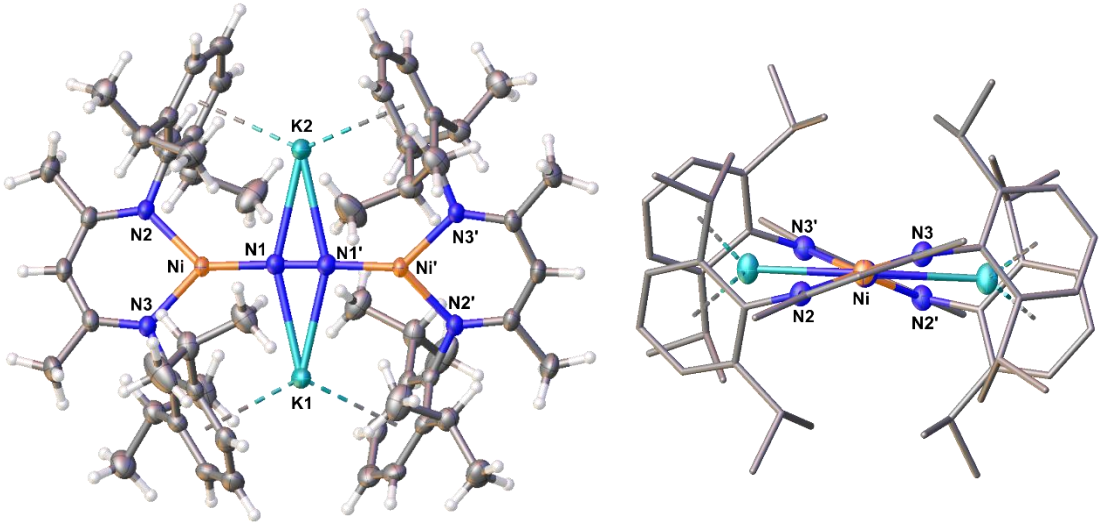


Figure S4.27. Molecular structure of **6** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]:Ni···K1 3.4757(9), Ni···K2 3.5923(9), Ni-N2 1.928(2), Ni-N3 1.919(2), Ni-N1 1.725(3), N1-N1' 1.195(5), N1-K1 2.709(3), N1-K2 2.751(3), Ni-N1-N1' 177.4(2).

4.5.5.9. [(K@18-crown-6)(thf)$_2$][L^{3}Ni($\eta^{1:1}$-P_4)] (**7a**)

Compound **7a** crystallized from a concentrated solution in thf layered with hexane at - 30 °C in the non-centrosymmetric orthorhombic space group *P2$_1$2$_1$2$_1$* as orange needle. The asymmetric unit contains one molecule of **7a**, one potassium ions chelated by one molecule of 18-crown-6 and 2 molecules of thf (both disordered over two positions: 84:16 and 58:42). The structure in solid state is shown in Figure S4.28.

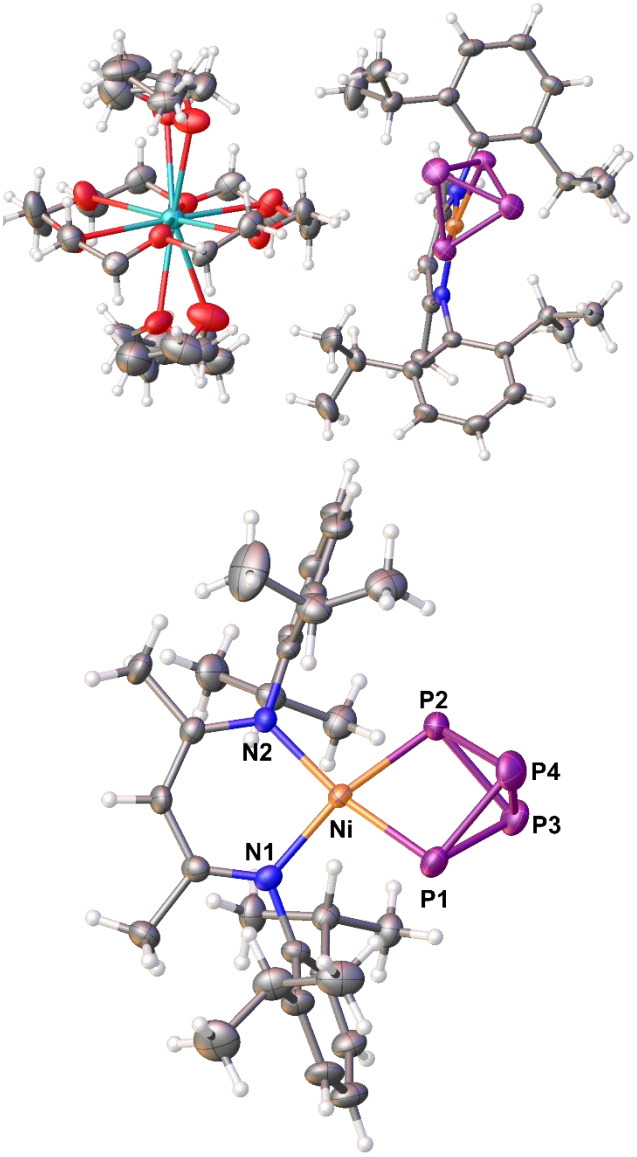


Figure S4.28. Molecular structure of **7a** in solid state. Top: view of the asymmetric unit. Bottom: best view. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Ni-P1 2.1935(12), Ni-P2 2.1886(12), P1···P2 2.6759(15), P1-P3 2.2255(15), P1-P4 2.2209(16), P2-P3 2.2115(16), P2-P4 2.2282(17), P3-P4 2.1567(18), Ni-N1 1.972(3), Ni-N2 1.982(3), P1-Ni-P2 75.27(4), N1-Ni-N2 94.50(13), P3-P1-P2 52.67(5), P4-P1-P2 53.15(5), P4-P1-P3 58.03(6), P3-P2-P1 53.15(4), P3-P2-P4 58.13(6), P4-P2-P1 52.90(5), P2-P3-P1 74.18(5), P4-P3-P1 60.88(5), P4-P3-P2 61.32(6), P1-P4-P2 73.95(5), P3-P4-P1 61.09(5), P3-P4-P2 60.55(6).

4.5.5.10. [K@cryptand][thf][L^3Ni($\eta^{1:1}$-As_4)] (**7b**)

Compound **7b** crystallized from a concentrated solution in thf layered with hexane at -30 °C in the triclinic space group $P\bar{1}$ as brown needles. The asymmetric unit contains one molecule of **7b**, one potassium ions chelated by one molecule of cryptand and one molecule of thf. The structure in solid state is shown in Figure S4.29.

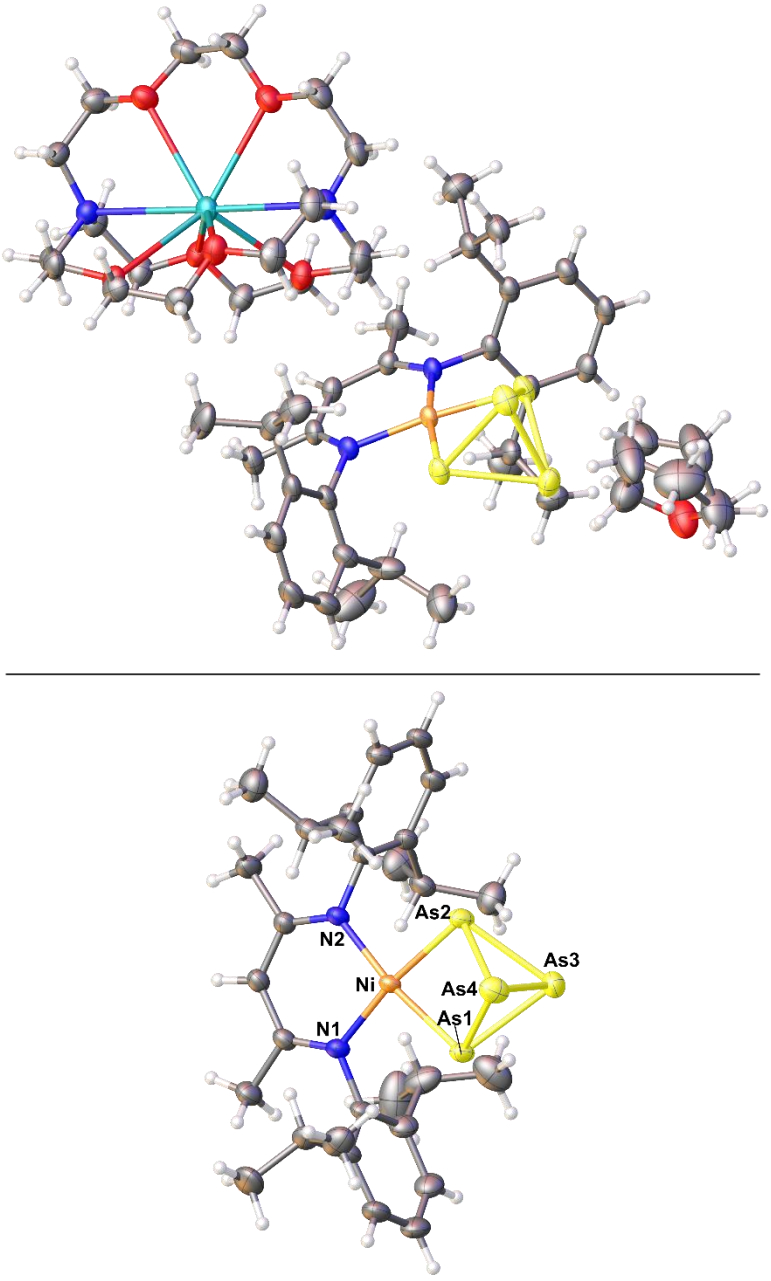


Figure S4.29. Molecular structure of **7b** in solid state. Top: view of the asymmetric unit. Bottom: best view. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Ni As1 2.3246(4), Ni-As2 2.3205(4), As1···As2 2.8963(3), As1-As3 2.4687(3), As1-As4 2.4506(4), As2-2.4596(3), As2-As3 2.4666(4), N1-Ni 1.9669(17), N2-Ni 1.9705(18), As1-Ni-As2 77.144(13), As4-As2-As3 58.066(11), As4-As1-As3 58.155(11), As2-As3-As1 71.866(10), As4-As3-As2 60.819(11), As4-As3-As1 60.544(11), As1-As4-As2 72.292(11), As3-As4-As2 61.115(11), As3-As4-As1 61.302(11).

4.5.5.11. Crystallographic information

Table S4.3. Crystallographic data and details of diffraction experiments for **2b**, **2c**, **3a** and **3b**.

Compound	**2b**	**2c**	**3a**	**3b**
CCDC	2109927	2109928	2109929	2109930
Formula	$C_{118}H_{169}As_8N_8Ni_4O_{0.5}$	$As_{2.26}C_{190}H_{286}N_{12}Ni_6O_4P_{9.74}$	$C_{58}H_{82}N_4Ni_2P_3$	$C_{58}H_{82}As_3N_4Ni_2$
$D_{calc.}$/ g cm^{-3}	1.433	1.254	1.231	1.377
μ/mm^{-1}	3.586	2.247	1.923	3.053
Formula Weight	2541.80	3625.52	1045.60	1177.45
Colour	dark green	green	green	brown
Shape	block-shaped	block-shaped	rod	rod
Size/mm^3	0.34×0.29×0.14	0.09×0.08×0.06	0.30×0.07×0.02	0.36×0.06×0.06
T/K	123.00(10)	100.01(10)	123.01(10)	123.00(10)
Crystal System	monoclinic	monoclinic	orthorhombic	orthorhombic
Space Group	$P2_1/c$	$C2/c$	$Pbca$	$Pbca$
a/Å	13.97930(10)	24.0518(2)	19.08692(18)	18.9860(2)
b/Å	15.8852(2)	35.9443(4)	23.0111(2)	23.1897(3)
c/Å	26.7832(2)	23.2698(3)	25.6877(3)	25.7976(3)
α/°	90	90	90	90
β/°	97.9450(10)	107.3190(10)	90	90
γ/°	90	90	90	90
V/Å^3	5890.49(10)	19205.2(4)	11282.35(19)	11358.2(2)
Z	2	4	8	8
Z'	0.5	0.5	1	1
Wavelength/Å	1.54184	1.54184	1.54184	1.54184
Radiation type	Cu K$_\alpha$	Cu K$_\alpha$	Cu K$_\alpha$	Cu K$_\alpha$
Θ_{min}/°	4.236	2.283	3.466	3.462
Θ_{max}/°	67.023	73.341	70.654	76.541
Measured Refl's.	111628	80701	77497	31637
Indep't Refl's	10449	18572	10687	11622
Refl's I≥2 σ(I)	9997	14666	8685	9969
R_{int}	0.0572	0.0562	0.0473	0.0273
Parameters	677	1098	651	678
Restraints	26	139	0	12
Largest Peak	0.589	0.972	0.494	0.526
Deepest Hole	-0.980	-0.516	-0.289	-0.767
GooF	1.159	1.111	1.016	1.027
wR_2 (all data)	0.1041	0.1665	0.0931	0.0947
wR_2	0.1028	0.1599	0.0852	0.0892
R_1 (all data)	0.0422	0.0657	0.0474	0.0428
R_1	0.0407	0.0545	0.0347	0.0344

Table S4.4. Crystallographic data and details of diffraction experiments for **4**, **5a**, **5b**.

Compound	**4**	**5a**	**5b**
CCDC	2109931	2109932	2109933
Formula	$C_{86}H_{114}K_2N_4Ni_2P_4$	$C_{82}H_{130}KN_4Ni_2O_9P_3$	$As_3C_{84}H_{134}KN_4Ni_2O_{9.5}$
Dcalc	1.251	1.226	1.315
μ/mm^{-1}	2.588	1.955	2.650
Formula Weight	1523.31	1565.32	1733.22
Colour	brown	clear brown	clear brown
Shape	block-shaped	plate-shaped	needle-shaped
Size/mm^3	0.21×0.16×0.06	0.36×0.30×0.10	0.21×0.04×0.03
T/K	123(1)	123.00(10)	123.01(10)
Crystal System	monoclinic	triclinic	monoclinic
Space Group	$P2_1/n$	P-1	$I2/a$
a/Å	14.29612(14)	12.98450(10)	35.6437(4)
b/Å	14.53816(13)	13.60660(10)	13.2844(2)
c/Å	19.69075(16)	24.7335(2)	37.2813(5)
α/°	90	103.0540(10)	90
β/°	98.7928(8)	94.0260(10)	97.1640(10)
γ/°	90	92.2980(10)	90
V/Å^3	4044.42(6)	4239.31(6)	17515.1(4)
Z	2	2	8
Z'	0.5	1	1
Wavelength/Å	1.54184	1.54184	1.54184
Radiation type	CuK_α	Cu K_α	Cu K_α
Θ_{min}/°	3.795	3.340	2.389
Θ_{max}/°	66.611	73.254	73.180
Measured Refl's.	16391	65154	60090
Indep't Refl's	6974	16397	16692
Refl's I≥2 σ(I)	6519	15036	12366
R_{int}	0.0238	0.0237	0.0581
Parameters	536	1052	1011
Restraints	210	138	219
Largest Peak	1.577	0.534	0.517
Deepest Hole	-0.415	-0.437	-0.574
GooF	1.041	1.057	1.114
wR_2 (all data)	0.1378	0.1050	0.1490
wR_2	0.1353	0.1032	0.1406
R_1 (all data)	0.0517	0.0419	0.0691
R_1	0.0495	0.0390	0.0511

Table S4.5. Crystallographic data and details of diffraction experiments for **6**, **7a** and **7b**.

Compound	**6**	**7a**	**7b**
CCDC	2109934	2109935	2109936
Formula	$C_{58}H_{82}K_2N_6Ni_2$	$C_{49}H_{81}KN_2NiO_8P_4$	$C_{51}H_{85}As_4KN_4NiO_7$
Dcalc	1.235	1.269	1.451
μ/mm^{-1}	2.431	2.692	4.064
Formula Weight	1058.91	1047.84	1263.71
Colour	dark violet	clear orange	clear dark brown
Shape	needle	needle-shaped	needle-shaped
Size/mm^3	0.35×0.03×0.02	0.17×0.14×0.05	0.66×0.08×0.06
T/K	123(1)	123.00(10)	100.00(10)
Crystal System	orthorhombic	orthorhombic	triclinic
Flack Parameter	-	-0.012(8)	-
Hooft Parameter	-	0.003(5)	-
Space Group	*Pbcn*	$P2_12_12_1$	*P*-1
a/Å	10.6599(2)	11.55370(10)	13.2378(2)
b/Å	23.0876(5)	19.6743(2)	14.9245(3)
c/Å	23.1458(4)	24.1351(3)	15.9101(3)
α/°	90	90	70.277(2)
β/°	90	90	78.6870(10)
γ/°	90	90	82.1540(10)
V/Å^3	5696.4(2)	5486.17(10)	2893.00(10)
Z	4	4	2
Z'	0.5	1	1
Wavelength/Å	1.54184	1.54184	1.54184
Radiation type	Cu K$_\alpha$	Cu K$_\alpha$	Cu K$_\alpha$
Θ_{min}/°	3.820	4.242	2.990
Θ_{max}/°	70.690	66.714	74.488
Measured Refl's.	15295	40235	117106
Indep't Refl's	5287	9591	11379
Refl's I≥2 σ(I)	4019	8495	10524
R_{int}	0.0504	0.0641	0.0496
Parameters	318	687	641
Restraints	0	134	75
Largest Peak	0.624	0.368	1.121
Deepest Hole	-0.434	-0.272	-0.777
GooF	1.029	0.975	1.079
wR_2 (all data)	0.1632	0.0999	0.0844
wR_2	0.1421	0.0980	0.0826
R_1 (all data)	0.0711	0.0443	0.0340
R_1	0.0529	0.0394	0.0312

4.5.6. DFT calculations

Gaussian 09 program[14] was used throughout. Density functional theory (DFT) in form of Becke's three-parameter hybrid functioncal B3LYP[15] or BP86[16] (Becke's exchange and Perdew 86 correlation functional) with def2-SVP all electron basis set was employed. The figures for the supporting information concerning the DFT calculations were created with Chemcraft.[17] For solvents effects has been accounted by using continuous polarizable continuum model (CPM).[18] The dielectric constant of thf (ε = 7.4257) has been used in the calculations of the anions (**4, 5a, 5b**). The Natural Bond Orbital (NBO) analysis has been performed with the NBO6 program.[19] The long range dispersion correction GD3BJ was applied.[20]

Table S4.6. Total energies for all optimized geometries of **2c-I** and **2c-II** (BP86/def2-SVP level of theory).

	total energy [Ha]
2c-I $[(L^3Ni)_2(AsP_3)]$	-8753.97439277
2c-II $[(L^3Ni)_2(AsP_3)]$	-8753.96934262

Table S4.7. Total energies for all optimized geometries of **3a** and **3b** (B3LYP/def2-SVP level of theory).

	total energy [Ha]
3a $[(L^3Ni)_2(\mu,\eta^{3:3}\text{-}P_3)]$	-6517.57987010
3b $[(L^3Ni)_2(\mu,\eta^{3:3}\text{-}As_3)]$	-12201.3925306

Table S4.8. Total energies for optimized geometries of **4**, **5a**, **5b** (BP86/def2-SVP level of theory).

	total energy [Ha]
4 $[(L^3Ni)_2(\mu,\eta^{2:2}\text{-}P_4)]^{2-}$ singlet state	-6859.54186686
5a $[(L^3Ni)_2(\mu,\eta^{3:3}\text{-}P_3)]^{-}$ singlet state	-6518.17456214
5b $[(L^3Ni)_2(\mu,\eta^{3:3}\text{-}As_3)]^{-}$ singlet state	-12201.9939337

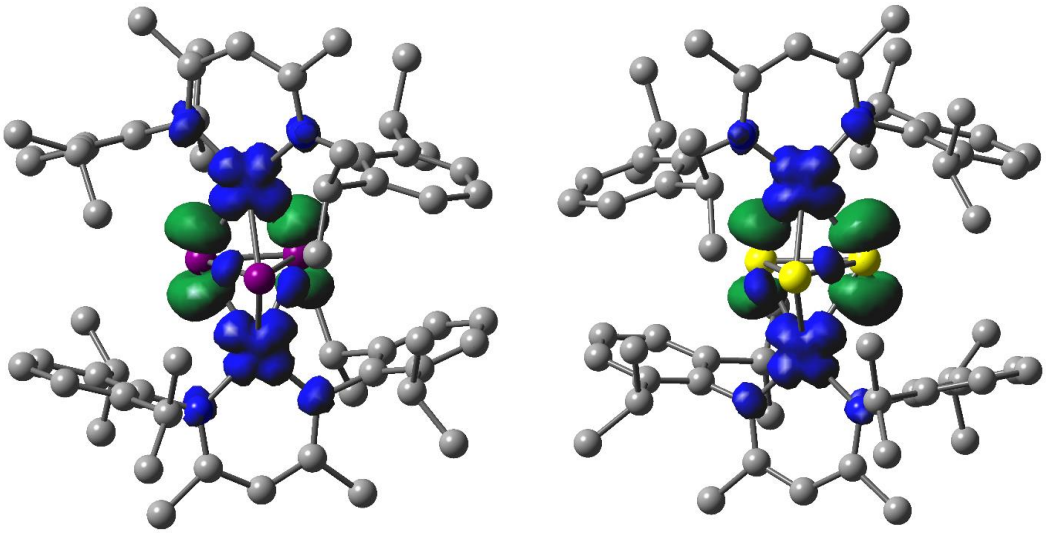
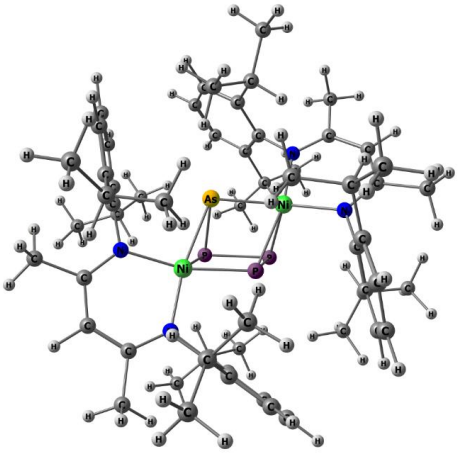


Figure S4.30. Isosurfaces of the calculated spin density in **3a** (left) and **3b** (right) B3LYP/def2-SVP level of theory.

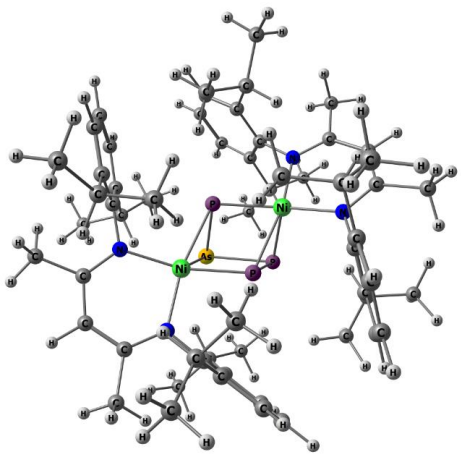
Table S4.9. Optimized geometry of **2c-I**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



Ni	-1.162682000	1.466706000	-0.187840000	Ni	1.234293000	-1.430385000	-0.160842000
P	1.109642000	0.798956000	-0.147456000	As	-1.153549000	-0.854001000	-0.148315000
P	0.033501000	1.116094000	-2.036876000	P	0.133057000	-1.098790000	-2.066735000
N	-0.897478000	3.335535000	0.343158000	N	0.993406000	-3.294364000	0.404995000
N	-3.085302000	1.620029000	-0.360091000	N	3.154957000	-1.558684000	-0.314453000
C	0.403845000	3.701357000	0.802207000	C	-0.313560000	-3.669458000	0.839386000
C	1.399793000	4.103975000	-0.128736000	C	-1.285105000	-4.090106000	-0.112336000
C	-3.785914000	2.764921000	-0.262262000	C	3.875495000	-2.685598000	-0.176482000
C	-3.203618000	4.010552000	0.043465000	C	3.312954000	-3.935660000	0.153916000
H	-3.890717000	4.866307000	0.090662000	H	4.016084000	-4.775923000	0.233119000
C	-1.861200000	4.269359000	0.394922000	C	1.972053000	-4.210760000	0.493238000
C	0.675083000	3.658334000	2.200221000	C	-0.632329000	-3.578457000	2.225137000
C	2.962711000	4.388040000	1.731894000	C	-2.911759000	-4.300125000	1.703540000
H	3.967672000	4.652145000	2.096881000	H	-3.931700000	-4.539973000	2.042361000
C	2.681853000	4.425595000	0.361409000	C	-2.584678000	-4.389543000	0.345637000
H	3.470457000	4.717982000	-0.347953000	H	-3.353019000	-4.696410000	-0.379468000
C	-3.809188000	0.411627000	-0.598720000	C	3.857252000	-0.338994000	-0.555841000
C	1.960581000	4.015426000	2.641784000	C	-1.937685000	-3.903456000	2.633267000
H	2.189331000	3.992752000	3.717630000	H	-2.203685000	-3.836757000	3.698724000
C	-3.890038000	-0.104382000	-1.926488000	C	3.986059000	0.146748000	-1.888946000
C	1.073141000	4.261010000	-1.610014000	C	-0.919889000	-4.255805000	-1.583431000

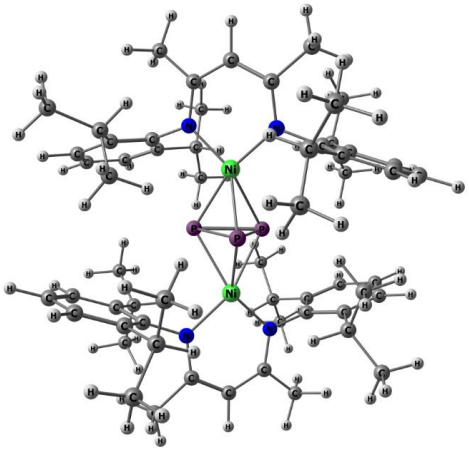
H	0.168868000	3.645164000	-1.805315000	H	-0.039144000	-3.602530000	-1.765686000
C	-1.552512000	5.660638000	0.920422000	C	1.676019000	-5.593200000	1.048138000
H	-1.596376000	5.665158000	2.031142000	H	1.681388000	-5.565885000	2.159362000
H	-2.296874000	6.392570000	0.553207000	H	2.447227000	-6.319085000	0.727406000
H	-0.536768000	6.000725000	0.646487000	H	0.677703000	-5.963877000	0.749926000
C	-5.296712000	2.740712000	-0.414076000	C	5.388528000	-2.636718000	-0.298035000
H	-5.634195000	2.008425000	-1.171242000	H	5.730875000	-1.891090000	-1.039299000
H	-5.678384000	3.744393000	-0.681395000	H	5.790119000	-3.632289000	-0.567207000
H	-5.770349000	2.444999000	0.545423000	H	5.836859000	-2.346660000	0.675457000
C	-0.411436000	3.200303000	3.170732000	C	0.419532000	-3.086672000	3.215996000
H	-1.383051000	3.569840000	2.780864000	H	1.406810000	-3.447283000	2.859525000
C	-4.364626000	-0.302813000	0.499976000	C	4.369212000	0.398427000	0.547389000
C	-4.578554000	-1.314900000	-2.131208000	C	4.682204000	1.352518000	-2.094199000
H	-4.659926000	-1.722982000	-3.149690000	H	4.803529000	1.736963000	-3.118043000
C	-3.225357000	0.642111000	-3.076628000	C	3.379091000	-0.630812000	-3.050508000
H	-2.353291000	1.158135000	-2.617258000	H	2.507266000	-1.168556000	-2.616594000
C	-4.218965000	0.201740000	1.933570000	C	4.183097000	-0.085723000	1.982832000
H	-3.673026000	1.167125000	1.890157000	H	3.655551000	-1.060860000	1.937311000
C	2.198591000	3.751437000	-2.520062000	C	-2.045657000	-3.808574000	-2.526742000
H	1.855077000	3.704996000	-3.574122000	H	-1.673334000	-3.743401000	-3.569802000
H	2.530861000	2.741232000	-2.214093000	H	-2.443234000	-2.817019000	-2.234724000
H	3.087911000	4.416863000	-2.491857000	H	-2.896373000	-4.523276000	-2.524629000
C	-5.029107000	-1.518132000	0.243108000	C	5.036828000	1.611211000	0.290851000
H	-5.455099000	-2.086065000	1.085355000	H	5.425747000	2.199921000	1.136684000
C	-5.150687000	-2.017359000	-1.059547000	C	5.210138000	2.080408000	-1.017232000
H	-5.678055000	-2.966670000	-1.241471000	H	5.743194000	3.026515000	-1.199832000
C	-0.499523000	1.665045000	3.182503000	C	0.482365000	-1.550454000	3.201443000
H	0.422349000	1.222682000	3.607980000	H	-0.467208000	-1.115225000	3.570313000
H	-0.611902000	1.269322000	2.149590000	H	0.645418000	-1.169292000	2.169462000
H	-1.365723000	1.313151000	3.779561000	H	1.310151000	-1.173064000	3.835734000
C	0.709850000	5.718305000	-1.961193000	C	-0.482271000	-5.698976000	-1.905700000
H	1.550326000	6.403840000	-1.719956000	H	-1.292605000	-6.420199000	-1.665454000
H	-0.183243000	6.068035000	-1.408784000	H	0.418846000	-5.995819000	-1.335696000
H	0.492141000	5.813113000	-3.045918000	H	-0.243672000	-5.799688000	-2.985410000
C	-5.584554000	0.450805000	2.603260000	C	5.528347000	-0.301460000	2.702783000
H	-6.219346000	1.139194000	2.009301000	H	6.194605000	-0.987386000	2.141285000
H	-5.451310000	0.893925000	3.612405000	H	5.367378000	-0.731970000	3.713441000
H	-6.151131000	-0.496480000	2.727725000	H	6.074577000	0.656977000	2.832629000
C	-0.247656000	3.752850000	4.593497000	C	0.222188000	-3.616394000	4.643419000
H	-1.124526000	3.477880000	5.215388000	H	1.078044000	-3.320409000	5.284527000
H	-0.155658000	4.858804000	4.597563000	H	0.142169000	-4.723068000	4.664207000
H	0.649939000	3.335468000	5.096977000	H	-0.693678000	-3.200857000	5.114537000
C	-3.378970000	-0.770614000	2.780649000	C	3.296739000	0.885313000	2.780489000
H	-3.884106000	-1.752278000	2.884655000	H	3.780944000	1.877181000	2.882024000
H	-3.208823000	-0.364345000	3.799856000	H	3.098102000	0.495845000	3.801290000
H	-2.393380000	-0.969952000	2.316276000	H	2.327941000	1.055264000	2.272398000
C	-2.687530000	-0.283096000	-4.176339000	C	2.850247000	0.267461000	-4.177162000
H	-2.061719000	-1.095335000	-3.752875000	H	2.188666000	1.065722000	-3.782963000
H	-2.058635000	0.293689000	-4.885245000	H	2.261699000	-0.334817000	-4.899549000
H	-3.501902000	-0.754870000	-4.766631000	H	3.669461000	0.757052000	-4.745758000
C	-4.127104000	1.738726000	-3.673938000	C	4.331534000	-1.705345000	-3.608818000
H	-5.069223000	1.304832000	-4.072261000	H	5.273479000	-1.246884000	-3.979222000
H	-3.607272000	2.254384000	-4.508504000	H	3.855054000	-2.241766000	-4.456107000
H	-4.391929000	2.507105000	-2.923367000	H	4.594839000	-2.460066000	-2.843856000

Table S4.10. Optimized geometry of **2C-II**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



Ni	0.933103000	-1.568059000	-0.057236000	Ni	-0.924331000	1.635331000	-0.129225000
P	-1.194998000	-0.573028000	-0.050240000	P	1.205251000	0.638289000	-0.092629000
As	-0.176051000	-1.136365000	-2.060598000	P	0.211599000	1.163795000	-1.986048000
N	0.388873000	-3.366522000	0.503739000	N	-0.383182000	3.451477000	0.384037000
N	2.803600000	-2.023224000	-0.251475000	N	-2.797965000	2.077767000	-0.312820000
C	-0.953310000	-3.528435000	0.962606000	C	0.959484000	3.624211000	0.837592000
C	-1.997716000	-3.813851000	0.041335000	C	2.005515000	3.879723000	-0.090221000
C	3.328500000	-3.253586000	-0.114337000	C	-3.325682000	3.310446000	-0.204129000
C	2.566493000	-4.389833000	0.226148000	C	-2.566493000	4.458316000	0.099622000
H	3.118816000	-5.336491000	0.301601000	H	-3.121896000	5.404579000	0.153057000
C	1.201842000	-4.434511000	0.579795000	C	-1.197680000	4.518292000	0.437080000
C	-1.217219000	-3.403675000	2.357407000	C	1.220472000	3.540225000	2.236363000
C	-3.585658000	-3.813018000	1.902968000	C	3.590373000	3.930443000	1.773834000
H	-4.618076000	-3.919252000	2.271392000	H	4.622369000	4.045663000	2.140833000
C	-3.312678000	-3.930857000	0.535496000	C	3.319781000	4.008690000	0.403137000
H	-4.134559000	-4.131609000	-0.168147000	H	4.142900000	4.187715000	-0.304808000
C	3.695521000	-0.940213000	-0.520102000	C	-3.687505000	0.989395000	-0.562973000
C	-2.539763000	-3.560750000	2.805002000	C	2.542613000	3.707344000	2.681354000
H	-2.761739000	-3.475073000	3.879118000	H	2.763099000	3.653099000	3.757763000
C	3.897824000	-0.509913000	-1.863374000	C	-3.865163000	0.526472000	-1.899514000
C	-1.703689000	-4.072147000	-1.433141000	C	1.714318000	4.092414000	-1.572659000
H	-0.703082000	-3.634303000	-1.640669000	H	0.717893000	3.642088000	-1.771945000
C	0.684964000	-5.748934000	1.137826000	C	-0.679159000	5.850864000	0.948840000
H	0.685447000	-5.716838000	2.248905000	H	-0.660145000	5.851687000	2.060093000
H	1.332151000	-6.590120000	0.824952000	H	-1.336183000	6.679058000	0.622206000
H	-0.357777000	-5.954927000	0.833756000	H	0.356878000	6.053078000	0.620370000
C	4.827457000	-3.455412000	-0.244085000	C	-4.825838000	3.502284000	-0.336851000
H	5.281791000	-2.778837000	-0.991322000	H	-5.272402000	2.822561000	-1.086336000
H	5.060482000	-4.504795000	-0.507089000	H	-5.065232000	4.549814000	-0.601112000
H	5.320557000	-3.233452000	0.725690000	H	-5.320948000	3.276364000	0.630863000
C	-0.075877000	-3.073543000	3.315777000	C	0.075750000	3.241248000	3.201201000
H	0.838591000	-3.566330000	2.924563000	H	-0.830644000	3.746038000	2.806331000
C	4.317918000	-0.265736000	0.567062000	C	-4.331947000	0.345445000	0.528779000
C	4.773681000	0.567215000	-2.094577000	C	-4.742752000	-0.551243000	-2.120008000
H	4.950411000	0.904060000	-3.127215000	H	-4.901598000	-0.914224000	-3.146379000
C	3.175828000	-1.202852000	-3.012610000	C	-3.093614000	1.174941000	-3.042496000
H	2.252113000	-1.630516000	-2.562856000	H	-2.130926000	1.500571000	-2.588706000
C	4.070129000	-0.690557000	2.012235000	C	-4.108303000	0.805138000	1.967113000
H	3.377842000	-1.557107000	1.987020000	H	-3.436374000	1.686896000	1.930397000
C	-2.723518000	-3.403250000	-2.365996000	C	2.737931000	3.396728000	-2.481051000
H	-2.380000000	-3.454564000	-3.420141000	H	2.397851000	3.416934000	-3.537098000
H	-2.877297000	-2.340772000	-2.096906000	H	2.886339000	2.341983000	-2.181383000
H	-3.715323000	-3.901159000	-2.318480000	H	3.730394000	3.894709000	-2.443730000
C	5.165869000	0.822284000	0.284388000	C	-5.179499000	-0.746458000	0.257516000
H	5.644473000	1.361440000	1.116912000	H	-5.675894000	-1.262833000	1.094175000
C	5.409122000	1.228791000	-1.033374000	C	-5.400837000	-1.183554000	-1.054014000
H	6.082930000	2.075768000	-1.235938000	H	-6.075433000	-2.031900000	-1.248350000
C	0.203546000	-1.561716000	3.303245000	C	-0.230397000	1.734607000	3.207703000
H	-0.652387000	-1.002022000	3.728460000	H	0.615262000	1.166186000	3.641221000
H	0.355398000	-1.194843000	2.264475000	H	-0.386959000	1.357683000	2.172910000
H	1.112109000	-1.312391000	3.888535000	H	-1.143998000	1.508129000	3.794266000
C	-1.604766000	-5.580827000	-1.739052000	C	1.614153000	5.591099000	-1.923739000
H	-2.554808000	-6.096970000	-1.483737000	H	2.561601000	6.117871000	-1.680213000
H	-0.790059000	-6.068068000	-1.169839000	H	0.795401000	6.093665000	-1.373754000
H	-1.405874000	-5.745825000	-2.818925000	H	1.419601000	5.722846000	-3.008980000
C	5.369397000	-1.130838000	2.714797000	C	-5.423403000	1.228140000	2.650369000
H	5.891542000	-1.936291000	2.159429000	H	-5.963827000	2.003991000	2.070680000
H	5.154871000	-1.504388000	3.738101000	H	-5.225114000	1.634335000	3.664423000
H	6.078928000	-0.281794000	2.810841000	H	-6.110459000	0.363369000	2.766234000
C	-0.297908000	-3.581847000	4.747181000	C	0.309042000	3.761719000	4.626314000
H	0.612148000	-3.413784000	5.359323000	H	-0.601786000	3.613142000	5.242280000
H	-0.531380000	-4.666619000	4.766278000	H	0.558089000	4.843163000	4.633440000
H	-1.130173000	-3.046505000	5.251301000	H	1.134859000	3.219537000	5.133772000
C	3.381628000	0.428610000	2.810305000	C	-3.400695000	-0.281591000	2.793073000
H	4.040426000	1.314362000	2.912711000	H	-4.035524000	-1.184343000	2.896613000
H	3.117203000	0.082411000	3.831784000	H	-3.162397000	0.086683000	3.813337000
H	2.459198000	0.772411000	2.303661000	H	-2.460645000	-0.606297000	2.305941000
C	2.749693000	-0.237740000	-4.128729000	C	-2.768720000	0.202581000	-4.185175000
H	2.195372000	0.634457000	-3.722911000	H	-2.331368000	-0.744204000	-3.805148000
H	2.084950000	-0.755254000	-4.851134000	H	-2.035349000	0.660364000	-4.880435000
H	3.618866000	0.151085000	-4.700640000	H	-3.669217000	-0.060587000	-4.780432000
C	3.977096000	-2.386407000	-3.588846000	C	-3.772837000	2.445068000	-3.590097000
H	4.960115000	-2.046575000	-3.979531000	H	-4.791180000	2.217735000	-3.971955000
H	3.422076000	-2.861719000	-4.424843000	H	-3.179476000	2.867561000	-4.427923000
H	4.163815000	-3.166667000	-2.826705000	H	-3.860564000	3.232605000	-2.818188000

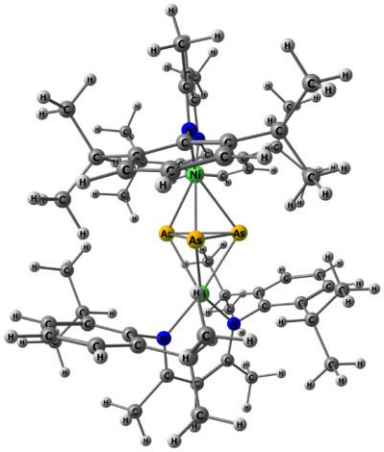
Table S4.11. Optimized geometry of **3a**. XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.



Ni	1.949424000	-0.209326000	0.107784000	C	-5.736854000	-1.613936000	-1.007735000
Ni	-1.932582000	0.191479000	-0.008134000	H	-5.508845000	-1.984010000	-2.026771000
P	-0.009592000	0.192725000	1.197275000	H	-6.729712000	-1.126049000	-1.018501000
P	-0.124919000	-1.189470000	-0.595433000	H	-5.803715000	-2.513388000	-0.360701000
P	0.190961000	0.978904000	-0.900162000	C	1.402957000	-5.094633000	0.470171000
N	2.953184000	-1.701960000	0.810871000	H	1.209406000	-5.842894000	-0.313926000
N	3.441895000	0.898527000	-0.375258000	C	-2.304743000	3.536027000	-1.529144000
N	-3.036924000	1.666686000	0.581649000	H	-2.323588000	2.427565000	-1.617354000
N	-3.362884000	-0.960360000	-0.620042000	C	2.075471000	-2.172713000	3.639988000
C	4.295702000	-1.699008000	0.935196000	H	2.575158000	-1.280422000	3.207294000
C	3.195804000	2.194964000	-0.947668000	C	5.842456000	1.523511000	-0.516753000
C	-2.413827000	2.903166000	0.975047000	H	5.840415000	1.706429000	-1.610349000
C	4.726761000	0.572289000	-0.119157000	H	6.829276000	1.114455000	-0.230519000
C	2.264087000	-2.917244000	1.157225000	H	5.718465000	2.517209000	-0.042022000
C	-3.049098000	-2.231401000	-1.210662000	C	-5.194613000	2.818447000	1.084047000
C	3.013005000	3.313875000	-0.079909000	H	-5.267938000	2.768692000	2.190648000
C	5.113801000	-0.631429000	0.503422000	H	-6.224762000	2.791565000	0.680910000
H	6.193151000	-0.763725000	0.658302000	H	-4.737394000	3.795845000	0.839910000
C	-3.147063000	-3.422565000	-0.427804000	C	-4.297887000	-4.615899000	1.539891000
C	-2.205686000	3.212604000	2.353316000	H	-5.176824000	-4.839791000	0.899274000
C	3.153730000	2.355381000	-2.365671000	H	-4.662596000	-4.459103000	2.576523000
C	2.018546000	-3.875910000	0.123111000	H	-3.656261000	-5.522369000	1.559739000
C	-2.063712000	3.841436000	-0.046352000	C	-3.585944000	2.810294000	4.473111000
C	-1.679447000	4.480113000	2.681109000	H	-3.183196000	3.688022000	5.021892000
H	-1.523760000	4.737976000	3.741368000	H	-3.864268000	2.047226000	5.230343000
C	-3.529132000	-3.372255000	1.055993000	H	-4.515363000	3.139015000	3.965961000
H	-4.200371000	-2.498854000	1.196662000	C	4.578286000	1.404770000	-4.260293000
C	2.776631000	4.578252000	-0.655953000	H	4.417841000	2.271712000	-4.936027000
H	2.629603000	5.449448000	0.003090000	H	4.748070000	0.512675000	-4.899697000
C	-2.655298000	-2.282378000	-2.582332000	H	5.513215000	1.595242000	-3.693791000
C	-4.384413000	1.643225000	0.557650000	C	-1.185018000	4.064348000	-2.444997000
C	1.869710000	-3.178561000	2.502891000	H	-1.176973000	5.174648000	-2.493653000
C	-5.137197000	0.554235000	0.062101000	H	-1.337248000	3.698839000	-3.482269000
H	-6.228425000	0.675848000	0.095042000	H	-0.182467000	3.730353000	-2.109511000
C	-4.672564000	-0.647870000	-0.506996000	C	3.850855000	-4.156860000	-1.635612000
C	3.367901000	1.182283000	-3.326933000	H	4.631253000	-3.699204000	-0.996990000
H	3.577394000	0.283886000	-2.709540000	H	4.123598000	-3.951059000	-2.692676000
C	5.017934000	-2.871848000	1.580561000	H	3.889050000	-5.257496000	-1.485422000
H	4.933458000	-2.812118000	2.686032000	C	2.100639000	0.888132000	-4.156564000
H	6.094633000	-2.855447000	1.326053000	H	1.225184000	0.701478000	-3.502150000
H	4.591811000	-3.849131000	1.284625000	H	2.247501000	-0.007356000	-4.796896000
C	-1.356206000	5.418048000	1.692752000	H	1.845637000	1.739268000	-4.823624000
H	-0.955432000	6.404874000	1.974667000	C	1.428109000	-4.140045000	-2.356704000
C	-2.542257000	2.237434000	3.487402000	H	1.422364000	-5.250528000	-2.398841000
H	-2.968338000	1.323136000	3.023332000	H	1.695337000	-3.782422000	-3.373292000
C	1.036258000	-5.375717000	1.794572000	H	0.395879000	-3.802679000	-2.134068000
H	0.566542000	-6.339852000	2.046834000	C	0.724954000	-1.709200000	4.227035000
C	-1.536238000	5.089320000	0.341578000	H	0.068451000	-1.288838000	3.438445000
H	-1.268173000	5.823571000	-0.433847000	H	0.878817000	-0.924267000	4.997388000
C	2.912706000	3.643068000	-2.886910000	H	0.180484000	-2.549972000	4.707524000
H	2.875845000	3.782590000	-3.979831000	C	-1.345729000	-1.030624000	-4.389966000
C	2.727015000	4.750009000	-2.046603000	H	-0.404943000	-1.282028000	-3.859530000
H	2.543319000	5.747486000	-2.476543000	H	-1.215632000	-0.035592000	-4.863975000
C	3.061609000	3.171657000	1.443801000	H	-1.481545000	-1.765222000	-5.212509000
H	3.208730000	2.094650000	1.667507000	C	1.730207000	3.594983000	2.090941000
C	-2.383908000	-3.542532000	-3.153836000	H	1.524231000	4.674866000	1.939455000
H	-2.087251000	-3.601870000	-4.212540000	H	1.748398000	3.408401000	3.185469000
C	-2.545340000	-1.008719000	-3.425222000	H	0.875976000	3.033813000	1.662145000
H	-2.381879000	-0.174878000	-2.707775000	C	-3.675755000	4.061137000	-2.012528000
C	-2.851698000	-4.652501000	-1.048963000	H	-4.519516000	3.599576000	-1.463876000
H	-2.918522000	-5.581925000	-0.463240000	H	-3.818294000	3.836850000	-3.091068000

C	2.439647000	-3.607418000	-1.325645000	H	-3.746391000	5.162893000	-1.883933000
H	2.482606000	-2.500964000	-1.432486000	C	2.972218000	-2.725855000	4.769650000
C	-1.279403000	1.818734000	4.271365000	H	2.493210000	-3.586180000	5.283918000
H	-0.516180000	1.371519000	3.603924000	H	3.158383000	-1.944853000	5.537019000
H	-1.534493000	1.069365000	5.050437000	H	3.956841000	-3.073620000	4.396205000
H	-0.815911000	2.689253000	4.783092000	C	-3.850728000	-0.706486000	-4.193689000
C	-2.482970000	-4.720289000	-2.400476000	H	-4.103603000	-1.535276000	-4.889718000
H	-2.267458000	-5.694974000	-2.866435000	H	-3.744465000	0.221027000	-4.795608000
C	-2.288977000	-3.114423000	1.936460000	H	-4.710334000	-0.561688000	-3.509828000
H	-1.544540000	-3.931717000	1.838325000	C	4.237524000	3.953489000	2.068853000
H	-2.575163000	-3.031160000	3.006630000	H	5.218051000	3.640563000	1.654937000
H	-1.790116000	-2.170238000	1.640772000	H	4.271100000	3.793813000	3.167511000
C	1.262537000	-4.418989000	2.792189000	H	4.135265000	5.046162000	1.894956000
H	0.960578000	-4.639115000	3.829122000				

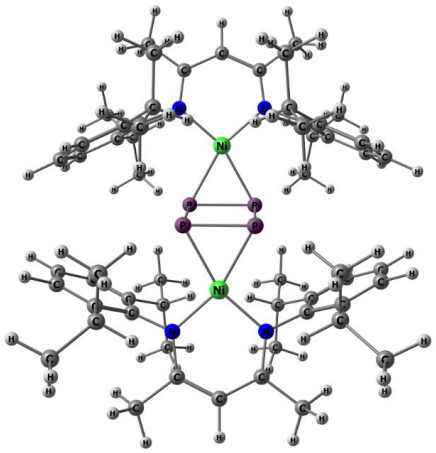
Table S4.12. Optimized geometry of **3b**. XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.



As	0.001618000	0.125976000	-1.382069000	H	-6.614550000	-2.140003000	0.365953000
As	-0.017927000	1.072340000	0.920228000	H	-5.681037000	-2.260223000	1.890426000
As	-0.011363000	-1.349643000	0.604082000	C	-4.637334000	-1.239199000	0.280709000
C	5.518493000	2.462898000	0.727124000	C	-5.213551000	-0.105682000	-0.322473000
H	5.302835000	2.810355000	1.756521000	H	-6.308722000	-0.121044000	-0.416803000
H	5.395477000	3.348851000	0.070560000	C	-4.580542000	1.072648000	-0.782525000
H	6.575316000	2.140635000	0.671086000	C	-5.535629000	2.121926000	-1.341897000
C	4.590501000	1.335652000	0.301338000	H	-5.057622000	3.099362000	-1.527390000
C	5.198603000	0.228557000	-0.325270000	H	-6.389916000	2.269592000	-0.650679000
H	6.289044000	0.288678000	-0.443099000	H	-5.966260000	1.759146000	-2.299263000
C	4.599959000	-0.968657000	-0.775843000	C	-2.865205000	-2.633668000	1.033442000
C	5.551136000	-2.008614000	-1.350528000	C	-2.796240000	-2.793877000	2.449384000
H	5.361252000	-3.021516000	-0.946226000	C	-2.383669000	-4.042228000	2.961824000
H	6.601964000	-1.732439000	-1.142852000	H	-2.325691000	-4.182395000	4.053640000
H	5.429477000	-2.088424000	-2.449833000	C	-2.050763000	-5.107272000	2.114625000
C	2.795645000	2.617610000	1.183137000	H	-1.740483000	-6.075973000	2.537692000
C	2.602216000	3.820661000	0.439200000	C	-2.101607000	-4.928805000	0.723224000
C	2.144432000	4.964181000	1.125512000	H	-1.818142000	-5.761899000	0.061450000
H	1.981462000	5.898089000	0.564068000	C	-2.498228000	-3.702398000	0.155764000
C	1.898517000	4.941094000	2.505317000	C	-3.128353000	-1.655349000	3.418314000
H	1.550474000	5.849920000	3.021465000	H	-3.501384000	-0.803652000	2.811885000
C	2.094035000	3.752887000	3.224493000	C	-1.864990000	-1.169961000	4.161723000
H	1.896827000	3.739223000	4.308006000	H	-1.438180000	-1.973037000	4.800100000
C	2.535063000	2.574867000	2.588661000	H	-2.102167000	-0.307326000	4.820110000
C	2.846499000	3.892695000	-1.071335000	H	-1.076641000	-0.851666000	3.449626000
H	3.386245000	2.969575000	-1.367554000	C	-4.232431000	-2.035067000	4.428369000
C	1.514213000	3.902129000	-1.847573000	H	-5.156664000	-2.386310000	3.924482000
H	0.899099000	3.012777000	-1.602903000	H	-4.501957000	-1.160993000	5.058281000
H	1.695298000	3.902797000	-2.943665000	H	-3.901900000	-2.844619000	5.113667000
H	0.907733000	4.798314000	-1.602248000	C	-2.512336000	-3.509540000	-1.363345000
C	3.719378000	5.097723000	-1.481059000	H	-2.405491000	-2.414512000	-1.526730000
H	3.199718000	6.063595000	-1.305682000	C	-1.327656000	-4.197075000	-2.063621000
H	3.960174000	5.049924000	-2.563982000	H	-0.356813000	-3.908769000	-1.612558000
H	4.677449000	5.131338000	-0.921115000	H	-1.301141000	-3.912616000	-3.136285000
C	2.748124000	1.291844000	3.398266000	H	-1.403259000	-5.305101000	-2.026980000
H	2.715571000	0.454390000	2.667856000	C	-3.845758000	-3.949503000	-2.007414000
C	1.638214000	1.046172000	4.437928000	H	-3.811731000	-3.800522000	-3.107694000
H	1.661970000	1.792039000	5.260947000	H	-4.709316000	-3.372982000	-1.622133000
H	1.761285000	0.045891000	4.903177000	H	-4.042418000	-5.027179000	-1.819023000
H	0.631254000	1.083217000	3.973306000	C	-2.756430000	2.573689000	-1.102127000

C	4.136532000	1.260465000	4.075374000	C	-2.439429000	2.878252000	-2.461049000
H	4.254295000	2.109808000	4.782359000	C	-2.055603000	4.198558000	-2.777949000
H	4.960456000	1.317893000	3.336650000	H	-1.825415000	4.453154000	-3.825168000
H	4.270036000	0.319897000	4.651072000	C	-1.973154000	5.194804000	-1.796586000
C	2.857509000	-2.538095000	-1.081256000	H	-1.684883000	6.221991000	-2.071722000
C	2.782282000	-3.537721000	-0.058864000	C	-2.248274000	4.872238000	-0.460319000
C	2.504746000	-4.866331000	-0.439014000	H	-2.166218000	5.652623000	0.312270000
H	2.453671000	-5.647525000	0.335237000	C	-2.637708000	3.571051000	-0.083749000
C	2.300531000	-5.215541000	-1.781744000	C	-2.548009000	1.847114000	-3.590593000
H	2.099808000	-6.262891000	-2.058024000	H	-2.706892000	0.854819000	-3.117242000
C	2.331107000	-4.219320000	-2.765688000	C	-1.260037000	1.769282000	-4.437575000
H	2.144158000	-4.493322000	-3.816781000	H	-1.089224000	2.705206000	-5.011100000
C	2.597306000	-2.871341000	-2.444887000	H	-1.330306000	0.941407000	-5.174284000
C	3.021979000	-3.197999000	1.417611000	H	-0.364162000	1.591343000	-3.808916000
H	2.799596000	-2.113192000	1.525885000	C	-3.753606000	2.127312000	-4.516956000
C	4.492939000	-3.406698000	1.844189000	H	-4.710594000	2.159256000	-3.961887000
H	4.809962000	-4.458988000	1.678217000	H	-3.838777000	1.341119000	-5.297087000
H	4.616545000	-3.184174000	2.925419000	H	-3.637478000	3.102814000	-5.036346000
H	5.188691000	-2.746963000	1.290481000	C	-2.971260000	3.267749000	1.380733000
C	2.085510000	-3.968324000	2.369172000	H	-2.883911000	2.165506000	1.498263000
H	1.022046000	-3.883053000	2.065619000	C	-1.993568000	3.928970000	2.371057000
H	2.179429000	-3.570051000	3.401161000	H	-0.936353000	3.700619000	2.126835000
H	2.339519000	-5.049156000	2.417382000	H	-2.192368000	3.568387000	3.402199000
C	2.587745000	-1.828140000	-3.568559000	H	-2.105161000	5.034394000	2.389564000
H	2.781485000	-0.839466000	-3.101075000	C	-4.423337000	3.660702000	1.735365000
C	1.207170000	-1.762962000	-4.258446000	H	-4.582490000	4.752037000	1.597444000
H	0.981704000	-2.703640000	-4.804950000	H	-4.644430000	3.418083000	2.796561000
H	1.177023000	-0.933301000	-4.996016000	H	-5.165368000	3.130379000	1.108572000
H	0.392178000	-1.596691000	-3.524998000	N	3.262249000	1.428591000	0.523370000
C	3.675777000	-2.076045000	-4.637207000	N	3.272526000	-1.209084000	-0.712751000
H	4.698419000	-2.090575000	-4.209963000	N	-3.306406000	-1.391847000	0.459053000
H	3.648404000	-1.278923000	-5.409831000	N	-3.249078000	1.270757000	-0.735904000
H	3.519036000	-3.046214000	-5.155396000	Ni	1.989254000	0.086587000	-0.047130000
C	-5.602799000	-2.301849000	0.783587000	Ni	-2.005127000	-0.075267000	-0.099844000
H	-5.270185000	-3.328024000	0.535000000				

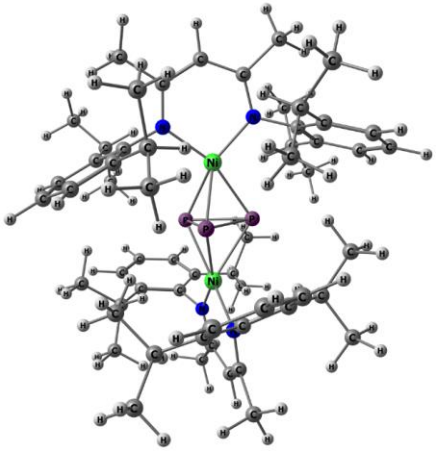
Table S4.13. Optimized geometries of **4** singlet state. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



C	4.210666000	-3.312457000	3.540938000	C	-4.210666000	3.312457000	-3.540938000
H	4.357905000	-4.351207000	3.895210000	H	-4.357905000	4.351207000	-3.895210000
H	5.203125000	-2.909743000	3.246552000	H	-5.203125000	2.909743000	-3.246552000
H	3.859328000	-2.690796000	4.389152000	H	-3.859328000	2.690796000	-4.389152000
C	3.235554000	-3.264448000	2.376924000	C	-3.235554000	3.264448000	-2.376924000
C	2.938013000	-4.486083000	1.725172000	C	-2.938013000	4.486083000	-1.725172000
H	3.457135000	-5.379295000	2.103179000	H	-3.457135000	5.379295000	-2.103179000
C	1.971935000	-4.704171000	0.711383000	C	-1.971935000	4.704171000	-0.711383000
C	1.747385000	-6.139716000	0.265647000	C	-1.747385000	6.139716000	-0.265647000
H	2.029745000	-6.854241000	1.063721000	H	-2.029745000	6.854241000	-1.063721000
H	0.691909000	-6.317651000	-0.020006000	H	-0.691909000	6.317651000	0.020006000
H	2.365408000	-6.375419000	-0.627546000	H	-2.365408000	6.375419000	0.627546000
C	2.882204000	-0.929261000	2.805965000	C	-2.882204000	0.929261000	-2.805965000
C	4.042078000	-0.117544000	2.654578000	C	-4.042078000	0.117544000	-2.654578000
C	4.143591000	1.070484000	3.406155000	C	-4.143591000	-1.070484000	-3.406155000
C	3.131274000	1.456254000	4.296175000	C	-3.131274000	-1.456254000	-4.296175000
C	1.989113000	0.648387000	4.438526000	C	-1.989113000	-0.648387000	-4.438526000
C	1.842614000	-0.546605000	3.711760000	C	-1.842614000	0.546605000	-3.711760000

C	5.135367000	-0.481848000	1.653006000	C	-5.135367000	0.481848000	-1.653006000
H	4.870490000	-1.475740000	1.235901000	H	-4.870490000	1.475740000	-1.235901000
C	6.523908000	-0.584027000	2.313043000	C	-6.523908000	0.584027000	-2.313043000
H	6.525275000	-1.291022000	3.168800000	H	-6.525275000	1.291022000	-3.168800000
H	7.285194000	-0.929863000	1.581239000	H	-7.285194000	0.929863000	-1.581239000
H	6.860383000	0.402779000	2.698071000	H	-6.860383000	-0.402779000	-2.698071000
C	5.162674000	0.510859000	0.475245000	C	-5.162674000	-0.510859000	-0.475245000
H	5.468278000	1.523853000	0.815655000	H	-5.468278000	-1.523853000	-0.815655000
H	5.878850000	0.182337000	-0.308596000	H	-5.878850000	-0.182337000	0.308596000
H	4.147042000	0.598556000	0.034660000	H	-4.147042000	-0.598556000	-0.034660000
C	0.587102000	-1.407679000	3.822659000	C	-0.587102000	1.407679000	-3.822659000
H	0.338507000	-1.670072000	2.765237000	H	-0.338507000	1.670072000	-2.765237000
C	0.832541000	-2.727606000	4.582089000	C	-0.832541000	2.727606000	-4.582089000
H	1.213020000	-2.529440000	5.608196000	H	-1.213020000	2.529440000	-5.608196000
H	-0.116981000	-3.295552000	4.679575000	H	0.116981000	3.295552000	-4.679575000
H	1.555381000	-3.381300000	4.059308000	H	-1.555381000	3.381300000	-4.059308000
C	-0.617201000	-0.677379000	4.426509000	C	0.617201000	0.677379000	-4.426509000
H	-0.813198000	0.266415000	3.879970000	H	0.813198000	-0.266415000	-3.879970000
H	-1.523720000	-1.312041000	4.336433000	H	1.523720000	1.312041000	-4.336433000
H	-0.472996000	-0.457195000	5.507777000	H	0.472996000	0.457195000	-5.507777000
C	0.209070000	-3.979147000	-0.758558000	C	-0.209070000	3.979147000	0.758558000
C	0.457699000	-4.189743000	-2.144400000	C	-0.457699000	4.189743000	2.144400000
C	-0.638844000	-4.363224000	-3.011661000	C	0.638844000	4.363224000	3.011661000
H	-0.451977000	-4.507020000	-4.089162000	H	0.451977000	4.507020000	4.089162000
C	-1.956895000	-4.338500000	-2.535831000	C	1.956895000	4.338500000	2.535831000
H	-2.801375000	-4.462592000	-3.231560000	H	2.801375000	4.462592000	3.231560000
C	-2.193795000	-4.127659000	-1.166949000	C	2.193795000	4.127659000	1.166949000
H	-3.229481000	-4.080217000	-0.798834000	H	3.229481000	4.080217000	0.798834000
C	-1.132424000	-3.946847000	-0.261163000	C	1.132424000	3.946847000	0.261163000
C	1.877210000	-4.199131000	-2.705142000	C	-1.877210000	4.199131000	2.705142000
H	2.562279000	-4.046895000	-1.845270000	H	-2.562279000	4.046895000	1.845270000
C	2.217977000	-5.543411000	-3.378044000	C	-2.217977000	5.543411000	3.378044000
H	1.591623000	-5.706559000	-4.281684000	H	-1.591623000	5.706559000	4.281684000
H	3.280743000	-5.567928000	-3.701743000	H	-3.280743000	5.567928000	3.701743000
H	2.046807000	-6.402274000	-2.697102000	H	-2.046807000	6.402274000	2.697102000
C	2.110042000	-3.029784000	-3.680497000	C	-2.110042000	3.029784000	3.680497000
H	1.868799000	-2.069636000	-3.178540000	H	-1.868799000	2.069636000	3.178540000
H	3.164917000	-3.007620000	-4.030041000	H	-3.164917000	3.007620000	4.030041000
H	1.456651000	-3.117824000	-4.575886000	H	-1.456651000	3.117824000	4.575886000
C	-1.375698000	-3.670765000	1.220053000	C	1.375698000	3.670765000	-1.220053000
H	-0.653010000	-2.856940000	1.470094000	H	0.653010000	2.856940000	-1.470094000
C	-1.041682000	-4.884416000	2.110798000	C	1.041682000	4.884416000	-2.110798000
H	0.021804000	-5.177511000	2.037145000	H	-0.021804000	5.177511000	-2.037145000
H	-1.247431000	-4.647396000	3.176213000	H	1.247431000	4.647396000	-3.176213000
H	-1.666489000	-5.761434000	1.832690000	H	1.666489000	5.761434000	-1.832690000
C	-2.788097000	-3.166249000	1.537790000	C	2.788097000	3.166249000	-1.537790000
H	-3.557654000	-3.954581000	1.381265000	H	3.557654000	3.954581000	-1.381265000
H	-2.845728000	-2.857194000	2.603012000	H	2.845728000	2.857194000	-2.603012000
H	-3.031250000	-2.284266000	0.911395000	H	3.031250000	2.284266000	-0.911395000
N	2.689291000	-2.091653000	2.010254000	N	-2.689291000	2.091653000	-2.010254000
N	1.275873000	-3.705521000	0.143069000	N	-1.275873000	3.705521000	-0.143069000
P	-0.514957000	0.875734000	1.217201000	P	0.514957000	-0.875734000	-1.217201000
P	1.514131000	0.377037000	0.261371000	P	-1.514131000	-0.377037000	-0.261371000
Ni	1.532906000	-1.863579000	0.523980000	Ni	-1.532906000	1.863579000	-0.523980000
H	1.184817000	0.967259000	5.118059000	H	-1.184817000	-0.967259000	-5.118059000
H	3.219800000	2.393965000	4.867041000	H	-3.219800000	-2.393965000	-4.867041000
H	5.030054000	1.713569000	3.276171000	H	-5.030054000	-1.713569000	-3.276171000

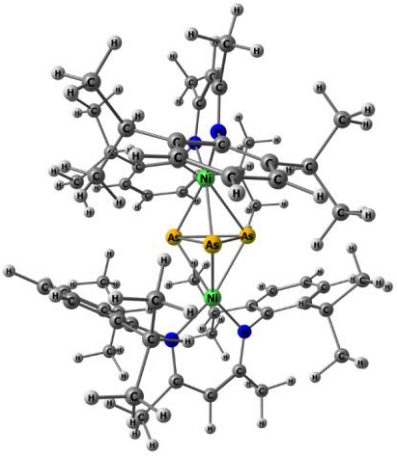
Table S4.14. Optimized geometries of **5a** singlet. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



Ni	1.795214000	0.692075000	-0.272480000	C	-5.900562000	-0.564173000	-1.419376000
Ni	-1.760749000	-0.744108000	-0.276882000	H	-5.783483000	-0.101620000	-2.418371000
P	0.504081000	-1.177298000	-0.512630000	H	-6.343920000	0.214056000	-0.762595000
P	-0.370736000	0.745466000	-1.304299000	H	-6.624139000	-1.399341000	-1.487512000
P	-0.140864000	0.460852000	0.895014000	C	-3.278521000	2.467724000	1.531541000
N	2.475606000	2.302456000	0.496178000	H	-2.294035000	2.016275000	1.290013000
N	-2.353043000	-2.228943000	0.789998000	H	-3.472162000	2.304101000	2.612171000
N	3.405981000	0.203805000	-1.182625000	H	-3.199253000	3.561432000	1.361388000
N	-3.462173000	-0.309094000	-1.025790000	C	-1.016405000	4.223293000	-0.886629000
C	3.682957000	2.831053000	0.247230000	H	-1.616003000	3.343183000	-0.588568000
C	-1.441568000	-2.669021000	1.790830000	H	-1.082567000	4.304391000	-1.990905000
C	1.636410000	2.899926000	1.474514000	H	-1.498435000	5.130609000	-0.461097000
C	-3.611896000	0.980535000	-1.604349000	C	3.906331000	-3.482724000	-1.031457000
C	4.596549000	2.255784000	-0.668213000	H	4.115001000	-4.262416000	-0.283393000
H	5.538814000	2.800378000	-0.822826000	C	5.713657000	0.478544000	-2.034825000
C	-0.615673000	-3.812009000	1.594154000	H	6.057710000	-0.495811000	-1.629949000
C	3.506632000	-1.149536000	-1.608838000	H	6.548933000	1.201542000	-1.974518000
C	4.498049000	0.985415000	-1.279024000	H	5.478287000	0.301518000	-3.104223000
C	-3.578505000	-2.769241000	0.716074000	C	2.916682000	-0.468196000	-4.006499000
C	0.594797000	3.769359000	1.039968000	H	3.050007000	0.527391000	-3.534765000
C	-3.251759000	1.191460000	-2.967192000	C	0.611388000	-4.732264000	-0.442849000
C	-4.575908000	-1.048057000	-0.852851000	H	0.489480000	-5.314791000	-1.380568000
C	4.150800000	4.050298000	1.021486000	H	1.412535000	-5.221715000	0.150869000
H	4.964553000	4.572777000	0.482131000	H	0.963083000	-3.716218000	-0.708161000
H	4.547355000	3.745965000	2.014100000	C	-1.662669000	0.379882000	4.109701000
H	3.327366000	4.764223000	1.216576000	H	-1.512645000	0.025768000	5.152590000
C	-4.603347000	-2.246144000	-0.109582000	H	-2.338574000	1.257686000	4.158338000
H	-5.563282000	-2.781641000	-0.087287000	H	-0.690257000	0.728780000	3.709725000
C	-4.118073000	2.048330000	-0.808876000	C	-1.169843000	-6.114528000	0.686912000
C	1.783671000	2.558170000	2.847610000	H	-1.341681000	-6.705781000	-0.237616000
C	-0.268272000	4.316406000	2.007581000	H	-2.105309000	-6.124001000	1.280158000
H	-1.076969000	4.990973000	1.687260000	H	-0.394126000	-6.644437000	1.280417000
C	2.840640000	1.551398000	3.294942000	C	3.747096000	-3.848304000	-2.379292000
H	3.463526000	1.315863000	2.407509000	H	3.845887000	-4.903229000	-2.681476000
C	-2.666172000	0.041968000	-3.781018000	C	-5.776592000	2.411007000	1.101487000
H	-1.995406000	-0.499442000	-3.073535000	H	-6.598900000	1.994129000	0.483193000
C	3.779174000	-2.144345000	-0.620165000	H	-5.818046000	3.517593000	1.010721000
C	-1.347260000	-1.899868000	2.991864000	H	-5.986395000	2.160529000	2.162633000
C	0.288830000	-4.170521000	2.614468000	C	-3.734121000	-0.966572000	-4.250309000
H	0.924154000	-5.060413000	2.476775000	H	-3.262472000	-1.774519000	-4.849310000
C	0.442538000	4.070212000	-0.446813000	H	-4.498241000	-0.472137000	-4.888621000
H	0.851534000	3.172822000	-0.960690000	H	-4.250147000	-1.444297000	-3.396370000
C	-3.436155000	2.474720000	-3.517374000	C	1.426116000	-0.602431000	-4.367314000
H	-3.162078000	2.657788000	-4.567133000	H	0.786715000	-0.487621000	-3.468179000
C	0.889493000	3.123020000	3.777875000	H	1.212327000	-1.597322000	-4.814357000
H	0.984264000	2.860839000	4.844458000	H	1.129822000	0.173796000	-5.102521000
C	0.396343000	-3.421983000	3.794076000	C	3.764363000	2.117128000	4.389121000
H	1.118132000	-3.714374000	4.573211000	H	4.572518000	1.394954000	4.631589000
C	-0.713507000	-4.680934000	0.341490000	H	3.206408000	2.318439000	5.328770000
H	-1.478752000	-4.219068000	-0.316747000	H	4.239540000	3.068782000	4.072673000
C	3.308869000	-1.510899000	-2.967381000	C	-1.825872000	0.520907000	-4.970383000
C	-0.417132000	-2.292167000	3.971999000	H	-2.452431000	1.000378000	-5.753424000
H	-0.328564000	-1.701754000	4.896065000	H	-1.307378000	-0.336739000	-5.444275000
C	-0.124666000	4.003851000	3.369350000	H	-1.057509000	1.251102000	-4.646787000
H	-0.814926000	4.435585000	4.111649000	C	2.193187000	0.229973000	3.749553000
C	-3.939546000	-3.996954000	1.535603000	H	2.970801000	-0.518106000	4.012000000
H	-3.791262000	-4.915963000	0.929765000	H	1.554892000	-0.199599000	2.951289000
H	-5.005863000	-3.972641000	1.834363000	H	1.554093000	0.382353000	4.644777000

H	-3.312063000	-4.093225000	2.441334000	C	-3.655997000	-1.131672000	3.732604000
C	-3.967719000	3.527231000	-2.753858000	H	-3.572959000	-1.634740000	4.720426000
H	-4.108983000	4.521905000	-3.205999000	H	-4.161679000	-1.825588000	3.034650000
C	-2.270510000	-0.702806000	3.210337000	H	-4.313087000	-0.244051000	3.854981000
H	-2.422206000	-0.261603000	2.200303000	C	3.419927000	-2.863271000	1.798211000
C	-4.292601000	3.310995000	-1.407196000	H	2.424594000	-3.258927000	1.520483000
H	-4.678727000	4.146038000	-0.800546000	H	3.343005000	-2.479811000	2.835792000
C	-4.404992000	1.854881000	0.678685000	H	4.144310000	-3.706644000	1.809836000
H	-4.404632000	0.764542000	0.881374000	C	3.794828000	-0.523440000	-5.270190000
C	3.847104000	-1.740669000	0.849425000	H	3.643582000	-1.469784000	-5.832148000
H	3.095868000	-0.919773000	0.944553000	H	4.875212000	-0.449706000	-5.025644000
C	1.283414000	5.285759000	-0.883624000	H	3.542165000	0.311114000	-5.957558000
H	2.362504000	5.134073000	-0.687897000	C	5.211522000	-1.155083000	1.259177000
H	0.964127000	6.204820000	-0.345282000	H	6.025724000	-1.898361000	1.115071000
H	1.162825000	5.470229000	-1.972457000	H	5.199207000	-0.868801000	2.332699000
C	3.430432000	-2.868185000	-3.330018000	H	5.461884000	-0.246564000	0.678085000
H	3.274245000	-3.161500000	-4.381160000				

Table S4.15. Optimized geometries of **5b** singlet. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



Ni	-1.785945000	0.817613000	0.261120000	H	3.599150000	2.660447000	4.333679000
Ni	1.745243000	-0.850210000	0.266288000	C	-0.628361000	2.815387000	-3.879537000
N	3.490276000	-0.536220000	0.983239000	H	-0.732563000	2.404813000	-4.896147000
N	-3.464943000	0.477127000	1.110487000	C	1.842859000	-0.072369000	-4.255034000
N	2.170476000	-2.456268000	-0.716634000	H	2.604688000	0.728473000	-4.345914000
N	-2.271724000	2.494443000	-0.547272000	H	0.902617000	0.398695000	-3.905806000
C	4.527239000	-1.383651000	0.830597000	H	1.674420000	-0.478589000	-5.275636000
C	4.422592000	-2.624603000	0.169657000	C	-0.111599000	4.379497000	0.153753000
H	5.329521000	-3.247049000	0.162679000	H	-0.688486000	3.711953000	0.829918000
C	-3.435417000	3.125953000	-0.332544000	C	0.718383000	-5.925586000	-0.111155000
C	3.769571000	0.770942000	1.468974000	H	0.686278000	-6.409422000	0.888388000
C	-4.507368000	1.328112000	1.101967000	H	1.768330000	-5.921714000	-0.455612000
C	-4.456070000	2.603652000	0.499316000	H	0.136999000	-6.562100000	-0.813031000
H	-5.359607000	3.223105000	0.598903000	C	3.646227000	-1.769552000	-3.765982000
C	3.345146000	-3.095923000	-0.621678000	H	3.494107000	-2.339218000	-4.708333000
C	1.218472000	-2.854752000	-1.700077000	H	4.084194000	-2.455105000	-3.017964000
C	0.194177000	-3.799309000	-1.399767000	H	4.393253000	-0.971906000	-3.966244000
C	5.908464000	-0.982403000	1.321477000	C	5.914704000	1.769155000	-1.400593000
H	6.389509000	-0.288704000	0.599837000	H	6.128911000	2.858106000	-1.348465000
H	6.561996000	-1.870212000	1.422920000	H	6.036690000	1.459124000	-2.459961000
H	5.870676000	-0.447434000	2.289834000	H	6.690313000	1.246971000	-0.802205000
C	-4.262187000	-1.834521000	0.809079000	C	-2.487809000	-0.069299000	3.748852000
C	1.257915000	-2.206838000	-2.974525000	H	-2.061424000	0.629867000	2.995854000
C	-1.384800000	2.952155000	-1.562928000	C	-2.151298000	0.239932000	-4.072471000
C	4.303130000	1.748651000	0.580776000	H	-2.961530000	-0.506688000	-4.203722000
C	4.493639000	1.446686000	-0.904257000	H	-1.280860000	-0.284669000	-3.629014000
H	4.320361000	0.360350000	-1.045866000	H	-1.866346000	0.596141000	-5.085442000
C	-3.661366000	-0.833286000	1.623938000	C	0.565949000	4.210079000	-2.296001000
C	-1.526826000	2.407768000	-2.876859000	H	1.398654000	4.894845000	-2.071000000
C	0.116259000	-4.505881000	-0.047204000	C	3.437057000	2.186997000	-1.744994000
H	0.721731000	-3.901095000	0.661653000	H	2.409692000	1.892757000	-1.450047000
C	3.616567000	-4.377906000	-1.396107000	H	3.560521000	1.958267000	-2.823896000
H	3.690079000	-5.235453000	-0.694562000	H	3.522258000	3.286506000	-1.619122000
H	4.590211000	-4.319096000	-1.923723000	C	0.410842000	3.717884000	-3.599447000
H	2.826866000	-4.599638000	-2.136621000	H	1.112277000	4.019713000	-4.393482000

C	2.322857000	-1.151366000	-3.274261000
H	2.530998000	-0.659754000	-2.297316000
C	3.496368000	1.095772000	2.831036000
C	-3.196657000	-1.144275000	2.934549000
C	-0.752348000	-4.103736000	-2.398941000
H	-1.548486000	-4.830838000	-2.175409000
C	-3.741013000	4.458854000	-0.999778000
H	-2.990411000	4.726578000	-1.765497000
H	-3.764741000	5.268170000	-0.239340000
H	-4.743289000	4.442559000	-1.474379000
C	-0.708377000	-3.497276000	-3.660931000
H	-1.462894000	-3.746200000	-4.423947000
C	0.292151000	-2.552857000	-3.938101000
H	0.313724000	-2.060876000	-4.921944000
C	-5.834707000	0.896942000	1.701778000
H	-6.368288000	0.208803000	1.011857000
H	-6.489213000	1.771426000	1.881252000
H	-5.700600000	0.342013000	2.651132000
C	4.597204000	3.030289000	1.084196000
H	5.006082000	3.795479000	0.404036000
C	-0.313366000	3.838730000	-1.258363000
C	-4.615338000	-1.548821000	-0.647899000
H	-4.525340000	-0.453648000	-0.800352000
C	-4.034168000	-3.429354000	2.656241000
H	-4.186599000	-4.442429000	3.061338000
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H	-3.049030000	-2.696124000	4.445972000
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H	2.140404000	-0.498718000	3.086062000
C	-2.622586000	1.382878000	-3.162202000
H	-2.874463000	0.938062000	-2.174095000
C	4.365602000	3.353423000	2.429014000
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C	-4.444382000	-3.121928000	1.349598000
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C	2.064714000	0.671498000	4.900167000
H	2.729465000	1.183268000	5.629300000
H	1.519071000	-0.117464000	5.455648000
H	1.321302000	1.409188000	4.534283000
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C	-3.593581000	-2.221708000	-1.585118000
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C	-1.321611000	-0.620809000	4.577822000
H	-1.657407000	-1.325428000	5.369172000
H	-0.787856000	0.209426000	5.081629000
H	-0.594500000	-1.144259000	3.922780000
C	-6.053768000	-1.960166000	-1.009142000
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C	-3.470650000	0.726063000	4.629407000
H	-4.263590000	1.206484000	4.023105000
H	-2.939361000	1.527123000	5.186411000
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C	-0.666432000	5.811110000	0.302345000
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H	-0.548932000	6.171244000	1.346655000
H	-1.739370000	5.871784000	0.039565000
As	0.532226000	0.979829000	1.212993000
As	-0.613998000	-1.173792000	0.837732000
As	0.075810000	0.232570000	-1.090664000

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Preface

The following chapter has not been published until the submission of this thesis.

Authors

M. Haimerl, M. Piesch, R. Yadav, P. W. Roesky and M. Scheer*

Author contribution

The main part of the manuscript was done by the first author (M. Haimerl). All synthesis and characterizations of compound **3b**, **3c**, **4b**, **4c**, **5a**, **6a**, **6b**, **7a** and **7b** were done by M. Haimerl. M. Piesch performed the DFT calculations and contributed the corresponding part in the Supporting Information. The EPR sample was prepared by the first author and measured with help of S. Dinauer. R. Yadav of the working group P. W. Roesky synthesize [L^3Al] for us. M. Scheer supervised the research and revised the manuscript.

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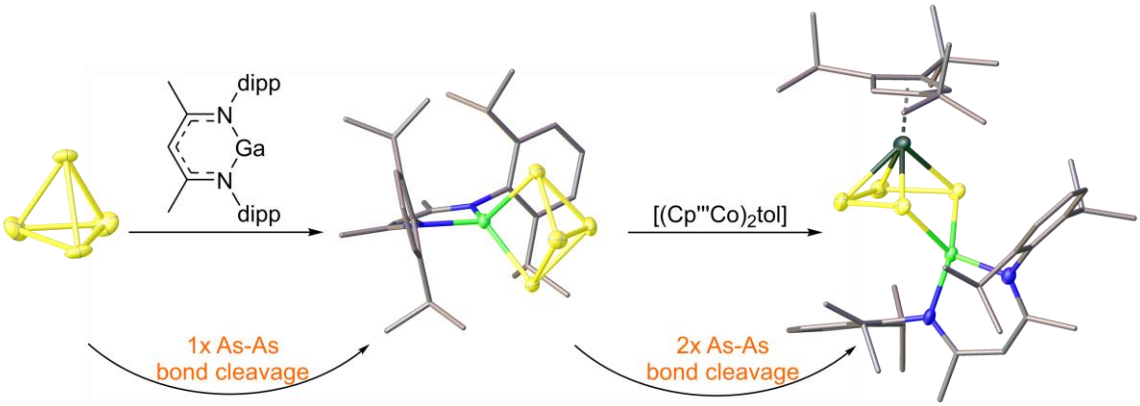

dipp
N
Ga
N
dipp
[(Cp'''Co)2tol]
1x As-As
bond cleavage
2x As-As
bond cleavage

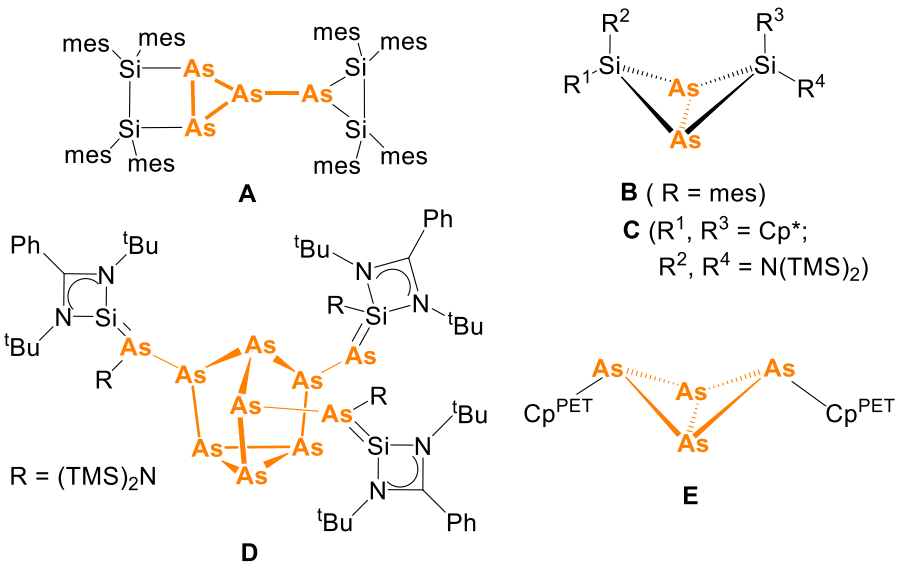
5. Reactivity of E_4 (E_4 = P_4, As_4, AsP_3) towards low valent Al(I) and Ga(I) compounds

Abstract: *The reactivity of yellow arsenic and the interpnictogen compound AsP_3 towards low valent group 13 compounds was investigated. The reactions of [L^3Al] (**1**, L^3 = [{N($C_6H_3{}^iPr_2$-2,6)C(Me)}$_2$CH]$^-$) with As_4 and AsP_3 leads to [(L^3Al)$_2$(μ,$\eta^{1:1:1:1}$-E_4)] (E_4 = As_4 (**3b**), AsP_3 (**3c**)) by insertion of two fragments into two of the six E-E edges of the E_4 tetrahedra. Furthermore, the reaction of [L^3Ga] (**2**) with E_4 afforded [L^3Ga($\eta^{1:1}$-E_4)] (E_4 = As_4 (**4b**), AsP_3 (**4c**)). In this compound only one E-E bond of the E_4 tetrahedra is cleaved. These compounds represent the first examples of the conversion of yellow arsenic and AsP_3 with group 13 compounds. Furthermore, the reactivity of the gallium complexes towards unsaturated transition metal units or polypnictogen (E_n) ligand complexes were investigated. This leads to the heterobimetallic compounds [(L^3Ga)(μ,$\eta^{2:1:1}$-P_4)(L^3Ni)] (**5a**), [(Cp'''Co)(μ,$\eta^{4:1:1}$-E_4)(L^3Ga)] (E = P (**6a**), As (**6b**), Cp''' = η^5-$C_5H_2{}^tBu_3$) and [(Cp'''Ni)($\eta^{3:1:1}$-E_3)(L^3Ga)] (E = P (**7a**), As (**7b**)), which combines two different ligand systems in one compound (nacnac and Cp) as well as two different types of metals (main group and transition metals). The compounds were characterized by crystallographic and spectroscopic methods.*

5.1. Introduction

Yellow arsenic (As_4) is the isostructural higher homolog of white phosphorus, both of them represent at room temperature stable but the most reactive group 15 allotropes. While the reactivity of white phosphorus towards transition metal and main group compounds was extensively investigated,[1] there are just a few examples of the conversion of As_4 with main group compounds.[2] The reason for this lies in the instability, the light- and air sensitivity and the lack of storage possibilities of yellow arsenic.[2d] Another problem is the lack of characterization of product mixtures, since the ^{75}As NMR method only works for very symmetric compounds such as As_4. *West et al.* reported the reactivity of yellow arsenic with silicon compounds.[2a] The reaction of [$Mes_2Si{=}SiMes_2$] with As_4 leads to 1-arsa-2,3-disilacyclopropyl-1,4,5-triarsa-2,3,-disilabicyclo [2.1.0] pentane (**A**, Scheme 5.1) and 1,3-diarsa-2,4-disilabicyclobutane products (**B**, Scheme 5.1). By heating this mixture at 95 °C, there is a conversion to the Si_2As_2 butterfly compound **B**. The reaction of P_4 with different disilenes leads to products similar to **B**. A totally different outcome was observed by the reaction of yellow arsenic with silylene [PhC(N^tBu)$_2$SiN($SiMe_3$)$_2$] as well as the disilene [(Me_3Si)$_2$N(η^1-Me_5C_5)Si=Si(η^1-Me_5C_5)N($SiMe_3$)$_2$][2c] in comparison to the reaction with white phosphorus. Thus, the reaction with As_4 leads to an As_{10} cage with a nortricyclane core stabilized by three arsasilene fragments (**D**, Scheme 5.1) and [Cp*{($SiMe_3$)$_2$N}SiAs]$_2$ (**C**, Cp* = η^5-C_5Me_5, Scheme 5.1) with a butterfly-like central core. By using a main group radical ($Cp^{PET\cdot}$, Cp^{PET} = η^5-C_5(4-EtC_6H_4)$_5$) the first organo-substituted As_4 butterfly compound [$Cp^{PET}{}_2As_4$][2b] (**E**, Scheme 5.1) was synthesized. This compound was able to release yellow arsenic under thermal or photochemical conditions. All known examples of the activation of yellow arsenic with main group compounds are examples of group 14 reactives. In contrast to yellow arsenic, the binary interpnictogen compound AsP_3[3] is

stable, isolobal and as easy to handle as P_4. Within the last decade, a few examples of the activation of AsP_3 with main group and transition metal compounds were reported.[4]



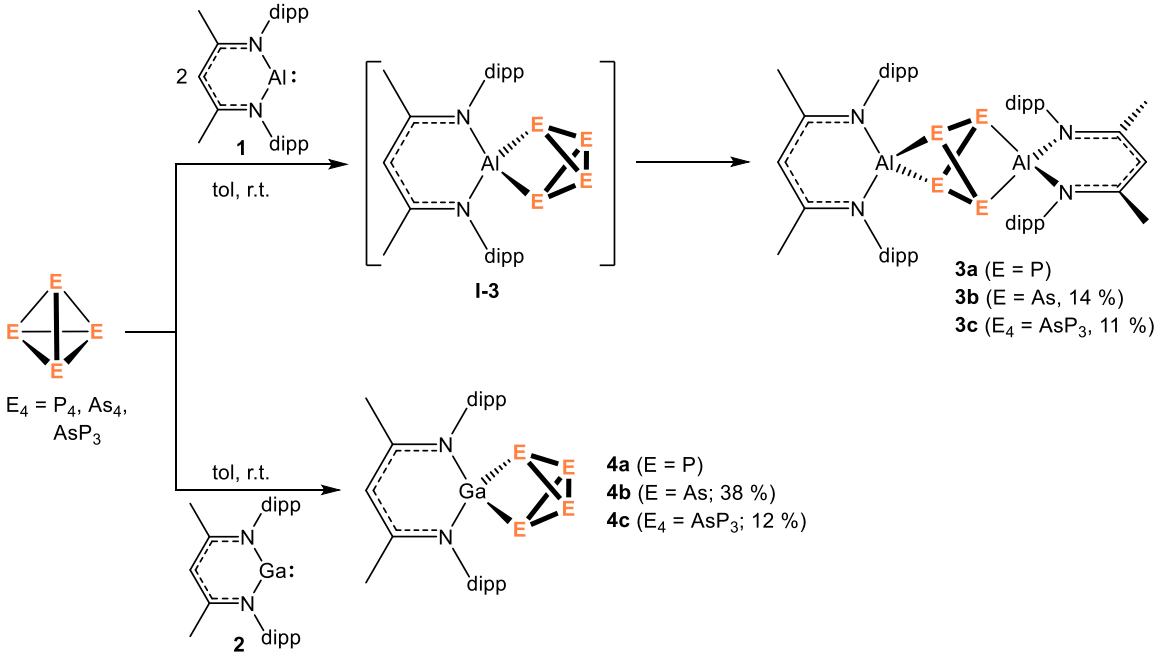
Scheme 5.1. Examples of the conversion of yellow arsenic with main group compounds.

Moreover the groups of *H. W. Roesky, R. A. Fischer* and *J. J. Weigand* reported the reaction of the main group metal compounds [L^3Al] (**1**, L^3 = [{N($C_6H_3{}^iPr_2$-2,6)C(Me)}$_2$CH]$^-$)[5] and [L^3Ga] (**2**)[6] with white phosphorus. Here the formation of [(L^3Al)$_2$(μ,$\eta^{1:1:1:1}$-P_4)] (**3a**)[7], [L^3Ga($\eta^{1:1}$-P_4)] (**4a**)[8] and other polyphosphanes stabilized by two {L^3Ga} fragments are obtained.[9] Moreover, **2** was reacted with the antimony reagent [Cp*Sb]$_4$ to form [(L^3Ga)$_2$(μ,$\eta^{1:1:1:1}$-Sb_4)].[10]

Motivated by the results of the reactivity of white phosphorus towards group 13 metal complexes, the question arose if there are similarities or differences in their reactivity towards yellow arsenic. Furthermore, the reactivity of such products towards unsaturated metal fragments were of interest. On the basis of our results about the reactivity of Cu(I) nacnac complexes towards E_n ligand complexes,[11] the question arose as to what extent the E-E bonds in E_n ligand complexes can be activated or cleaved by {L^3Ga} fragments. Herein, we present the conversion of yellow arsenic and AsP_3, respectively, with the Al(I) and Ga(I) nacnac compounds **1** and **2**. Thereby result the first examples of the conversion of yellow arsenic and AsP_3 with group 13 metal compounds [(L^3Al)$_2$(μ,$\eta^{1:1:1:1}$-E_4)] (E_4 = As_4 (**3b**), AsP_3 (**3c**)) and [L^3Ga($\eta^{1:1}$-E_4)] (E_4 = As_4 (**4b**), AsP_3 (**4c**)). Furthermore, the reactivity of gallium compounds towards unsaturated metal compounds and E_n ligand complexes were investigated.

5.2. Results and Discussion

The reaction of [L^3Al] (**1**) and [L^3Ga] (**2**) with an excess of yellow arsenic in toluene at room temperature leads to [$(L^3Al)_2(\mu,\eta^{1:1:1:1}\text{-}As_4)$] (**3b**) and [$L^3Ga(\eta^{1:1}\text{-}As_4)$] (**4b**), which are isolated as orange (**3b**) or yellow (**4b**) air-sensitive solids in crystalline yields of 14 % and 38 %, respectively (Scheme 5.2). Reacting **1** and **2** with AsP_3, yields [$(L^3Al)_2(\mu,\eta^{1:1:1:1}\text{-}AsP_3)$] (**3c**) and [$L^3Ga(\eta^{1:1}\text{-}AsP_3)$] (**4c**), respectively, as orange or yellow air-sensitive solids in isolated crystalline yields of 11 % (**3c**) and 12 % (**4c**) (Scheme 5.2).



Scheme 5.2. Reaction of As_4 and AsP_3 with **1** and **2** (dipp = 2,6-diisopropylphenyl).

The reaction of **1** with an excess of P_4 also leads to **3a**, the $^{31}P\{^1H\}$ NMR spectrum show only traces of a monomeric species (**I-3a**, see Supporting Information). According to DFT calculations at the B3LYP/def2-SVE level of theory, the formation of the dimeric species are in the case of aluminum by 112 kJ · mol^{-1} (**3a**), 95 kJ · mol^{-1} (**3b**) and 116 kJ · mol^{-1} (**3c**) more likely than the formation of the monomeric species. A similar behavior is calculated for the gallium compounds, the dimeric species should be favored by 25 kJ · mol^{-1} (**4a**), 31 kJ · mol^{-1} (**4b**) and 29 kJ · mol^{-1} (**4c**). Even by changing the reaction conditions (e.g. temperature, stoichiometry), the reaction of **2** with As_4 leads to the monomeric species **4b**.[12] In comparison with the lighter homolog phosphorus the reaction of **2** with white phosphorus in a 1:0.75 ratio at 180 °C[13] leads to the formation of **4a** and [$(L^3Ga)_2(P_n)$] (n = 4, 6, 8, 12, 14, 16).[9] Freshly dissolved **3b** in C_6D_6 was characterized by ^1H NMR spectroscopy at room temperature, which shows one set of signals for the two equivalent nacnac ligands. Similarly, the ^1H NMR spectrum of **4b** (C_6D_6, r.t.) reveals a full set of signals for the nacnac ligand. The $^{31}P\{^1H\}$ NMR spectra of the crude reaction mixture of **3c** and **4c** show the formation of various compounds (see Supporting Information) but only **3c** and **4c**, respectively, could be isolated (vide infra). The $^{31}P\{^1H\}$ NMR spectrum of

crystals of **4c** dissolved in C_6D_6 show two sets of signals corresponding to two isomers, indicating different chemical and magnetic environments, which can be explained by the different position of the arsenic atom in the AsP_3 unit (Figure 5.1). The formation of the isomers of **4c** depend on the successive bond cleavage of the AsP_3 tetrahedron. According to DFT calculations, the cleavage of an As-P bond is preferred by 6 kcal·mol^{-1} vs a P-P bond.[4d] If the P-As bond is broken than the major isomer **4c1** is formed, with the gallium coordinated arsenic atom (Figure 5.3). A P-P bond cleavage leads to the formation of the minor isomer **4c2**, with the arsenic atom in the bridgehead position of the ligand (Figure 5.3). In the $^{31}P\{^1H\}$ NMR spectrum of **4c**, both isomers are visible. For the major isomer **4c1**, a triplet at δ = 179.1 ppm and a doublet at δ = -319.8 ppm ($^1J_{PP}$ = 155 Hz) in an integral ratio of 1:2 can be detected. The signals for the isomer **4c2** revealing a doublet at δ = 227.6 ppm and a triplet at -279.4 ppm ($^1J_{PP}$ = 164 Hz) in an integral ratio of 2:1. The ratio between compounds **4c1** to **4c2** in the $^{31}P\{^1H\}$ NMR spectrum of the crystals is 1:0.1. There are also traces of **4a** visible ($^{31}P\{^1H\}$: δ = -328.7 (t) and 212.7 ppm (t)), due to P_4 impurities in AsP_3.

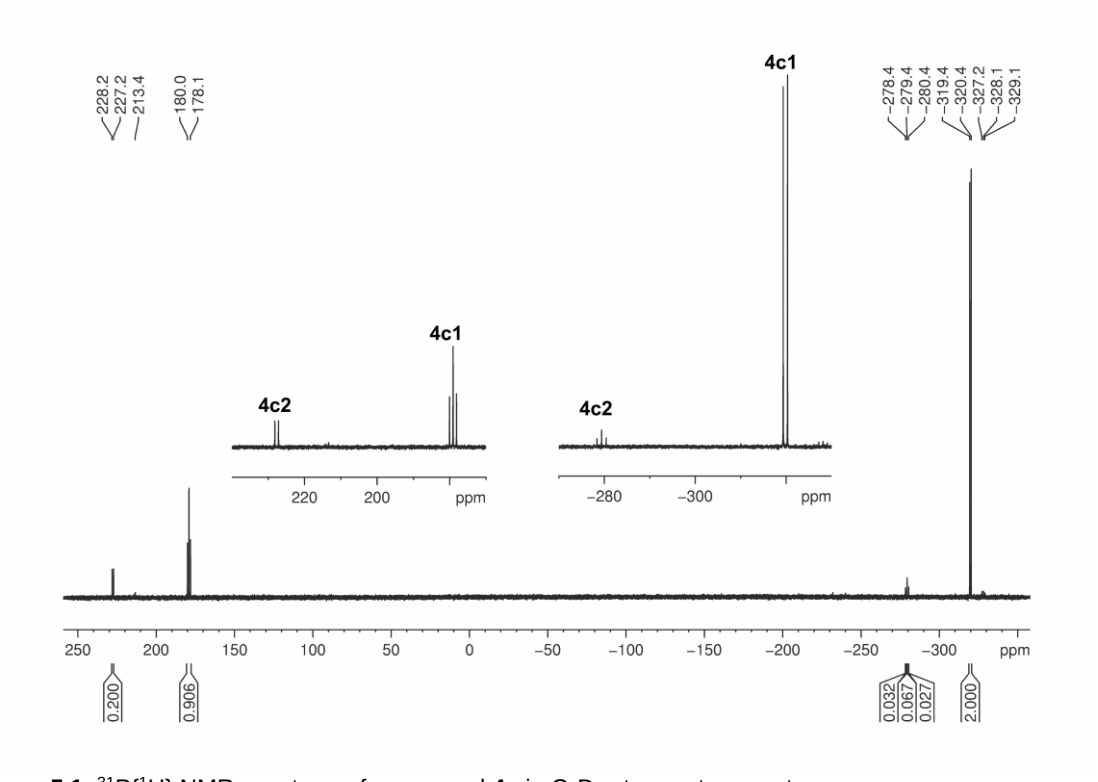


Figure 5.1. $^{31}P\{^1H\}$ NMR spectrum of compound **4c** in C_6D_6 at room temperature.

The $^{31}P\{^1H\}$ NMR spectrum of the crude reaction solution of [L^{3}Al] with AsP_3 show two set of signals corresponding to two monomeric isomers (**I-3c**, Scheme 5.2) of a compound analogous to **4c**. For one isomer a doublet at δ = 117.7 ppm ($^1J_{PP}$ = 162 Hz, 2P) and a triplet at δ = -284.8 ppm ($^1J_{PP}$ = 162 Hz, 1P) can be detected, while for the other isomer there is a triplet at δ = 67.4 ppm ($^1J_{PP}$ = 151 Hz, 1P) and a doublet at δ = -324.9 ppm ($^1J_{PP}$ = 151 Hz, 2P). Both isomers are in an integral ratio of 3:2. Based on the striking similarity of the $^{31}P\{^1H\}$ NMR spectroscopic date of the two isomers and **4c** (vide supra) the two

isomers represent the analogs of **3c** in which the As atom possessing wingtip as well as in bridgehead position. Furthermore, there are signals for **3c** visible, which was the only product that was obtained by crystallization regardless of numerous attempts. The ^{1}H NMR spectrum of a sample prepared by dissolved crystals of **3c** in C_6D_6 at room temperature show two sets of signals for the Me-groups and the α-H atoms, due to the magnetically non equivalent ligands. This is caused by the position of the arsenic atom within the AsP_3 unit. In the $^{31}P\{^{1}H\}$ NMR spectrum of the same sample of **3c** a doublet at δ = 62.1 ppm ($^{1}J_{PP}$ = 24 Hz) and a triplet at δ = 50.0 ppm ($^{1}J_{PP}$ = 24 Hz) in an integral ration of 2:1 can be detected. In the $^{31}P\{^{1}H\}$ NMR spectrum of **3c** also a signal for **3a** is visible (**3a**: $^{31}P\{^{1}H\}$: δ = 78.6 ppm[7]). The small $^{1}J_{PP}$ coupling constants could be explained by the pronounced 3p character of the P-P bond and the mainly 3s character of the phosphorus lone-pairs, which lead to a small s-overlap integral for the P-P bond and was reported also for diphosphines.[14] NBO analysis nicely show the high p character of the E-E bonds of **3c** (P1-P2: $sp^{9.2}$, P2-As3: sp^{10}, As3-P4: sp^{10}, P1-P4: $sp^{9.2}$). In the LIFDI-MS spectra of **3b**, **4b** and **4c**, respectively, the corresponding molecular ion peak are detected.

The molecular structures of **3b** and **3c** reveal dinuclear compounds bearing a strongly folded As_4 or AsP_3 ring, coordinating in a $\eta^{1:1}$ fashion to both {L^3Al} fragments, which are twisted (**3b**: 97.70(11)°; **3c**: 81.99(11)°) to each other (Figure 5.2). The arsenic atom in **3c** is disordered over all four pnictogen positions (occupation of the phosphorus and arsenic positions see Table 5.1). The As-As distances in **3b** are between 2.5096(6) and 2.5220(6) Å, which is elongated in comparison to an As-As single bond.[15] The Wiberg Bond Indices show the integrity of the As-As bonds (WBIs all-around 0.93). A similar M_2As_4 core has been observed in [(Cp*Co(CO))$_2$(μ,$\eta^{1:1:1:1}$-As_4)] (**F**).[16] The As1···As3 and As2···As4 distances (3.329 and 3.341 Å) of **3b** are clearly longer than those in **F** (2.838(2) and 2.881(2) Å), which indicates a complete bond cleavage of two As-As edges of the As_4 tetrahedra. The P-As distances in **3c** are in the range of 2.280(18) and 2.561(14) Å, the P-P distances are within 2.301(7) and 2.407(8) Å (WBIs between 0.93 and 0.96). The average Al-As distance in **3b** is 2.4513 Å, which is comparable to the recently reported compound [L^3Al(AsH_2)$_2$] (L^3 = [{N($C_6H_3{}^{i}Pr_2$-2,6)C(Me)}$_2$CH]$^-$) of our group (Al-$As_{(av.)}$ 2.474(3) Å).[17]

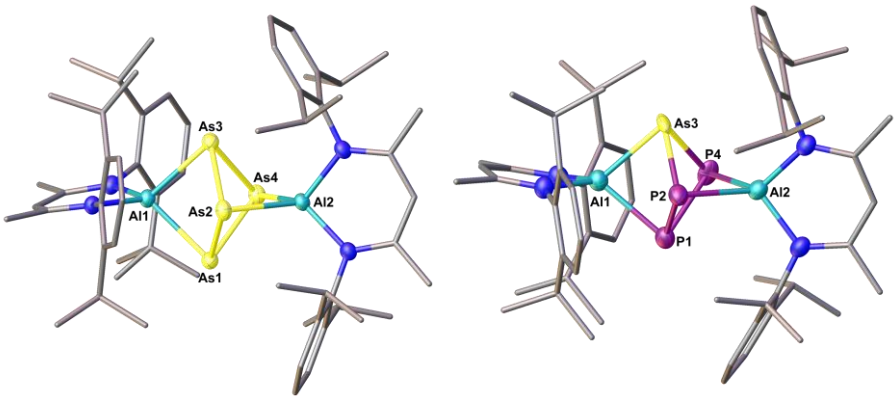


Figure 5.2. Molecular structure of **3b** (left) and **3c** (right, one of the four isomers) in the solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms are omitted for clarity.

The molecular structures of **4b** and **4c** reveal mononuclear compounds bearing an As_4 or AsP_3 butterfly ligand, coordinating in a $\eta^{1:1}$ fashion to the {L^{3}Ga} fragment (Figure 5.3). The arsenic atom in **4c** is disordered over all four pnictogen positions. The major isomer **4c1**, with the gallium coordinated arsenic atom and the minor isomer **4c2**, with the arsenic atom in the bridgehead position of the ligand, were determined to be in a ratio of 85:6 (9 % are **4a**) in the solid state (occupation of the phosphorus and arsenic positions see Table 5.1). According to DFT calculations at the B3LYP/def2-SVE level of theory, **4c1** is just by 0.3 kJ·mol^{-1} more stable than **4c2**.

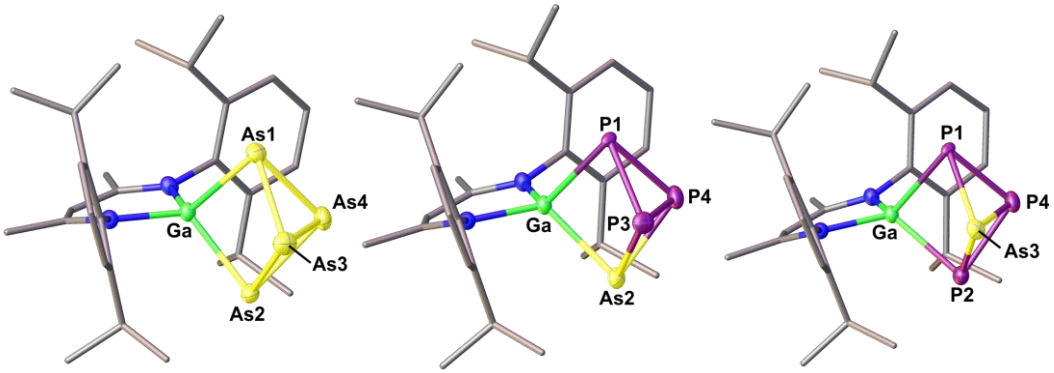


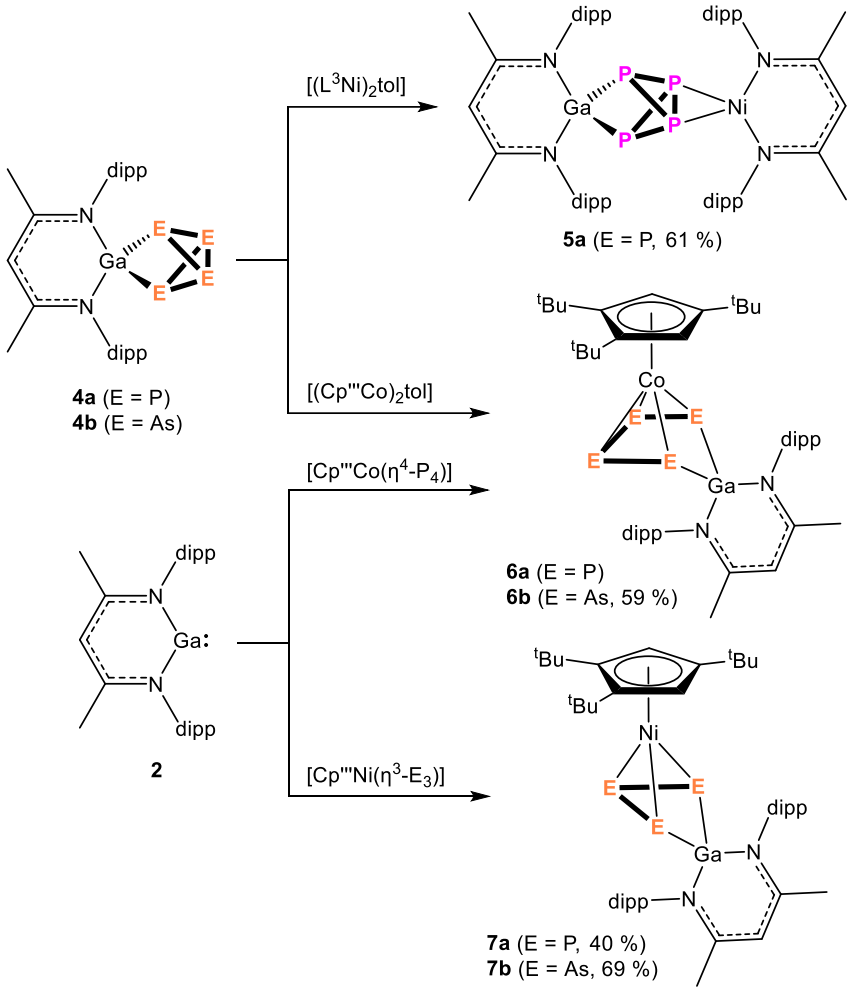
Figure 5.3. Molecular structure of **4b** (left), one of the major isomers **4c1** (middle) and one of the minor isomers **4c2** (right) in the solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms are omitted for clarity.

Table 5.1. Occupation of the phosphorus and arsenic positions in compound **3c** and **4c**.

	Atom	1	2	3	4
3c	P	0.91	0.90	0.69	0.67
	As	0.09	0.10	0.31	0.33
4c	P	0.49	0.65	0.98	0.97
	As	0.51	0.35	0.02	0.03

The six-membered GaN_2C_3 ring is nearly perpendicular oriented (**4b**: 91.8°; **4c**: 87.9°) to the E1-Ga-E2 plane. The As1···As2 distance with 3.452 Å lies in a non-bonding area for **4b** (WBI: 0.1). The E1···E2 distances of **4c** are 3.291(13), 3.365(10) and 3.295(13) Å and in a non-bonding area, respectively. The As-As distances of **4b** are all between 2.4608(5) and 2.4693(6) Å, except of the As3-As4 length, which is shortened to 2.3830(6) Å. A similar trend of the As-As distances within the As_4 butterfly moiety was also found in [Cp*Co(CO)($\eta^{1:1}$-As_4)][16] and [($Cp^R M(CO)_n)_2$($\mu,\eta^{1:1}$-As_4)][18] (Cp''', M = Fe, n = 2; Cp*, M = Cr, n = 3). The P-As distances in **4c** are in the range between 2.315(4) and 2.52(4) Å, the P-P distances are within 2.155(4) and 2.301(5) Å which fits well to the values of **4a**.[8] Moreover, the WBIs of all E-E bonds distances were calculated and show the integrity of the bonds. The Ga-As distances are 2.4259(5)/2.4415(5) Å for **4b** and 2.412(3)/2.421(8) Å for compound **4c**. This is comparable to the Ga-As distances found in [(η^1-L^3Ga(Cp*))(η^2-L^3Ga)(μ-As_3)], which exhibit Ga-As bond lengths of the η^2 coordinated Ga of 2.4183(3) and 2.4224(3) Å.[19]

The E-E bond in the bridgehead of the butterfly unit of **4a** can be further activated in the case of phosphorus with another molecule of **2**.[9] Such a reactivity could not be observed for the arsenic compound **4b**. Thus, the question arose if such gallium complexes are able to react further with unsaturated transition metal fragments and this also in case of the As_4 derivative **4b**. We focus especially on the synthesis of heterometallic mixed main group (group 13 metals) and transition metal complexes, which are little explored.[20] In order to investigate the reactivity of **4a** and **4b** towards unsaturated transition metal fragments, they were reacted with 0.5 equivalent of [(L^3Ni)$_2$tol][21] and [(Cp'''Co)$_2$($\mu,\eta^{4:4}$-C_7H_8)][22] to deliver just one metal fragment. This leads to the quantitative formation of [(L^3Ga)($\mu,\eta^{2:1:1}$-P_4)(L^3Ni)] (**5a**) and [(Cp'''Co)($\mu,\eta^{4:1:1}$-E_4)(L^3Ga)] (E = P (**6a**), As (**6b**)), which are isolated as orange (**5a**) or green (**6a**, **6b**) air-sensitive solids in crystalline yields of 61 % (**5a**, Scheme 5.3) and 59 % (**6b**, Scheme 5.3), respectively. The reaction of **4a** with [(Cp'''Co)$_2$tol] is not as selective as in the case of **4b**. In addition to [(Cp'''Co)($\mu,\eta^{4:1:1}$-P_4)(L^3Ga)] (**6a**), [(Cp'''Co)($\mu,\eta^{2:2}$-P_2)$_2$] (**G**) is also formed in this reaction showing that **4a** can deliver P_4 units to {Cp'''Co} fragments.[23] To examine if [L^3Ga] is also able to open an E-E bond of a *cyclo*-E_n complex, we react [Cp'''Co(η^4-P_4)] (**H**) and [Cp'''Ni(η^3-E_3)] (**I**) with **2** (Scheme 5.3). The reaction of **H** with **2** leads to the selective formation of **6a**. By the reaction of **I** with **2** compound [(Cp'''Ni)($\eta^{3:1:1}$-E_3)(L^3Ga)] (E = P (**7a**), As (**7b**)) is formed as orange air sensitive solid in crystalline yields of 40 % (**7a**) and 69 % (**7b**) (Scheme 5.3). These compounds are novel neutral, heterometallic compounds containing mixed main group and transition metals.



Scheme 5.3. Reaction of **4a** and **4b** with unsaturated transition metal complexes and reaction of **2** with E_n ligand complexes (dipp = 2,6-diisopropylphenyl, Cp''' = $C_5H_2{}^tBu_3$).

Whereas the $^{31}P\{^1H\}$ NMR spectrum of **5a** in C_6D_6 at room temperature is silent, the ^1H NMR spectrum displays broad and shifted signals revealing a paramagnetic compound. The effective magnetic moment (μ_{eff}) was determined by the Evans method to be 2.29 μ_B corresponding approximately to one unpaired electron. The paramagnetic nature of **5a** was confirmed by X-band EPR spectroscopy at room temperature and at 77 K (r.t.: g = 2.156, 77K: g_1 = 2.236, g_2 = 2.121 and g_3 = 2.038, Figure 5.4). DFT calculations (B3LYP/def2-SVE level) show that the spin density is delocalized over the nickel atom and all four phosphorus atoms (Figure 5.4), which is in agreement with the observed hyperfine coupling. The ^1H NMR spectrum of the reaction of **4b** with $[(L^3Ni)_2tol]$ exhibit similar broad and shifted signals to **5a** but regardless of numerous attempts crystallization was not possible.

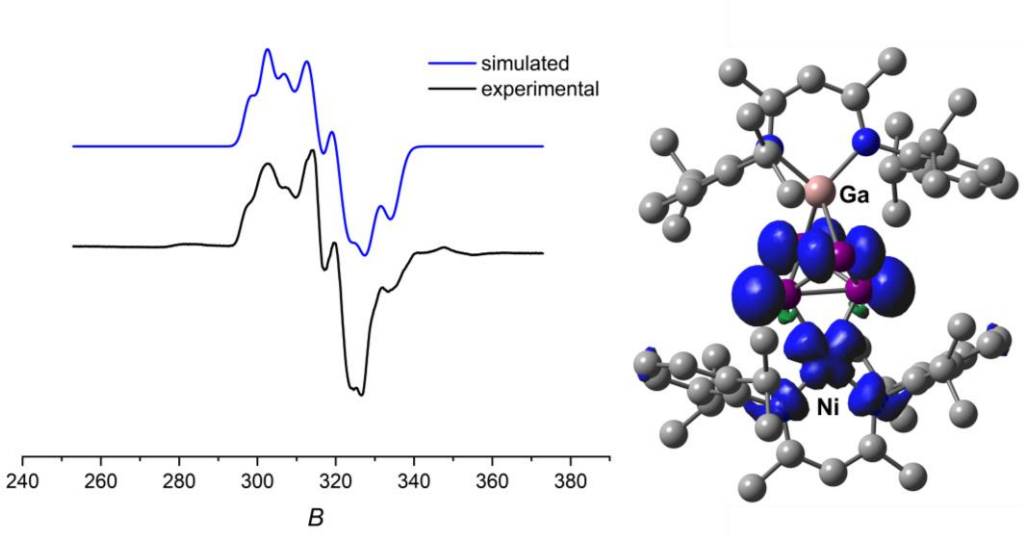


Figure 5.4. left: X-band EPR spectrum of **5a** (B in [mT], frozen toluene solution 77 K (black), simulation (blue)); right: Spin density distribution in **5a**, calculated at the B3LYP/def2-SVE level.

The ^{1}H NMR spectra of the reaction solutions of **6b** and **7b**, respectively, in C_6D_6 indicate that the reactions are very selective, they exhibit four doublets centered at δ = 1.90, 1.63, 1.19 and 0.82 ppm (**6b**); δ = 1.67, 1.60, 1.14 and 1.04 ppm (**7b**) and two septets centered at δ = 3.95 and 2.58 (**6b**) or δ = 1.56 and 1.48 (**7b**) for the isopropyl groups, respectively. This indicates that the chemical environment of all isopropyl groups is different. Similar signals could be obtained for **6a** and **7a** in the ^{1}H NMR spectrum. The ^{31}P{^{1}H} NMR spectrum of **6a** in C_6D_6 reveals two multiplets centered at δ = 94.0 and -54.0 ppm, respectively, with an integral ratio of 1:1 displaying an AA'XX' spin system (see Supporting Information). This show high similarities to the anionic heterobimetallic complex [K(dme)$_2${(^{Mes}BIAN)Co(μ,η$^{4:1:1}$-P_4)(L^3Ga)] (^{Mes}BIAN = 1,2-bis(2,4,6-dimethylphenylimino)acenaphthene).[20b] The ^{31}P{^{1}H} NMR spectrum of **7a** in C_6D_6 reveals a doublet at δ = 163.8 ppm (2P, $^{1}J_{PP}$ = 325 Hz) and a triplet at δ = 109.1 ppm (1P, $^{1}J_{PP}$ = 325 Hz).

The molecular structure of **5a** displays a heterobimetallic complex bearing a P_4 butterfly unit, coordinating in a η$^{1:1}$ fashion to the {L^3Ga} fragment and in a η^2 fashion to the {L^3Ni} fragment (Figure 5.5). The P1···P2 distances of compound **5a** is 3.1784(17) Å, which is in the same range than for **4a** (3.173(3) Å[8]) and in a non-bonding area (WBI: P1···P2 0.12). The P-P bond distances of **5a** are all between 2.2366(18) and 2.2391(17) Å (WBIs all around 0.9), except of the P3-P4 bond distance, which is elongated to 2.2566(15) Å (WBI: 0.78). Compound **5a** is a rare example of a mixed main group-transition metal nacnac complex. To the best of our knowledge, only one example of a similar compound with mixed metal nacnac ligands is known, the nickel silicon compound [(L^3Si)(μ,η$^{2:1:1}$-P_4)(L^3Ni)].[20c]

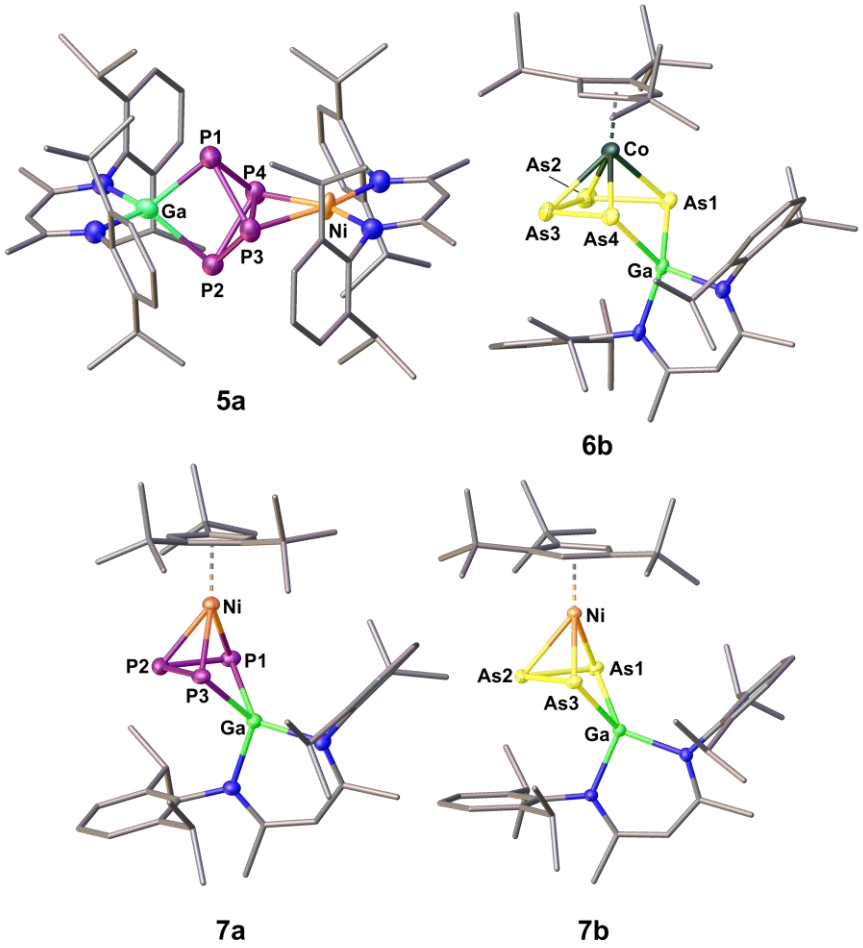


Figure 5.5. Molecular structures of **5a**, **6b**, **7a** and **7b** in the solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

Compound **6b**, **7a** and **7b** are heterodinuclear sandwich complexes with a {Cp'''M} fragment η^4- or η^3-coordinated to the As_4 or E_3 chain and a $\{L^3Ga\}$ fragment in a $\eta^{1:1}$ coordination mode (Figure 5.5). In comparison to **4b**, in **6b** two more As-As bonds are broken. Compound **7a** and **7b** shows an insertion of the $\{L^3Ga\}$ fragment into the *cyclo*-E_3 unit. The butadiene-like As_4 unit of **6b** is nearly planar (deviation 2.8 °). The As1-As2 and As3-As4 distances in **6b** are 2.3227(6) and 2.3270(6) Å, the As2-As3 bond distance is slightly longer (2.4018(6) Å). The E-E bond distances are 2.1586(11) and 2.1818(11) Å for **7a** and 2.4059(4) and 2.4095(4) Å for **7b**, respectively. The As1···As4 (**6b**), P1···P3 (**7a**) and As1···As3 (**7b**) distances are with 3.4434(6) Å (**6b**), 3.0939(9) Å (**7a**) and 3.2753(6) Å (**7b**) in the non-bonding area and slightly shorter than the comparable distance in **4b** (3.452 Å). Compound **6b** reveals a similar Ga-As distance (2.4271(5) and 2.4481(5) Å) as **4b**. The six-membered GaN_2C_3 ring is nearly perpendicular (**6b**: 92.4 °, **7a**: 95.9 ° **7b**: 89.6 °) to the E1-Ga-E4/E3 plane and this plane is folded by 113.7 ° (**6b**), 126.0 ° (**7a**) or 120.5° (**7b**) to the $E_{4/3}$ unit. Compound **6b** contains a similar core as the homodinuclear compound [(Cp*Co)(μ,$\eta^{4:1:1}$-As_4)(Co(CO)Cp*)].[16]

5.3. Conclusion

In conclusion, we reported the synthesis of novel homobimetallic compounds $[(L^3Al)_2(\mu,\eta^{1:1:1:1}\text{-}E_4)]$ (E = As (**3b**), AsP_3 (**3c**)) and the mononuclear compounds $[L^3Ga(\eta^{1:1}\text{-}E_4)]$ (E = As (**4b**), AsP_3 (**4c**)), the first examples of the conversion of yellow arsenic and AsP_3 with low valent group 13 compounds. We have shown that in the case of AsP_3 an As-P bond activation occurs more likely than a P-P- bond activation. The $^{31}P\{^1H\}$ NMR of **4c** show two isomers in dependence of the position of the arsenic atom. The crude reaction solution of **3c** also indicates the formation of a mononuclear compound in solution, which represent the first step on the reaction pathway to the double substitution. Furthermore, in the case of the gallium complexes a further reactivity towards unsaturated metal complexes or E_n (n = 3, 4) ligand complexes could be investigated. Thus, the heterometallic compounds $[(L^3Ga)(\mu,\eta^{2:1:1}\text{-}P_4)(L^3Ni)]$ (**5a**), $[(Cp'''Co)(\mu,\eta^{4:1:1}\text{-}E_4)(L^3Ga)]$ (E = P (**6a**), As (**6b**)) and $[(Cp'''Ni)(\mu,\eta^{3:1:1}\text{-}E_3)(L^3Ga)]$ (E = P (**7a**), As (**7b**)) were synthesized, these complexes unite different ligand systems (Cp and nacnac) and also different merge metal moieties, main group as well as transition metals.

5.4. References

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5.5. Supporting Information

5.5.1. Synthesis and Characterization

General Remarks

All manipulations were performed with rigorous exclusion of oxygen and moisture using standard Schlenk techniques on a dual manifold Schlenk line with Argon or N_2 inert gas or glove box filled with nitrogen containing a high-capacity recirculator (<0.1 ppm O_2). Traces of oxygen and moisture in the inert gas were removed by passing it through a drying column filled with Cu/$MgSO_4$ catalyst as well as, concentrated H_2SO_4 and orange gel, respectively. All solvents were degassed and purified by standard procedures. All NMR spectra have been recorded using deuterated d_6-benzene or toluene-d_8 that were dried (over Na/K or CaH_2), refluxed for three hours and then distilled under inert atmosphere.

Characterization methods

Mass spectrometry was performed using a Jeol AccuTOF GCX LIFDI mass spectrometer by the MS department of the University of Regensburg. The compounds were dissolved in the corresponding solvent in a glove box under N_2 atmosphere. The observed fragments were assigned according to the mass/charge (m/z) ratio and the corresponding isotope pattern. Elemental analysis (CHN) were performed by the department of central analyses of the University of Regensburg on a Vario micro cube and a MT5 micro scale device. The compounds were filled in tin capsules in a glove box under N_2 atmosphere.

^{1}H and ^{31}P NMR spectra were recorded on a Bruker Avance III HD 400 (^{1}H: 400.130 MHz, ^{31}P: 161.976 MHz) spectrometer at the NMR department of the University of Regensburg. The chemical shifts are reported in ppm relative to external TMS (^{1}H) or 85 % H_3PO_4 (^{31}P). The chemical shifts δ are given in parts per million [ppm] and coupling constants J in [Hz].

Starting materials

The compounds [L^3Al][1] (**1**), [L^3Ga][2] (**2**), As_4[3], AsP_3[4], [(Cp'''Co)$_2$(μ,$\eta^{4:4}$-C_7H_8)][5a], [(L^3Ni)$_2$tol][5b], [(L^3Al)$_2$($\eta^{1:1:1:1}$-P_4)][6] (**3a**), [L^3Ga($\eta^{1:1}$-P_4)][7] (**4a**), [Cp'''Co(η^4-P_4)][8a] (**H**) and [Cp'''Ni(η^3-E_3)][8b,8c] (**I**) were prepared according to literature procedures. (L^3 = [{N($C_6H_3{}^iPr_2$-2,6)C(Me)}$_2$CH]$^-$, Cp''' = η^5-$C_5H_2{}^tBu_3$)

5.5.1.1. Synthesis of $[(L^3Al)_2(\mu,\eta^{1:1:1:1}\text{-}As_4)]$ (**3b**)

All preparations were performed under exclusion of light. 60 mg [L^3Al] (**1**) (0.13 mmol, 1 eq) were dissolved in 5 mL of toluene and added to an excess of freshly precipitated As_4. The mixture was stirred at room temperature for 2 hours and the colour changed from yellow to orange. The reaction mixture was filtered, and the solvent was removed in vacuum. The orange residue was stored at least over night to ensure the degradation of the excess of unreacted As_4 into As_{grey}. After dissolving the orange residue in 2 mL of Et_2O, the solution was filtered again over diatomaceous earth to remove the insoluble As_{grey}. By storing the orange solution for two days at -30 °C, compound $[(L^3Al)_2(\mu,\eta^{1:1:1:1}\text{-}As_4)]$ (**3b**) crystallized as orange plates, suitable for X-Ray analysis.

Crystalline yield: 11 mg (0.01 mmol, 14 %)

^{1}H NMR (C_6D_6, 300 K): δ [ppm] = 7.11-7.03 (m, 12H, H_{aryl}), 4.97 (s, 2H, H_β), 3.70 (sept, 8H, C*H*Me_2), 1.67 (s, 12H, α-*Me*), 1.25 (d, 24H, CH*Me*Me'), 1.12 (d, 24H, CHMe*Me'*).

LIFDI-MS (toluene): m/z (%) = 1188.30 (100, $[M]^+$).

EA calculated for $C_{58}H_{82}N_2Al_2As_4$: C: 58.59, H: 6.95, N: 4.71, found [%]: C: 58.35, H: 7.11, N: 4.54.

5.5.1.2. Synthesis of $[(L^3Al)_2(\mu,\eta^{1:1:1:1}\text{-}AsP_3)]$ (**3c**)

10 mg AsP_3 (0.06 mmol,0.5 eq) were dissolved in toluene and added to a solution of 53 mg [L^3Al] (**1**) (0.12 mmol, 1 eq) in 5 mL of toluene. The red solution was stirred at room temperature for one week. The reaction mixture was filtered, and the solvent was removed in vacuum. After dissolving the orange residue in 2 mL of Et_2O, the solution was stored for two days at -30 °C, compound $[(L^3Al)_2(\mu,\eta^{1:1:1:1}\text{-}AsP_3)]$ (**3c**) crystallized as orange plates, suitable for X-Ray analysis.

Crystalline Yield: 7 mg (0.006 mmol, 11 %)

^{1}H NMR (C_6D_6, 300 K) δ [ppm] = 7.11 – 7.00 (m, 12H), 5.03 (s, 1H), 5.00 (s, 1H), 3.64 (m, 8H), 1.70 (s, 6H), 1.68 (s, 6H), 1.22 – 1.12 (m, 48H).

^{31}P{^{1}H} NMR (C_6D_6, 300 K): δ [ppm] = 79.3 (s, 0.1P, $[(L^3Al)_2P_4]$ (**3a**)), 62.3 (d, 2P, $^1J_{PP}$ = 24 Hz), 50.1 ppm (t, $^1J_{PP}$ = 24 Hz).

5.5.1.3. Synthesis of [$L^3Ga(\eta^{1:1}$-$As_4)$] (**4b**)

All manipulations were performed under exclusion of light. 200 mg [L^3Ga] (0.4 mmol, 1 eq) were dissolved in 20 mL of toluene and added to an excess of freshly precipitated As_4. The mixture was stirred for 1 day, during this time the colour change from yellow to orange. The solvent was removed in vacuum and the orange residue was dissolved in a toluene/n-hexane (2:1) mixture at 55 °C. The orange solution was filtered warm over diatomaceous earth. By storing the orange solution for ten days at -30 °C, compound [$L^3Ga(\eta^{1:1}$-$As_4)$] (**4b**) crystallized as yellow blocks, suitable for X-Ray analysis.

Crystalline yield: 124 mg (0.15 mmol, 38 %)

^{1}H NMR (C_6D_6, 300 K): δ [ppm] = 7.26-7.33 (m, 6H, *H$_{aryl}$*), 4.63 (s, 1H, *H$_\beta$*), 3.35 (sept, 4H, C*H*Me_2), 1.65 (d, 12H, CH*Me*Me'), 1.54 (s, 6H, α-*Me*),1.16 (d, 12H, CHMe*Me'*).

LIFDI-MS (toluene): m/z (%) = 785.94 (100, $[M]^+$).

EA calculated for $C_{29}H_{41}N_2GaAs_4$: C: 44.26, H: 5.25, N: 3.56, found [%]: C: 44.10, H: 4.98, N: 3.41.

5.5.1.4. Synthesis of [$L^3Ga(\eta^{1:1}$-$AsP_3)$] (**4c**)

All manipulations were performed under exclusion of light. 30 mg [L^3Ga] (0.06 mmol, 1 eq) and 10.3 mg AsP_3 (0.06 mmol, 1 eq) were dissolved in 3 mL of toluene and stirred for 1 day. During this time the colour change from yellow to orange. The solvent was removed in vacuum and the orange residue was dissolved in toluene/n-hexane (2:1) mixture at 55 °C. The orange solution was filtered warm. By storing the orange solution for 2 weeks at -30 °C, compound [$L^3Ga(\eta^{1:1}$-$AsP_3)$] (**4c**) crystallized as yellow blocks, suitable for X-Ray analysis.

Crystalline yield: 5 mg (0.007 mmol, 12 %)

^{1}H NMR (C_6D_6, 300 K): δ [ppm] = 7.3 - 7.15 (m, 6H, *H$_{aryl}$*), 4.66 (s, 1H, *H$_\beta$*), 3.33 (sept, 2H, C*H*Me_2), 3.27 (sept, 2H, C*H*Me_2), 1.65 (d, 6H, CH*Me*Me'), 1.59 (d, 6H, CH*Me*Me'), 1.52 (d, 6H, α-*Me*), 1.06 (d, 6H, CHMe*Me'*), 1.04 (d, 6H, CHMe*Me'*).

^{31}P{^{1}H} NMR (C_6D_6, 300 K): δ [ppm] = 227.6 (d, 2P, $^1J_{PP}$ = 164 Hz), 213 (t, traces of [$L^3Ga(\eta^{1:1}$-$P_4)$]), 179.1 (t, 1P, $^1J_{PP}$ = 155.07 Hz), -279.4 (t, 1P, $^1J_{PP}$ = 164 Hz), -319.8 (d, 2P, $^1J_{PP}$ = 155.1 Hz), -328 (t, traces of [$L^3Ga(\eta^{1:1}$-$P_4)$]).

LIFDI-MS (toluene): m/z (%) = 654.10 (100, $[M]^+$).

5.5.1.5. Synthesis of [(L^3Ga)(μ,$\eta^{2:1:1}$-P_4)(L^3Ni)] (**5a**)

[(L^3Ni)$_2$tol] (42.7 mg, 0.04 mmol, 0.5 eq) was dissolved in toluene and cooled to -70 °C. A solution of [L^3Ga($\eta^{1:1}$-P_4)] (**4a**, 50 mg, 0.08 mmol, 1 eq) in toluene was added drop by drop and stirred for 1h at -70 °C. After stirring for a further hour at room temperature the reaction solution was filtrated over diatomaceous earth and concentrated to approximately 1 mL. By storing the orange solution at -30 °C, compound [(L^3Ga)($\eta^{2:1:1}$-P_4)(L^3Ni)] (**5a**) crystallized as orange plates, suitable for X-Ray analysis.

Crystalline yield: 54 mg (0.05 mmol, 61 %)

^{1}H NMR (C_6D_6, 300 K): δ [ppm] = 16.71 (b, 4H, *H*$_{aryl}$), 7.52 (b, 2H, *H*$_{aryl}$), 4.38 (b, 12H, CH*Me*Me), 3.67 (b, 2H, *H*$_{\beta}$), 3.18 (b, 12H, CH*Me*Me'), 2.92 (b, 6H, α-*Me*), 1.35 (b, 6H, α-*Me*), 1.21 (b, 12H, CH*Me*Me'), 1.12 (b, 12H, CH*Me*Me'), -16.35 (b, 4H, C*H*MeMe), some signals are missing due to line broadening caused by the paramagnetic nature of **5a** (measured range: 170 ppm to -140 ppm).

^{1}H NMR (Evans-method, C_6D_6, 300 K): $\Delta\nu$ = 21.7 Hz, μ_{eff} = 2.29 μ_B, n = 1.5.

^{31}P{^{1}H} NMR (C_6D_6, 300 K): silent, measured range: +600 to -600 ppm.

LIFDI-MS (toluene): m/z (%) = 1087.32 (100, $[M]^+$).

EA calculated for $C_{58}H_{82}N_4GaNiP_4$: C: 64.05, H: 7.60, N: 5.15, found [%]: C: 64.26, H: 7.1, N: 5.14.

5.5.1.6. Synthesis of [(Cp'''Co)(μ,$\eta^{4:1:1}$-P_4)(L^3Ga)] (**6a**)

[Cp'''Co(η^4-P_4)] (50 mg, 0.1 mmol, 1 eq) were dissolved in toluene and cooled to -80 °C. A toluene solution of [L^3Ga] (**2**) (58 mg, 0.1 mmol, 1 eq) were added drop by drop and the reaction solution was allowed to warm to room temperature overnight. The green reaction mixture was filtered over diatomaceous earth. The solution was layered under acetonitrile (1:2).

^{1}H NMR (C_6D_6, 300 K): δ [ppm] = 7.31 – 7.19 (m, 4H, *H*$_{aryl,meta}$ + toluene), 7.11-7.00 (m, 2H, *H*$_{aryl,para}$ + toluene), 4.69 (s, 1H, *H*$_{\beta}$), 4.48 (s, 2H, Cp(^{t}Bu$_2$^{t}Bu*H*$_2$)), 3.89 (sept. 2H, C*H*Me$_2$), 2.59 (sept, 2H, C*H*Me$_2$), 2.11 (toluene), 1.89 (d, 6H, CH*Me*Me'), 1.66 (d, 6H, CH*Me*Me'), 1.54 (s, 3H, *α*-Me), 1.35 (s, 3H, *α*-Me'), 1.27 (s, 18H, Cp(*^{t}Bu$_2$*^{t}BuH$_2$)), 1.20 (d, 6H, CHMe*Me'*), 1.01 (s, 9H, Cp(^{t}Bu$_2$*^{t}Bu*H$_2$)), 0.84 (d, 6H, CHMe*Me'*).

^{31}P{^{1}H} NMR (C_6D_6, 300 K): δ [ppm] = 94.05 ppm (m, 2P), -54.0 ppm (m, 2P). Corresponding coupling constants are taken from simulation (Figure S5.12) and given in table S5.1.

5.5.1.7. Synthesis of [(Cp'''Co)(μ,$\eta^{4:1:1}$-As_4)(L^3Ga)] (**6b**)

[(Cp'''Co)$_2$tol] (12.1 mg, 0.02 mmol, 1 eq) and [L^3Ga($\eta^{1:1}$-As_4)] (**4**) (31 mg, 0.04 mmol, 2 eq) were dissolved in 5 mL ortho-difluorobenzene or toluene. The green reaction mixture was stirred for 2 hours and then filtered over diatomaceous earth. The solution was layered with acetonitrile (1:2). By storing the layering by -30 °C, compound [(Cp'''Co)(μ,$\eta^{4:1:1}$-As_4)(L^3Ga)] (**6b**) crystallized as green plates, suitable for X-ray analysis.

Crystalline Yield: 35 mg (0.03 mmol, 83 %)

^{1}H NMR (C_6D_6, 300 K): δ [ppm] = 7.33 – 7.17 (m, 4H, *H*$_{aryl,meta}$), 7.11-6.99 (m, 2H, *H*$_{aryl,para}$), 4.65 (s, 1H, *H*$_{\beta}$), 4.13 (s, 2H, Cp(^{t}Bu$_2$^{t}Bu*H*$_2$)), 3.95 (sept. 2H, C*H*Me$_2$), 2.58 (sept, 2H, C*H*Me$_2$), 1.90 (d, 6H, CH*Me*Me'), 1.63 (d, 6H, CH*Me*Me'), 1.55 (s, 3H, *α*-Me), 1.33 (s, 3H, *α*-Me'), 1.22 (s, 18H, Cp(*^{t}Bu$_2$*^{t}BuH$_2$)), 1.19 (d, 6H, CHMe*Me'*), 1.02 (s, 9H, Cp(^{t}Bu$_2$*^{t}Bu*H$_2$)), 0.82 (d, 6H, CHMe*Me'*).

LIFDI-MS (toluene): m/z (%) = 1078.07 (100, $[M]^+$).

EA calculated for $C_{46}H_{70}N_2GaAs_4Co$ + 1x toluene (visible in the ^{1}H NMR): C: 54.35, H: 6.71, N: 2.39, found [%]: C: 54.06, H: 6.64, N: 2.27.

5.5.1.8. Synthesis of [(Cp'''Ni)(μ,$\eta^{3:1:1}$-P_3)(L^3Ga)] (**7a**)

[Cp'''Ni(η^3-P_3)] (50 mg, 0.13 mmol, 1 eq) and [L^3Ga] (**2**) (128 mg, 0,26 mmol, 2 eq) were dissolved in 5 mL toluene. The green reaction mixture was refluxed for 2 hours and then filtered over diatomaceous earth. The solution was layered with acetonitrile (1:2). The layering was stored at -30 °C. By storing the orange solution at -30 °C, compound [(Cp'''Ni)($\eta^{3:1:1}$-P_3)(L^3Ga)] (**7a**) crystallized as orange-brown plates, suitable for X-Ray analysis.

Crystalline Yield: 45 mg (0.05 mmol, 40 %)

^{1}H NMR (C_6D_6, 300 K): δ [ppm] = 7.21 – 7.10 (m, 6H), 5.48 (s, 2H, Cp(^{t}Bu$_2$^{t}Bu*H*$_2$)), 4.71 (s, 1H, *H*$_{\beta}$), 3.46 (sept, 2H, $^3J_{HH}$ = 7 Hz, C*H*Me$_2$), 3.41 (sept, 2H, $^3J_{HH}$ = 7 Hz, C*H*Me$_2$), 1.67 (d, 6H, CH*Me*Me', $^3J_{HH}$ = 7 Hz), 1.59 (d, 6H, CH*Me*Me', $^3J_{HH}$ = 7 Hz), 1.54 (s, 3H, *α*-Me), 1.44 (s, 3H, *α*-Me'), 1.26 (s, 18H, Cp(*^{t}Bu$_2$*^{t}BuH$_2$)), 1.13 (d, 6H, CHMe*Me'*, $^3J_{HH}$ = 7 Hz), 1.11 (s, 9H, Cp(^{t}Bu$_2$*^{t}Bu*H$_2$)), 1.04 (d, 6H, CHMe*Me'*, $^3J_{HH}$ = 7 Hz).

^{31}P{^{1}H} NMR (C_6D_6, 300 K): δ [ppm] = 163.8 ppm (d, 2P, $^1J_{PP}$ = 325 Hz), 109.1 ppm (t, 1P, $^1J_{PP}$ = 324 Hz).

LIFDI-MS (toluene): m/z (%) = 904.26 (100, $[M+O_2]^+$).

EA calculated for $C_{46}H_{70}N_2GaP_3Ni$: C: 63.33, H: 8.09, N: 3.21, found [%]: C: 63.21, H: 7.97, N: 3.20.

5.5.1.9. Synthesis of [(Cp'''Ni)(μ,$\eta^{3:1:1}$-As_3)(L^3Ga)] (**7b**)

[Cp'''Ni(η^3-As_3)] (21 mg, 0.04mmol, 1 eq) and [L^3Ga] (**2**) (40 mg, 0.08 mmol, 2 eq) were dissolved in 5 mL toluene. The green reaction mixture was refluxed for 2 hours and then filtered over diatomaceous earth. The solution was layered with acetonitrile (1:2). By storing the layering by -30 °C, compound [(Cp'''Ni)(μ,$\eta^{3:1:1}$-As_3)(L^3Ga)] (**7b**) crystallized as orange plates, suitable for X-ray analysis.

Crystalline Yield: 31 mg (0.003 mmol, 76 %)

^{1}H NMR (C_6D_6, 300 K): δ [ppm] = 7.19 (t, 2H, $^3J_{HH}$ = 7 Hz, $H_{aryl,para}$), 7.14 (d, 4H, $H_{aryl,meta}$), 5.32 (s, 2H, Cp(^{t}Bu$_2$^{t}BuH_2)), 4.71 (s, 1H, $H_{ß}$), 3.54 (sept, 2H, $^3J_{HH}$ = 7 Hz, CHMe$_2$), 3.45 (sept, 2H, $^3J_{HH}$ = 7 Hz, CHMe$_2$), 2.11 (toluene, 3H), 1.67 (d, 6H, CH*Me*Me'), 1.60 (d, 6H, CH*Me*Me'), 1.56 (s, 3H, *α*-Me), 1.48 (s, 3H, *α*-Me'), 1.28 (s, 18H, Cp(^{t}*Bu*$_2$^{t}BuH$_2$)), 1.14 (d, 6H, CHMe*Me'*), 1.11 (s, 9H, Cp(^{t}Bu$_2$^{t}*Bu*H$_2$)), 1.04 (d, 6H, CHMe*Me'*).

LIFDI-MS (toluene): m/z (%) = 1036.08 (100, $[M+O_2]^+$).

EA calculated for $C_{46}H_{70}N_2GaAs_3Ni$ + 1x toluene: C: 58.06, H: 7.17, N: 2.56, found [%]: C: 58.38, H: 6.65, N: 2.59.

5.5.2. NMR studies

5.5.2.1. [L^3Al] (**1**) with an excess of P_4

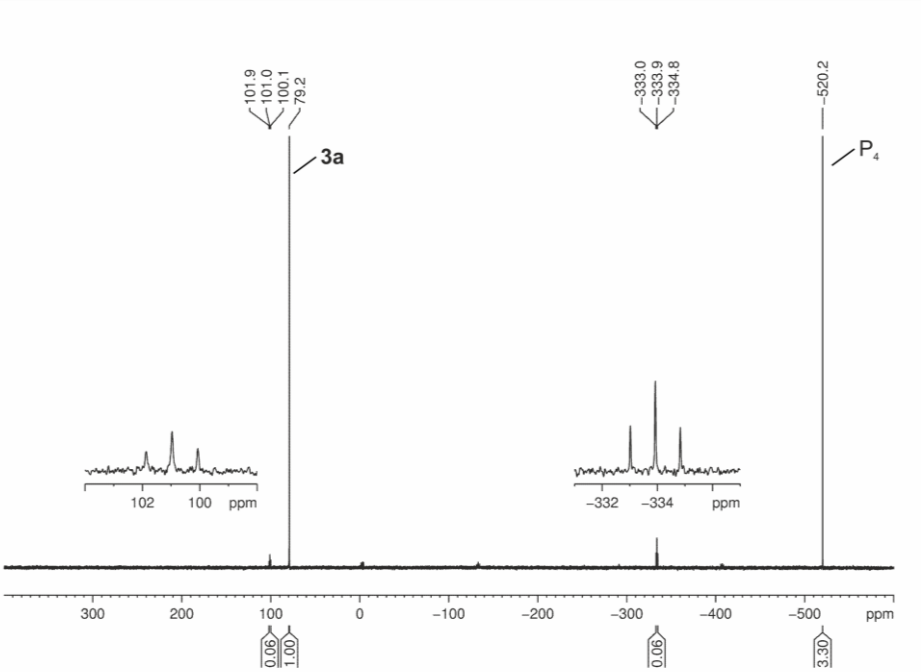


Figure S5.1. $^{31}P\{^1H\}$ NMR spectrum of the reaction of [LAl] with an excess of P_4.

5.5.2.2. [$(L^3Al)_2(\mu,\eta^{1:1:1:1}\text{-}As_4)$] (**3b**)

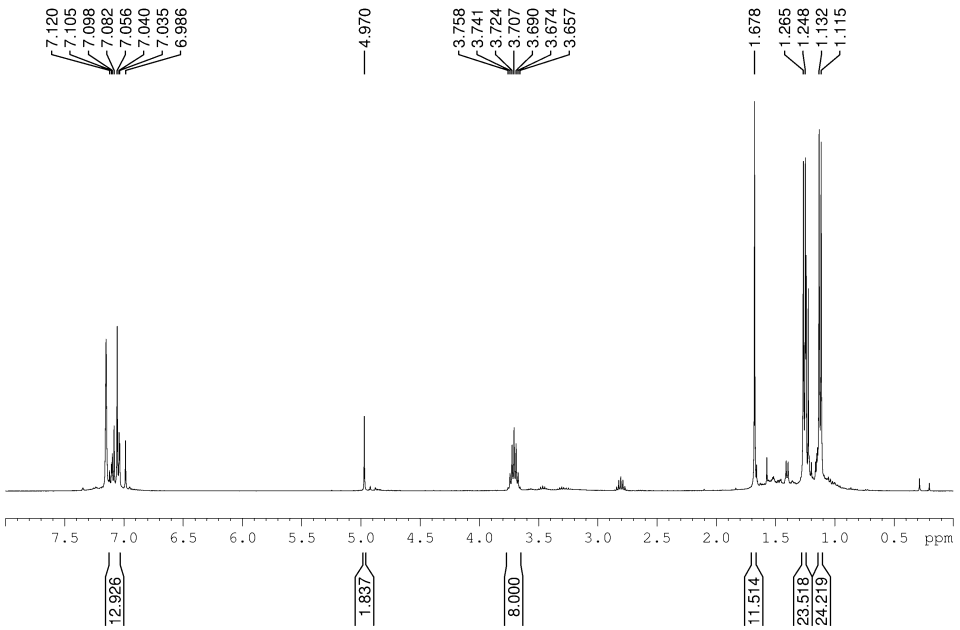


Figure S5.2. ^1H NMR spectrum of **3b** in C_6D_6 at room temperature.

5.5.2.3. $[(L^3Al)_2(\mu,\eta^{1:1:1:1}\text{-}AsP_3)]$ (**3c**)

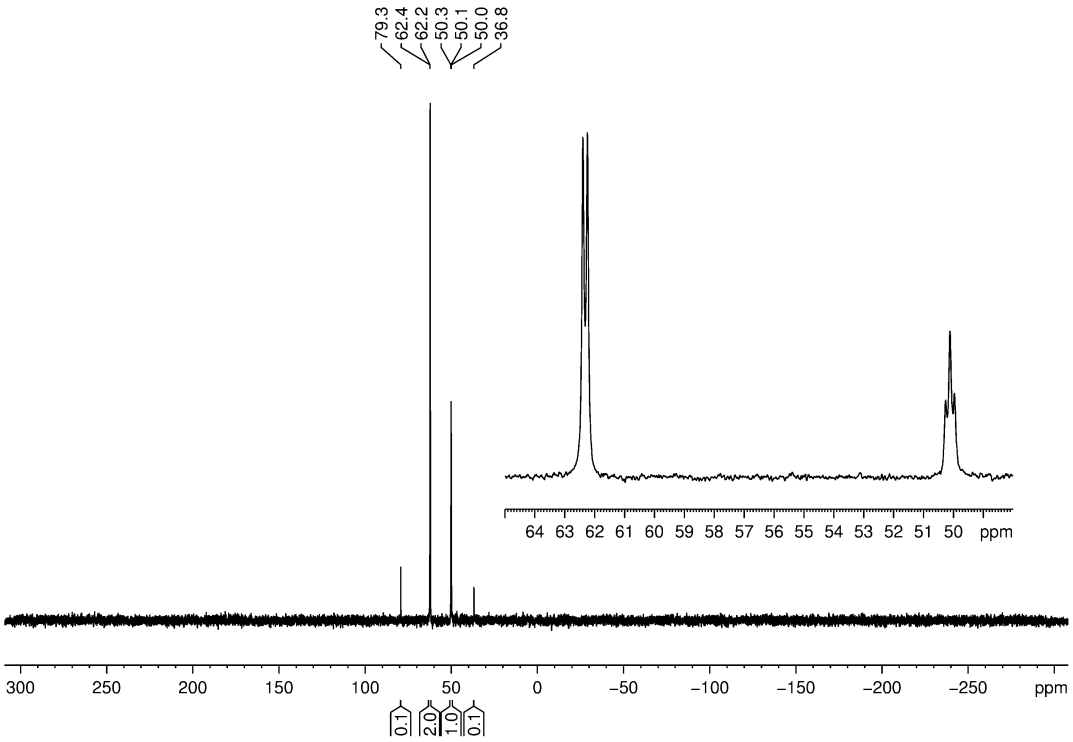


Figure S5.3. $^{31}P\{^1H\}$ NMR spectrum of **3c** in C_6D_6 at room temperature.

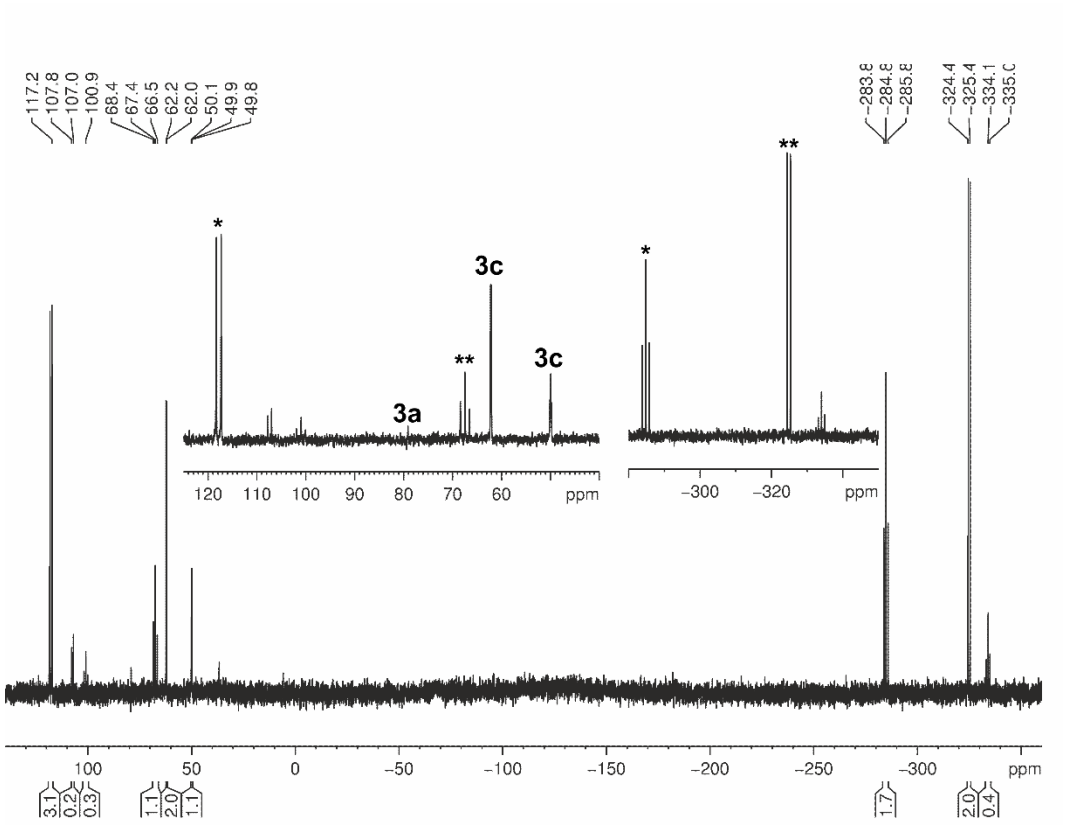


Figure S5.4. $^{31}P\{^1H\}$ NMR spectrum of the reaction solution of $[L^3Al]$ with AsP_3 in C_6D_6 at room temperature. (* = **I-3c1** and ** = **I-3c2**)

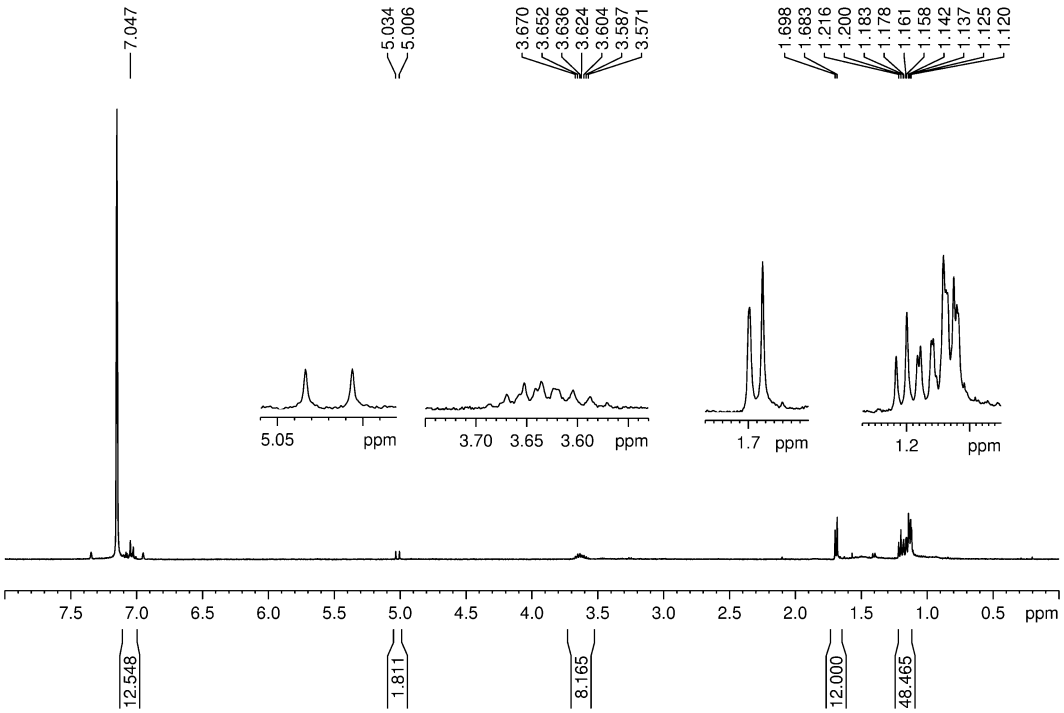


Figure S5.5. ^{1}H NMR spectrum of **3c** in C_6D_6 at room temperature.

5.5.2.4. [$L^3Ga(\eta^{1:1}$-$As_4)$] (**4b**)

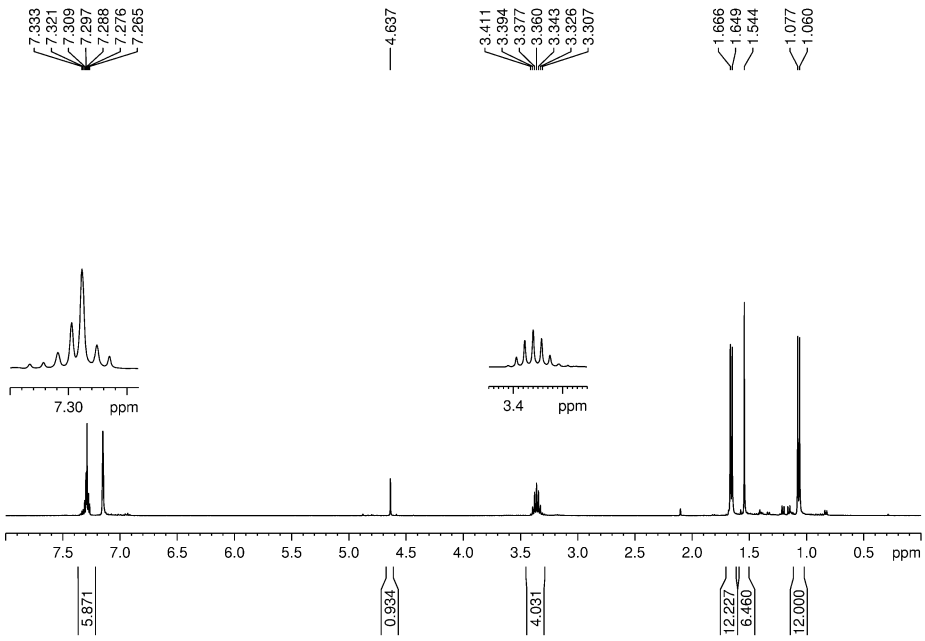


Figure S5.6. ^{1}H NMR spectrum of **4b** in C_6D_6 at room temperature.

5.5.2.5. [$L^3Ga(\eta^{1:1}\text{-}AsP_3)$] (**4c**)

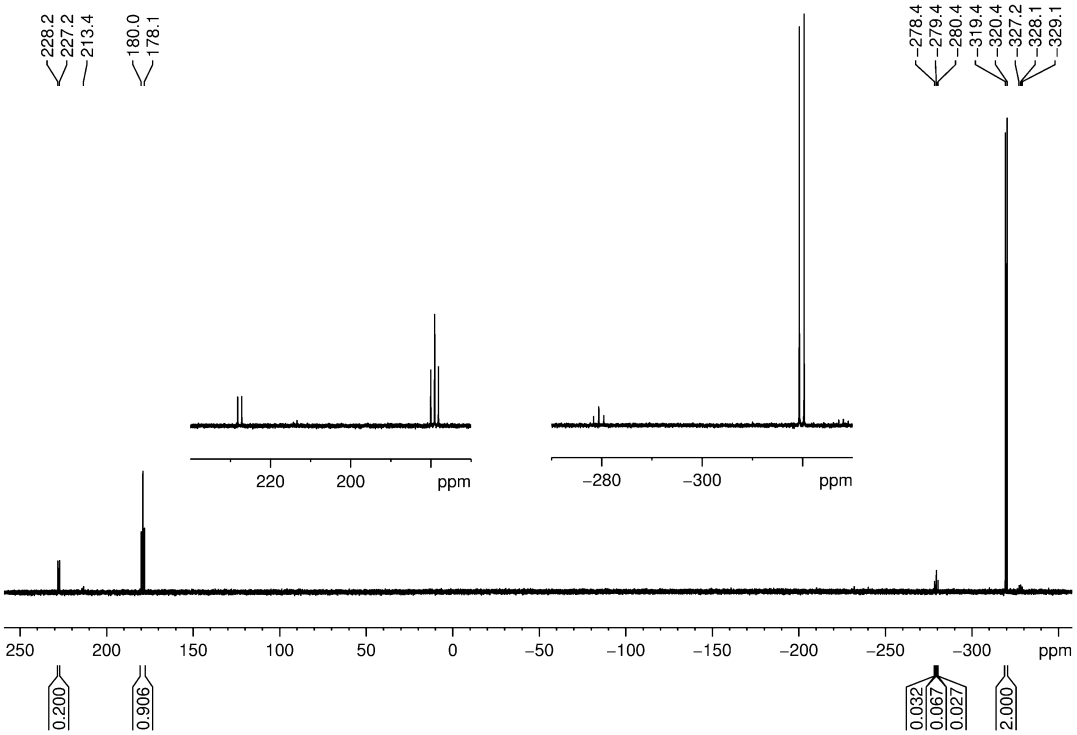


Figure S5.7. $^{31}P\{^1H\}$ NMR spectrum of crystals of **4c** in C_6D_6 at room temperature.

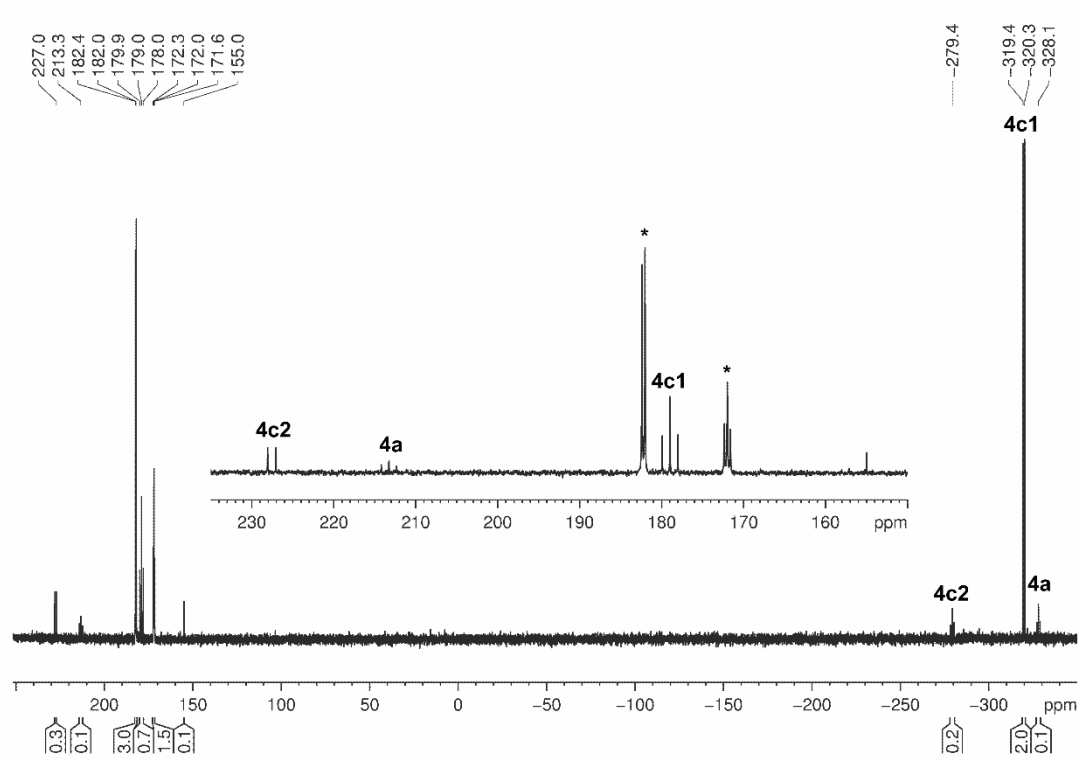


Figure S5.8. $^{31}P\{^1H\}$ NMR spectrum of the reaction solution of [L^3Ga] with AsP_3 in C_6D_6 at room temperature.

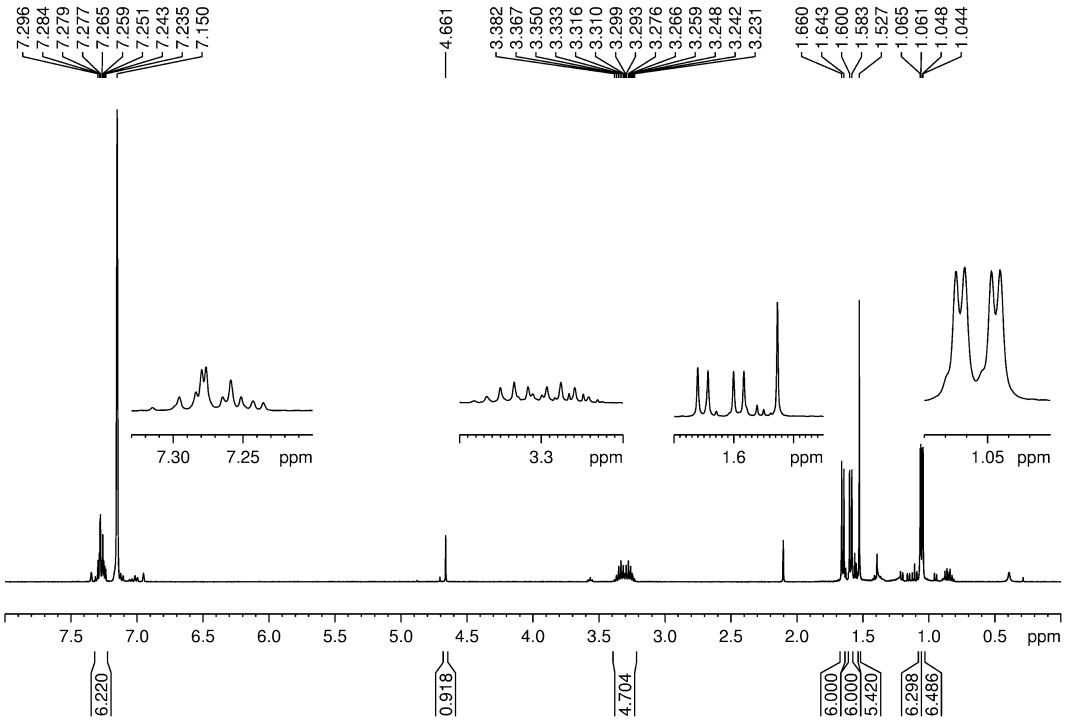


Figure S5.9. ^{1}H NMR spectrum of compound **4c** in C_6D_6 at room temperature.

5.5.2.6. [(L^{3}Ga)(μ,η$^{2:1:1}$-P$_4$)(L^{3}Ni)] (**5a**)

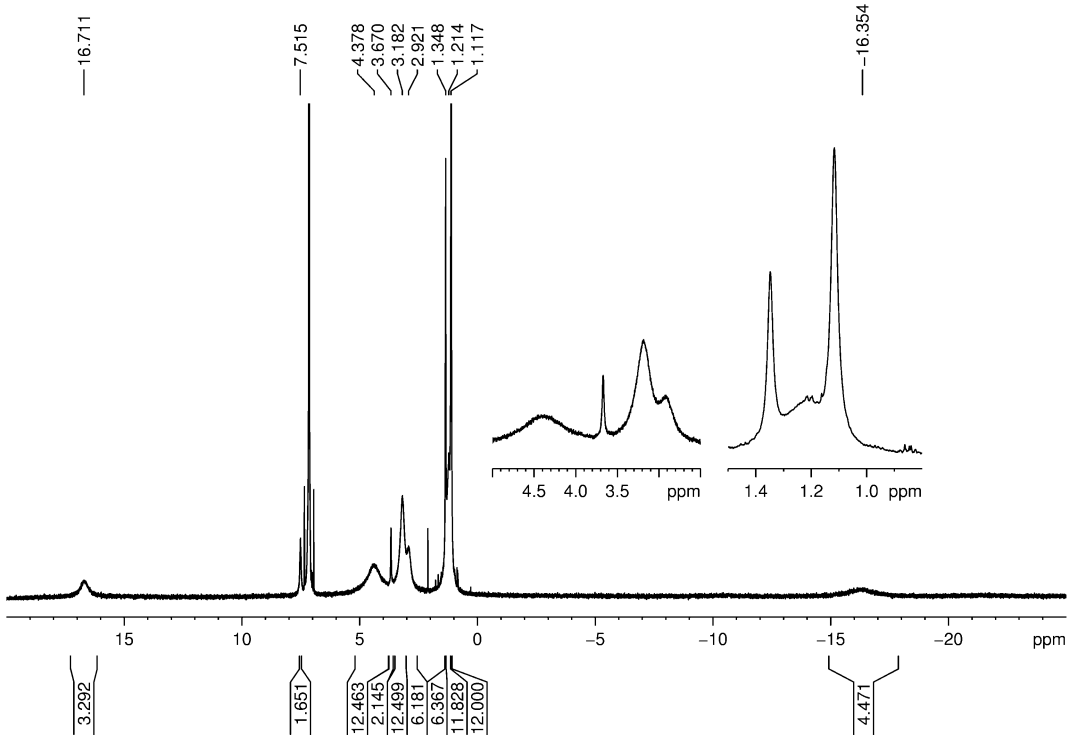


Figure S5.10. ^{1}H NMR spectrum of **5a** in C_6D_6 at room temperature.

5.5.2.7. [(Cp'''Co)(μ,$\eta^{4:1:1}$-P_4)(L^3Ga)] (**6a**)

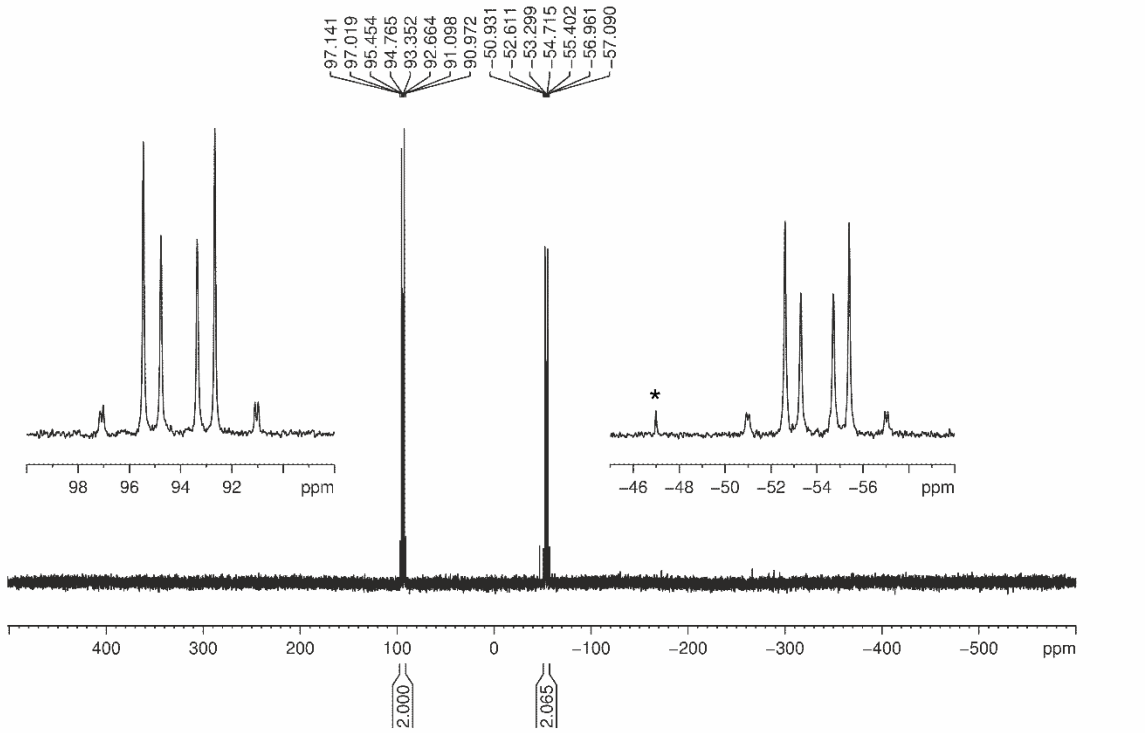


Figure S5.11. $^{31}P\{^1H\}$ NMR spectrum of **6a** in C_6D_6 at room temperature. * = traces of [(Cp'''Co)$_2$(μ,$\eta^{2:2}$-P_2)$_2$]

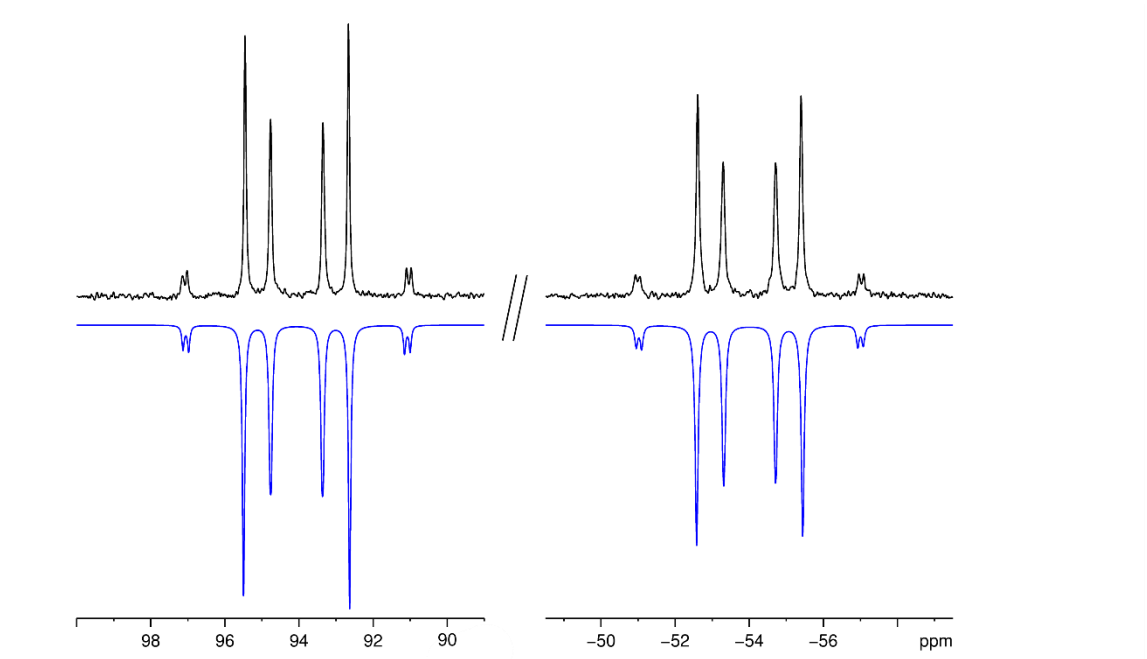


Figure S5.12. $^{31}P\{^1H\}$ NMR spectrum of **6a** in C_6D_6 at room temperature (measured top (black) and simulated bottom (blue)).

Table S5.1. Coupling constants obtained from the simulation in Figure S5.12.

[(Cp'''Co)(μ,η$^{4:1:1}$-P$_4$)(L^{3}Ga)]		
$^1J_{PAPA'}$ = 371 Hz	$^1J_{PAPX}$ = $^1J_{PA'PX'}$ = 466 Hz	$^2J_{PA'PX}$ = -8 Hz
$^2J_{PAPX'}$ = 3 Hz	$^3J_{PXPX'}$ = $^3J_{PX'PX}$= -15 Hz	
δ = AA' = 94.05 ppm	XX' = -54.0 ppm	

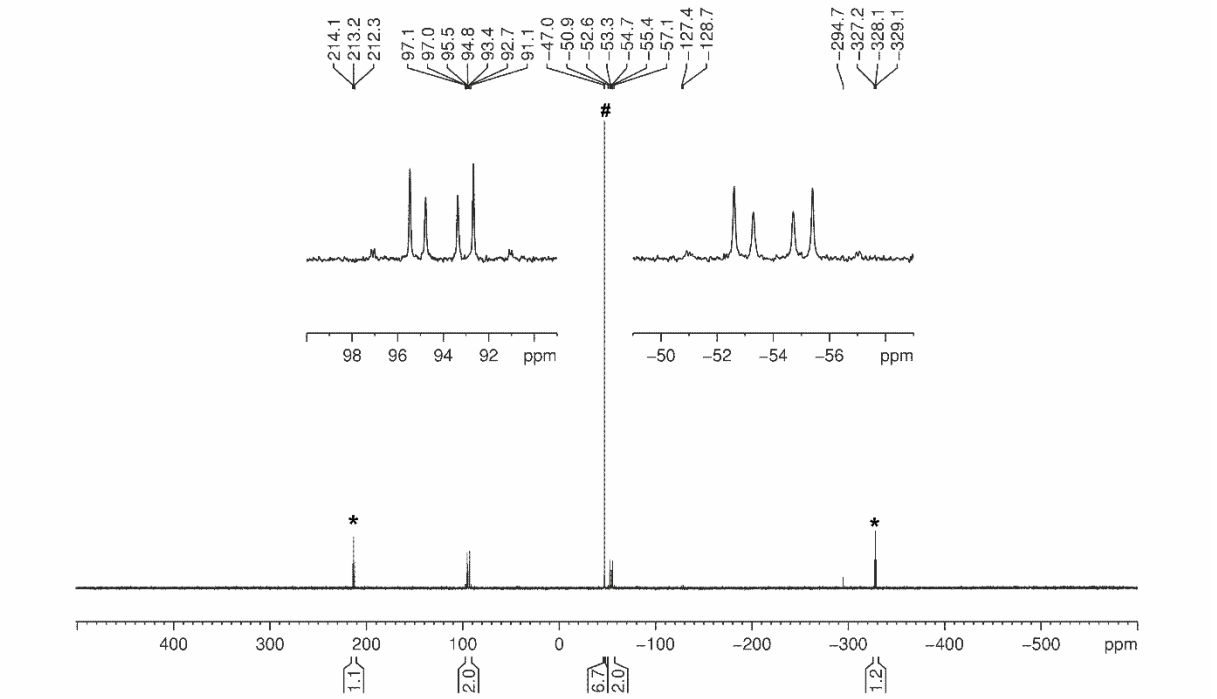


Figure S5.13. $^{31}P\{^1H\}$ NMR spectrum of the reaction solution of [(Cp'''Co)$_2$tol] with [L^{3}Ga(η$^{1:1}$-P$_4$)] (**4a**) in C_6D_6 at room temperature (* = **4a**, # = [(Cp'''Co)$_2$(μ,η$^{2:2}$-P$_2$)$_2$]).

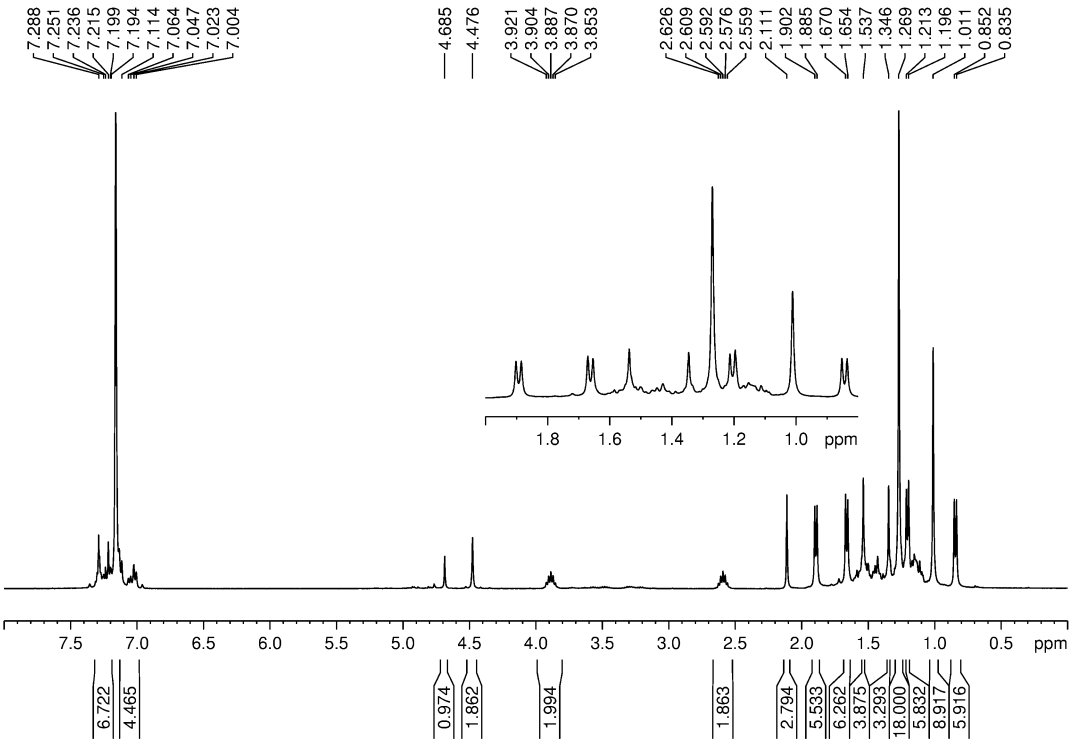


Figure S5.14. ^{1}H NMR spectrum of the reaction solution of [Cp'''Co(η^4-P_4)] with [L^3Ga] in C_6D_6 at room temperature.

5.5.2.8. [(Cp'''Co)(μ,$\eta^{4:1:1}$-As_4)(L^3Ga)] (**6b**)

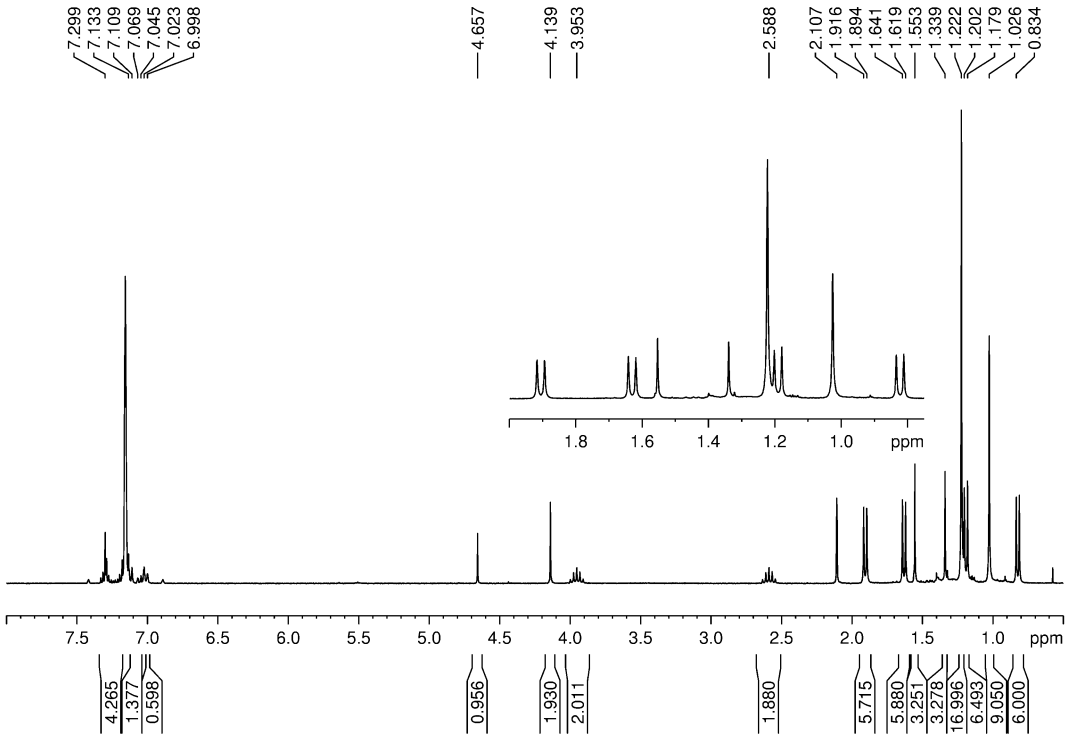


Figure S5.15. ^{1}H NMR spectrum of compound **6b** in C_6D_6 at room temperature.

5.5.2.9. [(Cp'''Ni)(μ,$\eta^{3:1:1}$-P_3)(L^3Ga)] (**7a**)

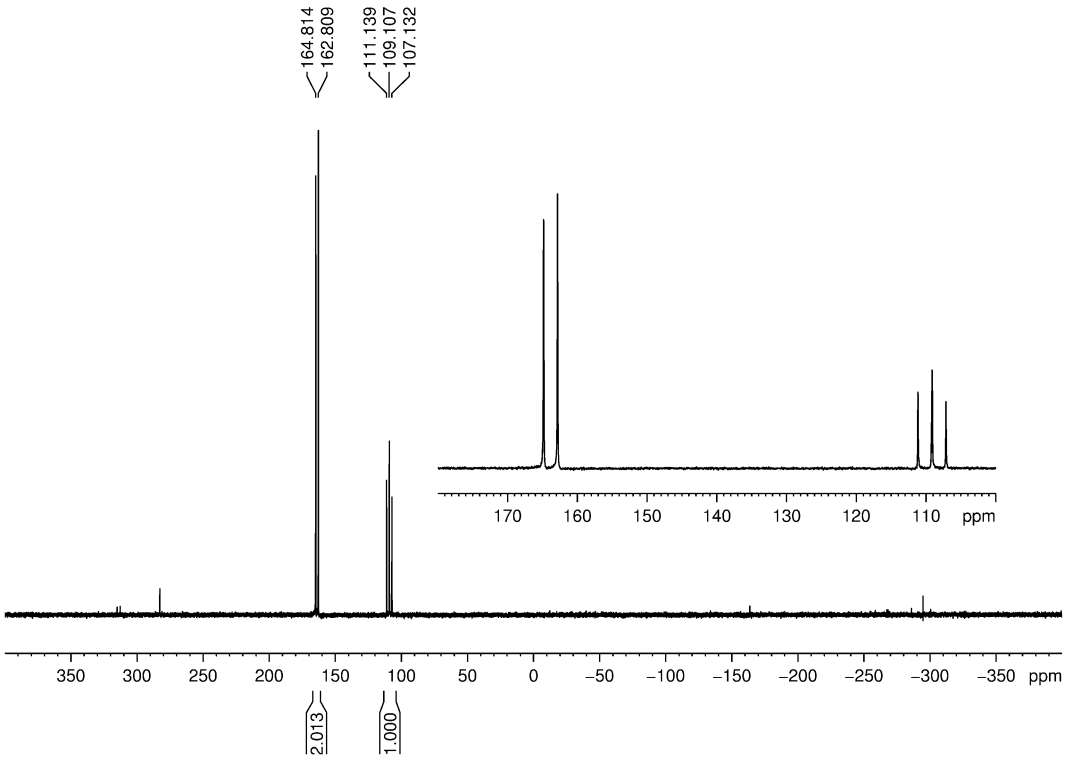


Figure S5.16. $^{31}P\{^1H\}$ NMR spectrum of **7a** in C_6D_6 at room temperature.

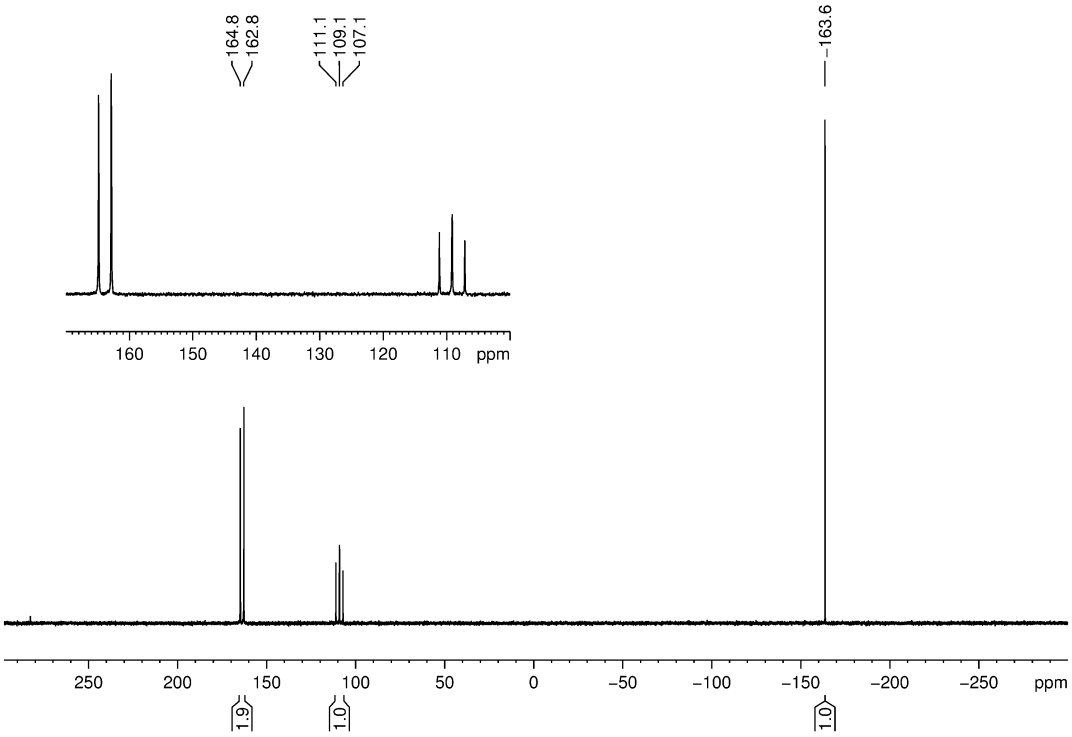


Figure S5.17. $^{31}P\{^1H\}$ NMR spectrum of 1 equivalent [L^3Ga] and 1 equivalent [Cp'''Ni(η^3-P_3)] after refluxing for 2 hours in C_6D_6 at room temperature.

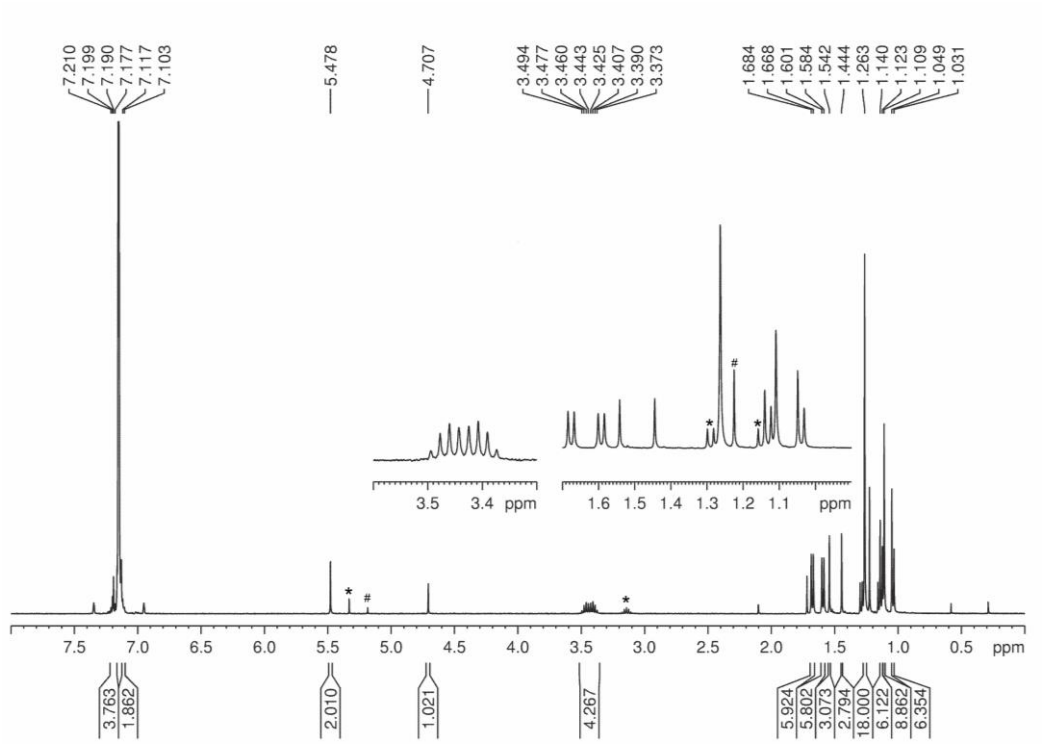


Figure S5.18. ^{1}H NMR spectrum of **7a** in C_6D_6 at room temperature. Contaminated with * = [L^{3}Ga] and # = [Cp'''Ni(η^3-P_3)].

5.5.2.10. [(Cp'''Ni)(μ,$\eta^{3:1:1}$-As_3)(L^{3}Ga)] (**7b**)

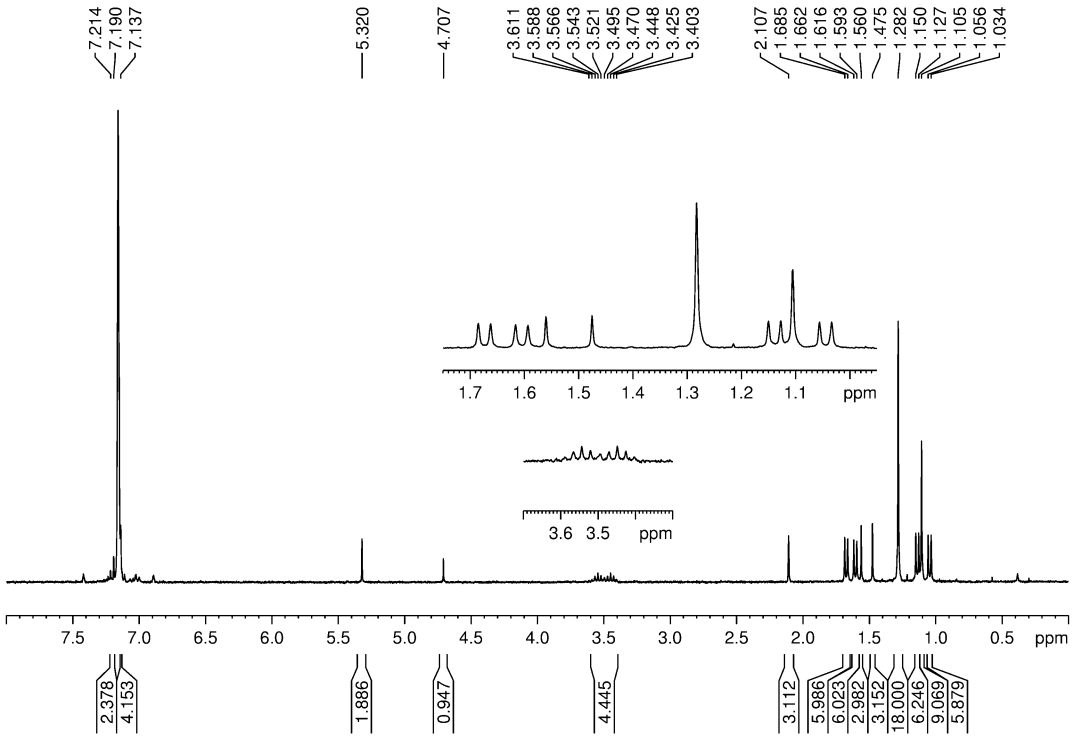


Figure S5.19. ^{1}H NMR spectrum of compound **7b** in C_6D_6 at room temperature.

5.5.3. Magnetic Measurements in Solution

5.5.3.1. Evans Method

The effective magnetic moment (μ_{eff}) of paramagnetic compounds were determined by the Evans method.[9] The Evans method is based on the chemical shift difference of the residual solvent peak between the inner tube containing a solution of the paramagnetic species and the outer tube, which contains the pure deuterated solvent. The ^{1}H NMR spectra are recorded at room temperature[10] on a Bruker Avance III HD 400 (^{1}H: 400.13 MHz) spectrometer.

The molar paramagnetic susceptibility χ_P was obtained from the measured molar magnetic susceptibility χ_M after the correction for diamagnetic contribution χ_D according to equation (*1*).[11] The magnetic susceptibility χ_M and the effective magnetic moment μ_{eff} of the paramagnetic compounds was determined according, to equation (*2*)[10] and (*3*)[11].

$$\boldsymbol{\chi_P = \chi_M - \chi_D} \qquad (1)$$

$$\boldsymbol{\chi_M = \frac{3000 * \Delta\nu}{4\pi * \nu_0 * c}} \qquad (2)$$

$$\boldsymbol{\mu_{eff} = \sqrt{8 \cdot T \cdot \chi_p}} \qquad (3)$$

Finally, the number of unpaired electrons is calculated by the 'spin-only' formula[12] (equation 4):

$$\mathbf{n = -1 + \sqrt{\mu_{eff}^2 + 1}} \qquad (4)$$

Where

χ_M is the measured susceptibility of the sample in emu · mol^{-1},

χ_P is the molar paramagnetic susceptibility of the sample in emu · mol^{-1},

χ_D is the molar diamagnetic susceptibility of the sample in emu · mol^{-1},

$\Delta\nu$ is the chemical shift difference between the solvent in presence of paramagnetic solute and pure solvent in [Hz],

ν_0 is the measuring frequency of the NMR spectrometer [Hz],

c is the concentration of paramagnetic sample in mol · L^{-1},

T is the absolute temperature in K,

μ_{eff} is the effective magnetic moment in μ_B, and

n is the number of unpaired electrons.

5.5.3.2. EPR (Electrone Paramagnetic Resonance) measurements

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. The compounds were dissolved in a glovebox under N_2 inert gas atmosphere, placed in tip-sealed pasteur pipettes, and were rubber plugged. The measurements were conducted at room temperature and 77 K, respectively. With EPR, a magnetic field is applied to the sample, which interacts with the unpaired electrons. The simulation has been performed using the EasySpin[13] program.

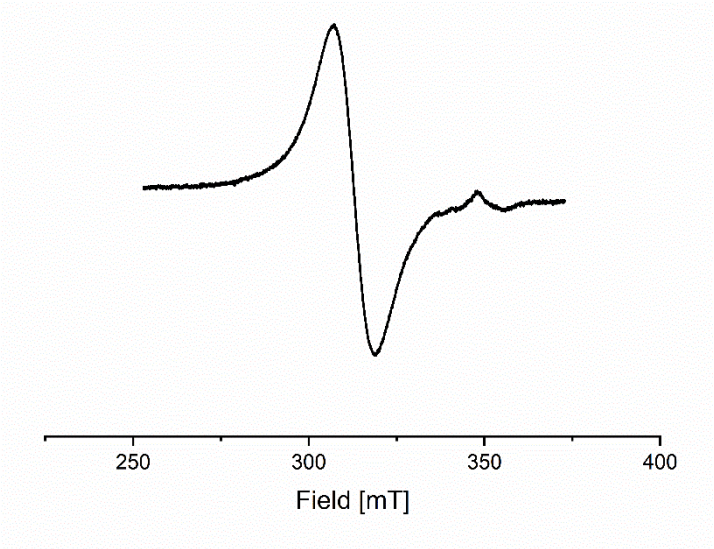


Figure S5.20. EPR spectrum of **5a** in toluene solution, room temperature (g = 2.156, B = 312.89 mT)

Table S5.2. Experimental parameters for the X-band EPR measurement of **5a** at 77 K, see Figure 5.4 (Paper).

Sys.g = [2.2364 2.1212 2.038]	*Exp.Range = [252.87 – 372.90]*
Sys.lw = [3.5]	*Exp.nPoints 4096*
Sys.A = [120 178 20; 150 60 180]	*Exp.mwFreq = 9.440920*
Sys.HStrain = [40 20 100]	*Exp.Temperature= 77*
Sys.Astrain [6 20 20]	*Exp.ModAmp = 0.2*

5.5.4. Details on single crystal X-ray structure analysis

The X-ray diffraction experiments were performed on either a Gemini Ultra diffractometer (Oxford diffraction) with an AtlasS2 detector (λ = 1.54178 Å) (**3b**), on a SuperNova Dualflex diffractometer (Rigaku, formerly Agilent Technologies) equipped with a TitanS2 detector (λ = 1.54178 Å) (**4b**, **4c**) or XtaLAB Synergy R, DW system (Rigaku) equipped with a HyPix Arc 150° detector (**3c**, **5a**, **6b**, **7a**, **7b**). All measurements were performed at 123 K. Data collection and reduction were performed with CrysAlisPro[14] (Version 171.38.41, 2015 (**3b**), 171.41.21a, 2019 (**4b**), 171.41.54a, 2020 (**4c**), 171.41.76a, 2020 (**6b**), 171.41.88a, 2020 (**5a**, **7b**), 171.41.90a, 2020 (**3c**), 171.41.118a, 2021 (**7a**)). For the compound (**3b**) an analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid was applied.[15] For the compounds (**3c**, **4b**, **4c**, **5a**, **6b**, **7a**, **7b**) a gaussian absorption correction based on gaussian integration over a multifaceted crystal model was applied. Using Olex2,[16] were the structures solved by direct methods with ShelXT[17] and refined by full-matrix least-squares method against F^2 in anisotropic approximation using ShelXL[18]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined in calculated positions using riding on pivot atom model.

Figures were created with Olex2.[16]

5.5.4.1. $[(L^3Al)_2(\eta^{1:1:1:1}\text{-}As_4)]$ (**3b**)

Compound **3b** crystallizes from a concentrated solution in Et_2O at -30 °C in the non-centrosymmetric orthorhombic space group $P2_12_12_1$ as orange plate. The asymmetric unit contains one molecule of **3b** and a molecule of Et_2O, which is 0.65 occupied. The structure in the solid state is given in Figure S5.21.

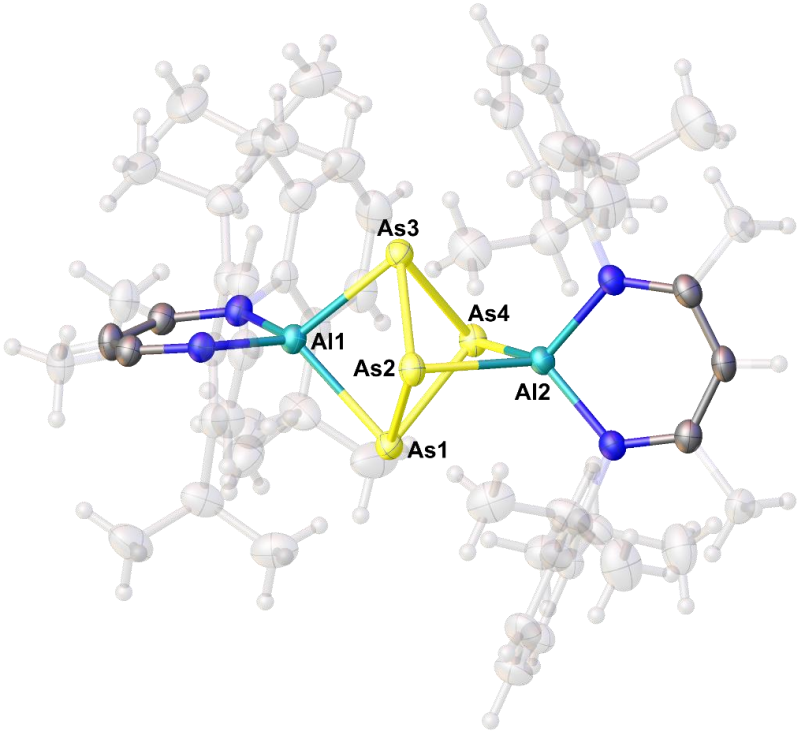


Figure S5.21. Molecular structure of **3b** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Al1-As1 2.4412(11), Al1-As3 2.4649(11), Al2-As2 2.4582(11), Al2-As4 2.4408(11), As1-As2 2.5220(6), As2-As3 2.5097(6), As3-As4 2.5096(6), As1-As4 2.5200(6), N1-Al1 1.920(3), N2-Al1 1.917(3), N3-Al2 1.922(3), N4-Al2 1.919(3), As4-As3-As2 83.456(18), As3-As2-As1 82.844(17), As4-As1-As2 82.996(18), As3-As4-As1 82.887(18), Al1-As3-As2 80.22(3), Al1-As3-As4 77.21(3), Al1-As1-As2 80.43(3), Al1-As1-As4 77.44(3), Al2-As2-As3 80.18(3), Al2-As2-As1 76.51(3), Al2-As4-As3 80.52(3), Al2-As4-As1 76.86(3).

5.5.4.2. $[(L^3Al)_2(\mu,\eta^{1:1:1:1}\text{-}AsP_3)]$ (**3c**)

Compound **3c** crystallizes from a concentrated solution in Et_2O at -30 °C in the non-centrosymmetric orthorhombic space group $P2_12_12_1$ as orange plate. The asymmetric unit contains one molecule of **3c** and a molecule of Et_2O, which is 0.8 occupied. The structure in the solid state is given in Figure S5.22.

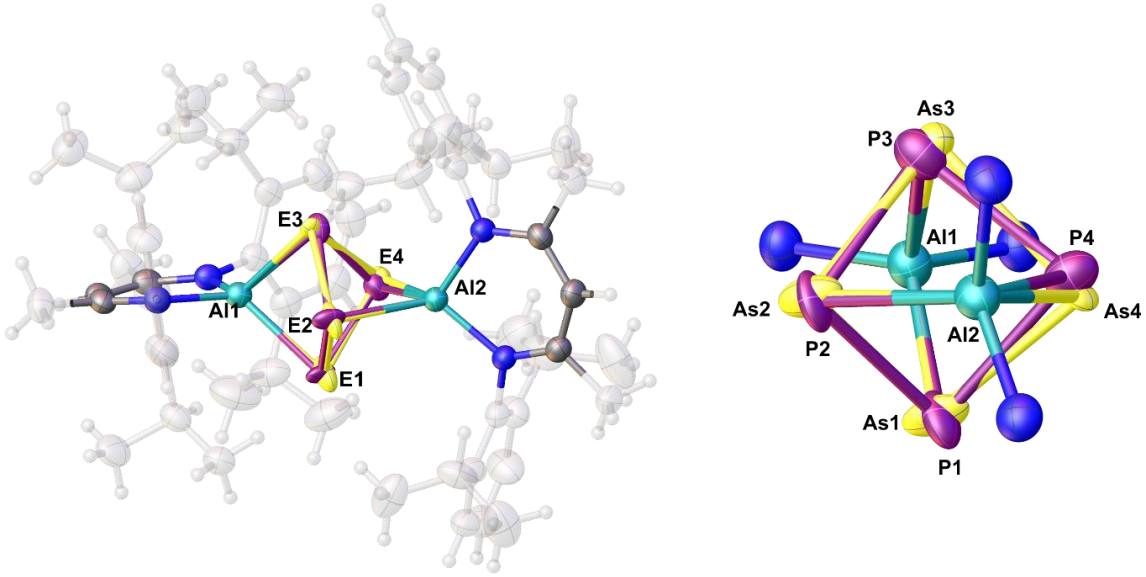


Figure S5.22. Molecular structure of **3c** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Al1-As1 2.398(16), Al1-As3 2.492(5), Al2-As2 2.43(2), Al2-As4 2.404(4), Al1-P1 2.380(4), Al1-P3 2.418(4), Al2-P2 2.370(6), Al2-P4 2.482(5), P1-P2 2.301(7), P2-P3 2.332(7), P3-P4 2.407(8), P4-P1 2.393(6), As1-P2 2.561(14), As1-P4 2.306(13), As2-P3 2.557(18), P1-As2 2.280(17), P2-As3 2.287(7), As3-P4 2.435(7), P3-As4 2.366(7), P1-As4 2.411(6), N1-Al1 1.909(4), N2-Al1 1.918(3), N3-Al2 1.915(3), N4-Al2 1.907(3), P1-P2-P3 85.2(2), P2-P3-P4 83.9(2), P3-P4-P1 81.5(2), P4-P1-P2 84.9(2), As1-P2-P3 82.4(4), P4-As1-P2 81.1(4), P3-P4-As1 86.5(4), P1-As2-P3 80.6(5), As2-P3-P4 83.5(5), P4-P1-As2 90.1(5), P1-P2-As3 87.0(2), P2-As3-P4 84.3(3), As3-P4-P1 81.7(2), P2-P3-As4 83.2(2), P3-As4-P1 82.03(18), As4-P1-P2 82.9(2).

5.5.4.3. [$L^3Ga(\eta^{1:1}\text{-}As_4)$] (**4b**)

Compound **4b** crystallizes from a concentrated solution in a toluene:n-hexane (1:2) mixture at -30 °C in the tetragonal space group *P4₃2₁2* as yellow blocks The asymmetric unit contains one molecule of **4b**. The structure in the solid state is given in Figure S5.23.

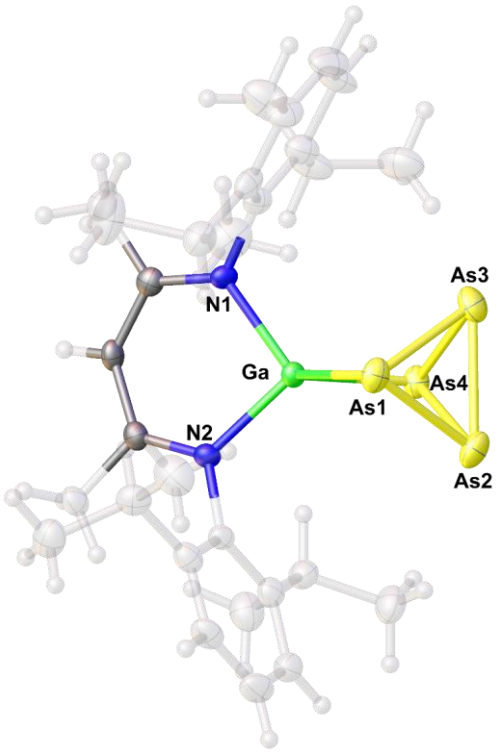


Figure S5.23. Molecular structure of **4b** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Ga-As1 2.4259(5), Ga-As4 2.4415(5), As1-As2 2.4693(6), As2-As3 2.3830(6), As3-As4 2.4612(6), As1-As3 2.4678(5), As2-As4 2.4608(5), Ga-N1 1.973 (3), Ga-N2 1.960(2), As3-As1-As2 57.720(17), As4-As3-As1 88.927(16), As2-As3-As1 61.172(16), As2-As3-As4 61.033(17), As4-As2-As1 88.902(18), As3-As2-As1 61.108(16), As3-As2-As4 61.050(17), Ga-As1-As2 83.876(17), Ga-As1-As3 81.665(16), Ga-As4-As3 81.489(17), Ga-As4-As2 83.732(17), As1-Ga-As4 90.359(17).

5.5.4.4. [$L^3Ga(\eta^{1:1}$-AsP_3)] (**4c**)

Compound **4c** crystallizes from a concentrated solution in a toluene:*n*-hexane (2:1) mixture -30 °C in the tetragonal space group $P4_32_12$ as yellow blocks The asymmetric unit contains one molecule of **4c**. The structure in the solid state is given in Figure S5.24.

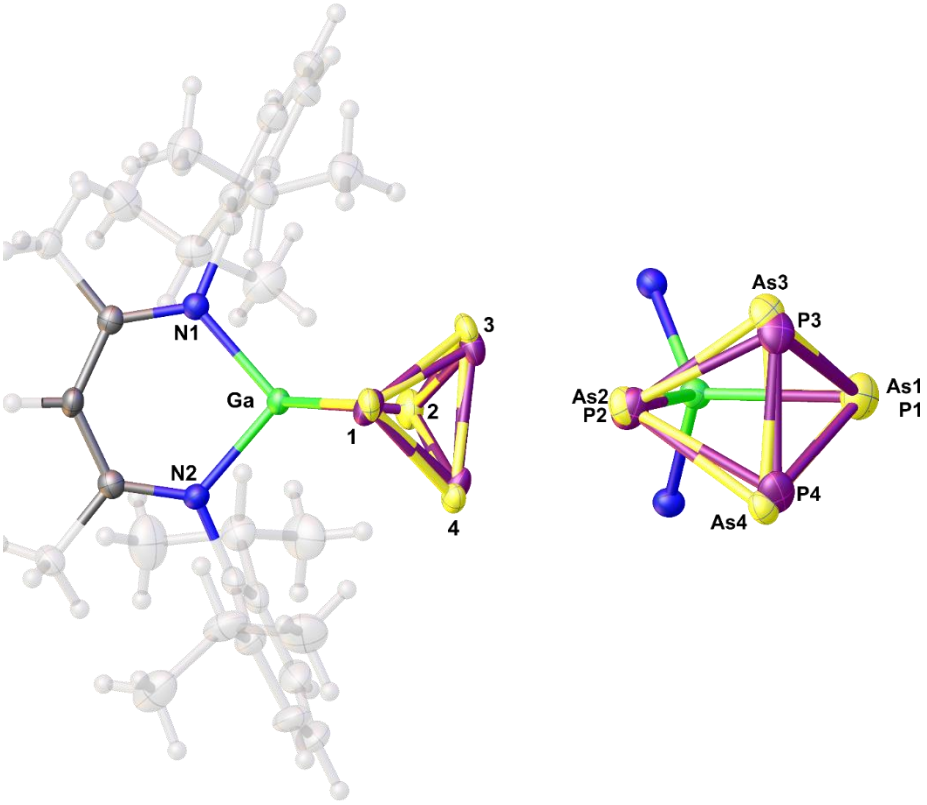


Figure S5.24. Molecular structure of **4c** in solid state (left: best view, right: disordered AsP_3 ligand). Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å]: Ga-P1 2.451(6), Ga-P2 2.365(11), Ga-As1 2.412(3), Ga-As2 2.421(8), As1-P3 2.321(3), As1-P4 2.315(4), P2-P3 2.296(9), P2-P4 2.277(12), P3-P4 2.155(4), P1-P3 2.301(5), P1-P4 2.290(6), As2-P3 2.323(6), As2-P4 2.340(9), P1-As3 2.47(4), P2-As3 2.30(4), As3-P4 2.41(3), P1-As4 2.52(4), P2-As4 2.25(4), P3-As4 2.34(4).

5.5.4.5. $[(L^3Ga)(\mu,\eta^{2:1:1}\text{-}P_4)(L^3Ni)]$ (**5a**)

Compound **5a** crystallizes from a concentrated toluene solution at -30 °C in the monoclinic space group *C2/c.* The asymmetric unit contains half a molecule of **5a** as an inversion twin. One dipp group of the ligand is disordered over two positions (0.67:0.33). The structure in the solid state is shown in Figure S5.25 and S5.26.

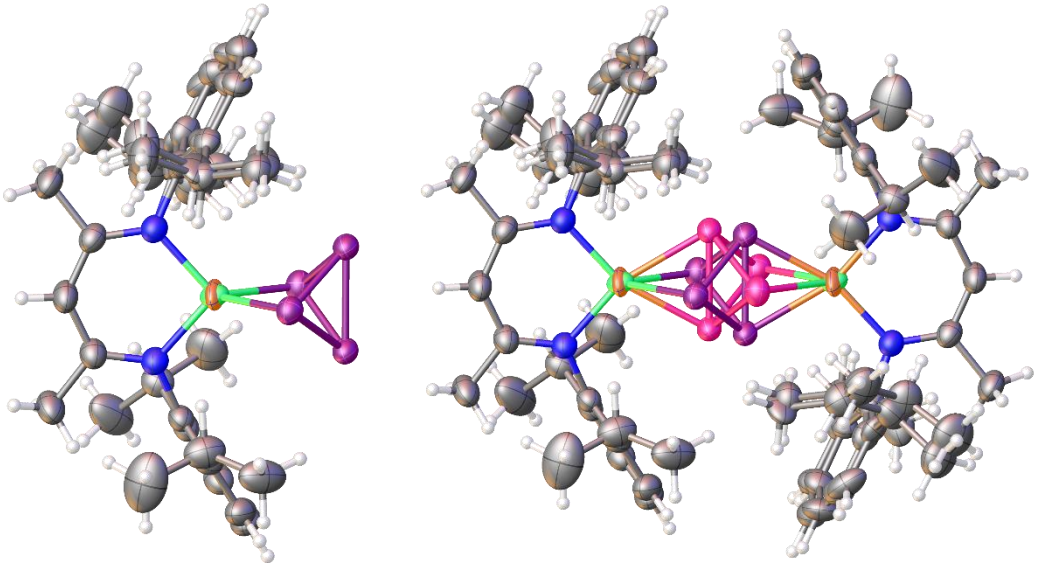


Figure S5.25. Molecular structure of **5a** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Left: Asymmetric unit of **5a**. Right: growed structure of the inversion twin of **5a**.

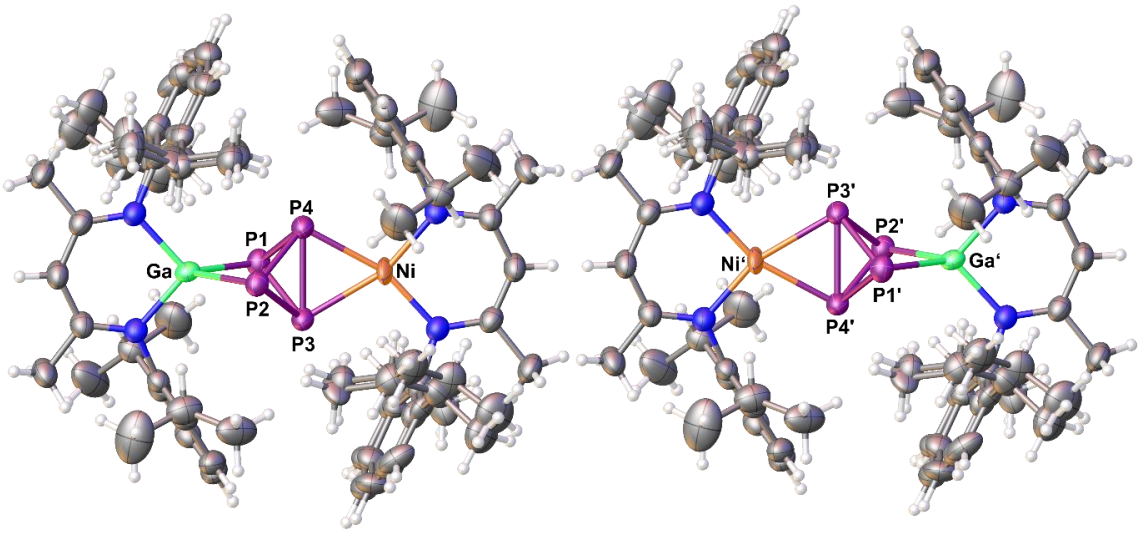


Figure S5.26. Selected bond lengths [Å] and angles [°]: N1-Ni 1.926(3), N2-Ni 1.923(4), N1-Ga 1.920(3), N2-Ga 1.928(3), Ga-P1 2.298(2), Ga-P2 2.386(2), Ni-P3 2.317(3), Ni-P4 2.297(3), P1···P2 3.1784(17), P1-P3 2.2366(18), P1-P4 2.2386(17), P3-P2 2.2372(16), P3-P4 2.2566(15), P2-P4 2.2391(17), P3-P1-P4 60.56(5), P1-P3-P2 90.54(6), P1-P3-P4 59.76(6), P2-P3-P4 59.77(5), P3-P2-P4 60.55(5), P1-P4-P3 59.68(6), P1-P4-P2 90.44(6), P2-P4-P3 59.68(5).

5.5.4.6. [(Cp'''Co)(μ,$\eta^{4:1:1}$-As_4)(L^3Ga)] (**6b**)

Compound **6b** crystallizes from a concentrated orthodiflurobenzene solution layered with acetonitril at -30 °C in the monoclinic space group *P2₁/n*. The asymmetric unit contains one molecule of **6b**. The Cp''' ring is disordered over two positions with an occupancy of 50:50. The structure in the solid state is shown in Figure S5.27.

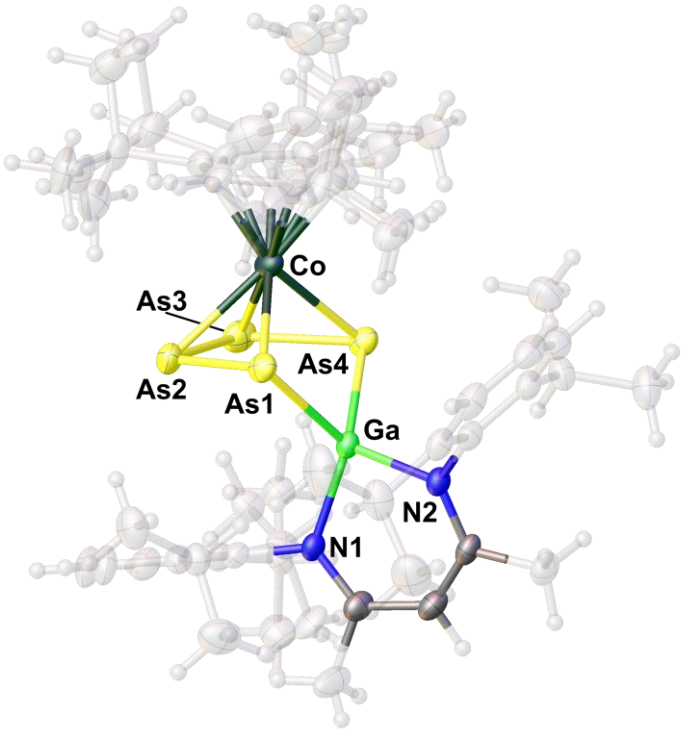


Figure S5.27. Molecular structure of **6b** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å]: Ga-As1 2.4271(5), Ga-As2 2.4481(5), As1-As2 2.3270(6), As2-As3 2.4018(6), As3-As4 2.3227(6), Co-As1 2.5002(7), Co-As2 2.4093(8), Co-As3 2.4431(8), Co-As4 2.4817(7), Ga-N1 1.978(3), Ga-N2 1.983(3), As1-As2-As3 102.77(2), As2-As3-As4 103.07(2), As1-Ga-As4 89.870(19).

5.5.4.7. [(Cp'''Ni)(μ,$\eta^{3:1:1}$-P_3)(L^3Ga)] (**7a**)

Compound **7a** crystallizes from a concentrated toluene solution layered with acetonitrile at -30 °C in the monoclinic space group *P2₁/n*. The asymmetric unit contains one molecule of **7a**. The structure in the solid state is shown in Figure S5.28.

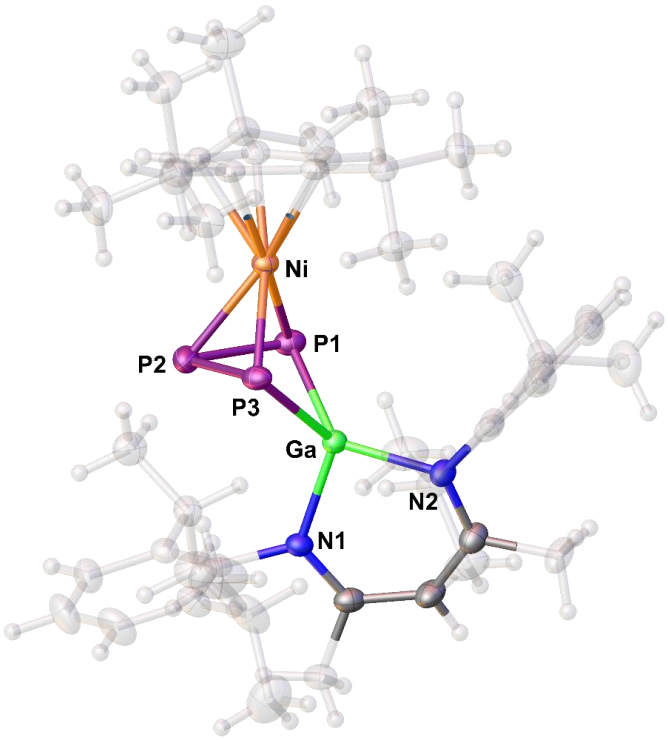


Figure S5.28. Molecular structure of **7a** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å]: P1-P2 2.1818(11), P2-P3 2.1586(11), P1 ⋯ P3 3.0939(9), P1-Ga 2.3295(7), P3-Ga 2.3474(8), P1-Ni 2.2911(8), P2-Ni 2.2134(8), P3-Ni 2.3062(8), Ga-N1 1.987(2), Ga-N2 1.961(2), P1-P2-P3 90.93(4).

5.5.4.8. [(Cp'''Ni)(μ,$\eta^{3:1:1}$-As_3)(L^3Ga)] (**7b**)

Compound **7b** crystallizes from a concentrated toluene solution layered with acetonitrile at -30 °C in the orthorhombic space group *Pbca*. The asymmetric unit contains one molecule of **7b** and toluene. The structure in the solid state is shown in Figure S5.29.

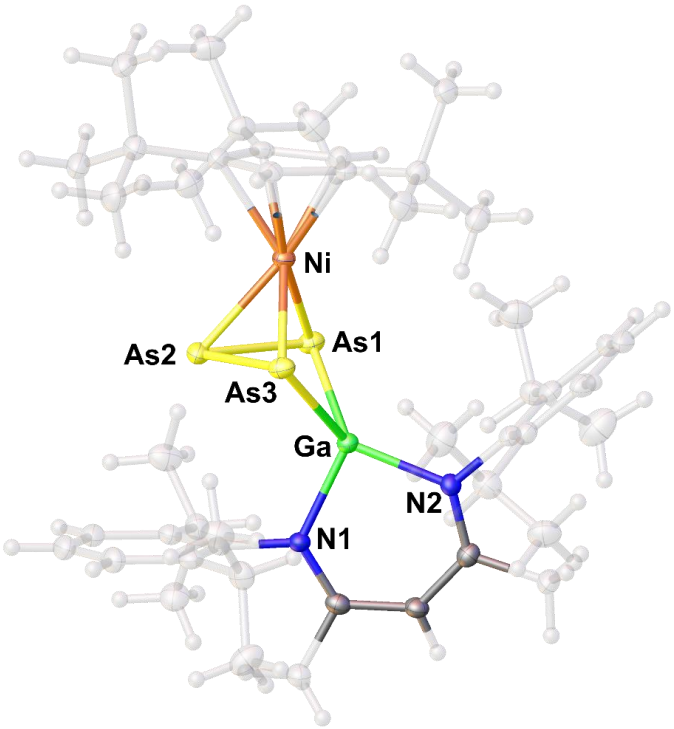


Figure S5.29. Molecular structure of **7b** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Solvent molecule is omitted for clarity. Selected bond lengths [Å]: As1-As2 2.4163(5), As2-As3 2.4059 (4), As1 ⋯ As3 3.2753(6), As1-Ga 2.4311(4), As3-Ga 2.4480(4), As1-Ni 2.3989(5), As2-Ni 2.3241(5), As3-Ni 2.3928(5), Ga-N1 2.000(2), Ga-N2 1.979(2), As1-As2-As3 85.562(14).

5.5.4.9. Crystallographic information

Table S5.3. Crystallographic data and details of diffraction experiments for **3b**, **3c**, **4b** and **4c**.

Compound	**3b** · 0.65 Et_2O	**3c** · 0.8 Et_2O	**4b**	**4c**
Formula	$C_{60.6}H_{88.5}Al_2As_4N_4O_{0.65}$	$C_{61.2}H_{90}Al_2As_{0.83}N_4O_{0.8}P_{3.17}$	$As_4C_{29}GaH_{41}N_2$	$As_{0.92}C_{39}GaH_{56}N_2P_{3.08}$
$D_{calc.}$/ g cm^{-3}	1.290	1.166	1.522	1.404
μ/mm^{-1}	3.013	1.959	5.048	3.393
Formula Weight	1237.09	1108.89	869.96	786.89
Colour	orange	clear orange	yellow	yellow
Shape	plate	plate	block	block
Size/mm^3	0.35×0.18×0.07	0.09×0.08×0.04	0.49×0.32×0.24	0.25×0.20×0.17
T/K	123(1)	123.00(10)	122.9(2)	123.00(10)
Crystal System	orthorhombic	orthorhombic	tetragonal	tetragonal
Flack Parameter	-0.029(9)	-0.040(8)	-0.009(9)	-0.003(8)
Hooft Parameter	-0.002(9)	-0.026(7)	0.002(9)	0.003(7)
Space Group	$P2_12_12_1$	$P2_12_12_1$	$P4_32_12$	$P4_32_12$
a/Å	13.89960(10)	13.89988(12)	20.14280(10)	19.99220(10)
b/Å	14.26410(10)	14.24724(14)	20.14280(10)	19.99220(10)
c/Å	32.1342(3)	31.8996(3)	18.7094(2)	18.62610(10)
α/°	90	90	90	90
β/°	90	90	90	90
γ/°	90	90	90	90
V/Å^3	6371.10(9)	6317.23(10)	7591.01(11)	7444.63(8)
Z	4	4	8	8
Z'	1	1	1	1
Wavelength/Å	1.54184	1.54184	1.54184	1.54184
Radiation type	Cu K$_\alpha$	Cu K$_\alpha$	Cu K$_\alpha$	Cu K$_\alpha$
Θ_{min}/°	3.390	2.770	3.901	3.926
Θ_{max}/°	71.862	73.579	75.421	73.482
Measured Refl's.	22680	37292	37319	32622
Ind't Refl's	12051	12049	7675	7414
Refl's with I > 2(I)	11496	10601	7634	7273
R_{int}	0.0261	0.0389	0.0428	0.0324
Parameters	690	716	335	375
Restraints	0	49	0	12
Largest Peak	0.526	0.543	0.532	0.173
Deepest Hole	-0.271	-0.301	-0.544	-0.158
GooF	1.040	1.061	1.050	1.019
wR_2 (all data)	0.0736	0.1189	0.0635	0.0454
wR_2	0.0719	0.1152	0.0634	0.0451
R_1 (all data)	0.0312	0.0505	0.0246	0.0196
R_1	0.0290	0.0436	0.0244	0.0190

Table S5.4. Crystallographic data and details of diffraction experiments for **5a**, **6b**, **7a** and **7b**.

Compound	**5a**	**6b**	**7a**	**7b** · 1 tol
Formula	$C_{58}H_{82}GaN_4NiP_4$	$C_{46}H_{70}As_4CoGaN_2$	$C_{46}H_{70}GaN_2NiP_3$	$C_{53}H_{78}As_3GaN_2Ni$
$D_{calc.}$/ g cm^{-3}	1.247	1.502	1.249	1.413
μ/mm^{-1}	2.308	6.730	2.425	3.491
Formula Weight	1087.58	1079.37	872.38	1096.36
Colour	clear orange	green	brown	clear orange
Shape	plate-shaped	plate	plate-shaped	plate
Size/mm^3	0.14×0.12×0.04	0.19×0.11×0.03	0.15×0.11×0.04	0.46×0.18×0.06
T/K	123.01(10)	100.01(10)	122.99(10)	100.00(10)
Crystal System	monoclinic	monoclinic	monoclinic	orthorhombic
Space Group	$C2/c$	$P2_1/n$	$P2_1/n$	$Pbca$
a/Å	25.1414(5)	12.2766(3)	13.6409(2)	22.4679(4)
b/Å	13.2693(2)	26.9810(7)	24.3945(4)	18.7909(3)
c/Å	17.4724(3)	14.8138(4)	14.3521(2)	24.4157(4)
α/°	90	90	90	90
β/°	96.234(2)	103.482(2)	103.775(2)	90
γ/°	90	90	90	90
V/Å^3	5794.48(18)	4771.6(2)	4638.48(13)	10308.1(3)
Z	4	4	4	8
Z'	0.5	1	1	1
Wavelength/Å	1.54184	1.54184	1.54184	1.54184
Radiation type	Cu K$_\alpha$	Cu K$_\alpha$	Cu K$_\alpha$	Cu K$_\alpha$
Θ_{min}/°	3.537	3.276	3.624	3.561
Θ_{max}/°	73.288	73.461	73.899	75.384
Measured Refl's.	21770	38782	9680	62074
Indep't Refl's	5580	9043	9680	10433
Refl's I≥2 σ(I)	4759	7117	8557	9053
R_{int}	0.0230	0.0425	.	0.0497
Parameters	456	688	498	561
Restraints	102	202	0	0
Largest Peak	0.296	0.505	0.893	0.654
Deepest Hole	-0.419	-0.631	-0.402	-0.597
GooF	1.072	1.056	1.047	1.070
wR_2 (all data)	0.1040	0.0961	0.1214	0.0882
wR_2	0.1000	0.0903	0.1186	0.0844
R_1 (all data)	0.0493	0.0542	0.0475	0.0472
R_1	0.0407	0.0382	0.0422	0.0380

5.5.5. DFT calculations

The geometry of the molecules has been optimized with Gaussian 09,[19] using the B3LYP functional[20] together with the def2-SVP basis set for all atoms.[21] The Natural Bond Orbital (NBO) analysis has been performed with the NBO6 program.[22] The figures for the supporting information concerning the DFT calculations were created with Chemcraft.[23]

Table S5.5. Total energies for all optimized geometries (B3LYP/def2-SVP level of theory).

	total energy [Ha] B3LYP-def2SVP
P_4	-1365,087187
As_4	-8942,661612
AsP_3	-3259,478111
[L^3Ga] (**2**)	-3163,117881
[$L^3Ga(\eta^{1:1}\text{-}P_4)$] (**4a**)	-4528,227746
[$L^3Ga(\eta^{1:1}\text{-}As_4)$] (**4b**)	-12105,80203
[$L^3Ga(\eta^{1:1}\text{-}AsP_3)$] (**4c1**, Isomer 1)	-6422,619313
[$L^3Ga(\eta^{1:1}\text{-}AsP_3)$] (**4c2**, Isomer 2)	-6422,619195
[$(L^3Ga)_2(P_4)$]	-7.691,355143
[$(L^3Ga)_2(As_4)$]	-15268,93152
[$(L^3Ga)_2(AsP_3)$]	-9585,748073
[L^3Al] (**1**)	-1480,828028
[$L^3Al(P_4)$] (**I-3a**)	-2845,978289
[$L^3Al(As_4)$](**I-3b**)	-10423,54925
[$L^3Al(AsP_3)$] (**I-3c1**, Isomer 1)	-4740,368153
[$L^3Al(AsP_3)$] (**I-3c2**, Isomer 2)	-4740,369903
[$(L^3Al)_2(\mu,\eta^{1:1:1:1}\text{-}P_4)$] (**3a**)	-4326,849138
[$(L^3Al)_2(\mu,\eta^{1:1:1:1}\text{-}As_4)$] (**3b**)	-11904,41336
[$(L^3Al)_2(\mu,\eta^{1:1:1:1}\text{-}AsP_3)$] (**3c**)	-6221,240485
[$(L^3Ga)(\eta^{2:1:1}\text{-}P_4)(L^3Ni)$] (**5a**)	-727533923258

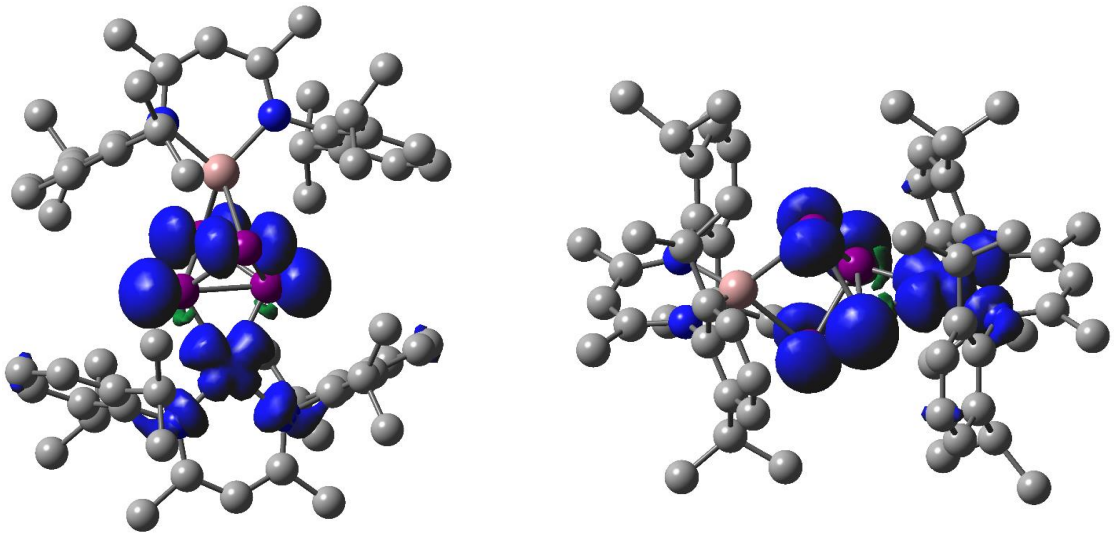
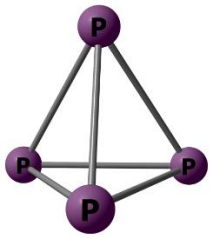
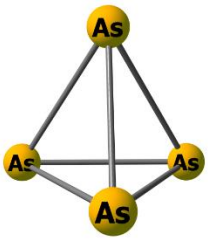


Figure S5.30. Isosurfaces of the calculated spin density in **5a** (two different views) B3LYP/def2-SVP level of theory.

Table S5.6. Optimized geometries of P_4 (left) and As_4 (right). XYZ coordinated in angstroms. BP86/def2-SVP level of theory.

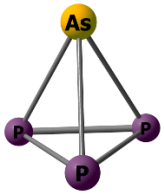


P	1.774510000	3.039595000	4.823887000
P	-0.256548000	3.323675000	3.963479000
P	0.364366000	4.479935000	5.757796000
P	1.263272000	4.932895000	3.777338000



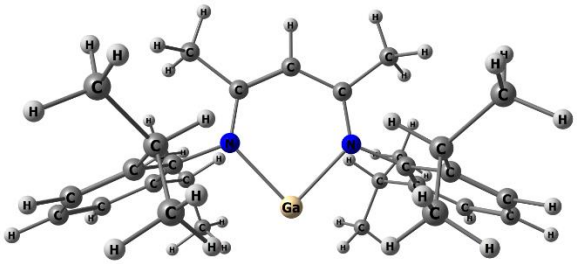
As	1.882073000	2.946629000	4.859868000
As	-0.360804000	3.250359000	3.889766000
As	0.305682000	4.538626000	5.879164000
As	1.318648000	5.040486000	3.693701000

Table S5.7. Optimized geometries of AsP_3. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



As	1.848412000	2.963746000	4.841668000
P	-0.287009000	3.348462000	3.956520000
P	0.339628000	4.506261000	5.755142000
P	1.244569000	4.957631000	3.769170000

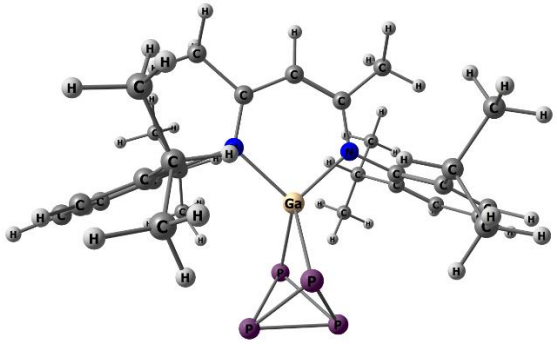
Table S5.8. Optimized geometries of **2**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



Ga	0.000046000	-0.000672000	-0.992426000
N	-1.466621000	0.000046000	0.536401000
N	1.466614000	0.000029000	0.536408000
C	1.271869000	0.000389000	1.857240000
C	2.798649000	0.000036000	0.003790000
C	-1.271891000	0.000226000	1.857227000
C	-2.469605000	0.000193000	2.786747000
H	-3.104939000	0.880373000	2.605510000
H	-2.159716000	0.000281000	3.839506000
H	-3.104815000	-0.880086000	2.605600000
C	3.434474000	-1.232487000	-0.299168000
C	3.434433000	1.232572000	-0.299303000
C	4.705578000	-1.203740000	-0.890811000
H	5.205896000	-2.145168000	-1.131371000
C	-3.434385000	-1.232494000	-0.299353000
C	-3.434517000	1.232566000	-0.299124000
C	2.768082000	-2.580626000	-0.026447000
H	1.849794000	-2.387671000	0.547049000
C	-0.000009000	0.000441000	2.464453000
H	-0.000015000	0.000582000	3.553582000
C	-2.767955000	-2.580633000	-0.026773000
H	-1.849525000	-2.387704000	0.546512000
C	-2.798651000	0.000031000	0.003792000
C	2.469586000	0.000829000	2.786750000
H	2.159708000	0.000245000	3.839513000
C	2.767908000	2.580705000	-0.026890000
H	1.849841000	2.387854000	0.546999000
C	-2.768024000	2.580683000	-0.026612000
H	-1.850053000	2.387836000	0.547423000
C	-2.347101000	-3.268031000	-1.339134000
H	-3.222126000	-3.493551000	-1.970772000
H	-1.826690000	-4.218290000	-1.133751000
H	-1.670068000	-2.627585000	-1.926117000
C	3.646560000	-3.513878000	0.825244000
H	3.096615000	-4.435133000	1.078088000
H	3.954290000	-3.035511000	1.768656000
H	4.562784000	-3.816429000	0.292551000
C	2.346136000	3.267353000	-1.339361000
H	1.825576000	4.217573000	-1.134170000
H	1.668962000	2.626441000	-1.925672000
H	3.220766000	3.492770000	-1.971583000
C	2.346874000	-3.267989000	-1.338714000
H	3.221735000	-3.493628000	-1.970537000
H	1.669787000	-2.627486000	-1.925569000
H	1.826404000	-4.218189000	-1.133201000
C	-4.705507000	-1.203738000	-0.890965000
H	-5.205777000	-2.145159000	-1.131660000
C	-5.342772000	0.000021000	-1.184025000
H	-6.333361000	0.000012000	-1.646031000
C	-2.346064000	3.267274000	-1.339060000

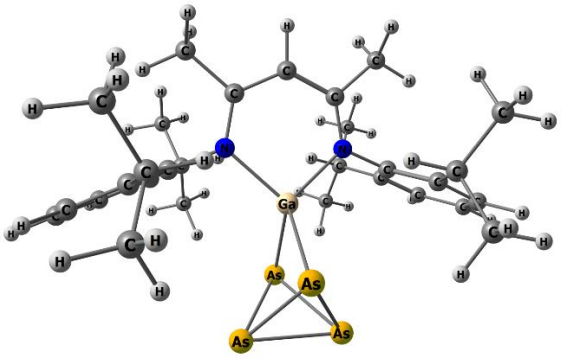
H	3.104209000	0.881604000	2.605888000	H	-1.668735000	2.626385000	-1.925220000
H	3.105486000	-0.878861000	2.605215000	H	-1.825627000	4.217557000	-1.133857000
C	4.705544000	1.203803000	-0.890901000	H	-3.220613000	3.492546000	-1.971446000
H	5.205863000	2.145210000	-1.131540000	C	3.646461000	3.514535000	0.824068000
C	5.342751000	0.000021000	-1.184075000	H	4.562382000	3.817177000	0.290910000
H	6.333326000	0.000026000	-1.646108000	H	3.954700000	3.036620000	1.767543000
C	-4.705639000	1.203806000	-0.890692000	H	3.096334000	4.435721000	1.076763000
H	-5.206019000	2.145224000	-1.131166000	C	-3.646691000	3.514583000	0.824150000
C	-3.646251000	-3.513824000	0.825178000	H	-4.562534000	3.817198000	0.290833000
H	-3.953693000	-3.035385000	1.768646000	H	-3.096595000	4.435792000	1.076828000
H	-3.096264000	-4.435081000	1.077925000	H	-3.955075000	3.036767000	1.767628000
H	-4.562636000	-3.816360000	0.292756000				

Table S5.9. Optimized geometries of **4a**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



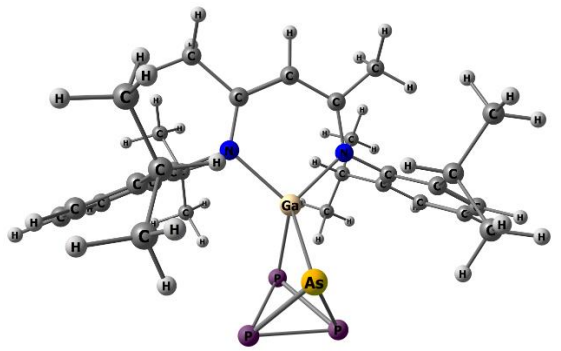
Ga	0.000052000	-0.170791000	-0.281874000	H	1.714233000	2.578947000	0.330638000
P	0.000012000	-2.258499000	-1.455844000	C	2.597898000	3.339923000	-1.464850000
P	1.094427000	-1.115496000	-3.089450000	H	3.582510000	3.559918000	-1.908551000
P	-1.094978000	-1.115715000	-3.089165000	H	2.043197000	4.290989000	-1.410800000
P	-0.000428000	0.782235000	-2.475291000	H	2.057092000	2.674865000	-2.154769000
N	1.493139000	0.239239000	0.996210000	C	3.458739000	3.697862000	0.883127000
N	-1.493069000	0.239402000	0.996282000	H	3.559187000	3.291032000	1.900443000
C	1.276147000	0.559534000	2.275540000	H	2.909822000	4.651445000	0.950905000
C	0.000097000	0.669603000	2.860266000	H	4.473684000	3.925177000	0.517978000
H	0.000109000	0.928049000	3.919659000	C	-2.830745000	0.183069000	0.455754000
C	-1.276020000	0.559528000	2.275604000	C	-3.524339000	-1.056204000	0.438186000
C	2.434758000	0.869165000	3.203587000	C	-4.807185000	-1.090857000	-0.127386000
H	3.407586000	0.590589000	2.785626000	H	-5.358061000	-2.033533000	-0.145244000
H	2.293214000	0.351508000	4.163549000	C	-5.394822000	0.050708000	-0.667676000
H	2.451091000	1.949344000	3.420105000	H	-6.394276000	-0.001337000	-1.106864000
C	-2.434502000	0.868671000	3.203991000	C	-4.702174000	1.258032000	-0.644246000
H	-2.448861000	1.948213000	3.423746000	H	-5.169600000	2.150721000	-1.066323000
H	-2.294286000	0.347905000	4.162487000	C	-3.417822000	1.354893000	-0.088574000
H	-3.407652000	0.593002000	2.784875000	C	-2.949878000	-2.331832000	1.056325000
C	2.830863000	0.182824000	0.455784000	H	-1.872372000	-2.170545000	1.208658000
C	3.524252000	-1.056574000	0.438198000	C	-3.102925000	-3.561951000	0.145916000
C	4.807172000	-1.091407000	-0.127186000	H	-4.157586000	-3.860835000	0.032595000
H	5.357883000	-2.034177000	-0.145053000	H	-2.566942000	-4.421722000	0.578836000
C	5.395073000	0.050100000	-0.667317000	H	-2.688955000	-3.380154000	-0.856365000
H	6.394573000	-0.002081000	-1.106384000	C	-3.571993000	-2.616187000	2.437990000
C	4.702625000	1.257534000	-0.643890000	H	-3.425764000	-1.782417000	3.139989000
H	5.170236000	2.150160000	-1.065904000	H	-3.122095000	-3.517026000	2.886683000
C	3.418226000	1.354590000	-0.088348000	H	-4.657281000	-2.791406000	2.352244000
C	2.949423000	-2.332173000	1.056062000	C	-2.731329000	2.721062000	-0.062229000
H	1.871862000	-2.170796000	1.207904000	H	-1.713495000	2.578835000	0.330212000
C	3.102807000	-3.562253000	0.145657000	C	-2.597747000	3.340777000	-1.464542000
H	2.689413000	-3.380329000	-0.856840000	H	-2.057355000	2.675913000	-2.154974000
H	2.566458000	-4.421972000	0.578219000	H	-2.042800000	4.291685000	-1.410240000
H	4.157490000	-3.861282000	0.032900000	H	-3.582467000	3.561248000	-1.907762000
C	3.570835000	-2.616640000	2.438010000	C	-3.457621000	3.697655000	0.884002000
H	4.656204000	-2.791657000	2.352847000	H	-4.472783000	3.925072000	0.519518000
H	3.120846000	-3.517632000	2.886303000	H	-2.908691000	4.651226000	0.951887000
H	3.424033000	-1.783038000	3.140091000	H	-3.557454000	3.290364000	1.901191000
C	2.731929000	2.720861000	-0.062276000				

Table S5.10. Optimized geometries of **4b**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



As	-0.000555000	-2.350362000	0.885466000	H	-3.639884000	-0.469909000	4.545202000
As	0.000162000	-0.664887000	-2.165120000	H	-5.069504000	-0.155986000	3.533690000
Ga	0.000216000	0.053487000	0.218084000	C	2.413285000	2.606993000	-1.555443000
As	-1.213549000	-2.677079000	-1.287828000	H	1.395436000	2.566150000	-1.139810000
As	1.212497000	-2.677869000	-1.287717000	C	-2.412981000	2.607202000	-1.555432000
N	-1.497229000	1.238957000	0.888420000	H	-1.395171000	2.566543000	-1.139688000
N	1.497627000	1.238801000	0.888356000	C	-3.484667000	-2.150421000	2.383715000
C	1.276106000	2.250802000	1.732174000	H	-4.557668000	-2.401312000	2.360090000
C	2.824413000	0.957414000	0.395672000	H	-3.063467000	-2.607832000	3.293309000
C	-1.275562000	2.251055000	1.732042000	H	-3.005494000	-2.625664000	1.515993000
C	-2.424759000	3.075488000	2.282890000	C	3.981097000	-0.004355000	3.605853000
H	-3.404199000	2.751400000	1.917108000	H	3.641030000	-0.471063000	4.544871000
H	-2.282617000	4.134441000	2.018803000	H	3.804833000	1.077776000	3.684271000
H	-2.420546000	3.018092000	3.382515000	H	5.070526000	-0.157729000	3.533020000
C	3.661727000	0.041728000	1.086196000	C	2.303654000	2.307528000	-3.060247000
C	3.262179000	1.581693000	-0.802291000	H	1.607828000	3.016056000	-3.538546000
C	4.934746000	-0.221597000	0.558473000	H	1.929308000	1.289802000	-3.248743000
H	5.594398000	-0.918673000	1.079966000	H	3.274035000	2.410784000	-3.572389000
C	-3.661422000	0.042127000	1.086416000	C	3.484213000	-2.151006000	2.382985000
C	-3.261897000	1.582057000	-0.802099000	H	4.557067000	-2.402469000	2.358673000
C	3.254309000	-0.629815000	2.398413000	H	3.004296000	-2.625766000	1.515411000
H	2.175779000	-0.461252000	2.536830000	H	3.063276000	-2.608420000	3.292701000
C	0.000306000	2.659827000	2.165262000	C	-4.934505000	-0.221075000	0.558820000
H	0.000355000	3.488149000	2.875138000	H	-5.594177000	-0.918090000	1.080363000
C	-3.253927000	-0.629351000	2.398648000	C	-5.377330000	0.386456000	-0.613459000
H	-2.175260000	-0.461328000	2.536638000	H	-6.372969000	0.163911000	-1.005574000
C	-2.824071000	0.957739000	0.395797000	C	-2.303222000	2.307266000	-3.060138000
C	2.425477000	3.074782000	2.283336000	H	-1.928636000	1.289564000	-3.248304000
H	2.421440000	3.016701000	3.382926000	H	-1.607552000	3.015797000	-3.538663000
H	2.283444000	4.133917000	2.019921000	H	-3.273627000	2.410111000	-3.572322000
H	3.404814000	2.750802000	1.917187000	C	2.941919000	4.038072000	-1.334413000
C	4.544037000	1.278389000	-1.283158000	H	3.955538000	4.154313000	-1.752564000
H	4.897251000	1.754826000	-2.200449000	H	2.994413000	4.297390000	-0.266824000
C	5.377503000	0.385870000	-0.613850000	H	2.289360000	4.774981000	-1.830957000
H	6.373076000	0.163218000	-1.006076000	C	-2.941731000	4.038313000	-1.334894000
C	-4.543850000	1.278893000	-1.282834000	H	-3.955263000	4.154426000	-1.753290000
H	-4.897104000	1.755390000	-2.200081000	H	-2.289094000	4.775116000	-1.831491000
C	-3.979967000	-0.003209000	3.606184000	H	-2.994460000	4.297891000	-0.267378000
H	-3.803079000	1.078837000	3.684331000				

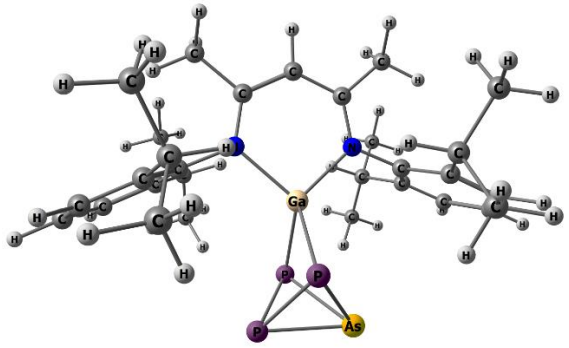
Table S5.11. Optimized geometries of **4c1**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



Ga	-0.000117000	-0.223945000	-0.122658000	H	3.577704000	-0.828936000	3.437968000
P	0.001695000	0.082429000	-2.493397000	C	2.277258000	3.122221000	-2.140629000
As	-0.000886000	-2.661544000	-0.648252000	H	3.233820000	3.343916000	-2.640926000
P	1.099533000	-1.898374000	-2.637736000	H	1.622737000	3.997853000	-2.282476000

N	-1.494404000	0.562957000	0.974155000	H	1.814313000	2.268471000	-2.658297000
N	1.494199000	0.562723000	0.974518000	C	-4.575921000	1.479835000	-0.943742000
C	3.291813000	1.574130000	-0.387308000	H	-4.953404000	2.299695000	-1.559503000
C	2.822195000	0.499387000	0.411952000	C	-4.905214000	-0.685085000	0.056569000
C	-1.275434000	1.142785000	2.158290000	H	-5.541296000	-1.557004000	0.222613000
C	4.904407000	-0.686560000	0.056569000	C	3.445187000	-3.187741000	0.860387000
H	5.539989000	-1.558927000	0.222141000	H	3.040669000	-3.243202000	-0.160494000
C	1.275105000	1.142535000	2.158594000	H	2.975350000	-3.988216000	1.453925000
C	2.427039000	1.685655000	2.982984000	H	4.523386000	-3.410711000	0.811835000
H	3.409395000	1.407116000	2.588424000	C	-2.471257000	2.839537000	-0.642363000
H	2.341145000	1.327724000	4.019914000	H	-1.473101000	2.684267000	-0.207222000
H	2.368538000	2.785026000	3.018374000	C	3.095428000	4.064065000	0.058721000
C	3.172077000	-1.819130000	1.507584000	H	3.225956000	3.899907000	1.138914000
H	2.083223000	-1.729319000	1.637817000	H	2.457919000	4.953351000	-0.075340000
C	4.576409000	1.479118000	-0.942533000	H	4.086995000	4.300256000	-0.360910000
H	4.954384000	2.299112000	-1.557812000	C	-5.380712000	0.365010000	-0.725512000
C	-2.427427000	1.686232000	2.982395000	H	-6.378962000	0.312497000	-1.167410000
H	-3.409766000	1.407897000	2.587682000	C	-3.446522000	-3.186647000	0.860648000
H	-2.368651000	2.785596000	3.017694000	H	-4.524736000	-3.409430000	0.811598000
H	-2.341799000	1.328407000	4.019387000	H	-2.977085000	-3.987197000	1.454404000
C	3.626907000	-0.649222000	0.634362000	H	-3.041565000	-3.242203000	-0.160055000
C	-0.000227000	1.337526000	2.723067000	C	-3.812551000	-1.763541000	2.909884000
H	-0.000302000	1.802379000	3.709770000	H	-3.580136000	-0.827722000	3.438085000
C	-3.627685000	-0.648189000	0.634338000	H	-3.451349000	-2.599227000	3.531480000
C	-3.173511000	-1.818051000	1.507958000	H	-4.910308000	-1.844921000	2.845121000
H	-2.084716000	-1.728407000	1.638774000	C	-2.275977000	3.121190000	-2.142576000
C	-2.822341000	0.499863000	0.411394000	H	-1.813575000	2.266965000	-2.659947000
C	2.472534000	2.839876000	-0.640540000	H	-1.620921000	3.996355000	-2.284824000
H	1.474334000	2.685069000	-0.205314000	H	-3.232440000	3.343298000	-2.642875000
C	-3.291300000	1.574410000	-0.388523000	C	-3.093290000	4.064348000	0.056575000
C	5.380521000	0.363686000	-0.724944000	H	-4.084783000	4.300984000	-0.362982000
H	6.378731000	0.310814000	-1.166891000	H	-2.455260000	4.953204000	-0.077856000
C	3.810335000	-1.764759000	2.909873000	H	-3.223751000	3.900601000	1.136840000
H	4.908121000	-1.846233000	2.845720000	P	-1.097913000	-1.897394000	-2.639230000
H	3.448696000	-2.600431000	3.531237000				

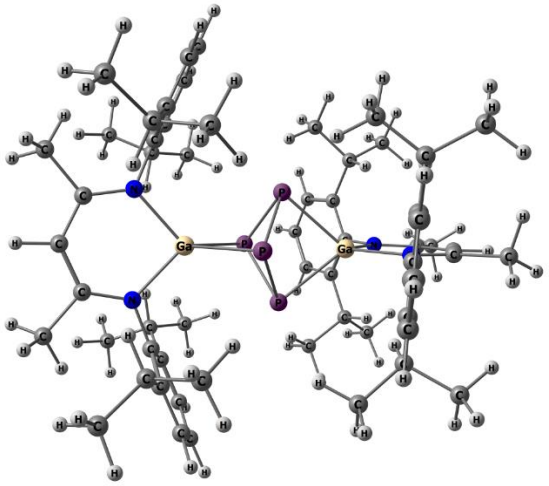
Table S5.12. Optimized geometries of **4c2**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory



Ga	-0.060331000	-0.156641000	-0.076330000	H	3.554577000	2.998059000	-2.715385000
P	-0.039009000	0.068818000	-2.457393000	H	1.933780000	3.711989000	-2.608772000
N	-1.623334000	0.591813000	0.948814000	H	2.113945000	1.951860000	-2.789276000
N	1.364252000	0.708647000	1.047994000	C	-4.766939000	0.954113000	-1.052507000
C	3.297461000	1.461440000	-0.297649000	H	-5.224424000	1.653699000	-1.755847000
C	2.726980000	0.528774000	0.607336000	C	-4.872464000	-1.107344000	0.186545000
C	-1.470096000	1.309997000	2.064705000	H	-5.413296000	-2.018366000	0.451416000
C	4.774334000	-0.765732000	0.580225000	C	3.104644000	-3.069666000	1.610356000
H	5.358642000	-1.625298000	0.915803000	H	2.693547000	-3.248149000	0.606322000
C	1.079510000	1.415209000	2.146489000	H	2.592105000	-3.751742000	2.307608000
C	2.184202000	2.048132000	2.971783000	H	4.169472000	-3.353720000	1.601393000
H	3.188171000	1.773737000	2.632635000	C	-2.829020000	2.564361000	-0.903079000
H	2.071550000	1.757708000	4.027147000	H	-1.807037000	2.547998000	-0.496061000
H	2.090113000	3.144655000	2.930315000	C	3.141691000	3.986404000	-0.136157000
C	2.904822000	-1.610827000	2.055536000	H	3.138465000	3.936341000	0.962748000
H	1.820949000	-1.438724000	2.132197000	H	2.559939000	4.872979000	-0.437517000
C	4.611751000	1.243536000	-0.736638000	H	4.184342000	4.147817000	-0.455934000
H	5.068219000	1.953775000	-1.429914000	C	-5.448763000	-0.210418000	-0.709717000
C	-2.673528000	1.837085000	2.823505000	H	-6.430010000	-0.420623000	-1.142749000
H	-3.628123000	1.500764000	2.406470000	C	-3.140024000	-3.324501000	1.273611000
H	-2.658543000	2.938097000	2.819277000	H	-4.183356000	-3.673794000	1.209609000
H	-2.612836000	1.521238000	3.876050000	H	-2.615755000	-3.993118000	1.975015000
C	3.463774000	-0.600987000	1.051906000	H	-2.675959000	-3.448371000	0.284447000
C	-0.223511000	1.655167000	2.621466000	C	-3.739359000	-1.731999000	3.137756000
H	-0.277046000	2.239100000	3.541201000	H	-3.645611000	-0.716675000	3.549484000
C	-3.613696000	-0.866613000	0.756345000	H	-3.296626000	-2.433064000	3.864210000
C	-3.051794000	-1.869532000	1.764800000	H	-4.815313000	-1.961595000	3.064086000
H	-1.985700000	-1.637056000	1.905613000	C	-2.710396000	2.741138000	-2.426892000

C	-2.933437000	0.328540000	0.402525000	H	-2.180159000	1.897909000	-2.894094000
C	2.557269000	2.711193000	-0.775457000	H	-2.150142000	3.661208000	-2.660473000
H	1.511298000	2.626607000	-0.445100000	H	-3.698683000	2.830447000	-2.906290000
C	-3.506116000	1.249600000	-0.513554000	C	-3.554538000	3.774799000	-0.282568000
C	5.348087000	0.142885000	-0.306075000	H	-4.578638000	3.869076000	-0.679728000
H	6.370655000	-0.007476000	-0.661531000	H	-3.019405000	4.709551000	-0.517443000
C	3.506456000	-1.400682000	3.459449000	H	-3.632160000	3.694544000	0.811706000
H	4.595453000	-1.573259000	3.451515000	P	-0.988816000	-2.006581000	-2.456121000
H	3.061696000	-2.106288000	4.180212000	P	0.038528000	-2.514705000	-0.481572000
H	3.336202000	-0.381943000	3.836634000	As	1.314598000	-1.910185000	-2.419022000
C	2.542237000	2.843581000	-2.308113000				

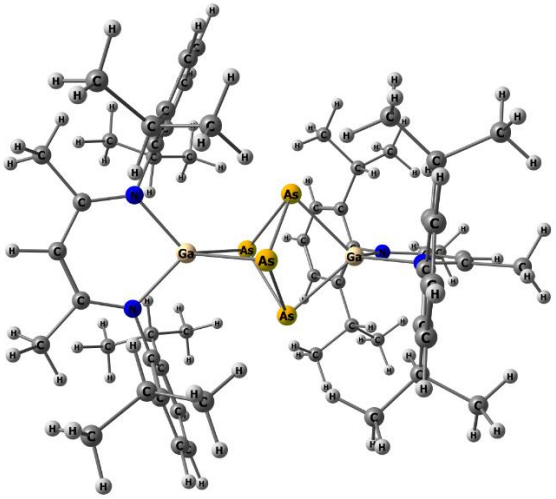
Table S5.13. Optimized geometries of $[(L^3Ga)_2(P_4)]$. XYZ coordinated in angstroms. BP86/def2-SVP level of theory



Ga	-2.274977000	0.033126000	-0.031683000	H	-1.128228000	-3.933938000	0.630513000
Ga	2.276310000	-0.003310000	-0.001107000	C	-4.510403000	-4.537216000	-0.012982000
P	0.390694000	1.087267000	1.089333000	H	-5.358857000	-3.983166000	-0.440963000
P	-0.369676000	1.113352000	-1.095145000	H	-4.767859000	-4.794212000	1.027794000
P	-0.410551000	-1.080723000	1.063897000	H	-4.411608000	-5.480060000	-0.576478000
P	0.388182000	-1.069865000	-1.107551000	C	4.976269000	0.896130000	-0.865755000
N	-3.642795000	1.098431000	1.015603000	C	5.560923000	-0.033541000	0.013051000
N	-3.646969000	-1.011782000	-1.093357000	H	6.650362000	-0.045114000	0.017882000
N	3.659166000	1.078879000	-1.008182000	C	4.951724000	-0.952557000	0.888861000
N	3.632225000	-1.109328000	1.020252000	C	5.948176000	1.689979000	-1.715709000
C	-4.959368000	0.994406000	0.815375000	H	6.098764000	1.173451000	-2.677354000
C	-5.556940000	0.116930000	-0.108419000	H	6.925500000	1.761644000	-1.220520000
H	-6.645422000	0.158531000	-0.147556000	H	5.583598000	2.697731000	-1.946135000
C	-4.963133000	-0.807245000	-0.987683000	C	5.912185000	-1.763202000	1.737692000
C	-5.926927000	1.874897000	1.582831000	H	5.461530000	-2.675758000	2.142371000
H	-6.835573000	1.310300000	1.834637000	H	6.249257000	-1.149761000	2.589436000
H	-6.234974000	2.720078000	0.945836000	H	6.805424000	-2.027410000	1.154563000
H	-5.493458000	2.289034000	2.499567000	C	3.165807000	2.092210000	-1.908917000
C	-5.933597000	-1.569893000	-1.869253000	C	2.871119000	3.383169000	-1.395333000
H	-6.227543000	-0.935180000	-2.721241000	C	2.365041000	4.348484000	-2.276592000
H	-6.849237000	-1.807266000	-1.309894000	H	2.137122000	5.348442000	-1.901146000
H	-5.508044000	-2.494271000	-2.274490000	C	2.144385000	4.059027000	-3.621435000
C	-3.119900000	2.008587000	2.004452000	H	1.742358000	4.825280000	-4.289338000
C	-2.871141000	3.361569000	1.661863000	C	2.440161000	2.789838000	-4.110200000
C	-2.304185000	4.198104000	2.634401000	H	2.268310000	2.570596000	-5.166921000
H	-2.101673000	5.243171000	2.387172000	C	2.955946000	1.786176000	-3.277199000
C	-1.998153000	3.727833000	3.908320000	C	3.131763000	3.764434000	0.063201000
H	-1.554501000	4.397742000	4.649414000	H	3.267987000	2.831531000	0.629448000
C	-2.265439000	2.400255000	4.236062000	C	1.955017000	4.513323000	0.708557000
H	-2.033977000	2.041171000	5.241132000	H	1.800865000	5.507412000	0.257783000
C	-2.824148000	1.516578000	3.302789000	H	2.149204000	4.668548000	1.781989000
C	-3.231500000	3.956311000	0.299541000	H	1.018058000	3.945940000	0.620117000
H	-3.671408000	3.155342000	-0.312777000	C	4.428275000	4.585579000	0.210606000
C	-2.001425000	4.480975000	-0.460262000	H	5.309138000	4.045691000	-0.167159000
H	-2.301592000	4.887270000	-1.440255000	H	4.614009000	4.827500000	1.270102000
H	-1.265376000	3.684984000	-0.643899000	H	4.358685000	5.537092000	-0.342672000
H	-1.497712000	5.289553000	0.094081000	C	3.289398000	0.424795000	-3.889271000
C	-4.287776000	5.071440000	0.432817000	H	3.709536000	-0.208565000	-3.093866000
H	-5.179390000	4.733225000	0.982188000	C	2.041074000	-0.293624000	-4.430551000
H	-4.611588000	5.417640000	-0.562458000	H	1.292191000	-0.462180000	-3.643726000
H	-3.883476000	5.945153000	0.969636000	H	2.314798000	-1.277843000	-4.845264000
C	-3.156203000	0.084932000	3.727180000	H	1.561159000	0.285636000	-5.236207000
H	-3.318702000	-0.501916000	2.811236000	C	4.351362000	0.542843000	-5.000459000
C	-2.022167000	-0.600498000	4.505147000	H	3.961689000	1.094242000	-5.871641000
H	-1.079300000	-0.592333000	3.940523000	H	4.653879000	-0.456845000	-5.352865000

H	-2.282830000	-1.653166000	4.700663000	H	5.254918000	1.070142000	-4.658143000
H	-1.843663000	-0.123104000	5.482523000	C	3.099165000	-2.105352000	1.916902000
C	-4.464352000	0.035859000	4.542199000	C	2.860347000	-1.779143000	3.275313000
H	-4.365960000	0.608135000	5.479794000	C	2.292506000	-2.758694000	4.102786000
H	-4.716055000	-1.003922000	4.808781000	H	2.099104000	-2.524394000	5.152537000
H	-5.316234000	0.454834000	3.986598000	C	1.973328000	-4.023543000	3.616913000
C	-3.131996000	-2.012387000	-1.995443000	H	1.529466000	-4.770865000	4.279717000
C	-2.871544000	-1.680730000	-3.348853000	C	2.227122000	-4.334165000	2.282572000
C	-2.320391000	-2.667525000	-4.179116000	H	1.984041000	-5.331966000	1.910803000
H	-2.109642000	-2.428968000	-5.224569000	C	2.787276000	-3.393253000	1.407575000
C	-2.038482000	-3.944273000	-3.701717000	C	3.232621000	-0.426116000	3.883094000
H	-1.606640000	-4.696667000	-4.366735000	H	3.654776000	0.198191000	3.081753000
C	-2.314429000	-4.260312000	-2.372994000	C	2.013092000	0.323839000	4.445368000
H	-2.101690000	-5.267520000	-2.008149000	H	1.258111000	0.513486000	3.668826000
C	-2.859657000	-3.312978000	-1.495597000	H	2.319924000	1.300159000	4.855376000
C	-3.200625000	-0.313423000	-3.949730000	H	1.529943000	-0.240788000	5.259349000
H	-3.628351000	0.311579000	-3.151940000	C	4.313011000	-0.575709000	4.972632000
C	-1.951966000	0.415507000	-4.474747000	H	4.640739000	0.414120000	5.330552000
H	-1.458875000	-0.154528000	-5.279011000	H	5.198988000	-1.114990000	4.604657000
H	-1.213592000	0.585432000	-3.678128000	H	3.929062000	-1.130894000	5.844124000
H	-2.228670000	1.400111000	-4.886506000	C	3.095628000	-3.800325000	-0.034445000
C	-4.257246000	-0.427286000	-5.066622000	H	3.289971000	-2.879962000	-0.604538000
H	-3.863916000	-0.978544000	-5.936381000	C	1.925100000	-4.517926000	-0.724780000
H	-4.556233000	0.573576000	-5.418992000	H	1.704822000	-5.491934000	-0.258285000
H	-5.162753000	-0.953045000	-4.727660000	H	2.170904000	-4.710664000	-1.781535000
C	-3.200340000	-3.725368000	-0.062380000	H	1.009208000	-3.910386000	-0.704478000
H	-3.363467000	-2.804738000	0.516783000	C	4.369036000	-4.666785000	-0.108882000
C	-2.070391000	-4.500187000	0.633505000	H	5.245006000	-4.155805000	0.317410000
H	-1.887353000	-5.478689000	0.160286000	H	4.604539000	-4.920380000	-1.155655000
H	-2.337621000	-4.692536000	1.685130000	H	4.235446000	-5.612143000	0.443053000

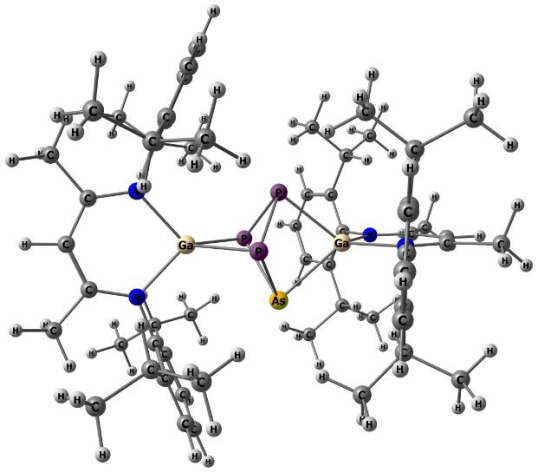
Table S5.14. Optimized geometries of [(L^3Ga)$_2$(As_4)]. XYZ coordinated in angstroms. BP86/def2-SVP level of theory



Ga	-2.341488000	-0.045501000	0.044056000	H	-1.199150000	4.059151000	-0.526558000
Ga	2.342153000	0.008272000	-0.007293000	C	-4.630098000	4.475462000	-0.007670000
As	0.464532000	-1.198271000	-1.177885000	H	-5.465102000	3.878232000	0.386110000
As	-0.436663000	-1.218931000	1.208624000	H	-4.864616000	4.730756000	-1.054284000
As	-0.488621000	1.166143000	-1.156594000	H	-4.594603000	5.416114000	0.567032000
As	0.463774000	1.165791000	1.209799000	C	5.061378000	-0.868177000	0.847447000
N	-3.718005000	-1.115446000	-1.012940000	C	5.628639000	0.052958000	-0.052042000
N	-3.723955000	1.009160000	1.106971000	H	6.719171000	0.067627000	-0.067487000
N	3.749714000	-1.053192000	1.016777000	C	5.011947000	0.959213000	-0.934018000
N	3.691574000	1.108569000	-1.066877000	C	6.074204000	-1.657342000	1.658929000
C	-5.033149000	-1.002661000	-0.812030000	H	6.613591000	-0.972144000	2.331723000
C	-5.627688000	-0.124529000	0.113315000	H	6.824422000	-2.101574000	0.987967000
H	-6.716728000	-0.165091000	0.149711000	H	5.622989000	-2.450321000	2.263460000
C	-5.038720000	0.801898000	0.993072000	C	5.979442000	1.777675000	-1.771154000
C	-6.018234000	-1.860607000	-1.586522000	H	5.488121000	2.552368000	-2.368198000
H	-6.830042000	-1.232739000	-1.982085000	H	6.526373000	1.107809000	-2.453200000
H	-6.481610000	-2.588989000	-0.902130000	H	6.728904000	2.250173000	-1.118840000
H	-5.557604000	-2.411254000	-2.412959000	C	3.266966000	-2.034030000	1.957127000
C	-6.022899000	1.564241000	1.861743000	C	3.002629000	-3.355793000	1.510112000
H	-6.375343000	0.906650000	2.672815000	C	2.519188000	-4.287809000	2.439309000
H	-6.905464000	1.849105000	1.271617000	H	2.317155000	-5.310852000	2.114425000
H	-5.591501000	2.460956000	2.318880000	C	2.292055000	-3.938045000	3.768283000
C	-3.206674000	-2.027652000	-2.006039000	H	1.911520000	-4.680411000	4.474597000
C	-2.949977000	-3.379670000	-1.661284000	C	2.553145000	-2.637894000	4.191753000
C	-2.427303000	-4.229173000	-2.647553000	H	2.377248000	-2.371229000	5.236680000
H	-2.225114000	-5.274165000	-2.400189000	C	3.041031000	-1.664009000	3.308147000

C	-2.163232000	-3.771952000	-3.935438000	C	3.282398000	-3.809614000	0.076493000
H	-1.754033000	-4.451896000	-4.687124000	H	3.417439000	-2.906365000	-0.536408000
C	-2.424706000	-2.443079000	-4.261574000	C	2.122542000	-4.607363000	-0.541247000
H	-2.221625000	-2.092401000	-5.275688000	H	1.976694000	-5.578229000	-0.040146000
C	-2.943873000	-1.547375000	-3.316387000	H	2.331174000	-4.817667000	-1.602592000
C	-3.260122000	-3.961303000	-0.281068000	H	1.174345000	-4.053075000	-0.492106000
H	-3.587664000	-3.135172000	0.366956000	C	4.587264000	-4.626581000	-0.009498000
C	-2.026056000	-4.597139000	0.380588000	H	5.453640000	-4.067959000	0.372775000
H	-2.274220000	-4.950058000	1.394857000	H	4.800882000	-4.906349000	-1.054337000
H	-1.199363000	-3.877882000	0.471007000	H	4.508912000	-5.557463000	0.576647000
H	-1.660106000	-5.465457000	-0.190968000	C	3.354097000	-0.268468000	3.850700000
C	-4.410235000	-4.986251000	-0.344638000	H	3.608997000	0.374716000	2.995464000
H	-5.316073000	-4.565333000	-0.804934000	C	2.151322000	0.374847000	4.560791000
H	-4.673961000	-5.334472000	0.667612000	H	1.271179000	0.424976000	3.903934000
H	-4.122297000	-5.871979000	-0.934512000	H	2.396513000	1.403945000	4.870040000
C	-3.267350000	-0.114287000	-3.741953000	H	1.866596000	-0.182006000	5.468369000
H	-3.389646000	0.481777000	-2.825707000	C	4.572441000	-0.292037000	4.795196000
C	-2.147858000	0.543763000	-4.564387000	H	4.363482000	-0.890977000	5.696902000
H	-1.180457000	0.504402000	-4.043280000	H	4.826211000	0.728702000	5.125598000
H	-2.385864000	1.604499000	-4.744105000	H	5.462212000	-0.722992000	4.313599000
H	-2.025144000	0.067202000	-5.550685000	C	3.154065000	2.077070000	-1.990272000
C	-4.598807000	-0.046978000	-4.516646000	C	2.901336000	1.703937000	-3.335728000
H	-4.538267000	-0.623787000	-5.454703000	C	2.350920000	2.661831000	-4.199680000
H	-4.841625000	0.995835000	-4.779646000	H	2.152732000	2.392155000	-5.239798000
H	-5.439433000	-0.450614000	-3.934275000	C	2.055063000	3.950071000	-3.762824000
C	-3.221322000	2.012932000	2.012111000	H	1.624362000	4.679682000	-4.453444000
C	-2.967234000	1.685585000	3.368842000	C	2.314611000	4.304814000	-2.441182000
C	-2.452848000	2.684767000	4.208625000	H	2.089108000	5.319829000	-2.106724000
H	-2.251710000	2.450108000	5.256788000	C	2.861920000	3.388757000	-1.531716000
C	-2.195377000	3.968850000	3.737918000	C	3.254349000	0.324950000	-3.896066000
H	-1.793496000	4.730889000	4.410668000	H	3.565154000	-0.310896000	-3.054103000
C	-2.454419000	4.278276000	2.404361000	C	2.057388000	-0.365923000	-4.570091000
H	-2.256876000	5.289741000	2.043101000	H	1.206909000	-0.466953000	-3.880624000
C	-2.964524000	3.319841000	1.517812000	H	2.338711000	-1.378067000	-4.903553000
C	-3.266206000	0.309715000	3.966316000	H	1.712426000	0.188791000	-5.457693000
H	-3.613054000	-0.343533000	3.152083000	C	4.439151000	0.404343000	-4.879692000
C	-2.017832000	-0.347589000	4.579375000	H	4.729035000	-0.603991000	-5.218394000
H	-1.631356000	0.234242000	5.431864000	H	5.323100000	0.876620000	-4.426923000
H	-1.207479000	-0.446978000	3.843089000	H	4.174059000	0.991451000	-5.774424000
H	-2.258813000	-1.357391000	4.949808000	C	3.183522000	3.854401000	-0.110485000
C	-4.390959000	0.380725000	5.018511000	H	3.378864000	2.958081000	0.496395000
H	-4.077708000	0.967149000	5.897836000	C	2.023078000	4.611023000	0.555854000
H	-4.653621000	-0.629860000	5.372223000	H	1.816550000	5.571400000	0.056030000
H	-5.303178000	0.848787000	4.620234000	H	2.272083000	4.837639000	1.605075000
C	-3.285326000	3.726206000	0.078349000	H	1.096023000	4.019982000	0.555047000
H	-3.386495000	2.802228000	-0.509476000	C	4.458896000	4.720995000	-0.083106000
C	-2.175731000	4.561876000	-0.579925000	H	5.328744000	4.193903000	-0.500704000
H	-2.075723000	5.556265000	-0.114976000	H	4.706239000	5.014259000	0.950507000
H	-2.407501000	4.723824000	-1.644855000	H	4.318843000	5.644692000	-0.669002000

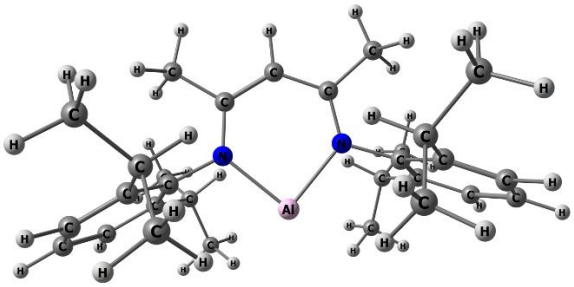
Table S5.15. Optimized geometries of $[(L^3Ga)_2(AsP_3)]$. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



Ga	-2.297474000	0.085367000	-0.016023000	H	-1.147254000	2.280666000	-3.071620000
Ga	2.282083000	-0.041591000	-0.005345000	C	-4.215680000	3.948569000	-3.226538000
As	0.345195000	-1.665543000	-0.014560000	H	-5.101528000	4.067204000	-2.584796000
P	-0.448382000	0.018639000	1.558297000	H	-4.541304000	3.490472000	-4.175031000
P	-0.437752000	0.033982000	-1.576601000	H	-3.840516000	4.958775000	-3.459055000
P	0.406795000	1.498110000	0.000722000	C	4.972315000	-0.010430000	1.266211000
N	-3.731373000	-1.346513000	-0.029236000	C	5.566307000	-0.015335000	-0.009534000

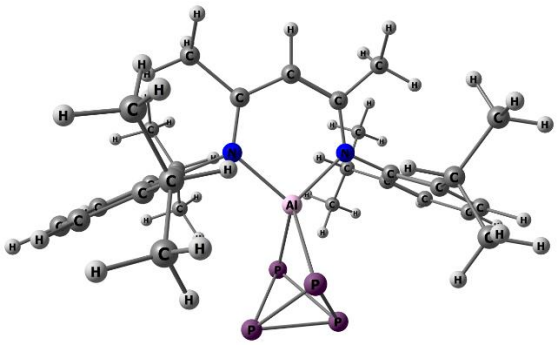
N	-3.603435000	1.637054000	-0.010105000
N	3.654983000	-0.025174000	1.486869000
N	3.651233000	-0.010624000	-1.501318000
C	-5.038611000	-1.071091000	-0.058976000
C	-5.578628000	0.227411000	-0.062221000
H	-6.667681000	0.274821000	-0.086844000
C	-4.928362000	1.475640000	-0.042432000
C	-6.063253000	-2.188593000	-0.121179000
H	-6.468281000	-2.254080000	-1.144078000
H	-6.907317000	-1.963990000	0.546491000
H	-5.648423000	-3.167577000	0.140632000
C	-5.856107000	2.675787000	-0.085292000
H	-6.689836000	2.530985000	0.616977000
H	-6.294204000	2.760695000	-1.092849000
H	-5.351207000	3.619213000	0.146452000
C	-3.270721000	-2.712544000	-0.000163000
C	-3.019724000	-3.329998000	1.253320000
C	-2.522956000	-4.640782000	1.260090000
H	-2.327478000	-5.133869000	2.215112000
C	-2.274127000	-5.328834000	0.074600000
H	-1.880141000	-6.348023000	0.103400000
C	-2.536328000	-4.714081000	-1.146803000
H	-2.349254000	-5.263447000	-2.072744000
C	-3.039298000	-3.406626000	-1.215193000
C	-3.331383000	-2.642475000	2.583854000
H	-3.523762000	-1.580505000	2.373022000
C	-2.163975000	-2.698666000	3.582239000
H	-2.422286000	-2.141862000	4.497562000
H	-1.253096000	-2.244184000	3.166347000
H	-1.927841000	-3.732078000	3.883998000
C	-4.609078000	-3.223247000	3.222483000
H	-5.478183000	-3.146596000	2.552162000
H	-4.854225000	-2.687932000	4.154602000
H	-4.477173000	-4.288877000	3.473517000
C	-3.360929000	-2.810712000	-2.586540000
H	-3.700553000	-1.776134000	-2.431574000
C	-2.134738000	-2.751040000	-3.513198000
H	-1.326255000	-2.143120000	-3.081840000
H	-2.409531000	-2.297859000	-4.479797000
H	-1.733358000	-3.756127000	-3.721710000
C	-4.508034000	-3.577664000	-3.274668000
H	-4.208169000	-4.609883000	-3.519350000
H	-4.792115000	-3.083527000	-4.218360000
H	-5.404421000	-3.638276000	-2.639444000
C	-3.025609000	2.958336000	0.028159000
C	-2.711052000	3.538119000	1.284936000
C	-2.105334000	4.802025000	1.299475000
H	-1.858773000	5.266102000	2.257030000
C	-1.811144000	5.479498000	0.118313000
H	-1.332713000	6.461716000	0.153158000
C	-2.135141000	4.901968000	-1.106308000
H	-1.910724000	5.443171000	-2.028701000
C	-2.746592000	3.642143000	-1.182399000
C	-3.064717000	2.862715000	2.610937000
H	-3.315534000	1.814305000	2.393106000
C	-1.899175000	2.847409000	3.612754000
H	-1.620672000	3.863352000	3.937312000
H	-1.007425000	2.363454000	3.189241000
H	-2.185192000	2.283639000	4.515496000
C	-4.309029000	3.511105000	3.250219000
H	-4.117612000	4.567104000	3.503903000
H	-4.584175000	2.987838000	4.180875000
H	-5.180692000	3.485283000	2.579610000
C	-3.125020000	3.088532000	-2.556921000
H	-3.541513000	2.081029000	-2.410672000
C	-1.913758000	2.946447000	-3.494084000
H	-1.443518000	3.921671000	-3.700808000
H	-2.228295000	2.519681000	-4.460698000
H	6.656459000	-0.007624000	-0.010912000
C	4.969020000	0.001855000	-1.283805000
C	5.948994000	0.052486000	2.425483000
H	6.326282000	1.083001000	2.527370000
H	6.817047000	-0.591117000	2.223976000
H	5.499944000	-0.235919000	3.381786000
C	5.943288000	0.075386000	-2.444522000
H	5.491174000	-0.199603000	-3.403302000
H	6.809325000	-0.573927000	-2.252763000
H	6.324419000	1.105593000	-2.534291000
C	3.136590000	-0.021682000	2.832710000
C	2.814837000	-1.258500000	3.451444000
C	2.270802000	-1.233312000	4.742821000
H	2.020718000	-2.174558000	5.236979000
C	2.040508000	-0.032111000	5.409999000
H	1.608553000	-0.035788000	6.414085000
C	2.366494000	1.172209000	4.792752000
H	2.189993000	2.110424000	5.324465000
C	2.920189000	1.208358000	3.504484000
C	3.095307000	-2.604581000	2.781301000
H	3.247288000	-2.414435000	1.708657000
C	1.928180000	-3.597212000	2.902881000
H	1.769340000	-3.922731000	3.943901000
H	2.137067000	-4.500955000	2.308181000
H	0.986652000	-3.165721000	2.533737000
C	4.390402000	-3.241929000	3.323257000
H	5.264520000	-2.589457000	3.182883000
H	4.597343000	-4.195500000	2.809953000
H	4.303459000	-3.453425000	4.402104000
C	3.301141000	2.563110000	2.905541000
H	3.698628000	2.384713000	1.895586000
C	2.093849000	3.504932000	2.757886000
H	1.314942000	3.073284000	2.112760000
H	2.408082000	4.459855000	2.305312000
H	1.638325000	3.735486000	3.734698000
C	4.411232000	3.249647000	3.726314000
H	4.053574000	3.524424000	4.732144000
H	4.741725000	4.176628000	3.229430000
H	5.290945000	2.601599000	3.856975000
C	3.129875000	0.005090000	-2.846082000
C	2.808913000	-1.226254000	-3.476016000
C	2.263775000	-1.189718000	-4.766616000
H	2.014185000	-2.126620000	-5.269178000
C	2.031211000	0.017368000	-5.422238000
H	1.598454000	0.022551000	-6.425982000
C	2.355294000	1.216267000	-4.793631000
H	2.176211000	2.159235000	-5.315970000
C	2.909981000	1.241124000	-3.505546000
C	3.089443000	-2.578184000	-2.817862000
H	3.239223000	-2.397719000	-1.743220000
C	1.922959000	-3.570245000	-2.950739000
H	0.979581000	-3.141063000	-2.583784000
H	2.129527000	-4.477633000	-2.360769000
H	1.769273000	-3.889412000	-3.994538000
C	4.385851000	-3.209982000	-3.363040000
H	4.591870000	-4.168434000	-2.858517000
H	5.259548000	-2.558781000	-3.214526000
H	4.301235000	-3.411082000	-4.444065000
C	3.287722000	2.590940000	-2.893619000
H	3.681108000	2.404189000	-1.883551000
C	2.079457000	3.531196000	-2.743376000
H	1.630256000	3.772248000	-3.720623000
H	2.391248000	4.481229000	-2.278951000
H	1.296171000	3.093106000	-2.108033000
C	4.400802000	3.284884000	-3.704082000
H	5.281856000	2.638912000	-3.835718000
H	4.727991000	4.208497000	-3.198798000
H	4.047186000	3.566676000	-4.709418000

Table S5.16. Optimized geometries of **1**. XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



Al	-0.000025000	-0.000734000	-0.965994000	C	2.733010000	2.583854000	-0.114325000
N	-1.425662000	-0.000188000	0.462125000	H	1.803341000	2.394454000	0.441984000
N	1.425618000	-0.000026000	0.462057000	C	-2.733458000	2.583702000	-0.113484000
C	1.262857000	0.000023000	1.791566000	H	-1.803890000	2.394324000	0.442994000
C	2.761459000	0.000100000	-0.083467000	C	-2.341463000	-3.281845000	-1.430149000
C	-1.262850000	-0.000228000	1.791624000	H	-3.229863000	-3.508333000	-2.042397000
C	-2.474099000	-0.000295000	2.698936000	H	-1.821921000	-4.233077000	-1.227046000
H	-3.106250000	0.879786000	2.507732000	H	-1.672270000	-2.647033000	-2.031910000
H	-2.179806000	-0.000569000	3.756179000	C	3.604300000	-3.504359000	0.760052000
H	-3.106412000	-0.880176000	2.507350000	H	3.057557000	-4.429002000	1.007222000
C	3.396276000	-1.232721000	-0.383166000	H	3.890918000	-3.019410000	1.706826000
C	3.395893000	1.233062000	-0.383515000	H	4.532659000	-3.801425000	0.245699000
C	4.669673000	-1.203443000	-0.970124000	C	2.340079000	3.281356000	-1.429918000
H	5.170731000	-2.144693000	-1.209333000	H	1.820624000	4.232630000	-1.226818000
C	-3.396066000	-1.232923000	-0.383606000	H	1.670564000	2.646256000	-2.031035000
C	-3.396198000	1.232863000	-0.382913000	H	3.228055000	3.507595000	-2.042882000
C	2.733844000	-2.583668000	-0.113601000	C	2.341482000	-3.281812000	-1.429019000
H	1.803989000	-2.394389000	0.442444000	H	3.229686000	-3.507981000	-2.041676000
C	0.000026000	-0.000142000	2.411973000	H	1.671899000	-2.647170000	-2.030540000
H	0.000056000	-0.000206000	3.500934000	H	1.822301000	-4.233178000	-1.225673000
C	-2.733381000	-2.583836000	-0.114523000	C	-4.669421000	-1.203658000	-0.970637000
H	-1.803309000	-2.394517000	0.441139000	H	-5.170231000	-2.144908000	-1.210375000
C	-2.761541000	-0.000078000	-0.083322000	C	-5.307295000	0.000114000	-1.260801000
C	2.474176000	0.000436000	2.698787000	H	-6.299398000	0.000189000	-1.719563000
H	2.179973000	-0.000449000	3.756059000	C	-2.340318000	3.281163000	-1.429055000
H	3.105444000	0.881251000	2.507906000	H	-1.670772000	2.645997000	-2.030063000
H	3.107307000	-0.878739000	2.506792000	H	-1.820821000	4.232410000	-1.225932000
C	4.669273000	1.204011000	-0.970499000	H	-3.228221000	3.507419000	-2.042109000
H	5.170026000	2.145335000	-1.210046000	C	3.603309000	3.505238000	0.758767000
C	5.307266000	0.000337000	-1.260839000	H	4.531367000	3.802562000	0.244030000
H	6.299379000	0.000439000	-1.719578000	H	3.890470000	3.020712000	1.705597000
C	-4.669581000	1.203793000	-0.969910000	H	3.056216000	4.429701000	1.005828000
H	-5.170523000	2.145121000	-1.209060000	C	-3.603906000	3.505041000	0.759453000
C	-3.603388000	-3.504666000	0.759434000	H	-4.532036000	3.802158000	0.244731000
H	-3.889381000	-3.019915000	1.706505000	H	-3.056956000	4.429630000	1.006373000
H	-3.056597000	-4.429418000	1.006096000	H	-3.890932000	3.020621000	1.706379000
H	-4.532107000	-3.801468000	0.245592000				

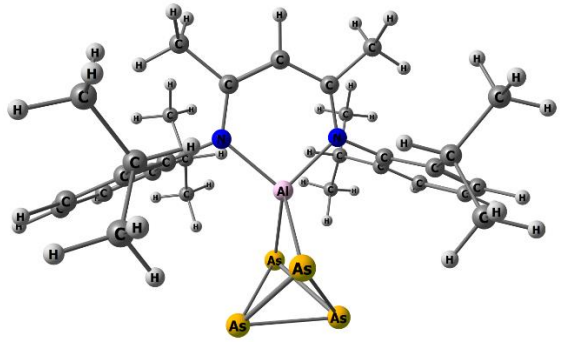
Table S5.17. Optimized geometries of [L^3Al(P_4)] (**I-3a**). XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



Al	0.000075000	-0.224606000	-0.252826000	C	2.608523000	2.723775000	-0.109333000
P	-0.000223000	-2.335789000	-1.329254000	H	1.592177000	2.547869000	0.273483000
P	1.090799000	-1.221676000	-2.991611000	C	2.466693000	3.354334000	-1.506033000
P	-1.091569000	-1.221575000	-2.991293000	H	3.446868000	3.615318000	-1.937067000
P	-0.000222000	0.699515000	-2.429904000	H	1.878104000	4.284400000	-1.445515000
N	1.457297000	0.203743000	0.962189000	H	1.955481000	2.678700000	-2.208177000
N	-1.457182000	0.203865000	0.962244000	C	3.297395000	3.711951000	0.852943000
C	1.268482000	0.513330000	2.253100000	H	3.396254000	3.300312000	1.868433000

C	0.000109000	0.608922000	2.852872000
H	0.000113000	0.855249000	3.915133000
C	-1.268320000	0.513354000	2.253133000
C	2.437352000	0.823857000	3.165277000
H	3.408910000	0.595484000	2.715934000
H	2.334160000	0.262640000	4.105746000
H	2.422108000	1.893658000	3.427957000
C	-2.437094000	0.823282000	3.165668000
H	-2.419327000	1.891942000	3.432721000
H	-2.335868000	0.258030000	4.103966000
H	-3.408886000	0.598909000	2.714838000
C	2.795328000	0.187409000	0.404664000
C	3.531489000	-1.026817000	0.384294000
C	4.810494000	-1.016539000	-0.191434000
H	5.393653000	-1.939490000	-0.213085000
C	5.353850000	0.144133000	-0.736441000
H	6.351071000	0.126524000	-1.183349000
C	4.620100000	1.326700000	-0.707868000
H	5.053233000	2.234726000	-1.133451000
C	3.337380000	1.379397000	-0.142815000
C	3.013052000	-2.323825000	1.008483000
H	1.933937000	-2.201604000	1.184059000
C	3.188431000	-3.543786000	0.088139000
H	2.748324000	-3.370659000	-0.904120000
H	2.689162000	-4.422354000	0.526955000
H	4.250053000	-3.806881000	-0.046830000
C	3.674837000	-2.595527000	2.374282000
H	4.763065000	-2.734665000	2.263734000
H	3.264748000	-3.513954000	2.825293000
H	3.517270000	-1.772471000	3.086212000
H	2.722442000	4.650019000	0.921099000
H	4.310308000	3.968554000	0.501845000
C	-2.795177000	0.187865000	0.404618000
C	-3.531793000	-1.026072000	0.384364000
C	-4.810756000	-1.015375000	-0.191456000
H	-5.394265000	-1.938109000	-0.213029000
C	-5.353635000	0.145441000	-0.736624000
H	-6.350841000	0.128163000	-1.183581000
C	-4.619430000	1.327733000	-0.708165000
H	-5.052194000	2.235872000	-1.133876000
C	-3.336716000	1.379997000	-0.143068000
C	-3.013930000	-2.323213000	1.008738000
H	-1.934869000	-2.201246000	1.184844000
C	-3.189162000	-3.543094000	0.088259000
H	-4.250793000	-3.805820000	-0.047339000
H	-2.690443000	-4.421845000	0.527339000
H	-2.748422000	-3.370086000	-0.903738000
C	-3.676512000	-2.594793000	2.374173000
H	-3.519525000	-1.771580000	3.086042000
H	-3.266599000	-3.513102000	2.825585000
H	-4.764654000	-2.734081000	2.262973000
C	-2.607331000	2.724087000	-0.109554000
H	-1.590733000	2.547606000	0.272314000
C	-2.466394000	3.355352000	-1.506015000
H	-1.956121000	2.679821000	-2.208945000
H	-1.877252000	4.285064000	-1.445468000
H	-3.446779000	3.617132000	-1.936081000
C	-3.295017000	3.711938000	0.853900000
H	-4.308287000	3.968794000	0.504007000
H	-2.719872000	4.649903000	0.921855000
H	-3.392787000	3.299843000	1.869305000

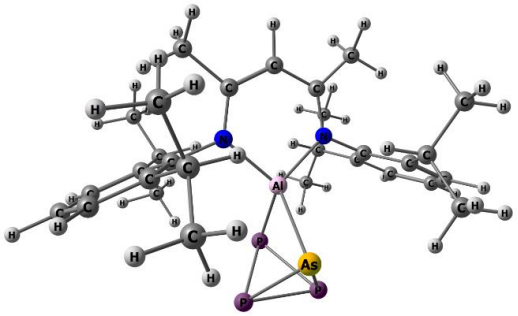
Table S5.18. Optimized geometries of [L^3Al(As_4)] (**I-3b**). XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



Al	0.000120000	0.062309000	0.239579000
As	0.000101000	-0.498229000	-2.169113000
As	-0.000456000	-2.345626000	0.813212000
As	1.209579000	-2.551447000	-1.380084000
N	-1.463588000	1.162716000	0.935269000
N	1.463938000	1.162482000	0.935190000
C	3.220823000	1.564429000	-0.752918000
C	2.797059000	0.900419000	0.429248000
C	-1.268912000	2.135226000	1.837512000
C	4.920964000	-0.258029000	0.546083000
H	5.591383000	-0.962055000	1.044148000
C	1.269431000	2.135041000	1.837479000
C	2.433440000	2.890397000	2.447119000
H	3.388630000	2.684077000	1.954002000
H	2.525101000	2.615126000	3.509972000
H	2.238786000	3.972175000	2.413993000
C	3.271046000	-0.733550000	2.391205000
H	2.206550000	-0.534192000	2.585716000
C	4.501890000	1.287314000	-1.250551000
H	4.844529000	1.791529000	-2.156358000
C	-2.432821000	2.890716000	2.447186000
H	-3.387959000	2.684864000	1.953780000
H	-2.237834000	3.972449000	2.414528000
H	-2.524787000	2.615043000	3.509912000
C	3.649518000	-0.021347000	1.091524000
C	0.000308000	2.537023000	2.290367000
H	0.000378000	3.327795000	3.041222000
C	-3.649473000	-0.020625000	1.091435000
C	-3.271291000	-0.732999000	2.391104000
H	-2.206736000	-0.533995000	2.585672000
C	-2.796743000	0.900953000	0.429261000
C	2.358413000	2.608121000	-1.464959000
H	3.967935000	0.893734000	3.712443000
C	2.347004000	2.443808000	-2.993769000
H	3.325397000	2.682076000	-3.441371000
H	1.612009000	3.131852000	-3.441919000
H	2.075189000	1.420230000	-3.291298000
C	-4.501320000	1.288298000	-1.250691000
H	-4.843772000	1.792594000	-2.156519000
C	-4.920915000	-0.257021000	0.545843000
H	-5.591527000	-0.960927000	1.043812000
C	3.444240000	-2.259953000	2.299328000
H	2.901334000	-2.679351000	1.440967000
H	3.057006000	-2.742549000	3.211039000
H	4.505149000	-2.543215000	2.204554000
C	-2.357454000	2.608530000	-1.464909000
H	-1.322094000	2.476546000	-1.116862000
C	2.790843000	4.039422000	-1.089231000
H	2.746628000	4.214909000	-0.004655000
H	2.140039000	4.782869000	-1.578219000
H	3.826177000	4.234030000	-1.414591000
C	-5.348048000	0.385044000	-0.612729000
H	-6.342202000	0.182313000	-1.019065000
C	-3.444990000	-2.259350000	2.299200000
H	-4.506016000	-2.542278000	2.204716000
H	-3.057668000	-2.742086000	3.210797000
H	-2.902452000	-2.678918000	1.440690000
C	-4.076169000	-0.192541000	3.590351000
H	-3.967718000	0.894409000	3.712453000
H	-3.744092000	-0.673960000	4.524756000
H	-5.151488000	-0.405081000	3.472322000
C	-2.346213000	2.444364000	-2.993738000
H	-2.075047000	1.420646000	-3.291372000
H	-1.610823000	3.132001000	-3.441859000

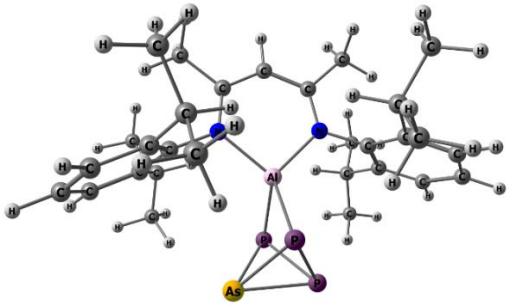
H	1.323020000	2.476587000	-1.116837000	H	-3.324482000	2.683271000	-3.441275000
C	-3.220234000	1.565093000	-0.752942000	C	-2.789242000	4.039989000	-1.089010000
C	5.348355000	0.383897000	-0.612480000	H	-3.824622000	4.234976000	-1.413978000
H	6.342509000	0.180930000	-1.018695000	H	-2.138334000	4.783183000	-1.578242000
C	4.076021000	-0.193275000	3.590465000	H	-2.744514000	4.215458000	-0.004459000
H	5.151277000	-0.406197000	3.472555000	As	-1.210611000	-2.550733000	-1.380071000
H	3.743705000	-0.674486000	4.524892000				

Table S5.19. Optimized geometries of [L^3Al(AsP_3)] (**I-3c1**, Isomer 1). XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



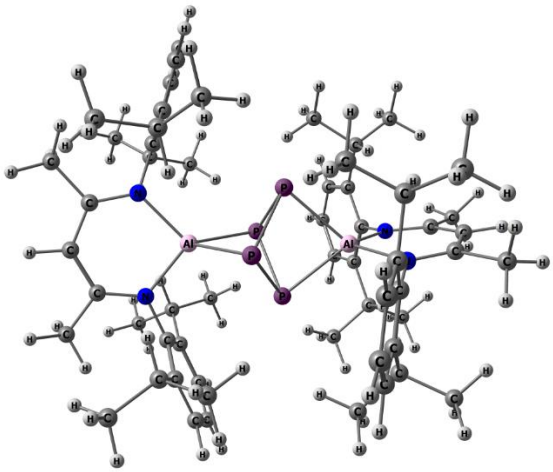
Al	0.000073000	-0.070139000	-0.177466000	H	3.457598000	-1.416602000	3.354555000
P	-0.000545000	0.815000000	-2.374792000	C	2.646626000	3.326970000	-1.733481000
As	0.000588000	-2.306097000	-1.232127000	H	3.659414000	3.561476000	-2.098893000
P	1.096012000	-1.079822000	-2.982317000	H	2.059113000	4.258177000	-1.781888000
N	-1.460344000	0.418663000	1.017344000	H	2.188637000	2.607493000	-2.428153000
N	1.460327000	0.418763000	1.017337000	C	-4.676815000	1.314411000	-0.689416000
C	3.379485000	1.441996000	-0.170534000	H	-5.136987000	2.168349000	-1.191436000
C	2.804644000	0.320730000	0.483108000	C	-4.812662000	-0.967593000	0.063595000
C	-1.269077000	0.831575000	2.278924000	H	-5.379518000	-1.897066000	0.149418000
C	4.812999000	-0.966770000	0.063748000	C	3.118303000	-3.421986000	0.509511000
H	5.380110000	-1.896070000	0.149750000	H	2.700797000	-3.320092000	-0.502831000
C	1.269038000	0.831788000	2.278913000	H	2.592409000	-4.251509000	1.008962000
C	2.436105000	1.186067000	3.178609000	H	4.175400000	-3.718538000	0.413833000
H	3.410813000	0.981832000	2.724939000	C	-2.670074000	2.791399000	-0.290647000
H	2.356803000	0.627300000	4.123310000	H	-1.624435000	2.649122000	0.020606000
H	2.388124000	2.255544000	3.436670000	C	3.292415000	3.838543000	0.653327000
C	2.959936000	-2.126891000	1.325119000	H	3.294046000	3.502916000	1.700686000
H	1.881866000	-1.964099000	1.474162000	H	2.733673000	4.787393000	0.601943000
C	4.676498000	1.315055000	-0.689695000	H	4.337233000	4.051817000	0.373561000
H	5.136426000	2.169019000	-1.191891000	C	-5.391890000	0.125422000	-0.575710000
C	-2.436156000	1.185512000	3.178750000	H	-6.401428000	0.049501000	-0.987513000
H	-3.410860000	0.981139000	2.725138000	C	-3.117432000	-3.422428000	0.509034000
H	-2.388329000	2.254954000	3.436960000	H	-4.174473000	-3.719088000	0.413134000
H	-2.356672000	0.626624000	4.123373000	H	-2.591521000	-4.251952000	1.008471000
C	3.518766000	-0.900924000	0.600439000	H	-2.699784000	-3.320354000	-0.503233000
C	-0.000013000	0.990897000	2.862613000	C	-3.597566000	-2.302345000	2.717138000
H	-0.000042000	1.326081000	3.900424000	H	-3.457130000	-1.417516000	3.354356000
C	-3.518462000	-0.901478000	0.600323000	H	-3.155913000	-3.167413000	3.238417000
C	-2.959330000	-2.127414000	1.324812000	H	-4.682268000	-2.481123000	2.633139000
H	-1.881287000	-1.964423000	1.473840000	C	-2.647417000	3.327123000	-1.732746000
C	-2.804667000	0.320391000	0.483181000	H	-2.189032000	2.607934000	-2.427456000
C	2.669265000	2.791494000	-0.291283000	H	-2.060270000	4.258573000	-1.780905000
H	1.623624000	2.648876000	0.019818000	H	-3.660238000	3.561287000	-2.098286000
C	-3.379838000	1.441628000	-0.170224000	C	-3.293798000	3.838049000	0.654039000
C	5.391922000	0.126295000	-0.575744000	H	-4.338663000	4.050932000	0.374153000
H	6.401491000	0.050602000	-0.987513000	H	-2.735446000	4.787143000	0.602889000
C	3.598269000	-2.301473000	2.717447000	H	-3.295449000	3.502252000	1.701342000
H	4.683017000	-2.479949000	2.633429000	P	-1.096295000	-1.080456000	-2.981863000
H	3.156878000	-3.166599000	3.238853000				

Table S5.20. Optimized geometries of [$L^3Al(AsP_3)$] (**I-3c2**, Isomer 2). XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



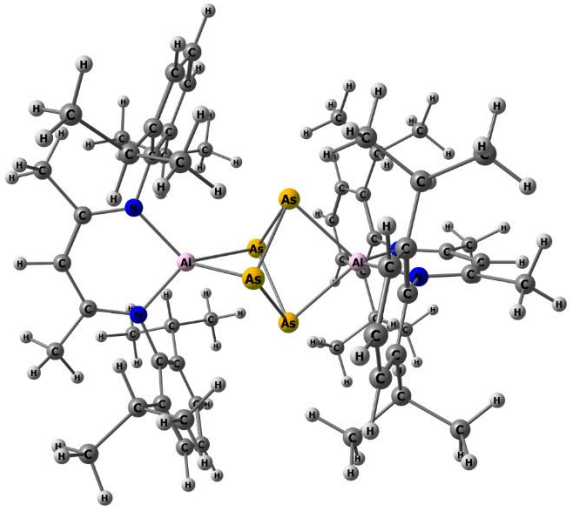
Al	-0.061687000	-0.224676000	-0.014771000
P	-0.070247000	-0.041274000	-2.372911000
N	-1.587840000	0.502999000	0.955361000
N	1.324429000	0.659682000	1.028696000
C	3.143364000	1.550625000	-0.391075000
C	2.680849000	0.571193000	0.525972000
C	-1.463468000	1.182901000	2.104393000
C	4.812403000	-0.570451000	0.397208000
H	5.470788000	-1.388456000	0.697696000
C	1.068412000	1.326308000	2.163472000
C	2.180615000	1.965640000	2.970104000
H	3.174386000	1.805145000	2.540638000
H	2.167462000	1.566514000	3.995977000
H	2.002165000	3.049216000	3.047890000
C	3.084987000	-1.561851000	1.947063000
H	2.001878000	-1.452673000	2.106618000
C	4.449490000	1.432292000	-0.888132000
H	4.823270000	2.179962000	-1.591273000
C	-2.679562000	1.701870000	2.843425000
H	-3.616651000	1.246979000	2.506513000
H	-2.758999000	2.791199000	2.698408000
H	-2.561037000	1.530124000	3.923145000
C	3.515507000	-0.504705000	0.928258000
C	-0.224934000	1.509338000	2.685232000
H	-0.277201000	2.052993000	3.629115000
C	-3.618526000	-0.884760000	0.635087000
C	-3.103446000	-1.968285000	1.584104000
H	-2.022164000	-1.811707000	1.710856000
C	-2.899410000	0.310973000	0.368747000
C	2.298173000	2.751509000	-0.818983000
H	1.269452000	2.578875000	-0.469117000
C	-3.435215000	1.310338000	-0.485202000
C	5.280496000	0.383590000	-0.502617000
H	6.294620000	0.309918000	-0.903495000
C	3.780490000	-1.349989000	3.306826000
H	4.871865000	-1.476521000	3.214993000
H	3.420627000	-2.087207000	4.043058000
H	3.598300000	-0.346602000	3.717469000
C	2.234798000	2.924272000	-2.346313000
H	3.221657000	3.165409000	-2.773448000
H	1.556408000	3.753255000	-2.605740000
H	1.858972000	2.016973000	-2.842688000
C	-4.694223000	1.085953000	-1.061985000
H	-5.121627000	1.843522000	-1.723153000
C	-4.874846000	-1.049644000	0.033541000
H	-5.445347000	-1.959818000	0.228873000
C	3.330726000	-2.998450000	1.453765000
H	2.853708000	-3.180687000	0.480689000
H	2.912402000	-3.722088000	2.171622000
H	4.406200000	-3.218941000	1.356988000
C	-2.723658000	2.631572000	-0.782024000
H	-1.738399000	2.602450000	-0.293617000
C	2.797981000	4.048891000	-0.152922000
H	2.813160000	3.970497000	0.944432000
H	2.149789000	4.898641000	-0.423168000
H	3.822044000	4.292835000	-0.480372000
C	-5.411757000	-0.079461000	-0.809206000
H	-6.390908000	-0.233310000	-1.269805000
C	-3.292596000	-3.390727000	1.030261000
H	-4.355113000	-3.681909000	0.999273000
H	-2.774729000	-4.117887000	1.675372000
H	-2.879413000	-3.490321000	0.016510000
C	-3.751958000	-1.857289000	2.978440000
H	-3.562952000	-0.882817000	3.451372000
H	-3.356685000	-2.637233000	3.649630000
H	-4.844723000	-1.991182000	2.915857000
C	-2.481621000	2.841742000	-2.287442000
H	-1.906056000	2.013105000	-2.726715000
H	-1.916867000	3.773251000	-2.456991000
H	-3.429993000	2.927334000	-2.842064000
C	-3.492565000	3.832079000	-0.195478000
H	-4.471455000	3.957865000	-0.686246000
H	-2.925272000	4.765150000	-0.346033000
H	-3.678951000	3.718304000	0.882899000
P	-0.975114000	-2.138640000	-2.286235000
P	0.071764000	-2.573511000	-0.298979000
As	1.319155000	-1.997564000	-2.269805000

Table S5.21. Optimized geometries of [$(L^3Al)_2(\mu,\eta^{1:1:1:1}\text{-}P_4)$] (**3a**). XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



Al	-2.167004000	-0.508042000	0.254895000
Al	2.178430000	0.512611000	0.219611000
P	0.618478000	-0.949727000	-0.842798000
P	-0.135799000	-1.180871000	1.353758000
P	-0.635325000	1.010828000	-0.768513000
P	0.183286000	1.121912000	1.416535000
N	-3.128514000	-1.870809000	-0.781220000
N	-3.745196000	0.219625000	1.154506000
N	3.780898000	-0.242515000	1.050668000
N	3.114642000	1.909948000	-0.797577000
C	-4.411591000	-2.186339000	-0.561793000
C	-5.226938000	-1.536646000	0.383278000
H	-6.242797000	-1.921393000	0.470394000
C	-4.948774000	-0.376534000	1.123147000
C	-5.113842000	-3.252900000	-1.378916000
H	-5.801529000	-2.766284000	-2.089587000
H	-5.727410000	-3.884652000	-0.720340000
H	-4.429277000	-3.885686000	-1.951778000
C	-6.131160000	0.232868000	1.847731000
H	-6.858449000	-0.547078000	2.110911000
H	-6.640633000	0.948489000	1.183406000
H	-5.843273000	0.781022000	2.751330000
C	-2.402078000	-2.579572000	-1.816351000
C	-1.740029000	-3.794244000	-1.500947000
C	-1.052996000	-4.457789000	-2.526956000
H	-0.542104000	-5.397661000	-2.305674000
C	-1.001564000	-3.942695000	-3.820007000
H	-0.454896000	-4.475581000	-4.602367000
C	-1.649622000	-2.745211000	-4.110217000
H	-1.607313000	-2.346229000	-5.126491000
C	-2.361028000	-2.042630000	-3.126930000
C	-1.768523000	-4.422533000	-0.105854000
H	-2.204133000	-3.686011000	0.584957000
C	-0.361287000	-4.754106000	0.419364000
H	-0.419804000	-5.115114000	1.458675000
H	0.292810000	-3.871277000	0.412667000
H	0.121868000	-5.545186000	-0.177279000
C	-2.656093000	-5.682422000	-0.063256000
H	-3.691305000	-5.476650000	-0.372210000
H	-2.686793000	-6.096590000	0.957879000
H	-2.261355000	-6.467965000	-0.728983000
C	-3.088748000	-0.756449000	-3.519929000
H	-3.486272000	-0.302570000	-2.599997000
C	-2.154189000	0.280205000	-4.165911000
H	-1.320122000	0.545757000	-3.499891000
H	-2.709750000	1.206066000	-4.387807000
H	-1.732588000	-0.085951000	-5.116200000
C	-4.286786000	-1.049744000	-4.444314000
H	-3.953940000	-1.471582000	-5.407090000
H	-4.844865000	-0.124267000	-4.662359000
H	-4.987477000	-1.769800000	-3.995153000
C	-3.639863000	1.498365000	1.827859000
C	-3.181642000	1.540440000	3.170937000
C	-3.125295000	2.786191000	3.810873000
H	-2.782095000	2.842604000	4.844646000
C	-3.484789000	3.960090000	3.151771000
H	-3.426459000	4.920438000	3.670642000
C	-3.909486000	3.904521000	1.828253000
H	-4.181635000	4.829430000	1.314072000
C	-4.002897000	2.684699000	1.140474000
C	-2.767515000	0.277784000	3.931118000
H	-2.372562000	-0.432648000	3.188140000
C	-1.641536000	0.534881000	4.943752000
H	-1.998286000	1.096415000	5.823076000
H	-0.814408000	1.094461000	4.484870000
H	-1.244654000	-0.423497000	5.313134000
C	-3.951192000	-0.410905000	4.638952000
H	-4.441418000	0.278160000	5.347175000
H	-3.594857000	-1.282541000	5.211946000
H	-4.713733000	-0.772396000	3.935651000
C	-4.501587000	2.704484000	-0.306718000
H	-4.559090000	1.664957000	-0.661514000
C	-3.530881000	3.450550000	-1.240535000
H	-3.435458000	4.510790000	-0.954017000
H	-3.899960000	3.420096000	-2.279335000
H	-2.526511000	3.002363000	-1.227885000
C	-5.913921000	3.310870000	-0.426391000
H	-6.641333000	2.813577000	0.233397000
H	-6.282160000	3.224083000	-1.461700000
H	-5.915889000	4.381970000	-0.166993000
C	4.977623000	0.369175000	1.029882000
C	5.238157000	1.546456000	0.312867000
H	6.251820000	1.937301000	0.394524000
C	4.399609000	2.224280000	-0.593114000
C	6.139894000	-0.203230000	1.811512000
H	6.030129000	0.045030000	2.878429000
H	7.090150000	0.219946000	1.462111000
H	6.185823000	-1.297445000	1.744916000
C	5.080680000	3.322748000	-1.385290000
H	4.382692000	3.964981000	-1.930794000
H	5.766915000	2.866602000	-2.117139000
H	5.693687000	3.941110000	-0.713399000
C	3.679279000	-1.543898000	1.680909000
C	3.812515000	-2.702871000	0.870215000
C	3.693654000	-3.958569000	1.482353000
H	3.795046000	-4.860809000	0.875613000
C	3.454048000	-4.080391000	2.849292000
H	3.361350000	-5.069722000	3.304811000
C	3.337585000	-2.935625000	3.631950000
H	3.151962000	-3.037858000	4.703879000
C	3.448248000	-1.652890000	3.075385000
C	4.145118000	-2.632523000	-0.622028000
H	3.932765000	-1.608384000	-0.961450000
C	3.287304000	-3.575812000	-1.480412000
H	3.494901000	-4.636495000	-1.263599000
H	3.506068000	-3.414692000	-2.548501000
H	2.213517000	-3.391861000	-1.330900000
C	5.643513000	-2.896162000	-0.872807000
H	6.286602000	-2.175443000	-0.345941000
H	5.874430000	-2.824736000	-1.948536000
H	5.928715000	-3.906424000	-0.534964000
C	3.319084000	-0.442596000	4.000718000
H	3.488553000	0.462616000	3.398741000
C	1.906503000	-0.332904000	4.597428000
H	1.140741000	-0.317316000	3.811096000
H	1.809821000	0.587078000	5.196536000
H	1.686432000	-1.187380000	5.258596000
C	4.365194000	-0.456171000	5.132756000
H	4.188328000	-1.287938000	5.833636000
H	4.311828000	0.478311000	5.714968000
H	5.393930000	-0.561938000	4.755477000
C	2.369253000	2.637199000	-1.806668000
C	2.329044000	2.139205000	-3.132797000
C	1.596401000	2.857311000	-4.089160000
H	1.553773000	2.488176000	-5.116656000
C	0.928989000	4.033479000	-3.758555000
H	0.366509000	4.579075000	-4.520687000
C	0.981770000	4.510994000	-2.451375000
H	0.455104000	5.433756000	-2.197912000
C	1.687689000	3.829209000	-1.450640000
C	3.078116000	0.880405000	-3.571632000
H	3.505651000	0.413801000	-2.671817000
C	2.153302000	-0.161061000	-4.224088000
H	1.339825000	-0.462138000	-3.547683000
H	2.724356000	-1.068111000	-4.482023000
H	1.703360000	0.219643000	-5.155466000
C	4.249591000	1.222805000	-4.513153000
H	4.824495000	0.315859000	-4.762898000
H	4.942335000	1.949356000	-4.062195000
H	3.887354000	1.657397000	-5.459441000
C	1.712836000	4.412644000	-0.036669000
H	2.157146000	3.658377000	0.629007000
C	0.303230000	4.712637000	0.501321000
H	-0.182043000	5.530037000	-0.057022000
H	0.357560000	5.022021000	1.557261000
H	-0.346061000	3.828092000	0.446125000
C	2.589781000	5.677894000	0.044756000
H	3.626280000	5.490226000	-0.272050000
H	2.618543000	6.060347000	1.078296000
H	2.187643000	6.480394000	-0.595874000

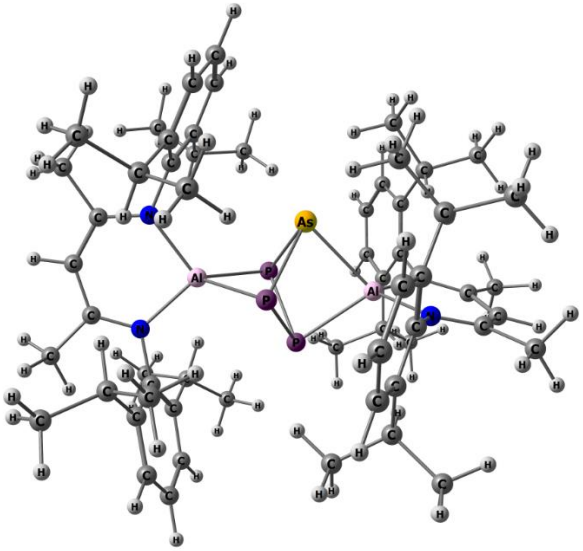
Table S5.22. Optimized geometries of [$(L^3Al)_2(\mu,\eta^{1:1:1:1}\text{-}As_4)$] (**3b**). XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



Al	-2.290424000	-0.047349000	0.054285000	H	-1.191816000	-3.720377000	0.786236000
Al	2.294420000	0.006072000	-0.010655000	C	-4.269344000	-5.116726000	-0.157324000
As	0.454127000	1.232710000	1.166123000	H	-5.179134000	-4.795537000	-0.703953000
As	-0.480000000	1.126007000	-1.220013000	H	-4.574757000	-5.428552000	0.863972000
As	-0.417178000	-1.176405000	1.275676000	H	-3.877002000	-6.018252000	-0.674320000
As	0.449772000	-1.260603000	-1.138755000	C	4.940723000	0.904333000	-0.984667000
N	-3.623189000	1.024696000	1.051778000	C	5.574009000	0.047115000	-0.057894000
N	-3.626108000	-1.151402000	-0.906104000	H	6.672749000	0.060715000	-0.073914000
N	3.600056000	1.029519000	-1.091624000	C	4.989318000	-0.824627000	0.886981000
N	3.655869000	-0.983155000	1.032691000	C	5.866903000	1.671916000	-1.909807000
C	-4.957064000	0.815866000	1.002962000	H	6.156414000	1.023109000	-2.764085000
C	-5.565330000	-0.162243000	0.186015000	H	6.799926000	1.948727000	-1.381643000
H	-6.661264000	-0.215564000	0.246386000	H	5.398833000	2.580239000	-2.330077000
C	-4.959701000	-1.074017000	-0.706878000	C	5.960300000	-1.567745000	1.785687000
C	-5.897273000	1.625856000	1.875696000	H	5.529018000	-2.490331000	2.214262000
H	-6.080931000	1.082143000	2.827081000	H	6.252019000	-0.913587000	2.635114000
H	-6.877534000	1.754035000	1.377585000	H	6.887387000	-1.815975000	1.233475000
H	-5.486665000	2.617013000	2.141159000	C	3.054864000	1.969730000	-2.051448000
C	-5.906682000	-2.012630000	-1.431460000	C	2.737775000	3.292324000	-1.615349000
H	-6.863904000	-1.501763000	-1.652312000	C	2.176111000	4.184999000	-2.550434000
H	-6.142935000	-2.879908000	-0.778515000	H	1.928133000	5.209943000	-2.232999000
H	-5.478837000	-2.413155000	-2.368312000	C	1.924897000	3.795669000	-3.872750000
C	-3.109208000	2.097369000	1.881146000	H	1.477796000	4.508188000	-4.584207000
C	-2.860830000	3.370020000	1.281665000	C	2.249830000	2.498330000	-4.286129000
C	-2.322837000	4.392741000	2.088668000	H	2.058522000	2.199741000	-5.329512000
H	-2.126737000	5.381035000	1.644289000	C	2.821459000	1.563084000	-3.398168000
C	-2.032646000	4.178664000	3.442714000	C	3.046986000	3.782865000	-0.196229000
H	-1.605241000	4.990733000	4.052318000	H	3.194133000	2.883962000	0.439405000
C	-2.294020000	2.929571000	4.017597000	C	1.898232000	4.597065000	0.428601000
H	-2.072416000	2.768928000	5.085053000	H	1.730043000	5.557930000	-0.103049000
C	-2.837237000	1.869278000	3.262281000	H	2.135879000	4.844666000	1.484162000
C	-3.222799000	3.670757000	-0.177333000	H	0.946461000	4.027982000	0.426776000
H	-3.324328000	2.695531000	-0.699192000	C	4.359060000	4.600479000	-0.160086000
C	-2.138789000	4.472999000	-0.921571000	H	5.227413000	4.018940000	-0.528337000
H	-2.410927000	4.579597000	-1.992378000	H	4.587430000	4.927481000	0.876626000
H	-1.153426000	3.965975000	-0.878002000	H	4.275281000	5.511686000	-0.790871000
H	-2.021694000	5.498604000	-0.510948000	C	3.201610000	0.177498000	-3.931018000
C	-4.584720000	4.396516000	-0.276680000	H	3.611558000	-0.408625000	-3.081797000
H	-5.408400000	3.808748000	0.175065000	C	1.986178000	-0.596944000	-4.479441000
H	-4.849925000	4.586807000	-1.338428000	H	1.205685000	-0.739340000	-3.703469000
H	-4.549059000	5.377752000	0.243944000	H	2.294619000	-1.603939000	-4.831732000
C	-3.140692000	0.543051000	3.967674000	H	1.521410000	-0.069972000	-5.339628000
H	-3.560488000	-0.152859000	3.211152000	C	4.298746000	0.271036000	-5.016949000
C	-1.872463000	-0.117079000	4.545406000	H	3.920728000	0.784505000	-5.926641000
H	-1.118162000	-0.317172000	3.756827000	H	4.632435000	-0.742980000	-5.323595000
H	-2.123183000	-1.087331000	5.024002000	H	5.188578000	0.833650000	-4.668845000
H	-1.396251000	0.524606000	5.316815000	C	3.163054000	-1.935172000	2.009295000
C	-4.194211000	0.722563000	5.085449000	C	2.960635000	-1.532788000	3.362251000
H	-3.798569000	1.347138000	5.914549000	C	2.438292000	-2.480532000	4.267152000
H	-4.475530000	-0.260944000	5.518030000	H	2.270843000	-2.185357000	5.315603000
H	-5.119052000	1.212663000	4.718888000	C	2.132126000	-3.785634000	3.864063000
C	-3.112118000	-2.105330000	-1.869497000	H	1.723011000	-4.507682000	4.588670000
C	-2.836486000	-1.659612000	-3.197964000	C	2.352982000	-4.170325000	2.535001000
C	-2.300799000	-2.586556000	-4.114510000	H	2.119532000	-5.200978000	2.225199000
H	-2.084080000	-2.260873000	-5.143813000	C	2.865040000	-3.265500000	1.583404000
C	-2.036030000	-3.911274000	-3.742793000	C	3.322890000	-0.137901000	3.883216000
H	-1.608964000	-4.616517000	-4.473551000	H	3.696017000	0.456458000	3.022784000

C	-2.321993000	-4.335022000	-2.439697000	C	2.104902000	0.608506000	4.464012000
H	-2.120389000	-5.380368000	-2.155020000	H	1.299916000	0.731393000	3.710298000
C	-2.866417000	-3.455383000	-1.480578000	H	2.399553000	1.622615000	4.807770000
C	-3.165892000	-0.237677000	-3.665547000	H	1.676318000	0.071033000	5.336414000
H	-3.261326000	0.393906000	-2.756666000	C	4.450966000	-0.204301000	4.939056000
C	-2.061263000	0.387551000	-4.537983000	H	4.769064000	0.817668000	5.235724000
H	-1.952497000	-0.135262000	-5.512240000	H	5.344012000	-0.746549000	4.567526000
H	-1.078704000	0.372665000	-4.024323000	H	4.109852000	-0.725105000	5.859112000
H	-2.305607000	1.446877000	-4.761864000	C	3.142893000	-3.749027000	0.155496000
C	-4.522064000	-0.193740000	-4.406980000	H	3.245851000	-2.846950000	-0.484237000
H	-4.493246000	-0.823120000	-5.322525000	C	1.997161000	-4.593869000	-0.432970000
H	-4.764591000	0.844644000	-4.718106000	H	1.874686000	-5.560352000	0.101121000
H	-5.357009000	-0.559565000	-3.776814000	H	2.206268000	-4.832451000	-1.496647000
C	-3.200514000	-4.001158000	-0.087892000	H	1.030536000	-4.052307000	-0.395953000
H	-3.618403000	-3.165207000	0.511288000	C	4.474677000	-4.530991000	0.077558000
C	-1.952444000	-4.518057000	0.655914000	H	5.338533000	-3.925746000	0.417034000
H	-1.474639000	-5.360405000	0.112147000	H	4.678134000	-4.853257000	-0.965816000
H	-2.227557000	-4.885303000	1.667261000	H	4.435957000	-5.443217000	0.711236000

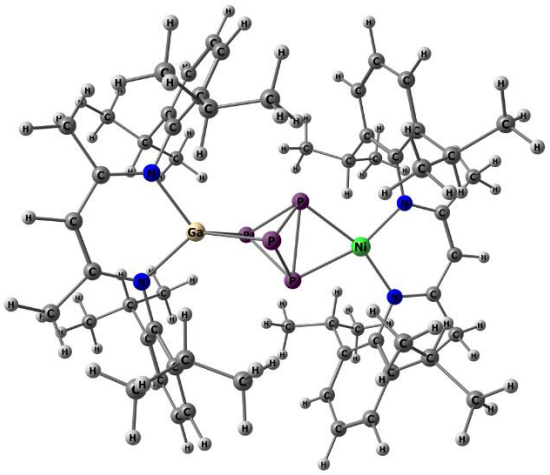
Table S5.23. Optimized geometries of [$(L^3Al)_2(\mu,\eta^{1:1:1:1}\text{-}AsP_3)$] (**3c**). XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



Al	-2.181255000	-0.442730000	0.356197000	H	-2.549300000	2.947875000	-1.491537000
Al	2.207990000	0.496803000	0.130608000	C	-5.911808000	3.308568000	-0.617978000
As	0.590442000	-1.106084000	-0.873434000	H	-6.612470000	2.883048000	0.116390000
P	-0.156490000	-1.096732000	1.469687000	H	-6.312443000	3.104223000	-1.624322000
P	-0.688423000	0.981694000	-0.837835000	H	-5.917250000	4.401901000	-0.479309000
P	0.226870000	1.186558000	1.299224000	C	5.018973000	0.397910000	0.916677000
N	-3.232495000	-1.872012000	-0.490594000	C	5.274044000	1.524540000	0.120396000
N	-3.705176000	0.427370000	1.240247000	H	6.292701000	1.909863000	0.158346000
N	3.820707000	-0.204748000	0.995239000	C	4.419336000	2.166092000	-0.796304000
N	3.127931000	1.852991000	-0.956931000	C	6.192306000	-0.113777000	1.725028000
C	-4.511246000	-2.125767000	-0.174388000	H	6.172518000	0.343605000	2.727285000
C	-5.258643000	-1.365390000	0.741548000	H	7.141375000	0.168112000	1.250602000
H	-6.275080000	-1.711792000	0.923562000	H	6.167145000	-1.200457000	1.866516000
C	-4.918396000	-0.138348000	1.336151000	C	5.087928000	3.231057000	-1.643542000
C	-5.273237000	-3.236523000	-0.866427000	H	4.385557000	3.809936000	-2.250591000
H	-5.727401000	-2.842703000	-1.790459000	H	5.814704000	2.751560000	-2.318550000
H	-6.089346000	-3.597924000	-0.226566000	H	5.656630000	3.916212000	-0.997384000
H	-4.637421000	-4.079052000	-1.157125000	C	3.710157000	-1.454905000	1.719802000
C	-6.052351000	0.572710000	2.046362000	C	3.821840000	-2.672791000	0.995964000
H	-6.780614000	-0.158513000	2.422712000	C	3.682660000	-3.877526000	1.699244000
H	-6.579666000	1.226680000	1.334427000	H	3.766474000	-4.824277000	1.161933000
H	-5.711130000	1.205540000	2.872991000	C	3.444997000	-3.893848000	3.072301000
C	-2.600330000	-2.709286000	-1.491911000	H	3.335569000	-4.845333000	3.599089000
C	-1.934731000	-3.898276000	-1.091902000	C	3.352877000	-2.693136000	3.769131000
C	-1.337498000	-4.687893000	-2.084262000	H	3.171299000	-2.712128000	4.846373000
H	-0.825533000	-5.608683000	-1.796021000	C	3.484536000	-1.457149000	3.118956000
C	-1.376447000	-4.322870000	-3.427824000	C	4.157975000	-2.712335000	-0.496536000
H	-0.897588000	-4.952002000	-4.182633000	H	3.907233000	-1.727886000	-0.918214000
C	-2.028819000	-3.152035000	-3.802981000	C	3.345832000	-3.754792000	-1.281136000
H	-2.058675000	-2.870787000	-4.858515000	H	3.611188000	-4.786362000	-0.997914000
C	-2.655049000	-2.328008000	-2.856059000	H	3.549266000	-3.654346000	-2.359544000
C	-1.866477000	-4.370603000	0.363035000	H	2.264042000	-3.622010000	-1.133752000
H	-2.214040000	-3.545013000	1.000669000	C	5.666699000	-2.937536000	-0.721850000
C	-0.432725000	-4.708345000	0.806949000	H	6.279290000	-2.153501000	-0.253080000
H	-0.415257000	-4.941626000	1.883387000	H	5.900800000	-2.944894000	-1.799243000

H	0.251981000	-3.865370000	0.640485000	H	5.986171000	-3.905805000	-0.301685000
H	-0.034771000	-5.586917000	0.273073000	C	3.396594000	-0.179592000	3.953585000
C	-2.789714000	-5.578387000	0.621124000	H	3.560196000	0.674449000	3.279467000
H	-3.844403000	-5.357191000	0.401436000	C	2.005637000	-0.001071000	4.583186000
H	-2.727991000	-5.888947000	1.677050000	H	1.214856000	-0.025124000	3.821950000
H	-2.494802000	-6.442097000	0.002164000	H	1.944573000	0.961079000	5.117097000
C	-3.383215000	-1.075128000	-3.345316000	H	1.791078000	-0.800904000	5.311192000
H	-3.800367000	-0.562076000	-2.466126000	C	4.479769000	-0.126951000	5.048890000
C	-2.433376000	-0.085520000	-4.042619000	H	4.316230000	-0.903871000	5.813415000
H	-1.611203000	0.225028000	-3.381417000	H	4.458006000	0.847644000	5.563556000
H	-2.980214000	0.823253000	-4.343280000	H	5.492833000	-0.275294000	4.645180000
H	-1.992116000	-0.523175000	-4.953061000	C	2.354720000	2.549720000	-1.966669000
C	-4.562356000	-1.425932000	-4.273790000	C	2.265807000	2.002734000	-3.271307000
H	-4.213078000	-1.893296000	-5.208973000	C	1.505319000	2.688937000	-4.228936000
H	-5.121522000	-0.516489000	-4.548420000	H	1.426380000	2.282353000	-5.239918000
H	-5.267747000	-2.126522000	-3.800828000	C	0.855779000	3.881070000	-3.920634000
C	-3.554060000	1.776158000	1.749829000	H	0.270188000	4.401164000	-4.683146000
C	-3.036315000	1.972390000	3.057545000	C	0.956224000	4.407132000	-2.635363000
C	-2.949801000	3.284902000	3.541849000	H	0.444553000	5.342846000	-2.399604000
H	-2.562049000	3.461739000	4.545779000	C	1.692756000	3.759463000	-1.633703000
C	-3.335838000	4.375493000	2.764779000	C	2.998909000	0.727087000	-3.688276000
H	-3.253961000	5.389658000	3.164491000	H	3.417161000	0.268536000	-2.779851000
C	-3.814208000	4.168017000	1.475266000	C	2.066404000	-0.312364000	-4.332548000
H	-4.102499000	5.028149000	0.866151000	H	1.229869000	-0.576466000	-3.668944000
C	-3.939386000	2.876071000	0.941170000	H	2.623195000	-1.237765000	-4.553141000
C	-2.589461000	0.805000000	3.942370000	H	1.644854000	0.050473000	-5.284041000
H	-2.199272000	0.022910000	3.271998000	C	4.178238000	1.041047000	-4.630188000
C	-1.445621000	1.182357000	4.895003000	H	4.739109000	0.122740000	-4.870406000
H	-1.786830000	1.843477000	5.708918000	H	4.881550000	1.760390000	-4.184894000
H	-0.628946000	1.683071000	4.355670000	H	3.823510000	1.472956000	-5.580598000
H	-1.038586000	0.274835000	5.367052000	C	1.774770000	4.402743000	-0.247898000
C	-3.746724000	0.181356000	4.747229000	H	2.234333000	3.672974000	0.434617000
H	-4.233781000	0.934612000	5.389410000	C	0.389464000	4.745828000	0.326188000
H	-3.364598000	-0.619009000	5.401838000	H	-0.107838000	5.541023000	-0.253124000
H	-4.517555000	-0.265572000	4.104937000	H	0.486975000	5.106294000	1.362724000
C	-4.489213000	2.730670000	-0.480035000	H	-0.271490000	3.868326000	0.341289000
H	-4.543989000	1.657243000	-0.714119000	C	2.668307000	5.659066000	-0.255612000
C	-3.560701000	3.378780000	-1.523533000	H	3.689024000	5.444720000	-0.604290000
H	-3.474496000	4.465879000	-1.361733000	H	2.741679000	6.085474000	0.758317000
H	-3.961732000	3.226378000	-2.539543000	H	2.250018000	6.437878000	-0.914812000

Table S5.24. Optimized geometries of [(L^3Ga)(μ,$\eta^{2:1:1}$-P_4)(L^3Ni)] (**5a**)). XYZ coordinated in angstroms. BP86/def2-SVP level of theory.



P	-0.776735000	0.002816000	1.446504000	H	-0.812817000	2.873152000	-4.150792000
N	-3.700100000	1.491485000	-0.520349000	H	-0.822284000	4.474029000	-3.358967000
N	-3.702473000	-1.488399000	-0.516951000	Ni	2.524281000	-0.001258000	0.214350000
C	-3.253005000	-2.825645000	-0.199505000	N	3.791959000	-1.429192000	0.422714000
C	-4.985583000	1.281781000	-0.869495000	N	3.792791000	1.425328000	0.426387000
C	-3.443872000	-3.340264000	1.118031000	C	3.303996000	2.760723000	0.251585000
C	-2.595019000	-3.598971000	-1.203760000	C	5.104819000	-1.267847000	0.683503000
C	-2.979392000	-4.642194000	1.399445000	C	3.438504000	3.406410000	-1.014013000
H	-3.118057000	-5.053939000	2.411973000	C	2.663668000	3.421449000	1.345094000
C	-4.987614000	-1.277336000	-0.866536000	C	2.949152000	4.721392000	-1.152702000
C	-4.124926000	-2.542134000	2.234817000	H	3.047241000	5.234155000	-2.123441000
H	-4.450007000	-1.571291000	1.805590000	C	5.105481000	1.262514000	0.687206000
C	-2.157729000	-4.895649000	-0.864374000	C	4.046847000	2.684882000	-2.219602000
H	-1.649728000	-5.506443000	-1.626255000	H	4.574269000	1.787642000	-1.835121000
C	-2.345879000	-5.418685000	0.421563000	C	2.195755000	4.736936000	1.152326000
H	-1.991325000	-6.433130000	0.663172000	H	1.702242000	5.262160000	1.984989000

C	-5.546823000	0.002413000	-1.092930000
H	-6.600358000	0.002879000	-1.403770000
C	-5.932483000	2.460906000	-0.982375000
H	-5.432334000	3.365279000	-1.376609000
H	-6.797175000	2.207889000	-1.624724000
H	-6.326592000	2.727438000	0.021239000
C	-5.936448000	-2.455198000	-0.976694000
H	-6.329962000	-2.719677000	0.027694000
H	-6.801359000	-2.201881000	-1.618614000
H	-5.438037000	-3.360934000	-1.370031000
C	-2.385075000	-3.083288000	-2.631300000
H	-2.488617000	-1.977319000	-2.599794000
C	-0.976874000	-3.396435000	-3.174278000
H	-0.832854000	-4.483498000	-3.351600000
H	-0.818387000	-2.883767000	-4.145579000
H	-0.184697000	-3.056493000	-2.477936000
C	-3.147143000	-2.231610000	3.388259000
H	-2.251437000	-1.682832000	3.029442000
H	-3.640238000	-1.607701000	4.163480000
H	-2.794534000	-3.161980000	3.881740000
C	-5.381819000	-3.258042000	2.778285000
H	-5.119545000	-4.211098000	3.284507000
H	-5.902537000	-2.620782000	3.523796000
H	-6.107060000	-3.502399000	1.974777000
C	-3.461899000	-3.620500000	-3.601689000
H	-4.486526000	-3.323435000	-3.301357000
H	-3.288608000	-3.232635000	-4.627763000
H	-3.433165000	-4.730264000	-3.650955000
P	0.538541000	-1.149048000	-0.046748000
P	-0.419215000	-0.003805000	-1.792539000
P	0.540386000	1.146856000	-0.051541000
Ga	-2.363866000	0.000747000	-0.359319000
C	-2.971143000	4.647340000	1.390457000
H	-3.109323000	5.061283000	2.402153000
C	-3.438717000	3.346055000	1.111177000
C	-4.122742000	2.551839000	2.228934000
H	-4.450144000	1.581059000	1.801337000
C	-5.378192000	3.272141000	2.769979000
H	-6.101942000	3.517218000	1.965345000
H	-5.901428000	2.637560000	3.516019000
H	-5.113773000	4.225274000	3.274937000
C	-3.146893000	2.240899000	3.383903000
H	-2.792800000	3.171245000	3.876371000
H	-3.642231000	1.619275000	4.159534000
H	-2.251972000	1.689642000	3.026940000
C	-3.248303000	2.828515000	-0.205302000
C	-2.588280000	3.598554000	-1.210717000
C	-2.335171000	5.420462000	0.411501000
H	-1.978131000	6.434419000	0.651478000
C	-2.147902000	4.894725000	-0.873458000
H	-1.638157000	5.502915000	-1.636264000
C	-2.379493000	3.080043000	-2.637411000
H	-2.486752000	1.974477000	-2.604366000
C	-3.454116000	3.619552000	-3.608953000
H	-3.421055000	4.729098000	-3.660361000
H	-3.282225000	3.229050000	-4.634259000
H	-4.479947000	3.327115000	-3.308177000
C	-0.970043000	3.387699000	-3.180279000
H	-0.179331000	3.046048000	-2.483130000
C	2.341711000	5.390167000	-0.080551000
H	1.972812000	6.420595000	-0.208187000
C	5.712033000	-0.003035000	0.834469000
H	6.787521000	-0.003645000	1.058744000
C	6.019049000	-2.479815000	0.779978000
H	5.577535000	-3.292363000	1.389775000
H	6.997058000	-2.196795000	1.214001000
H	6.206581000	-2.913601000	-0.225419000
C	6.020167000	2.473770000	0.787980000
H	6.206764000	2.912078000	-0.215590000
H	6.998490000	2.188634000	1.219894000
H	5.579379000	3.283700000	1.401806000
C	2.484800000	2.715627000	2.692111000
H	2.494611000	1.625224000	2.468467000
C	1.141792000	3.040890000	3.371116000
H	1.097972000	4.091768000	3.730443000
H	0.993187000	2.387582000	4.256018000
H	0.287510000	2.878218000	2.683195000
C	2.938689000	2.179695000	-3.168241000
H	2.231252000	1.509394000	-2.637424000
H	3.371956000	1.610377000	-4.018267000
H	2.354383000	3.026411000	-3.587638000
C	5.076407000	3.540571000	-2.985013000
H	4.604632000	4.413982000	-3.484027000
H	5.565432000	2.938527000	-3.779706000
H	5.872088000	3.930238000	-2.315997000
C	3.655866000	2.992632000	3.660865000
H	4.625055000	2.649549000	3.248815000
H	3.497774000	2.462304000	4.624143000
H	3.742504000	4.078663000	3.881898000
C	2.943772000	-4.721676000	-1.161332000
H	3.040306000	-5.232870000	-2.133041000
C	3.434495000	-3.407367000	-1.020870000
C	4.041919000	-2.683819000	-2.225679000
H	4.573097000	-1.789452000	-1.839668000
C	5.066913000	-3.539951000	-2.996664000
H	5.862948000	-3.934423000	-2.330887000
H	5.555864000	-2.936529000	-3.790352000
H	4.591285000	-4.410080000	-3.497759000
C	2.932666000	-2.171862000	-3.169383000
H	2.344600000	-3.015322000	-3.590083000
H	3.365251000	-1.600811000	-4.018600000
H	2.228761000	-1.501339000	-2.634093000
C	3.301929000	-2.763860000	0.245989000
C	2.662265000	-3.425890000	1.339135000
C	2.336898000	-5.391741000	-0.089648000
H	1.966928000	-6.421616000	-0.218660000
C	2.192940000	-4.740592000	1.144586000
H	1.699842000	-5.266864000	1.976834000
C	2.485608000	-2.722006000	2.687461000
H	2.495894000	-1.631261000	2.465347000
C	3.657733000	-3.001302000	3.654257000
H	3.743320000	-4.087634000	3.874224000
H	3.501712000	-2.471615000	4.618223000
H	4.626759000	-2.659106000	3.241100000
C	1.143236000	-3.047106000	3.367795000
H	0.288112000	-2.882122000	2.681472000
H	0.996705000	-2.395347000	4.254187000
H	1.098715000	-4.098617000	3.725158000

5.5.6. References

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Preface

The following chapter has not been published until the submission of this thesis.

Authors

M. Haimerl, F. Spitzer, A. Y. Timoshkin, M. Seidl and M. Scheer

Author contribution

The main part of the manuscript was done by the first author (M. Haimerl). F. Spitzer performed the synthesis and characterization of compound **1a**, **2a**, **3b**, **4** and **5**, which was already part of his PhD thesis. M. Haimerl performed the synthesis and characterization of **1b**, **1c**, **2b**, **2c** and **3a**. Compound **2b** and **3a** were already part of the master thesis of M. Haimerl. The refinement of the structures was done by M. Seidl, he also checked all crystallographic files and data. A. Y. Timoshkin performed the DFT calculations and contributed the corresponding part in the paper and Supporting Information. M. Scheer supervised the research and revised the manuscript.

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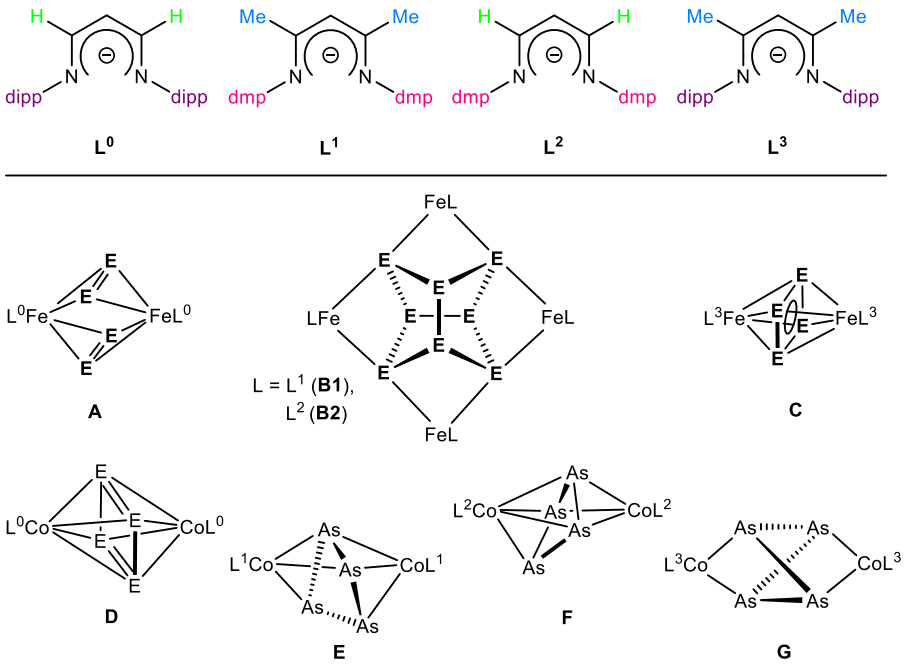
6. Reactivity of Cu(I) Nacnac Complexes Towards E_4, E_4S_3 (E = P, As), and red selenium

6. Reactivity of Cu(I) Nacnac Complexes Towards E_4, E_4S_3 (E = P, As) and red selenium

Abstract: *The nacnac Cu(I) compound [L^1Cu(MeCN)] (L^1 = [{N(C_6H_3Me-2,6)C(Me)}$_2$CH]$^-$) was reacted with E_4 (E_4 = P_4, As_4 and AsP_3) yielding the homobimetallic complexes [(L^1Cu)$_2$($\eta^{2:2}$-E_4)] (E_4 = P_4 (**1a**), As_4 (**1b**), AsP_3 (**1c**)) and the mononuclear complexes [L^1Cu(η^2-E_4)] (E_4 = P_4 (**2a**), As_4 (**2b**), AsP_3 (**2c**)), revealing neutral and intact side-on coordinated E_4 units. Furthermore, the reaction of [L^1Cu(MeCN)] with Se_{red} and E_4S_3 (E = P, As) afforded [(LCu)$_2$(μ,$\eta^{2:2}$-Se_2)] (L^1 = **3a**, L^3 = **3b**) and [(L^3Cu)$_2$(E_4S_3)] (E = P (**4**), As (**5**)). These complexes are examples of the coordination of group 11 metals with polypnictogen, chalcogen and mixed E15/Q16 compounds*

6.1. Introduction

The conversion of white phosphorus and yellow arsenic in the coordination sphere of transition metal or main group complexes is an active topic in current research.[1] In dependence of the ligand, the metal and the preparation conditions different E_n (E = P, As) ligand complexes are formed. Numerous research articles give insight into the stepwise degeneration of E_4 by successive bond cleavage or aggregation (n>4) of E_4 units.[1-2] In the case of *β*-diiminato ligands (nacnac) the aromatic flanking groups and backbone substituents play an important role to tune the properties of the resulting product. Recently, a systematic investigation of the *β*-diiminato ligand design of iron(I)[3] and cobalt(I)[4] complexes was reported which influences the reaction outcome towards white phosphorus and yellow arsenic. The steric and electronic properties of the ligand have a strong impact on the reactivity and the resulting structure of the complexes. Using the ligand L^0 (Scheme 6.1) *Driess et al*. synthesized the dinuclear iron complex [(L^0Fe)$_2$(μ,$\eta^{2:2}$-P_2)$_2$] (**A**, [{N($C_6H_3{}^iPr_2$-2,6)C(H)}$_2$CH]$^-$), which contains two anionic P_2^{2-} units.[3a] An analogues arsenic derivative has also been reported.[3c] By changing the aromatic flanking groups from dipp (2,6-diisopropylphenyl) to dmp (2,6-dimethylphenyl) groups, compound [(LFe)$_4$(μ,$\eta^{2:2:2:2}$-E_8)] (L = L^1 = [{N($C_6H_3Me_2$-2,6)C(Me)}$_2$CH]$^-$ (**B1**); L^2 = [{N($C_6H_3Me_2$-2,6)C(H)}$_2$CH]$^-$ (**B2**))[3b, 3c] could be obtained. These complexes show an E_8 unit which is coordinated by four iron(II) centers. Furthermore, by using the sterically most demanding ligand in this series - L^3 (L^3 = [{N($C_6H_3{}^iPr_2$-2,6)C(Me)}$_2$CH]$^-$) – under the same reaction conditions lead to the formation of [(L^3Fe)$_2$(μ,$\eta^{4:4}$-E_4)] (**C**)[3b, 3c] which contains an $[E_4]^{2-}$ unit. All in all, this demonstrate the impact of the ligand substitution pattern. A similar study with Co(I) nacnac complexes demonstrate for the phosphorus conversion that ligand design does not automatically influence the experimental outcome.[4] With all four ligands L^0 – L^3 a rectangular-shaped $[P_4]^0$ moiety (**D**) is stabilized by two {LCo} fragments.[4a,4b] Interestingly, a different outcome is realized by the reaction with yellow arsenic. Under ambient conditions, the dinuclear compounds **E**, **F** and **G** could be obtained. Each of them has a $[Co_2As_4]$ core, which is distinct octahedral (**E**), prismatic (**F**) or asterane-like (**G**) shaped.[4c,4d]



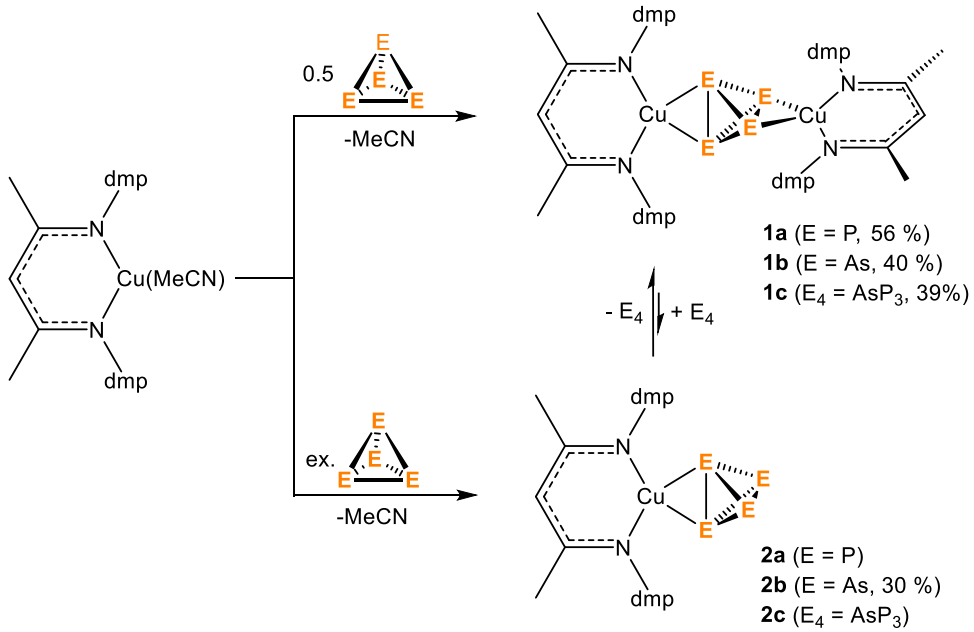
Scheme 6.1. Top: Set of *β*-diiminato ligands (L^0 – L^3) with different backbone substituents and flanking groups. Bottom: Selected E_n ligand complexes obtained by iron(I) and cobalt(I) complexes with E_4 (E = P, As).

Recently, we reported the synthesis and characterization of the first neutral and molecular complexes containing an intact E_4 tetrahedron, $[(L^3Cu)_2(\mu_2,\eta^{2:2}\text{-}E_4)]$ and $[L^3Cu(\eta^2\text{-}P_4)]$. Motivated by these studies about the impact of the ligand design towards the reaction outcome, the question arose if the E_4 structural motif in the case of Cu(I) nacnac could be affected in the same manner. Furthermore, we intend to investigate the reactivity of the interpnictogen compound AsP_3[5] towards Cu(I) nacnac complexes. This compound is closing the gap between white phosphorus and yellow arsenic, the coordination behavior of phosphorus and arsenic could be investigated at the same time. Besides the conversion of E_4, we were also interested in the activation of chalcogens and mixed group E15/Q16 (E = P, As; Q = S, Se) cage compounds with Cu(I) nacnac complexes. The reaction of chalcogens with some M(I) nacnac complexes were already reported.[6] Especially the activation of O_2 with Cu(I) nacnac complexes, in which the ligand design is responsibly for diverse peroxo and/or bis(μ-oxo)dicopper compounds.[7] To the best of our knowledge, there are no examples of the reaction of M(I) nacnac complexes with E_4Q_3. But in general, a different coordination behavior for E_4Q_3 is reported: There are compounds known in which one basal E-E bond is cleaved,[8] one basal E-atom is replaced by a metal fragment,[9] {LM} is coordinated to an intact E_4Q_3[10] cage or a fragmentation of the cage compound[11] take place. The question arose at what extend the E-E and E-Q bonds here are activated, opened up or still be intact. In the following we report the room temperature reactions of P_4, As_4, AsP_3, Se_{red}, P_4S_3 and As_4S_3 with [LCu(NCMe)] (L = L^1, L^3). These results in the formation of a series of dicopper compounds $[(L^1Cu)_2(\mu,\eta^{2:2}\text{-}E_4)]$ (E = P (**1a**), As (**1b**), AsP_3 (**1c**)) and mononuclear compounds $[L^1Cu(\eta^2\text{-}E_4)]$ (E = P (**2a**), As (**2b**), AsP_3

(**2c**)), and further the diselenium compounds [$(LCu)_2(\mu,\eta^{2:2}\text{-}Se_2)$] (L = L^1 (**3a**), L^3 (**3b**)] and the cage compounds [$(L^3Cu)_2(E_4S_3)$] (E = P (**4**), As (**5**)).

6.2. Results and Discussion

The reaction of [L^1Cu(MeCN)] with 0.5 eq of E_4 (E_4 = P_4, As_4, AsP_3) in toluene at room temperature leads to the quantitative formation of [$(L^1Cu)_2(\mu,\eta^{2:2}\text{-}E_4)$] (E = P (**1a**), As (**1b**), AsP_3 (**1c**)), in crystalline yields of 56 % (**1a**), 40 % (**1b**) and 39% (**1c**) (Scheme 6.2). Performing the reaction with an excess of E_4 leads to the formation of the neutral mononuclear compounds [$L^1Cu(\eta^2\text{-}E_4)$] (E = P (**2a**), As (**2b**), AsP_3 (**2c**)). **2b** is obtained as yellow air-sensitive solid in crystalline yields of 30 %, **2a** and **2c** were only synthesized in solution.[12]



Scheme 6.2. Reaction of E_4 with [L^1Cu(MeCN)]. (dmp = 2,6-dimethylphenyl)

The $^{31}P\{^1H\}$ NMR spectra at room temperature show a singlet at δ = -430 ppm for **1a** (C_6D_6) and broad singlets for **1c** (δ = -406 ppm, $\omega_{1/2}$ = 954 Hz, toluene-d_8), **2a** (δ = -479 ppm, $\omega_{1/2}$ = 2152 Hz, CD_2Cl_2) and **2c** (δ = -452 ppm, $\omega_{1/2}$ = 954 Hz, toluene-d_8). Dissolving compound **1c** at -80 °C and recording the $^{31}P\{^1H\}$ NMR spectrum at this temperature, a triplet (δ = -401 ppm, 1P, $^1J_{PP}$ = 183 Hz) and a doublet (δ = -410 ppm, 2P, $^1J_{PP}$ = 183 Hz) can be detected indicating a dynamic behavior of **1c** in solution at room temperature. Preparing a fresh solution of **2a** (CD_2Cl_2) and **2c** (toluene-d_8) at room temperature and cool it stepwise to 193 K (VT NMR spectra see Supporting Information) the broad signal splits for **2a** into two triplets centered at δ = −450 ppm ($P_{coordinated}$, 2P, $^1J_{PP}$ = 178 Hz) and −500 ppm ($P_{non\text{-}coordinated}$, 2P, $^1J_{PP}$ = 178 Hz), for **2c** the broad signal splits into a triplet at δ = −421 ppm ($P_{coordinated}$, $^1J_{PP}$ = 184 Hz) and a doublet at δ = −466 ppm ($P_{non\text{-}coordinated}$, $^1J_{PP}$ = 184 Hz) with an integral ratio of 1:2, respectively. This indicating that the dynamic

process is frozen at low temperature. The ^{1}H NMR spectrum of **1b** displays one set of signals for the ligand. Freshly dissolved **2b** was investigated by ^{1}H NMR spectroscopy (r.t., C_6D_6), which shows an equilibrium between the dinuclear (**1b**) and the mononuclear (**2b**) compound (Scheme 6.2). Dissolution at -70 °C (CD_2Cl_2) also leads to an equilibrium of **1b** and **2b** monitored by NMR spectroscopy. This shows that the partly disproportionation occurs even at low temperature. In the LIFDI-MS spectra of **1a**, **1b**, **1c** and **2b** the corresponding molecular ion peaks are detected. Computational studies indicate, that the gas phase reaction **1b** + As_4 = 2 **2b** is slightly endothermic at M06/def2-TZVPP level of theory but is exergonic due to the entropy increase. Values of equilibrium constants at 25 °C and -70 °C are 26 and 6, respectively, in agreement with the experimental observations.

The molecular structure of **1a**, **1b** and **1c** reveals a dinuclear copper complex, bridging an intact E_4 tetrahedron in a $\eta^{2:2}$ coordination mode (Figure 6.1). The arsenic atom in **1c** is disordered over all four pnictogen positions (ratio: 35:35:20:10). In **2b** the {L^1Cu} fragment is bonded in a η^2 fashion side-on to the As_4 tetrahedra (Figure 6.1), this complex is a rare example for a neutral, intact side-on coordinated As_4 unit. Some cationic complexes with one or two intact As_4 ligands are known which are used as transfer reagent for As_4 units.[13] In comparison to the previously reported compounds [(L^3Cu)$_2$(μ,$\eta^{2:2}$-E_4)] (E = P (**1a-L^3**), As (**1b-L^3**)) and [L^3Cu(μ,η^2-P_4)] (**2a-L^3**), no significant deviations are found in the bond distances.[14] The structural parameter of the L^1Cu compounds are summarized in table 6.1. To mention are the copper coordinated E-E bond lengths (**1a**: 2.3649(6) and 2.4566(6) Å, **1b**: 2.6575(3) and 2.6885(3) Å, **2b**: 2.6754(13) Å), which deviate from the ones in **1a-L^3** (2.4121(8) and 2.4286(9) Å) and **1b-L^3** (2.6491(8) Å), this is attributed to the different coordination geometry of the Cu centers ($Cu_{twist\text{-}angle}$ = N-Cu-N to E-Cu-E twist angle: **1a**: 16.27(4) and 41.87(4)°, **1a-L^3**: 10.15(6) and 17.40(6)°, **1b**: 29.63(5) and 5.16(5)°, **1b-L^3**: 2.69(15)°). Which is an effect of the different twisting angles of the {LCu} fragments (ϕ = plane to plane (CuNCCCN) twist angle = **1a**: 61.40(4)°, **1a-L^3**: 82.98(6)°, **1b** 61.09(6)°, **1b-L^3**: 83.8(2)°). Wiberg Bond Indices (WBI) of the copper coordinated E-E bonds in **1a**-**2b** are 0.60-0.69 and non-coordinated E-E bonds are 0.93-1.00. These values are in agreement with a weakening of the bonds through coordination. Recently we investigated the reactivity of [L^1Cu(NCMe)] towards polypnictogen complexes, which show also an elongation of the coordinated E-E bonds (P: between 2.2100(10) and 2.3387(9) Å; As: between 2.4039(6) and 2.5625(3) Å) but no bond cleavage.[15]

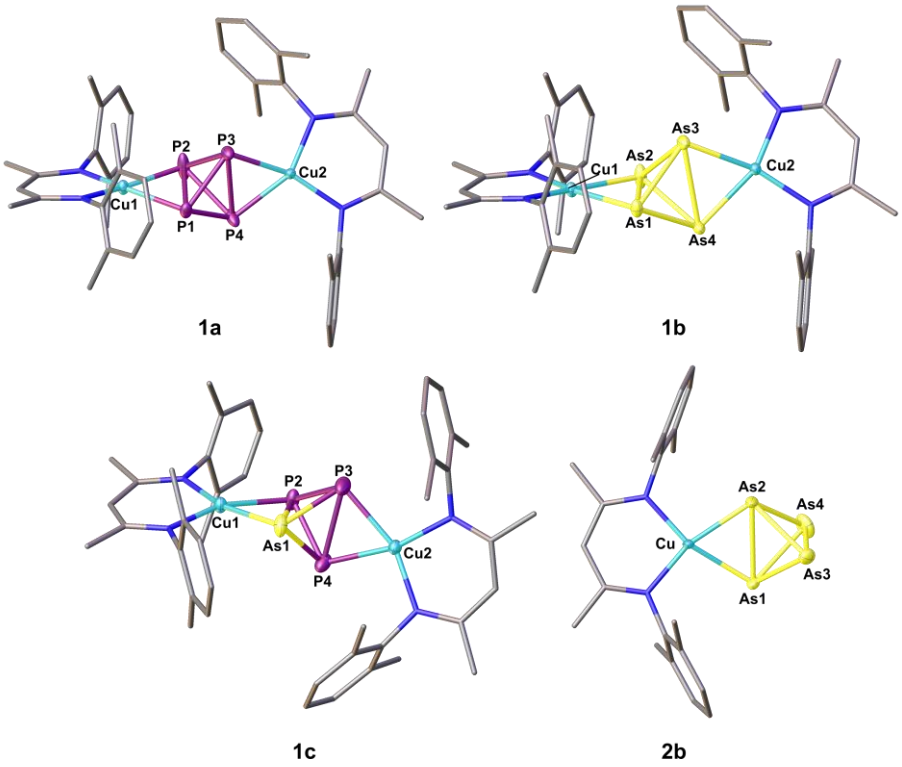


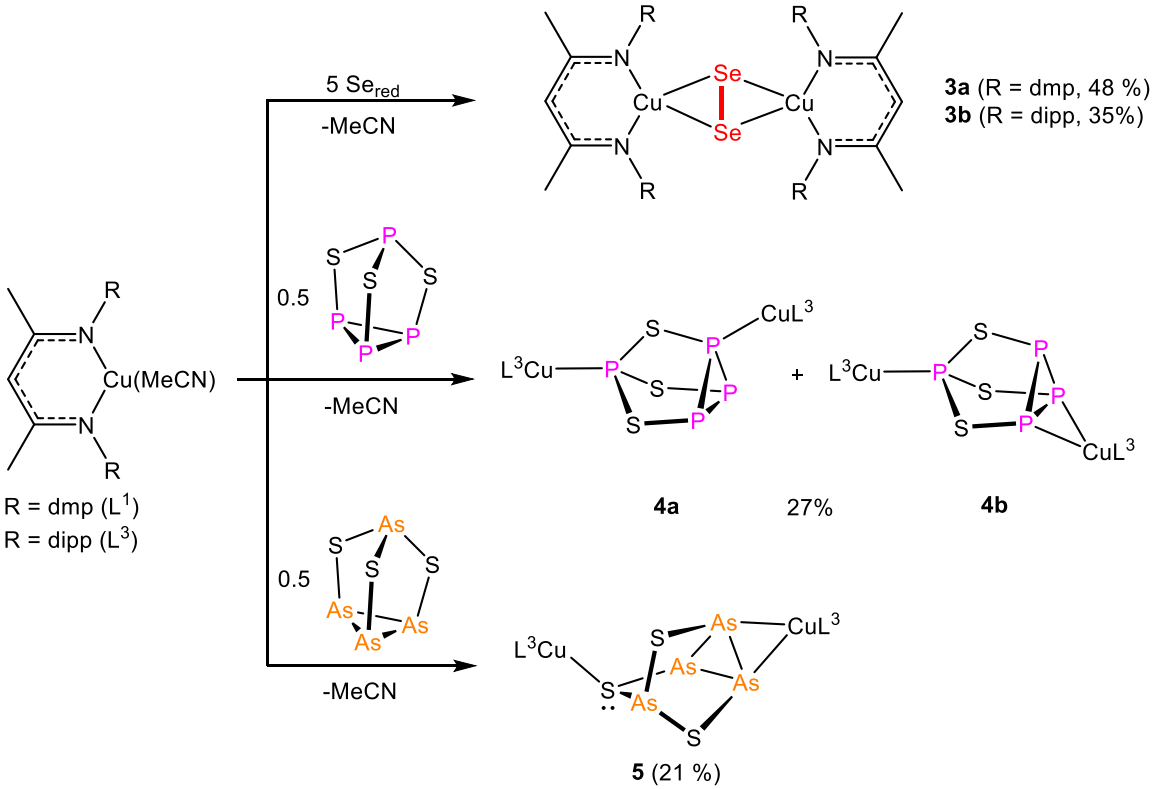
Figure 6.1. Molecular structure of **1a**, **1b**, **1c** and **2b** in the solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms are omitted for clarity.

Table 6.1. Comparison of the structural parameters of **1a**, **1b**, **1c** and **2b**. Cu $_{twist\_angle}$ = N-Cu-N to E-Cu-E twist angle, ϕ = plane to plane (CuNCCCN) twist angle.

Compound	**1a**	**1b**	**1c**	**2b**[14]
d(Cu···Cu)/ [Å]	5.1646(4)	5.3835(4)	5.2244(4)	-
d(E-E)/ [Å]	2.1917(7) – 2.2091(8)	2.4321(4) – 2.4510(4)	2.146(12) – 2.466(10)	2.3946(16)– 2.4322(14)
d(E-E)/ [Å] coordinated	2.3649(6) 2.4566(6)	2.6575(3) 2.6885(3)	2.429(11)- 2.625(10)	2.6754(13)
d(Cu-E)/ [Å]	2.2408(5)– 2.2750(5)	2.3551(4)– 2.3899(4)	2.288(2)- 2.333(6)	2.3645(14) 2.3769(14)
Cu $_{twist\_angel}$/ [°]	16.27(4) 41.87(4)	29.63(5) 174.84(5)	3.3(3) – 14.87(19)	24.91(14)
Φ [°]	61.40(4)	61.09(6)	116.12(5)	-

In order to investigate if the reactivity of [LCu(MeCN)] (L = L^1, L^3) can be extended to chalcogens and mixed cage compounds, [LCu(NCMe)] was reacted with red selenium and E_4S_3 (E = P, As). The reaction of [LCu(NCMe)] with an excess of red selenium in toluene at room temperature leads to the selective formation of compound [$(LCu)_2(\mu,\eta^{2:2}\text{-}Se_2)$]

(L^1 = **3a**, L^3 = **3b**, Scheme 6.3), which are isolated as green air-sensitive solids in crystalline yields of 48 % (**3a**) and 35 % (**3b**). Compound **3** was formed by fragmentation of the Se_8 rings into Se_2 units. Performing the reaction of [L^3Cu(NCMe)] with 0.5 equivalent of E_4S_3 at room temperature in toluene leads to the formation of [(L^3Cu)$_2$(E_4S_3)] (E = P (**4**), As (**5**), Scheme 6.3), which are isolated as air sensitive yellow (**4**) or red (**5**) solids in crystalline yields of 27 % (**4**) and 21 % (**5**).



Scheme 6.3. Reaction of [LCu(MeCN)] with red selenium and E_4S_3.

The formation of **3a** and **3b** are quantitative, which was proven by ^{1}H NMR spectroscopy, for which one set of signals for the nacnac ligand is found. The ^{77}Se NMR spectrum displays a single, sharp peak at δ = 1132 ppm (**3a**) and 1246 ppm (**3b**), respectively, which indicates that the two selenium atoms are chemically and magnetically equivalent. At room temperature, the ^{31}P{^{1}H} NMR spectrum of **4** in toluene-d_8 shows two broad signals at δ = 71 ppm ($\omega_{1/2}$ = 166 Hz) and -125 ppm ($\omega_{1/2}$ = 244 Hz) with an integral ratio of 1:3 for the apical and basal phosphorus atoms of the intact P_4S_3 unit (^{31}P{^{1}H} NMR of P_4S_3 in toluene-d_8: δ = 66 ppm (q, $^2J_{PP}$ = 70 Hz), -125 ppm (d, $^2J_{PP}$ = 71 Hz)). Furthermore, the composition of **3a**, **3b** and **4** were proofed by elemental analysis and the LIFDI mass spectrometer shows the molecular ion peak of **3a**, **3b**, **4** and **5**.

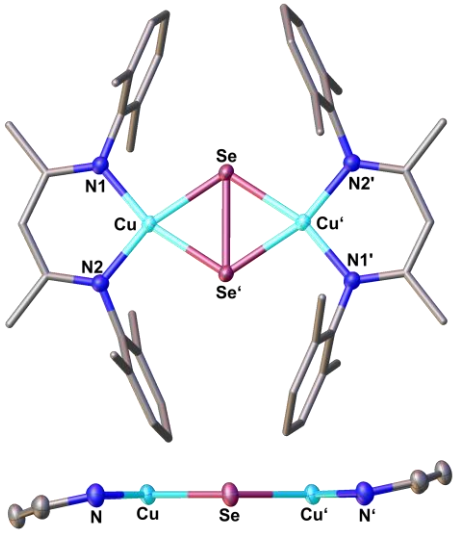


Figure 6.2. Top: Molecular structure of **3a** in the solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms are omitted for clarity. Bottom: side view presentation of **3a**, dipp groups are omitted for clarity.

The molecular structure of **3a** (Figure 6.2) and **3b** reveals a dinuclear centrosymmetric complex in which a Se_2 ligand is η^2 coordinated by two {LCu} fragments (Figure 6.2, just **3a** is depicted). The Cu···Cu distance is 3.8848(7) Å for **3a** and 3.9849(7) Å for **3b**, respectively, which is in a non-bonding area (covalent radius of Cu: 1.12 Å[17]; van der Waal radius of Cu: 1.40 Å[18]). The Cu-Se distances are 2.3075(3) and 2.3070(3) Å for **3a** and 2.3350(3) and 2.3441(3) Å for **3b**. The central $[Cu_2Se_2]$ core is planar for both compounds and the copper atoms are coordinated in a square-planar coordination mode. The overall complex is folded by 12.62(17)° (**3a**) and 10.04(10)° (**3b**) (Figure 6.2, bottom). Interestingly, the Se-Se bond distance is 2.4910(4) Å for **3a** and 2.4527(4) Å for **3b**, respectively, which is longer than the values for a Se-Se single bond (e.g. α-Se_8: 2.33 Å[18] or H_2Se_2: 2.346 Å[17]) or a Se=Se double bond (2.166 Å[19]). The selenide compound $[(CpNiSePh)_2]$[20] possess a Se···Se distance of 3.292(1) Å, this excludes any bonding interaction and is elongated in comparison to the bond distances found in **3** (2.4910(4) Å (**3a**) and 2.4527(4) Å (**3b**)). A Se-Se distance which is also longer than those found in **3** was reported for the $[Se_2]^{3-}$ unit in $[(({}^{i}Pr_4C_5H)Ni)_2(\mu\text{-}Se_2)]$ (2.915(2) Å).[21] The structural related compound $[(L^3Ni)_2(\mu,\eta^{2:2}\text{-}Se_2)]$ (**H**),[6c] is described as a $[Se_2]^{2-}$ unit with a Se-Se bond distance of 2.3304(6) Å which is shorter than those found in **3**. The different bond distances could be explained by the geometry of **H**, which is bend by approximately 134° along the Se-Se edge. A Se-Se distance which is comparable to **3** is found in $[K(18\text{-crown-}6)]_2(Se_2)\cdot en$[22] (en = ethylenediamine), this compound contain a $[Se_2]^{2-}$ unit (2.4063(4) Å) and is $\mu,\eta^{2:2}$ coordinated. Optimized Se-Se distances in **3a** and **3b** are 2.45 and 2.43 Å with WBI of 0.93 and 0.96, respectively which is close to single bond in gaseous Se_2^{2-} (2.54 Å, WBI 1.01), although Mulliken partial charges on Se atoms are only slightly negative.

The molecular structure of **4** and **5** are displaying a dinuclear copper complex coordinating an intact E_4S_3 unit. In **4** the P_4S_3 ligand is disordered over two positions in a ratio of 93:7, the major isomer (**4a**) is η^1-coordinated to one basal and the apical phosphorus atom, each, the minor isomer (**4b**) shows a η^1-coordination to the apical phosphorus atom and a η^2-coordination to two basal phosphorus atoms (Figure 6.3).

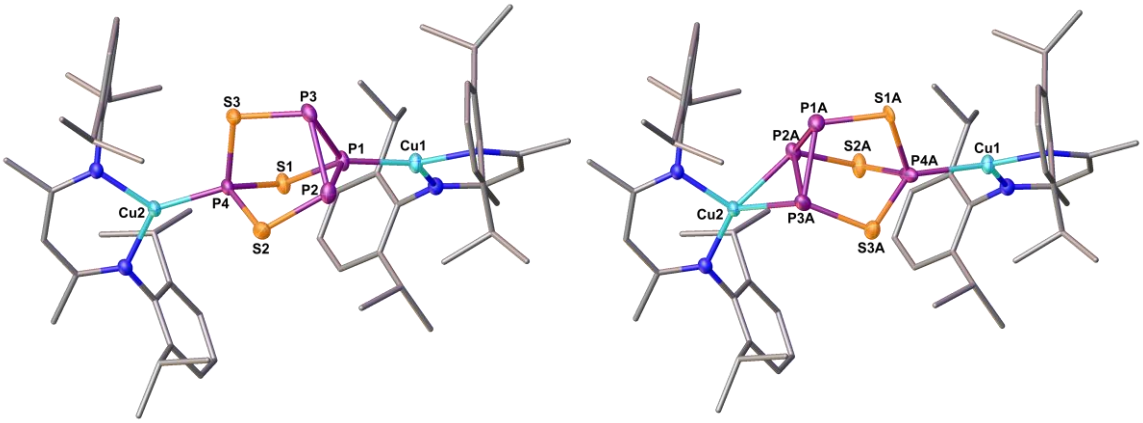


Figure 6.3. Molecular structure of **4** in the solid state. Right: $\mu,\eta^{1:1}$-coordination mode, major isomer (93%), left: $\mu,\eta^{2:1}$-coordination mode, minor isomer (7%). Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms are omitted for clarity.

The As_4S_3 ligand in **5**[23] (Figure 6.4) exhibit a disorder over two positions in a ratio of 65:35. The As_4S_3 unit is η^2-coordinated to two basal arsenic atoms and η^1-coordinated to the sulfur atom whose basal arsenic atom is not coordinated by a $\{L^3Cu\}$ fragment. This is due to the fact that sulfur is more electronegative than arsenic (S: χ_P = 2.64; As: χ_P = 2.25).[24]

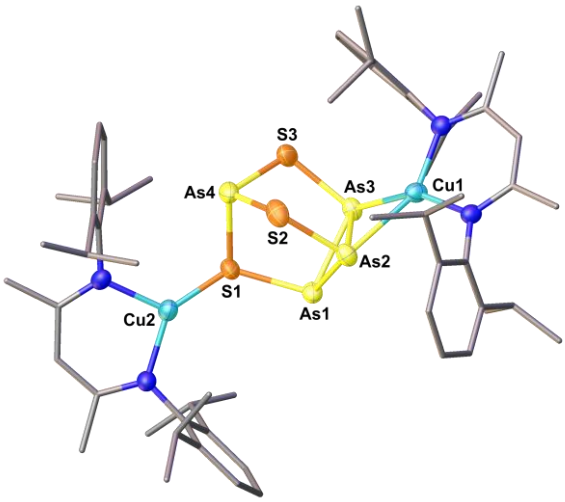


Figure 6.4. Molecular structure of **5** in the solid state.

The Cu···Cu distances are 7.1974(4) Å for **4** and 7.2197(6) Å for **5**, respectively. The E-E and E-Q bond distances are in the range of an E_4S_3[25] molecule (Table 6.2), expect from the basal η^2-coordinated E-E bond distance which are elongated to 2.404(9) Å (**4b**), 2.7273(7) Å (**5a**) and 2.7801(13) Å (**5b**), respectively. This bond elongation is reflected in

the smaller WBI values for these bonds (0.74 and 0.60 in optimized **4b** and **5**), but the overall structure of the E_4S_3 moiety is only slightly affected by the complexation.

Table 6.2. Comparison of structural parameters in **4**, **5** and E_4S_3 (E = P, As). ϕ = plane to plane (CuNCCCN) twist angle.

Compound	**4a** (93%)	**4b** (7%)	**5** (65%)	**5** (35%)	$\mathbf{P_4S_3}$[23a]	$\mathbf{As_4S_3}$[23b]
$d(E_{basal}\text{-}E_{basal})$/ [Å]	2.2296(16) 2.230(3) 2.257(2)	2.24(3) 2.26(3) 2.404(9)	2.4573(7) 2.4637(8) 2.7273(7)	2.4608(14) 2.4538(13) 2.7801(13)	2.240 2.246	2.460(7) 2.480(7)
$d(E_{apical}\text{-}S)$/ [Å]	2.0950(9) 2.0965(7) 2.101(2)	2.077(19) 2.104(11) 2.14(4)	2.2147(15) 2.2298(13) 2.2579(13)	2.223(3) 2.223(3) 2.260(2)	2.091 2.096	2.230(8) 2.234(16)
$d(E_{basal}\text{-}S)$/ [Å]	2.0927(7) 2.091(3) 2.0975(16)	2.04(4) 2.090(9) 2.104(11)	2.2099(13) 2.2322(16) 2.2379(13)	2.221(3) 2.235(2) 2.209(3)	2.089 2.097	2.218(10) 2.221(12)
$d(Cu\text{-}E_{apical})$/ [Å]	2.1048(5)	2.34(2)	-	-	-	-
$d(Cu\text{-}E_{basal})$/ [Å]	2.0977(17)	2.336(6) 2.428(7)	2.3700(6) 2.5208(7)	2.3933(10) 2.5820(10)	-	-
$d(Cu\text{-}S_{coord})$/ [Å]	-	-	2.0812(12)	2.023(2)	-	-
d(Cu···Cu)/ [Å]	7.1974(4)		7.2197(6)		-	-
Φ/ [°]	48.59(5)		42.78(8)		-	-

6.3. Conclusion

In summary, we report the synthesis of the dinuclear and mononuclear complexes $[(L^1Cu)_2(\mu,\eta^{2:2}\text{-}E_4)]$ (E = P (**1a**), As (**1b**), AsP_3 (**1c**)) and $[L^1Cu(\eta^2\text{-}E_4)]$ (E = P (**2a**), As (**2b**), AsP_3 (**2c**)). These complexes contain rare examples of intact, neutral η^2 coordinated E_4 tetrahedra. There dynamic behavior in solution was investigated by variable-temperature NMR spectroscopy. The integrity of the copper coordinated E-E bonds was elucidated by DFT calculations. Furthermore, the homodinuclear copper compounds $[(LCu)_2(\mu,\eta^{2:2}\text{-}Se_2)]$ (L^1 = **3a**, L^3 = **3b**) and $[(L^3Cu)_2(E_4S_3)]$ (E = P (**4**), As (**5**)) were synthesized, representing rare examples of group 11 complexes coordinating to chalcogens and mixed cage compounds. The latter show a coordination of copper compounds towards intact E_4S_3 cage units.

6.4. References

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6.5. Supporting Information

6.5.1. Synthesis and Characterization

General Remarks

All manipulations were performed with rigorous exclusion of oxygen and moisture using standard Schlenk techniques on a dual manifold Schlenk line with Argon or N_2 inert gas or glove box filled with nitrogen containing a high-capacity recirculator (<0.1 ppm O_2). Traces of oxygen and moisture in the inert gas were removed by passing it through a drying column filled with Cu/$MgSO_4$ catalyst as well as, concentrated H_2SO_4 and orange gel, respectively.

All solvents were degassed and purified by standard procedures. All NMR spectra have been recorded using deuterated d_6-benzene, CD_2Cl_2 or toluene-d_8 that were dried (over Na/K or CaH_2), refluxed for three hours and then distilled under inert atmosphere.

Characterization methods

Mass spectrometry was performed using a Jeol AccuTOF GCX LIFDI mass spectrometer by the MS department of the University of Regensburg. The compounds were dissolved in the corresponding solvent in a glove box under N_2 atmosphere. The observed fragments were assigned according to the mass/charge (m/z) ratio and the corresponding isotope pattern. Elemental analysis (CHN) were performed by the department of central analyses of the University of Regensburg on a Vario micro cube and a MT5 micro scale device. The compounds were filled in tin capsules in a glove box under N_2 atmosphere.

^1H and ^{31}P NMR spectra were recorded on a Bruker Avance III HD 400 (^1H: 400.130 MHz, ^{31}P: 161.976 MHz) spectrometer at the NMR department of the University of Regensburg. The chemical shifts are reported in ppm relative to external TMS (^1H) or 85 % H_3PO_4 (^{31}P). The chemical shifts δ are given in parts per million [ppm] and coupling constants J in [Hz].

Starting Material

The compounds [LCu(MeCN)] (L = L^1, L^3)[1], P_4, As_4[2], AsP_3[3], P_4S_3[4], As_4S_3[5] were prepared according to literature procedures.

6.5.1.1. Synthesis of $[(L^1Cu)_2(\mu,\eta^{2:2}\text{-}P_4)]$ (**1a**)

30 mg (0.24 mmol, 0.5 eq) P_4 were dissolved in 10 mL toluene. The colourless solution was transferred into a yellow solution of 213 mg (0.52 mmol, 1 eq, 10 mL toluene) $[L^1Cu(MeCN)]$. The mixture was stirred at room temperature for 35 minutes and the colour change from yellow to red was observed. The solvent was removed in vacuum, the orange solid was dissolved in 5 mL ^{n}hexane and filtered over diatomaceous earth. The intense reddish-orange filtrate was stored at + 8 °C for 2 days to yield crystalline orange blocks.

Crystalline Yield: 125.0 mg (0.14 mmol, 56 %)

^{1}H NMR (400 MHz, CD_2Cl_2, 300 K): δ [ppm] = 7.10 (d, $^3J_{HH}$ = 7 Hz, 8H, *d*), 6.96 (t, $^3J_{HH}$ = 7 Hz, 4H, *e*), 4.79 (s, 2H, *a*), 1.94 (s, 24H, *c*), 1.60 (s, 12H, *b*).

^{1}H NMR (400 MHz, CD_2Cl_2, 193 K): δ [ppm] = 7.11 (d, $^3J_{HH}$ = 7 Hz, 8H, *d*), 6.97 (t, $^3J_{HH}$ = 7 Hz, 4H, *e*), 4.79 (s, 2H, *a*), 1.83 (s, 24H, *c*), 1.53 (s, 12H, *b*). Assignment according to Figure S6.1.

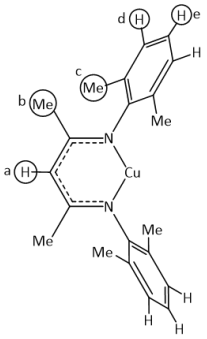


Figure S6.1. $[L^1Cu]$

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 300 K): δ [ppm] = −430.3 (s, *P*).

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 193 K): δ [ppm] = −431.4 (s, *P*). Measured range: 600 to −600 ppm.

Elemental analysis for $C_{42}H_{50}Cu_2N_4P_4$**:** C 58.53, H 5.85, N 6.50; found [%]: C 58.81, H 6.02, N 6.39.

LIFDI-MS (toluene): m/z (%): 860.2 (78%, $[M]^+$), 770.3 (5, $[(L^1Cu)_2(OH)_2]^+$), 736.3 (100, $[L^1Cu]_2^+$), 492.0 (9, $[(L^1Cu)P_4]^+$).

6.5.1.2. Synthesis of $[(L^1Cu)_2(\mu,\eta^{2:2}\text{-}As_4)]$ (**1b**)

All preparations were performed *under exclusion of light*. 220 mg (0.5 mmol) $[L^1Cu(MeCN)]$ were dissolved in 10 mL toluene. The yellow solution was transferred into a freshly prepared solution of As_4 in toluene. The mixture was stirred at room temperature over night. The solvent was removed in vacuum and the orange residue was stored at least over night to ensure the degradation of the excess of unreacted As_4 into As_{grey}. After dissolving the orange solid in 20 mL ^{n}hexane, the solution was filtered over diatomaceous earth to remove the insoluble As_{grey} and stored at + 4 °C for 4 days to yield yellow needle-shaped crystals of **1b**.

Crystalline yield: 110 mg (0.1 mmol, 40 %)

^{1}H NMR (C_6D_6, 300 K): δ [ppm] = 7.03 ppm (d, 8H, $^3J_{HH}$ = 7 Hz, *d*), 6.89 ppm (t, 4H, $^3J_{HH}$ = 7 Hz, *e*), 4.85 ppm (s, 2H, *a*), 1.97 (s, 24H, *c*), 1.59 (s, 12H, *b*). Assignment according to Figure S6.1.

LIFDI-MS (toluene): m/z (%) = 1037.87 (65.94, [M$^+$]), 736.1 (100, [L^{1}Cu]$_2^+$).

6.5.1.3. Synthesis of [(L^{1}Cu)$_2$(μ,η$^{2:2}$-AsP$_3$)] (**1c**)

40 mg (0.1 mmol, 1 eq) [L^{1}Cu(MeCN)] and 8.2 mg (0.05 mmol, 0.5 eq) AsP_3 were dissolved in 1 mL toluene. The red solution was stirred at room temperature for 12 hours under exclusion of light. The mixture was filtrated and was stored at -30 °C for 4 days to yield crystalline orange blocks, suited for X-Ray analysis.

Crystalline Yield: 17 mg (0.02 mmol, 39 %)

^{1}H NMR (C_6D_6, 300 K): δ [ppm] = 7.04 ppm (d, 8H, $^3J_{HH}$ = 7Hz, *d*), 6.92 ppm (t, 4H, $^3J_{HH}$ = 7Hz *e*), 4.85 ppm (s, 2H, *a*), 1.99 ppm (s, 24H, *c*), 1.59 (s, 12H, *b*).

^{1}H NMR (tol-d_8, 193 K): δ [ppm] = 6.93 (m, 6H, *d*+*e*), 4.83 (s, 2H, *a*), 1.95 (d, 24H, $^3J_{HH}$ = 46 Hz, *c*), 1.56 (d, 12H, $^3J_{HH}$ = 17 Hz, *b*). Assignment according to Figure S6.1.

^{31}P{^{1}H} NMR (C_6D_6, 300 K): δ [ppm] = -406.2 ppm (b, 3P). Measured range: 500 ppm to -600 ppm.

^{31}P{^{1}H} NMR (tol-d_8, 193 K): δ [ppm] = -400.5 ppm (t, 1P, $^1J_{PP}$ = 183 Hz), -410.3 ppm (d, 2P, $^1J_{PP}$ = 183 Hz).

^{31}P{^{1}H} NMR (tol-d_8, 300 K): δ [ppm] = -406.0 ppm (b, 3P).

LIFDI-MS (toluene): m/z (%) = 904.11 (41.41, [M]$^+$), 736.30 (100, [LCu]$_2$).

6.5.1.4. Synthesis of [L^{1}Cu(η^2-P$_4$)] (**2a**)

18 mg (0.021 mmol, 1 eq) of **1a** and 9 mg (0.073 mmol, 3.5 eq) P_4 were stirred in 1 mL CD_2Cl_2. The colour of the reaction mixtures turned bright yellow. The reaction was monitored by ^{31}P NMR spectroscopy and shows a total conversion from **1a** to **2a**.

^{1}H NMR (CD_2Cl_2, 300 K): δ [ppm] = *δ* [ppm] = 7.15 (d, $^3J_{HH}$ = 7 Hz, 4H, *d*), 6.96 (t, $^3J_{HH}$ = 7 Hz, 2H, *e*), 4.89 (s, 1H, *a*), 2.07 (s, 12H, *c*), 1.69 (s, 6H, *b*).

^{1}H NMR (CD_2Cl_2, 193 K): *δ* [ppm] = 7.13 (d, $^3J_{HH}$ = 7 Hz, 4H, *d*), 6.94 (t, $^3J_{HH}$ = 7 Hz, 2H, *e*), 4.88 (s, 1H, *a*), 1.95 (s, 12H, *c*), 1.61 (s, 6H, *b*). Assignment according to Figure S6.1.

^{31}P{^{1}H} NMR (CD_2Cl_2, 300 K). *δ* [ppm] = −479.19 (s, $\omega_{1/2}$ = 2152 Hz).

^{31}P NMR (CD_2Cl_2, 300 K): δ [ppm] = −478.97 (s, $\omega_{1/2}$ = 2153 Hz).

^{31}P{^{1}H} NMR (CD_2Cl_2, 193 K): δ [ppm] = −449.63 (t, 2P, $^1J_{PP}$ = 178 Hz, η^2-*P2*), −499.62 (t, 2P, $^1J_{PP}$ = 178 Hz, *P2*). Contamination with $P_{4,solv}$ and precipitation of $P_{4,solid}$ (vide Figure S6.9).

6.5.1.5. Synthesis of [L^{1}Cu(η^2-As$_4$)] (**2b**)

All preparations were performed *under exclusion of light*. This synthesis was very challenging. 190 mg (0.46 mmol) [L^{1}Cu(NCMe)] were dissolved in 10 mL toluene. The yellow solution was transferred into a freshly prepared solution of As_4 in toluene, with great excess of As_4. The mixture was stirred at room temperature for 40 minutes. The solvent was removed in vacuum and the orange residue was stored at least over night to ensure the degradation of the excess of unreacted As_4 into As_{grey}. After dissolving the orange solid in 20 mL ^{n}hexane, the solution was filtered over diatomaceous earth to remove the insoluble As_{grey} and concentrated to a volume of 15 mL. The orange solution was stored at -30 °C for 11 days to yield yellow needle-shaped crystals of **2b**.

Crystalline yield: 72 mg (0.07 mmol, 30 %)

^{1}H NMR (400 MHz, CD_2Cl_2, 203 K) δ [ppm] = 7.16 (d, 4H, $^3J_{HH}$ = 8 Hz, *d*), 6.94 (m, *e*), 4.88 (s, 1H, *a*), 1.97 (s, 12H, *c*), 1.63 (s, 6H, *b*), δ [ppm] (**1b**) =7.11 (d, 8H, $^3J_{HH}$ = 8 Hz, *d*), 6.94 (m, *e*), 4.77 (s, 2H, *a*), 1.83 (s, 24H, *c*), 1.54 (s, 12H, *b*). Assignment according to Figure S6.1.

EPR silent for r.t. and 77 K.

LIFDI-MS (toluene): m/z (%) = 1035.89(100, $[(LCu)_2As_4]^+$), 736.24 (40.3, $[(LCu)_2]^+$), 667.77 (4.8, $[(LCu)As_4]^+$).

6.5.1.6. [L^{1}Cu(η^2-AsP$_3$)] (**2c**)

15 mg of [L^{1}Cu(MeCN)] (0.04 mmol, 1 eq) and 6.5 mg of AsP_3 (0.04 mmol, 1.1 eq) were dissolved 0.7 mL toluene-d_8. The colour of the reaction mixture turned orange. The reaction was monitored by ^{31}P{^{1}H} NMR spectroscopy at different temperatures.

^{31}P{^{1}H} NMR (toluene-d_8, 300 K): δ [ppm] = -452.3 ppm (br).

^{31}P{^{1}H} NMR (toluene-d_8, 197 K): δ [ppm] = -420.6 ppm (t, 1P, $^1J_{PP}$ = 184 Hz), -465.9 ppm (d, 2P, $^1J_{PP}$ = 184 Hz).

6.5.1.7. $[(L^1Cu)_2(\mu,\eta^{2:2}\text{-}Se_2)]$ (**3a**)

A solution of 150 mg (0.37 mmol) $[L^1Cu(MeCN)]$ in 7 mL toluene was added to a slurry of 147 mg (1.8 mmol, 5 eq) Se_{red} in 5 mL toluene. The reaction mixture was stirred for one hour at room temperature and filtered over diatomaceous earth. The solvent was reduced to 7 mL. Storing the solution for one day at 4 °C, leads to the formation of crystalline green blocks, suited for X-Ray analysis.

Crystalline Yields: 78 mg (0.09 mmol, 48 %)

^{1}H NMR (400 MHz, C_6D_6, 300 K): δ [ppm] = 6.92 – 6.98 (m, 12H, *d* + *e*), 4.82 (s, 2H, *a*), 2.05 (s, 24H, *c*), 1.42 (s, 12H, *b*). Assignment according to Figure S6.1.

^{77}Se NMR (162 MHz, C_6D_6, 300K): δ [ppm] = 1132 (s)

Measured range: 3000 to -600 ppm.

^{1}H NMR (Evans-method, C_6D_6, 300K): No solvent shift was detected.

EPR: silent at r.t. and 77K.

Elemental analysis for $C_{42}H_{50}N_4Cu_2Se_2$: C56.31, H 5.63, N 6.25; found [%]: C56.71, H 5.47, N 6.32.

LIFDI-MS (toluene): m/z (%) = 896.1 (100, $[M]^+$).

6.5.1.8. $[(L^3Cu)_2(\mu,\eta^{2:2}\text{-}Se_2)]$ (**3b**)

A solution of 100 mg (0.192 mmol) $[L^3Cu(MeCN)]$ in 5 mL toluene was added to a slurry of 76 mg (0.962 mmol, 5 eq) Se_{red} in 5 mL toluene. The reaction mixture was stirred for 20 hours at room temperature and filtered over diatomaceous earth. The solvent was reduced to 7 mL. Storing the solution for one day at -30 °C, leads to the formation of crystalline green blocks, suited for X-Ray analysis.

Crystalline yields: 38 mg (0.034 mmol, 35 %)

^{1}H NMR (400 MHz, C_6D_6, 300K): δ [ppm] = 7.13 (t, $^3J_{HH}$ = 7.6 Hz, 4H, *e*), 7.01 (d, $^3J_{HH}$ = 7.6 Hz, 8H, *d*), 4.90 (s, 2H, *a*), 3.11 (sept, $^3J_{HH}$ = 6.8 Hz, 8H, *f*), 1.58 (s, 12H, *b*), 1.23 (d, $^3J_{HH}$ = 6.7 Hz, 24H, *c*), 1.11 (d, $^3J_{HH}$ = 6.7 Hz, 24H, *c*). Assignment according to Figure S6.2.

^{77}Se{^{1}H} NMR (76 MHz, C_6D_6, 300K): δ [ppm] = 1246 (s)

Measured range: 3000 to -600 ppm.

EPR: silent at r.t. and 77K.

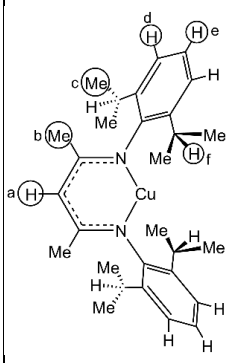


Figure S6.2. $[L^3Cu]$

Elemental analysis for $C_{58}H_{82}N_4Cu_2Se_2$: C 62.18, H 7.38, N 5.00; found [%]: C62.58, H 7.20, N 4.86.

LIFDI-MS (toluene): m/z (%) = 1120.6 (100, $[M]^+$).

6.5.1.9. $[(L^3Cu)_2(P_4S_3)]$ (**4**)

A solution of 150 mg (0.29 mmol) $[L^3Cu(NCMe)]$ in 5 mL toluene was added to a slurry of 33 mg (0.15 mmol) P_4S_3 in 4 mL toluene. The colour of the reaction solution turned from yellow to orange. The reaction solution was stirred for approximately 16 hours, filtered over diatomaceous earth and the solvent was removed. The solid was redissolved in n-hexane and stored at -30 °C to yield crystalline yellow blocks, suited for X-Ray analysis.

Crystalline yields: 45 mg (0.038 mmol, 27 %)

$^{31}P\{^1H\}$ NMR (162 MHz, d_8-toluene, 300 K): δ [ppm] = 71.0 (s, $\omega_{1/2}$ = 166 Hz, 1P, $\underline{P}_{apical}$), -124.9 (s, $\omega_{1/2}$ = 244 Hz, 3P, $\underline{P}_{basal}$).

Elemental analysis for $C_{58}H_{82}N_4Cu_2P_4S_3$: C 58.91, H 6.99, N 4.74, S 8.14; found [%]: C 58.71, H 7.00, N 4.55, S 7.97.

LIFDI-MS (toluene): m/z (%) = 1182.4 (100, $[M]^+$), 700.2 (6.95, $[(L^3Cu)(P_4S_3)]^+$).

6.5.1.10. $[(L^3Cu)_2(As_4S_3)]$ (**5**)

A solution of 150 mg (0.29 mmol) $[L^3Cu(NCMe)]$ in 8 mL toluene was added to a slurry of 56.5 mg (0.14 mmol) As_4S_3 in 8 mL toluene. The colour of the reaction solution turned from yellow to intense blood-red. The reaction solution was stirred for approximately 20 hours and the solvent was removed. The residue was dissolved in 25 mL n-hexane and filtered over diatomaceous earth. The solution was reduced to a volume of 4 mL and stored at room temperature to yield crystalline dark red blocks, suited for X-Ray analysis.

Crystalline yields: 40.5 mg (0.03 mmol, 21 %)

LIFDI-MS (toluene): m/z (%) = 1357.9 (100, $[M]^+$).

6.5.2. NMR studies

6.5.2.1. $[(L^1Cu)_2(\mu,\eta^{2:2}\text{-}P_4)]$ (**1a**)

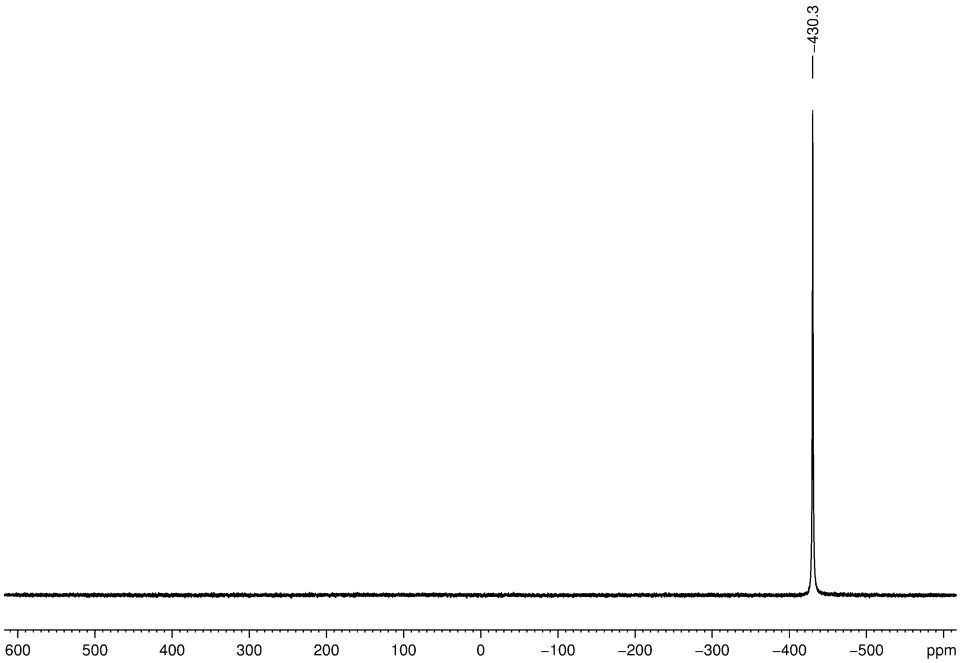


Figure S6.3. $^{31}P\{^1H\}$ NMR spectrum of **1a** in CD_2Cl_2 at room temperature.

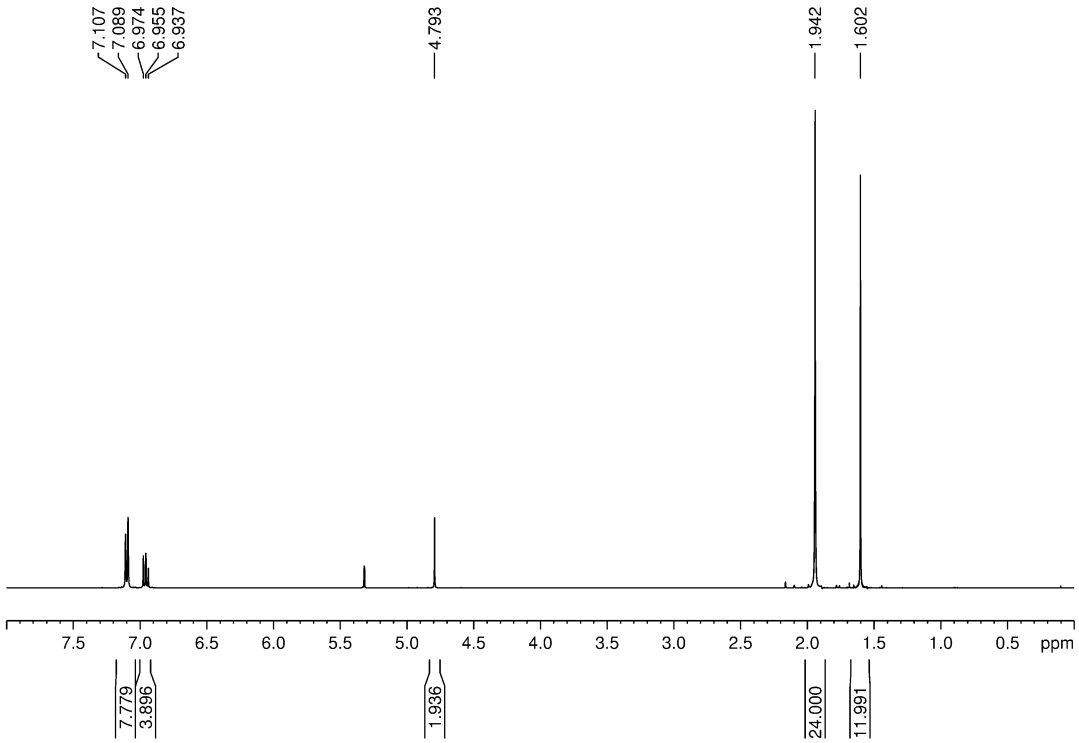


Figure S6.4. ^1H NMR spectrum of **1a** in CD_2Cl_2 at room temperature.

6.5.2.2. $[(L^1Cu)_2(\mu,\eta^{2:2}\text{-}As_4)]$ (**1b**)

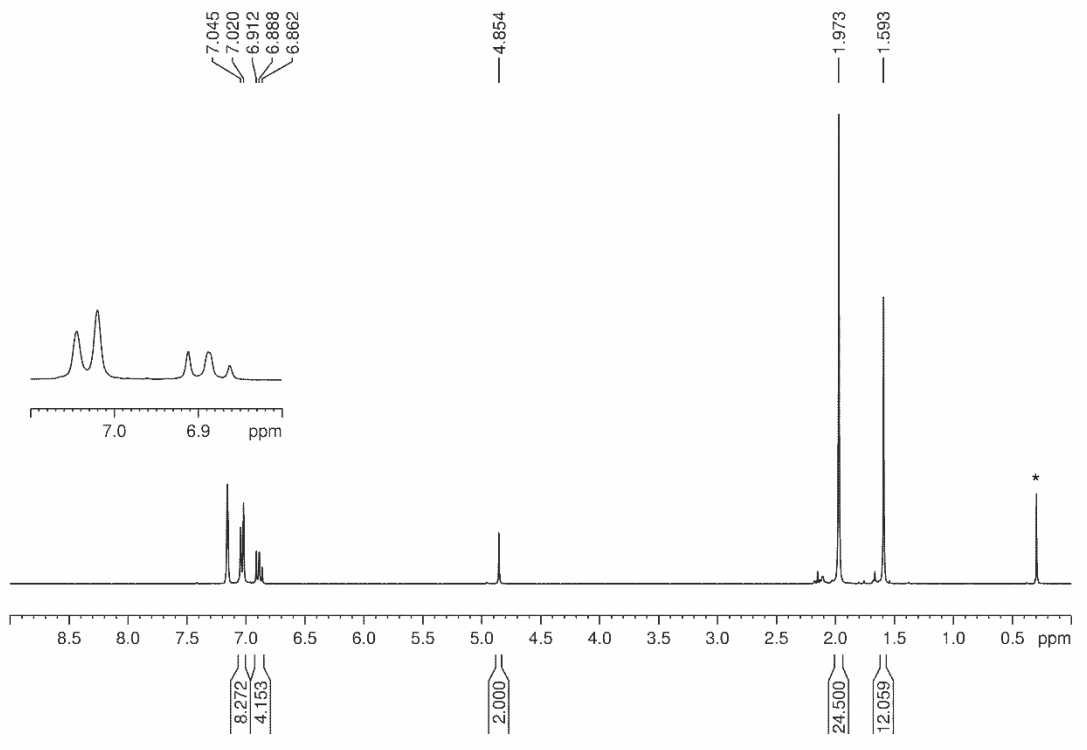


Figure S6.5. ^{1}H NMR spectrum of **1b** in C_6D_6 at room temperature.

6.5.2.3. $[(L^1Cu)_2(\mu,\eta^{2:2}\text{-}AsP_3)]$ (**1c**)

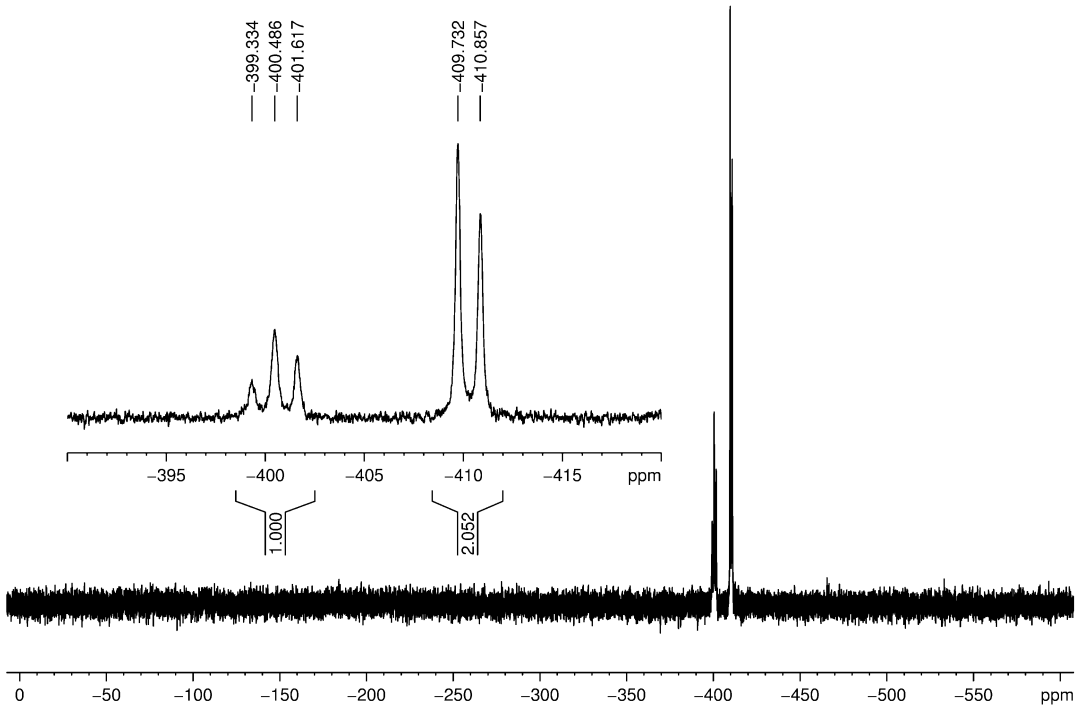


Figure S6.6. $^{31}P\{^1H\}$ NMR spectrum of compound **1c** in tol-d_8 at 193 K.

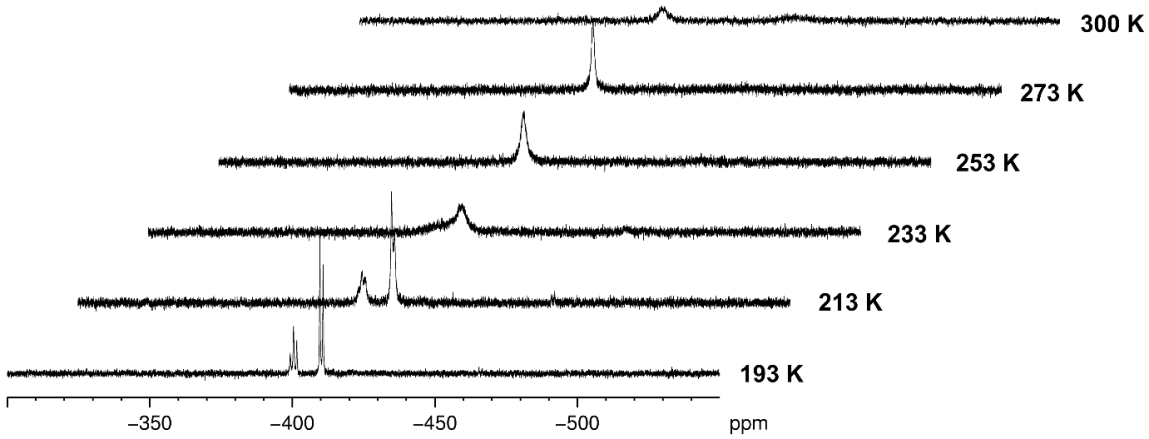


Figure S6.7. VT $^{31}P\{^1H\}$ NMR spectrum of **1c** in toluene-d_8 at different temperatures between 193 K and 300 K.

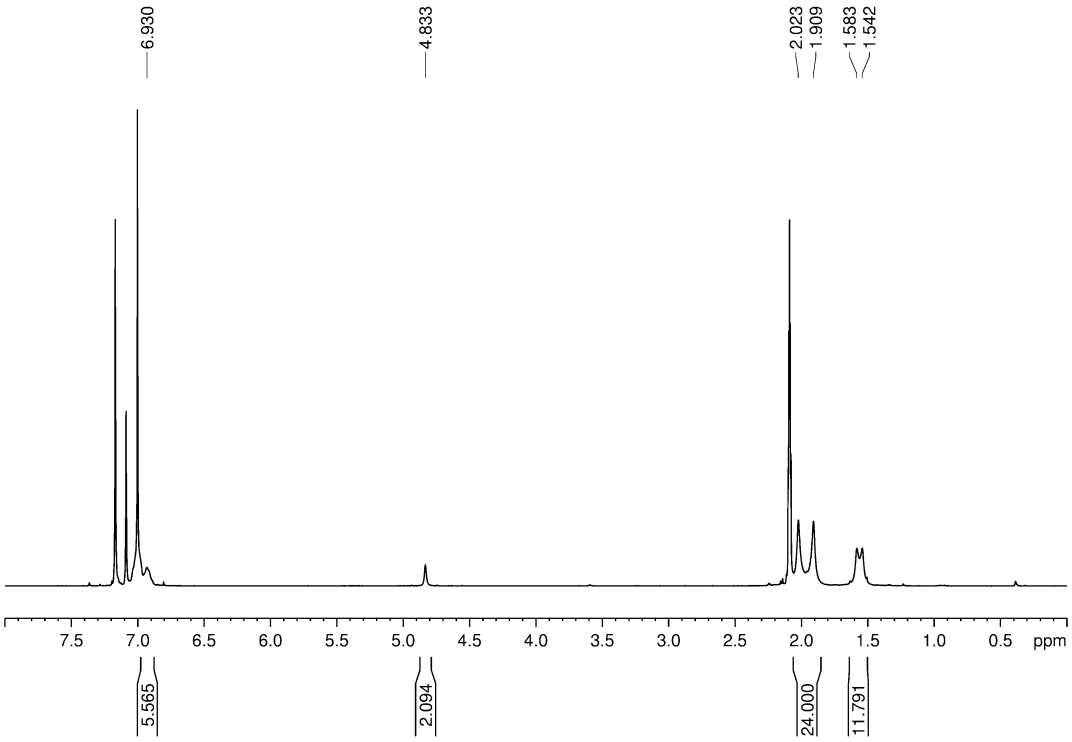


Figure S6.8. ^1H NMR spectrum of **1c** in toluene-d_8 at 193K.

6.5.2.4. $[L^1Cu(\eta^2\text{-}P_4)]$ (**2a**)

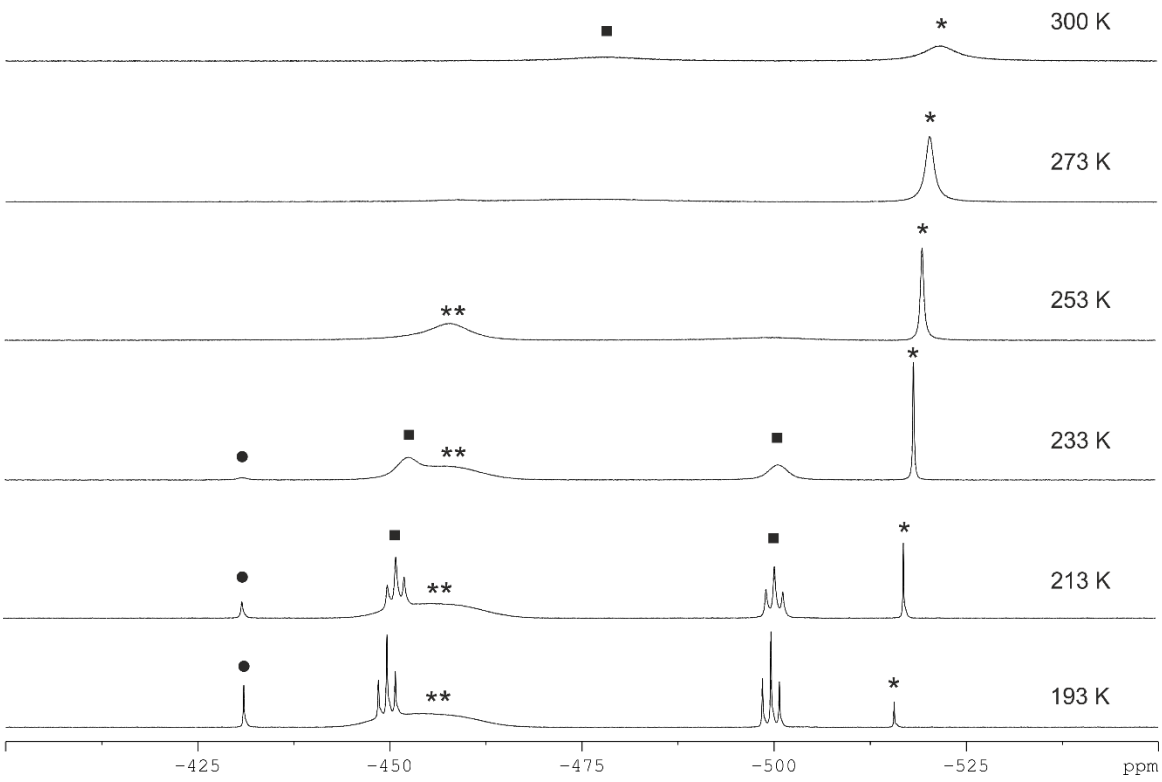


Figure S6.9. $^{31}P\{^1H\}$ NMR spectra of a freshly prepared solution of complex **2a** in CD_2Cl_2 in the temperature range of 300 K to 193 K. The signal at δ = −522 ppm is assigned to $P_{4,solv}$ (*) and the one at δ = −431 ppm is assigned to **1a** (●). At δ = −455 ppm $P_{4,solid}$ (**) is detected, which precipitates from solution with successively decreasing the temperature. At 300 K compound **2a** (■) is assigned to the broad signal at δ = −479.2 ppm. Successive decrease of the temperature leads to the breakdown of the coalescence signal and a final signal splitting at δ = −449.6 ppm (P^A) and −499.6 ppm (P^B) at 193 K.

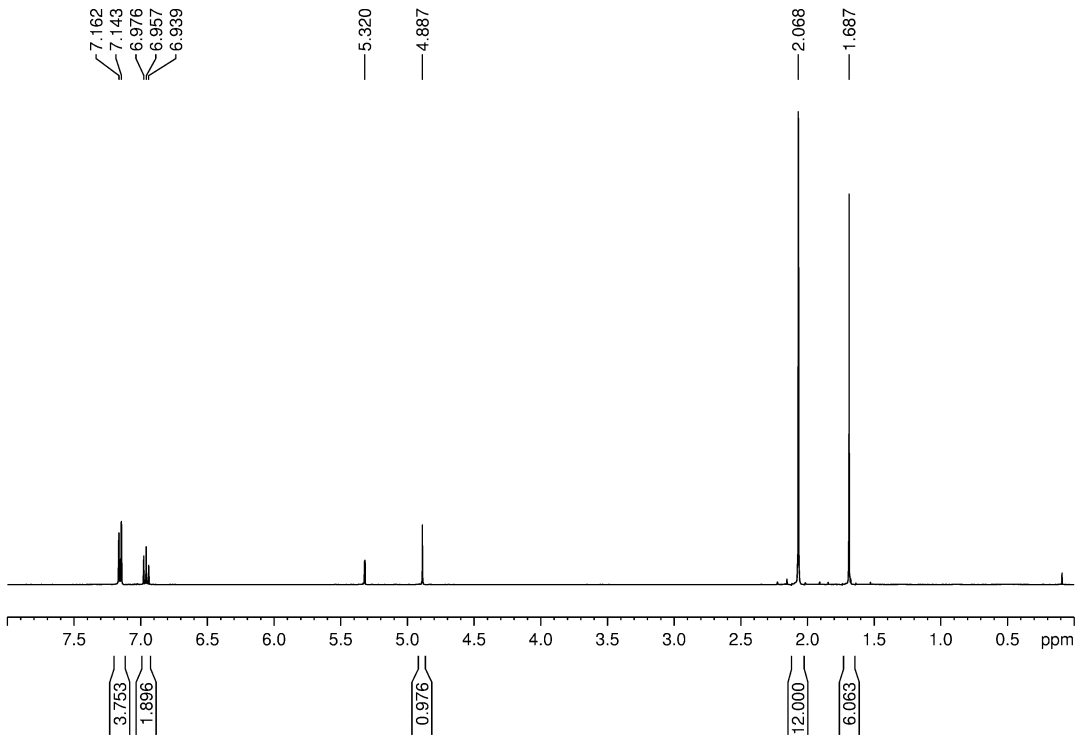


Figure S6.10. ^{1}H NMR of **2a** in CD_2Cl_2 at room temperature.

6.5.2.5. [$L^1Cu(\eta^2\text{-}As_4)$] (**2b**)

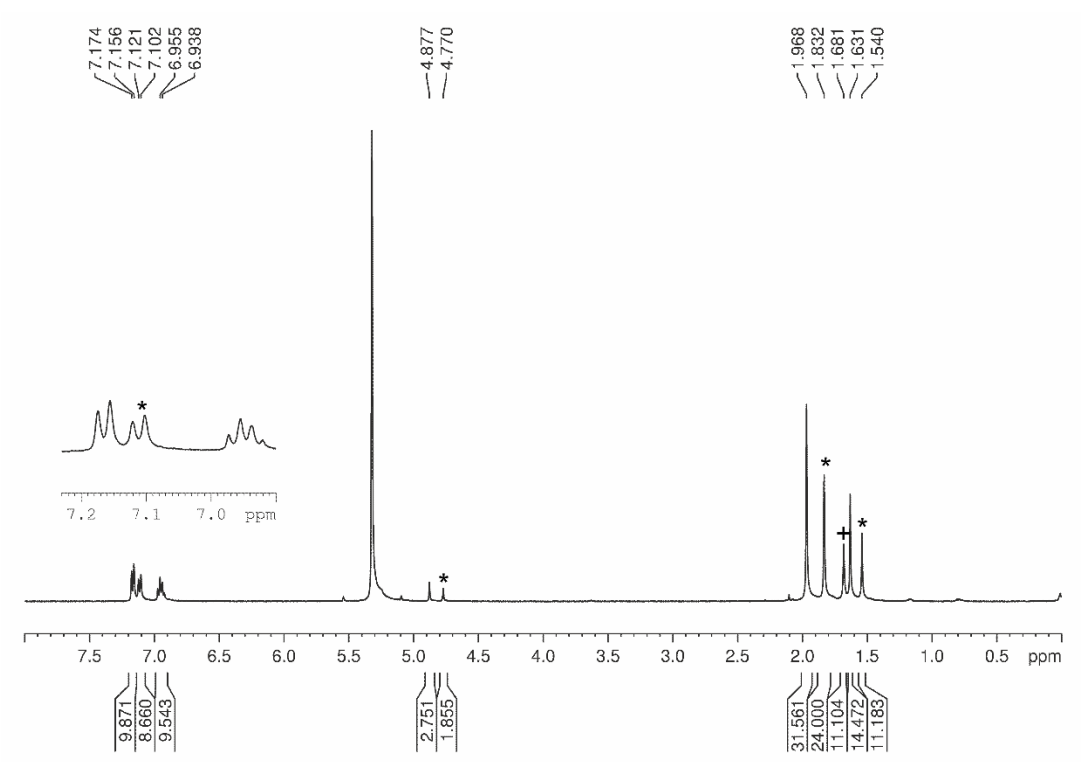


Figure S6.11. ^{1}H NMR spectrum of **2b** in CD_2Cl_2 at 203 K (signal assignment: * = **1b**, + = impurity).

6.5.2.6. [$L^1Cu(\eta^2\text{-}AsP_3)$] (**2c**)

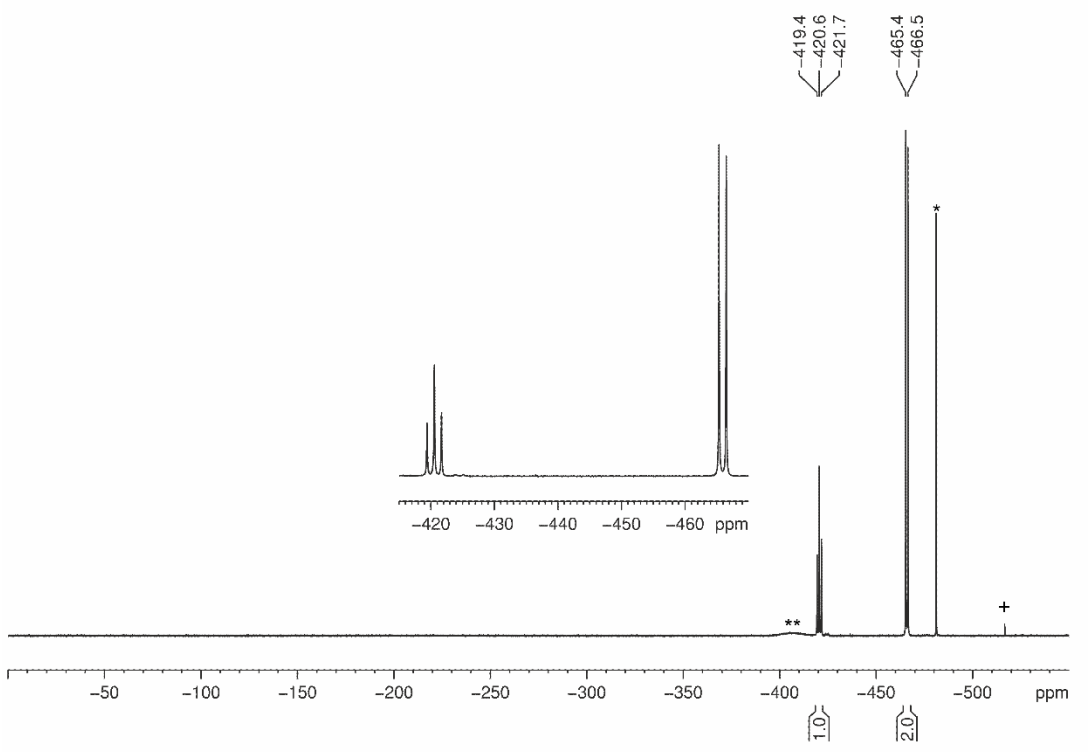


Figure S6.12. $^{31}P\{^1H\}$ NMR spectrum of **2c** in toluene-d_8 at 193 K. * = AsP_3; ** = AsP_3, solid; + P_4.

6.5.2.7. [$(L^1Cu)_2(\mu,\eta^{2:2}\text{-}Se_2)$] (**3a)**

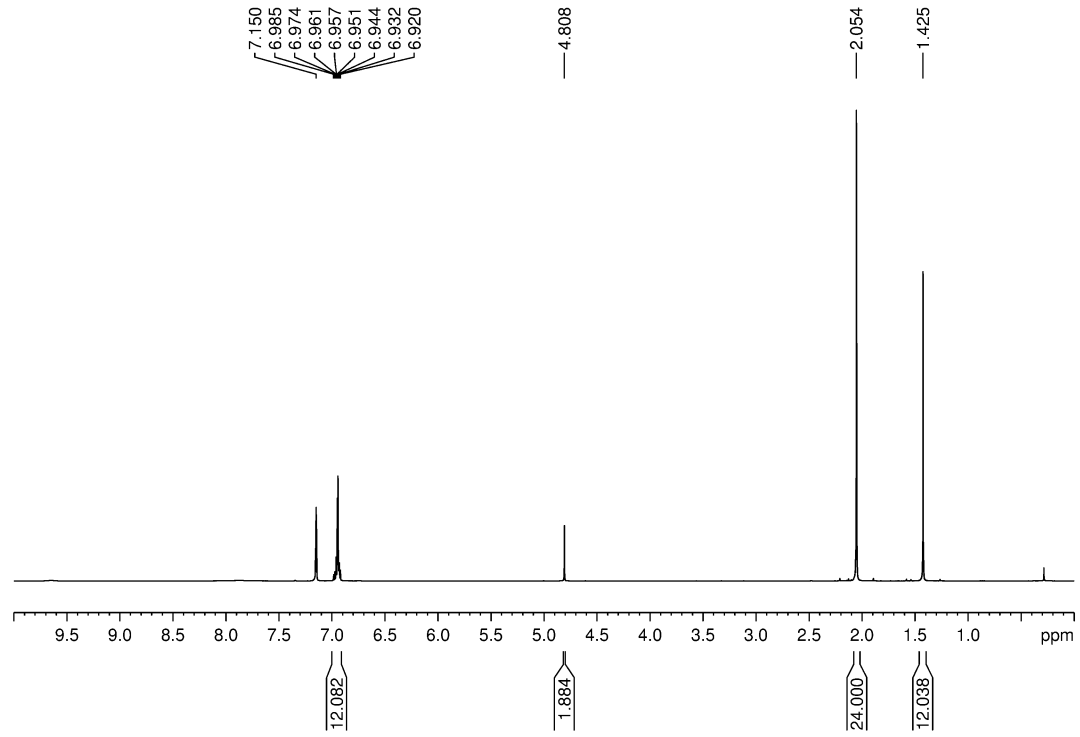


Figure S6.13. ^1H NMR spectrum of **3a** in C_6D_6 at room temperature.

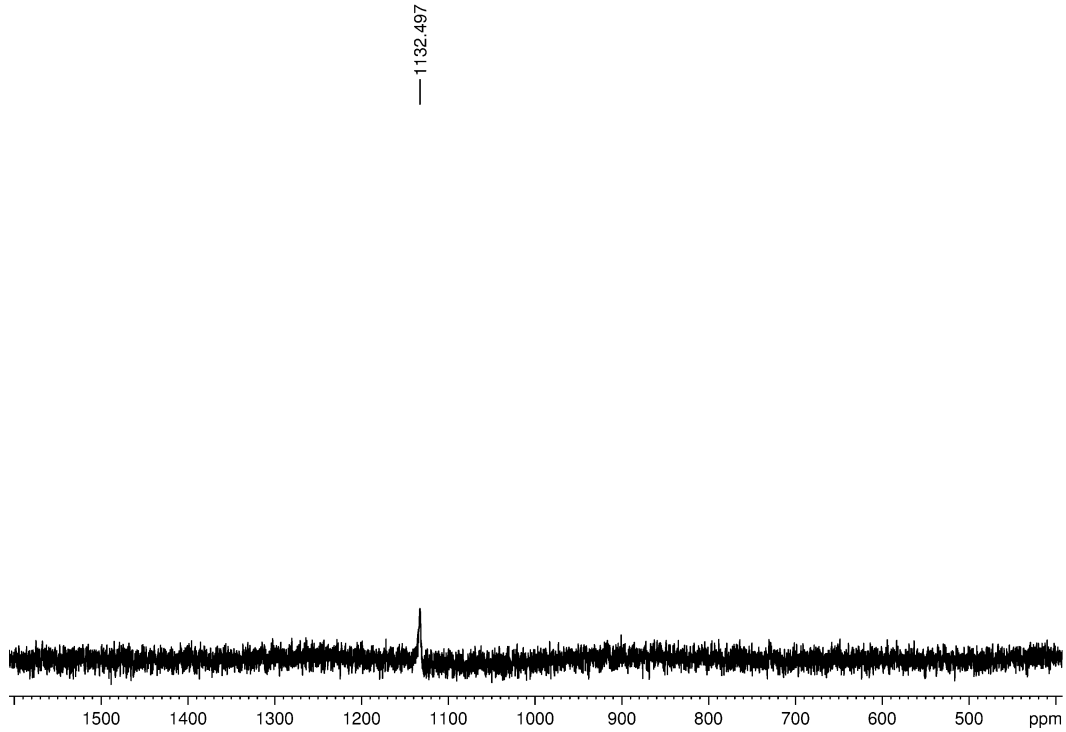


Figure S6.14. ^{77}Se NMR spectrum of **3a** in C_6D_6 at room temperature.

6.5.2.8. $[(L^3Cu)_2(\mu,\eta^{2:2}\text{-}Se_2)]$ (**3b**)

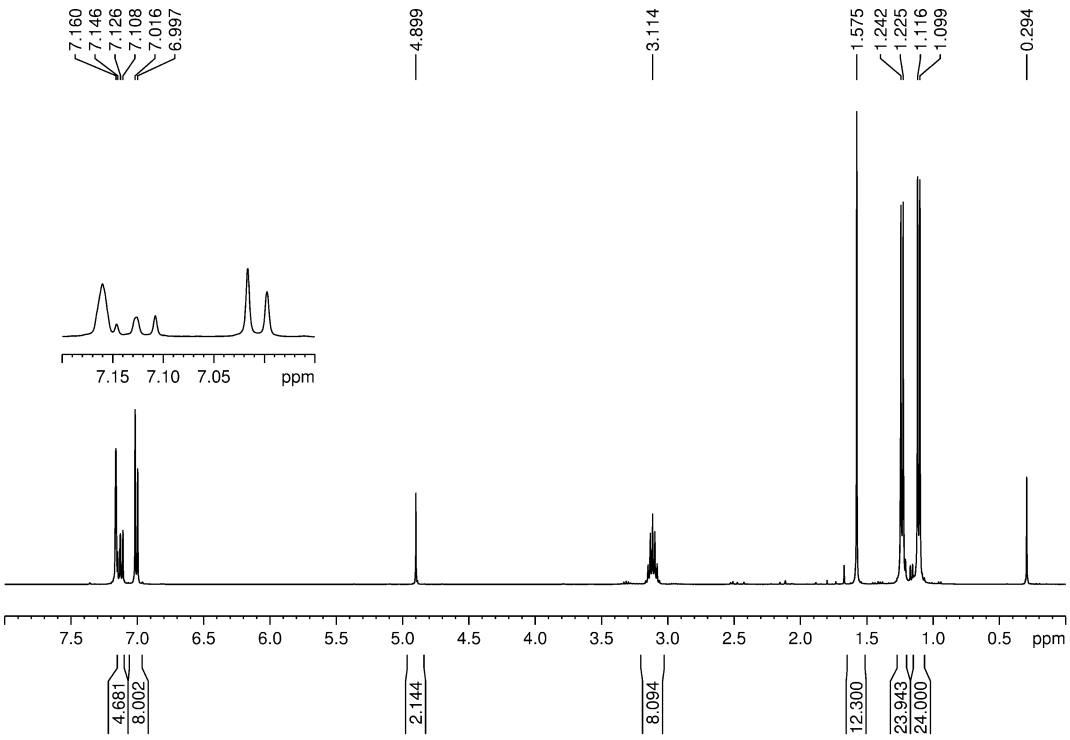


Figure S6.15. ^{1}H NMR spectrum of **3b** in C_6D_6 at room temperature.

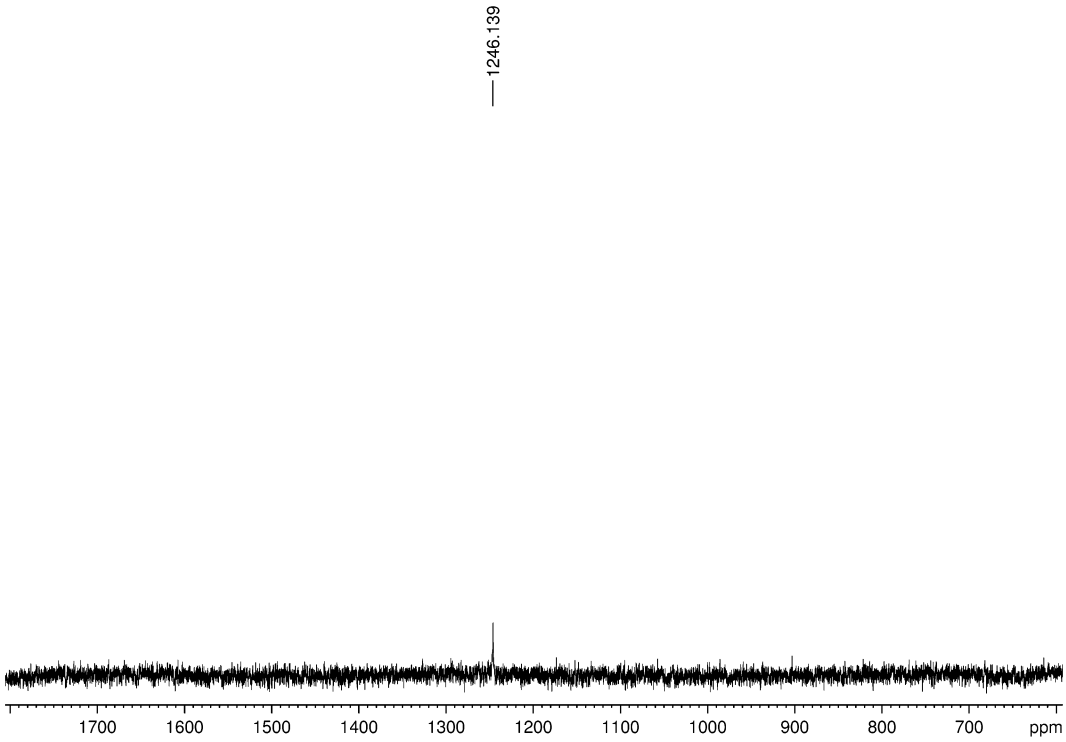


Figure S6.16. ^{77}Se NMR spectrum of **3b** in C_6D_6 at room temperature.

6.5.2.9. $[(L^3Cu)_2(P_4S_3)]$ (**4**)

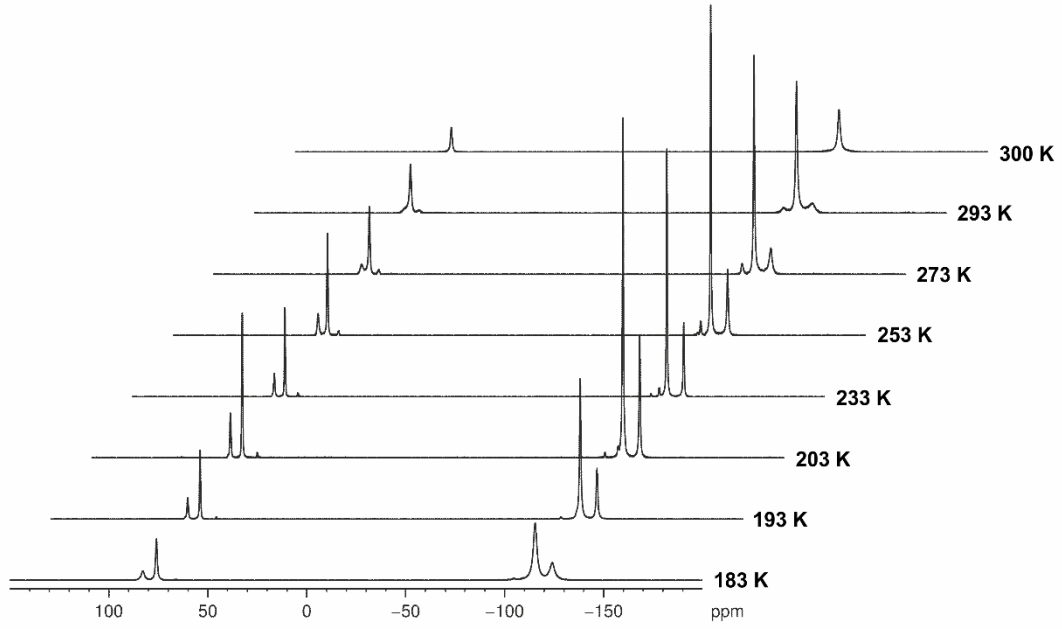


Figure S6.17. VT $^{31}P\{^1H\}$ NMR spectra of **4** in toluene-d_8 at different temperature between 183 K and 300 K.

6.5.3. Details on single crystal X-ray structure analysis

The X-ray diffraction experiments were performed on either a Gemini Ultra diffractometer (Oxford diffraction) with an AtlasS2 detector Cu-K*α* radiation (λ = 1.54178 Å) (**2b**, **4**, **5**), on a GV 50 diffractometer (Rigaku, formerly Agilent Technologies) with TitanS2 detector from applying Cu-K*α* radiation (λ = 1.54178 Å) (**1a**, **1b**, **1c**, **3a**, **3b**). All measurements were performed at 123 K. Data collection and reduction were performed with CrysAlisPro[7] (Version 171.38.41, 2015 (**1c**), 171.38.43, 2015 (**1a**, **3b, 4**), 171.38.46, 2015 (**3a**), 171.39.37b, 2017 (**1b**), 171.40.14a, 2018 (**2b**), 171.41.90a, 2020 (**5**). For the compounds (**2b**, **5**) an analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid was applied.[8] For the compounds (**1a**, **1b**, **1c**, **3a**, **3b**, **4**) a gaussian absorption correction based on gaussian integration over a multifaceted crystal model was applied. All structures were solved by direct methods with ShelXT[9] and Olex2[10] and refined by full-matrix least-squares method against F^2 in anisotropic approximation using ShelXL[11]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined in calculated positions using riding on pivot atom model.

6.5.3.1. $[(L^1Cu)_2(\mu,\eta^{2:2}\text{-}P_4)]$ (**1a**)

Compound **1a** crystallizes from a concentrated solution in n-hexane at -30 °C in the monoclinic space group $P2_1/n$ as orange block. The asymmetric unit contains one molecule of **1a**. The structure in solid state is given in Figure S6.18.

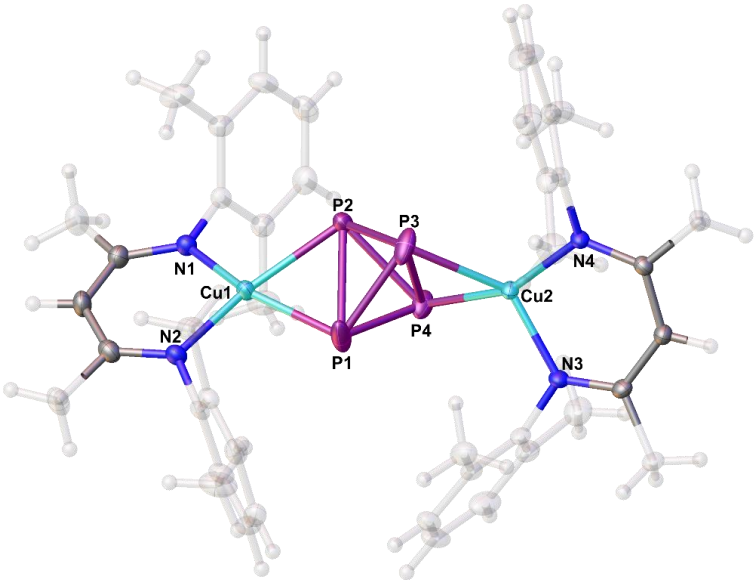


Figure S6.18. Molecular structure of **1a** in solid state. Solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu1-P1 2.2501(5), Cu1-P2 2.2540(5), Cu2-P3 2.2750(5), Cu2-P4 2.2408(5), P1-P2 2.3649(6), P1-P3 2.2047(6), P2-P3 2.1992(6), P3-P4 2.4566(6), P1-P4 2.1917(7), P2-P4 2.2091(8), P1-Cu1-P2 63.344(17), P3-Cu2-P4 65.909(17), P1-P3-P4 55.78(2), P2-P3-P1 64.96(2), P2-P3-P4 56.33(2), P3-P1-P2 57.409(19), P4-P1-P3 67.94(2), P4-P1-P2 57.85(3), P3-P2-P1 57.631(19), P3-P2-P4 67.73(2), P4-P2-P1 57.14(2), P1-P4-P3 56.279(19), P1-P4-P2 65.01(2), P2-P4-P3 55.94(2).

6.5.3.2. $[(L^1Cu)_2(\mu,\eta^{2:2}\text{-}As_4)]$ (**1b**)

Compound **1b** crystallizes from a concentrated solution in n-hexane at -30 °C in the monoclinic space group $P2_1/n$ as orange plate. The asymmetric unit contains one molecule of **1b**. The structure in solid state is given in Figure S6.19.

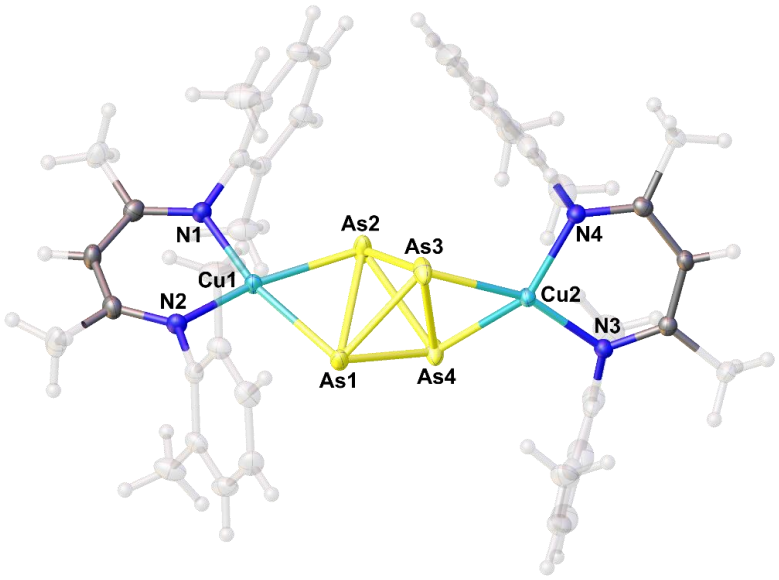


Figure S6.19. Molecular structure of **1b** in solid state. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu1-As1 2.3899(4), Cu1-As2 2.3551(4), Cu2-As3 2.3592(4), Cu2-As4 2.3684(4), As1-As2 2.6885(3), As1-As3 2.4480(3), As1-As4 2.4411(3), As2-As3 2.4321(4), As2-As4 2.4510(4), As3-As4 2.6575(3), As3-As1-As2 56.286(10), As4-As1-As3 65.851(10), As4-As1-As2 56.840(10), As1-As3-As4 56.948(9), As2-As3-As1 66.858(10), As2-As3-As4 57.372(10), As1-As4-As3 57.200(9), As1-As4-As2 66.674(10), As2-As4-As3 56.686(10), As3-As2-As1 56.855(9), As3-As2-As4 65.942(10), As4-As2-As1 56.486(9).

6.5.3.3. $[(L^1Cu)_2(\mu,\eta^{2:2}\text{-}AsP_3)]$ (**1c**)

Compound **1c** crystallizes from a concentrated solution in toluene at -30 °C in the monoclinic space group $P2_1/n$ as orange plate. The asymmetric unit contains one molecule of **1c**. The structure in solid state is given in Figure S6.20.

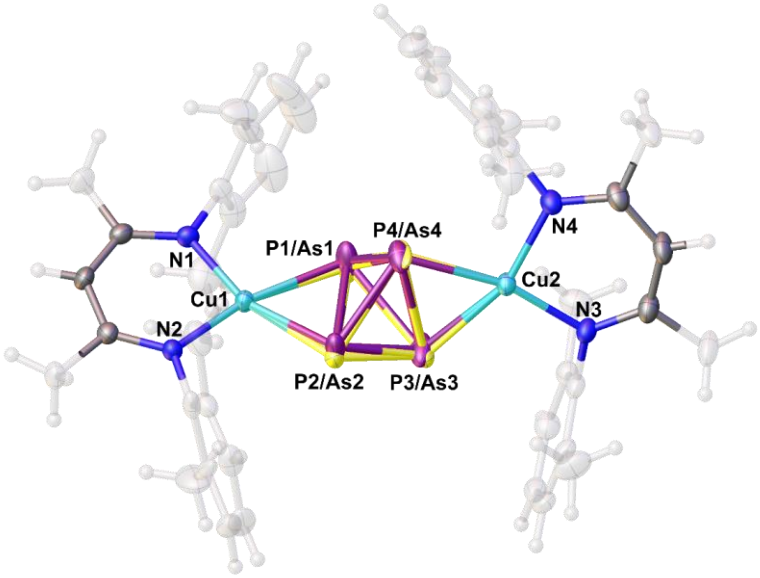


Figure S6.20. Molecular structure of **1c** in solid state. Solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu1-P1 2.311(7), Cu1-P2 2.302(4), Cu1-As1 2.333(6), Cu1-As2 2.332(8), Cu2-P3 2.315(6), Cu2-P4 2.288(2), Cu2-As3 2.317(4), Cu2-As4 2.230(10), P1-P2 2.546(8), P1-P3 2.199(8), P1-P4 2.329(11), P2-P3 2.272(8), P2-P4 2.182(6), P3-P4 2.456(7), As1-P2 2.546(7), As1-P3 2.231(10), As1-P4 2.286(6), As2-P1 2.625(10), As2-P3 2.219(10), As2-P4 2.382(8), As3-P1 2.466(10), As3-P2 2.319(6), As3-P4 2.540(5), As4-P1 2.146(12), As4-P2 2.250(12), As4-P3 2.429(11).

6.5.3.4. [L^1Cu(η^2-As_4)] (**2b**)

Yellow needle-like twinned crystals of **2b** were obtained by crystallization from *n*-hexane at - 30 °C in the triclinic space group $P\bar{1}$ as light yellow block. The asymmetric unit contains two molecules of **2b**. The crystal structure of **2b** was refined as a two-component twin. The As_4 ligand in **2b** is disordered over two positions with chemical occupancy of 96.5:3.5. The structure in solid state is given in Figure S6.21.

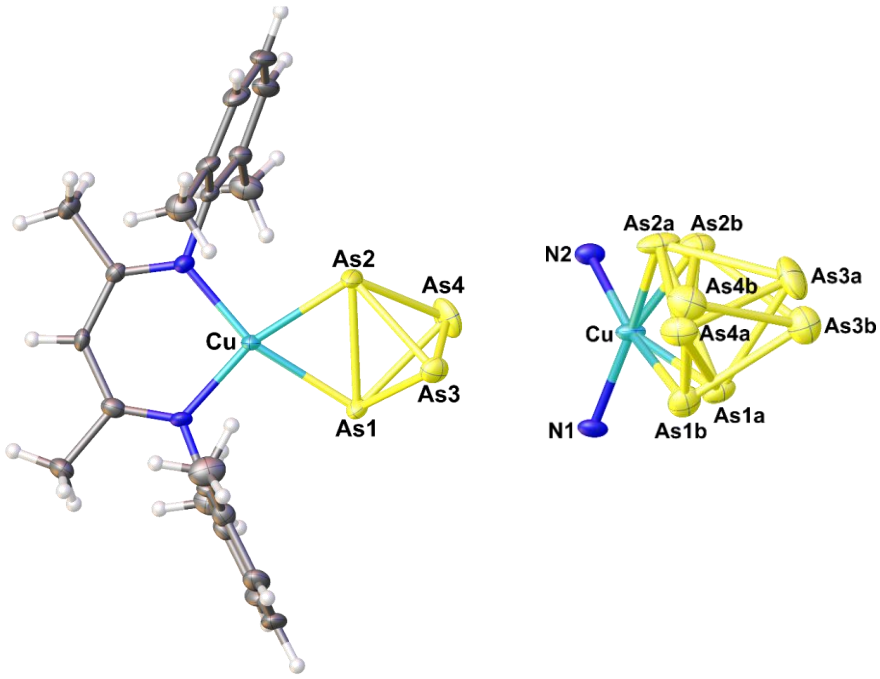


Figure S6.21. Molecular structure of **2b** in the solid state. From the two molecules of the asymmetric unit only molecule 1 is depicted. Selected bond lengths [Å] and angles [°]:

Molecule 1: As1a-As2a 2.6754(13), As1a-As3a 2.4265(15), As1a-As4a 2.4322(14), As2a-As3a 2.4271(13), As2a-As4a 2.4218(18), As3a-As4a 2.3946(16), As1b-As2b 2.64(2), As1b-As3b 2.42(2), As1b-As4b 2.43(2), As2b-As3b 2.42(2), As2b-As4b 2.44(2), As3b-As4b 2.38(3), Cu1-As1a 2.3769(14), Cu1-As2a 2.3645(14), Cu1-As1b 2.39(3), Cu1-As2b 2.31(3), Cu1-N1 1.957(6), Cu1-N2 1.947(6),

Molecule 2: As5a-As6a 2.6569(11), As5a-As7a 2.4193(15), As5a-As8a 2.4321(15), As6a-As7a 2.4285(15), As6a-As8a 2.4162(15), As7a-As8a 2.3992(19), As5b-As6b 2.60(3), As5b-As7b 2.37(3), As5b-As8b 2.38(4), As6b-As7b 2.38(4), As6b-As8b 2.37(3), As7b-As8b 3.32(3), Cu2-As5a 2.3721(13), Cu2-As6a 2.3837(13), Cu2-As5b 2.34(3), Cu2-As6b 2.2.28(2), Cu2-N3 1.956(6), Cu2-N4 1.931(6).

6.5.3.5. $[(L^1Cu)_2(\mu,\eta^{2:2}\text{-}Se_2)]$ (**3a**)

Compound **3a** crystallizes from a concentrated solution in toluene at -30 °C in the monoclinic space group C2/c as green blocks. The asymmetric unit contains one molecule of **3a**. The structure in solid state is given in Figure S6.22.

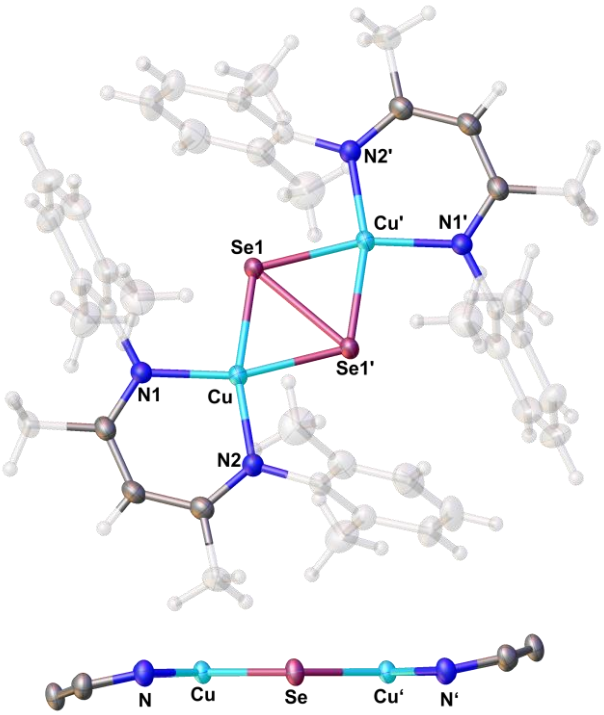


Figure S6.22. Molecular structure of **3a** in solid state. Solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Se-Se’ 2.4910(4), Cu-Se 2.3075(3), Cu-Se’ 2.3070(3), Cu-N1 1.9080(17), Cu-N2 1.9074(16), Se-Cu-Se’ 65.342(11), Cu-Se-Cu’ 114.656(11).

6.5.3.6. $[(L^3Cu)_2(\mu,\eta^{2:2}\text{-}Se_2)]$ (**3b**)

Compound **3b** crystallizes from a concentrated solution in toluene at -30 °C in the monoclinic space group $P2_1/n$ as green blocks. The asymmetric unit contains one molecule of **3b**. The structure in solid state is given in Figure S6.23.

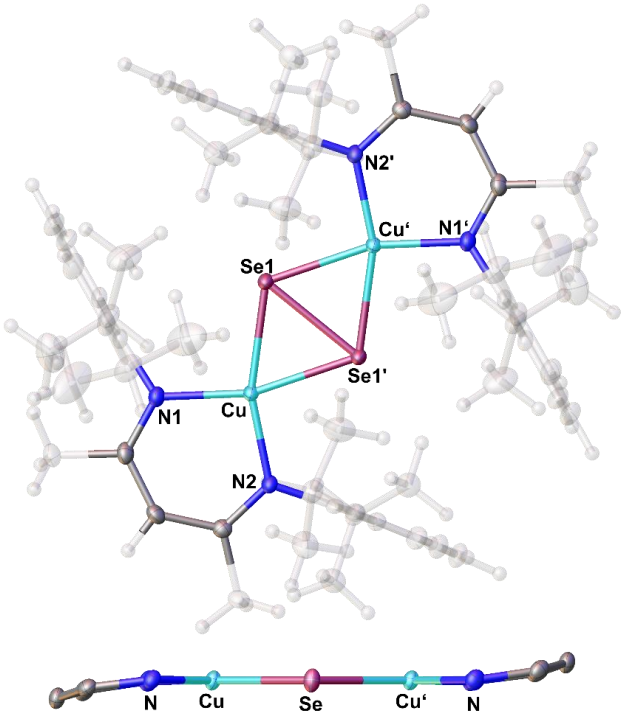


Figure S6.23. Molecular structure of **3b** in solid state. Solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Se-Se' 2.4527(4), Cu-Se 2.3350(3), Cu-Se' 2.3441(3), Cu-N1 1.9246(15), Cu-N2 1.9373(16), Se-Cu-Se' 63.225(10), Cu-Se-Cu' 116.773(10).

6.5.3.7. $[(L^3Cu)_2(P_4S_3)]$ (**4**)

Compound **4** crystallizes from a concentrated solution in toluene at -30 °C in the triclinic space group $P\bar{1}$ as yellow blocks. The asymmetric unit contains one molecule of **4**. The P_4S_3 unit is disordered over two positions: 93:7 (**4a**:**4b**). The structure in solid state is given in Figure S6.24.

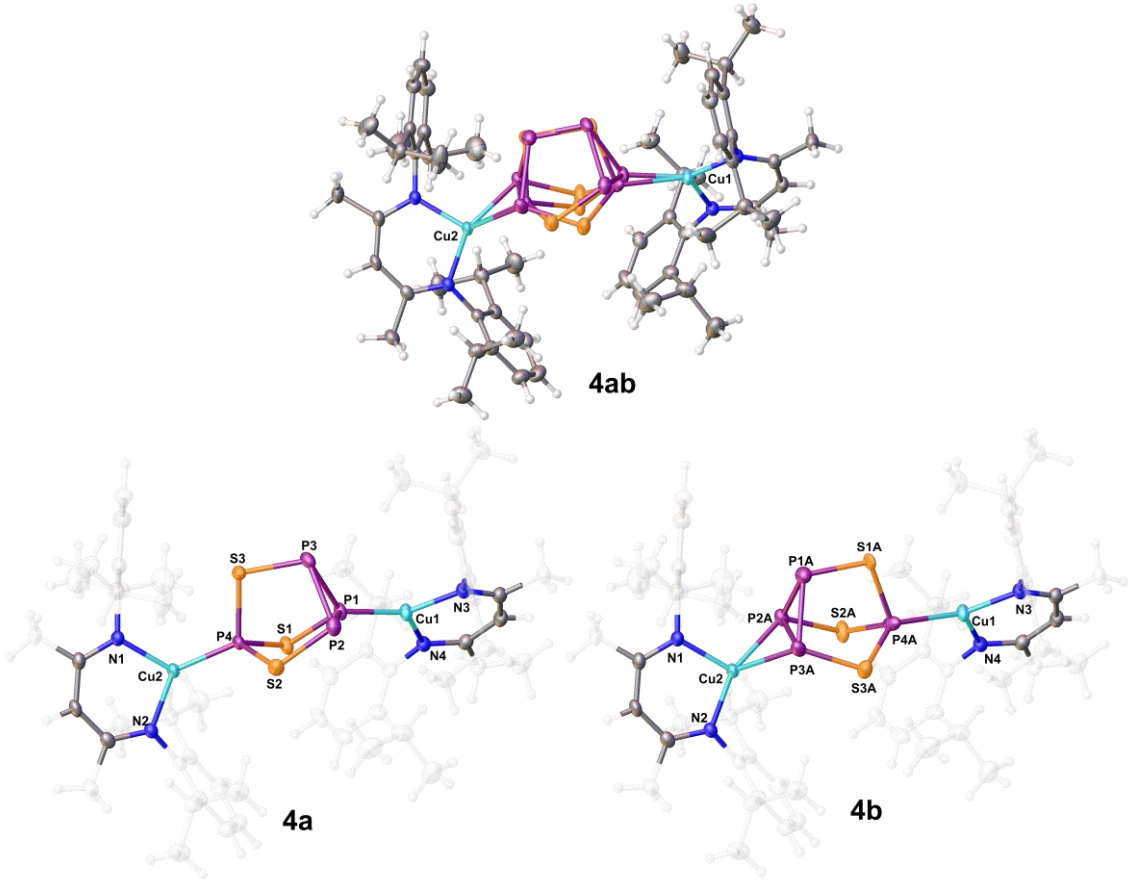


Figure S6.24. Molecular structure of **4** in solid state (left: major isomer **4a**, right: minor isomer **4b**). Solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu1-N1 1.9149(14), Cu1-N2 1.9090(14), Cu2-N3 1.9313(14), Cu2-N4 1.9236(14); **4a**: Cu1-P1 2.0977(17), Cu2-P4 2.1048(5), S3-P3 2.091(3), S3-P4 2.101(2), P1-S1 2.0975(16), P1-P3 2.230(3), P1-P2 2.2296(16), S1-P4 2.0950(9), P3-P2 2.257(2), P4-S2 2.0965(7), S2-P2 2.0927(7), P3-S3-P4 102.02(11), S1-P1-P3 105.39(9), S1-P1-P2 105.86(6), P2-P1-P3 60.81(7), P4-S1-P1 99.56(6), S3-P3-P1 102.56(11), S3-P3-P2 103.04(11), P1-P3-P2 59.58(7), S1-P4-S3 101.21(6), S1-P4-S2 101.15(3), S2-P4-S3 100.18(4), P2-S2-P4 102.04(3), P1-P2-P3 59.61(6), S2-P2-P1 101.99(4), S2-P2-P3 103.56(6); **4b**: Cu1-P4A 2.34(2), Cu2-P2A 2.336(6), Cu2-P3A 2.428(7), P2A-P3A 2.404(9), P2A-P1A 2.26(3), P2A-S2A 2.104(11), P3A-P1A 2.24(3), P3A-S3A 2.090(9), S1A-P1A 2.04(4), S1A-P4A 2.14(4), S3A-P4A 2.077(19), P1A-P2A-P3A57.4(8), S2A-P2A-P3A 99.5(4), S2A-P2A-P1A 103.0(9), P1A-P3A-P2A 58.0(7), S3A-P3A-P2A 102.1(4), S3A-P3A-P1A 101.9(8), P1A-S1A-P4A 100.9(17), P3A-P1A-P2A 64.7(9), S1A-P1A-P2A 106.1(17), S1A-P1A-P3A 106.4(16), P4A-S3A-P3A 104.1(8), S1A-P4A-S2A 100.4(13), S3A-P4A-S1A 100.9(12), P2A-S2A-P4A 103.0(8).

6.5.3.8. $[(L^3Cu)_2(As_4S_3)]$ (**5**)

Compound **5** crystallizes from a concentrated solution in toluene at room temperature in the triclinic space group $P\bar{1}$ as yellow blocks. The asymmetric unit contains two molecules of **5**. The As_4S_3 unit is disordered over two positions: 65:35 (**5a**:**5b**) for one molecule and over three positions for the other molecule 88:4:8 (**5c**:**5d**:**5e**). The structure in solid state is given in Figure S25-S27.

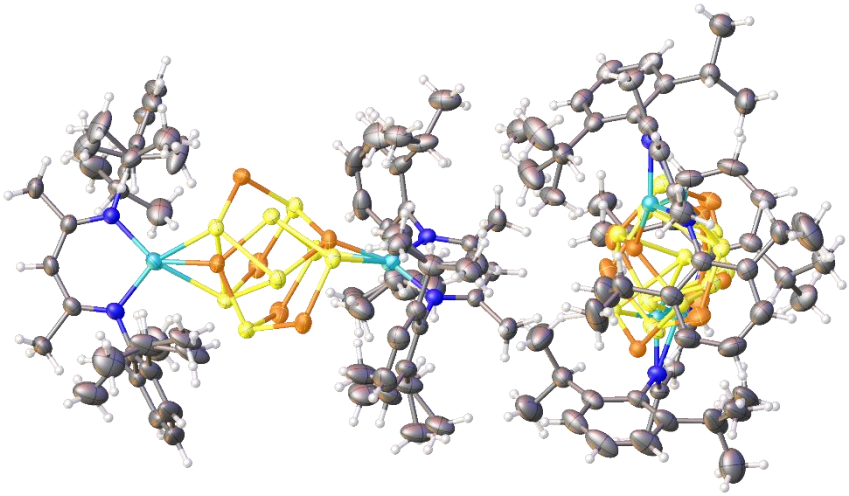


Figure S6.25. Asymmetric unit of **5**. Left: **5ab**, right: **5cde**.

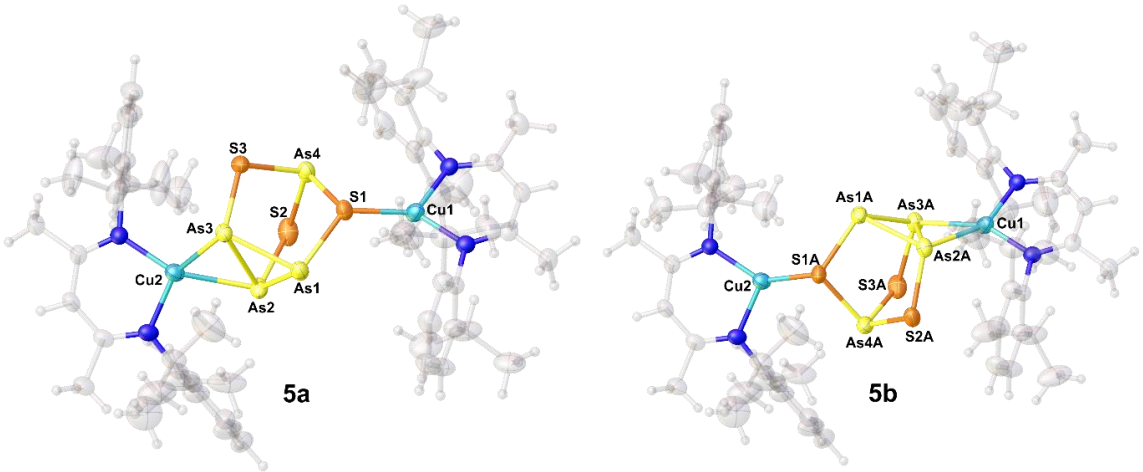


Figure S6.26. Molecular structure of **5a** and **5b** in solid state. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu2-N1 1.933(2), Cu2-N2 1.924(3), Cu1-N3 1.945(3), Cu1-N4 1.945(3), **5a**: Cu2-As3 2.3700(6), Cu2-As2 2.5208(7), Cu1-S1 2.0812(12), As3-As1 2.4573(7), As3-As2 2.7273(7), As3-S3 2.2099(13), As1-As2 2.4637(8), As1-S1 2.2379(13), As4-S1 2.2579(13), As4-S3 2.2298(13), As4-S2 2.2147(15), As2-S2 2.2322(16), As1-As3-As2 56.237(15), S3-As3-As1 103.63(3), S3-As3-As2 99.95(3), As3-As1-As2 67.848(16), S1-As1-As3 98.89(3), S1-As1-As2 104.79(3), As1-As2-As3 55.915(16), S2-As2-As3 96.94(5), S2-As2-As1 99.03(3), S3-As4-S1 96.35(4), S3-As4-S2 99.58(5), S2-As4-S1 97.90(5), As1-S1-As4 104.76(4), As3-S3-As4 106.55(4), As2-S2-As4 109.65(7), **5b**: Cu2-S1A 2.023(2), Cu1-As2A 2.3933(10), Cu1-As3A 2.5820(10), S3A-As4A 2.223(3), S3A-As3A 2.221(3), As4A-S1A 2.260(2), As4A-S2A 2.223(3), S1A-As1A 2.235(2), As1A-As2A 2.4608(14), As1A-As3A 2.4538(13), As2A-S2A 2.209(3), As2A-As3A 2.7801(13), As2A-As3A-As1A 55.56(17), S3A-As3A-As1A 96.2(4), S3A-As3A-As2A 99.2(4), As2A-As1A-As3A 55.68(17), S1A-As1A-As3A 99.8(4), S1A-As1A-As2A 102.8(4), As1A-As2A-As3A 68.76(18), S2A-As2A-As3A 104.5(4),

S2A-As2A-As1A 99.5(4), S1A-As4A-S3A 99.4(5), S1A-As4A-S2A 96.2(5), S3A-As4A-S2A 97.3(5), As4A-S1A-As1A 107.3(6), As3A-S3A-As4A 109.8(5), As2A-S2A-As4A 105.3(4).

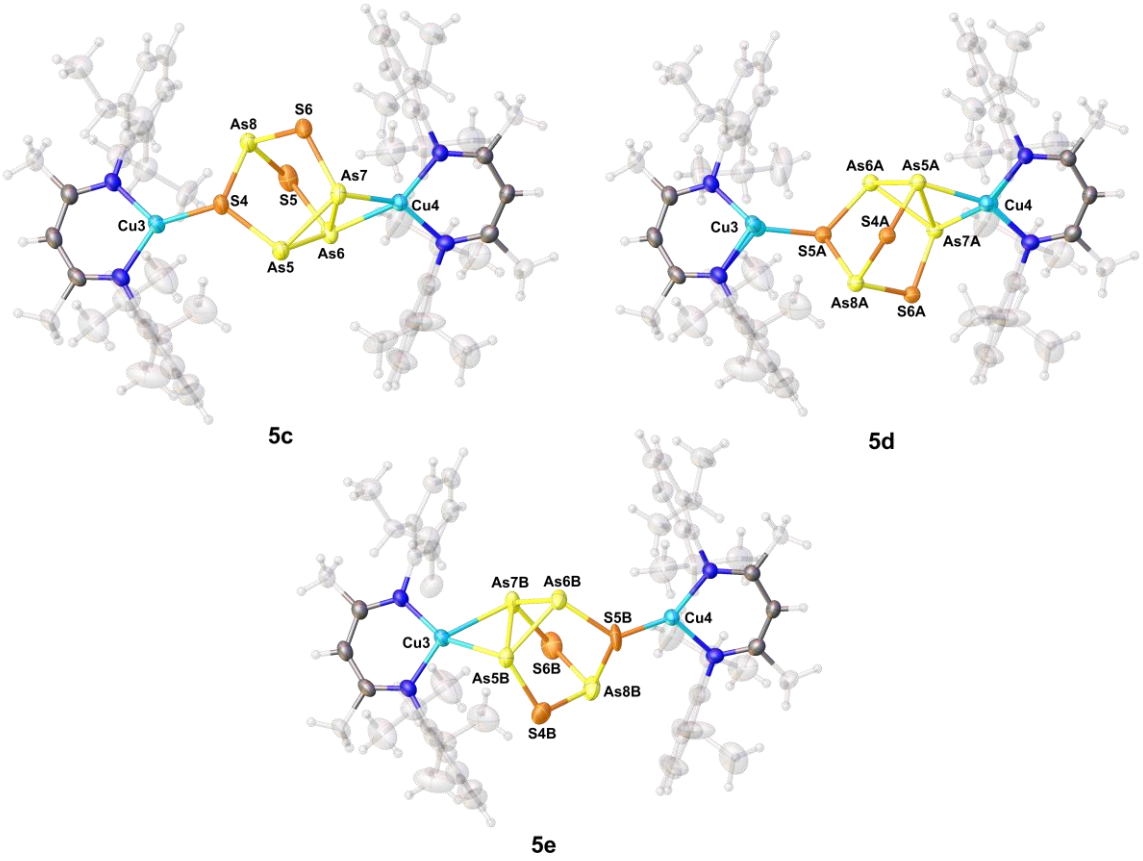


Figure S6.27. Molecular structure of **5** in the solid state. Second molecule of the asymmetric unit. Molecular structure of **5c**, **5d** and **5e** in solid state. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu4-N7 1.956(2), Cu4-N8 1.954(3), Cu3-N5 1.909(3), Cu3-N6 1.924(3); **5c**: Cu3-S4 2.1127(9), Cu4-As7 2.3651(6), Cu4-As6 2.4522(6), As7-As5 2.4527(6), As7-As6 2.7429(5), As7-S6 2.2126(10), As5-As6 2.4620(6), As5-S4 2.2345(9), As6-S5 2.226(2), As8-S4 2.2587(10, As8-S6 2.2221(10), As8-S5 2.2263(16), **5d**: Cu3A-S5A 2.10(2), Cu4A- As7A 2.316(15), Cu4A-As5A 2.488(15), As5A-As6A 2.480(19), As5A-As7A 2.769(11), As5A-S4A 2.176(16), As6A-As7A 2.469(18), As6A-S5A 2.204(18), As7A-S6A 2.198(16), S4A-As8A 2.233(17), S5A-As8A 2.227(16), As8A-S6A 2.219(17), **5e**: Cu4-S5B 1.935(10), Cu3-As7B 2.621(4), Cu3-As5B 2.455(4), As7B-As5B 2.767(6), As7B-As6B 2.452(6), As7B-S6B 2.229(13), As5B-As6B 2.449(6), As5B-S4B 2.213(13), As6B-S5B 2.215(12), As8B-S4B 2.208(15), As8B-S6B 2.230(15), As8B-S5B 2.255(13)

6.5.3.9. Crystallographic information

Table S6.1. Crystallographic data and details of diffraction experiments for **1a**, **1b**, **1c** and **2b**.

Compound	**1a**	**1b**	**1c**	**2b**
Formula	$C_{42}H_{50}Cu_2N_4P_4$	$C_{42}H_{50}As_4Cu_2N_4$	$C_{63}H_{74}AsCu_2N_4P_3$	$C_{42}H_{50}As_8Cu_2N_4$
$D_{calc.}$/ g cm^{-3}	1.373	1.633	1.335	1.897
μ/mm^{-1}	2.971	4.985	2.604	7.668
Formula Weight	861.82	1037.62	1182.17	1337.30
Colour	clear orange	clear orange	clear yellow	light yellow
Shape	block-shaped	plate	block	block
Size/mm^3	0.40×0.22×0.09	0.13×0.07×0.04	0.47×0.31×0.21	0.34×0.15×0.06
T/K	122.97(11)	122.9(2)	122.96(13)	123(1)
Crystal System	monoclinic	monoclinic	triclinic	triclinic
Space Group	$P2_1/n$	$P2_1/n$	P-1	P-1
a/Å	13.50049(6)	13.70410(10)	13.0852(3)	13.0657(5)
b/Å	14.42791(5)	14.26150(10)	13.9315(2)	13.8591(3)
c/Å	21.44106(10)	21.6146(2)	16.6663(3)	13.9850(3)
α/°	90	90	99.300(2)	67.600(2)
β/°	93.6512(4)	92.4720(10)	94.585(2)	89.757(3)
γ/°	90	90	99.426(2)	89.251(3)
V/Å^3	4167.90(3)	4220.45(6)	2940.07(10)	2341.11(12)
Z	4	4	2	2
Z'	1	1	1	1
Wavelength/Å	1.54184	1.54184	1.54184	1.54184
Radiation type	Cu K□	Cu K$_a$	Cu K$_a$	Cu K$_a$
Θ_{min}/°	3.695	3.714	3.445	3.383
Θ_{max}/°	74.441	75.245	74.278	66.155
Measured Refl's.	132557	18204	33331	15213
Indep't Refl's	8426	8288	11614	15213
Refl's I≥2 σ(I)	8169	7399	10980	13524
R_{int}	0.0849	0.0263	0.0277	.
Parameters	481	481	879	591
Restraints	0	0	18	211
Largest Peak	0.437	0.804	0.513	1.687
Deepest Hole	-0.584	-0.812	-0.396	-1.763
GooF	1.028	1.036	1.056	1.174
wR_2 (all data)	0.0907	0.0630	0.0778	0.2560
wR_2	0.0898	0.0606	0.0766	0.2242
R_1 (all data)	0.0335	0.0296	0.0320	0.0749
R_1	0.0327	0.0249	0.0301	0.0648

Table S6.2. Crystallographic data and details of diffraction experiments for **3a**, **3b**, **4** and **5**.

Compound	**3a**	**3b**	**4**	**5**
Formula	$C_{42}H_{50}Cu_2N_4Se_2$	$C_{58}H_{82}Cu_2N_4Se_2$	$C_{58}H_{82}Cu_2N_4P_4S_3$	$C_{116}H_{163}As_8Cu_4N_8S_6$
$D_{calc.}$/ g cm^{-3}	1.479	1.357	1.281	1.458
μ/mm^{-1}	3.624	2.764	3.089	4.460
Formula Weight	895.86	1120.27	1182.41	2715.41
Colour	dark black	brownish green	yellow	dark red
Shape	block-shaped	block-shaped	block-shaped	block-shaped
Size/mm^3	0.20×0.13×0.09	0.12×0.09×0.07	0.57×0.21×0.16	0.27×0.26×0.24
T/K	133.7(4)	123.0(2)	123(1)	123.3(8)
Crystal System	monoclinic	monoclinic	triclinic	triclinic
Space Group	*C*2/*c*	$P2_1/n$	*P*-1	*P*-1
a/Å	23.7168(6)	9.07280(10)	12.3168(3)	16.91500(12)
b/Å	10.7136(3)	14.2744(2)	16.3685(4)	17.09987(11)
c/Å	15.9081(4)	21.1898(2)	16.9091(5)	22.02781(14)
α/°	90	90	104.138(2)	97.8005(5)
β/°	95.677(2)	92.2040(10)	93.023(2)	101.3538(6)
γ/°	90	90	110.306(2)	90.1207(5)
V/Å^3	4022.30(18)	2742.23(6)	3064.66(15)	6186.20(7)
Z	4	2	2	2
Z'	0.5	0.5	1	1
Wavelength/Å	1.54184	1.54184	1.54184	1.54184
Radiation type	Cu K□	CuK□	CuK□	Cu K□
Θ_{min}/°	3.746	3.735	3.442	3.547
Θ_{max}/°	74.056	74.256	66.707	67.023
Measured Refl's.	11111	23846	30599	24918
Indep't Refl's	3961	5499	10714	24918
Refl's I≥2 σ(I)	3759	5123	10072	23673
R_{int}	0.0401	0.0499	0.0285	.
Parameters	232	308	724	1602
Restraints	0	0	36	237
Largest Peak	0.594	0.655	0.717	0.919
Deepest Hole	-0.779	-0.511	-0.723	-0.539
GooF	1.045	1.044	1.033	1.079
wR_2 (all data)	0.0829	0.0861	0.0858	0.1081
wR_2	0.0815	0.0839	0.0839	0.1059
R_1 (all data)	0.0328	0.0338	0.0337	0.0432
R_1	0.0315	0.0318	0.0316	0.0407

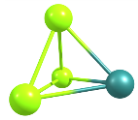
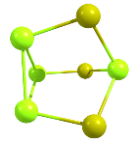
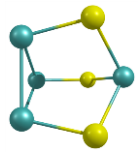
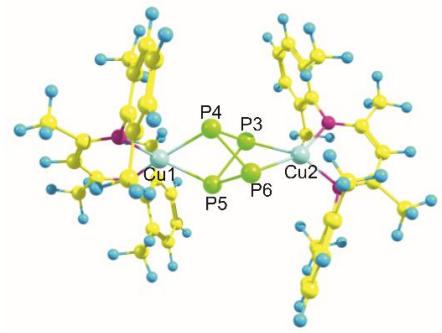
6.5.4. DFT calculations

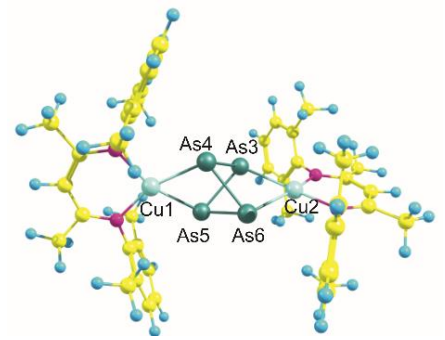
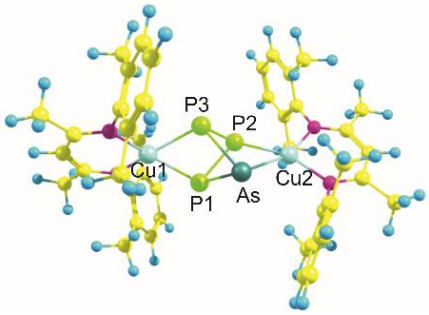
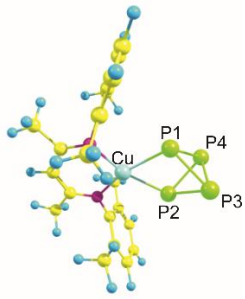
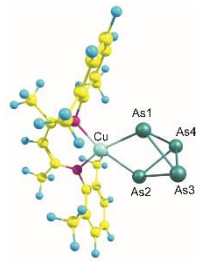
The geometries of compounds have been optimized using DFT in the form of Becke's three-parameter hybrid functional B3LYP[12] with def2-SVP basis set[13]. All structures have been fully optimized and verified to be minima on respective potential energy surfaces by subsequent vibrational analysis. Geometry was re-optimized at M06[14]/def2-TZVPP[13] level of theory, but due to large computational demands, vibrational analysis at this level of theory was not possible for the complexes. Therefore, ZPVE and thermal contributions to the standard enthalpies and standard entropies were taken from the B3LYP/def2-SVP level of theory. The Gaussian 16 suite of programs[15] was used throughout.

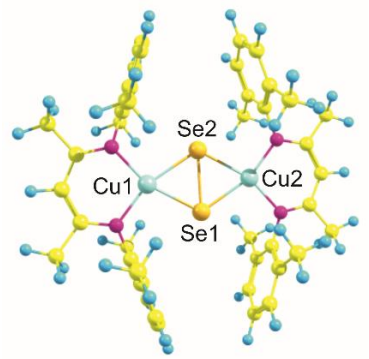
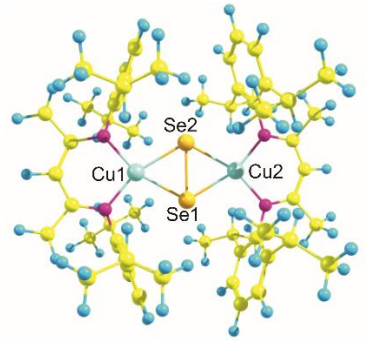
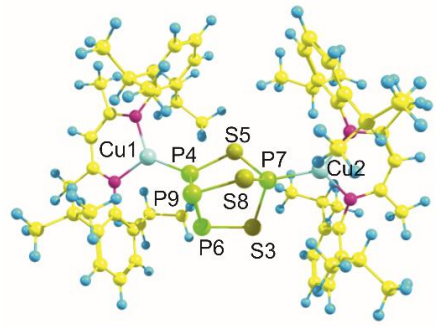
Table S6.3. Total Energies E_0, Standard enthalpies H^o_{298} (all in Hartree), Standard entropies $S°_{298}$ (in cal mol^{-1} K^{-1}) for studied compounds. B3LYP/def2-SVP level of theory if not otherwise indicated.

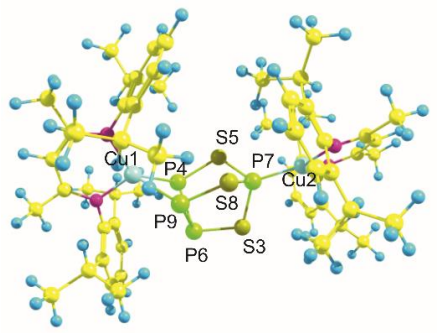
Compound	E_0	H^o_{298}	$S°_{298}$	E_0 (M06/def2-TZVPP)
P_4	-1365.087187	-1365.075594	66.904	-1365.4738757
As_4	-8942.661644	-8942.651479	78.259	-8943.3896554
AsP_3	-3259.4781213	-3259.466939	72.535	-3259.9493964
P_4S_3	-2559.4129108	-2559.391543	88.837	-2560.1241645
As_4S_3	-10136.9891716	-10136.9693	101.08	-10138.0544248
MeCN	-132.6548635	-132.605239	57.993	-132.7108660
$[Se_2]^{2-}$	-4802.4713388	-4802.467012	59.806	-4802.8768939
Se_2 singlet state	-4802.5614244	-4802.556925	58.206	-4802.9365759
Se_2 triplet state	-4802.5947975	-4802.590294	60.369	-4802.9671808
Se_8	-19210.5031502	-19210.481341	129.865	-19212.0147561
[nacnac^{1}Cu·MeCN]	-2697.2079968	-2696.723104	203.088	-2697.7088202
[nacnac^{3}Cu·MeCN]	-3011.4769644	-3010.755343	258.428	-3012.0748290
1a	-6494.1813563	-6493.298541	329.231	-6495.4819156
1b	-14071.7619194	-14070.88089	347.892	-14073.4116034
1c	-8388.5744513	-8387.692514	341.331	-8389.9640673
2a	-3929.6343144	-3929.187321	206.574	-3930.4776884
2b	-11507.2122745	-11506.76666	217.658	-11508.3999881
3a	-9931.7200269	-9930.845072	312.706	-9933.0090799
3b	-10560.2424175	-10558.8924	416.504	-10561.7422951
4a	-8317.0393438	-8315.673337	462.258	-8318.8663056
4b	-8317.0315998	-8315.665603	460.37	-8318.8668072
5_1	-15894.6051182	-15893.24107	470.662	-15896.7991560
5_5	-15894.6058900	-15893.24174	467.967	-15896.7999974

Table S6.4. Selected interatomic distances R, Wiberg Bond Indices (WBI) and Mulliken partial charges q for studied compounds. B3LYP/def2-SVP level of theory.

Compound	WBI	q, ē	R, Å
P_4	P-P 1.008		P-P 2.222
As_4	As-As 1.000		As-As 2.462
 AsP_3	As-P 0.997 P-P 1.013	q_P +0.006 q_{As} -0.018	As-P 2.343 P-P 2.228
 P_4S_3	P1-S 0.972 P3-S 1.032 P-P 0.929	q_{P1} 0.202 q_{P3} 0.084 q_S -0.151	S-P1 2.148 P3-S 2.134 P-P 2.285
 As_4S_3	As1-S 0.944 As3-S 1.014 As-As 0.913	q_{As1} 0.329 q_{As3} 0.120 q_S -0.229	S-As1 2.273 As3-S 2.246 As-As 2.521
Se_2 singlet	Se-Se 2.023		Se-Se 2.196
Se_2 triplet	Se-Se 2.024		Se-Se 2.192
Se_2^{2-}	Se-Se 1.011		Se-Se 2.543
[nacnac^{1}Cu·MeCN]	Cu-N 0.409	q_{Cu} +0.325 $q_{N\text{-}Cu}$ -0.317 $q_{N(AN)}$ +0.118	Cu-N 1.895
[nacnac^{3}Cu·MeCN]	Cu-N 0.396	q_{Cu} +0.327 $q_{N\text{-}Cu}$ -0.332 $q_{N(AN)}$ +0.118	Cu-N 1.903
 **1a**	Cu1-P(4,5) 0.478 Cu2-P(3,6) 0.477 P3-P(4,5) 0.947 P3-P6 0.652 P4-P5 0.651	q_{Cu} +0.188 q_P +0.050 q_N -0.314	Cu1-P(4,5) 2.355 Cu2-P(3,6) 2.355 P3-P(4,5) 2.239 P3-P6 2.466 P4-P5 2.467

 **1b**	Cu1-As(4,5) 0.469 Cu2-As(3,6) 0.469 As3-As(4,5) 0.933 As3-As6 0.628 As4-As5 0.628	q_{Cu} +0.151 q_{As} +0.074 q_{N} -0.308	Cu1-As(4,5) 2.469 Cu2-As(3,6) 2.469 As3-As(4,5) 2.479 As3-As6 2.701 As4-As5 2.701
 **1c**	Cu1-P1 0.461 Cu1-P3 0.464 Cu2-As 0.488 Cu2-P2 0.500 As-P1 0.929 As-P3 0.929 As-P2 0.601 P1-P3 0.686 P3-P2 0.954 P1-P2 0.954	q_{Cu1} +0.187 $q_{N(Cu1)}$ -0.314 $q_{N(Cu1)}$ -0.314 q_{Cu2} +0.171 $q_{N(Cu2)}$ -0.310 $q_{N(Cu2)}$ -0.312 q_{P1} +0.034 q_{P2} +0.060 q_{P3} +0.036 q_{As} +0.097	Cu1-P1 2.360 Cu1-P3 2.357 Cu2-As 2.451 Cu2-P2 2.359 As-P1 2.363 As-P3 2.361 As-P2 2608 P1-P3 2.452 P3-P2 2.244 P1-P2 2.242
 **2a**	Cu-P(1,2) 0.480 P1-P2 0.635 P1-P(3,4) 0.975 P3-P4 1.001	q_{Cu} +0.181 q_{N} -0.314 $q_{P1,2}$ +0.026 $q_{P3,4}$ +0.023	Cu-P(1,2) 2.366 P1-P2 2.486 P1-P(3,4) 2.232 P3-P4 2.216
 **2b**	Cu-As(1,2) 0.473 As1-As2 0.616 As1-As(3,4) 0.963 As3-As4 0.999	q_{Cu} +0.150 q_{N} -0.308 $q_{As1,2}$ +0.081 $q_{As3,4}$ -0.010	Cu-As(1,2) 2.474 As1-As2 2.720 As1-As(3,4) 2.472 As3-As4 2.450

 **3a**	Cu1-Se1 0.506 Cu1-Se2 0.506 Cu2-Se1 0.506 Cu2-Se2 0.506 Se1-Se2 0.933 Cu-Cu 0.078	q_{Cu} +0.246 q_{Se} -0.045 q_{N} -0.318	Cu1-Se1 2.410 Cu1-Se2 2.411 Cu2-Se1 2.411 Cu2-Se2 2.410 Se1-Se2 2.455 Cu-Cu 4.149
 **3b**	Cu1-Se1 0.481 Cu1-Se2 0.481 Cu2-Se1 0.481 Cu2-Se2 0.481 Se1-Se2 0.966 Cu-Cu 0.080	q_{Cu} +0.275 q_{Se} -0.057 q_{N} -0.328	Cu1-Se1 2.438 Cu1-Se2 2.438 Cu2-Se1 2.438 Cu2-Se2 2.438 Se1-Se2 2.429 Cu-Cu 4.229
 **4a**	Cu1-P4 0.514 Cu2-P7 0.537 P4-S5 0.972 P4-P9 0.876 P4-P6 0.857 P4-S8 0.052 P4-S3 0.049 P7-S5 0.939 P7-S8 0.915 P7-S3 0.907 P6-P9 0.903 P6-S3 1.057 P6-S8 0.060 P6-S5 0.067 P9-S8 1.045 P9-S3 0.060 P9-S5 0.064	q_{Cu1} +0.316 q_{NCu1} -0.339 q_{NCu1} -0.342 q_{Cu2} +0.299 q_{NCu2} -0.336 q_{NCu2} -0.340 q_{S3} -0.096 q_{P4} +0.006 q_{S5} -0.081 q_{P6} +0.141 q_{P7} +0.155 q_{S8} -0.120 q_{P9} +0.107	Cu1-P4 2.209 Cu2-P7 2.200 P4-S5 2.137 P4-P9 2.282 P4-P6 2.281 P4-S8 3.444 P4-S3 3.447 P7-S5 2.143 P7-S8 2.153 P7-S3 2.158 P6-P9 2.308 P6-S3 2.121 P6-S8 3.489 P6-S5 3.498 P9-S8 2.126 P9-S3 3.474 P9-S5 3.491

 **4b**	Cu1-P4 0.383	q_{Cu1} +0.250	Cu1-P4 2.380
	Cu1-P9 0.394	q_{NCu1} -0.345	Cu1-P9 2.360
	Cu2-P7 0.530	q_{NCu1} -0.318	Cu2-P7 2.210
	P4-S5 0.994	q_{Cu2} +0.305	P4-S5 2.143
	P4-P9 0.741	q_{NCu2} -0.337	P4-P9 2.441
	P4-P6 0.897	q_{NCu2} -0.342	P4-P6 2.274
	P4-S8 0.057	q_{S3} -0.132	P4-S8 3.549
	P4-S3 0.054	q_{P4} +0.083	P4-S3 3.457
	P7-S5 0.931	q_{S5} -0.116	P7-S5 2.143
	P7-S8 0.908	q_{P6} +0.163	P7-S8 2.156
	P7-S3 0.908	q_{P7} +0.158	P7-S3 2.159
	P6-P9 0.886	q_{S8} -0.086	P6-P9 2.266
	P6-S3 1.049	q_{P9} +0.072	P6-S3 2.119
	P6-S8 0.062		P6-S8 3.477
	P6-S5 0.060		P6-S5 3.472
	P9-S8 1.022		P9-S8 2.128
	P9-S3 0.053		P9-S3 3.461
	P9-S5 0.056		P9-S5 3.532

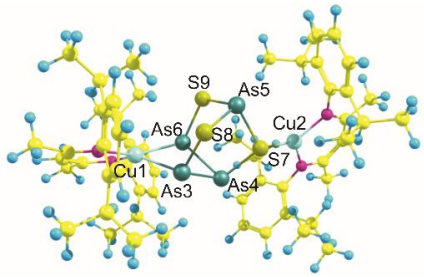
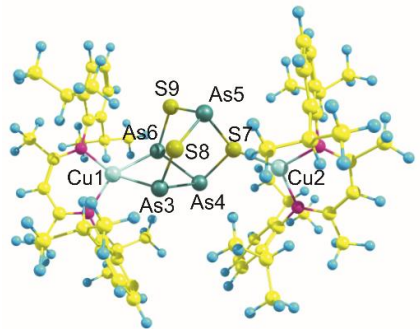
Compound	WBI	q, ē	R, Å
 **5_1**	Cu1-As3 0.435 Cu1-As6 0.420 Cu2-S7 0.422 As3-As4 0.904 As3-S8 0.976 As6-As4 0.906 As6-S9 0.955 S7-As4 0.885 S7-As5 0.804 As5-S8 0.967 As5-S9 0.966 As3-As6 0.599	q_{Cu1} +0.196 q_{NCu1} -0.326 q_{NCu1} -0.314 q_{Cu2} +0.324 q_{NCu2} -0.334 q_{NCu2} -0.335 q_{As3} +0.153 q_{As4} +0.183 q_{As5} +0.385 q_{As6} +0.187 q_{S7} -0.258 q_{S8} -0.215 q_{S9} -0.234	Cu1-As3 2.473 Cu1-As6 2.505 Cu2-S7 2.227 As3-As4 2.502 As3-S8 2.261 As6-As4 2.498 As6-S9 2.276 S7-As4 2.292 S7-As5 2.323 As5-S8 2.262 As5-S9 2.260 As3-As6 2.790
 **5_5**	Cu1-As3 0.421 Cu1-As6 0.430 Cu2-S7 0.419 As3-As4 0.907 As3-S8 0.956 As6-As4 0.905 As6-S9 0.974 S7-As4 0.886 S7-As5 0.803 As5-S8 0.964 As5-S9 0.968 As3-As6 0.597	q_{Cu1} +0.209 q_{NCu1} -0.323 q_{NCu1} -0.325 q_{Cu2} +0.324 q_{NCu2} -0.334 q_{NCu2} -0.335 q_{As3} +0.179 q_{As4} +0.184 q_{As5} +0.384 q_{As6} +0.151 q_{S7} -0.259 q_{S8} -0.231 q_{S9} -0.214	Cu1-As3 2.502 Cu1-As6 2.478 Cu2-S7 2.228 As3-As4 2.498 As3-S8 2.275 As6-As4 2.501 As6-S9 2.261 S7-As4 2.289 S7-As5 2.325 As5-S8 2.261 As5-S9 2.262 As3-As6 2.793

Table S6.5. Reaction energies (ΔE^o_0, kJ mol^{-1}), standard enthalpies (ΔH^o_{298}, kJ mol^{-1}), entropies (ΔS^o_{298}, J mol^{-1} K^{-1}) and Gibbs energies (ΔG^o_{298}, kJ mol^{-1}) for the gas phase processes. B3LYP/def2-SVP level of theory.

Process	ΔE^o_0	ΔH^o_{298}	ΔS^o_{298}	ΔG^o_{298}
2 [nacnac^{1}Cu·MeCN] + P_4 = **1a** + 2 MeCN	31.8	33.6	-116.6	68.3
2 [nacnac^{1}Cu·MeCN] + As_4 = **1b** + 2 MeCN	15.7	16.6	-86.0	42.2
2 [nacnac^{1}Cu·MeCN] + AsP_3 = **1c** + 2 MeCN	26.1	26.7	-89.5	53.4
[nacnac^{1}Cu·MeCN] + P_4 = **2a** + MeCN	15.8	16.1	-22.7	22.9
[nacnac^{1}Cu·MeCN] + As_4 = **2b** + MeCN	6.6	7.1	-23.8	14.2
1a + P_4 = 2 **2a**	-0.2	-1.3	71.2	-22.6
1b + As_4 = 2 **2b**	-2.6	-2.5	38.3	-13.9
2 [nacnac^{1}Cu·MeCN] + ¼ Se_8 = **3a** + 2 MeCN	31.6	28.9	-10.3	31.9
2 [nacnac^{3}Cu·MeCN] + ¼ Se_8 = **3b** + 2 MeCN	72.4	73.9	-70.4	94.9
2 [nacnac^{1}Cu·MeCN] + Se_2 = **3a** + 2 MeCN	-49.8	-50.0	-127.1	-12.1
2 [nacnac^{3}Cu·MeCN] + Se_2 = **3b** + 2 MeCN	-9.0	-5.0	-187.2	50.8
2 [nacnac^{3}Cu·MeCN] + P_4S_3 = **4a**+ 2 MeCN	46.7	48.3	-114.8	82.6
2 [nacnac^{3}Cu·MeCN] + P_4S_3 = **4b**+ 2 MeCN	67.0	68.7	-122.7	105.2
2 [nacnac^{3}Cu·MeCN] + As_4S_3 = **5** + 2 MeCN	72.2	72.9	-142.2	115.3

Table S6.6. Reaction energies (ΔE^o_0, kJ mol^{-1}), standard enthalpies (ΔH^o_{298}, kJ mol^{-1}), entropies (ΔS^o_{298}, J mol^{-1} K^{-1}) and Gibbs energies (ΔG^o_{298}, kJ mol^{-1}) for the gas phase processes at M06/def2-TZVPP level of theory (with ZPVE and thermal contributions to enthalpy and standard entropies from B3LYP/def2-SVP level).

Process	ΔE^o_0	ΔH^o_{298}	ΔS^o_{298}	ΔG^o_{298}
2 [nacnac^{1}Cu·MeCN] + P_4 = **1a** + 2 MeCN	-31.9	-30.0	-116.6	4.7
2 [nacnac^{1}Cu·MeCN] + As_4 = **1b** + 2 MeCN	-68.4	-67.5	-86.0	-41.9
2 [nacnac^{1}Cu·MeCN] + AsP_3 = **1c** + 2 MeCN	-49.3	-48.7	-89.5	-22.0
[nacnac^{1}Cu·MeCN] + P_4 = **2a** + MeCN	-15.4	-15.0	-22.7	-8.3
[nacnac^{1}Cu·MeCN] + As_4 = **2b** + MeCN	-32.5	-32.0	-23.8	-24.9
1a + P_4 = 2 **2a**	1.1	0.0	71.2	-21.2
1b + As_4 = 2 **2b**	3.4	3.5	38.3	-8.0
2 [nacnac^{1}Cu·MeCN] + ¼ Se_8 = **3a** + 2 MeCN	-24.9	-27.6	-10.3	-24.5
2 [nacnac^{3}Cu·MeCN] + ¼ Se_8 = **3b** + 2 MeCN	-28.0	-26.6	-70.4	-5.6
2 [nacnac^{1}Cu·MeCN] + Se_2 = **3a** + 2 MeCN	-120.7	-121.0	-127.1	-83.1
2 [nacnac^{3}Cu·MeCN] + Se_2 = **3b** + 2 MeCN	-123.9	-119.9	-187.2	-64.1
2 [nacnac^{3}Cu·MeCN] + P_4S_3 = **4a**+ 2 MeCN	-37.3	-35.6	-114.8	-1.4
2 [nacnac^{3}Cu·MeCN] + P_4S_3 = **4b**+ 2 MeCN	-38.6	-37.0	-122.7	-0.4
2 [nacnac^{3}Cu·MeCN] + As_4S_3 = **5** + 2 MeCN	-46.3	-45.6	-142.2	-3.2

Table S6.7. Optimized gas phase geometries (xyz coordinates in Å) for studied compounds.

B3LYP/def2-SVP level of theory				M06/def2-TZVPP level of theory			
P_4				**P_4**			
15	0.785664000	0.785664000	0.785664000	15	0.770545000	0.770545000	0.770545000
15	-0.785664000	-0.785664000	0.785664000	15	-0.770545000	-0.770545000	0.770545000
15	0.785664000	-0.785664000	-0.785664000	15	0.770545000	-0.770545000	-0.770545000
15	-0.785664000	0.785664000	-0.785664000	15	-0.770545000	0.770545000	-0.770545000
As_4				**As_4**			
33	0.870401000	0.870401000	0.870401000	33	0.859077000	0.859077000	0.859077000
33	-0.870401000	-0.870401000	0.870401000	33	-0.859077000	-0.859077000	0.859077000
33	0.870401000	-0.870401000	-0.870401000	33	0.859077000	-0.859077000	-0.859077000
33	-0.870401000	0.870401000	-0.870401000	33	-0.859077000	0.859077000	-0.859077000
AsP_3				**AsP_3**			
33	0.000000000	0.000000000	1.130046000	33	0.000000000	0.000000000	1.107556000
15	0.000000000	1.286185000	-0.828700000	15	0.000000000	1.263838000	-0.812208000
15	-1.113869000	-0.643093000	-0.828700000	15	-1.094516000	-0.631919000	-0.812208000
15	1.113869000	-0.643093000	-0.828700000	15	1.094516000	-0.631919000	-0.812208000
P_4S_3				**P_4S_3**			
15	0.000000000	0.000000000	1.735000000	15	0.000000000	0.000000000	1.700003000
16	0.000000000	1.890489000	0.715004000	16	0.000000000	1.861712000	0.704582000
16	1.637212000	-0.945245000	0.715004000	16	1.612290000	-0.930856000	0.704582000
16	-1.637212000	-0.945245000	0.715004000	16	-1.612290000	-0.930856000	0.704582000
15	1.142438000	-0.659587000	-1.341004000	15	1.120110000	-0.646696000	-1.318222000
15	0.000000000	1.319174000	-1.341004000	15	0.000000000	1.293392000	-1.318222000
15	-1.142438000	-0.659587000	-1.341004000	15	-1.120110000	-0.646696000	-1.318222000
As_4S_3				**As_4S_3**			
33	0.000000000	0.000000000	2.097592000	33	0.000000000	0.000000000	2.065592000
16	0.000000000	1.989236000	0.998643000	16	0.000000000	1.962965000	0.987609000
16	1.722729000	-0.994618000	0.998643000	16	1.699977000	-0.981482000	0.987609000
16	-1.722729000	-0.994618000	0.998643000	16	-1.699977000	-0.981482000	0.987609000
33	1.260535000	-0.727770000	-1.183388000	33	1.241051000	-0.716521000	-1.167372000
33	0.000000000	1.455540000	-1.183388000	33	0.000000000	1.433042000	-1.167372000
33	-1.260535000	-0.727770000	-1.183388000	33	-1.241051000	-0.716521000	-1.167372000
MeCN				**MeCN**			
6	0.000000000	0.000000000	0.280868000	6	0.000000000	0.000000000	0.278154000
7	0.000000000	0.000000000	1.439066000	7	0.000000000	0.000000000	1.426018000
6	0.000000000	0.000000000	-1.178992000	6	0.000000000	0.000000000	-1.168138000
1	0.000000000	1.031931000	-1.561573000	1	0.000000000	1.021026000	-1.547407000
1	-0.893679000	-0.515966000	-1.561573000	1	-0.884234000	-0.510513000	-1.547407000
1	0.893679000	-0.515966000	-1.561573000	1	0.884234000	-0.510513000	-1.547407000
$[Se_2]^{2-}$				**$[Se_2]^{2-}$**			
34	0.000000000	0.000000000	1.271337000	34	0.000000000	0.000000000	1.245492000
34	0.000000000	0.000000000	-1.271337000	34	0.000000000	0.000000000	-1.245492000
Se_2 singlet state				**Se_2 singlet state**			
34	0.000000000	0.000000000	1.097975000	34	0.000000000	0.000000000	1.084769000
34	0.000000000	0.000000000	-1.097975000	34	0.000000000	0.000000000	-1.084769000
Se_2 triplet state				**Se_2 triplet state**			
34	0.000000000	0.000000000	1.096238000	34	0.000000000	0.000000000	1.084898000
34	0.000000000	0.000000000	-1.096238000	34	0.000000000	0.000000000	-1.084898000
Se_8				**Se_8**			
34	0.000000000	2.696428000	0.579350000	34	0.000000000	2.633636000	0.589672000
34	-1.906663000	1.906663000	-0.579350000	34	-1.862262000	1.862262000	-0.589672000
34	1.906663000	1.906663000	-0.579350000	34	1.862262000	1.862262000	-0.589672000
34	-2.696428000	0.000000000	0.579350000	34	-2.633636000	0.000000000	0.589672000
34	2.696428000	0.000000000	0.579350000	34	2.633636000	0.000000000	0.589672000
34	1.906663000	-1.906663000	-0.579350000	34	1.862262000	-1.862262000	-0.589672000
34	-1.906663000	-1.906663000	-0.579350000	34	-1.862262000	-1.862262000	-0.589672000
34	0.000000000	-2.696428000	0.579350000	34	0.000000000	-2.633636000	0.589672000
[nacnac^{1}Cu·MeCN]				**[nacnac^{1}Cu·MeCN]**			
29	0.000146000	0.455091000	-0.000445000	29	0.163705000	0.554901000	0.112924000
7	1.506201000	-0.824368000	0.001493000	7	1.732337000	-0.535313000	0.044450000
7	-1.505593000	-0.824859000	0.001444000	7	-1.233281000	-0.913579000	0.047045000
6	2.818817000	-0.291599000	-0.000398000	6	2.983934000	0.117686000	-0.000919000
6	-2.818353000	-0.292470000	-0.000421000	6	-2.572576000	-0.519668000	-0.002490000
6	-1.283354000	-2.136970000	0.004693000	6	-0.860961000	-2.172119000	-0.022043000
6	1.284363000	-2.136554000	0.004736000	6	1.662239000	-1.854319000	-0.011610000
6	0.000602000	-2.732315000	0.006459000	6	0.475694000	-2.600395000	-0.024874000
1	0.000780000	-3.822152000	0.009148000	1	0.611310000	-3.672149000	-0.067097000
6	-3.454510000	0.019056000	1.226615000	6	-3.271268000	-0.275962000	1.189203000
6	3.454873000	0.020180000	1.226624000	6	3.664231000	0.407364000	1.186699000
6	3.453850000	0.014043000	-1.229501000	6	3.495632000	0.532267000	-1.235967000
6	-3.453458000	0.013082000	-1.229510000	6	-3.165439000	-0.226410000	-1.240039000

6	2.472128000	-3.084738000	0.006690000
1	3.110625000	-2.917327000	-0.875021000
1	2.149877000	-4.133990000	0.009882000
1	3.111831000	-2.912301000	0.886550000
6	-2.470818000	-3.085530000	0.006611000
1	-3.110641000	-2.913245000	0.886412000
1	-2.148238000	-4.134680000	0.009882000
1	-3.109302000	-2.918370000	-0.875159000
6	2.751264000	-0.248365000	2.533313000
1	1.753758000	0.222131000	2.545064000
1	3.331700000	0.137650000	3.384425000
1	2.579683000	-1.324845000	2.701799000
6	-4.728051000	0.595669000	-1.209171000
1	-5.219673000	0.828640000	-2.158572000
6	-5.371729000	0.883761000	-0.004369000
1	-6.367009000	1.335754000	-0.005887000
6	4.728277000	0.596993000	-1.209181000
1	5.219845000	0.830053000	-2.158589000
6	-4.729092000	0.601503000	1.202366000
1	-5.221512000	0.839117000	2.150198000
6	-2.748712000	-0.261796000	-2.534277000
1	-1.751136000	0.208504000	-2.547459000
1	-3.328361000	0.120160000	-3.387755000
1	-2.577117000	-1.339095000	-2.697443000
6	2.749210000	-0.261124000	-2.534266000
1	2.578126000	-1.338500000	-2.697475000
1	3.328668000	0.121132000	-3.387738000
1	1.751409000	0.208700000	-2.547417000
6	5.371858000	0.885348000	-0.004391000
1	6.367005000	1.337630000	-0.005929000
6	4.729289000	0.602986000	1.202355000
1	5.221629000	0.840801000	2.150178000
6	-2.750846000	-0.249383000	2.533296000
1	-2.579243000	-1.325849000	2.701855000
1	-3.331264000	0.136672000	3.384404000
1	-1.753348000	0.221126000	2.544976000
6	-0.002004000	3.509268000	-0.001654000
7	-0.000909000	2.350221000	-0.001649000
6	-0.003451000	4.964541000	-0.000631000
1	0.884240000	5.348475000	-0.526902000
1	0.011856000	5.338803000	1.034584000
1	-0.907212000	5.346902000	-0.500025000

[nacnac^{3}Cu·MeCN]

29	0.000123000	0.001261000	0.447485000
7	1.510179000	0.000066000	-0.836318000
7	-1.509867000	-0.003852000	-0.836418000
6	-2.831622000	-0.006195000	-0.313162000
6	-3.490037000	1.225147000	-0.044465000
6	-3.461170000	-1.236349000	0.017251000
6	1.285022000	0.001421000	-2.149053000
6	-1.284663000	-0.011736000	-2.149112000
6	2.762692000	2.572637000	-0.226289000
1	1.870046000	2.370241000	-0.835122000
6	2.831968000	0.004370000	-0.313130000
6	0.000200000	-0.006608000	-2.742527000
1	0.000241000	-0.009155000	-3.832259000
6	3.490551000	-1.226012000	-0.040262000
6	-4.731377000	-1.209061000	0.610167000
1	-5.221698000	-2.151082000	0.870446000
6	-4.759053000	1.197742000	0.549746000
1	-5.271967000	2.138912000	0.763677000
6	-5.383737000	-0.006064000	0.875504000
1	-6.375837000	-0.005753000	1.334687000
6	-2.762546000	-2.574135000	-0.217491000
1	-1.870227000	-2.373932000	-0.827526000
6	3.461391000	1.235698000	0.013007000
6	2.468925000	0.010735000	-3.100941000
1	3.108541000	0.889226000	-2.922253000
1	2.143344000	0.021504000	-4.149008000
1	3.108163000	-0.871817000	-2.941100000
6	2.811493000	-2.563492000	-0.329609000
1	1.993666000	-2.369304000	-1.038316000
6	-2.468520000	-0.025889000	-3.100996000
1	-3.106886000	-0.904713000	-2.919382000
1	-2.142904000	-0.039817000	-4.149013000
1	-3.109042000	0.856249000	-2.944130000
6	4.759613000	-1.196401000	0.553675000
1	5.272687000	-2.136736000	0.770781000
6	-2.811097000	2.561576000	-0.338797000
1	-1.991230000	2.364211000	-1.044253000
6	2.164127000	-3.130038000	0.947920000
1	2.924198000	-3.336072000	1.720334000
1	1.629370000	-4.071546000	0.737560000
1	1.439980000	-2.414969000	1.367580000
6	5.384207000	0.008610000	0.875239000

6	2.941027000	-2.643362000	-0.075449000
1	3.516040000	-2.389037000	-0.968029000
1	2.743905000	-3.712504000	-0.086624000
1	3.583799000	-2.416320000	0.776662000
6	-1.912973000	-3.242422000	-0.124025000
1	-2.653306000	-3.145827000	0.672194000
1	-1.477495000	-4.238011000	-0.077822000
1	-2.459160000	-3.151143000	-1.066153000
6	3.075917000	0.025285000	2.505595000
1	2.087102000	0.473810000	2.638063000
1	3.713712000	0.354226000	3.325939000
1	2.932888000	-1.053502000	2.601701000
6	-4.466289000	0.257442000	-1.267679000
1	-4.926436000	0.469393000	-2.226954000
6	-5.176416000	0.467890000	-0.097066000
1	-6.196116000	0.830606000	-0.133924000
6	4.711325000	1.201146000	-1.265706000
1	5.111261000	1.519498000	-2.222272000
6	-4.571140000	0.206886000	1.121368000
1	-5.115121000	0.378250000	2.044228000
6	-2.381883000	-0.412176000	-2.498145000
1	-1.433292000	0.131812000	-2.450253000
1	-2.941338000	-0.063853000	-3.366135000
1	-2.116159000	-1.458790000	-2.666644000
6	2.725573000	0.281616000	-2.491590000
1	2.562052000	-0.782755000	-2.675986000
1	3.242904000	0.698428000	-3.355620000
1	1.729790000	0.732809000	-2.435324000
6	5.407817000	1.468039000	-0.101260000
1	6.356083000	1.989129000	-0.140340000
6	4.877740000	1.077563000	1.114794000
1	5.408806000	1.298593000	2.034304000
6	-2.602641000	-0.511367000	2.503971000
1	-2.284403000	-1.549062000	2.624377000
1	-3.266110000	-0.261641000	3.331837000
1	-1.694328000	0.091978000	2.592771000
6	-1.828632000	2.752079000	0.115925000
7	-0.854292000	2.145642000	0.140008000
6	-3.066208000	3.486835000	0.083966000
1	-3.107669000	4.119704000	-0.801684000
1	-3.157409000	4.114209000	0.969772000
1	-3.900347000	2.779386000	0.057730000

[nacnac^{3}Cu·MeCN]

29	0.142375000	0.047725000	0.496669000
7	1.673585000	0.011315000	-0.655880000
7	-1.285343000	0.008817000	-0.925783000
6	-2.611062000	-0.013170000	-0.473438000
6	-3.265532000	1.191641000	-0.162712000
6	-3.229278000	-1.246287000	-0.196908000
6	1.564286000	-0.019655000	-1.972605000
6	-0.965684000	-0.012505000	-2.200520000
6	2.907388000	2.535013000	-0.066419000
1	2.195741000	2.358175000	-0.877713000
6	2.949659000	0.003768000	-0.046144000
6	0.353221000	-0.021560000	-2.679411000
1	0.450666000	-0.038720000	-3.755980000
6	3.539128000	-1.218027000	0.308620000
6	-4.484566000	-1.248990000	0.397302000
1	-4.969248000	-2.195412000	0.612234000
6	-4.520960000	1.138834000	0.430597000
1	-5.035479000	2.063531000	0.669935000
6	-5.132965000	-0.068299000	0.714436000
1	-6.117247000	-0.089466000	1.165906000
6	-2.523340000	-2.550585000	-0.490495000
1	-1.696831000	-2.337377000	-1.173212000
6	3.579967000	1.220120000	0.255179000
6	2.819102000	-0.056540000	-2.798734000
1	3.446322000	0.813808000	-2.593335000
1	2.593133000	-0.080130000	-3.861891000
1	3.421581000	-0.933024000	-2.549217000
6	2.823744000	-2.524160000	0.051062000
1	2.075684000	-2.349618000	-0.727843000
6	-2.063726000	-0.040535000	-3.225850000
1	-2.643724000	-0.963394000	-3.142372000
1	-1.671759000	0.029305000	-4.237967000
1	-2.764997000	0.780280000	-3.061200000
6	4.763733000	-1.199685000	0.962642000
1	5.229976000	-2.136269000	1.246851000
6	-2.619504000	2.529815000	-0.443281000
1	-1.701744000	2.342455000	-1.007112000
6	2.077615000	-2.957843000	1.308130000
1	2.782586000	-3.150006000	2.121533000
1	1.504221000	-3.870683000	1.130957000
1	1.385629000	-2.179915000	1.644058000
6	5.397950000	-0.008848000	1.260483000

1	6.376365000	0.009960000	1.334295000
6	4.731683000	1.210589000	0.605904000
1	5.221903000	2.153558000	0.862924000
6	2.270025000	3.180612000	1.099986000
1	1.590818000	2.486989000	1.619352000
1	1.723984000	4.122629000	0.923922000
1	3.112230000	3.399785000	1.777698000
6	3.632303000	3.574354000	-1.003939000
1	4.520828000	3.884964000	-0.429787000
1	3.057807000	4.486867000	-1.234030000
1	3.985240000	3.148998000	-1.956884000
6	-3.632443000	-3.578819000	-0.990965000
1	-4.520456000	-3.887704000	-0.415081000
1	-3.057839000	-4.491962000	-1.218260000
1	-3.986236000	-3.156933000	-1.945132000
6	3.743995000	-3.596579000	-0.981041000
1	4.220436000	-3.195812000	-1.889982000
1	3.177221000	-4.498122000	-1.266007000
1	4.547583000	-3.922230000	-0.300271000
6	-2.167628000	3.135304000	0.937491000
1	-2.929842000	3.344752000	1.706862000
1	-1.633045000	4.076124000	0.723598000
1	-1.444073000	2.422934000	1.362741000
6	-2.269139000	-3.177170000	1.110768000
1	-1.589644000	-2.481658000	1.627245000
1	-1.723097000	-4.119779000	0.937951000
1	-3.111038000	-3.393960000	1.789635000
6	-3.742653000	3.590476000	-0.998184000
1	-4.216025000	3.184685000	-1.906497000
1	-3.175935000	4.491145000	-1.286038000
1	-4.548603000	3.918720000	-0.321447000
6	-0.000873000	0.010147000	3.509767000
7	-0.000480000	0.006445000	2.350411000
6	-0.001136000	0.015937000	4.964685000
1	-0.039037000	1.051938000	5.335121000
1	0.912611000	-0.463215000	5.349157000
1	-0.877999000	-0.528155000	5.348573000

1	6.354372000	-0.013614000	1.768186000
6	4.803390000	1.188844000	0.910411000
1	5.301853000	2.120097000	1.153775000
6	2.106901000	3.016621000	1.138667000
1	1.365208000	2.272563000	1.444664000
1	1.582500000	3.948407000	0.914346000
1	2.770735000	3.195615000	1.988821000
6	3.875374000	3.612320000	-0.528169000
1	4.544963000	3.927398000	0.275360000
1	3.327171000	4.498092000	-0.854337000
1	4.492357000	3.268568000	-1.360811000
6	-3.426679000	-3.572251000	-1.163906000
1	-4.216447000	-3.922361000	-0.494922000
1	-2.849501000	-4.448355000	-1.465040000
1	-3.905494000	-3.158866000	-2.053795000
6	3.746079000	-3.631289000	-0.433549000
1	4.319283000	-3.321616000	-1.309686000
1	3.166913000	-4.516758000	-0.702365000
1	4.456552000	-3.934077000	0.338867000
6	-2.222609000	3.231509000	0.849817000
1	-3.100651000	3.421396000	1.473932000
1	-1.750781000	4.193969000	0.641181000
1	-1.517351000	2.630766000	1.427206000
6	-1.910905000	-3.127827000	0.780227000
1	-1.185646000	-2.437767000	1.217361000
1	-1.395726000	-4.068580000	0.573362000
1	-2.685567000	-3.327092000	1.527359000
6	-3.510530000	3.433724000	-1.284650000
1	-3.834792000	2.938578000	-2.201542000
1	-2.976613000	4.344693000	-1.561841000
1	-4.406783000	3.736157000	-0.737475000
6	-1.681833000	0.073092000	2.846574000
7	-0.761726000	0.081781000	2.160409000
6	-2.861412000	0.060608000	3.671434000
1	-3.193462000	1.082413000	3.855208000
1	-2.664035000	-0.428082000	4.624771000
1	-3.659750000	-0.469605000	3.146441000

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29	-2.708749000	-0.000169000	-0.000449000
29	2.708767000	-0.000553000	0.000970000
15	0.701545000	1.159811000	0.415685000
15	-0.702960000	-0.417316000	1.160771000
15	-0.702335000	0.413787000	-1.161653000
15	0.702840000	-1.162052000	-0.415352000
7	-4.017089000	-1.092639000	1.028846000
7	4.015614000	1.030777000	1.093345000
7	-4.015513000	1.094283000	-1.029519000
7	4.017243000	-1.029961000	-1.091231000
6	-5.330447000	-0.936273000	0.870589000
6	-5.329068000	0.939934000	-0.870848000
6	3.508086000	-1.950378000	-2.046585000
6	3.163724000	-1.496392000	-3.342996000
6	-5.926722000	0.002494000	0.000121000
1	-7.015988000	0.003452000	0.000262000
6	-3.507865000	-2.049453000	1.947665000
6	5.329186000	0.872507000	0.938848000
6	-3.505211000	2.049495000	-1.949438000
6	-6.279384000	-1.817199000	1.664721000
1	-6.091392000	-2.882247000	1.457442000
1	-7.327005000	-1.594075000	1.425801000
1	-6.131141000	-1.683435000	2.747460000
6	-3.158035000	3.344753000	-1.494248000
6	3.266166000	3.294886000	1.671580000
6	-3.162685000	-3.344863000	1.491454000
6	3.505041000	1.951032000	2.048084000
6	3.268838000	-3.294244000	-1.670426000
6	3.158858000	1.496965000	3.343961000
6	-6.276854000	1.821689000	-1.665496000
1	-6.085954000	2.886682000	-1.460634000
1	-7.324723000	1.601638000	-1.424803000
1	-6.130358000	1.685351000	-2.748155000
6	-3.269232000	-1.675496000	3.292254000
6	5.926865000	0.000981000	0.001940000
1	7.016132000	0.001204000	0.002532000
6	2.712673000	4.173377000	2.614556000
1	2.528945000	5.212588000	2.326871000
6	5.330578000	-0.871075000	-0.935349000
6	2.617267000	-2.408557000	-4.255855000
1	2.356492000	-2.062230000	-5.260123000
6	2.398526000	-3.741100000	-3.901722000
1	1.969796000	-4.438830000	-4.625509000
6	2.392402000	3.741504000	3.901566000
1	1.962533000	4.439146000	4.624761000
6	-3.267487000	1.674311000	-3.293848000
6	2.716934000	-4.172890000	-2.614256000

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29	-2.719519000	-0.057994000	-0.053853000
29	2.715418000	0.081146000	-0.027209000
15	0.672865000	1.133089000	0.251714000
15	-0.708001000	-0.372572000	1.051746000
15	-0.733131000	0.279328000	-1.200754000
15	0.760530000	-1.116536000	-0.400999000
7	-4.000918000	-1.149671000	0.946054000
7	3.925427000	1.105609000	1.126617000
7	-4.015944000	1.053037000	-1.012802000
7	4.083089000	-0.875092000	-1.050649000
6	-5.304008000	-1.008909000	0.801544000
6	-5.316441000	0.923295000	-0.835017000
6	3.625836000	-1.825292000	-1.986088000
6	3.190468000	-1.400630000	-3.246609000
6	-5.909966000	-0.041861000	-0.011133000
1	-6.990721000	-0.037539000	0.002379000
6	-3.451736000	-2.115376000	1.813381000
6	5.236101000	0.995076000	1.043100000
6	-3.482220000	2.025350000	-1.882355000
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6	2.559688000	-3.671437000	-3.762937000
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1b

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6	-2.210101000	4.771378000	-2.341216000
1	-2.607732000	5.654166000	-1.857186000

1c

29	-2.775717000	0.000246000	-0.011922000
29	2.702789000	0.095591000	0.018110000
15	-0.756747000	-0.358033000	1.149453000
7	3.929785000	1.327093000	1.004403000
7	-4.097582000	1.125121000	-0.988790000
7	-4.069663000	-1.154318000	0.969694000
7	4.102757000	-1.005876000	-0.877136000
6	-3.544887000	-2.142955000	1.844278000
6	5.253215000	1.218972000	0.907370000
6	-3.598073000	2.119146000	-1.872284000
6	5.923759000	0.268625000	0.105850000

1c

29	2.779577000	0.136468000	-0.294704000
29	-2.657972000	-0.012385000	0.055581000
15	0.823019000	0.445965000	0.926265000
7	-3.617466000	-1.478176000	0.961241000
7	3.597197000	-1.512382000	-1.003666000
7	4.399240000	0.988488000	0.370331000
7	-4.230936000	1.037696000	-0.446236000
6	4.228782000	2.173485000	1.114330000
6	-4.932632000	-1.517607000	1.032198000
6	2.699544000	-2.448215000	-1.551286000
6	-5.783967000	-0.568648000	0.448922000

1	7.010940000	0.329987000	0.130300000	1	-6.841074000	-0.765094000	0.559613000
6	-3.314315000	-1.826882000	3.205278000	6	4.111974000	2.100233000	2.508115000
6	3.351201000	2.333802000	1.824450000	6	-2.815337000	-2.447544000	1.597503000
6	-2.498440000	4.045259000	-3.593038000	6	0.695824000	-4.075612000	-2.580469000
1	-2.073896000	4.796811000	-4.263476000	1	-0.088884000	-4.705053000	-2.980817000
6	3.680374000	-2.083653000	-1.702006000	6	-3.982042000	2.301825000	-1.018564000
6	-3.172942000	-3.408561000	1.329482000	6	4.058668000	3.391045000	0.446322000
6	-3.377861000	1.801627000	-3.234603000	6	2.401573000	-2.401665000	-2.919668000
6	-5.408488000	0.954419000	-0.827678000	6	4.894442000	-1.722348000	-0.932454000
6	5.401604000	-0.751242000	-0.717126000	6	-5.461896000	0.615892000	-0.222736000
6	-2.698606000	4.341183000	-2.243561000	6	0.999465000	-4.113963000	-1.231500000
1	-2.427198000	5.327520000	-1.856238000	1	0.445377000	-4.769247000	-0.567252000
6	6.133308000	2.165098000	1.706131000	6	-5.586834000	-2.633958000	1.795878000
1	5.932645000	3.214369000	1.440423000	1	-5.311676000	-3.606797000	1.384763000
1	7.197903000	1.959296000	1.536940000	1	-6.670315000	-2.544442000	1.780473000
1	5.926177000	2.075408000	2.784024000	1	-5.252720000	-2.633812000	2.835431000
6	-3.240485000	3.392202000	-1.366086000	6	1.998294000	-3.310521000	-0.697446000
6	-2.740896000	-2.799204000	4.037758000	6	3.856322000	3.265296000	3.218319000
1	-2.563650000	-2.558355000	5.089985000	1	3.763959000	3.211526000	4.297526000
6	-5.993147000	-0.030118000	-0.000174000	6	5.814033000	-0.802592000	-0.406018000
1	-7.082441000	-0.038869000	0.005122000	1	6.849748000	-1.108839000	-0.454720000
6	-2.830858000	2.780053000	-4.077501000	6	1.398009000	-3.223954000	-3.414067000
1	-2.661860000	2.538132000	-5.130852000	1	1.162670000	-3.184805000	-4.471927000
6	-5.384698000	-1.005563000	0.820751000	6	5.588216000	0.441103000	0.200836000
6	3.341562000	-1.840463000	-3.055496000	6	-3.676828000	2.395596000	-2.381586000
6	6.416933000	-1.600037000	-1.463098000	6	-6.611036000	1.452640000	-0.708974000
1	6.328470000	-2.661829000	-1.185774000	1	-6.627612000	2.424058000	-0.211095000
1	7.442723000	-1.270163000	-1.255191000	1	-7.563701000	0.959496000	-0.531708000
1	6.246557000	-1.550122000	-2.549944000	1	-6.514344000	1.655517000	-1.777336000
6	-2.605062000	-4.351638000	2.196716000	6	3.807178000	4.533864000	1.192700000
1	-2.322863000	-5.332345000	1.802755000	1	3.681410000	5.479587000	0.677118000
6	-2.393190000	-4.056947000	3.544732000	6	3.710809000	4.479031000	2.571447000
1	-1.948287000	-4.803653000	4.207344000	1	3.512602000	5.378792000	3.139852000
6	3.065828000	3.607760000	1.276842000	6	-2.455210000	-3.617382000	0.918169000
6	-3.719403000	0.430976000	-3.763681000	6	3.129568000	-1.454697000	-3.818052000
1	-3.273653000	-0.359057000	-3.137693000	1	3.081406000	-0.430191000	-3.438769000
1	-3.360283000	0.303615000	-4.795326000	1	2.709572000	-1.470669000	-4.823380000
1	-4.806704000	0.243784000	-3.761260000	1	4.192696000	-1.695663000	-3.896441000
6	3.515832000	-3.374399000	-1.142126000	6	-3.908330000	3.429106000	-0.190337000
6	-3.674190000	-0.464877000	3.744320000	6	4.226914000	0.783611000	3.207359000
1	-3.249979000	0.335595000	3.116791000	1	3.575254000	0.033353000	2.749275000
1	-3.305269000	-0.335432000	4.772220000	1	3.960041000	0.877386000	4.259703000
1	-4.764721000	-0.297848000	3.755539000	1	5.238509000	0.372417000	3.156922000
6	-3.371477000	-3.725110000	-0.131948000	6	4.122029000	3.442566000	-1.045374000
1	-4.431226000	-3.666500000	-0.430331000	1	5.068941000	3.058834000	-1.431145000
1	-3.006367000	-4.734303000	-0.372091000	1	3.993831000	4.462367000	-1.407350000
1	-2.835089000	-3.003671000	-0.771525000	1	3.340578000	2.820365000	-1.494518000
6	-6.368595000	1.869319000	-1.568708000	6	5.444462000	-3.027444000	-1.433858000
1	-6.181765000	2.923557000	-1.310748000	1	4.988352000	-3.863287000	-0.899055000
1	-7.413022000	1.631097000	-1.330203000	1	6.523073000	-3.082107000	-1.307447000
1	-6.231927000	1.790115000	-2.658315000	1	5.209727000	-3.172372000	-2.490065000
6	3.470508000	-0.454667000	-3.636782000	6	-3.693547000	1.172938000	-3.239770000
1	2.867293000	0.273580000	-3.068726000	1	-2.954109000	0.440610000	-2.898033000
1	3.138304000	-0.432119000	-4.684775000	1	-3.470242000	1.420035000	-4.277137000
1	4.508375000	-0.084547000	-3.600375000	1	-4.658075000	0.661880000	-3.208992000
6	3.835053000	-3.623481000	0.311101000	6	-4.169703000	3.305535000	1.276344000
1	4.911117000	-3.508823000	0.524868000	1	-5.206932000	3.036581000	1.491829000
1	3.539282000	-4.638526000	0.613396000	1	-3.954172000	4.241263000	1.791009000
1	3.318437000	-2.900568000	0.963799000	1	-3.557993000	2.515556000	1.723570000
6	-3.424986000	3.710397000	0.096761000	6	2.305565000	-3.342136000	0.764909000
1	-4.478423000	3.627651000	0.411175000	1	3.326281000	-3.680908000	0.960249000
1	-3.080162000	4.728877000	0.327224000	1	1.616832000	-4.002046000	1.293000000
1	-2.861074000	3.005549000	0.731136000	1	2.229908000	-2.346417000	1.213997000
6	-6.322465000	-1.937390000	1.569264000	6	6.800700000	1.181734000	0.691476000
1	-6.121972000	-2.987951000	1.306527000	1	6.817067000	2.199827000	0.297983000
1	-7.372961000	-1.715087000	1.342344000	1	7.718578000	0.678121000	0.397801000
1	-6.175577000	-1.858770000	2.657579000	1	6.791761000	1.272325000	1.779456000
6	2.875458000	-2.906317000	-3.837849000	6	-3.330789000	3.633836000	-2.905441000
1	2.619016000	-2.722874000	-4.885198000	1	-3.098969000	3.709906000	-3.961897000
6	3.044750000	-4.411773000	-1.960680000	6	-3.555784000	4.649411000	-0.752538000
1	2.919706000	-5.410248000	-1.531948000	1	-3.496412000	5.523397000	-0.113603000
6	3.409639000	3.916679000	-0.158793000	6	-2.969796000	-3.884663000	-0.458541000
1	4.498576000	3.916900000	-0.335037000	1	-4.054842000	-4.012689000	-0.479674000
1	3.021047000	4.901486000	-0.455972000	1	-2.517256000	-4.785167000	-0.874060000
1	2.991035000	3.157701000	-0.839982000	1	-2.749096000	-3.050713000	-1.130810000
6	2.732449000	-4.187103000	-3.301562000	6	-3.274103000	4.758453000	-2.101933000
1	2.367222000	-5.006506000	-3.925704000	1	-3.000087000	5.716339000	-2.525030000
6	2.374328000	3.019354000	3.935828000	6	-1.400964000	-3.067185000	3.436528000
1	2.097277000	2.787921000	4.968357000	1	-0.983274000	-2.845412000	4.412158000
6	2.450501000	4.570543000	2.090093000	6	-1.585298000	-4.506709000	1.537397000
1	2.231367000	5.556796000	1.670963000	1	-1.315687000	-5.421252000	1.019853000
6	3.241283000	0.651700000	3.721561000	6	-2.599747000	-0.866424000	3.534777000
1	2.739225000	-0.124343000	3.119318000	1	-2.234803000	-0.012238000	2.952971000
1	2.874512000	0.573434000	4.755287000	1	-2.144416000	-0.818413000	4.523473000
1	4.313089000	0.393252000	3.720092000	1	-3.675924000	-0.715840000	3.644447000
6	2.112118000	4.286801000	3.413241000	6	-1.063084000	-4.242681000	2.789591000

1	1.633462000	5.048614000	4.033731000	1	-0.386362000	-4.946658000	3.257365000
33	0.725222000	-1.276549000	-0.442513000	33	-0.844179000	1.589691000	-0.207385000
15	-0.765884000	0.400309000	-1.182431000	15	0.721010000	0.337000000	-1.362856000
15	0.648135000	1.203777000	0.360176000	15	-0.554246000	-0.931877000	-0.104052000
6	2.986625000	2.027363000	3.157594000	6	-2.272248000	-2.156810000	2.855601000
2a				**2a**			
29	0.000001000	0.077020000	0.000034000	29	0.000000000	-0.039288000	0.000205000
6	1.278298000	-2.555945000	-0.000353000	6	1.264407000	2.570117000	0.000383000
6	2.465371000	-3.503983000	-0.000513000	6	2.451154000	3.491705000	0.000376000
1	3.104295000	-3.335110000	-0.881099000	1	3.080138000	3.311303000	0.874276000
1	2.139967000	-4.552032000	-0.000705000	1	2.145203000	4.534911000	0.000656000
1	3.104278000	-3.335429000	0.880147000	1	3.079797000	3.311690000	-0.873851000
7	1.499274000	-1.242102000	-0.000163000	7	1.473546000	1.267181000	0.000250000
6	2.829462000	-0.740852000	-0.000097000	6	2.786744000	0.752543000	0.000064000
6	3.469438000	-0.449768000	1.228545000	6	3.404965000	0.442112000	-1.216285000
7	-1.499273000	-1.242101000	-0.000099000	7	-1.473546000	1.267181000	0.000226000
6	4.760928000	0.095751000	1.206004000	6	4.660636000	-0.150240000	-1.195494000
1	5.259221000	0.318755000	2.153858000	1	5.142067000	-0.391204000	-2.136800000
6	-1.278298000	-2.555945000	-0.000264000	6	-1.264407000	2.570118000	0.000365000
6	-2.465372000	-3.503983000	-0.000431000	6	-2.451154000	3.491706000	0.000354000
1	-3.104291000	-3.335412000	0.880215000	1	-3.079860000	3.311615000	-0.873812000
1	-2.139968000	-4.552031000	-0.000601000	1	-2.145202000	4.534911000	0.000529000
1	-3.104283000	-3.335126000	-0.881030000	1	-3.080074000	3.311379000	0.874316000
6	4.760860000	0.096262000	-1.205949000	6	4.660918000	-0.150402000	1.195056000
1	5.259102000	0.319669000	-2.153735000	1	5.142569000	-0.391497000	2.136215000
6	0.000000000	-3.154579000	-0.000400000	6	0.000000000	3.171373000	0.000491000
1	0.000000000	-4.243803000	-0.000567000	1	0.000000000	4.252280000	0.000604000
6	3.469371000	-0.449248000	-1.228653000	6	3.405249000	0.441940000	1.216223000
6	2.764032000	-0.707816000	-2.536628000	6	2.704479000	0.716294000	2.506840000
1	2.561843000	-1.780312000	-2.695599000	1	2.502496000	1.780833000	2.649089000
1	3.361330000	-0.347710000	-3.386864000	1	3.295666000	0.369505000	3.353877000
1	1.782320000	-0.206353000	-2.564729000	1	1.729887000	0.218814000	2.540611000
6	2.764169000	-0.708905000	2.536444000	6	2.703898000	0.716670000	-2.506698000
1	1.782424000	-0.207520000	2.564771000	1	1.729292000	0.219206000	-2.540329000
1	3.361472000	-0.349097000	3.386802000	1	3.294887000	0.370009000	-3.353926000
1	2.562056000	-1.781479000	2.694997000	1	2.501894000	1.781235000	-2.648731000
6	-3.469340000	-0.449422000	1.228567000	6	-3.404942000	0.442074000	-1.216319000
6	-3.469468000	-0.449592000	-1.228631000	6	-3.405272000	0.441979000	1.216188000
6	-2.829462000	-0.740851000	-0.000047000	6	-2.786744000	0.752543000	0.000031000
6	-2.764248000	-0.708587000	-2.536585000	6	-2.704527000	0.716381000	2.506809000
1	-1.782468000	-0.207269000	-2.564860000	1	-1.729931000	0.218913000	2.540615000
1	-3.361547000	-0.348615000	-3.386876000	1	-3.295727000	0.369615000	3.353847000
1	-2.562216000	-1.781153000	-2.695298000	1	-2.502560000	1.780928000	2.649024000
6	-4.760960000	0.095918000	-1.205981000	6	-4.660938000	-0.150367000	1.195016000
1	-5.259281000	0.319045000	-2.153791000	1	-5.142605000	-0.391435000	2.136174000
6	5.410812000	0.360847000	0.000066000	6	5.293843000	-0.438366000	-0.000314000
1	6.417606000	0.786048000	0.000129000	1	6.272991000	-0.900011000	-0.000461000
6	-5.410812000	0.360845000	0.000010000	6	-5.293842000	-0.438366000	-0.000356000
1	-6.417607000	0.786044000	0.000034000	1	-6.272991000	-0.900010000	-0.000506000
6	-4.760828000	0.096094000	1.205972000	6	-4.660616000	-0.150275000	-1.195533000
1	-5.259043000	0.319377000	2.153802000	1	-5.142030000	-0.391265000	-2.136840000
6	-2.763953000	-0.708133000	2.536489000	6	-2.703848000	0.716583000	-2.506729000
1	-2.561735000	-1.780644000	2.695324000	1	-2.501826000	1.781140000	-2.648795000
1	-3.361230000	-0.348142000	3.386787000	1	-3.294827000	0.369902000	-3.353956000
1	-1.782251000	-0.206652000	2.564619000	1	-1.729249000	0.219103000	-2.540326000
15	-1.242855000	2.090292000	-0.000599000	15	-1.169106000	-2.070228000	-0.000026000
15	1.242854000	2.090292000	0.001103000	15	1.169106000	-2.070229000	-0.000039000
15	-0.000778000	3.577333000	1.108263000	15	-0.000008000	-3.563484000	-1.089736000
15	0.000777000	3.577561000	-1.107453000	15	0.000008000	-3.564045000	1.088895000
2b				**2b**			
29	-0.000091000	0.594762000	0.000026000	29	-0.000001000	0.607202000	0.000263000
6	1.278558000	3.233499000	0.000309000	6	1.263267000	3.230800000	0.000535000
6	2.462624000	4.185985000	0.000388000	6	2.449297000	4.153799000	0.000839000
1	3.102393000	4.019972000	0.880893000	1	3.078528000	3.974507000	0.874719000
1	2.133179000	5.232764000	0.000664000	1	2.141694000	5.196519000	0.001372000
1	3.102165000	4.020377000	-0.880356000	1	3.078316000	3.975367000	-0.873372000
7	1.503786000	1.920221000	0.000153000	7	1.472232000	1.927912000	0.000329000
6	2.838614000	1.430825000	-0.000004000	6	2.788269000	1.421326000	0.000098000
6	3.482443000	1.146974000	-1.229092000	6	3.411475000	1.118710000	-1.216567000
7	-1.504164000	1.919989000	-0.000067000	7	-1.472239000	1.927905000	0.000114000
6	4.778677000	0.612301000	-1.206187000	6	4.672201000	0.536377000	-1.195499000
1	5.279258000	0.394632000	-2.154053000	1	5.156197000	0.301038000	-2.136869000
6	-1.279144000	3.233299000	0.000258000	6	-1.263280000	3.230794000	0.000112000
6	-2.463353000	4.185608000	0.000290000	6	-2.449316000	4.153787000	-0.000301000
1	-3.102587000	4.020152000	-0.880717000	1	-3.078275000	3.974710000	-0.874424000
1	-2.134065000	5.232436000	0.000944000	1	-2.141718000	5.196509000	-0.000486000
1	-3.103378000	4.019262000	0.880533000	1	-3.078604000	3.975132000	0.873668000
6	4.778776000	0.611871000	1.205727000	6	4.672193000	0.535275000	1.194881000
1	5.279435000	0.393876000	2.153476000	1	5.156189000	0.299072000	2.136033000
6	-0.000338000	3.830464000	0.000419000	6	-0.000008000	3.832934000	0.000444000
1	-0.000423000	4.919650000	0.000601000	1	-0.000011000	4.913761000	0.000545000
6	3.482541000	1.146529000	1.228927000	6	3.411464000	1.117573000	1.216483000
6	2.777605000	1.402758000	2.537652000	6	2.712382000	1.389845000	2.508584000
1	2.556543000	2.472634000	2.688057000	1	2.495092000	2.452116000	2.644290000

1	3.385272000	1.060839000	3.388040000
1	1.805661000	0.883159000	2.574739000
6	2.777410000	1.403707000	-2.537667000
1	1.805119000	0.884757000	-2.574570000
1	3.384692000	1.061448000	-3.388194000
1	2.557024000	2.473740000	-2.687984000
6	-3.482671000	1.146203000	-1.229171000
6	-3.482820000	1.146202000	1.228848000
6	-2.838911000	1.430373000	-0.000126000
6	-2.777947000	1.402772000	2.537539000
1	-1.805501000	0.884109000	2.574347000
1	-3.385179000	1.060091000	3.387931000
1	-2.557892000	2.472830000	2.688182000
6	-4.778996000	0.611396000	1.205715000
1	-5.279643000	0.393492000	2.153493000
6	5.430680000	0.351971000	-0.000303000
1	6.440968000	-0.064785000	-0.000422000
6	-5.430850000	0.351220000	-0.000282000
1	-6.441092000	-0.065649000	-0.000341000
6	-4.778847000	0.611393000	-1.206200000
1	-5.279379000	0.393492000	-2.154037000
6	-2.777640000	1.402787000	-2.537775000
1	-2.557493000	2.472839000	-2.688325000
1	-3.384811000	1.060201000	-3.388249000
1	-1.805232000	0.884050000	-2.574511000
33	-1.359688000	-1.472515000	0.000780000
33	1.360066000	-1.472340000	-0.000824000
33	-0.000452000	-3.133374000	-1.224913000
33	0.001037000	-3.133249000	1.225046000

1	3.313561000	1.058135000	3.354643000
1	1.745992000	0.877309000	2.552212000
6	2.712410000	1.392202000	-2.508422000
1	1.745887000	0.879955000	-2.552442000
1	3.313483000	1.061049000	-3.354774000
1	2.495378000	2.454639000	-2.643256000
6	-3.411027000	1.117776000	-1.216847000
6	-3.411919000	1.118491000	1.216203000
6	-2.788274000	1.421317000	-0.000180000
6	-2.713336000	1.391750000	2.508367000
1	-1.746809000	0.879536000	2.552636000
1	-3.314704000	1.060395000	3.354431000
1	-2.496407000	2.454170000	2.643503000
6	-4.672639000	0.536161000	1.194569000
1	-5.156977000	0.300654000	2.135720000
6	5.306969000	0.251502000	-0.000441000
1	6.289613000	-0.202564000	-0.000647000
6	-5.306972000	0.251496000	-0.000770000
1	-6.289618000	-0.202569000	-0.000998000
6	-4.671763000	0.535476000	-1.195813000
1	-5.155416000	0.299440000	-2.137183000
6	-2.711443000	1.390279000	-2.508626000
1	-2.494016000	2.452564000	-2.644002000
1	-3.312317000	1.058797000	-3.354989000
1	-1.745065000	0.877692000	-2.551983000
33	-1.334469000	-1.443226000	0.002269000
33	1.334473000	-1.443223000	-0.001931000
33	-0.001954000	-3.085880000	-1.211067000
33	0.001961000	-3.086263000	1.210882000

3a

34	1.004385000	-0.067537000	0.702021000
29	0.825631000	-1.377419000	-1.313425000
7	0.098149000	-2.134001000	-2.973249000
7	2.554415000	-2.306413000	-1.254799000
6	-1.178621000	-1.718102000	-3.461476000
6	3.483498000	-2.047909000	-0.200198000
6	2.879685000	-3.186125000	-2.202803000
6	0.793442000	-3.038049000	-3.664228000
6	2.066157000	-3.524050000	-3.303097000
1	2.488233000	-4.264629000	-3.980270000
6	4.433819000	-1.011331000	-0.348138000
6	-1.262885000	-0.602836000	-4.326705000
6	-2.342623000	-2.407664000	-3.050119000
6	3.424427000	-2.814641000	0.986404000
6	0.199808000	-3.604931000	-4.942099000
1	-0.768517000	-4.090627000	-4.747546000
1	0.875304000	-4.339061000	-5.398833000
1	0.002082000	-2.806206000	-5.673226000
6	4.221057000	-3.894229000	-2.122023000
1	5.050609000	-3.170953000	-2.120121000
1	4.355887000	-4.580848000	-2.967109000
1	4.309707000	-4.466499000	-1.185947000
6	-0.023506000	0.164837000	-4.712258000
1	0.480777000	0.569383000	-3.818660000
1	-0.272043000	1.006640000	-5.374709000
1	0.716999000	-0.467354000	-5.229524000
6	4.358036000	-2.555518000	1.999574000
1	4.321627000	-3.147930000	2.918063000
6	5.321047000	-1.556757000	1.853283000
1	6.042212000	-1.368773000	2.652517000
6	-3.582763000	-1.987429000	-3.550996000
1	-4.487067000	-2.518226000	-3.240626000
6	5.348221000	-0.786556000	0.690321000
1	6.089660000	0.009898000	0.580829000
6	2.370395000	-3.878914000	1.160531000
1	1.359591000	-3.444261000	1.086499000
1	2.461518000	-4.366683000	2.141870000
1	2.433630000	-4.660058000	0.385182000
6	-2.251653000	-3.558572000	-2.079895000
1	-1.606953000	-4.370857000	-2.453438000
1	-3.246231000	-3.981015000	-1.875871000
1	-1.817090000	-3.229175000	-1.121240000
6	-3.676765000	-0.907454000	-4.428827000
1	-4.651625000	-0.594451000	-4.810645000
6	-2.523582000	-0.217187000	-4.803149000
1	-2.596050000	0.641881000	-5.476025000
6	4.451631000	-0.157380000	-1.590960000
1	4.627249000	-0.749839000	-2.504032000
1	5.236056000	0.610869000	-1.529545000
1	3.483443000	0.351651000	-1.730607000
34	-1.004385000	0.067537000	-0.702021000
29	-0.825631000	1.377419000	1.313425000
7	-0.098149000	2.134001000	2.973249000
7	-2.554415000	2.306413000	1.254799000
6	1.178621000	1.718102000	3.461476000

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7	3.270121000	-1.431800000	0.210134000
7	3.235414000	1.505239000	0.209032000
6	2.807884000	-2.745923000	-0.056572000
6	2.742213000	2.808098000	-0.057115000
6	4.526915000	1.312348000	0.404059000
6	4.555873000	-1.208835000	0.410181000
6	5.128965000	0.058840000	0.550101000
1	6.193661000	0.071804000	0.733223000
6	2.637939000	3.227409000	-1.387200000
6	2.723942000	-3.170527000	-1.386551000
6	2.362224000	-3.558924000	0.990393000
6	2.288663000	3.614596000	0.991729000
6	5.495611000	-2.379386000	0.460717000
1	5.148836000	-3.136438000	1.164680000
1	6.496491000	-2.064320000	0.745409000
1	5.553803000	-2.867963000	-0.514180000
6	5.440043000	2.504172000	0.441047000
1	5.472008000	2.992336000	-0.535260000
1	6.451989000	2.213018000	0.711816000
1	5.085941000	3.254162000	1.148933000
6	3.112510000	-2.253547000	-2.500049000
1	2.443223000	-1.387565000	-2.534795000
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1	4.123174000	-1.854870000	-2.387918000
6	1.759192000	4.861688000	0.685816000
1	1.400063000	5.489047000	1.493853000
6	1.677771000	5.301836000	-0.621493000
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6	1.860743000	-4.816749000	0.682901000
1	1.510107000	-5.450526000	1.489649000
6	2.107136000	4.482696000	-1.649364000
1	2.027049000	4.813579000	-2.678825000
6	2.343552000	3.132148000	2.404419000
1	1.779842000	2.203066000	2.524055000
1	1.920313000	3.873093000	3.082193000
1	3.364638000	2.920341000	2.730503000
6	2.397202000	-3.073720000	2.402650000
1	3.410453000	-2.834141000	2.733694000
1	1.990239000	-3.824837000	3.079202000
1	1.807805000	-2.160330000	2.517813000
6	1.797646000	-5.260885000	-0.624076000
1	1.405508000	-6.246200000	-0.844609000
6	2.220262000	-4.436533000	-1.650537000
1	2.155239000	-4.771149000	-2.679807000
6	3.033743000	2.316722000	-2.503285000
1	4.046006000	1.922562000	-2.390538000
1	2.972116000	2.828367000	-3.463363000
1	2.367899000	1.448228000	-2.542872000
34	0.013173000	-1.226447000	0.001967000
29	-2.000402000	-0.022087000	-0.132088000
7	-3.270729000	1.431540000	-0.209709000
7	-3.235440000	-1.505339000	-0.207904000
6	-2.808571000	2.745679000	0.056874000

6	-3.483498000	2.047909000	0.200198000
6	-2.879685000	3.186125000	2.202803000
6	-0.793442000	3.038049000	3.664228000
6	-2.066157000	3.524050000	3.303097000
1	-2.488233000	4.264629000	3.980270000
6	-4.433819000	1.011331000	0.348138000
6	1.262885000	0.602836000	4.326705000
6	2.342623000	2.407664000	3.050119000
6	-3.424427000	2.814641000	-0.986404000
6	-0.199808000	3.604931000	4.942099000
1	0.768517000	4.090627000	4.747546000
1	-0.875304000	4.339061000	5.398833000
1	-0.002082000	2.806206000	5.673226000
6	-4.221057000	3.894229000	2.122023000
1	-5.050609000	3.170953000	2.120121000
1	-4.355887000	4.580848000	2.967109000
1	-4.309707000	4.466499000	1.185947000
6	0.023506000	-0.164837000	4.712258000
1	-0.480777000	-0.569383000	3.818660000
1	0.272043000	-1.006640000	5.374709000
1	-0.716999000	0.467354000	5.229524000
6	-4.358036000	2.555518000	-1.999574000
1	-4.321627000	3.147930000	-2.918063000
6	-5.321047000	1.556757000	-1.853283000
1	-6.042212000	1.368773000	-2.652517000
6	3.582763000	1.987429000	3.550996000
1	4.487067000	2.518226000	3.240626000
6	-5.348221000	0.786556000	-0.690321000
1	-6.089660000	-0.009898000	-0.580829000
6	-2.370395000	3.878914000	-1.160531000
1	-1.359591000	3.444261000	-1.086499000
1	-2.461518000	4.366683000	-2.141870000
1	-2.433630000	4.660058000	-0.385182000
6	2.251653000	3.558572000	2.079895000
1	1.606953000	4.370857000	2.453438000
1	3.246231000	3.981015000	1.875871000
1	1.817090000	3.229175000	1.121240000
6	3.676765000	0.907454000	4.428827000
1	4.651625000	0.594451000	4.810645000
6	2.523582000	0.217187000	4.803149000
1	2.596050000	-0.641881000	5.476025000
6	-4.451631000	0.157380000	1.590960000
1	-4.627249000	0.749839000	2.504032000
1	-5.236056000	-0.610869000	1.529545000
1	-3.483443000	-0.351651000	1.730607000

6	-2.741469000	-2.808079000	0.057407000
6	-4.527192000	-1.312855000	-0.401388000
6	-4.556650000	1.208270000	-0.408579000
6	-5.129672000	-0.059530000	-0.547375000
1	-6.194564000	-0.072746000	-0.729332000
6	-2.634384000	-3.227144000	1.387376000
6	-2.724672000	3.170381000	1.386794000
6	-2.363292000	3.558811000	-0.990183000
6	-2.289714000	-3.614692000	-0.992193000
6	-5.496326000	2.378839000	-0.459955000
1	-5.150429000	3.134149000	-1.166237000
1	-6.497692000	2.063377000	-0.742517000
1	-5.552931000	2.869812000	0.513856000
6	-5.440165000	-2.504840000	-0.436264000
1	-5.469869000	-2.992876000	0.540173000
1	-6.452750000	-2.213916000	-0.704857000
1	-5.087557000	-3.254932000	-1.144753000
6	-3.113305000	2.253780000	2.500594000
1	-2.445375000	1.386780000	2.534852000
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1	-4.124744000	1.856697000	2.389759000
6	-1.759746000	-4.861728000	-0.687041000
1	-1.402122000	-5.489252000	-1.495624000
6	-1.675730000	-5.301642000	0.620169000
1	-1.261583000	-6.278293000	0.838922000
6	-1.861707000	4.816668000	-0.682760000
1	-1.510947000	5.450410000	-1.489496000
6	-2.102744000	-4.482226000	1.648764000
1	-2.020310000	-4.812756000	2.678151000
6	-2.346753000	-3.132448000	-2.404890000
1	-1.782210000	-2.204022000	-2.525770000
1	-1.925531000	-3.873947000	-3.083319000
1	-3.368145000	-2.919592000	-2.729267000
6	-2.398542000	3.073601000	-2.402451000
1	-3.411663000	2.832499000	-2.732762000
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1	-1.807967000	2.161024000	-2.518068000
6	-1.798504000	5.260823000	0.624203000
1	-1.405927000	6.245990000	0.844676000
6	-2.221213000	4.436546000	1.650665000
1	-2.156207000	4.771164000	2.679945000
6	-3.028078000	-2.316371000	2.504145000
1	-4.041055000	-1.923313000	2.394051000
1	-2.963389000	-2.827699000	3.464184000
1	-2.363051000	-1.447187000	2.541723000

3b

34	0.030369000	-0.834711000	-0.881836000
29	-0.148281000	-1.534524000	1.446973000
7	-0.278606000	-1.425964000	3.420988000
7	-0.186837000	-3.502685000	1.234386000
6	-0.412103000	-4.285354000	2.290449000
6	-0.490560000	-2.530059000	4.138594000
6	-0.623856000	-3.826768000	3.605443000
1	-0.820342000	-4.608103000	4.338514000
6	-1.121904000	0.722075000	4.285234000
6	-0.046858000	-0.188517000	4.103337000
6	0.404842000	2.235254000	5.437354000
1	0.579224000	3.178553000	5.961295000
6	-0.523738000	-2.454288000	5.656604000
1	0.504433000	-2.499338000	6.051115000
1	-1.076804000	-3.306968000	6.072652000
1	-0.966063000	-1.522230000	6.027348000
6	0.126392000	-4.106872000	-0.025992000
6	-2.533250000	0.403613000	3.789757000
1	-2.425038000	-0.326693000	2.973229000
6	-0.867790000	1.924357000	4.961238000
1	-1.682088000	2.634768000	5.115102000
6	-0.373531000	-5.797503000	2.136953000
1	-0.753687000	-6.137099000	1.166456000
1	-0.947520000	-6.281075000	2.938701000
1	0.667965000	-6.150085000	2.213961000
6	-0.900317000	-4.281534000	-0.991925000
6	1.255651000	0.120047000	4.576150000
6	1.454273000	1.340618000	5.236883000
1	2.451445000	1.594414000	5.604820000
6	-3.400934000	-0.255527000	4.879999000
1	-2.984305000	-1.212389000	5.224071000
1	-4.414268000	-0.456274000	4.494603000
1	-3.500400000	0.405250000	5.757542000
6	1.460154000	-4.508143000	-0.300683000
6	0.738691000	-5.279680000	-2.497051000
1	0.975993000	-5.739892000	-3.459656000
6	-3.258196000	1.629450000	3.215078000
1	-3.535936000	2.352223000	4.000050000
1	-4.192437000	1.317364000	2.721003000

3b

34	0.018677000	-0.831300000	-0.882101000
29	-0.166112000	-1.475665000	1.389420000
7	-0.307846000	-1.374978000	3.324631000
7	-0.229877000	-3.406028000	1.182177000
6	-0.448227000	-4.194019000	2.219243000
6	-0.518449000	-2.459640000	4.047548000
6	-0.661084000	-3.748490000	3.526310000
1	-0.858356000	-4.523469000	4.254157000
6	-1.022642000	0.816507000	4.126517000
6	-0.011703000	-0.145039000	3.972878000
6	0.586293000	2.278124000	5.177952000
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6	-0.537544000	-2.368278000	5.548632000
1	0.474057000	-2.520256000	5.933751000
1	-1.168102000	-3.149855000	5.968921000
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6	-2.439597000	0.543783000	3.674669000
1	-2.389016000	-0.205325000	2.878902000
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1	-1.461967000	2.779577000	4.857241000
6	-0.395270000	-5.687443000	2.048914000
1	-0.699363000	-6.010785000	1.055513000
1	-1.018848000	-6.177967000	2.794176000
1	0.630805000	-6.033233000	2.199379000
6	-0.812001000	-4.116669000	-1.079336000
6	1.300186000	0.109137000	4.396447000
6	1.573151000	1.327997000	5.004249000
1	2.583474000	1.543566000	5.334240000
6	-3.278325000	-0.038976000	4.807276000
1	-2.894225000	-0.998642000	5.154297000
1	-4.308936000	-0.192157000	4.480473000
1	-3.294764000	0.646339000	5.659439000
6	1.485021000	-4.337044000	-0.275888000
6	0.905024000	-5.022272000	-2.515753000
1	1.200322000	-5.432378000	-3.473875000
6	-3.125804000	1.773413000	3.102866000
1	-3.356623000	2.509334000	3.877930000
1	-4.071748000	1.488943000	2.637710000

1	-2.639357000	2.153021000	2.473251000	1	-2.505704000	2.260659000	2.348486000
6	2.438350000	-0.828029000	4.372185000	6	2.423190000	-0.877860000	4.163896000
1	2.035990000	-1.786154000	4.014478000	1	1.989724000	-1.811175000	3.791128000
6	-2.345069000	-3.867701000	-0.708616000	6	-2.257768000	-3.736819000	-0.850216000
1	-2.306111000	-3.093651000	0.073096000	1	-2.272657000	-2.967398000	-0.072414000
6	-0.565641000	-4.875302000	-2.217757000	6	-0.406355000	-4.646135000	-2.298080000
1	-1.341112000	-5.021841000	-2.971921000	1	-1.130851000	-4.764039000	-3.094563000
6	1.739030000	-5.089424000	-1.545807000	6	1.839681000	-4.862402000	-1.511595000
1	2.760701000	-5.402556000	-1.774700000	1	2.871450000	-5.140539000	-1.695885000
6	3.205269000	-1.113267000	5.675517000	6	3.188847000	-1.199256000	5.440207000
1	3.716488000	-0.214601000	6.057174000	1	3.729292000	-0.325919000	5.812026000
1	3.979556000	-1.879105000	5.504938000	1	3.926395000	-1.982445000	5.255180000
1	2.538908000	-1.477764000	6.473263000	1	2.525037000	-1.538515000	6.237734000
6	2.591338000	-4.309809000	0.709018000	6	2.546816000	-4.119786000	0.779947000
1	2.133087000	-4.028206000	1.667398000	1	2.049630000	-3.877980000	1.723948000
6	3.395670000	-0.312048000	3.282500000	6	3.374950000	-0.362461000	3.090921000
1	2.867278000	-0.138040000	2.333027000	1	2.850096000	-0.157712000	2.153749000
1	4.202309000	-1.040917000	3.098521000	1	4.161935000	-1.092833000	2.891564000
1	3.865252000	0.638903000	3.582186000	1	3.854760000	0.565805000	3.411277000
6	-3.043444000	-3.252180000	-1.929845000	6	-2.921540000	-3.151575000	-2.085706000
1	-2.438756000	-2.452247000	-2.379202000	1	-2.320954000	-2.351482000	-2.521744000
1	-4.012732000	-2.820692000	-1.632143000	1	-3.898630000	-2.741205000	-1.823179000
1	-3.251955000	-4.003068000	-2.709761000	1	-3.087148000	-3.908890000	-2.856877000
6	-3.187152000	-5.033463000	-0.153708000	6	-3.067713000	-4.925150000	-0.342257000
1	-3.216879000	-5.873488000	-0.867929000	1	-3.013910000	-5.753675000	-1.054172000
1	-4.225209000	-4.706843000	0.023615000	1	-4.118218000	-4.650494000	-0.226484000
1	-2.794896000	-5.415158000	0.799219000	1	-2.711284000	-5.286163000	0.622747000
6	3.517507000	-3.149969000	0.300775000	6	3.424089000	-2.927829000	0.417174000
1	4.041841000	-3.371198000	-0.642952000	1	3.966722000	-3.116174000	-0.512782000
1	4.282071000	-2.973024000	1.075374000	1	4.159645000	-2.738026000	1.201751000
1	2.952912000	-2.216575000	0.156768000	1	2.830154000	-2.020526000	0.275489000
6	3.405241000	-5.592952000	0.952405000	6	3.402839000	-5.356602000	1.013936000
1	2.761364000	-6.440138000	1.237062000	1	2.793971000	-6.235524000	1.234845000
1	4.135970000	-5.435733000	1.762605000	1	4.083428000	-5.194343000	1.851782000
1	3.973293000	-5.895936000	0.057871000	1	4.015592000	-5.591552000	0.140869000
34	-0.030369000	0.834711000	0.881836000	34	-0.018677000	0.831300000	0.882101000
29	0.148281000	1.534524000	-1.446973000	29	0.166112000	1.475665000	-1.389420000
7	0.278606000	1.425964000	-3.420988000	7	0.307846000	1.374978000	-3.324631000
7	0.186837000	3.502685000	-1.234386000	7	0.229877000	3.406028000	-1.182177000
6	0.412103000	4.285354000	-2.290449000	6	0.448227000	4.194019000	-2.219243000
6	0.490560000	2.530059000	-4.138594000	6	0.518449000	2.459640000	-4.047548000
6	0.623856000	3.826768000	-3.605443000	6	0.661084000	3.748490000	-3.526310000
1	0.820342000	4.608103000	-4.338514000	1	0.858356000	4.523469000	-4.254157000
6	1.121904000	-0.722075000	-4.285234000	6	1.022642000	-0.816507000	-4.126517000
6	0.046858000	0.188517000	-4.103337000	6	0.011703000	0.145039000	-3.972878000
6	-0.404842000	-2.235254000	-5.437354000	6	-0.586293000	-2.278124000	-5.177952000
1	-0.579224000	-3.178553000	-5.961295000	1	-0.819120000	-3.224684000	-5.650439000
6	0.523738000	2.454288000	-5.656604000	6	0.537544000	2.368278000	-5.548632000
1	-0.504433000	2.499338000	-6.051115000	1	-0.474057000	2.520256000	-5.933751000
1	1.076804000	3.306968000	-6.072652000	1	1.168102000	3.149855000	-5.968921000
1	0.966063000	1.522230000	-6.027348000	1	0.876210000	1.399373000	-5.909498000
6	-0.126392000	4.106872000	0.025992000	6	-0.146920000	3.975966000	0.064381000
6	2.533250000	-0.403613000	-3.789757000	6	2.439597000	-0.543783000	-3.674669000
1	2.425038000	0.326693000	-2.973229000	1	2.389016000	0.205325000	-2.878902000
6	0.867790000	-1.924357000	-4.961238000	6	0.696788000	-2.022749000	-4.733547000
1	1.682088000	-2.634768000	-5.115102000	1	1.461967000	-2.779577000	-4.857241000
6	0.373531000	5.797503000	-2.136953000	6	0.395270000	5.687443000	-2.048914000
1	0.753687000	6.137099000	-1.166456000	1	0.699363000	6.010785000	-1.055513000
1	0.947520000	6.281075000	-2.938701000	1	1.018848000	6.177967000	-2.794176000
1	-0.667965000	6.150085000	-2.213961000	1	-0.630805000	6.033233000	-2.199379000
6	0.900317000	4.281534000	0.991925000	6	0.812001000	4.116669000	1.079336000
6	-1.255651000	-0.120047000	-4.576150000	6	-1.300186000	-0.109137000	-4.396447000
6	-1.454273000	-1.340618000	-5.236883000	6	-1.573151000	-1.327997000	-5.004249000
1	-2.451445000	-1.594414000	-5.604820000	1	-2.583474000	-1.543566000	-5.334240000
6	3.400934000	0.255527000	-4.879999000	6	3.278325000	0.038976000	-4.807276000
1	2.984305000	1.212389000	-5.224071000	1	2.894225000	0.998642000	-5.154297000
1	4.414268000	0.456274000	-4.494603000	1	4.308936000	0.192157000	-4.480473000
1	3.500400000	-0.405250000	-5.757542000	1	3.294764000	-0.646339000	-5.659439000
6	-1.460154000	4.508143000	0.300683000	6	-1.485021000	4.337044000	0.275888000
6	-0.738691000	5.279680000	2.497051000	6	-0.905024000	5.022272000	2.515753000
1	-0.975993000	5.739892000	3.459656000	1	-1.200322000	5.432378000	3.473875000
6	3.258196000	-1.629450000	-3.215078000	6	3.125804000	-1.773413000	-3.102866000
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1	4.192437000	-1.317364000	-2.721003000	1	4.071748000	-1.488943000	-2.637710000
1	2.639357000	-2.153021000	-2.473251000	1	2.505704000	-2.260659000	-2.348486000
6	-2.438350000	0.828029000	-4.372185000	6	-2.423190000	0.877860000	-4.163896000
1	-2.035990000	1.786154000	-4.014478000	1	-1.989724000	1.811175000	-3.791128000
6	2.345069000	3.867701000	0.708616000	6	2.257768000	3.736819000	0.850216000
1	2.306111000	3.093651000	-0.073096000	1	2.272657000	2.967398000	0.072414000
6	0.565641000	4.875302000	2.217757000	6	0.406355000	4.646135000	2.298080000
1	1.341112000	5.021841000	2.971921000	1	1.130851000	4.764039000	3.094563000
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1	-2.760701000	5.402556000	1.774700000	1	-2.871450000	5.140539000	1.695885000
6	-3.205269000	1.113267000	-5.675517000	6	-3.188847000	1.199256000	-5.440207000
1	-3.716488000	0.214601000	-6.057174000	1	-3.729292000	0.325919000	-5.812026000
1	-3.979556000	1.879105000	-5.504938000	1	-3.926395000	1.982445000	-5.255180000

1	-2.538908000	1.477764000	-6.473263000
6	-2.591338000	4.309809000	-0.709018000
1	-2.133087000	4.028206000	-1.667398000
6	-3.395670000	0.312048000	-3.282500000
1	-2.867278000	0.138040000	-2.333027000
1	-4.202309000	1.040917000	-3.098521000
1	-3.865252000	-0.638903000	-3.582186000
6	3.043444000	3.252180000	1.929845000
1	2.438756000	2.452247000	2.379202000
1	4.012732000	2.820692000	1.632143000
1	3.251955000	4.003068000	2.709761000
6	3.187152000	5.033463000	0.153708000
1	3.216879000	5.873488000	0.867929000
1	4.225209000	4.706843000	-0.023615000
1	2.794896000	5.415158000	-0.799219000
6	-3.517507000	3.149969000	-0.300775000
1	-4.041841000	3.371198000	0.642952000
1	-4.282071000	2.973024000	-1.075374000
1	-2.952912000	2.216575000	-0.156768000
6	-3.405241000	5.592952000	-0.952405000
1	-2.761364000	6.440138000	-1.237062000
1	-4.135970000	5.435733000	-1.762605000
1	-3.973293000	5.895936000	-0.057871000

1	-2.525037000	1.538515000	-6.237734000
6	-2.546816000	4.119786000	-0.779947000
1	-2.049630000	3.877980000	-1.723948000
6	-3.374950000	0.362461000	-3.090921000
1	-2.850096000	0.157712000	-2.153749000
1	-4.161935000	1.092833000	-2.891564000
1	-3.854760000	-0.565805000	-3.411277000
6	2.921540000	3.151575000	2.085706000
1	2.320954000	2.351482000	2.521744000
1	3.898630000	2.741205000	1.823179000
1	3.087148000	3.908890000	2.856877000
6	3.067713000	4.925150000	0.342257000
1	3.013910000	5.753675000	1.054172000
1	4.118218000	4.650494000	0.226484000
1	2.711284000	5.286163000	-0.622747000
6	-3.424089000	2.927829000	-0.417174000
1	-3.966722000	3.116174000	0.512782000
1	-4.159645000	2.738026000	-1.201751000
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6	-3.402839000	5.356602000	-1.013936000
1	-2.793971000	6.235524000	-1.234845000
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1	-4.015592000	5.591552000	-0.140869000

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29	3.750599000	0.204897000	-0.019258000
29	-3.687720000	-0.067941000	0.025191000
16	-0.979627000	-2.516505000	-0.486362000
15	1.687728000	-0.335290000	-0.595208000
16	-0.001756000	0.506709000	0.407181000
15	1.015589000	-2.428788000	-1.201164000
15	-1.619135000	-0.459824000	-0.614456000
16	-1.059743000	-0.026192000	-2.648184000
15	0.955801000	-0.697940000	-2.726233000
7	-4.825931000	1.538343000	0.012468000
7	4.522048000	1.894796000	0.623268000
7	5.331539000	-0.968313000	-0.031722000
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6	-4.482228000	-2.756272000	0.944095000
6	5.189642000	-2.337344000	-0.403227000
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1	7.767644000	1.112718000	0.959828000
6	-4.666727000	-3.682675000	-0.117882000
6	-6.073715000	1.452605000	0.475477000
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6	-3.135519000	3.177181000	1.712877000
1	-3.182851000	2.075974000	1.750356000
6	-4.323898000	2.760353000	-0.524880000
6	3.682511000	3.025269000	0.851038000
6	-6.657783000	0.277501000	1.006422000
1	-7.684109000	0.400314000	1.351006000
6	4.752892000	-3.286596000	0.559047000
6	3.316065000	3.864059000	-0.233881000
6	3.164427000	3.268891000	2.152032000
6	-4.610911000	3.122605000	-1.867303000
6	-4.159336000	-4.981457000	0.025548000
1	-4.290293000	-5.700278000	-0.787616000
6	-3.321409000	-4.464079000	2.222494000
1	-2.797536000	-4.777854000	3.129384000
6	3.495440000	2.352023000	3.329503000
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6	-3.490537000	-5.376997000	1.183018000
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6	4.728570000	-5.003615000	-1.172484000
1	4.545792000	-6.038609000	-1.472516000
6	-5.381099000	-3.290782000	-1.411166000
1	-5.807285000	-2.288800000	-1.260030000
6	5.410648000	-2.734169000	-1.750043000
6	-3.477954000	3.574729000	0.277051000
6	-6.985627000	2.667414000	0.415586000
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6	4.527714000	-4.608494000	0.148784000
1	4.188108000	-5.345770000	0.881245000
6	3.897719000	3.118782000	4.600194000
1	4.724291000	3.821095000	4.407214000
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1	6.187297000	4.087329000	0.592052000

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29	3.582465000	0.176783000	-0.063970000
29	-3.568371000	-0.042025000	-0.148626000
16	-0.960390000	-2.526692000	-0.577576000
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6	-4.480000000	-2.526544000	0.945349000
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6	-3.777646000	-2.820972000	2.124645000
6	6.506459000	0.622487000	0.980123000
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1	-7.463115000	0.820730000	1.277523000
6	4.136324000	-3.278327000	0.645991000
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6	3.227576000	2.180065000	3.242779000
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1	-6.016407000	-2.281858000	-1.127913000
6	5.046925000	-2.830271000	-1.572953000
6	-2.830231000	3.344138000	0.391643000
6	-6.468315000	3.030288000	0.456164000
1	-5.809862000	3.841911000	0.766268000
1	-7.330100000	2.999834000	1.119305000
1	-6.823773000	3.281182000	-0.546855000
6	3.757258000	-4.540787000	0.204898000
1	3.255553000	-5.214049000	0.891437000
6	3.245476000	2.856054000	4.603769000
1	3.947307000	3.692033000	4.630000000
1	3.538887000	2.141153000	5.374291000
1	2.259914000	3.237770000	4.880609000
6	4.640757000	-4.096900000	-1.968659000
1	4.831569000	-4.425111000	-2.983678000
6	6.306921000	3.039338000	1.474708000
1	6.125818000	3.838756000	0.752958000

1	7.534861000	3.211498000	1.371806000	1	7.379108000	2.929425000	1.617658000
1	6.043510000	3.587518000	2.274420000	1	5.864570000	3.369405000	2.417620000
6	5.872301000	-1.737885000	-2.813244000	6	5.714372000	-1.891381000	-2.553473000
1	6.177884000	-0.818702000	-2.293818000	1	6.294858000	-1.165113000	-1.978804000
6	7.721809000	-1.385434000	0.376512000	6	7.291361000	-1.722842000	0.798040000
1	7.542505000	-2.241310000	1.045488000	1	6.947659000	-2.517031000	1.464788000
1	8.617153000	-0.853233000	0.721686000	1	8.192862000	-1.282673000	1.217079000
1	7.928660000	-1.809945000	-0.617736000	1	7.544126000	-2.204458000	-0.149398000
6	1.937315000	5.187574000	1.279516000	6	1.859601000	5.053012000	1.167110000
1	1.261376000	6.029854000	1.447386000	1	1.185187000	5.890725000	1.297011000
6	2.445223000	4.936489000	0.006607000	6	2.439104000	4.809958000	-0.061996000
1	2.158307000	5.589497000	-0.821989000	1	2.207524000	5.461033000	-0.897753000
6	4.515990000	-2.900768000	2.018399000	6	3.825242000	-2.856326000	2.065126000
1	4.808314000	-1.846734000	2.129221000	1	4.267126000	-1.867979000	2.226578000
6	-5.443239000	2.222654000	-2.780546000	6	-4.966705000	2.608270000	-2.704106000
1	-5.977464000	1.503371000	-2.144078000	1	-5.728265000	2.101157000	-2.107619000
6	-7.088060000	-2.063496000	1.737409000	6	-7.023133000	-1.672227000	1.732291000
1	-7.269105000	-2.883647000	1.025695000	1	-7.216637000	-2.535367000	1.091302000
1	-8.053153000	-1.616407000	2.007128000	1	-7.967747000	-1.183533000	1.958087000
1	-6.651422000	-2.526317000	2.635283000	1	-6.604366000	-2.066193000	2.661382000
6	2.295401000	4.352679000	2.337716000	6	2.141577000	4.217808000	2.232986000
1	1.887292000	4.548483000	3.332287000	1	1.672273000	4.406649000	3.191404000
6	-4.066285000	4.311862000	-2.372698000	6	-3.209046000	4.339979000	-2.187733000
1	-4.277171000	4.602663000	-3.404703000	1	-3.334367000	4.724551000	-3.193054000
6	-3.586866000	-2.185108000	3.292571000	6	-3.553118000	-1.765884000	3.185769000
1	-4.092355000	-1.243243000	3.035050000	1	-4.255414000	-0.946934000	3.001166000
6	2.331043000	1.386514000	3.617798000	6	2.176709000	1.075424000	3.213052000
1	1.420632000	1.934879000	3.911276000	1	1.171651000	1.497458000	3.309114000
1	2.587158000	0.692248000	4.435495000	1	2.328738000	0.364984000	4.028839000
1	2.082696000	0.785310000	2.729857000	1	2.215847000	0.519701000	2.271356000
6	-4.533855000	1.398312000	-3.709835000	6	-4.252849000	1.531158000	-3.512464000
1	-3.949343000	2.051019000	-4.378990000	1	-3.429896000	1.961517000	-4.089807000
1	-5.126807000	0.711602000	-4.336712000	1	-4.938844000	1.041017000	-4.206829000
1	-3.819525000	0.793927000	-3.130687000	1	-3.836313000	0.762027000	-2.854904000
6	3.830209000	3.617338000	-1.650771000	6	3.903194000	3.485468000	-1.614974000
1	4.499524000	2.745848000	-1.607635000	1	4.648019000	2.691482000	-1.509352000
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1	-2.846290000	6.055878000	-1.999250000	1	-1.655907000	5.733970000	-1.710900000
6	-2.964169000	4.755528000	-0.276744000	6	-2.074187000	4.407329000	-0.083863000
1	-2.316575000	5.394758000	0.326354000	1	-1.310249000	4.846235000	0.544991000
6	3.028785000	-3.000936000	2.402160000	6	2.323417000	-2.730465000	2.297337000
1	2.403912000	-2.371515000	1.749757000	1	1.870645000	-1.984455000	1.636984000
1	2.869151000	-2.669537000	3.441504000	1	2.115717000	-2.431046000	3.326632000
1	2.657063000	-4.035621000	2.320262000	1	1.814017000	-3.681454000	2.118185000
6	-1.720863000	3.592883000	2.142297000	6	-1.234189000	3.117901000	2.357004000
1	-0.958076000	3.279380000	1.414107000	1	-0.408336000	2.908854000	1.673622000
1	-1.470981000	3.135776000	3.113466000	1	-1.068467000	2.545048000	3.272588000
1	-1.631275000	4.683982000	2.270858000	1	-1.178582000	4.176284000	2.627633000
6	7.086391000	-2.237000000	-3.614995000	6	6.672205000	-2.595395000	-3.501691000
1	7.922228000	-2.517370000	-2.954579000	1	7.393742000	-3.210521000	-2.960532000
1	7.445312000	-1.450500000	-4.298840000	1	7.224645000	-1.861864000	-4.091233000
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6	-4.171451000	3.703112000	2.724992000	6	-3.677732000	3.153058000	2.767400000
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6	-6.545151000	-4.237271000	-1.752892000	6	-6.405079000	-4.287052000	-1.713455000
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1	-7.263908000	-4.314836000	-0.921818000	1	-7.080342000	-4.546656000	-0.895824000
6	5.386219000	-3.721994000	2.986520000	6	4.436455000	-3.809669000	3.084075000
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1	2.107759000	2.398904000	-2.252466000	1	2.325528000	2.099792000	-2.181397000
1	3.073748000	3.019454000	-3.615727000	1	3.258832000	2.732296000	-3.546376000
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6	4.717241000	-1.353765000	-3.754316000	6	4.672696000	-1.105832000	-3.342025000
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1	5.038632000	-0.596671000	-4.488681000	1	5.147531000	-0.438224000	-4.064313000
1	3.870746000	-0.932745000	-3.190433000	1	4.052960000	-0.491073000	-2.680566000
6	-2.095166000	-1.860005000	3.489671000	6	-2.149613000	-1.182372000	3.077781000
1	-1.517344000	-2.759494000	3.759167000	1	-1.390390000	-1.956693000	3.220614000
1	-1.960094000	-1.121872000	4.297607000	1	-1.989114000	-0.403399000	3.827471000
1	-1.647451000	-1.445075000	2.574334000	1	-1.984268000	-0.739242000	2.092519000
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1	-3.595787000	-2.463706000	-2.384592000	1	-3.814570000	-2.042727000	-2.195298000
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6	4.652894000	4.801360000	-2.189106000	6	4.607966000	4.706889000	-2.187802000
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1	-3.067383000	-3.027907000	4.891508000

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29	-3.603631000	-0.014621000	-0.043446000
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7	4.258737000	1.659672000	0.854772000
7	-4.397227000	1.715114000	-0.573756000
7	-5.196649000	-0.963697000	0.628168000
7	5.084664000	-1.121140000	-0.187298000
6	4.947406000	-2.437724000	-0.720392000
6	-5.097600000	-2.324348000	1.051355000
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6	5.004210000	-2.658815000	-2.123421000
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6	4.685555000	-3.522207000	0.165435000
6	5.584785000	1.719834000	0.995996000
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6	3.465020000	3.507105000	-1.250328000
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6	-3.368040000	2.709842000	-2.578134000
6	3.007430000	2.945209000	2.555645000
6	4.494533000	-4.801228000	-0.375343000
1	4.299586000	-5.641874000	0.293896000
6	4.803417000	-3.959889000	-2.609019000
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1	-4.590178000	-6.042305000	2.131093000
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6	-4.720432000	-2.627307000	2.386423000
6	3.034085000	3.688465000	0.204951000
6	6.221890000	2.951065000	1.620007000
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1	7.285971000	3.018972000	1.358108000
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6	-5.125693000	-4.695464000	0.526737000
1	-5.284273000	-5.507844000	-0.186857000
6	-4.939226000	2.395850000	-4.557518000
1	-5.676797000	3.074523000	-4.101172000
1	-5.491083000	1.648698000	-5.151530000
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1	-4.251352000	-4.215455000	3.772204000
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6	-4.515853000	-1.536194000	3.436554000
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6	-7.603690000	-1.072788000	1.140450000
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1	-8.474187000	-0.406918000	1.194248000
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6	-6.347575000	1.363473000	0.062088000
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1	6.802790000	2.838899000	2.250338000
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1	-4.998911000	3.063209000	-4.306041000
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1	-6.782107000	3.722289000	-0.786950000
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1	-5.337942000	-0.380025000	2.976322000
6	-7.585806000	-0.562618000	1.002872000
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6	-1.094349000	4.077085000	-2.462467000
1	-0.300766000	4.648337000	-2.928816000
6	-1.336766000	4.203907000	-1.107050000
1	-0.718398000	4.870380000	-0.517644000
6	-5.756847000	-2.725245000	-1.403910000
1	-6.164143000	-1.710191000	-1.420494000
6	2.611736000	2.225739000	3.697862000
1	3.516183000	1.617766000	3.621402000
6	7.365016000	-1.413907000	0.583656000
1	7.731239000	-1.711743000	1.568308000
1	8.121801000	-0.757540000	0.153243000
1	7.279611000	-2.303657000	-0.036883000
6	-1.871296000	3.220434000	-3.217186000
1	-1.678635000	3.123987000	-4.280067000
6	1.730830000	4.210057000	2.421405000
1	1.250742000	4.546502000	3.333308000

6	5.296979000	-1.534249000	-3.117427000
1	5.374216000	-0.598307000	-2.544995000
6	-3.069843000	0.736328000	-4.151822000
1	-2.363148000	1.268548000	-4.809886000
1	-3.599566000	-0.010903000	-4.765696000
1	-2.474536000	0.196328000	-3.400101000
6	2.132910000	1.157103000	4.121808000
1	1.379545000	1.817773000	4.581735000
1	2.414342000	0.398389000	4.871007000
1	1.646389000	0.642231000	3.280560000
6	-3.098785000	3.686393000	1.163690000
1	-3.942884000	3.022208000	1.398002000
6	1.827165000	4.972749000	1.890177000
1	1.210528000	5.835341000	2.155763000
6	2.236288000	4.781372000	0.570686000
1	1.927905000	5.499759000	-0.192118000
6	-4.548817000	-3.200161000	-2.289675000
1	-3.737387000	-2.516231000	-2.000298000
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1	-4.136027000	-4.222476000	-2.290800000
6	2.342338000	3.814660000	-2.254344000
1	1.410028000	3.286741000	-2.002368000
1	2.645347000	3.509626000	-3.269212000
1	2.109433000	4.891176000	-2.299332000
6	-5.561923000	-1.618777000	4.564173000
1	-6.590287000	-1.565237000	4.174751000
1	-5.430480000	-0.788959000	5.278265000
1	-5.470397000	-2.561056000	5.129241000
6	4.722444000	4.330183000	-1.589523000
1	4.537149000	5.408240000	-1.448304000
1	5.017358000	4.174122000	-2.640576000
1	5.578980000	4.050973000	-0.959381000
6	6.027414000	-3.588526000	2.321965000
1	6.338022000	-4.634103000	2.158628000
1	5.989615000	-3.413777000	3.409963000
1	6.810021000	-2.939036000	1.906587000
6	-6.917250000	-3.950310000	-1.796801000
1	-6.640215000	-5.014196000	-1.874094000
1	-7.255822000	-3.630049000	-2.795755000
1	-7.776128000	-3.880395000	-1.110413000
6	4.053552000	2.622437000	4.863764000
1	4.939238000	3.202460000	4.561622000
1	4.378202000	1.863660000	5.594617000
1	3.372081000	3.311436000	5.388982000
6	-1.866737000	3.120788000	1.892554000
1	-1.647416000	2.092241000	1.569512000
1	-2.031058000	3.102179000	2.982967000
1	-0.965090000	3.722902000	1.696189000
6	-3.094127000	-1.554228000	4.022749000
1	-2.896274000	-2.481133000	4.585968000
1	-2.948274000	-0.709335000	4.715932000
1	-2.332816000	-1.479539000	3.232777000
6	4.165374000	-1.349708000	-4.144601000
1	4.045622000	-2.239879000	-4.783409000
1	4.380456000	-0.494620000	-4.806207000
1	3.199803000	-1.158873000	-3.653514000
6	3.575940000	-4.160228000	2.387767000
1	2.585179000	-4.032900000	1.924948000
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6	6.638223000	-1.749699000	-3.844819000
1	7.471926000	-1.876355000	-3.138701000
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15	1.667504000	-0.129317000	-1.392598000
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16	-0.261886000	-0.863823000	1.473656000
15	-1.469108000	-0.542729000	-0.267478000
16	-0.207328000	0.873415000	-1.293352000

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29	-3.474878000	0.018721000	0.079480000
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33	-1.735066000	-0.787280000	-1.482333000
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33	0.858868000	-2.375296000	0.512569000
33	-1.175407000	0.677537000	0.824821000
16	1.892705000	-0.749148000	-0.785037000
16	-0.859425000	-2.788914000	-0.899586000
16	-0.175278000	-1.006735000	1.984537000

6	5.330465000	-0.626339000	-2.534170000
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6	-2.828369000	0.379864000	-4.012383000
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6	1.565023000	4.941695000	1.260989000
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6	2.135378000	4.496819000	0.083806000
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6	2.661173000	3.157680000	-2.465955000
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6	-5.457111000	-1.630817000	4.687924000
1	-6.488236000	-1.965527000	4.558544000
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1	-4.909323000	-2.427971000	5.195371000
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6	5.737085000	-4.412360000	1.912686000
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29	-3.344514000	-0.036226000	0.202535000
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33	0.913826000	-2.403884000	0.440369000
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16	1.864191000	-0.866298000	-0.943998000
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6	-5.806422000	1.571381000	0.900351000	6	-5.606360000	1.584216000	1.051270000
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6	6.619164000	-0.164370000	0.563724000	6	6.414303000	0.054865000	0.670076000
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6	-6.260284000	-0.826208000	0.095451000	6	-6.130295000	-0.803194000	0.371216000
6	6.412208000	3.502299000	-0.674885000	6	5.926961000	3.702988000	-0.421130000
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1	5.885711000	4.266683000	-0.081777000	1	5.308074000	4.401547000	0.146742000
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6	-6.605747000	0.451792000	0.587504000	6	-6.437342000	0.473588000	0.860977000
1	-7.671958000	0.595357000	0.763416000	1	-7.479315000	0.633461000	1.102605000
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6	5.075720000	-2.424316000	2.369299000	6	5.035432000	-2.444095000	2.216993000
6	5.351328000	-2.164949000	0.998916000	6	5.304701000	-2.046486000	0.896670000
6	-4.655570000	-3.500967000	1.585304000	6	-4.487728000	-3.508442000	1.646178000
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1	8.752901000	-0.247015000	0.974231000	1	8.513133000	0.095144000	1.151139000
1	8.025105000	-1.818940000	0.539516000	1	7.934032000	-1.449320000	0.506591000
6	-3.444471000	3.062963000	2.518904000	6	-3.110602000	3.114867000	2.341203000
6	-4.250504000	-5.027844000	-1.898242000	6	-4.128453000	-4.841577000	-1.892052000
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6	2.946219000	3.656512000	-0.207039000	6	2.494919000	3.557380000	-0.084261000
6	2.494418000	3.829159000	-2.975784000	6	2.093032000	3.658484000	-2.838865000
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6	4.884512000	-3.751123000	2.780070000	6	4.900819000	-3.797808000	2.490599000
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6	3.169698000	3.584621000	1.302790000	6	2.703573000	3.506844000	1.412574000
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6	5.435195000	-3.240130000	0.072810000	6	5.459164000	-3.001085000	-0.119810000
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1	5.304697000	-5.381404000	-0.168381000	1	5.430206000	-5.092799000	-0.573917000
6	-2.509055000	4.759130000	0.477148000	6	-2.153530000	4.470014000	0.099488000
1	-2.139255000	5.425397000	-0.304632000	1	-1.766163000	5.000769000	-0.761659000
6	-4.733847000	2.949663000	4.714092000	6	-3.961536000	3.300772000	4.711524000
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1	-5.570161000	3.497919000	4.254452000	1	-4.667033000	4.065388000	4.380632000
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1	-4.871609000	5.080866000	-1.679624000	1	-4.863467000	4.508289000	-1.814110000
1	-5.759005000	3.621856000	-1.177021000	1	-5.575115000	3.013342000	-1.188440000
1	-5.130387000	3.747430000	-2.833917000	1	-5.056557000	3.102821000	-2.869589000
6	-5.648482000	-4.493097000	2.216788000	6	-5.166981000	-4.709022000	2.286825000
1	-6.652900000	-4.406372000	1.773564000	1	-6.161688000	-4.879131000	1.869735000
1	-5.738421000	-4.310454000	3.300224000	1	-5.269208000	-4.554961000	3.362539000
1	-5.320460000	-5.537540000	2.088815000	1	-4.587485000	-5.624377000	2.147925000
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1	-1.477563000	3.358652000	-1.999192000	1	-1.394605000	3.072183000	-2.300642000
1	-2.362550000	4.845744000	-2.395121000	1	-2.448135000	4.410816000	-2.757980000
6	-4.106888000	-1.501254000	-4.414593000	6	-4.260412000	-1.227990000	-4.206188000
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1	-4.220534000	-0.556671000	-4.970565000	1	-4.408906000	-0.255796000	-4.680246000
1	-4.398687000	-2.313185000	-5.100357000	1	-4.624519000	-1.983110000	-4.906935000
6	-6.462588000	-1.364441000	-3.541684000	6	-6.509663000	-1.174090000	-3.154844000
1	-6.798664000	-2.274835000	-4.065569000	1	-6.864457000	-2.071332000	-3.669688000
1	-6.620301000	-0.508440000	-4.218627000	1	-6.724701000	-0.313400000	-3.791983000
1	-7.112501000	-1.219371000	-2.668196000	1	-7.087404000	-1.059671000	-2.238066000
6	3.381409000	4.969489000	1.937823000	6	2.563978000	4.867800000	2.077417000
1	2.475188000	5.594125000	1.879448000	1	1.533387000	5.229617000	2.044183000
1	4.197266000	5.521586000	1.444592000	1	3.197009000	5.617284000	1.598392000
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6	-2.735648000	1.452686000	4.358455000	6	-2.512245000	1.374099000	4.047809000
1	-2.167198000	0.829658000	3.652179000	1	-2.361070000	0.574859000	3.317976000
1	-3.100662000	0.794246000	5.163804000	1	-2.815383000	0.906107000	4.986674000
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1	4.748950000	-3.231076000	-3.356687000	1	4.883152000	-2.699954000	-3.518566000
1	3.612717000	-2.943976000	-2.017876000	1	3.697813000	-2.627129000	-2.210314000
6	4.990037000	2.957879000	-4.554193000	6	4.611375000	3.078422000	-4.378869000
1	4.278984000	3.492406000	-5.205331000	1	3.825640000	3.411836000	-5.060651000
1	5.619138000	2.326881000	-5.203310000	1	5.358970000	2.554467000	-4.977230000
1	5.640391000	3.712883000	-4.084817000	1	5.078633000	3.968660000	-3.953806000
6	3.382988000	1.035474000	-4.179340000	6	3.371872000	0.956035000	-3.923459000
1	2.925259000	0.365169000	-3.436016000	1	3.086390000	0.217331000	-3.170013000
1	3.976923000	0.413907000	-4.869981000	1	4.034109000	0.460416000	-4.636608000
1	2.569074000	1.498332000	-4.761940000	1	2.467742000	1.257430000	-4.459819000
6	3.501082000	-1.114817000	3.861694000	6	3.353747000	-1.049576000	3.397826000
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1	5.623136000	-2.372561000	5.194699000	1	4.787334000	-2.667724000	5.081631000
1	5.849402000	-0.613227000	5.266534000	1	5.302418000	-1.013866000	5.366773000
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6	4.720381000	-2.570977000	-2.273592000	6	4.651860000	-2.633478000	-2.041267000
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6	3.502244000	1.633235000	3.621116000	6	3.079203000	1.664141000	3.458294000
1	3.687758000	0.734211000	3.011593000	1	3.296039000	0.745314000	2.898407000
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1	1.653377000	5.814426000	2.514654000	1	1.120320000	5.655439000	2.044236000
6	-5.710416000	-3.005481000	-1.453066000	6	-5.854104000	-2.471161000	-1.629093000
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6	-2.475612000	3.893101000	-2.959394000	6	-1.889665000	3.657439000	-2.770681000
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6	3.953519000	3.784286000	-1.038195000	6	3.782669000	3.594163000	-1.180038000
1	4.674735000	2.959713000	-1.130660000	1	4.694155000	2.993212000	-1.120714000
6	4.606114000	-3.588456000	-0.027373000	6	4.570664000	-3.469620000	0.254814000
6	2.800144000	3.482018000	-2.011548000	6	2.823479000	2.856167000	-2.107183000
1	2.329574000	2.512775000	-1.781876000	1	2.667796000	1.826734000	-1.765814000
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6	-4.974728000	-1.277368000	3.346084000	6	-4.862501000	-1.414939000	3.240166000
1	-5.314418000	-0.356471000	2.851481000	1	-5.355464000	-0.479919000	2.961609000
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6	4.326584000	-4.821579000	-0.633222000	6	4.292738000	-4.735037000	-0.242549000
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6	6.456424000	-1.268943000	-3.604298000	6	6.364718000	-1.365744000	-3.367609000
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6.5.5. References

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Preface

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'Reactivity of Cu(I) Nacnac Complexes Towards [Cp*Ru(η^5-E$_5$)] (E = P, As)' DOI:10.1080/10426507.2021.2011888.

Authors

Maria Haimerl and Manfred Scheer*

Author contribution

M. Haimerl performed the experimental work. Prof. M. Scheer supervised, raised funding and directed the project. The manuscript was written through contributions of all authors.

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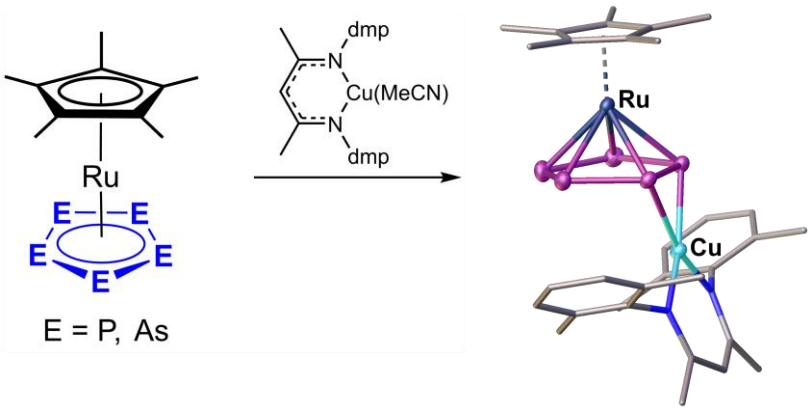
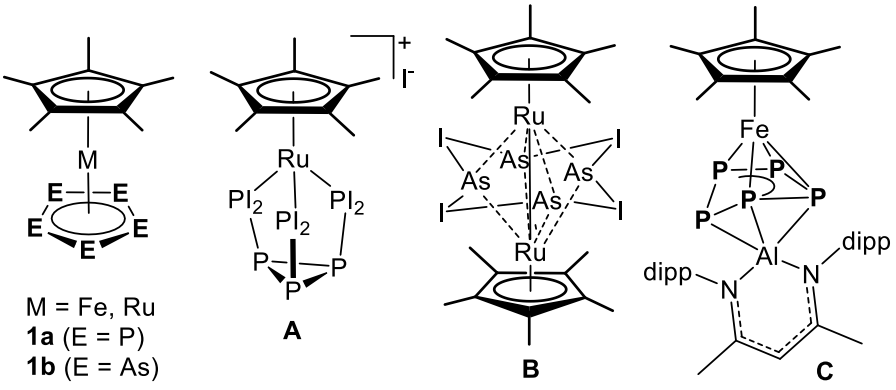

Ru
E
E
E
E
E
E = P, As
dmp
N
Cu(MeCN)
N
dmp
Ru
Cu

7. Reactivity of Cu(I) Nacnac Complexes Towards [Cp*Ru(η5-E5)] (E = P, As)

Abstract: *The reactivity of the nacnac Cu(I) compound [L1Cu(MeCN)] (**2**) (L1 = [{N(C6H3Me2-2,6)C(Me)}2CH]-) towards complexes containing aromatic cyclo-E5 ligands (E = P, As) was investigated. The copper complex was reacted with [Cp*Ru(η5-E5)] (E = P (**1a-Ru**), As (**1b-Ru**)), yielding the heterometallic complexes [(Cp*Ru)(μ,η5:2-E5)(L1Cu)] (E = P (**3a**), As (**3b**)). These neutral and molecular complexes represent rare examples of the coordination of group 11 metal complexes to cyclo-En units and are also rare examples of the coordination compounds of **1a-Ru** and **1b-Ru**. They were fully characterized by crystallographic and spectroscopic methods and compared to related compounds.*

7.1. Introduction

The conversion of white phosphorus and yellow arsenic is an active research topic. Decades of extensive studies have led to the formation of a plethora of polypnictogen (E_n) ligand complexes (E = P, As).[1] Of special interest are complexes with *cyclo*-E_n ligands which possess a special aromatic character. Such ligands were realized for n = 3-6 as end-decks or middle-decks.[2] The *cyclo*-E_5 ligand is present in the ferrocene analog pentaphosphaferrocene or pentaarsaferrocene [Cp*Fe(η5-E5)] (E = P (**1a-Fe**),[2h] As (**1b-Fe**),[2j] Scheme 7.1). These compounds were the subject of numerous research topics: The reactivity of **1a-Fe** and **1b-Fe** towards electrophiles, nucleophiles and their redox behavior,[3] and further their use as a building block for coordination polymers and spherical aggregates[4] was extensively studied. Similar complexes containing a *cyclo*-E_5 ligand are known for its heavier analogue ruthenium.[2i,2k,5] The chemistry of [Cp*Ru(η5-E5)] (E = P (**1a-Ru**), As (**1b-Ru**), Scheme 7.1) is less explored. Recently, our group reported the iodination of [Cp*M(η5-E5)] (M = Fe, Ru; E = P, As),[6] which leads in the case of **1a-Fe** and **1a-Ru** to the formation of a tripodal *cyclo*-$P_3(PI_2)_3$ ligand coordinating to a {Cp*M} fragment which represents a MP_6 core resembling the nortricyclane structure of P_7^{3-} (**A**, Scheme 7.1).



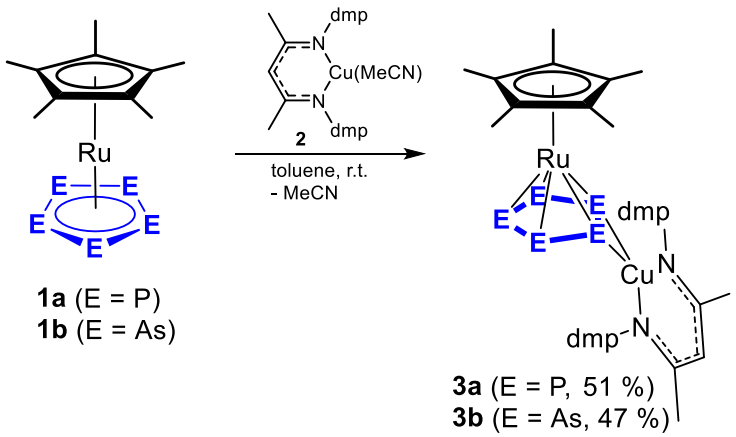
Scheme 7.1. Selected products of the reactivity of [Cp*M(η5-E5)] (M = Fe, Ru; E = P, As). dipp = 2,6-diisopropylphenyl.

Interestingly, a different outcome is realized by the reactions of the arsenic compounds **1b-Fe** and **1b-Ru**. While the reaction of **1b-Fe** with iodine leads to the formation of a di-cationic Fe-As triple decker complex with a *cyclo*-As_5 unit, the reaction of **1b-Ru** leads to three different products: a mono-cationic Ru-As triple decker complex, a Ru complex with a planar μ,$\eta^{4:4}$-As_4I_4 middle deck with a four-point star structural motif (**B**, Scheme 7.1), and $[(Cp^*Ru)_2As_8I_6]$. These results clearly show a different reactivity between the phosphorus and the arsenic compounds and also the impact of the metal center.

Furthermore, there are efforts to investigate the reactivity of *β*-diiminato M(I) complexes towards *cyclo*-E_n complexes. *Roesky et al.* reported the reaction of $[L^3Al]$ (L^3 = $[\{N(C_6H_3{}^iPr_2\text{-}2,6)C(Me)\}_2CH]^-$) with $[Cp^*Fe(\eta^5\text{-}P_5)]$ leading to $[(Cp^*Fe)(\mu,\eta^{5:3}\text{-}P_5)(L^3Al)]$ (**C**, Scheme 7.1) containing an envelope-shaped P_5 ring.[7] Recently, we reported the reactivity of Cu(I) nacnac complexes towards polypnictogen compounds, i.e. $[Cp^*Fe(\eta^5\text{-}E_5)]$ (E = P, As)[8] which leads to the formation of the heterobimetallic compounds $[(Cp^*Fe)(\mu,\eta^{5:2}\text{-}E_5)(L^1Cu)]$ (E = P, As) and $[(Cp^*Fe)(\mu,\eta^{5:2:1}\text{-}E_5)(L^1Cu)_2]$ (E = P, As). Such products are examples of the coordination of a group 11 metal by aromatic *cyclo*-E_n ligands. In this study, we varied the ring size of the $[Cp^RM(\textit{cyclo}\text{-}E_n)]$ complex and the metal (M = Fe, n = 5; M = Co, n = 4; M = Ni, n = 3). It turned out that the η^2-coordinating E-E bonds are elongated but still intact. Now the question arose as to what would happen when changing the metal to its higher homolog ruthenium by maintaining the *cyclo*-E_5 unit. In the following, we report on the reactivity of $[L^1Cu(MeCN)]$ (**2**) towards $[Cp^*Ru(\eta^5\text{-}E_5)]$ (E = P (**1a-Ru**), As (**1b-Ru**)), resulting in the formation of the new heterometallic compounds $[(Cp^*Ru)(\mu,\eta^{5:2}\text{-}E_5)(L^1Cu)]$ (E = P (**3a**), As (**3b**)).

7.2. Results and Discussion

The reaction of $[Cp^*Ru(\eta^5\text{-}E_5)]$[2i,2k] (E = P (**1a-Ru**), As (**1b-Ru**)) with one equivalent of $[L^1Cu(MeCN)]$[9] (**2**, L^1 = $[\{N(C_6H_3Me\text{-}2,6)C(Me)\}_2CH]^-$) leads to the formation of $[(Cp^*Ru)(\mu,\eta^{5:2}\text{-}E_5)(L^1Cu)]$ (E = P (**3a**), As (**3b**)) in good crystalline yields of 51 % (**3a**) and 47 % (**3b**), respectively (Scheme 7.2).



Scheme 7.2. Reaction of [Cp*Ru(η5-E5)] (E = P (**1a-Ru**), As (**1b-Ru**)) with [L1Cu(MeCN)] (**2**) (dmp = 2,6-dimethylphenyl).

The $^{31}P\{^{1}H\}$ NMR spectrum of **3a** in C_6D_6 at room temperature indicates a sharp singlet at δ = 58.3 ppm ($\omega_{1/2}$ = 13 Hz). One would expect at least three different phosphorus signals. Even though the low temperature of 193 K is not enough to freeze the ongoing dynamic behavior of **3a**, the $^{31}P\{^{1}H\}$ NMR spectrum still indicates a singlet which is broadened ($\omega_{1/2}$ = 166 Hz). Therefore, this highly dynamic behavior in solution of **3a** reflects either the tumbling of the {L1Cu} fragment around the *cyclo*-P_5 ring or a dissociation-reassociation process of the {L1Cu} fragment. Based on the results for [(Cp*Fe)(μ,η5:2:1-P5)(L1Cu)2][8] which show that its dynamic motion consists of an $\eta^1 \rightarrow \eta^2 \rightarrow \eta^1$ walk of the two {L1Cu} fragments around the *cyclo*-P_5 ring, we propose a similar behavior for the ruthenium complex. The ^{1}H NMR spectra of **3a** and **3b** (C_6D_6, r.t.) reveal a full set of signals for the nacnac ligand and a sharp signal for the Cp* ligand. In the LIFDI-MS spectra of **3a** and **3b**, the corresponding molecular ion peaks are detected.

The molecular structure of **3a** and **3b** reveals a dinuclear complex in which the {L1Cu} fragment is bonded in an η^2 fashion side-on to the {Cp*Ru(η5-E5)} unit (Figure 7.1). The {L1Cu} fragment is almost perpendicular to the E_5 plane (dihedral angle: **3a**: 82.46(3)°, **3b**: 96.15(3)°). The Cu-E distances are 2.2916(8)/2.2844(8) Å for **3a** and 2.3996(10)/2.3921(11) Å for **3b**. Four of the E-E distances are in the range between a single[10] and a double[11] bond (Table 7.1). The η^2-coordinated E-E distances are elongated (2.2327(10) Å (**3a**) and 2.4292(10) Å (**3b**)). All these values are in accordance with the reported complexes [(Cp*Fe)(μ,η5:2-E5)(L1Cu)][8] (E = P (**3a-Fe**), As (**3b-Fe**)) (Table 7.1) and reveal that the E-E bonds are still intact.

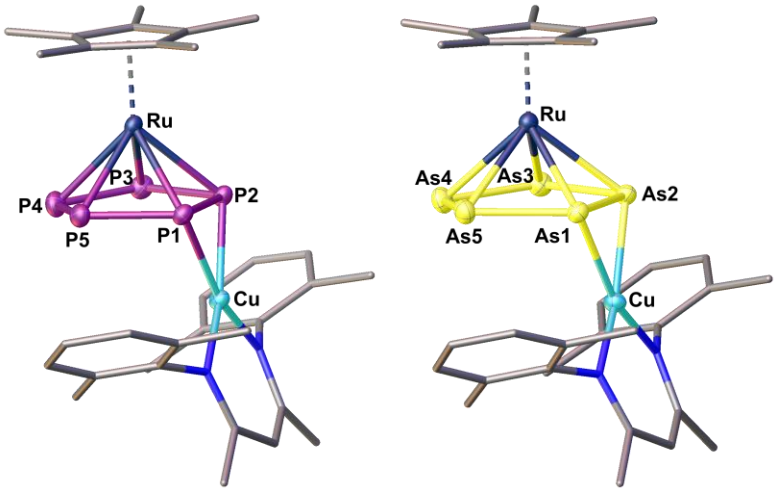


Figure 7.1. Molecular structures of **3a** (left) and **3b** (right) in the solid state. Thermal ellipsoids are shown at the 50 % probability level. Hydrogen atoms are omitted for clarity

Table 7.1. Comparison of selected atomic distances and angles in **3a**, **3b**, **3a-Fe** and **3b-Fe** (E = P, As; ϕ = angle between E$_5$ plane and E-Cu-E plane).

Compound	**3a**	**3b**	**3a-Fe**[8]	**3b-Fe**[8]
d(Cu-E)/ [Å]	2.2844(8) 2.2916(8)	2.3921(11) 2.3996(10)	2.2820(7) 2.2859(7)	2.4002(7) 2.4255(7)
d(E-E)/ [Å]	2.1301(10) - 2.1384(10)	2.3400(10) - 2.3475(10)	2.1172(13) - 2.1326(11)	2.3251(9) - 2.3425(8)
d(E1-E2)/ [Å]	2.2327(10)	2.4292(10)	2.2100(10)	2.4039(6)
Φ [°]	82.46(3)	96.15(3)	83.43(2)	94.29(2)

7.3. Conclusion

In summary, it was shown that the reactivity of copper nacnac compounds towards complexes containing a *cyclo*-E$_5$ ligand results in the synthesis of the heterometallic complexes [(Cp*Ru)(μ,η$^{5:2}$-E$_5$)(L^{1}Cu)] (E = P (**3a**), As (**3b**)). These compounds are rare examples of the reactivity of the ruthenium analogues of pentaphospha- and pentaarsaferrocene. Their structural characterization shows that the coordinated E-E bond of the *cyclo*-E$_5$ ligands are still intact. ^{31}P{^{1}H} NMR investigations for **3a** reveal a dynamic behavior in solution. Therefore, the reactivity of Cu(I) nacnac compounds is not affected by the choice of the metal center (Fe or Ru) and also the nature of the *cyclo*-E$_5$ ring shows the same reactivity.

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7.5. Supporting Information

7.5.1. Synthesis and Characterization

General Remarks

All manipulations were performed with rigorous exclusion of oxygen and moisture using standard Schlenk techniques on a dual manifold Schlenk line with Argon or N_2 inert gas or glove box filled with nitrogen containing a high-capacity recirculator (<0.1 ppm O_2). Traces of oxygen and moisture in the inert gas were removed by passing it through a drying column filled with Cu/$MgSO_4$ catalyst as well as, concentrated H_2SO_4 and orange gel, respectively.

All solvents were degassed and purified by standard procedures. All NMR spectra have been recorded using deuterated d_6-benzene that was dried (over Na/K), refluxed for three hours and then distilled under inert atmosphere.

Characterization methods

Mass spectrometry was performed using a Jeol AccuTOF GCX LIFDI mass spectrometer or an Agilent Q-TOF 6540 UHD ES mass spectrometer by the MS department of the University of Regensburg. The compounds were dissolved in the corresponding solvent in a glove box under N_2 atmosphere. The observed fragments were assigned according to the mass/charge (m/z) ratio and the corresponding isotope pattern. Elemental analysis (CHN) were performed by the department of central analyses of the University of Regensburg on a Vario micro cube and a MT5 micro scale device. The compounds were filled in tin capsules in a glove box under N_2 atmosphere.

^{1}H and ^{31}P NMR spectra were recorded on a Bruker Avance III HD 400 (^{1}H: 400.130 MHz, ^{31}P: 161.976 MHz) spectrometer at the NMR department of the University of Regensburg. The chemical shifts are reported in ppm relative to external TMS (^{1}H) or 85 % H_3PO_4 (^{31}P). The chemical shifts δ are given in parts per million [ppm] and coupling constants J in [Hz].

Starting materials

The compounds [Cp*Ru(η^5-E$_5$)][1] (E = P (**1a-Ru**), As (**1b-Ru**)) and [L^{1}Cu(MeCN)][2] (**2**, L^1 = [{N(C$_6$H$_3$Me$_2$-2,6)C(Me)}$_2$CH]$^-$) were prepared according to literature procedures.

7.5.1.1. Synthesis of [(Cp*Ru)(μ,η$^{5:2}$-P$_5$)(L^{1}Cu)] (**3a**)

[Cp*Ru(η^5-P$_5$)] (**1a-Ru**) (20 mg, 0.05 mmol, 1 eq) and [L^{1}Cu(MeCN)] (**2**) (21 mg, 0.05 mmol, 1 eq) were dissolved in Et$_2$O and stirred for 1 hour at room temperature. The reaction mixture was filtered over diatomaceous earth and transferred into a double Schlenk (with 1 mL of toluene on the other side). The solvent was reduced by slow evaporation at -30 °C. Compound [(Cp*Ru)(μ,η$^{5:2}$-P$_5$)(L^{1}Cu)] (**3a**) crystallized as orange needles, suitable for X-ray analysis.

Crystalline Yield: 20 mg (51 %, 0.026 mmol)

^{1}H NMR (C$_6$D$_6$, 300 K): δ [ppm] = 7.32 (d, 4H, *H*$_{meta}$, $^3J_{HH}$ = 7 Hz), 7.19 (t, 2H, *H*$_{para}$, $^3J_{HH}$ = 7 Hz), 4.74 (s, 1H, *H*$_β$), 2.10 (s, 12H, *ortho*-Me), 1.56 (s, 6H, α-Me), 1.10 (s, 15H, Cp*).

^{1}H NMR (tol-d$_8$, 193 K): δ [ppm] = 7.34 (d, 4H, *H*$_{meta}$, $^3J_{HH}$ = 7 Hz), 7.23 (t, 2H, *H*$_{para}$, $^3J_{HH}$ = 7 Hz), 4.69 (s, 1H, *H*$_β$), 2.08 (s, 12H, *ortho*-Me), 1.49 (s, 6H, α-Me), 0.99 (s, 15H, Cp*).

^{31}P{^{1}H} NMR (C$_6$D$_6$, 300 K): δ [ppm] = 58.3 ppm (s, 5P).

^{31}P{^{1}H} NMR (tol-d$_8$, 193 K): δ [ppm] = 54.84 ppm (s, 5P).

LIFDI-MS (toluene): m/z (%) = 759.98 (29.19, [M$^+$]), 1130.10 (100, [(Cp*Ru)(P$_5$)(L^{1}Cu)$_2$]).

EA calculated for C$_{31}$H$_{40}$CuN$_2$RuP$_5$: C: 48.98, H: 5.30, N: 3.69, found [%]: C: 48.93, H: 5.28, N: 3.63.

7.5.1.2. Synthesis of [(Cp*Ru)(μ,η$^{5:2}$-As$_5$)(L^{1}Cu)] (**3b**)

[Cp*Ru(η^5-As$_5$)] (**1b-Ru**) (20 mg, 0.03 mmol, 1 eq) and [L^{1}Cu(MeCN)] (13.4 mg, 0.03 mmol, 1 eq) were dissolved in Et$_2$O and stirred for 1 hour at room temperature. The reaction mixture was filtered over diatomaceous earth and transferred into a double Schlenk (with 1 mL of toluene on the other side). The solvent was reduced by slow evaporation at -30 °C. Compound [(Cp*Ru)(μ,η$^{5:2}$-As$_5$)(L^{1}Cu)] (**3b**) crystallized as orange needles, suitable for X-ray analysis.

Crystalline Yield: 15 mg (47 %, 0.015 mmol)

^{1}H NMR (C$_6$D$_6$, 300 K): δ [ppm] = 7.36 (d, 4H, *H*$_{meta}$, $^3J_{HH}$ = 7 Hz), 7.21 (t, 2H, *H*$_{para}$, $^3J_{HH}$ = 7 Hz), 4.73 (s, 1H, H$_β$), 3.25 (q, 2H, Et$_2$O), 2.02 (s, 12H, *ortho*-Me), 1.55 (s, 6H, α-Me), 1.07 (s, 15H, Cp*).

LIFDI-MS (toluene): m/z (%) = 979.69 (100, [M$^+$]).

7.5.2. NMR studies

7.5.2.1. [(Cp*Ru)(μ,η$^{5:2}$-P$_5$)(L^{1}Cu)] (**3a**)

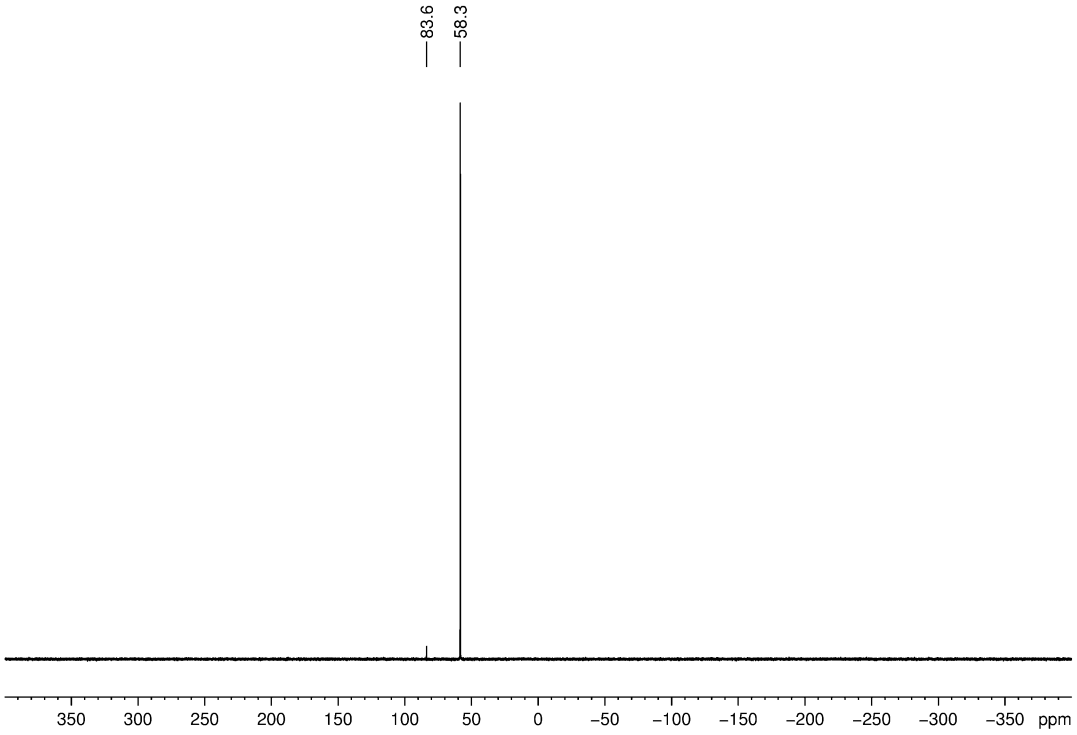

Figure S7.1. $^{31}P\{^1H\}$ NMR spectrum of **3a** in C_6D_6 at room temperature.

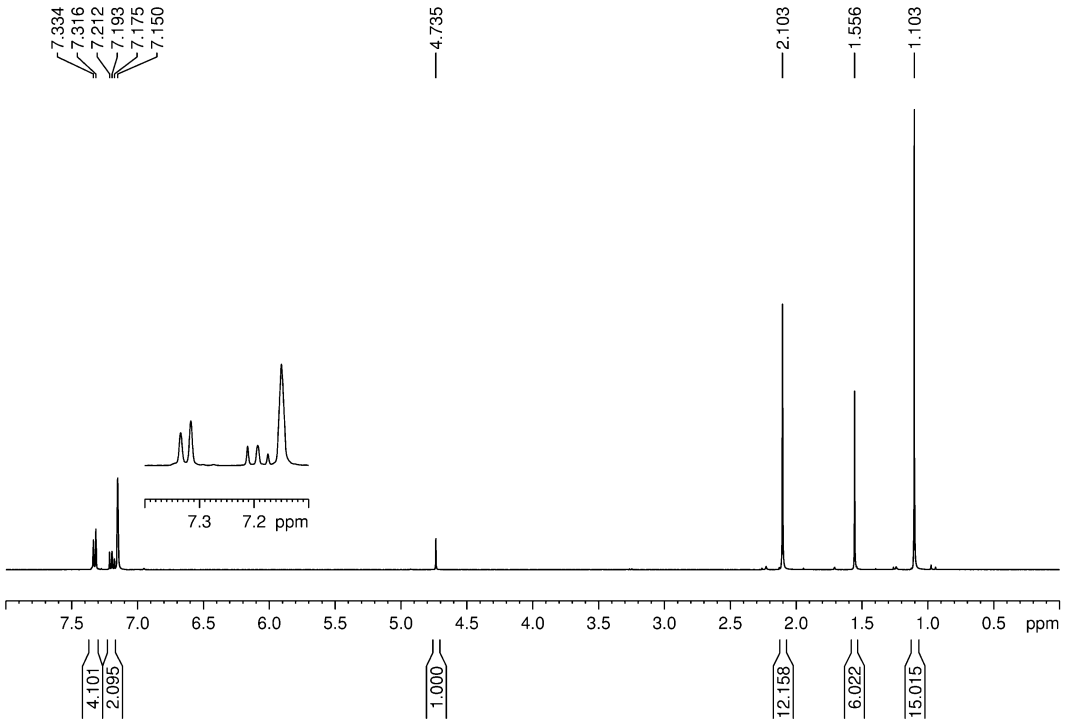

Figure S7.2. ^1H NMR spectrum of **3a** in C_6D_6 at room temperature.

7.5.2.2. [(Cp*Ru)(μ,η$^{5:2}$-As$_5$)(L^{1}Cu)] (**3b**)

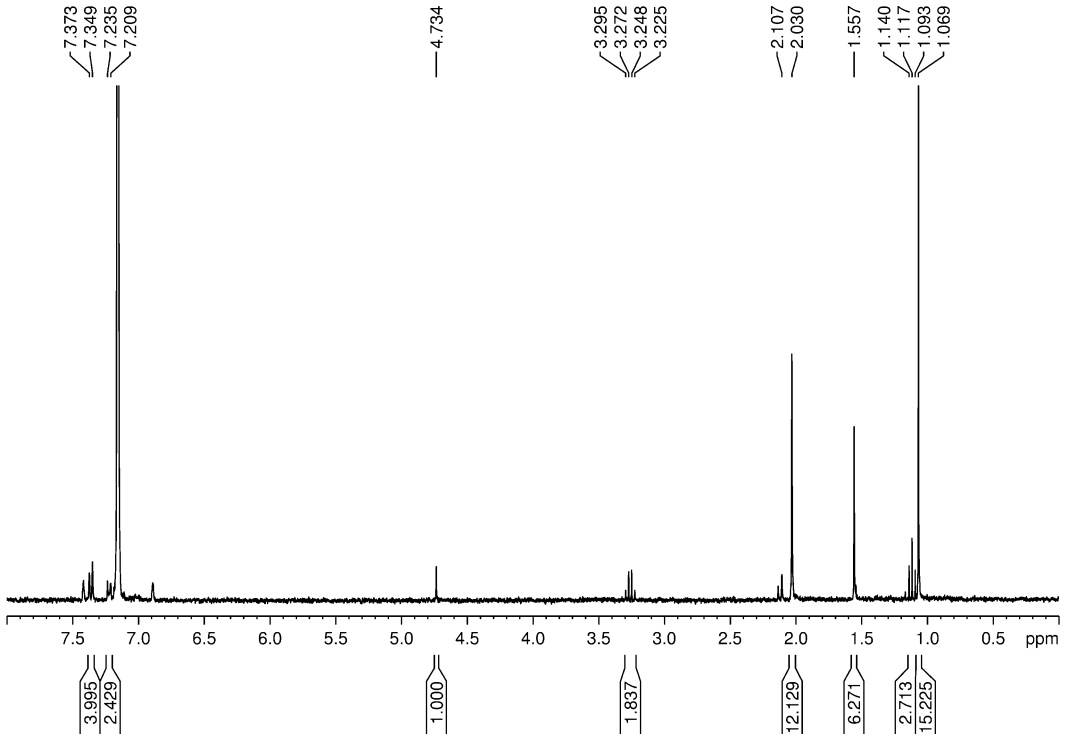

Figure S7.3. ^{1}H NMR spectrum of **3b** in C_6D_6 at room temperature.

7.5.3. Details on single crystal X-ray structure analysis

The X-ray diffraction experiments were performed on either a SuperNova Dualflex diffractometer (Rigaku) equipped with a TitanS2 CCD detector (**3a**), or a XtaLAB Synergy R, DW system (Rigaku) equipped with a HyPix Arc 150° detector (**3b**). All measurements were performed at 123 K, respectively. Data collection and reduction were performed with CrysAlisPro[3] (Version 171.41.90a, 2020 (**3a**, **3b**)). For the compounds **3a** and **3b** a gaussian absorption correction based on gaussian integration over a multifaceted crystal model was applied. Using Olex2, were the structures solved by direct methods with ShelXT[4] and refined by full-matrix least-squares method against F^2 in anisotropic approximation using ShelXL[5]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined in calculated positions using riding on pivot atom model.

Figures were created with Olex2.[6]

CCDC-2120088 (**3a**) and CCDC-2120089 (**3b**) 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).

7.5.3.1. [(Cp*Ru)(μ,η$^{5:2}$-P$_5$)(L^{1}Cu)] (**3a**)

Compound **3a** crystallizes from a concentrated diethyl ether solution at -30 °C in the monoclinic space group *P2$_1$/c*. The asymmetric unit contains one molecule of **3a**. The structure in the solid state is shown in Figure S7.4.

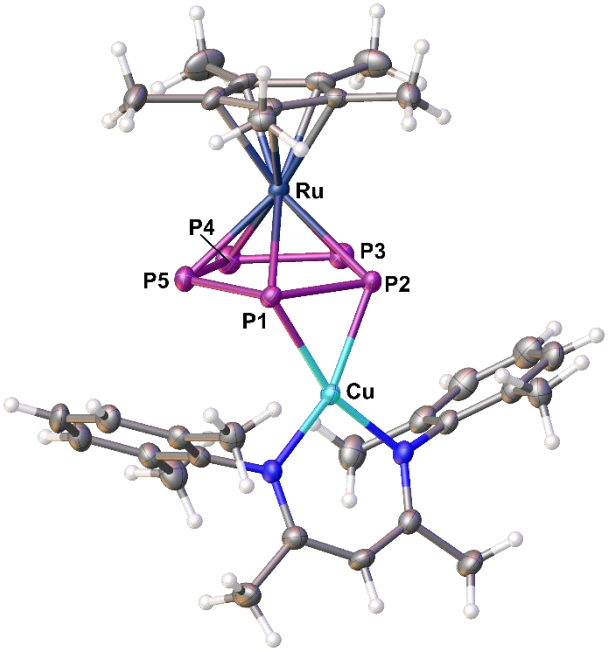

Figure S7.4. Molecular structure of **3a** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Ru-P1 2.4628(7), Ru-P2 2.4633(7), Ru-P3 2.4304(7), Ru-P4 2.4700(8), Ru-P5 2.4281(8), Cu-P1 2.2916(8), Cu-P2 2.2844(8), P1-P2 2.2327(10), P2-P3 2.1384(10), P3-P4 2.1301(10), P4-P5 2.1318(11), P5-P1 2.1364(10), P2-Cu-P1 58.41(3), P3-P2-P1 106.82(4), P5-P1-P2 107.02(4), P4-P5-P1 108.23(4), P4-P3-P2 108.33(4), P3-P4-P5 109.32(4).

7.5.3.2. [(Cp*Ru)(μ,η$^{5:2}$-As$_5$)(L^{1}Cu)] (**3b**)

Compound **3b** crystallizes from a concentrated diethyl ether solution at -30 °C in the monoclinic space group *P2$_1$/c*. The asymmetric unit contains one molecule of **3b**. The structure in the solid state is shown in Figure S7.5.

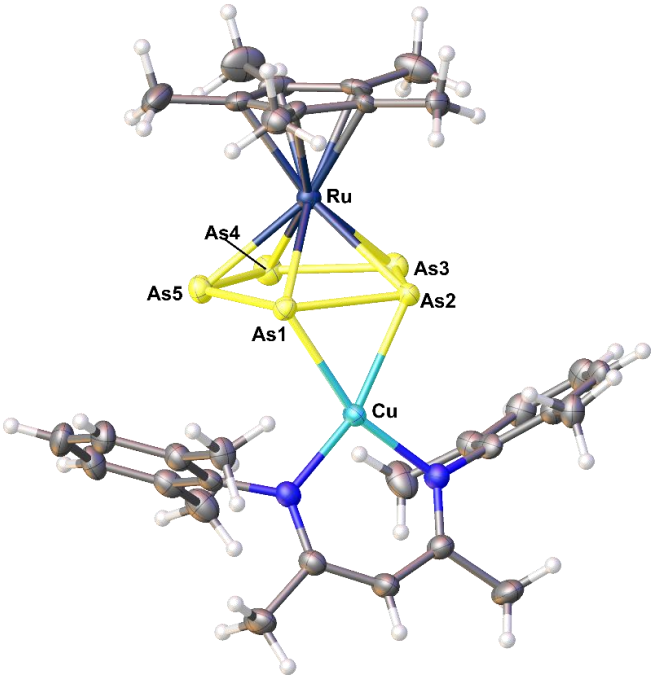

Figure S7.5. Molecular structure of **3b** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Ru-As1 2.5897(8), Ru-As2 2.5895(8), Ru-As3 2.5640(8), Ru-As4 2.6106(9), Ru-As5 2.5648(8), As1-As2 2.4292(10), As1-As5 2.3463(10), As2-As3 2.3475(10), As3-As4 2.3400(10), As4-As5 2.3435(10), Cu-As1 2.3996(10), Cu-As2 2.3921(11), As3-As2-As1 107.07(3), As5-As1-As2 107.22(3), As4-As3-As2 108.30(4), As4-As5-As1 108.17(4), As3-As4-As5 109.00(4), As2-Cu-As1 60.92(3).

7.5.3.3. Crystallographic Information

Table S7.1. Crystallographic data and details of diffraction experiments for **3a** and **3b**.

Compound	3a	3b
CCDC	2120088	2120089
Formula	$C_{31}H_{40}CuN_2P_5Ru$	$C_{31}H_{40}As_5CuN_2Ru$
$D_{calc.}$/ g cm^{-3}	1.512	1.899
μ/mm^{-1}	6.892	9.871
Formula Weight	760.11	979.86
Colour	orange	clear orange
Shape	needle	needle
Size/mm^3	0.15×0.06×0.04	0.18×0.04×0.03
T/K	123.00(10)	123.01(10)
Crystal System	monoclinic	monoclinic
Space Group	$P2_1/c$	$P2_1/c$
a/Å	7.98500(10)	8.11410(10)
b/Å	19.1630(3)	19.3060(3)
c/Å	22.1094(4)	22.2113(3)
α/°	90	90
β/°	99.285(2)	99.931(2)
γ/°	90	90
V/Å^3	3338.78(9)	3427.28(8)
Z	4	4
Z'	1	1
Wavelength/Å	1.54184	1.54184
Radiation type	Cu K$_\alpha$	Cu K$_\alpha$
Θ_{min}/°	4.052	3.053
Θ_{max}/°	66.859	73.339
Measured Refl's.	29913	20779
Indep't Refl's	5915	6496
Refl's I≥2 σ(I)	5194	5433
R_{int}	0.0373	0.0389
Parameters	372	372
Restraints	0	0
Largest Peak	1.693	2.389
Deepest Hole	-1.578	-2.132
GooF	1.023	1.087
wR_2 (all data)	0.0981	0.1806
wR_2	0.0929	0.1739
R_1 (all data)	0.0409	0.0662
R_1	0.0351	0.0586

7.5.4. References

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[5] G. M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3-8.

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Preface

The following chapter has not been published until submission of this thesis.

Authors

Maria Haimerl, Christoph Schwarzmaier, Alexey Timoshkin, Guy Bertrand and Manfred Scheer*

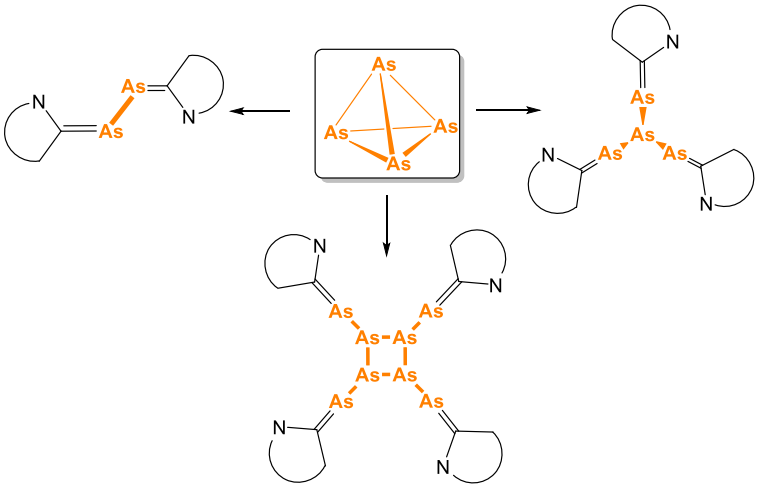
Author contribution

The main part of the manuscript was done by the first author (M. Haimerl). C. Schwarzmaier described the synthesis and characterization of compound **2** and **3** already in his PhD thesis. The synthesis and characterization of compound **1**, **4**, **5**, **6** and **7** were done by M. Haimerl. A. Timoshkin performed the DFT calculations and contributed the corresponding parts in the paper and in the Supporting Information. Samples for CV were prepared by the first author and measured with help of M. Weber. The group of G. Bertrand prepared CAAC-1 and CAAC-2. M. Scheer supervised the research and revised the manuscript.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft within the project Sch 384/40-1.

The nomenclature of the products of this chapter are adopted according to inorganic complexes to ensure clarity.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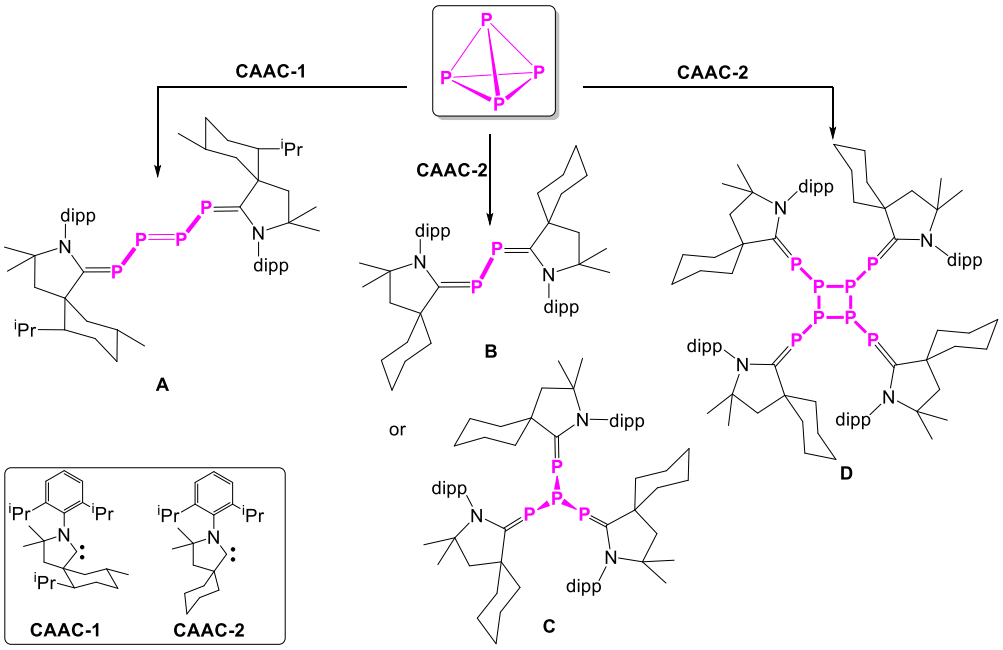
8. Reactivity of yellow arsenic towards Cyclic Alkyl Amino Carbenes (CAACs)

Abstract: *Different cyclic alkyl amino carbenes (CAACs) were reacted with yellow arsenic yielding the compounds [(CAAC-n)$_2$(μ,$\eta^{1:1}$-As$_2$)] (n = 1 (**1**), 4 (**2**)), [(CAAC-2)$_3$(μ_3,$\eta^{1:1:1}$-As$_4$)] (**3**) and [(CAAC-3)$_4$(μ_4,$\eta^{1:1:1:1}$-As$_8$)] (**6**) in dependence of the substituents. The products contain an As$_2$, As$_4$ or As$_8$ unit and represent the first examples of the reactivity of yellow arsenic towards CAACs. During our investigation also some phosphorus derivatives ([(CAAC-3)$_3$(μ_3,$\eta^{1:1:1}$-P$_4$)] (**4**) and [(CAAC-3)$_4$(μ_4,$\eta^{1:1:1:1}$-P$_8$)] (**7**)) and the interpnictogen compound [(CAAC-3)$_3$(μ_3,$\eta^{1:1:1}$-AsP$_3$)] (**5**) could be synthesized. The products were characterized by spectroscopic and crystallographic methods and DFT computations were performed to clarify the formation pathway of the products.*

8.1. Introduction

Since their discovery in 2005, the use of cyclic alkyl amino carbenes (CAACs) gained increasing attention and popularity.[1] They are the most nucleophilic and electrophilic stable carbenes known to date.[2] Their versatile applications in different research objectives ranges from coordination chemistry, transition metal catalysis to the activation of small molecules like H_2,[3] NH_3,[3] CO,[4] and most interestingly P_4.[5] Among others CAACs have the potential to activate, aggregate and fragmentate white phosphorus. In 2007, *Bertrand et al.* reported the first example of a 2,3,4,5-tetraphosphatriene derivative (**A**), stabilized by two menthyl substituted CAACs (**CAAC-1**) (Scheme 8.1).[6] The reaction of the less steric protected cyclohexyl-substituted CAAC (**CAAC-2**, Scheme 8.1) with P_4 leads depending on the reaction conditions to three different products: the P_2-dicarbene adduct (**B**),[5a] an isotetraphosphine adduct stabilized by three CAAC molecules (**C**)[5a] or the P_8 tetracarbene compound (**D**)[5b] (Scheme 8.1). For **D**, *Bertrand et al.* postulated a dimerization reaction of two molecules of type **A**. While the reactivity of white phosphorus towards transition metal and main group compounds was extensively studied,[7] the research about the conversion of yellow arsenic is limited by toxicity, impossibility to carry out stoichiometric reactions, light- and air-sensitivity of yellow arsenic. While there are several studies of the conversion of yellow arsenic with transition metal compounds containing e.g. Cp^R or nacnac ligands,[8] there are only few examples known with main group compounds.[8-9] Arsenic-arsenic bonds are weaker than phosphorus-phosphorus bonds, which results in less stable intermediates. In the case of yellow arsenic, most likely only the thermodynamically most stable compounds are formed, but there are a few examples of transient species which could be characterized.[9a] Interestingly, there are only few studies known in which the reactivity of white phosphorus and yellow arsenic is compared and different products could be realized.[9c,10] For example, the reaction of E_4 (E = P, As) with silylene [PhC(N*t*Bu)$_2$SiN(SiMe$_3$)$_2$)] and disilenen [(Me$_3$Si)$_2$NCp*Si=SiCp*N(SiMe$_3$)$_2$)] (Cp* = C_5Me_5) leads to very different compounds in the case of phosphorus and arsenic, respectively.[9c,10c]



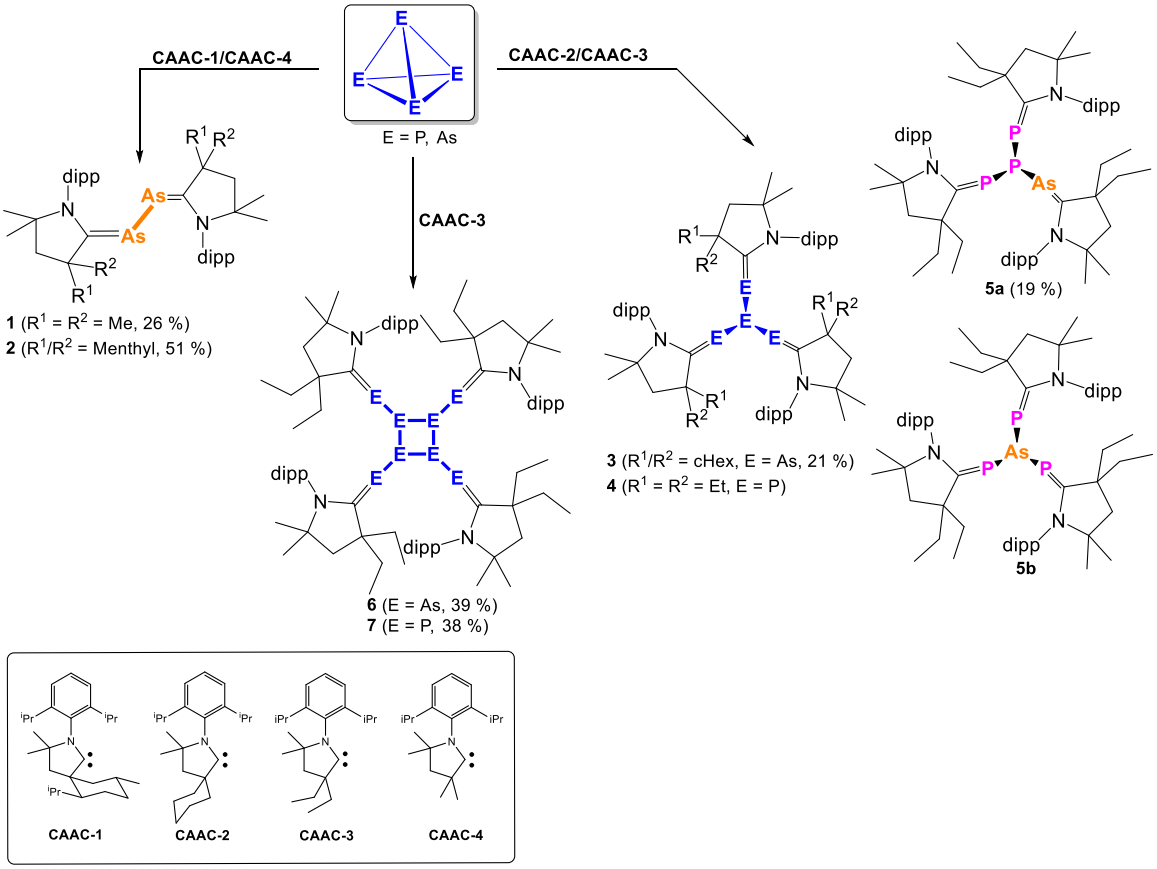
Scheme 8.1. Conversion of white phosphorus by different CAAC's.

Based on the known reaction behavior of CAACs with white phosphorus, the question arose if CAACs can also induce the conversion, aggregation, and fragmentation of yellow arsenic as well as what similarities or differences can be found between the reactivities of P_4 and As_4.

Interestingly, there have been efforts to find other ways to prepare arsenic containing compounds stabilized by CAACs. *Hudnall et al.* synthesized the dicarbene substituted diarsenic compound $[(CAAC\text{-}3)_2(\mu,\eta^{1:1}\text{-}As_2)]$ (**E**) by reacting CAAC-3 with $AsCl_3$ and subsequent reduction.[11] There is also one example with the heavier analogue antimony which is isostructural to $[(CAAC\text{-}n)_2E_2]$ (E = P (**B**), n = 2; As (**E**), n = 3).[12] This compound was synthesized by the stepwise reduction of $[(CAAC\text{-}2)SbCl_3]$ with potassium graphite. In contrast to yellow arsenic, the binary interpnictogen compound AsP_3[13] is stable, isolobal and similar to handle as P_4. This compound might close the gap between white phosphorus and yellow arsenic and in principle the reaction behavior of phosphorus and arsenic could be investigated at the same time. With such tools in hand, it is possible to monitor the formation of products by ^{31}P NMR spectroscopy, which is not possible at all for yellow arsenic. To note, there are only few examples reported of the conversion of AsP_3 with main group and transition metal compounds.[14] Herein, we present a comparative experimental and computational study of As_4 conversion by different CAAC's (**CAAC-1** – **CAAC-4**, Scheme 8.2) which results in a series of products. During our investigations we were able to synthesize and also characterize some new phosphorus products and an interpnictogen compound by the reaction of CAAC-3 with P_4 and AsP_3, respectively.

8.2. Results and Discussion

The reaction of **CAAC-1**, **CAAC-2**, **CAAC-3** and **CAAC-4** with an excess of yellow arsenic in toluene at room temperature leads to the formation of the 2,3-diarsabutadiene-derivate [(CAAC-4)$_2$(μ,η$^{1:1}$-As$_2$)] (**1**) and [(CAAC-1)$_2$(μ,η$^{1:1}$-As$_2$)] (**2**), the isotetraarsan adduct stabilized by three CAAC molecules (**3**) and [(CAAC-3)$_4$(μ$_4$,η$^{1:1:1:1}$- As$_8$)] (**6**) (Scheme 8.2). The products can be obtained as air, moisture and light sensitive yellow to red solids in crystalline yields of 26 % (**1**), 51 % (**2**), 21 % (**3**), 39 % (**6**), respectively (Scheme 8.2). Changing the reaction conditions (e.g. temperature) leads to the same products. By reacting **CAAC-3** with P$_4$ the isotetraphosphine adduct [(CAAC-3)$_3$(μ$_3$,η$^{1:1:1}$-P$_4$)] (**4**) and the P$_8$ tetracarbene [(CAAC-3)$_4$(μ$_4$,η$^{1:1:1:1}$-P$_8$)] (**7**) (Scheme 8.2) are obtained, **7** was isolated in crystalline yields of 38 %. Furthermore, we investigated also the reactivity of AsP$_3$ towards **CAAC-3**, which leads to [(CAAC-3)$_3$(μ$_3$,η$^{1:1:1}$-AsP$_3$)] (**5**) as yellow air sensitive solid in crystalline yields of 19 % (Scheme 8.2).

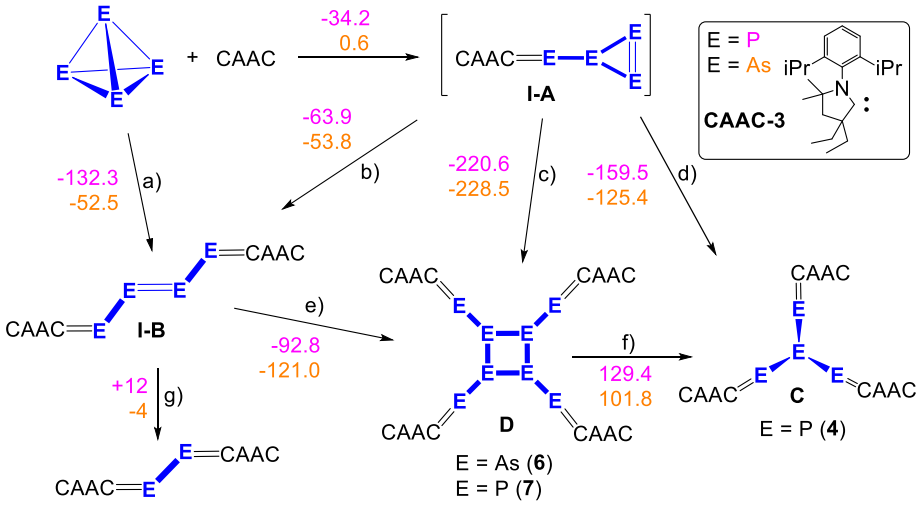


Scheme 8.2. Conversion of E$_4$ (E$_4$ = P$_4$, As$_4$, AsP$_3$) by different CAAC's (dipp = 2,6-diisopropylphenyl).

While the reaction of **CAAC-1** with P$_4$ leads to the formation of a carbene stabilized P$_4$ chain (**A**, Scheme 8.1), the reaction with yellow arsenic results in a carbene stabilized As$_2$ unit (**2**, Scheme 8.2). In order to clarify the difference in the reactivity, DFT computations at the B3LYP/def2-SVP level of theory were carried out (see SI for details). The formation

of *trans* isomers of compounds **A**, featuring an E_4 chain, is *exergonic* in solution by 81 and 3 kJ mol^{-1} for P and As, respectively. However, subsequent fragmentation of [(CAAC-1)$_2$E$_4$] (**I-B**, Scheme 8.3) to [(CAAC-1)$_2$E$_2$] and ½ E_4 is *endergonic* by 12 kJ mol^{-1} for P, but *exergonic* by 4 kJ mol^{-1} for As. Thus, the P_4 chain and the As_2 unit are thermodynamically the most favorable products.

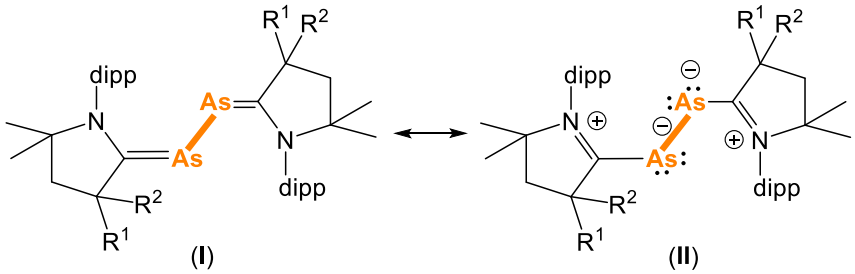
Via trapping reactions *Bertrand et al.* have shown that as an intermediate by the reaction of CAAC with P_4 an unstable monocarbene adduct **I-A** (Scheme 8.3) is formed.[5b] The formation of this intermediate and the following products (Scheme 8.3) were also computationally studied for **CAAC-2** and **CAAC-3** (Scheme 8.3). Experimentally, the reaction of **CAAC-2** with P_4 leads to the formation of **B**, **C** and **D** (Scheme 8.1), starting with **CAAC-3** compound **4** and **7** could be obtained. The formation of **3** and **6** by the reaction of yellow arsenic with CAAC-3 is independent of the stoichiometry. In the case of arsenic the formation of other products during the reaction can not be precluded but is hard to monitor this due to the poor NMR features of arsenic compounds. For the formation of **6** and **7** two different reaction pathways are proposed (Scheme 8.3). The first one includes the formation of **I-B** intermediate which is exergonic both for P and As (Scheme 8.3). Subsequent dimerization of two molecules of **I-B** to **6** and **7** is also exergonic by 93 and 121 kJ mol^{-1}, respectively. The second pathway includes formation of **I-A** as the first step and afterwards a direct formation of **6** and **7** or an indirect route via **I-B** (Scheme 8.3). By changing the stoichiometry, it was also possible to synthesize **4**, but not its arsenic analog [(CAAC-3)$_3$As$_4$]. Formation of [(CAAC-3)$_3$E$_4$] is expected to proceed via **I-A** intermediate. Since **I-A** formation for As is slightly *endergonic*, this reaction pathway would be less favorable than formation of **6** via **I-B** intermediate. This could explain the sole formation of **6** in case of the reaction with As_4.



Scheme 8.3. Standard Gibbs energies for the suggested reaction pathways ($\Delta G°_{298}$ values are in kJ mol^{-1} for **CAAC-3**, values for **CAAC-2** see SI). a) + 2 CAAC; b) 2x **I-A**, - P_4; c) 4x **I-A**, -2 P_4; d) + 2 CAAC; e) 2x **I-B**; f) for the reaction **D** = **C** + **I-A**; g) values for **CAAC-1**, -1/2 E_4.

In the ^{1}H NMR spectra of compounds **1**, **6** and **7** a set of signals for one CAAC unit is shown. The $^{31}P\{^{1}H\}$ NMR spectrum of **4** in C_6D_6 at room temperature reveals a doublet at δ = 69.9 ppm ($^{1}J_{PP}$ = 236 Hz) and a quartet at δ = -57.6 ppm ($^{1}J_{PP}$ = 236 Hz), this matching the expected signals in comparison to **C**. In the case of **5** there are two isomers visible in the $^{31}P\{^{1}H\}$ NMR spectrum this indicating a different chemical and magnetic environment which can be explained by the position of the arsenic atom. Which isomer is formed depends on the successive bond cleavage of the AsP_3 tetrahedron. The bond cleavage of an As-P bond in AsP_3 is 6 kJ · mol^{-1} less energy demanding than a P-P bond cleavage.[14d] Two As-P and one P-P bond cleavage lead to the formation of the major isomer **5a**, with the carbene coordinated arsenic atom (Scheme 8.2). Three P-P bond cleavages of the AsP_3 tetrahedron lead to the minor isomer **5b** where the arsenic atom is in the middle of the E_4 unit (Scheme 8.2). In the $^{31}P\{^{1}H\}$ NMR spectrum of **5**, a doublet at δ = 65.4 ppm and a triplet at δ = -58.9 ppm ($^{1}J_{PP}$ = 242 Hz) in an integral ratio of 2:1 for the major isomer **5a** and a singlet at δ = 74.18 ppm for the minor isomer **5b** can be detected (there are also the signals for **4** visible). Furthermore, the $^{31}P\{^{1}H\}$ NMR spectrum of **7** shows two multiplets at δ = 52.7 ppm and -54.9 ppm (comparable to **D**). In the LIFDI-MS spectra of **1**, **2**, **5** and **7**, respectively, the molecular ion peak is detected. Compound **3** is visible in traces in the LIFDI-MS spectrum and for **6** the LIFDI-MS spectrum show different fragments of ((CAAC-3)$_3As_7$), (CAAC-3)$_2As_n$) (n = 2, 3, 5)) but not the molecular ion peak, this shows the high sensitivity of arsenic containing compounds.

For **2** cyclic voltammetry measurements in thf were performed. It reveals a first reversible oxidation at -658 mV and a second irreversible oxidation at -350 mV (against $[Cp_2Fe]/[Cp_2Fe]^{+}$). Compared to the corresponding phosphorus analogues of **2** - **B** shows a reversible oxidation at - 536 mV and a second irreversible oxidation at 20 mV.[15] **2** is easier oxidized. This could be explained by the resonance form of **2** shown in Scheme 8.4. Due to the smaller tendency to form double bonds for arsenic the canonical form (I) might be less important than form (II), which contain an electron rich As_2 unit.



Scheme 8.4. Canonical forms of 2,3diarsabutadiene (I) and a charge separated diarsanediid (II).

The molecular structures of **1** and **2** reveal a central As_2 unit binding in an $\eta^{1:1}$ fashion to two CAAC fragments (Figure 8.1). The C2-As1-As2-C21/C28 dihedral angle is 175.6(1)° (**1**) and 165.7(1)° (**2**), respectively. Furthermore, the carbene carbon atoms reveal a typical planar geometry for the sp^2 hybridized carbon atoms (sum of angles; **1:** 360° for C1 and C21; **2**: 359.8° for C1 and 359.9° for C28). For **1** the diisopropylphenyl groups of the CAAC group are pointing away from the As_2 unit and in **2** they are pointing towards the As_2 unit. An explanation for this could be the steric effect of the bulky menthyl group which is larger than the steric effect of the diisopropylphenyl groups in **2** (buried volume for **CAAC-1**: 77.4 %, for **CAAC-4**: 71.9 %)[16]. The As1-As2 bond distance amounts to 2.4175(2) Å (**1**) and 2.4423(4) (**2**) Å, respectively, which is in the typical range of an As-As single bond (determined by electron diffraction:[17] 2.435(4) Å, by DFT computations:[18] 2.437 Å, by the sum of covalent radii:[19] 2.42 Å). The C-As bond distances are between a single[19] and a double bond[20] (**1**: 1.8520(14) and 1.8528(14) Å; **2**: 1.856(3) and 1.859(3) Å). The C1-N1 and C21/C28-N2 bond distances with 1.3645(17) Å and 1.3621(17) Å for compound **1**, 1.371(4) Å and 1.364(4) Å for compound **2**, respectively, are slightly shorter than the corresponding C-N bond distances in **B** (1.387(9) Å).[5a]

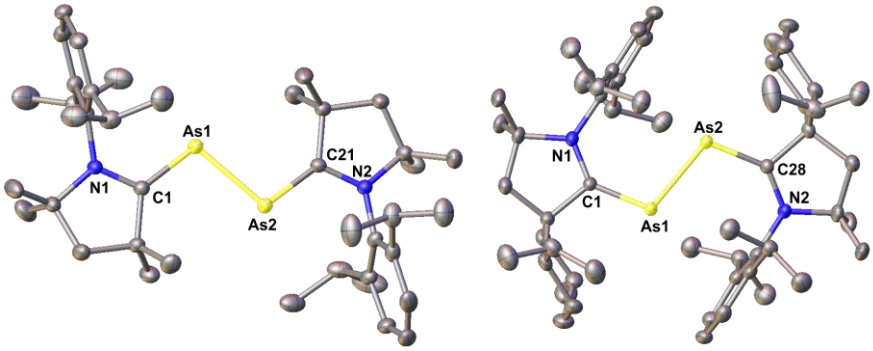


Figure 8.1. Molecular structure of **1** (left) and **2** (right) in the solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms are omitted for clarity.

The molecular structures of **3** and **5** reveal an iso-tetra-polypnictogen unit (E = As (**3**), AsP_3 (**5**)) that is stabilized by three CAAC substituents (Figure 8.2). The arsenic atom in **5** is disordered over all four pnictogen positions. The major isomer **5a**, with the carbene coordinated arsenic atom and the minor isomer **5b**, with the arsenic atom at position E4, are in a ratio of 79:5 (16 % corresponds to compound **4**) in the solid state (Scheme 8.2). DFT computations indicate, that in the gas phase the standard Gibbs energy for the equilibrium **5a** to **5b** is exergonic by 22.1 kJ mol^{-1}, indicating that isomer **5b** is the thermodynamically stable product (see SI). The higher amount of **5a** in the experiment is due to kinetic reasons. Reaction of **CAAC-3** with AsP_3 forming **I-A** via P atom is by 24.6 kJ mol^{-1} more exergonic than via As atom. The P-As bond breaking in the (CAAC-3)$PAsP_2$ intermediate is expected to proceed easier, than P-P bond breaking, resulting in **5a** rather than in **5b**. Formation of **4** upon reaction with AsP_3 can be explained by the thermodynamic favorability of the disproportionation of AsP_3: 4 AsP_3 = 3 P_4 + As_4 (computed gas phase

$\Delta G°_{298}$ = -13.6 kJ mol^{-1}). The formed As_4 can isomerize into unreactive grey arsenic and leave the reaction.

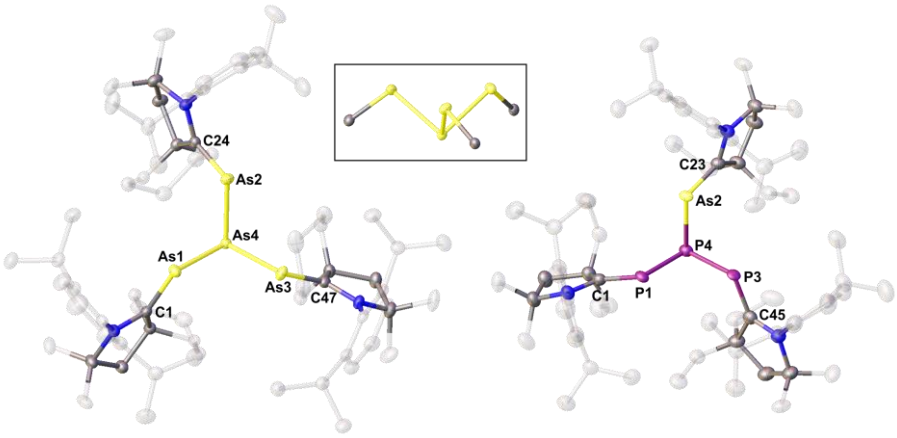


Figure 8.2. Molecular structure of **3** (left) and **5a** (right, one isomer of 5) in the solid state, side view E_4 unit (box). Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

Table 8.1. Occupation of the phosphorus and arsenic positions of compound **5**.

Atom	1	2	3	4
P	70	76	75	95
As	30	24	25	5

The angles around the central atom E4 are in the range of 89.28(1)° to 92.24(1)° for **3**, 86.81(1)° to 92.88(1)° for **5a** and 86.54(1)° to 86.99(1)° for **5b**. In comparison to **C** which has all three angles at 90.15(2)°, **3** and **5** show more deviation of the perfect local C_{3v} symmetry. In both structures the diisopropylphenyl groups of the CAAC substituents point away from the central atom E4 and the CAAC fragments itself are bent counter clockwise in the case of **3** and clockwise in the case of **5** (**C**: clockwise). In the case of arsenic the CAAC fragments are bent in the other direction than in the case of phosphorus. Interestingly, the mixed interpnictogen compound **5** has the same orientation of the CAAC units like the phosphorus analogue **C**. The As-As bond distances of **3** are between 2.4479(2) and 2.4520(2) Å which is in the range of an arsenic single bond.[19] The E-E bond distances of **5** are in the range of normal single bonds (P-P: 2.212(10) to 2.263(8) Å, P-As: 2.289(11) to 2.40(4) Å). The C-E bond distances are between a single and a double bond (**3**: 1.862(2) to 1.866(2) Å; **5**: C-P: 1.714(8) to 1.748(10) Å, C-As: 1.856(9) to 1.891(10) Å).

The molecular structures of **6** and **7** reveal a tetra(carbene)E_8 cage compound (E = As (**6**), P (**7**)), which contain a four membered E_4 ring where each pnictogen atom is connected to a further pnictogen atom and stabilized by four CAAC fragments.

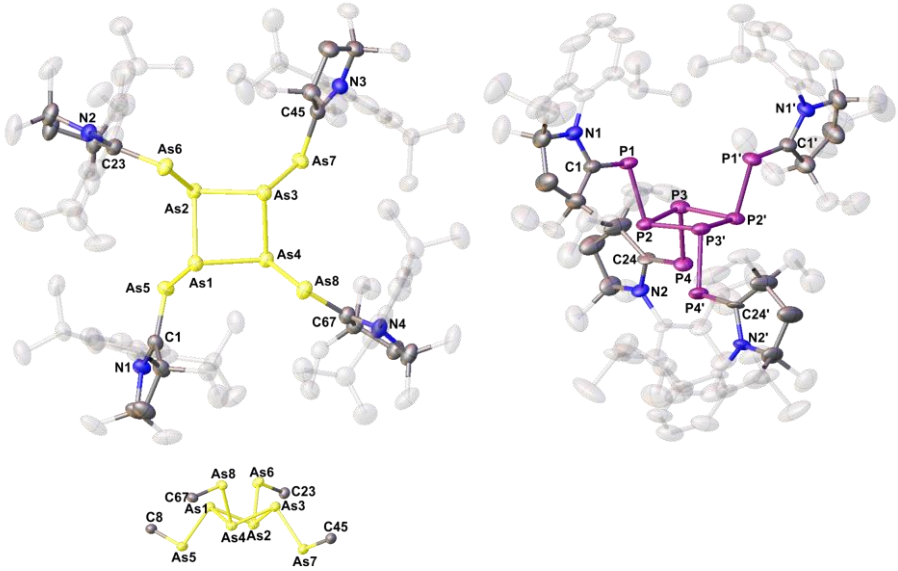


Figure 8.3. Molecular structure of **6** (left) and **7** (right) in the solid state (bottom: side view of the As_8 unit). Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms are omitted for clarity.

For the phosphorus compound **7**, the P_4 cycle is nearly planar (torsion angle: 171.8°) and almost right angles (P2-P3-P2' 89.70(3)° and P3-P2-P3' 90.01(3)°), this is in contrast to the already known compound **D**, which has the same structural P_8 motif but the P_4 cycle is folded by 47.90°. Compound **6** shows a similar structural E_8 motif as **D**, the As_4 cycle is folded 55.54° (As1-As2-As3 plane: As2-As3-As4 plane). The diisopropylphenyl groups of both compounds point away from the E_8 unit. The E-E-C angels are very similar for both compounds (**6**: 102.71(9) - 104.05(10)°; **7**: 101.01(4)/104.66(7)°). So the main difference here is the inner E_4 cycle. The E-E bond distances in the *cyclo*-E_4 unit are between 2.4538(5) and 2.4741(5) Å (**6**), 2.2335(8) and 2.2354(8) Å (**7**), respectively. This represents elongated single bonds. The other E-E bond distances are in the range of normal single bonds (**6**: between 2.4237(5) and 2.4334(5) Å, **7**: 2.1975(7) and 2.1987(7) Å). The C-E bond distances for **6** (between 1.862(3) and 1.864(3) Å) and **7** (1.731(2), 1.797(13) Å) are also between a single and a double bond.

8.3. Conclusion

In summary, we have demonstrated that the reaction of yellow arsenic with CAACs leads to the aggregation, fragmentation and rearrangement of As_4. By the reaction of different CAACs with As_4 the compounds $[(CAAC\text{-}4)_2(\mu,\eta^{1:1}\text{-}As_2)]$ (**1**), $[(CAAC\text{-}1)_2(\mu,\eta^{1:1}\text{-}As_2)]$ (**2**), $[(CAAC\text{-}2)_3(\mu_3,\eta^{1:1:1}\text{-}As_4)]$ (**3**) and $[(CAAC\text{-}3)_4(\mu_4,\eta^{1:1:1:1}\text{-}As_8)]$ (**6**) could be obtained. The products represent the first examples of the reactivity of yellow arsenic towards CAACs. By the activation of yellow arsenic with CAACs only the thermodynamically most stable compound could be obtained. The compounds are less stable than their phosphorus derivatives, which also affect the yields. DFT computations are in qualitative agreement with the experimental observations. Furthermore, the products $[(CAAC\text{-}3)_3(\mu_3,\eta^{1:1:1}\text{-}P_4)]$ (**4**), $[(CAAC\text{-}3)_4(\mu_4,\eta^{1:1:1:1}\text{-}P_8)]$ (**7**) and $[(CAAC\text{-}3)_3(\mu_3,\eta^{1:1:1}\text{-}AsP_3)]$ (**5**) were synthesized. The latest is the first example of the reactivity of AsP_3 towards CAACs. Moreover, the different reaction outcome and structural difference of the reactions with white phosphorus, yellow arsenic and the interpnictogen compound AsP_3 was treated.

8.4. References

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8.5. Supporting Information

8.5.1. Synthesis and Characterization

General Remarks

All manipulations were performed with rigorous exclusion of oxygen and moisture using standard Schlenk techniques on a dual manifold Schlenk line with Argon or N_2 inert gas or glove box filled with nitrogen containing a high-capacity recirculator (<0.1 ppm O_2). Traces of oxygen and moisture in the inert gas were removed by passing it through a drying column filled with Cu/$MgSO_4$ catalyst as well as, concentrated H_2SO_4 and orange gel, respectively.

All solvents were degassed and purified by standard procedures. All NMR spectra have been recorded using deuterated d_6-benzene or $CDCl_3$ that were dried (over Na/K or CaH_2), refluxed for three hours and then distilled under inert atmosphere.

Characterization methods

Mass spectrometry was performed using a Jeol AccuTOF GCX LIFDI mass spectrometer by the MS department of the University of Regensburg. The compounds were dissolved in the corresponding solvent in a glove box under N_2 atmosphere. The observed fragments were assigned according to the mass/charge (m/z) ratio and the corresponding isotope pattern. Elemental analysis (CHN) were performed by the department of central analyses of the University of Regensburg on a Vario micro cube and a MT5 micro scale device. The compounds were filled in tin capsules in a glove box under N_2 atmosphere.

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker Avance III HD 400 (^{1}H: 400.130 MHz, ^{13}C: 100.613 MHz, ^{31}P: 161.976 MHz) spectrometer at the NMR department of the University of Regensburg. The chemical shifts are reported in ppm relative to external TMS (^{1}H, ^{13}C) or 85 % H_3PO_4 (^{31}P). The chemical shifts δ are given in parts per million [ppm] and coupling constants J in [Hz].

Cyclic voltammetry measurements were performed in thf at 300 K in a three electrode setup, with a glassy carbon electrode (working electrode), an Ag-wire (pseudo-reference electrode) an a Pt (auxiliary electrode), in combination with a Methrom Autolab PGSTAT101 potentiostat. Bu_4NPF_6 (500 mg in 5 mL THF) was used as supporting electrolyte and all cyclic voltammograms are referenced against Cp_2Fe/Cp_2Fe^+ redox couple.

Starting Materials

[CAAC-n] (n = 1-4)

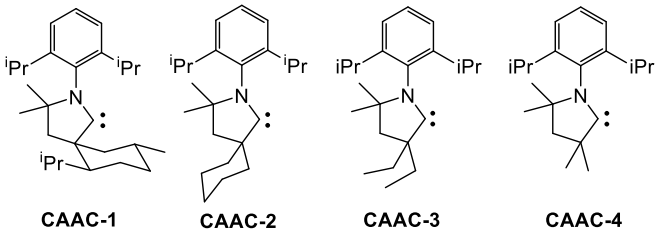

Figure S8.1. Used CAACs.

8.5.1.1. Synthesis of [(CAAC-4)$_2$(μ,η$^{1:1}$-As$_2$)] (**1**)

All preparations were performed *under exclusion of light.* **CAAC-4** (150 mg) in 15 mL toluene was added to a freshly prepared As_4 saturated toluene solution (250 mL) at room temperature. The colour of the reaction mixture turned immediately to red. The reaction mixture is stirred for 2 hours and the solvent was removed in vacuum. After dissolving the solid in 15-20 mL Et_2O the solution was filtered over diatomaceous earth to remove the insoluble As_{grey}. By storing the solution at + 4 °C, compound [(CAAC-4)$_2$(μ,η$^{1:1}$-As$_2$)] (**1**) crystallized as dark red blocks, suited for X-ray analysis.

Crystalline yield: 50 mg (0.07 mmol, 28 %)

^{1}H NMR ($CDCl_3$, 300 K): δ [ppm] = 7.34 (t, 2H, $^3J_{HH}$ = 7.7 Hz, C*H*$_{para}$), 7.19 (d, 4H, $^3J_{HH}$ = 7.7 Hz, C*H*$_{metha}$), 2.79 (m, 4H, dipp: C*H*(CH$_3$)$_2$), 2.07 (d, 4H, $^3J_{HH}$ = 3.7 Hz, C(C*H*$_2$CH$_3$)$_2$)), 1.65 (d, 12H, J_{HH} = 15.51 Hz, (C(*Me*)$_2$)), 1.45 (d, 6H, J_{HH} = 6.6 Hz, (C(*Me*)$_2$)), 1.29 (d, 6H, J_{HH} = 6.6 Hz, C(*Me*)$_2$), 1.20-1.25 (m, 24H).

LIFDI-MS (toluene): m/z (%) = 720.96 (12.96, [M]$^+$), 286.19 (100, [CAAC-H]).

8.5.1.2. Synthesis of [(CAAC-1)$_2$(μ,η$^{1:1}$-As$_2$)] (**2**)

All preparations were performed *under exclusion of light.* 280 mg (0.734 mmol) **CAAC-1** were dissolved in 20 mL toluene. A freshly prepared solution of As_4 in toluene (125 mL) was transferred to the solution. The pale green reaction mixture was stirred for 16 h, while the colour changed to bright yellow. The resulting solution shows thermochromic behaviour with a colour change from yellow to green upon cooling. The solvent was removed in vacuum to yield a bright yellow solid. After dissolving the solid in hexane, the solution was filtered over diatomaceous earth to remove the insoluble As_{grey} and again taken to dryness to remove last traces of toluene. The crude product is taken up in Et_2O (20 mL) and filtered from all insoluble by-products and concentrated. By storing the solution at 4 °C, compound **2** crystallized as yellow plates, suited for X-ray analysis.

Yield: 171 mg (0.187 mmol, 51 %)

Due to the highly complex nature of the CAAC ligands only partial assignments are made.

^{1}H NMR (C_6D_6, 300K): δ [ppm] = 0.80 – 1.40 (multiple signals), 3.15 (sept, $^{3}J_{HH}$ = 6.0 Hz, ^{i}Pr), 3.25 (sept, $^{3}J_{HH}$ = 6.3 Hz, ^{i}Pr), 3.64 (sept, $^{3}J_{HH}$ = 6.7 Hz, ^{i}Pr), 4.12 (sept, $^{3}J_{HH}$ = 6.8 Hz, ^{i}Pr), 7.16 (mult, H_{arom}).

FD-MS (toluene): m/z [%] = 912.4 (100) [M^{+}].

8.5.1.3. Synthesis of [(CAAC-2)$_3$(μ_3,$\eta^{1:1:1}$-As$_4$)] (**3**)

All preparations were performed *under exclusion of light.* 716 mg (0.734 mmol) **CAAC-2** were dissolved in 20 mL toluene. A freshly prepared solution of As_4 in toluene (250 mL) was transferred to the solution. The colourless reaction mixture was stirred for 16 h, while the colour changed to orange. The solvent was removed in vacuum to yield a bright yellow solid. After dissolving the solid in Et_2O, the solution was filtered over diatomaceous earth to remove the insoluble As_{grey} and again taken to dryness to remove last traces of toluene. The crude product is taken up in Et_2O (20 mL) and filtered from all insoluble by-products and concentrated. By storing the solution at -30 °C for 16h a brownish precipitate affords and was filtered off. Further concentration and storing at 4 °C afford **3** as yellow blocks, suited for X-Ray analysis.

Crystalline yield: 200 mg (0.16 mmol, 21 %)

^{1}H NMR (C_6D_6, 300 K): δ [ppm] = 1.09 (s, 18 H, -$(CH_3)_2$), 1.23 (d, 18 H, $^{3}J_{HH}$ = 7 Hz, ^{i}Pr), 1.41 (d, 18 H, $^{3}J_{HH}$ = 7 Hz, ^{i}Pr), 1.00 – 1.90 (m, ^{c}Hex), 1.97 (s, 6H, CH_2), 2.95 (sept., 6H, $^{3}J_{HH}$ = 7 Hz, ^{i}Pr), 3.34 (m, 6H, ^{c}Hex), 7.04 (s, 3H, H_{arom}), 7.06 (s, 3H, H_{arom}), 7.18 (s, 1H, H_{arom}), 7.19 (s, 1H, H_{arom}), 7.19 (s, 1H, H_{arom}).

LIFDI-MS (toluene): [m/z] (%) = 1275.4 (16) [M^{+}] (just in traces).

8.5.1.4. Synthesis of [(CAAC-3)$_3$(μ_3,$\eta^{1:1:1}$-P$_4$)] (**4**)

A solution of **CAAC-3** (20 mg, 4 eq) and P_4 (2 mg, 1 eq) were dissolved in 2 mL toluene at room temperature and stirred for 1 hour. The solvent was removed and the residue was taken up in C_6D_6.

^{31}P NMR (C_6D_6, 300 K): δ [ppm] = 67.4 (d, 3P, $^{1}J_{PP}$ = 237 Hz), -58.4 (q, 1P, $^{1}J_{PP}$ = 237 Hz)

8.5.1.5. Synthesis of [(CAAC-3)$_3$(μ$_3$,η$^{1:1:1}$-AsP$_3$)] (**5**)

CAAC-3 (40 mg, 1 eq) and AsP_3 (10mg, 0.5 eq) were dissolved in 1 mL of hexane and were stirred for 2 hours. The reaction mixture was filtered, concentrated and stored by + 4 °C. Compound [(CAAC-3)$_3$(μ$_3$,η$^{1:1:1}$-AsP$_3$)] (**5**) crystallized as dark red blocks, suited for X-ray analysis.

Crystallin Yield: 9 mg (0.008 mmol, 19 %)

^{1}H NMR (C_6D_6, 300 K): δ [ppm] = 7.19 (t, 2H, $^3J_{HH}$ = 8 Hz, C*H*$_{para}$), 7.08 (t, 4H, $^3J_{HH}$ = 8 Hz, C*H*$_{meta}$), 2.99 (m, 4H, dipp: C*H*(CH$_3$)$_2$), 2.28-2.64 (m, 8H, C(C*H*$_2$CH$_3$)$_2$), 1.32-1.39 (s, 12H, C(CH$_2$C*H*$_3$)$_2$), 1.21-1.28 (m, 24H, CH*MeMe'*), 1.06 (s, 12H, C(C*H*$_3$)$_2$), contaminated with CAAC-3.

^{31}P NMR (C_6D_6, 300 K): δ [ppm] = **5a**: 65.4 (d, 2P, $^2J_{PP}$ = 242.4 Hz), -58.9 (t, 1P, $^1J_{PP}$ = 243.3 Hz), **5b**: 74.2 (s, 0.15P (0.05 %)), **4**: 67.3 (d, 0.3P (0.1 %), $^2J_{PP}$ = 235 Hz), -57.7 (q, overlayered by **5a**).

LIFDI-MS (toluene): m/z (%) = 1107.58 (100, [M$^+$]), 763.36 (10.87, [$C_{44}H_{70}N_2P_2As$]$^+$), 719.41 (59.22, [$C_{44}H_{70}N_2P_3$]$^+$), 689.45 (, [$C_{44}H_{70}N_2P_2$]$^+$), 314.23 (14.61, [CAAC-3]$^+$).

8.5.1.6. Synthesis of [(CAAC-3)$_4$(μ$_4$,η$^{1:1:1:1}$-As$_8$)] (**6**)

All preparations were performed *under exclusion of light.* **CAAC-3** (200 mg) in 15 mL toluene was added to a freshly prepared As_4 saturated toluene solution (250 mL) at room temperature. The colour of the reaction mixture was turned immediately to orange. The reaction mixture was stirred over night and the solvent was removed in vacuum. After dissolving the solid in Et_2O the solution was filtered over diatomaceous earth to remove the insoluble As_{grey}. The orange solution was reduced to 5 mL. By storing the solution at + 4 °C, compound [(CAAC-3)$_4$(μ$_4$,η$^{1:1:1:1}$-As$_8$)] (**6**) crystallized as light orange needles, suited for X-ray analysis. Compound **6** crystallizes independently of the stoichiometry or reaction conditions.

Crystalline yield: 115 mg (39 %)

^{1}H NMR ($CDCl_3$, 300 K): δ [ppm] = 7.30 (t, 4H, C*H*$_{para}$), 7.17 (d, 8H, C*H*$_{metha}$), 2.86 (sept, 8H, dipp: C*H*(CH$_3$)$_2$), 2.15 (m, 8H, C(C*H*$_2$CH$_3$)$_2$), 1.94 (s, 8H, C*H*$_2$), 1.79 (m, 8H, C(C*H*$_2$CH$_3$)$_2$), 1.36 (d, 24H, CH*Me*Me')), 1.19 (d, 24H, CHMe*Me'*), 1.18 (s, 24H, C(C*H*$_3$)$_2$) 0.91 (t, 24H, C(CH$_2$C*H*$_3$)$_2$).

LIFDI-MS (toluene): m/z (%) = 314.27 (100, [CAAC-H]), 776.25 (4, [CAAC$_2$As$_2$]), 851.16 (3.9, [CAAC$_2$As$_3$]), 1000.96 ([CAAC$_2$As$_5$]), 1463.98 (3.2, [CAAC$_3$As$_7$]).

EA calculated for: $C_{88}H_{140}N_4As_8$: C: 57.03, H: 7.61, N: 3.02; found [%]: C: 57.38, H: 7.80, N: 2.79.

8.5.1.7. Synthesis of [(CAAC-3)$_4$(μ_4,$\eta^{1:1:1:1}$-P_8)] (**7**)

CAAC-3 (100 mg, 1 eq) in 5 ml ^{n}hexane was added to a stirred solution of P_4 (20 mg, 0.5 eq) in 5 mL ^{n}hexane at room temperature. The colour of the reaction mixture turned yellow. The reaction is stirred for 2 hours and then filtered over diatomaceous earth. The solvent is reduced to 3 mL. By storing the solution for four days at + 4 °C, compound [(CAAC-3)$_4$(μ_4,$\eta^{1:1:1:1}$-P_8)] (**7**) crystallized as clear yellow blocks, suited for X-ray analysis.

Crystalline yield: 45 mg (38 %, 0.3 mmol)

^{1}H NMR ($CDCl_3$, 300 K): δ [ppm] = 7.34 (t, 4H, C*H*$_{para}$), 7.17 (t, 8H, C*H*$_{metha}$), 2.83 (sept, 8H, dipp: C*H*(CH_3)$_2$), 2.13 (m, 8H, C(C*H*$_2$$CH_3$)$_2$), 1.91 (s, 8H, C*H*$_2$), 1.81 (m, 8H, C(C*H*$_2$$CH_3$)$_2$), 1.28 (d, 24H, CH*Me*Me')), 1.18 (d, 24H, CHMe*Me'*), 1.12 (s, 24H, C(C*H*$_3$)$_2$) 0.89 (t, 24H, C(CH_2C*H*$_3$)$_2$).

^{31}P{^{1}H} NMR ($CDCl_3$, 300 K): δ [ppm] = 59.3 (m, 4P), -55.93 (m, 4P).

LIFDI-MS (toluene): m/z (%) = 1500.95 (48.48, [M^+]), 781.41 (70.12, [$CAAC_2P_5$]), 719.45 (100, [$CAAC_2P_3$]).

8.5.2. NMR studies

8.5.2.1. [(CAAC-4)$_2$(μ,η$^{1:1}$-As$_2$)] (**1**)

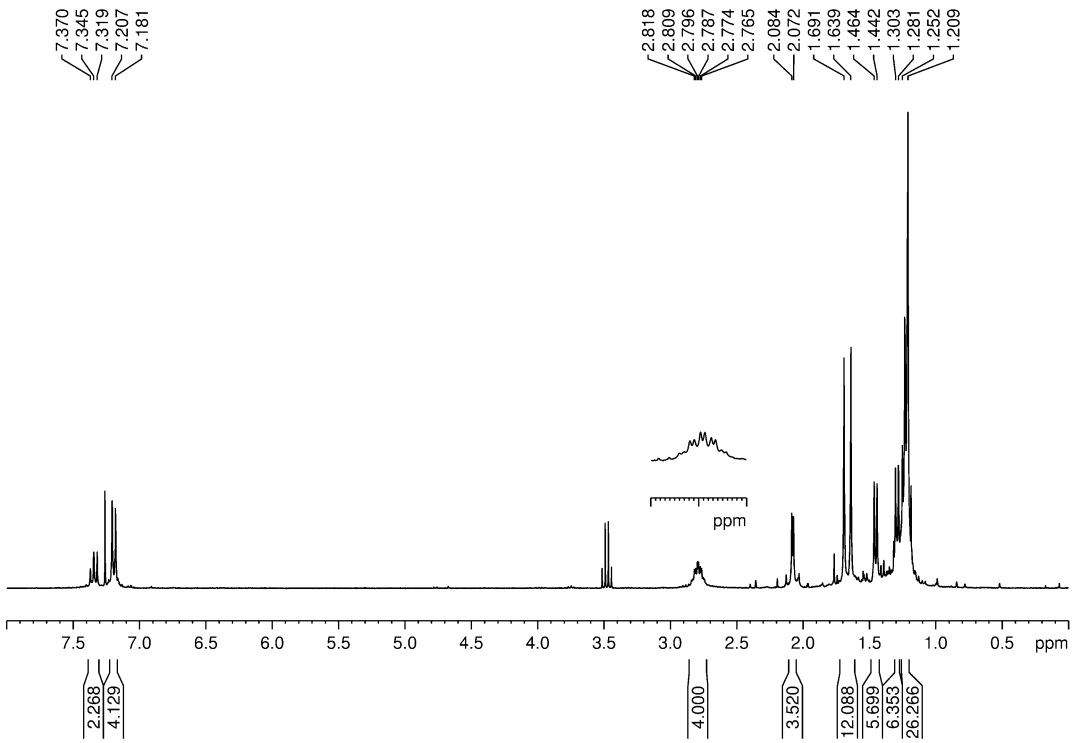

Figure S8.2. ^{1}H NMR spectrum of **1** in $CDCl_3$ at room temperature.

8.5.2.2. [(CAAC-1)$_2$(μ,η$^{1:1}$-As$_2$)] (**2**)

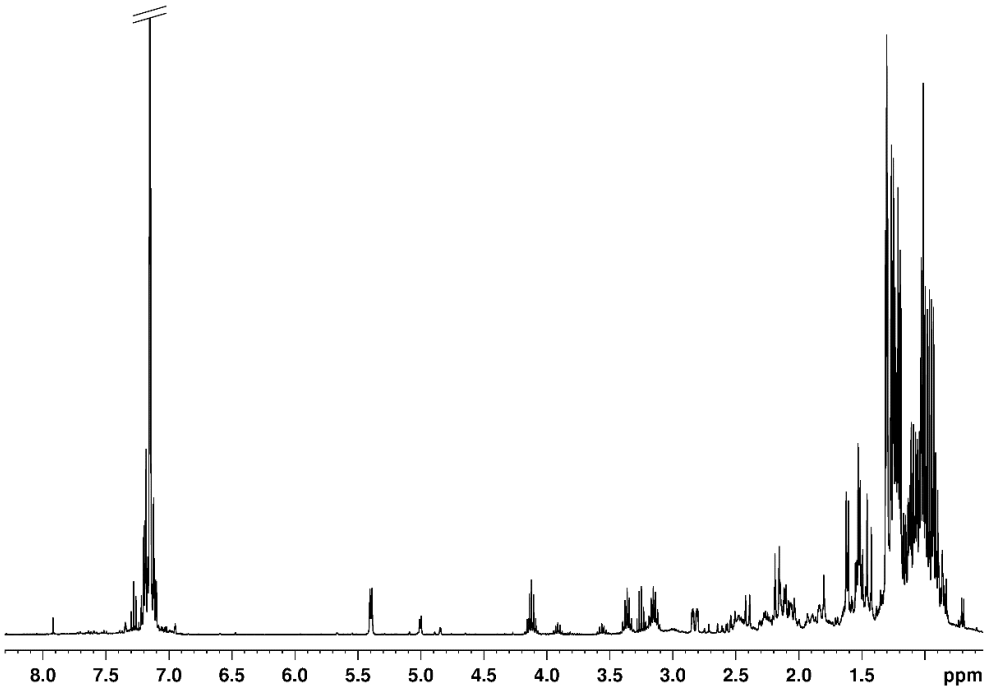

Figure S8.3. ^{1}H NMR spectrum of **2** in C_6D_6 at room temperature.

8.5.2.3. [(CAAC-2)$_2$(μ$_3$,η$^{1:1:1}$-As$_4$)] (**3**)

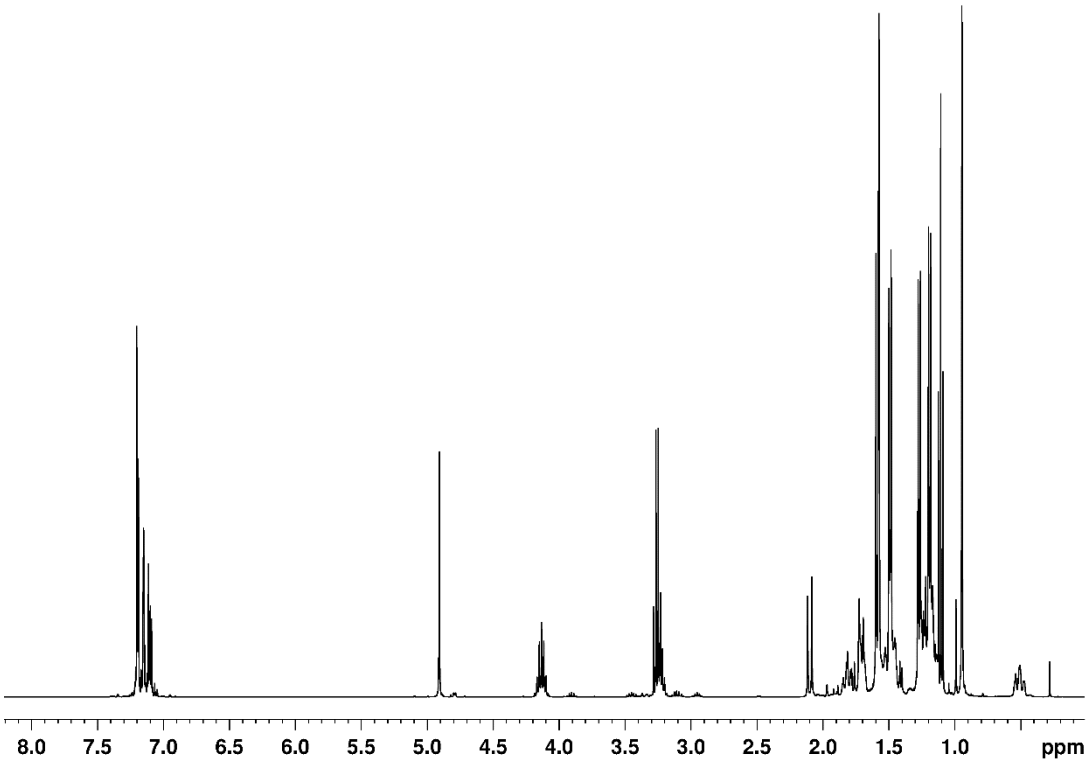

Figure S8.4. ^{1}H NMR spectra of **3** in C_6D_6 at room temperature.

8.5.2.4. [(CAAC-3)$_3$(μ$_3$,η$^{1:1:1}$-P$_4$)] (**4**)

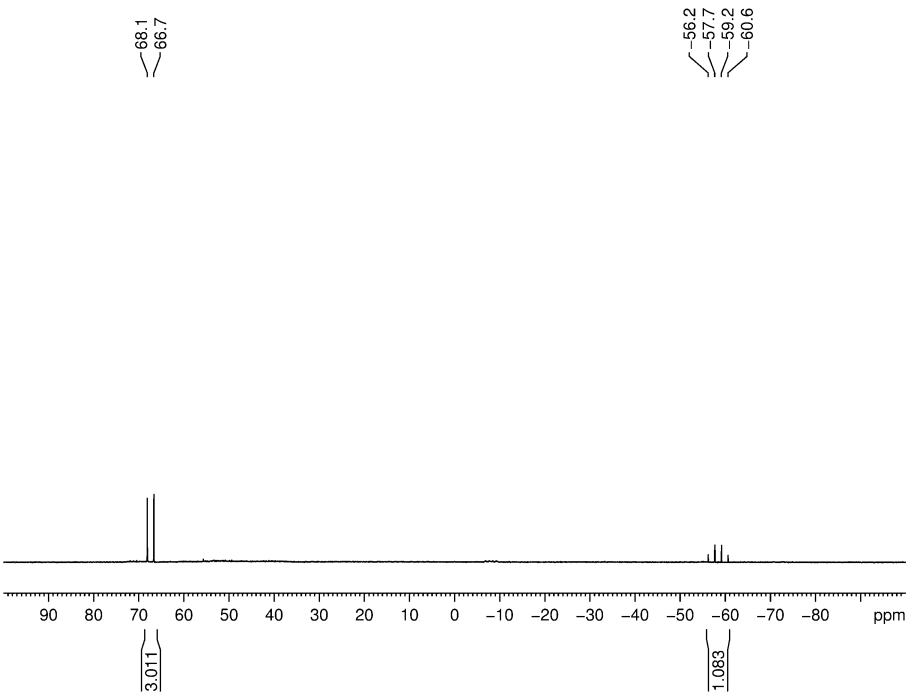

Figure S8.5. ^{31}P{^{1}H} NMR of compound **4** in C_6D_6 at room temperature.

8.5.2.5. [(CAAC-3)$_3$(μ_3,$\eta^{1:1:1}$-AsP$_3$)] (**5**)

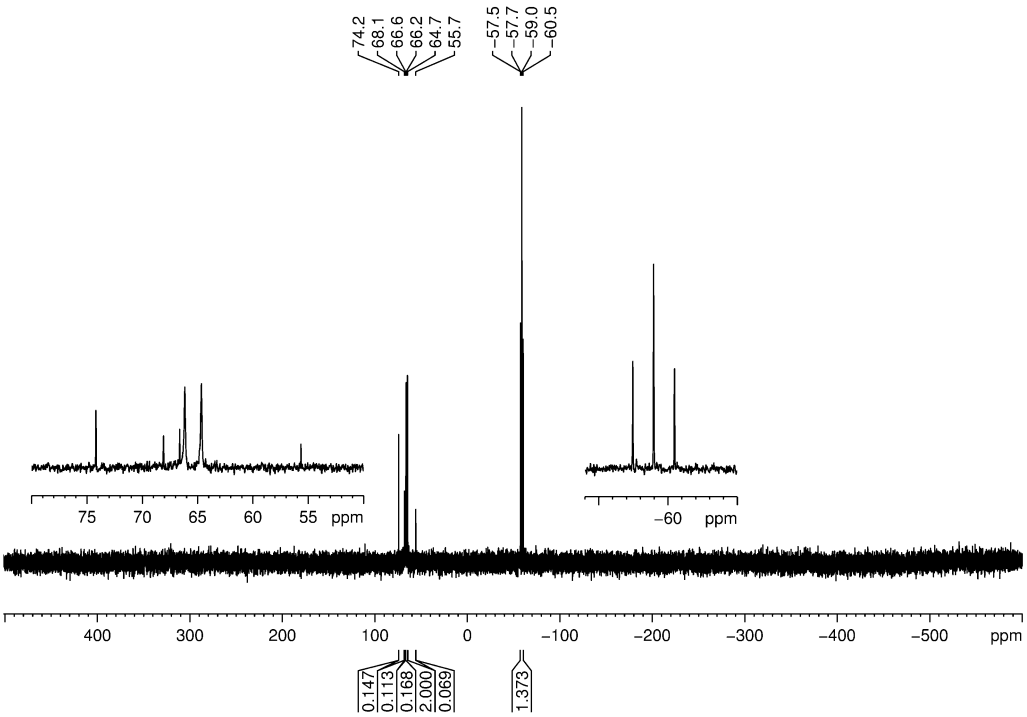

Figure S8.6. $^{31}P\{^1H\}$ NMR spectrum of **5** in C_6D_6 at room temperature.

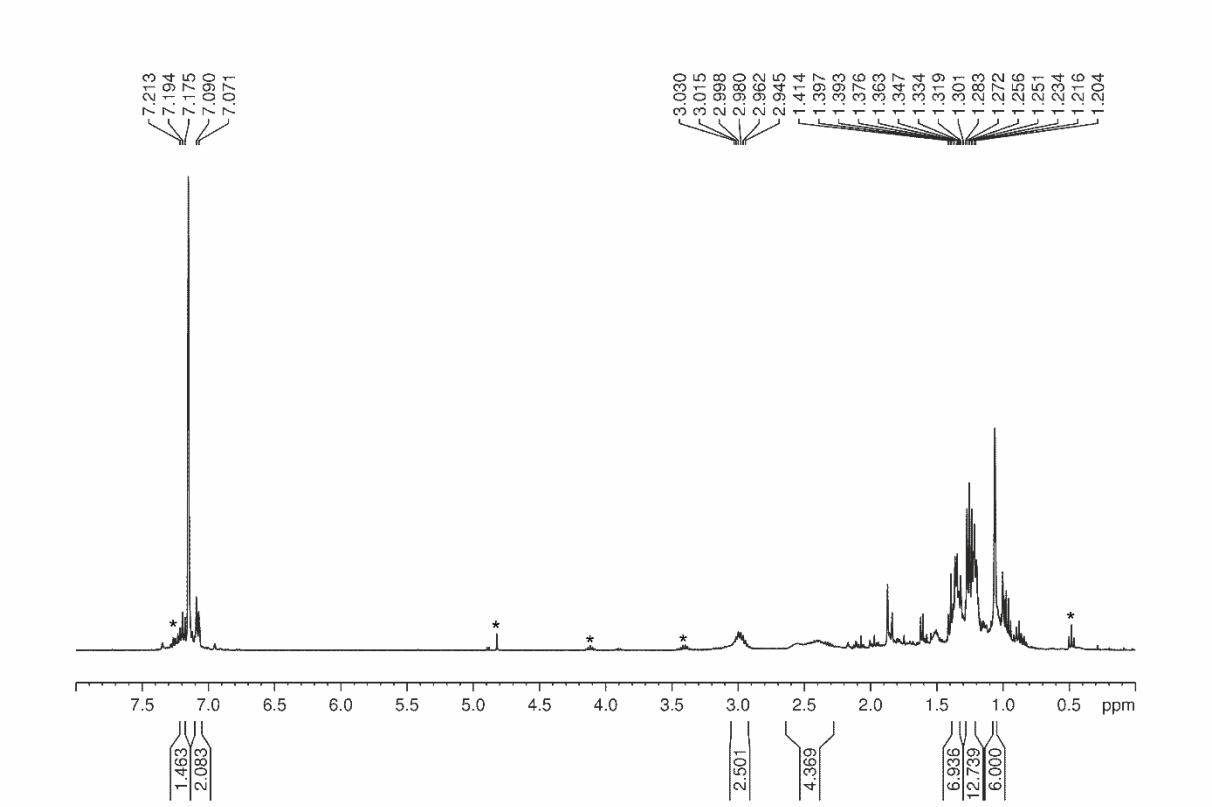

Figure S8.7. ^1H NMR spectrum of **5** in C_6D_6 at room temperature (* contamination with CAAC-3).

8.5.2.6. [(CAAC-3)$_4$(μ$_4$,η$^{1:1:1:1}$-As$_8$)] (**6**)

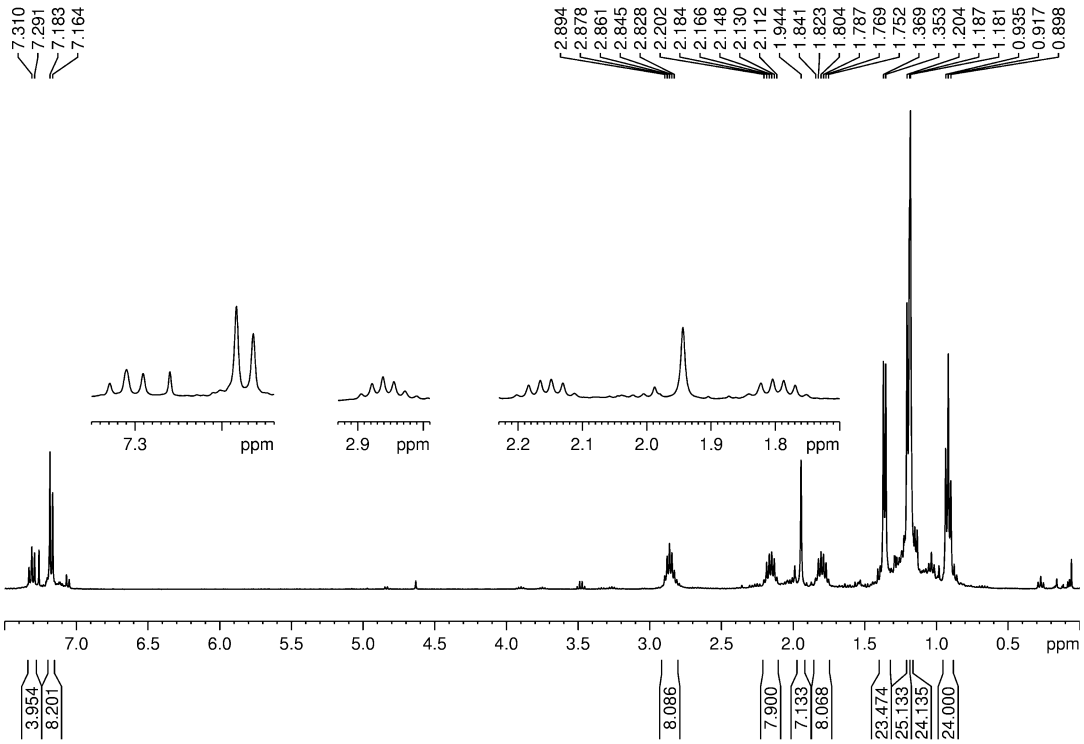

Figure S8.8. ^{1}H NMR spectrum of compound **6** in $CDCl_3$ at room temperature.

8.5.2.7. [(CAAC-3)$_4$(μ$_4$,η$^{1:1:1:1}$-P$_8$)] (**7**)

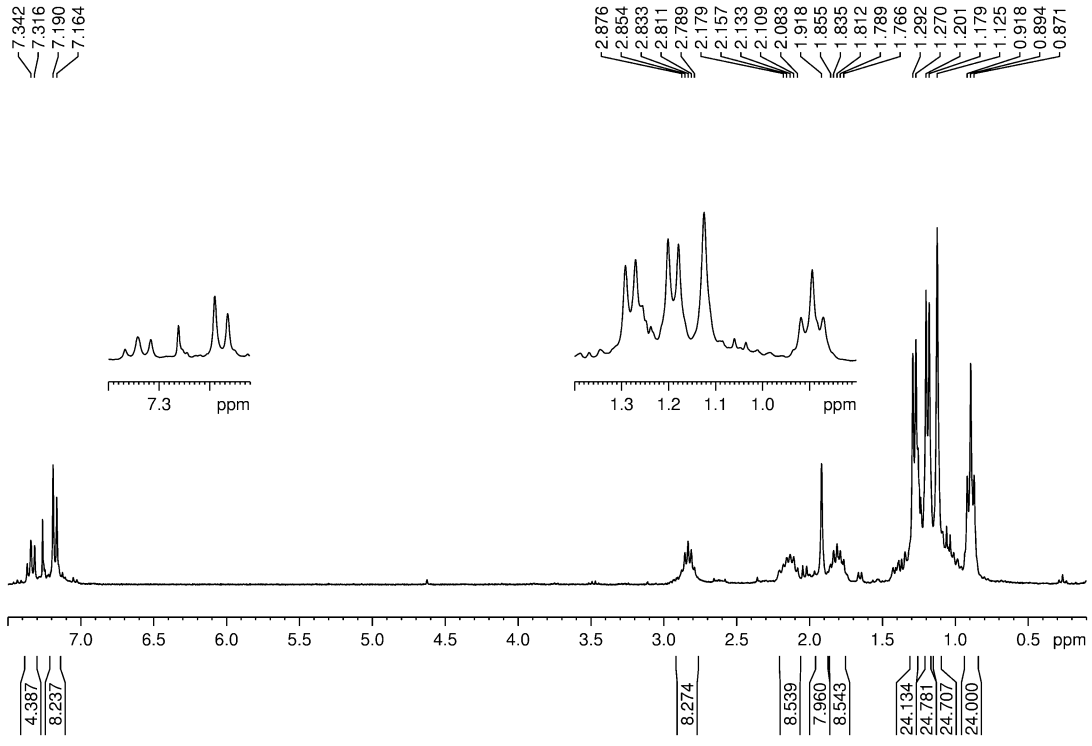

Figure S8.9. ^{1}H NMR spectrum of **7** in $CDCl_3$ at room temperature.

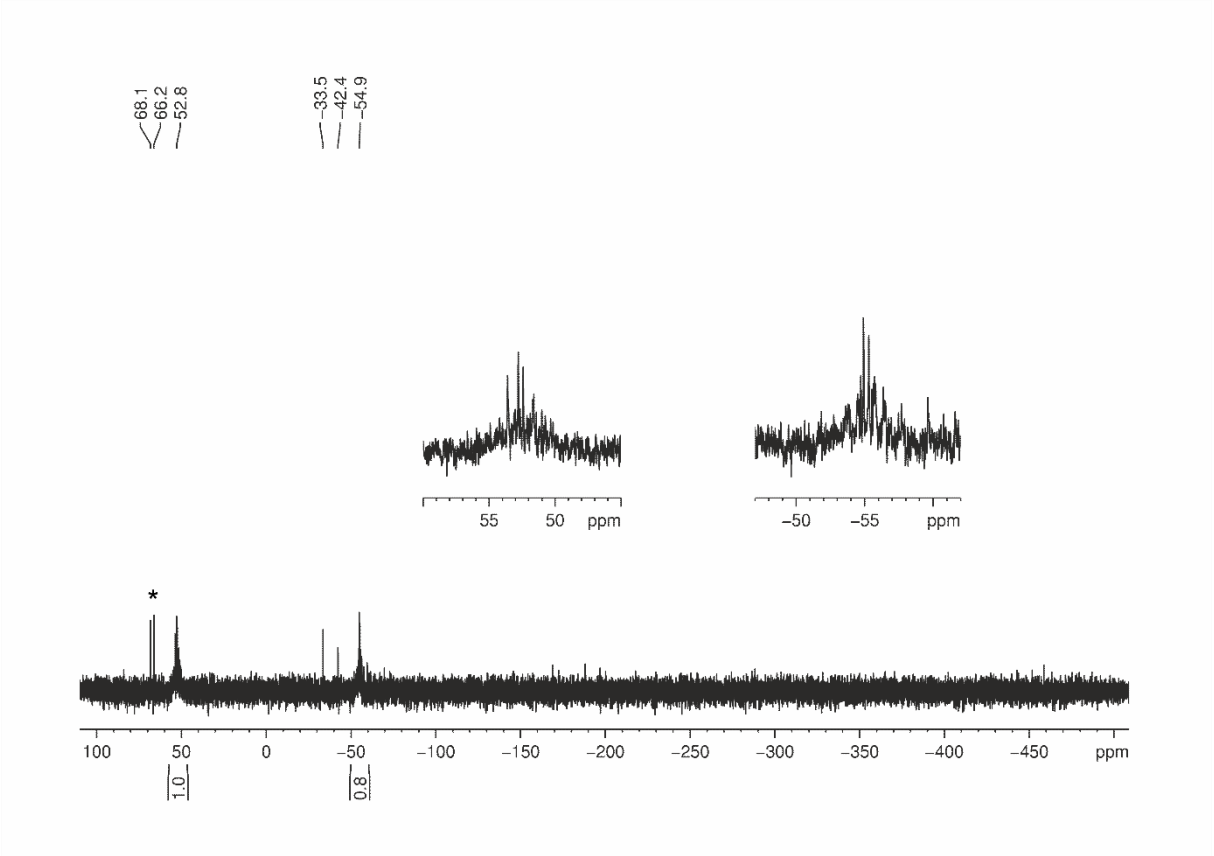

Figure S8.10. $^{31}P\{^{1}H\}$ NMR spectrum of **7** in C_6D_6 at room temperature (*contaminated with **4**).

8.5.3. Details on single crystal X-ray structure analysis

The X-ray diffraction experiments were performed on either a Gemini Ultra diffractometer (Oxford diffraction) with an AtlasS2 detector Cu-K*α* radiation (λ = 1.54178 Å) (**2**, **3**), SuperNova, Single source at offset, Atlas diffractometer Cu-K*α* radiation (λ = 1.54178 Å) (**5**) or on a GV 50 diffractometer (Rigaku, formerly Agilent Technologies) with TitanS2 detector from applying Cu-K*α* radiation (λ = 1.54178 Å) (**1**, **6**, **7**). All measurements were performed at 123 K. Data collection and reduction were performed with CrysAlisPro[1] (Version 17.34.36, 2010 (**2**, **3**), 171.38.41, 2015 (**1**, **6**), 171.40.14a, 2018 (**7**), 171.41.76a, 2020 (**5**)). For the compounds (**3**, **7**) an analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid was applied.[2] For the compounds (**1**, **5**, **6**) a gaussian absorption correction based on gaussian integration over a multifaceted crystal model was applied. All structures were solved by direct methods with ShelXT[3] and Olex2[4] and refined by full-matrix least-squares method against F^2 in anisotropic approximation using ShelXL[5]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined in calculated positions using riding on pivot atom model.

8.5.3.1. [(CAAC-4)$_2$(μ,η$^{1:1}$-As$_2$)] (**1**)

Compound **1** crystallizes from a concentrated solution in Et_2O at -30 °C in the monoclinic space group $P2_1/m$ as red blocks. The asymmetric unit contains one molecule of **1**. The structure in solid state is given in Figure S8.11.

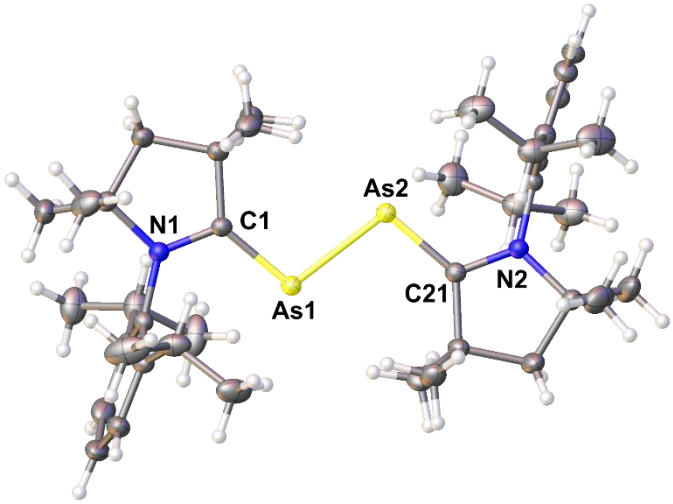

Figure S8.11. Molecular structure of **1** in solid state. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: As1-As2 2.4175(2), As1-C1 1.8520(14), As2-C21 1.8528(14), N2-C21 1.3621(17), N1-C1 1.3645(17), C1-As1-As2 102.57(4), C21-As2-As1 101.92(4), N1-C1-As1 118.56(9), C2-C1-As1 132.85(10), N2-C21-As2 118.68(10), C22-C21-As2 132.95(10).

8.5.3.2. [(CAAC-1)$_2$(μ,η$^{1:1}$-As$_2$)] (**2**)

Compound **2** crystallizes from a concentrated solution in Et_2O at -30 °C in the non-centrosymmetric space group $P2_1$ as pale yellow plates. The asymmetric unit contains one molecule of **2**. The structure in solid state is given in Figure S8.12.

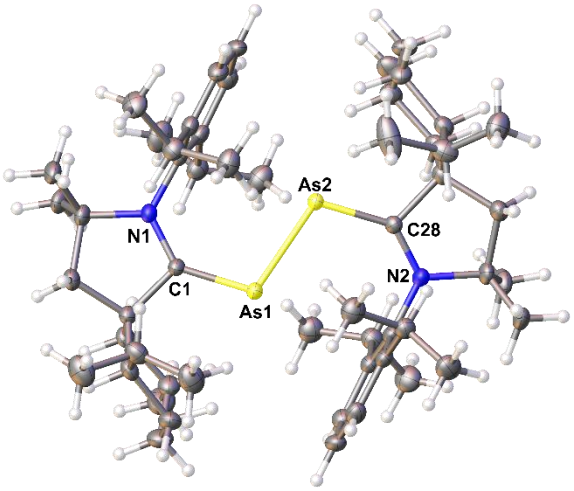

Figure S8.12. Molecular structure of **2** in solid state. Selected bond distances [Å] and angles [°]: As1-As2 2.4423(4), As1-C1 1.856(3), As2-C28 1.859(3), C28-N2 1.364(4), N1-C1 1.371(4), C1-As1-As2 107.23(9), C28-As2-As1 107.60(10), N2-C28-As2 134.2(2), C29-C28-As2 117.6(2).

8.5.3.3. [(CAAC-2)$_3$(μ_3,$\eta^{1:1:1}$-AsP$_3$)] (**3**)

Compound **3** crystallizes from a concentrated solution in Et_2O at -30 °C in space group $P\bar{1}$ as pale yellow plates. The asymmetric unit contains one molecule of **3**. The structure in solid state is given in Figure S8.13.

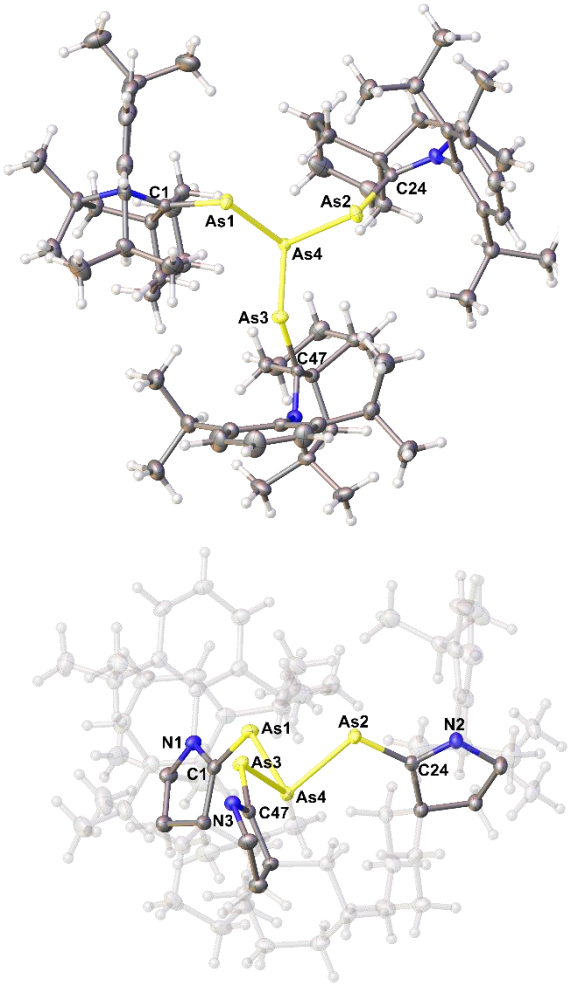

Figure S8.13. Molecular structure of **3** in solid state (top: topview, bottom: sideview). Selected bond distances [Å] and angles [°]: C1-N1 1.361(2), C24-N2 1.3553(19), C47-N3 1.357(2), C1-As1 1.8634(15), C24-As2 1.8663(15), C47-As3 1.8626(14), As1-As4 2.4520(2), As2-As4 2.4508(2), As3-As4 2.4479(2), As2-As4-As1 90.398(8), As3-As4-As1 89.288(7), As3-As4-As2 92.239(8).

8.5.3.4. [(CAAC-3)$_3$(μ_3,$\eta^{1:1:1}$-AsP$_3$)] (**5**)

Compound **5** crystallizes from a concentrated solution in Et_2O at -30 °C in space group $P\bar{1}$ as yellow needles. The asymmetric unit contains one molecule of **5** and 0.7 molecules of thf. The structure in solid state is given in Figure S8.14.

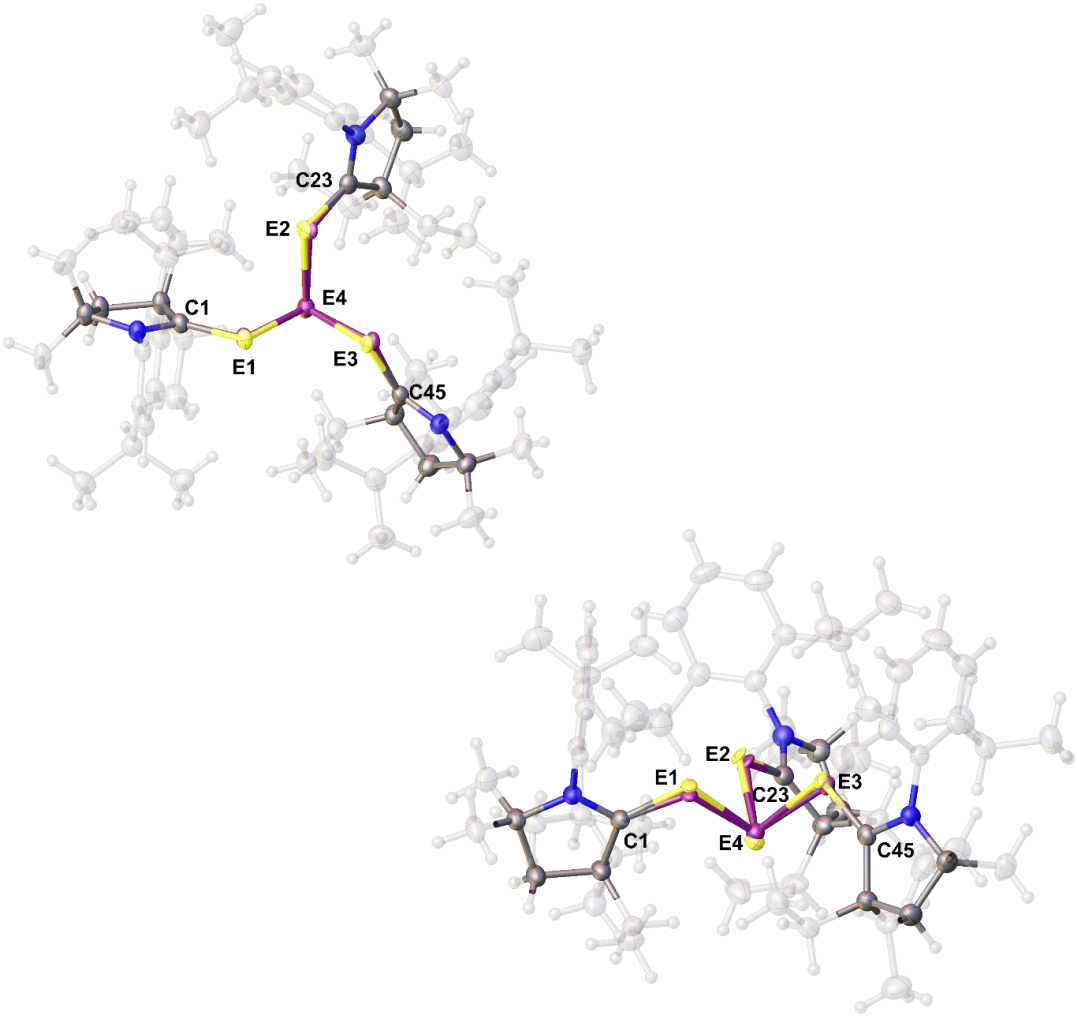

Figure S8.14. Molecular structure of **5** in solid state (top: topview, bottom: sideview). Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: As1-P4 2.358(10), P2-P4 2.225(9), P3-P4 2.263(8), As2-P4 2.339(12), As3-P4 2.289(11), P1-As4 2.32(4), P2-As4 2.34(4), P3-As4 2.40(4), C1-P1 1.748(10), C1-As1 1.859(10), C23-P2 1.714(8), C23-As2 1.891(10), C45-P3 1.740(8), C45-As3 1.856(9), N1-C1 1.360(3), N2-C23 1.360(3), N3-C45 1.366(3), P1-P4-P3 92.9(3), P1-P4-P2 92.4(4), P2-P4-P3 92.6(3), As1-P4-P2 90.3(4), As1-P4-P3 89.0(3), As2-P4-P1 86.8(4), As2-P4-P3 92.8(4), As3-P4-P1 87.2(3), As3-P4-P2 91.7(4), P1-As4-P2 87.0(13), P3-As4-P2 86.5(13), P3-As4-P1 87.0(12).

8.5.3.5. [(CAAC-3)$_4$(μ$_4$,η$^{1:1:1:1}$- As$_8$)] (**6**)

Compound **6** crystallizes from a concentrated solution in Et_2O at -30 °C in space group $P2_1/n$ as light orange needle. The asymmetric unit contains one molecule of **6**. The structure in solid state is given in Figure S8.15.

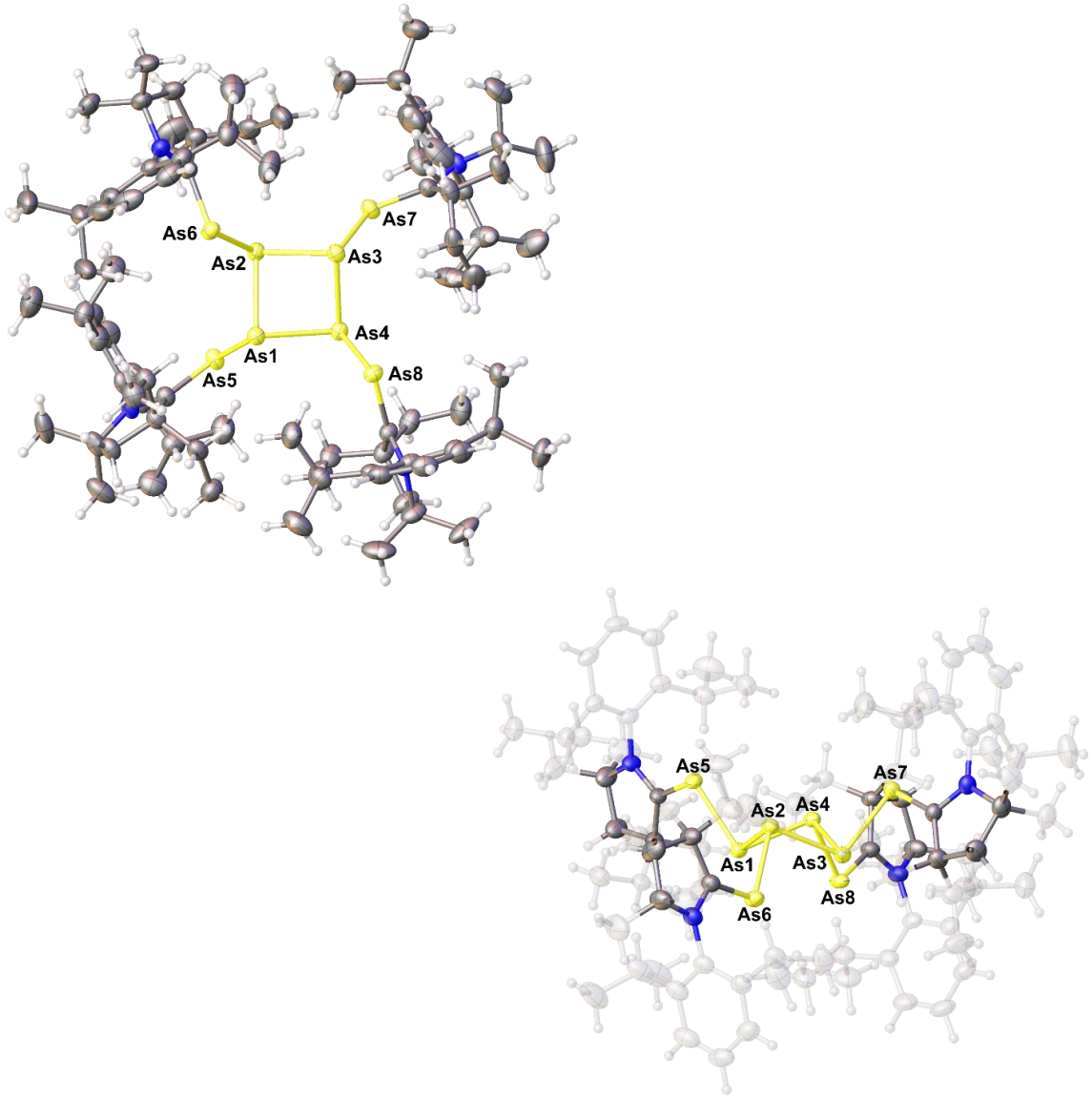

Figure S8.15. Molecular structure of **6** in solid state (top: topview, bottom: sideview). Selected bond distances [Å] and angles [°]: As1-As2 2.4741(5), As1-As5 2.4307(5), As1-As4 2.4658(5), As2-As3 2.4538(5), As2-As6 2.4248(5), As3-As4 2.4694(4), As4-As8 2.4334(5), As3-As7 2.4237(5), As5-C1 1.864(3), As6-C23 1.864(3), As7-C45 1.863(3), As8-C67 1.862(3), As5-As1-As2 96.525(17), As5-As1-As4 95.892(16), As4-As1-As2 83.178(16), As3-As2-As1 82.640(15), As6-As2-As1 102.695(18), As6-As2-As3 93.292(16), As1-As4-As3 82.492(15), As8-As4-As1 95.706(18), As8-As4-As3 93.591(16), As2-As3-As4 83.523(15), As7-As3-As2 92.399(17), As7-As3-As4 100.121(17), C1-As5-As1 103.15(9), C23-As6-As2 102.71(9), C45-As7-As3 103.85(11), C67-As8-As4 104.05(10).

8.5.3.6. [(CAAC-3)$_4$(μ_4,$\eta^{1:1:1:1}$- P$_8$)] (**7**)

Compound **7** crystallizes from a concentrated solution in Et_2O at -30 °C in the orthorhombic space group Pnna as clear yellow blocks. The asymmetric unit contains half a molecule of **7**. The structure in solid state is given in Figure S8.16.

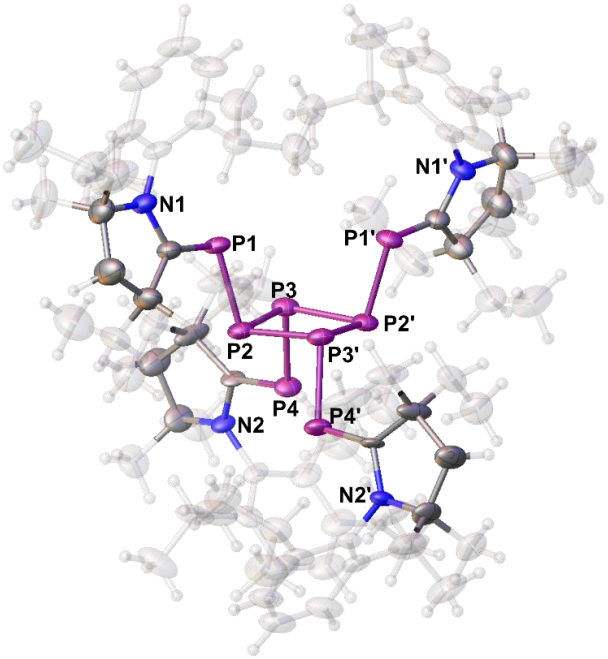

Figure S8.16. Molecular structure of **7** in solid state. Selected bond distances [Å] and angles [°]: P1-P2 2.1976(6), P2-P3 2.2354(8), P3-P4 2.1992(6), P3-P2' 2.2335(8), P1-C1 1.731(2), P4-C23A 1.797(13), P4-C23B 1.674(17), P1-P2-P3 92.50(3), P1-P2-P3' 101.65(3), P3-P2-P3' 90.01(3), P2-P3-P2' 89.70(3), P2-P3-P4 99.77(3), P2'-P3-P4 92.25(3), C1-P1-P2 104.66(7), C23A-P4-P3 101.0(4), C23B-P4-P3 109.9(4).

8.5.3.7. Crystallographic information

Table S8.1. Crystallographic data and details of diffraction experiments for **1**, **2**, and **3**.

Compound	**1**	**2**	**3**
Formula	$C_{40}H_{62}As_2N_2$	$C_{54}H_{86}As_2N_2$	$C_{77}H_{125}As_4N_3O_2$
$D_{calc.}$/ g cm^{-3}	1.259	1.206	1.256
μ/mm^{-1}	1.734	1.896	2.405
Formula Weight	720.75	913.08	1424.47
Colour	clear dark red	yellow	light yellow
Shape	block	plate	octahedral
Size/mm^3	0.23×0.17×0.17	0.58×0.30×0.04	0.42×0.32×0.21
T/K	123.00(10)	123(1)	123(1)
Crystal System	monoclinic	monoclinic	triclinic
Flack Parameter	-	-0.033(14)	-
Hooft Parameter	-	-0.009(10)	-
Space Group	$P2_1/c$	$P2_1$	P-1
a/Å	16.2753(2)	10.09320(10)	13.9899(3)
b/Å	14.99430(10)	21.7023(3)	15.6001(4)
c/Å	16.9642(2)	12.2533(2)	17.8266(4)
α/°	90	90	84.941(2)
β/°	113.2470(10)	110.470(2)	77.407(2)
γ/°	90	90	83.687(2)
V/Å^3	3803.78(7)	2514.55(7)	3765.65(16)
Z	4	2	2
Z'	1	1	1
Wavelength/Å	1.39222	1.54178	1.54178
Radiation type	Cu K	CuK_α	CuK_α
Θ_{min}/°	2.668	3.850	3.251
Θ_{max}/°	74.539	66.743	70.691
Measured Refl's.	30761	13138	27414
Ind't Refl's	10334	7068	13981
Refl's with I > 2(I)	9864	6968	13132
R_{int}	0.0297	0.0295	0.0228
Parameters	413	541	795
Restraints	0	1	0
Largest Peak	0.535	0.418	0.357
Deepest Hole	-0.726	-0.271	-0.270
GooF	1.044	1.022	1.064
wR_2 (all data)	0.0942	0.0692	0.0651
wR_2	0.0929	0.0688	0.0637
R_1 (all data)	0.0357	0.0276	0.0280
R_1	0.0344	0.0271	0.0258

Table S8.2. Crystallographic data and details of diffraction experiments for **5**, **6** and **7**.

Compound	**5**	**6**	**7**
Formula	$C_{68.8}H_{110.6}As_{0.84}N_3O_{0.7}P_{3.16}$	$C_{88}H_{140}As_8N_4$	$C_{88}H_{140}N_4P_8$
$D_{calc.}$/ g cm^{-3}	1.090	1.347	1.083
μ/mm^{-1}	1.542	2.773	1.665
Formula Weight	1151.79	1853.39	1573.94
Colour	yellow	light orange	clear yellow
Shape	needle	needle	block
Size/mm^3	0.35×0.08×0.06	0.42×0.12×0.02	0.41×0.15×0.08
T/K	123.01(10)	123.0(2)	122.9(3)
Crystal System	triclinic	monoclinic	orthorhombic
Space Group	P-1	$P2_1/n$	$Pnna$
a/Å	10.3895(3)	15.5624(3)	24.0622(9)
b/Å	14.6405(3)	30.5824(5)	23.3625(9)
c/Å	23.3361(6)	20.3894(5)	17.1780(5)
α/°	85.662(2)	90	90
β/°	86.143(2)	109.670(2)	90
γ/°	83.378(2)	90	90
V/Å^3	3509.67(15)	9137.8(3)	9656.7(6)
Z	2	4	4
Z'	1	1	0.5
Wavelength/Å	1.54184	1.39222	1.54184
Radiation type	Cu K$_\alpha$	Cu K	Cu K$_\alpha$
Θ_{min}/°	3.479	3.772	3.674
Θ_{max}/°	72.686	74.253	75.644
Measured Refl's.	39042	51164	28241
Ind't Refl's	13665	24299	9631
Refl's with I > 2(I)	11102	18772	7661
R_{int}	0.0408	0.0581	0.0377
Parameters	808	943	692
Restraints	177	0	375
Largest Peak	1.007	1.245	0.449
Deepest Hole	-0.307	-0.943	-0.210
GooF	1.071	0.995	1.032
wR_2 (all data)	0.1348	0.1277	0.1387
wR_2	0.1235	0.1163	0.1305
R_1 (all data)	0.0592	0.0659	0.0629
R_1	0.0459	0.0490	0.0499

8.5.4. DFT calculations

The geometries of compounds have been optimized using DFT in the form of Becke's three-parameter hybrid functional B3LYP[6] with def2-SVP[7] basis set. All structures have been fully optimized and verified to be minima on respective potential energy surfaces by subsequent vibrational analysis. The Gaussian 16 suite of programs[8] was used throughout. Standard entropies of the reactions in solution were estimated by taking into account the entropy of the solvation of one gaseous mole in the inert solvent (90 J mol^{-1} K^{-1}).[9]

Table S8.3. Total Energies E_0, Standard enthalpies H^o_{298} (all in Hartree), Standard entropies $S°_{298}$ (in cal mol^{-1} K^{-1}) for studied compounds. B3LYP/def2-SVP level of theory.

Compound	Point group	E_0	H^o_{298}	$S°_{298}$
P_2	$D_{\infty v}$	-682.510987	-682.505758	52.078
P_4	T_d	-1365.087187	-1365.075594	66.904
As_2	$D_{\infty v}$	-4471.292207	-4471.287606	57.464
As_4	T_d	-8942.661644	-8942.651479	78.259
AsP_3	C_{3v}	-3259.4781213	-3259.466939	72.535
CAAC-1	C_1	-1108.683255	-1108.009552	188.897
CAAC-2	C_1	-951.5511805	-950.995035	164.872
CAAC-3	C_1	-913.4593789	-912.912511	168.57
$(CAAC\text{-}1)_2P_2$	C_1	-2899.964896	-2898.605707	332.116
cis-$(CAAC\text{-}1)_2P_4$	C_1	-3582.449865	-3581.082928	352.854
trans-$(CAAC\text{-}1)_2P_4$	C_1	-3582.512137	-3581.146353	358.237
$(CAAC\text{-}1)_2As_2$	C_1	-6688.727153	-6687.369101	339.175
cis-$(CAAC\text{-}1)_2As_4$	C_1	-11159.99329	-11158.62835	368.025
trans-$(CAAC\text{-}1)_2As_4$	C_1	-11160.05476	-11158.69105	372.331
$(CAAC\text{-}2)P\text{-}P_3$	C_1	-2316.6512177	-2316.080402	192.973
$(CAAC\text{-}3)P\text{-}P_3$	C_1	-2278.5704960	-2278.008806	197.8
$(CAAC\text{-}2)As\text{-}As_3$	C_1	-9894.2125805	-9893.643350	204.906
$(CAAC\text{-}3)As\text{-}As_3$	C_s	-9856.1313270	-9855.571193	209.647
$(CAAC\text{-}3)As\text{-}P_3$	C_s	-4172.9517952	-4172.389708	200.996
$(CAAC\text{-}3)P\text{-}AsP_2$	C_s	-4172.9611736	-4172.398956	201.271
(CAAC-3)P-PAsP	C_1	-4172.9609704	-4172.398702	200.854
trans-$(CAAC\text{-}2)_2P_4$	C_1	-3268.2527570	-3267.123730	313.576
trans-$(CAAC\text{-}3)_2P_4$	C_1	-3192.0844085	-3190.970710	319.532
trans-$(CAAC\text{-}2)_2As_4$	C_2	-10845.7963987	-10844.669253	323.724
trans-$(CAAC\text{-}3)_2As_4$	C_2	-10769.6283901	-10768.516581	330.093
$P\{P=(CAAC\text{-}2)\}_3$	C_1	-4219.8704271	-4218.181797	422.64
$P\{P=(CAAC\text{-}3)\}_3$	C_3	-4105.5944012	-4103.928432	420.667
$As\{As=(CAAC\text{-}2)\}_3$	C_1	-11797.4082719	-11795.722141	441.005
$As\{As=(CAAC\text{-}3)\}_3$	C_3	-11683.1382242	-11681.475143	438.189
$As\{P=(CAAC\text{-}3)\}_3$	C_3	-5999.9864614	-5998.321417	427.063
$P\{As=(CAAC\text{-}3)\}\{P=(CAAC\text{-}3)\}_2$	C_1	-5999.9774617	-5998.312263	428.652
$\{P\text{-}P=(CAAC\text{-}2)\}_4$	D_2	-6536.5689237	-6534.306159	568.26
$\{P\text{-}P=(CAAC\text{-}3)\}_4$	C_1	-6384.2178120	-6381.988993	591.789
$\{As\text{-}As=(CAAC\text{-}2)\}_4$	D_2	-21691.6674243	-21689.409071	599.313
$\{As\text{-}As=(CAAC\text{-}3)\}_4$	C_1	-21539.3141107	-21537.088957	618.264

Table S8.4. Reaction energies (ΔE^o_0, kJ mol^{-1}), standard enthalpies (ΔH^o_{298}, kJ mol^{-1}), entropies (ΔS^o_{298}, J mol^{-1} K^{-1}) and Gibbs energies (ΔG^o_{298}, kJ mol^{-1}) for the gas phase processes. B3LYP/def2-SVP level of theory. Estimated Gibbs energies in solution (ΔG^o_{298}(solv), kJ mol^{-1}) are computed taking into account solvation entropy of one gaseous mole in the inert solvent as 90 J mol^{-1} K^{-1} (see ref [9] for details).

Process	ΔE^o_0	ΔH^o_{298}	ΔS^o_{298}	ΔG^o_{298}	ΔG^o_{298} (solv)
$P_4 = 2\ P_2$	171.2	168.2	155.9	121.8	148.6
$As_4 = 2\ As_2$	202.8	200.2	153.4	154.5	181.3
$4AsP_3 = 3P_4 + As_4$	-28.1	-27.6	-46.7	-13.6	-13.6
2(CAAC-1) + P_4 = *trans*-(CAAC-1)$_2P_4$	-153.4	-135.6	-361.8	-27.8	-81.4
2(CAAC-1) + P_4 = *cis*-(CAAC-1)$_2P_4$	10.1	30.9	-384.3	145.4	91.8
2(CAAC-1) + As_4 = *trans*-(CAAC-1)$_2As_4$	-69.8	-53.7	-350.3	50.7	-3.0
2(CAAC-1) + As_4 = *cis*-(CAAC-1)$_2As_4$	91.5	110.9	-368.3	220.7	167.0
trans-(CAAC-1)$_2P_4$ = (CAAC-1)$_2P_2$ + ½ P_4	9.6	7.5	30.7	-1.7	11.8
trans-(CAAC-1)$_2As_4$ = (CAAC-1)$_2As_2$ + ½ As_4	-8.5	-10.0	25.0	-17.4	-4.0
2(CAAC-1)$_2$ + ½ P_4 = (CAAC-1)$_2P_2$	-143.9	-128.1	-331.1	-29.4	-69.7
2(CAAC-1)$_2$ + ½ As_4 = (CAAC-1)$_2As_2$	-78.3	-63.7	-325.3	33.3	-7.0
2(CAAC-1)$_2$ + P_2 = (CAAC-1)$_2P_2$	-229.5	-212.3	-409.0	-90.3	-144.0
2(CAAC-1)$_2$ + As_2 = (CAAC-1)$_2As_2$	-179.7	-163.8	-402.0	-43.9	-97.6
P_4 + (CAAC-2) = (CAAC-2)P-P_3	-33.7	-25.7	-162.4	22.7	-4.1
P_4 + (CAAC-3) = (CAAC-3)P-P_3	-62.8	-54.4	-157.6	-7.4	-34.2
As_4 + (CAAC-2) = (CAAC-2)As-As_3	0.6	8.3	-159.9	56.0	29.2
As_4 + (CAAC-3) = (CAAC-3)As-As_3	-27.1	-18.9	-155.6	27.5	0.6
AsP_3 + (CAAC-3) = (CAAC-3)As-P_3	-37.5	-26.9	-167.8	23.1	-3.7
AsP_3 + (CAAC-3) = (CAAC-3)P-As-P_2	-62.2	-51.2	-166.7	-1.5	-28.4
AsP_3 + (CAAC-3) = (CAAC-3)P-P-AsP	-61.6	-50.5	-168.4	-0.3	-27.2
(CAAC-2)P-P_3 + 2(CAAC-2) = P{P=(CAAC-2)}$_3$	-306.8	-292.3	-418.7	-167.4	-221.1
(CAAC-3)P-P_3 + 2(CAAC-3) = P{P=(CAAC-3)}$_3$	-276.1	-248.4	-478.1	-105.8	-159.5
(CAAC-2)As-As_3 + 2(CAAC-2) = As{As=(CAAC-2)}$_3$	-245.0	-232.9	-391.8	-116.1	-169.8
(CAAC-3)As-As_3 + 2(CAAC-3) = As{As=(CAAC-2)}$_3$	-231.4	-207.2	-454.4	-71.8	-125.4
(CAAC-3)As-P_3 + 2(CAAC-3) = P{P=(CAAC-2)}$_2$ {As=(CAAC-2)}	-280.7	-256.1	-458.1	-119.5	-173.2
(CAAC-3)P-AsP_2 + 2(CAAC-3) = As{P=(CAAC-2)}$_3$	-279.7	-255.8	-465.9	-116.9	-170.6
(CAAC-3)P-P-AsP + 2(CAAC-3) = P{P=(CAAC-2)}$_2${As=(CAAC-2)}	-256.6	-232.5	-457.5	-96.1	-149.7
As{P=(CAAC-2)}$_3$ = P{P=(CAAC-2)}$_2${As=(CAAC-2)}	23.6	24.0	6.6	22.1	22.1
2(CAAC-2)P-P_3 = *trans*-(CAAC-2)$_2P_4$ + P_4	-98.5	-101.1	-22.9	-94.3	-94.3
2(CAAC-3)P-P_3 = *trans*-(CAAC-3)$_2P_4$ + P_4	-80.3	-75.3	-38.3	-63.9	-63.9
2(CAAC-2)As-As_3 = *trans*-(CAAC-2)$_2As_4$ + As_4	-86.3	-89.4	-32.8	-79.6	-79.6
2(CAAC-3)As-As_3 = *trans*-(CAAC-3)$_2As_4$ + As_4	-71.9	-67.4	-45.8	-53.8	-53.8
P_4 + 2(CAAC-2) = *trans*-(CAAC-2)$_2P_4$	-166.0	-152.5	-347.6	-48.8	-102.5
P_4 + 2 (CAAC-3) = *trans*-(CAAC-3)$_2P_4$	-206.0	-184.0	-353.6	-78.6	-132.3
As_4 + 2(CAAC-2) = *trans*-(CAAC-2)$_2As_4$	-85.0	-72.7	-352.6	32.4	-21.3
As_4 + 2(CAAC-3) = *trans*-(CAAC-3)$_2As_4$	-126.0	-105.2	-356.9	1.2	-52.5
4(CAAC-2)P-P_3 = {P-P=(CAAC-2)}$_4$ + 2P_4	-362.8	-356.4	-292.1	-269.3	-296.1
4(CAAC-3)P-P_3 = {P-P=(CAAC-3)}$_4$ + 2P_4	-289.1	-275.6	-274.5	-193.7	-220.6
4(CAAC-2)As-As_3 = {As-As=(CAAC-2)}$_4$ + 2As_4	-367.8	-364.0	-266.9	-284.4	-311.2
4(CAAC-3)As-As_3 = {As-As=(CAAC-3)}$_4$ + 2As_4	-294.3	-281.3	-267.0	-201.7	-228.5
2 *trans*-(CAAC-2)$_2P_4$= {P-P=(CAAC-2)}$_4$	-166.5	-154.1	-246.4	-80.6	-107.5
2 *trans*-(CAAC-3)$_2P_4$= {P-P=(CAAC-3)}$_4$	-128.6	-124.9	-197.8	-65.9	-92.8
2 *trans*-(CAAC-2)$_2As_4$= {As-As=(CAAC-2)}$_4$	-195.9	-185.3	-201.4	-125.2	-152.1
2 *trans*-(CAAC-3)$_2As_4$= {As-As=(CAAC-3)}$_4$	-150.5	-146.5	-175.4	-94.2	-121.0
{P-P=(CAAC-2)}$_4$ = P{P=(CAAC-2)}$_3$ + (CAAC-2)P-P_3	124.1	115.4	198.1	56.3	83.2
{P-P=(CAAC-3)}$_4$ = P{P=(CAAC-3)}$_3$ + (CAAC-3)P-P_3	138.9	135.9	111.6	102.6	129.4
{As-As=(CAAC-2)}$_4$ = As{As=(CAAC-2)}$_3$ + (CAAC-2)As-As_3	122.3	114.4	195.0	56.3	83.1
{As-As=(CAAC-3)}$_4$ = As{As=(CAAC-3)}$_3$ + (CAAC-3)As-As_3	117.0	111.9	123.7	75.0	101.8

Table S8.5. Optimized gas phase geometries (xyz coordinates in Å) for studied compounds. B3LYP/def2-SVP level of theory.

P_2

15	0.000000000	0.000000000	0.949347000
15	0.000000000	0.000000000	-0.949347000

As_2

33	0.000000000	0.000000000	1.053730000
33	0.000000000	0.000000000	-1.053730000

P_4

15	0.785664000	0.785664000	0.785664000
15	-0.785664000	-0.785664000	0.785664000
15	0.785664000	-0.785664000	-0.785664000
15	-0.785664000	0.785664000	-0.785664000

As_4

33	0.870401000	0.870401000	0.870401000
33	-0.870401000	-0.870401000	0.870401000
33	0.870401000	-0.870401000	-0.870401000
33	-0.870401000	0.870401000	-0.870401000

CAAC-1

6	-0.535894000	0.110882000	-0.323161000
7	0.515867000	-0.009533000	0.456430000
6	-1.762015000	0.171732000	0.580863000
6	0.284210000	-0.108895000	1.977986000
6	1.871119000	0.040788000	-0.069937000
6	-1.257161000	-0.186040000	2.014920000
6	-2.951304000	-0.736187000	0.110073000
6	-2.258259000	1.655059000	0.580391000
6	0.833649000	1.125331000	2.709700000
6	0.944659000	-1.358516000	2.570943000
6	2.552202000	-1.157907000	-0.395076000
6	2.489715000	1.302349000	-0.266312000
1	-1.668712000	0.497764000	2.772253000
1	-1.573523000	-1.197829000	2.303799000
6	-3.569711000	-0.225428000	-1.205238000
6	-2.649113000	-2.265114000	0.059545000
1	-3.718423000	-0.602273000	0.897755000
6	-2.885427000	2.157674000	-0.726177000
1	-3.012358000	1.743274000	1.385223000
1	-1.427129000	2.318801000	0.872183000
1	0.666418000	1.008373000	3.791938000
1	0.334564000	2.052058000	2.396149000
1	1.916347000	1.240360000	2.551005000
1	2.038451000	-1.336447000	2.453508000
1	0.561608000	-2.281931000	2.115211000
1	0.726385000	-1.404018000	3.649758000
6	3.895687000	-1.071894000	-0.792955000
6	1.858188000	-2.515842000	-0.474101000
6	3.832752000	1.329033000	-0.669388000
6	1.719530000	2.619003000	-0.189794000
6	-4.036627000	1.227890000	-1.123919000
1	-2.824018000	-0.309374000	-2.010534000
1	-4.417261000	-0.872918000	-1.486782000
6	-2.022410000	-2.740955000	-1.259439000
6	-3.903946000	-3.089657000	0.387273000
1	-1.918211000	-2.484068000	0.856788000
6	-3.334830000	3.616062000	-0.602342000
1	-2.116373000	2.095265000	-1.515254000
6	4.543502000	0.154679000	-0.904494000
1	4.438362000	-1.987045000	-1.040568000
6	1.639852000	-2.893264000	-1.953092000
6	2.601109000	-3.638359000	0.268689000
1	0.862379000	-2.415229000	-0.024160000
1	4.326815000	2.291296000	-0.818077000
6	1.304831000	3.055125000	-1.609261000
6	2.472979000	3.741563000	0.539860000
1	0.791476000	2.436158000	0.362614000
1	-4.851937000	1.321958000	-0.380464000
1	-4.462302000	1.543951000	-2.092246000
1	-1.660013000	-3.777554000	-1.161573000
1	-1.176081000	-2.104779000	-1.556998000
1	-2.753813000	-2.729496000	-2.083468000
1	-4.710224000	-2.905067000	-0.342582000
1	-4.299221000	-2.847765000	1.387539000
1	-3.685561000	-4.170065000	0.365064000
1	-4.095631000	3.734010000	0.189127000
1	-3.778361000	3.978014000	-1.544426000
1	-2.491008000	4.280885000	-0.353554000
1	5.592715000	0.197659000	-1.208111000
1	2.601683000	-3.037615000	-2.471896000
1	1.085267000	-2.104870000	-2.483165000
1	1.067202000	-3.831348000	-2.034722000
1	2.012588000	-4.569807000	0.238430000
1	2.781259000	-3.386874000	1.324810000
1	3.577288000	-3.859154000	-0.192366000
1	2.188843000	3.252639000	-2.237913000
1	0.702960000	3.978609000	-1.571871000
1	0.705355000	2.269869000	-2.093631000
1	2.794016000	3.433220000	1.547275000
1	1.824055000	4.625817000	0.647397000
1	3.369335000	4.067601000	-0.011818000

CAAC-2

6	-1.016697000	-0.141445000	-0.380978000
7	0.011683000	-0.081826000	0.432584000
6	-2.262021000	-0.308923000	0.481094000
6	-0.260006000	-0.156903000	1.948296000
6	1.363325000	0.068774000	-0.075325000
6	-1.741394000	-0.584264000	1.924001000
6	-3.119247000	-1.491986000	-0.038907000
6	-3.111759000	0.992893000	0.407065000
6	-0.052691000	1.214176000	2.610610000
6	0.641746000	-1.177089000	2.652354000
6	2.119999000	-1.093247000	-0.365562000
6	1.888015000	1.362118000	-0.312900000
1	-2.326739000	-0.056466000	2.692303000
1	-1.818915000	-1.660554000	2.146022000
6	-3.756607000	-1.242470000	-1.410410000
1	-3.913884000	-1.685467000	0.706813000
6	-3.749645000	1.243673000	-0.965199000
1	-3.910173000	0.908014000	1.167609000
1	-2.498358000	1.861020000	0.701932000
1	-0.259840000	1.131298000	3.689126000
1	-0.726084000	1.979255000	2.200142000
1	0.984483000	1.563335000	2.497797000
1	1.706132000	-0.912276000	2.561752000
1	0.500705000	-2.193949000	2.262279000
1	0.392979000	-1.196925000	3.725256000
6	3.449511000	-0.930505000	-0.781443000
6	1.502316000	-2.490274000	-0.376604000
6	3.224534000	1.466446000	-0.728417000
6	1.023141000	2.620239000	-0.278122000
6	-4.587995000	0.044879000	-1.421659000
1	-2.958002000	-1.165300000	-2.165867000
1	-4.383564000	-2.106803000	-1.689533000
1	-2.956166000	1.436130000	-1.705358000
6	4.009629000	0.335515000	-0.936955000
1	4.052937000	-1.812708000	-1.005107000
6	1.110404000	-2.869703000	-1.818575000
6	2.391356000	-3.567317000	0.263399000
1	0.567892000	-2.451906000	0.197252000
1	3.652100000	2.454472000	-0.911602000
6	0.596326000	2.991864000	-1.712280000
6	1.685678000	3.810071000	0.433017000
1	0.102434000	2.383429000	0.266801000
1	-5.458068000	-0.072148000	-0.747575000
1	-4.999138000	0.226957000	-2.429103000
1	5.050672000	0.440303000	-1.253491000
1	1.997555000	-2.918085000	-2.471483000
1	0.414561000	-2.127471000	-2.237952000
1	0.619241000	-3.856962000	-1.840448000
1	1.850810000	-4.526480000	0.312639000
1	2.692432000	-3.294396000	1.287135000
1	3.309831000	-3.746665000	-0.318255000
1	1.470893000	3.238114000	-2.336892000
1	-0.071208000	3.869755000	-1.703235000
1	0.060633000	2.154561000	-2.184232000
1	2.009036000	3.550535000	1.453566000
1	0.977825000	4.651596000	0.506304000
1	2.568797000	4.180197000	-0.112234000
1	-2.497560000	-2.403741000	-0.070733000
1	-4.373540000	2.152991000	-0.918722000

CAAC-3

6	-1.173517000	-0.123104000	-0.558468000	1	-2.980118000	-1.170904000	-2.516469000
7	-0.224322000	-0.070096000	0.346997000	1	-4.176050000	-2.432978000	-2.120361000
6	-2.497093000	-0.282733000	0.183186000	1	-2.306789000	2.193674000	-1.445015000
6	-0.638556000	-0.124360000	1.831323000	6	3.897807000	0.226460000	-0.630126000
6	1.173143000	0.040078000	-0.030926000	1	3.887594000	-1.922711000	-0.677667000
6	-2.106189000	-0.568575000	1.669883000	6	0.997263000	-2.905200000	-1.764222000
6	-3.256448000	-1.517931000	-0.380727000	6	2.068234000	-3.620830000	0.427064000
6	-3.349544000	1.024350000	0.085155000	1	0.289462000	-2.457090000	0.193476000
6	-0.501544000	1.258727000	2.487115000	1	3.598722000	2.354472000	-0.655349000
6	0.198086000	-1.124805000	2.636886000	6	0.673863000	2.975913000	-1.759989000
6	1.922127000	-1.144999000	-0.236685000	6	1.539103000	3.771075000	0.492654000
6	1.754609000	1.315958000	-0.225261000	1	-0.055442000	2.387463000	0.152016000
1	-2.767598000	-0.059944000	2.387708000	1	4.967411000	0.299763000	-0.843456000
1	-2.183835000	-1.647723000	1.875313000	1	1.937564000	-2.982036000	-2.334826000
6	-3.780374000	-1.450281000	-1.815408000	1	0.361765000	-2.148055000	-2.247735000
1	-4.097103000	-1.729324000	0.306550000	1	0.483624000	-3.879359000	-1.824400000
6	-3.317348000	1.820456000	-1.224715000	1	1.497549000	-4.563602000	0.435654000
1	-4.392974000	0.757201000	0.334486000	1	2.287638000	-3.347114000	1.471183000
1	-3.026909000	1.703055000	0.892189000	1	3.027875000	-3.832024000	-0.071492000
1	-0.828736000	1.197516000	3.536948000	1	1.618416000	3.206118000	-2.279997000
1	-1.118044000	2.019327000	1.988624000	1	0.025685000	3.865631000	-1.826559000
1	0.543792000	1.601748000	2.485315000	1	0.182060000	2.148314000	-2.292737000
1	1.263395000	-0.848875000	2.650237000	1	1.736598000	3.507668000	1.543813000
1	0.107691000	-2.148419000	2.249787000	1	0.853235000	4.633697000	0.483446000
1	-0.157517000	-1.132941000	3.679434000	1	2.489391000	4.111387000	0.050689000
6	3.289842000	-1.022401000	-0.521234000	1	-2.578434000	-2.386047000	-0.296065000
6	1.269723000	-2.525045000	-0.295182000	1	-3.991568000	2.690014000	-1.149240000
6	3.127994000	1.380099000	-0.507935000	1	-3.632773000	1.227237000	-2.092620000
6	0.926550000	2.597331000	-0.286886000	1	-4.601703000	-0.725571000	-1.924880000

(CAAC-1)$_2$P$_2$

15	-0.798428000	-0.794521000	0.154512000	1	3.298192000	4.019660000	1.866302000
15	0.798457000	0.794582000	0.154289000	6	2.527443000	1.804200000	3.437176000
6	-2.374352000	-0.069035000	-0.069635000	6	5.034375000	1.684473000	3.358823000
6	2.374352000	0.069056000	-0.069937000	1	3.664675000	0.310102000	2.454433000
7	-2.838909000	1.204360000	-0.349947000	6	3.165080000	3.852322000	-2.821867000
6	-3.610787000	-1.038853000	-0.052657000	1	1.838643000	2.914206000	-1.412394000
7	2.838862000	-1.204346000	-0.350302000	6	-0.622939000	4.832706000	-0.187288000
6	3.610792000	1.038864000	-0.053038000	1	-0.991121000	4.779294000	1.927877000
6	-4.326027000	1.282948000	-0.610829000	6	-1.291403000	1.984259000	3.179068000
6	-2.043690000	2.409770000	-0.303745000	6	-3.230753000	3.586300000	3.039096000
6	-4.790257000	-0.036244000	0.011286000	1	-3.070933000	1.690815000	2.043945000
6	-3.797252000	-2.044578000	1.151921000	1	-0.384107000	4.623867000	-2.310863000
6	-3.706313000	-1.851845000	-1.388430000	6	-0.229286000	1.877457000	-3.412408000
6	4.325955000	-1.282963000	-0.611365000	6	-2.289341000	3.229077000	-3.900344000
6	2.043622000	-2.409736000	-0.303966000	1	-2.204622000	1.402277000	-2.758332000
6	4.790294000	0.036263000	0.010599000	1	-4.311551000	-4.377690000	-0.363946000
6	3.797481000	2.044462000	1.151608000	1	-2.652685000	-4.994119000	-0.344901000
6	3.706016000	1.852034000	-1.388727000	1	-2.516979000	-1.220089000	4.371936000
6	-4.683438000	1.362620000	-2.109264000	1	-1.581303000	-1.617014000	2.913495000
6	-4.991348000	2.485604000	0.072527000	1	-2.556537000	-2.868682000	3.720996000
6	-1.861613000	3.066225000	0.946859000	1	-5.181066000	-2.769978000	3.497831000
6	-1.498638000	2.967641000	-1.492019000	1	-5.921519000	-1.297172000	2.833551000
1	-5.688718000	-0.433601000	-0.482614000	1	-5.009711000	-1.226594000	4.362353000
1	-5.058519000	0.152145000	1.059627000	1	-4.226854000	-4.138060000	-2.929648000
6	-3.002688000	-3.357230000	1.035337000	1	-2.565492000	-4.771937000	-2.916145000
6	-3.736724000	-1.402292000	2.583115000	1	-2.911973000	-3.197223000	-3.671764000
1	-4.850885000	-2.352147000	1.009773000	6	0.622837000	-4.832646000	-0.187286000
6	-2.911460000	-3.160129000	-1.479288000	1	0.383681000	-4.623797000	-2.310828000
1	-4.773027000	-2.101563000	-1.540386000	6	2.288484000	-3.229177000	-3.900644000
1	-3.419978000	-1.205969000	-2.232026000	6	0.228788000	-1.877177000	-3.412256000
6	4.683208000	-1.362746000	-2.109831000	1	2.204335000	-1.402340000	-2.758620000
6	4.991340000	-2.485579000	0.071990000	1	0.991341000	-4.779234000	1.927824000
6	1.498358000	-2.967593000	-1.492150000	6	1.291852000	-1.984325000	3.179029000
6	1.861695000	-3.066173000	0.946675000	6	3.231183000	-3.586346000	3.038642000
1	5.688649000	0.433630000	-0.483490000	1	3.071198000	-1.690796000	2.043627000
1	5.058788000	-0.152122000	1.058883000	1	4.311284000	4.377816000	-0.364048000
6	3.002797000	3.357075000	1.035383000	1	2.652370000	4.994105000	-0.344596000
6	3.737430000	1.402043000	2.582761000	1	2.518250000	1.219610000	4.371939000
1	4.851055000	2.352118000	1.009203000	1	1.582100000	1.616644000	2.913834000
6	2.911063000	3.160281000	-1.479255000	1	2.557544000	2.868270000	3.721150000
1	4.772691000	2.101798000	-1.540890000	1	5.181984000	2.769767000	3.497088000
1	3.419496000	1.206261000	-2.232338000	1	5.922307000	1.297033000	2.832499000
1	-5.775041000	1.266210000	-2.219637000	1	5.010994000	1.226333000	4.361593000
1	-4.217777000	0.567217000	-2.703133000	1	2.564668000	4.772224000	-2.915858000
1	-4.397503000	2.330294000	-2.537659000	1	2.911216000	3.197651000	-3.671737000
1	-4.594181000	3.441670000	-0.299239000	1	4.226104000	4.138544000	-2.929709000
1	-4.875998000	2.459282000	1.161977000	1	-0.076588000	5.778470000	-0.143088000
1	-6.070112000	2.463511000	-0.147272000	1	-0.586461000	2.779378000	3.470075000
6	-1.141726000	4.268573000	0.974240000	1	-0.720626000	1.194045000	2.674075000
6	-2.406534000	2.533434000	2.273283000	1	-1.721941000	1.562930000	4.102463000
6	-0.802346000	4.182529000	-1.403450000	1	-3.731744000	3.121099000	3.903841000
6	-1.602521000	2.311898000	-2.869226000	1	-4.002391000	4.053500000	2.409170000
6	-3.250228000	-4.067550000	-0.294226000	1	-2.592901000	4.393786000	3.433130000

1	-1.925767000	-3.166354000	1.149280000	1	0.416178000	2.747940000	-3.608644000
1	-3.297952000	-4.019903000	1.866231000	1	-0.353124000	1.335616000	-4.364381000
6	-2.526488000	-1.804586000	3.437117000	1	0.294970000	1.221822000	-2.703870000
6	-5.033440000	-1.684685000	3.359571000	1	-3.241424000	3.641367000	-3.534393000
1	-3.663912000	-0.310348000	2.454850000	1	-2.492976000	2.676859000	-4.832482000
6	-3.165779000	-3.851976000	-2.821940000	1	-1.646342000	4.084563000	-4.163222000
1	-1.839014000	-2.914121000	-1.412595000	1	0.076478000	-5.778402000	-0.142996000
1	4.397292000	-2.330469000	-2.538120000	1	1.645249000	-4.084524000	-4.163405000
1	5.774798000	-1.266286000	-2.220308000	1	3.240543000	-3.641684000	-3.534868000
1	4.217456000	-0.567416000	-2.703723000	1	2.492066000	-2.677002000	-4.832820000
1	4.876135000	-2.459172000	1.161452000	1	0.352504000	-1.335432000	-4.364301000
1	6.070077000	-2.463544000	-0.147949000	1	-0.295134000	-1.221370000	-2.703628000
1	4.594096000	-3.441664000	-0.299643000	1	-0.416918000	-2.747531000	-3.608266000
6	0.802070000	-4.182475000	-1.403477000	1	0.586967000	-2.779472000	3.470105000
6	1.602060000	-2.311861000	-2.869378000	1	0.720982000	-1.194082000	2.674187000
6	1.141800000	-4.268513000	0.974163000	1	1.722536000	-1.563055000	4.102381000
6	2.406840000	-2.533431000	2.273026000	1	3.732304000	-3.121207000	3.903344000
6	3.250000000	4.067580000	-0.294145000	1	4.002729000	-4.053500000	2.408566000
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15	0.960041000	0.250163000	-2.364364000	1	3.611025000	1.360015000	-3.069856000
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6	3.381606000	0.025458000	-0.524834000	1	5.492832000	-2.342501000	-2.010418000
15	-1.113137000	0.200806000	-2.436578000	1	6.045755000	-3.035146000	-0.458466000
15	-1.758344000	0.411347000	-0.350015000	1	7.589877000	-0.621317000	0.474997000
6	-3.490006000	0.087490000	-0.198939000	1	6.504344000	-1.592314000	1.488695000
7	-4.064926000	0.506639000	0.980256000	1	6.337637000	0.175003000	1.445207000
6	-5.540354000	0.260501000	1.075771000	1	-5.666944000	-0.733357000	3.017401000
6	-5.871553000	0.056530000	-0.411010000	1	-5.316656000	-1.856036000	1.687336000
6	-4.602710000	-0.515996000	-1.115305000	1	-6.952169000	-1.183330000	1.879970000
6	-3.350417000	1.240231000	2.006034000	1	-6.010959000	1.689177000	2.676360000
6	-5.877788000	-0.955345000	1.962288000	1	-7.386149000	1.208585000	1.657329000
6	-6.313443000	1.457510000	1.644392000	1	-6.189312000	2.357039000	1.031328000
1	-6.104349000	1.039619000	-0.845296000	6	-4.666895000	4.613056000	1.083426000
1	-6.761706000	-0.570992000	-0.539031000	1	-4.227001000	2.796779000	0.012799000
6	-4.463505000	0.055051000	-2.551557000	6	-2.499844000	4.058841000	-0.072416000
6	-4.764600000	-2.109040000	-1.154309000	1	-1.954915000	4.796059000	0.540219000
6	4.321686000	1.162614000	-1.033536000	1	-2.846524000	4.573867000	-0.983584000
6	5.586270000	0.307989000	-1.351731000	1	-1.794682000	3.270415000	-0.369530000
6	5.614345000	-0.882839000	-0.374076000	1	-4.156069000	5.393496000	1.669934000
7	4.160985000	-0.961475000	0.001083000	1	-5.519221000	4.259682000	1.681849000
6	4.645784000	2.118394000	0.164305000	1	-5.063493000	5.098351000	0.176606000
1	5.499623000	-0.081888000	-2.377357000	6	-1.259030000	-1.462109000	3.065739000
1	6.520980000	0.875903000	-1.292576000	1	-3.275787000	-1.387723000	2.365964000
6	6.553306000	-0.708786000	0.835426000	6	-3.332938000	-1.516711000	4.508468000
6	6.084413000	-2.148828000	-1.107479000	1	-3.354357000	-2.618683000	4.488648000
6	3.644997000	-2.063836000	0.794815000	1	-4.363119000	-1.160773000	4.662762000
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1	5.309016000	1.598434000	0.865764000	1	-0.638055000	-1.121728000	3.910551000
1	3.727887000	2.327278000	0.730395000	1	-0.800508000	-1.092398000	2.137368000
6	5.277581000	2.712642000	-2.749144000	1	-1.225099000	-2.563767000	3.049227000
6	6.221325000	3.981033000	0.873977000	1	4.276563000	0.113548000	2.191572000
1	4.507189000	4.200035000	-0.364002000	6	4.918759000	-0.723255000	4.056275000
6	6.068235000	3.388047000	-1.590444000	6	2.570573000	0.009723000	3.468797000
1	5.920447000	1.978105000	-3.254810000	1	1.826200000	0.136352000	2.669352000
1	5.037675000	3.456502000	-3.522356000	1	2.762730000	0.997347000	3.920028000
1	7.022941000	2.857893000	-1.429159000	1	2.127463000	-0.633139000	4.247003000
1	6.358413000	4.412474000	-1.876064000	1	5.859814000	-1.174361000	3.707488000
6	-3.571827000	-3.125804000	-1.225310000	1	4.543025000	-1.340646000	4.887918000
6	-5.858705000	-2.469470000	-2.203806000	1	5.152872000	0.270232000	4.472335000
1	-5.220289000	-2.364552000	-0.187683000	1	3.363925000	-2.551594000	-1.832086000
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6	-5.537088000	-0.348235000	-3.585949000	6	3.830596000	-4.657928000	-1.883523000
1	-3.497564000	-0.273293000	-2.956439000	1	0.928087000	-2.827691000	-1.277661000
1	-5.122624000	-0.041507000	-4.562618000	1	1.146999000	-4.599392000	-1.269542000
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6	-5.679719000	-1.878999000	-3.607429000	1	4.900802000	-4.604088000	-1.639553000
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1	-6.536931000	-2.171496000	-4.238758000	6	1.797452000	3.353454000	-1.158009000
1	-4.789341000	-2.311484000	-4.086978000	6	2.273413000	3.422366000	-3.621038000
6	-2.111482000	2.687402000	4.071587000	1	3.514119000	4.149255000	-2.067149000
6	-2.782829000	0.550551000	3.109711000	1	1.590231000	2.590192000	-3.849583000
6	-3.239046000	2.657600000	1.907791000	1	3.035184000	3.462811000	-4.416481000
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6	-2.183035000	1.300444000	4.133193000	1	1.395000000	4.380687000	-1.181231000
6	-2.713042000	-0.971284000	3.209239000	1	2.153438000	3.168997000	-0.136227000
6	-3.700813000	3.475222000	0.699389000	1	0.955918000	2.674211000	-1.338005000
1	-2.535445000	4.437097000	2.899818000	6	-2.747911000	-3.207250000	0.068083000
1	-1.748594000	0.779229000	4.989090000	6	-2.647757000	-3.094573000	-2.449530000
1	-1.641340000	3.252284000	4.880894000	1	-4.107521000	-4.092137000	-1.282496000
6	2.862557000	-4.228485000	2.401049000	1	-2.066083000	-2.163967000	-2.518062000
6	3.209569000	-3.271469000	0.180617000	1	-3.193176000	-3.223507000	-3.394679000
6	3.607840000	-1.917406000	2.208552000	1	-1.921169000	-3.921203000	-2.382953000

6	3.223518000	-3.019422000	2.986178000	1	-3.395693000	-3.316858000	0.953504000
6	2.841350000	-4.338105000	1.014142000	1	-2.112330000	-2.324842000	0.215659000
6	3.027349000	-3.466955000	-1.325954000	1	-2.087608000	-4.089492000	0.036821000
6	3.880899000	-0.595988000	2.927246000	1	6.622389000	4.979107000	0.632387000
1	3.196130000	-2.921578000	4.073591000	1	7.080916000	3.308079000	1.037371000
1	2.511786000	-5.274753000	0.559534000	1	5.675744000	4.063386000	1.828456000
1	2.573892000	-5.078453000	3.024867000	1	-7.495451000	0.033295000	-2.613948000
6	3.946999000	2.050698000	-2.280989000	1	-7.492461000	0.187936000	-4.376183000
6	2.900698000	3.249260000	-2.225596000	1	-6.761090000	1.460555000	-3.375203000

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15	2.352544000	0.899466000	-0.311956000	1	1.691932000	-2.761070000	-3.530328000
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15	-0.795217000	0.670104000	-0.254552000	1	1.868455000	-1.134378000	-2.835880000
15	-2.352525000	-0.899488000	-0.311763000	6	-3.947697000	-0.204324000	-0.120564000
7	4.407306000	-1.077883000	0.038911000	6	-5.908965000	1.198995000	0.153553000
7	-4.407333000	1.077886000	0.038829000	6	-6.299858000	-0.268029000	0.384923000
6	3.947701000	0.204322000	-0.120602000	1	-7.274649000	-0.507928000	-0.063827000
6	5.908924000	-1.199017000	0.153802000	1	-6.394793000	-0.436679000	1.465999000
6	6.299856000	0.268035000	0.384952000	6	-5.171341000	-1.165017000	-0.185875000
1	7.274654000	0.507845000	-0.063833000	6	-5.503615000	-1.521683000	-1.673896000
1	6.394803000	0.436833000	1.466005000	1	-6.572017000	-1.805740000	-1.707530000
6	5.171364000	1.164994000	-0.185942000	1	-5.406670000	-0.621060000	-2.299547000
6	5.503677000	1.521588000	-1.673973000	6	-4.700458000	-2.663207000	-2.309326000
1	6.572074000	1.805664000	-1.707595000	1	-3.636818000	-2.367468000	-2.319028000
1	5.406760000	0.620931000	-2.299578000	6	-4.828926000	-3.922348000	-1.446605000
6	4.700508000	2.663063000	-2.309476000	1	-5.884272000	-4.259099000	-1.453673000
1	3.636874000	2.367308000	-2.319170000	1	-4.238327000	-4.745291000	-1.884961000
6	4.828943000	3.922255000	-1.446825000	6	-4.372626000	-3.662244000	-0.010312000
1	4.238315000	4.745155000	-1.885222000	1	-3.290737000	-3.466158000	-0.008625000
1	5.884280000	4.259039000	-1.453922000	1	-4.528987000	-4.569812000	0.596411000
6	4.372667000	3.662227000	-0.010507000	6	-5.128554000	-2.497323000	0.656630000
1	4.529050000	4.569827000	0.596160000	1	-6.189992000	-2.808933000	0.635028000
1	3.290774000	3.466149000	-0.008789000	6	-3.555484000	2.244949000	0.072601000
6	5.128606000	2.497341000	0.656480000	6	-3.046549000	2.701426000	1.320884000
1	6.190045000	2.808940000	0.634804000	6	-2.248052000	3.853708000	1.332455000
6	3.555438000	-2.244933000	0.072700000	1	-1.847076000	4.215072000	2.282025000
6	3.046390000	-2.701287000	1.320979000	6	-1.939025000	4.537730000	0.161187000
6	2.247848000	-3.853537000	1.332594000	1	-1.311385000	5.431891000	0.195906000
1	1.846779000	-4.214791000	2.282167000	6	-2.414086000	4.062582000	-1.056369000
6	1.938887000	-4.537650000	0.161365000	1	-2.142969000	4.586249000	-1.975740000
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1	6.245602000	-2.826280000	-1.272422000	6	-5.142413000	-2.903148000	-3.755865000
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1	4.553199000	3.708914000	-4.222912000	6	-4.766736000	-2.303400000	2.174563000
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6	5.902185000	2.822325000	3.072631000	1	-5.669946000	-2.673977000	4.140550000
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1	6.859192000	2.316474000	2.863232000	1	-3.235144000	-2.644817000	3.676391000
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6	3.275261000	-1.982331000	2.652789000	1	-3.199912000	3.693752000	4.028373000
1	3.969166000	-1.150823000	2.469590000	1	-4.160112000	2.325901000	4.619310000
6	3.902098000	-2.903870000	3.717070000	1	-4.816399000	3.399204000	3.358060000
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1	4.159657000	-2.325439000	4.619464000	1	-1.525566000	0.657765000	2.499139000
1	4.815940000	-3.398972000	3.358407000	1	-2.188722000	0.821792000	4.144709000
6	1.977405000	-1.364030000	3.208097000	1	-1.227455000	2.139798000	3.433868000
1	1.227071000	-2.139364000	3.433675000	6	-3.620497000	2.427823000	-2.528287000
1	1.525349000	-0.657429000	2.498846000	1	-4.282604000	1.563010000	-2.401956000
1	2.188307000	-0.821333000	4.144509000	6	-2.407826000	1.943054000	-3.347117000
6	3.620616000	-2.428049000	-2.528185000	1	-1.691742000	2.760678000	-3.530362000
1	4.282701000	-1.563210000	-2.401913000	1	-2.741153000	1.565233000	-4.328026000
6	4.384794000	-3.501943000	-3.325926000	1	-1.868336000	1.134083000	-2.835716000
1	5.244287000	-3.906218000	-2.771037000	6	-4.384602000	3.501650000	-3.326188000
1	4.760026000	-3.081038000	-4.273096000	1	-5.244096000	3.906030000	-2.771377000
1	3.731732000	-4.350865000	-3.584340000	1	-4.759817000	3.080649000	-4.273322000
6	2.407986000	-1.943405000	-3.347148000	1	-3.731492000	4.350510000	-3.584679000

(CAAC-1)$_2$As$_2$

33	0.915245000	0.844916000	0.099776000	1	-3.707070000	-3.953935000	1.608399000
33	-0.915205000	-0.844805000	0.099814000	6	-2.792588000	-1.886073000	3.312006000
6	2.560276000	-0.038018000	-0.092370000	6	-5.286697000	-1.602651000	3.259578000
6	-2.560297000	0.038081000	-0.092139000	1	-3.835777000	-0.267964000	2.423523000
7	2.935182000	-1.347975000	-0.300026000	6	-3.530826000	-3.497620000	-3.064182000
6	3.850515000	0.848006000	-0.121048000	1	-2.179576000	-2.708673000	-1.592174000
7	-2.935324000	1.348002000	-0.299661000	6	0.414904000	-4.769486000	-0.065435000
6	-3.850493000	-0.848013000	-0.120717000	1	0.731507000	-4.662475000	2.056175000
6	4.418253000	-1.549410000	-0.519460000	6	1.204419000	-1.892297000	3.227041000
6	2.041042000	-2.481435000	-0.230687000	6	3.053775000	-3.599069000	3.178356000
6	4.966416000	-0.220535000	0.011251000	1	3.024022000	-1.724834000	2.124383000
6	4.088871000	1.911407000	1.022813000	1	0.236488000	-4.615375000	-2.199647000
6	3.999640000	1.572859000	-1.502394000	6	0.331148000	-1.916210000	-3.396050000
6	-4.418456000	1.549437000	-0.518706000	6	2.282449000	-3.445808000	-3.794049000
6	-2.041201000	2.481502000	-0.230943000	1	2.326477000	-1.575821000	-2.717785000
6	-4.966444000	0.220436000	0.011848000	1	4.723184000	4.120979000	-0.642248000
6	-4.088654000	-1.911493000	1.023094000	1	3.096881000	4.819187000	-0.660381000
6	-3.999751000	-1.572718000	-1.502124000	1	2.750637000	1.360997000	4.280631000
6	4.793344000	-1.765951000	-1.998735000	1	1.836366000	1.721168000	2.798958000
6	4.980806000	-2.740044000	0.268689000	1	2.887034000	2.961403000	3.530348000
6	1.767626000	-3.067580000	1.038612000	1	5.502444000	2.682655000	3.337887000
6	1.473886000	-3.033271000	-1.412315000	1	6.151781000	1.131367000	2.763180000
1	5.884434000	0.084243000	-0.511631000	1	5.230156000	1.204226000	4.285748000
1	5.229856000	-0.351014000	1.069441000	1	4.604008000	3.713944000	-3.207203000
6	3.371412000	3.257717000	0.821450000	1	2.982324000	4.443872000	-3.206453000
6	3.978745000	1.358871000	2.489030000	1	3.220929000	2.808248000	-3.866816000
1	5.159336000	2.149493000	0.874355000	6	-0.415253000	4.769743000	-0.066791000
6	3.261678000	2.905732000	-1.677755000	1	-0.237086000	4.614823000	-2.200963000
1	5.077908000	1.768726000	-1.652295000	6	-2.282776000	3.444405000	-3.794826000
1	3.696575000	0.888510000	-2.309272000	6	-0.331629000	1.914823000	-3.396067000
6	-4.793808000	1.766373000	-1.997841000	1	-2.327007000	1.574951000	-2.717677000
6	-4.980933000	2.739861000	0.269831000	1	-0.731499000	4.663495000	2.054915000
6	-1.474245000	3.032904000	-1.412871000	6	-1.203742000	1.893150000	3.226505000
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1	-5.884497000	-0.084323000	-0.510983000	1	-3.023710000	1.725593000	2.124499000
1	-5.229777000	0.350730000	1.070086000	1	-4.723249000	-4.120890000	-0.642121000
6	-3.371283000	-3.257816000	0.821508000	1	-3.096969000	-4.819143000	-0.660503000
6	-3.978248000	-1.359038000	2.489333000	1	-2.749930000	-1.361415000	4.280789000
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6	-3.261814000	-2.905583000	-1.677671000	1	-2.886844000	-2.961808000	3.530579000
1	-5.078033000	-1.768566000	-1.651943000	1	-5.502106000	-2.682558000	3.338319000
1	-3.696764000	-0.888276000	-2.308956000	1	-6.151215000	-1.131128000	2.763731000
1	5.890907000	-1.768261000	-2.088819000	1	-5.229435000	-1.204208000	4.286193000
1	4.407295000	-0.977009000	-2.655415000	1	-2.982630000	-4.443604000	-3.206521000
1	4.434096000	-2.734324000	-2.366648000	1	-3.221248000	-2.807925000	-3.866732000
1	4.516482000	-3.689924000	-0.035426000	1	-4.604295000	-3.713636000	-3.207066000
1	4.851978000	-2.617670000	1.350393000	1	-0.212060000	-5.662701000	-0.002164000
1	6.061267000	-2.817508000	0.069990000	1	0.453395000	-2.641900000	3.523979000
6	0.951017000	-4.206120000	1.088510000	1	0.684835000	-1.085989000	2.692290000
6	2.310000000	-2.524014000	2.361893000	1	1.637945000	-1.469777000	4.148575000
6	0.674106000	-4.180636000	-1.298199000	1	3.556415000	-3.138865000	4.044809000
6	1.655620000	-2.438411000	-2.809458000	1	3.814169000	-4.126898000	2.584049000
6	3.648196000	3.869019000	-0.551985000	1	2.359976000	-4.357986000	3.574382000
1	2.285682000	3.137830000	0.951520000	1	-0.381002000	-2.738639000	-3.572286000
1	3.707265000	3.953774000	1.608368000	1	0.514684000	-1.423273000	-4.365047000
6	2.793056000	1.885631000	3.311825000	1	-0.151869000	-1.194283000	-2.723821000
6	5.287231000	1.602711000	3.259139000	1	3.192612000	-3.919115000	-3.396941000
1	3.836475000	0.267778000	2.423186000	1	2.543469000	-2.946958000	-4.741789000
6	3.530557000	3.497890000	-3.064239000	1	1.575721000	-4.255550000	-4.036929000
1	2.179447000	2.708806000	-1.592180000	1	0.211629000	5.663046000	-0.003955000
1	-4.434415000	2.734771000	-2.365564000	1	-1.576074000	4.254112000	-4.037893000
1	-5.891386000	1.768938000	-2.087713000	1	-3.193076000	3.917761000	-3.398097000
1	-4.408054000	0.977511000	-2.654788000	1	-2.543554000	2.945143000	-4.742415000
1	-4.851932000	2.617255000	1.351487000	1	-0.515208000	1.421383000	-4.364799000
1	-6.061434000	2.817280000	0.071329000	1	0.151328000	1.193210000	-2.723456000
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6	-0.674561000	4.180392000	-1.299296000	1	-0.452542000	2.642740000	3.523036000
6	-1.656063000	2.437432000	-2.809744000	1	-0.684420000	1.086716000	2.691694000
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6	-2.309591000	2.524797000	2.361646000	1	-3.555388000	3.139955000	4.044914000
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1	-2.285534000	-3.137979000	0.951462000	1	-2.359052000	4.358932000	3.573887000

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33	1.101018000	-0.140350000	-2.421125000	1	3.848028000	1.067878000	-2.950875000
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6	3.603153000	0.010541000	-0.280024000	1	5.802795000	-2.439345000	-1.467934000
33	-1.187064000	-0.283848000	-2.522582000	1	6.361223000	-2.945111000	0.154002000
33	-1.874862000	0.444232000	-0.304923000	1	7.802898000	-0.414743000	0.860838000
6	-3.690357000	-0.028247000	0.005783000	1	6.713561000	-1.292280000	1.952221000
7	-4.325031000	0.665997000	1.004338000	1	6.512427000	0.456390000	1.708612000
6	-5.767325000	0.292405000	1.200078000	1	-5.832705000	-0.065588000	3.354572000
6	-6.046648000	-0.390788000	-0.148612000	1	-5.291578000	-1.483934000	2.434419000
6	-4.706661000	-1.005390000	-0.659408000	1	-7.006310000	-1.011129000	2.419378000

6	-3.716108000	1.762602000	1.730691000	1	-6.413454000	2.086727000	2.289616000
6	-5.974330000	-0.626457000	2.420516000	1	-7.716567000	1.149012000	1.527189000
6	-6.683542000	1.506897000	1.394511000	1	-6.674854000	2.175320000	0.526526000
1	-6.378179000	0.381000000	-0.858899000	6	-5.450269000	4.499929000	-0.114606000
1	-6.859837000	-1.122222000	-0.065834000	1	-4.777369000	2.514573000	-0.615380000
6	-4.588164000	-0.895610000	-2.201728000	6	-3.240607000	3.902270000	-1.155353000
6	-4.689155000	-2.540591000	-0.204161000	1	-2.782813000	4.842970000	-0.807589000
6	4.521756000	1.113232000	-0.890861000	1	-3.667965000	4.089939000	-2.154291000
6	5.816680000	0.268149000	-1.092002000	1	-2.447065000	3.149636000	-1.257698000
6	5.855671000	-0.812399000	0.004193000	1	-5.039849000	5.481322000	0.171975000
7	4.393169000	-0.894664000	0.355069000	1	-6.236457000	4.249188000	0.612187000
6	4.788899000	2.203631000	0.200039000	1	-5.924392000	4.624467000	-1.101893000
1	5.763064000	-0.229168000	-2.072395000	6	-1.354018000	-0.221205000	3.590478000
1	6.734625000	0.865443000	-1.074863000	1	-3.339458000	-0.593093000	2.898398000
6	6.760174000	-0.485019000	1.206936000	6	-3.460204000	-0.029010000	4.968675000
6	6.376435000	-2.131772000	-0.585317000	1	-3.369782000	-1.073842000	5.308062000
6	3.899681000	-1.919004000	1.262225000	1	-4.525470000	0.245970000	4.999806000
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1	3.847547000	2.460409000	0.705102000	1	-0.900047000	-0.123090000	2.594006000
6	5.483352000	2.487201000	-2.747516000	1	-1.211535000	-1.260491000	3.929000000
6	6.334436000	4.148390000	0.739167000	1	4.416761000	0.431637000	2.416226000
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6	6.233938000	3.302204000	-1.652893000	6	2.704529000	0.392183000	3.688459000
1	6.153335000	1.718322000	-3.158188000	1	1.966868000	0.410326000	2.873006000
1	5.246134000	3.138936000	-3.600105000	1	2.852587000	1.426758000	4.039841000
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1	-5.140746000	-2.538469000	0.797297000	1	3.664728000	-2.716215000	-1.292924000
1	-4.645267000	0.168063000	-2.487373000	6	1.904067000	-3.903860000	-1.026474000
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6	-7.003907000	-1.154052000	-3.158221000	1	1.787231000	-4.047122000	-2.112708000
6	-5.553240000	-3.185934000	-2.601170000	1	5.314332000	-4.646879000	-0.849891000
1	-6.730524000	-3.012257000	-0.811376000	1	4.175949000	-4.960114000	-2.181815000
1	-5.654585000	-4.391280000	-0.802981000	1	3.918610000	-5.711537000	-0.597873000
1	-6.355378000	-3.752878000	-3.105200000	6	1.932450000	3.188498000	-1.336677000
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6	-2.655164000	3.914658000	3.193800000	1	3.678261000	3.948116000	-2.226510000
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6	-2.854044000	0.131366000	3.562372000	1	2.235891000	3.077902000	-0.287635000
6	-4.343296000	3.429056000	-0.186983000	1	1.113962000	2.480850000	-1.511481000
1	-3.279408000	5.148008000	1.550262000	6	-2.621567000	-3.001411000	1.304300000
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6	3.182995000	-3.918411000	3.099226000	1	-1.917503000	-2.644129000	-1.435805000
6	3.524474000	-3.207697000	0.786672000	1	-2.894967000	-4.004559000	-2.030130000
6	3.834281000	-1.614430000	2.650010000	1	-1.615590000	-4.280296000	-0.839931000
6	3.484546000	-2.636246000	3.544887000	1	-3.295689000	-2.928385000	2.173980000
6	3.187878000	-4.186062000	1.734055000	1	-2.087651000	-2.047801000	1.198869000
6	3.375704000	-3.587162000	-0.688279000	1	-1.871391000	-3.774834000	1.537588000
6	4.044322000	-0.211659000	3.221652000	1	6.733611000	5.118473000	0.399996000
1	3.438457000	-2.415824000	4.613530000	1	7.195249000	3.504954000	0.991368000
1	2.905850000	-5.182175000	1.386840000	1	5.768575000	4.327692000	1.668220000
1	2.921013000	-4.703442000	3.813326000	1	-7.585988000	-1.272473000	-2.232556000
6	4.155710000	1.849430000	-2.237570000	1	-7.559256000	-1.674928000	-3.955591000
6	3.089397000	3.025041000	-2.335804000	1	-6.994530000	-0.080926000	-3.410243000

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33	-0.848314000	0.774920000	-0.106464000	1	2.040560000	-0.973630000	-2.772589000
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7	-4.735549000	1.101205000	-0.037724000	6	-6.673375000	-0.180865000	0.291191000
6	4.293206000	0.193141000	-0.074804000	1	-7.623799000	-0.441819000	-0.196424000
6	6.240814000	-1.255857000	-0.030981000	1	-6.836278000	-0.261734000	1.374152000
6	6.673308000	0.181023000	0.290837000	6	-5.528720000	-1.137514000	-0.135322000
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6	5.528540000	1.137627000	-0.135467000	1	-5.616017000	-0.768358000	-2.296522000
6	5.778647000	1.611816000	-1.607897000	6	-4.974829000	-2.822857000	-2.095678000
1	6.850993000	1.870872000	-1.686198000	1	-3.903793000	-2.554733000	-2.071752000
1	5.615516000	0.768519000	-2.296686000	6	-5.184544000	-4.000195000	-1.138630000
6	4.974470000	2.823060000	-2.095719000	1	-6.245908000	-4.314606000	-1.179374000
1	3.903416000	2.555025000	-2.071621000	1	-4.591137000	-4.869596000	-1.470386000
6	5.184442000	4.000361000	-1.138689000	6	-4.807798000	-3.628357000	0.295980000
1	4.591068000	4.869815000	-1.470360000	1	-3.722736000	-3.455192000	0.351319000
1	6.245829000	4.314680000	-1.179564000	1	-5.021017000	-4.479169000	0.964440000

6	4.807833000	3.628544000	0.295958000	6	-5.575440000	-2.397946000	0.813778000
1	5.021223000	4.479329000	0.964398000	1	-6.640410000	-2.688375000	0.737184000
1	3.722757000	3.455504000	0.351425000	6	-3.867093000	2.256936000	-0.017910000
6	5.575390000	2.398037000	0.813662000	6	-3.434124000	2.780067000	1.233277000
1	6.640384000	2.688365000	0.737014000	6	-2.634252000	3.931969000	1.232706000
6	3.867129000	-2.256934000	-0.018020000	1	-2.292478000	4.344071000	2.184690000
6	3.434338000	-2.780137000	1.233193000	6	-2.252826000	4.553722000	0.048113000
6	2.634485000	-3.932052000	1.232666000	1	-1.626747000	5.449250000	0.073640000
1	2.292848000	-4.344221000	2.184670000	6	-2.653237000	4.013656000	-1.169121000
6	2.252945000	-4.553763000	0.048090000	1	-2.325936000	4.488765000	-2.096506000
1	1.626898000	-5.449313000	0.073649000	6	-3.450938000	2.861249000	-1.236690000
6	2.653258000	-4.013679000	-1.169167000	6	-6.730207000	2.237961000	1.042031000
1	2.325922000	-4.488800000	-2.096534000	1	-6.449157000	1.919513000	2.052832000
6	3.450933000	-2.861259000	-1.236781000	1	-7.829625000	2.286172000	1.002403000
6	6.730265000	-2.237776000	1.041770000	1	-6.345513000	3.254332000	0.871199000
1	6.449139000	-1.919371000	2.052565000	6	-6.800154000	1.742097000	-1.380517000
1	7.829689000	-2.285847000	1.002178000	1	-6.458042000	2.759908000	-1.608603000
1	6.345706000	-3.254196000	0.870926000	1	-7.899266000	1.768986000	-1.319893000
6	6.799987000	-1.742015000	-1.380835000	1	-6.529476000	1.085247000	-2.215825000
1	6.457864000	-2.759838000	-1.608850000	6	-5.341797000	-3.175888000	-3.540005000
1	7.899107000	-1.768901000	-1.320335000	1	-6.408634000	-3.446806000	-3.628352000
1	6.529219000	-1.085199000	-2.216143000	1	-4.751311000	-4.033648000	-3.901132000
6	5.341240000	3.176063000	-3.540101000	1	-5.154926000	-2.330914000	-4.223170000
1	4.750724000	4.033836000	-3.901143000	6	-5.323923000	-2.094119000	2.335855000
1	5.154238000	2.331087000	-4.223227000	1	-5.241249000	-0.999575000	2.446912000
1	6.408072000	3.446948000	-3.628617000	6	-6.524581000	-2.548935000	3.182357000
6	5.323954000	2.094231000	2.335751000	1	-6.676472000	-3.638866000	3.095115000
1	5.240794000	0.999722000	2.446766000	1	-7.461260000	-2.060914000	2.865943000
6	6.524952000	2.548448000	3.182087000	1	-6.372210000	-2.323288000	4.250770000
1	6.677341000	3.638311000	3.094861000	6	-4.030423000	-2.675552000	2.928183000
1	7.461353000	2.059996000	2.865514000	1	-3.904789000	-2.320825000	3.964500000
1	6.372633000	2.322834000	4.250514000	1	-3.142683000	-2.366158000	2.359395000
6	4.030820000	2.676251000	2.928287000	1	-4.051165000	-3.776391000	2.963185000
1	3.905183000	2.321569000	3.964619000	6	-3.755591000	2.139622000	2.585893000
1	3.142855000	2.367277000	2.359623000	1	-4.451415000	1.309061000	2.406717000
1	4.052062000	3.777079000	2.963306000	6	-4.428598000	3.128172000	3.558082000
6	3.756074000	-2.139791000	2.585788000	1	-3.729562000	3.918491000	3.875412000
1	4.451913000	-1.309259000	2.406527000	1	-4.757094000	2.602514000	4.469596000
6	4.429223000	-3.128417000	3.557802000	1	-5.305541000	3.622579000	3.115581000
1	3.730250000	-3.918793000	3.875129000	6	-2.505080000	1.533041000	3.250580000
1	4.757801000	-2.602845000	4.469336000	1	-2.033814000	0.775920000	2.609403000
1	5.306135000	-3.622746000	3.115150000	1	-2.779348000	1.050861000	4.203516000
6	2.505717000	-1.533166000	3.250722000	1	-1.751007000	2.305730000	3.472223000
1	1.751686000	-2.305826000	3.472601000	6	-3.779515000	2.309703000	-2.626184000
1	2.034311000	-0.776082000	2.609603000	1	-4.459440000	1.459234000	-2.498345000
1	2.780220000	-1.050918000	4.203557000	6	-2.528920000	1.771846000	-3.348199000
6	3.779531000	-2.309763000	-2.626294000	1	-1.786634000	2.568294000	-3.519713000
1	4.459546000	-1.459362000	-2.498468000	1	-2.809315000	1.359748000	-4.331846000
6	4.478759000	-3.352688000	-3.519736000	1	-2.040402000	0.973733000	-2.772569000
1	5.354498000	-3.807212000	-3.033119000	6	-4.478885000	3.352533000	-3.519620000
1	4.816364000	-2.886782000	-4.459901000	1	-5.354767000	3.806832000	-3.033049000
1	3.793655000	-4.171489000	-3.791804000	1	-4.816298000	2.886633000	-4.459858000
6	2.528969000	-1.771774000	-3.348264000	1	-3.793923000	4.171498000	-3.791556000

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6	-1.059117000	-0.272052000	-0.213347000	1	-3.279585000	1.230603000	1.436805000
7	-0.132026000	-1.268803000	-0.086365000	6	4.041721000	-0.609628000	0.357154000
6	-2.465037000	-0.918178000	-0.370418000	1	4.113243000	-0.574740000	-1.789198000
6	-0.702378000	-2.667636000	-0.167135000	6	1.642092000	0.471304000	-3.192923000
6	1.283363000	-1.028067000	0.071213000	6	2.267561000	-1.961059000	-3.396409000
6	-2.084568000	-2.366427000	-0.762179000	1	0.491217000	-1.173914000	-2.472555000
6	-3.363004000	-0.340270000	-1.504450000	1	3.678675000	-0.628828000	2.473699000
6	-3.260922000	-0.888232000	0.975503000	6	1.005888000	0.414306000	3.372082000
6	-0.794946000	-3.354091000	1.208991000	6	1.512590000	-2.041464000	3.635195000
6	0.114761000	-3.590138000	-1.080775000	1	-0.012941000	-1.180253000	2.390375000
6	2.097741000	-0.889211000	-1.087746000	1	-5.730563000	0.026983000	0.017608000
6	1.846159000	-0.916680000	1.371584000	1	-5.467005000	1.744648000	0.349980000
1	-2.843627000	-3.095157000	-0.441539000	1	5.117261000	-0.450029000	0.468521000
1	-2.017922000	-2.426834000	-1.860380000	1	2.685362000	0.817949000	-3.270632000
6	-4.167287000	0.927594000	-1.190679000	1	1.073916000	1.228292000	-2.636052000
1	-4.083061000	-1.142437000	-1.752982000	1	1.229688000	0.420640000	-4.214138000
6	-4.006293000	0.418239000	1.269419000	1	1.767848000	-2.041433000	-4.375527000
1	-4.002781000	-1.706159000	0.925407000	1	2.274000000	-2.959014000	-2.934072000
1	-2.592372000	-1.127583000	1.816089000	1	3.315141000	-1.680534000	-3.590634000
1	-1.287532000	-4.331317000	1.087786000	1	2.017827000	0.725205000	3.678430000
1	-1.376994000	-2.775825000	1.936619000	1	0.384068000	0.359679000	4.280897000
1	0.203134000	-3.538935000	1.627809000	1	0.593518000	1.201146000	2.725920000
1	1.146260000	-3.712999000	-0.718503000	1	1.582600000	-3.030583000	3.157802000
1	0.145485000	-3.228709000	-2.115221000	1	0.824545000	-2.125745000	4.492085000
1	-0.356215000	-4.585278000	-1.090961000	1	2.508711000	-1.802179000	4.040868000
6	3.473605000	-0.685818000	-0.910883000	1	-2.746735000	-0.188712000	-2.405792000
6	1.556803000	-0.911915000	-2.519629000	1	-4.570976000	0.300414000	2.210065000
6	3.230362000	-0.717056000	1.481603000	15	-0.946776000	1.475908000	-0.212167000
6	1.024690000	-0.952477000	2.661201000	15	1.181663000	2.198233000	0.092294000
6	-4.945267000	0.800214000	0.122199000	15	0.857191000	4.168151000	-0.960608000

1	-3.489680000	1.793473000	-1.131571000
1	-4.856297000	1.124191000	-2.029961000
15	0.574247000	4.150245000	1.049820000

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6	-0.314203000	0.001601000	-0.809167000
7	1.044930000	0.001275000	-0.680928000
6	-0.690860000	0.004637000	-2.300717000
6	1.817152000	0.003794000	-1.976082000
6	1.716131000	-0.001271000	0.606575000
6	0.684061000	0.005843000	-3.030783000
6	-1.531132000	1.254278000	-2.702324000
6	-1.531447000	-1.243201000	-2.707338000
6	2.714917000	-1.235659000	-2.111764000
6	2.714919000	1.243768000	-2.106941000
6	2.040797000	1.232079000	1.238182000
6	2.040681000	-1.237125000	1.233331000
1	0.774322000	-0.871864000	-3.686028000
1	0.774523000	0.885866000	-3.682900000
6	-0.982831000	2.629860000	-2.329680000
1	-2.539450000	1.149702000	-2.272547000
6	-0.983520000	-2.620378000	-2.340062000
1	-2.539781000	-1.140060000	-2.277246000
1	-1.667507000	-1.181798000	-3.801924000
1	3.243044000	-1.192161000	-3.076962000
1	2.139378000	-2.169798000	-2.085462000
1	3.474479000	-1.268496000	-1.317688000
1	3.474493000	1.273500000	-1.312754000
1	2.139383000	2.177798000	-2.077000000
1	3.243049000	1.204020000	-3.072298000
6	2.769871000	1.196177000	2.435985000
6	1.578060000	2.599367000	0.734820000
6	2.769792000	-1.206013000	2.431243000
6	1.577781000	-2.602359000	0.724581000
1	0.013464000	2.821102000	-2.759724000
1	-1.652664000	3.418270000	-2.707820000
1	0.012817000	-2.810120000	-2.770674000
6	3.150239000	-0.006093000	3.022947000
1	3.032898000	2.136157000	2.925978000
6	0.528654000	3.208743000	1.686599000
6	2.737424000	3.591687000	0.529684000
1	1.083686000	2.451087000	-0.232512000
1	3.032763000	-2.147944000	2.917507000
6	0.528323000	-3.215321000	1.673989000
6	2.737026000	-3.593999000	0.515498000
1	1.083387000	-2.450219000	-0.242143000
1	3.722442000	-0.007946000	3.954289000
1	0.965714000	3.432514000	2.673622000
1	-0.319641000	2.525254000	1.833373000
1	0.142209000	4.154711000	1.272195000
1	2.363570000	4.524607000	0.077140000
1	3.523881000	3.189813000	-0.125567000
1	3.210731000	3.864328000	1.486590000
1	0.965422000	-3.443182000	2.660057000
1	0.141589000	-4.159506000	1.255804000
1	-0.319770000	-2.532194000	1.823606000
1	3.523504000	-3.189628000	-0.138192000
1	2.363048000	-4.525081000	0.059288000
1	3.210336000	-3.870469000	1.471305000
1	-1.667321000	1.197251000	-3.797131000
1	-1.653451000	-3.407132000	-2.721471000
1	-0.915967000	-2.746697000	-1.249039000
1	-0.915071000	2.751821000	-1.238173000
15	-1.318222000	-0.001362000	0.635560000
15	-3.455342000	0.000416000	-0.073999000
15	-4.320327000	-1.020639000	1.733301000
15	-4.320045000	1.013924000	1.737775000

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6	-1.355778000	0.879940000	-0.205678000
7	-2.055948000	-0.282616000	-0.076850000
6	-2.360972000	2.052600000	-0.359172000
6	-3.561005000	-0.120228000	-0.145646000
6	-1.437346000	-1.579110000	0.080899000
6	-3.654813000	1.291225000	-0.739796000
6	-2.060176000	3.071004000	-1.498854000
6	-2.542586000	2.832940000	0.984777000
6	-4.233525000	-0.218886000	1.236521000
6	-4.230633000	-1.159348000	-1.053246000
6	-1.098613000	-2.333424000	-1.078112000
6	-1.173208000	-2.088725000	1.381786000
1	-4.560487000	1.821665000	-0.410655000
1	-3.704752000	1.210851000	-1.837594000
6	-1.058753000	4.192173000	-1.196411000
1	-3.030355000	3.544267000	-1.740530000
6	-1.489869000	3.909881000	1.267920000
1	-3.532723000	3.321948000	0.937523000
1	-2.584530000	2.128232000	1.828761000
1	-5.309135000	-0.012120000	1.124387000
1	-3.830098000	0.499203000	1.960537000
1	-4.135136000	-1.229366000	1.654465000
1	-4.065948000	-2.184819000	-0.690526000
1	-3.880981000	-1.091425000	-2.089851000
1	-5.316497000	-0.977228000	-1.056881000
6	-0.545703000	-3.610147000	-0.899945000
6	-1.275502000	-1.826052000	-2.511911000
6	-0.621267000	-3.374421000	1.491958000
6	-1.418093000	-1.304534000	2.672330000
6	-1.385066000	4.911885000	0.115296000
1	-0.038668000	3.779152000	-1.143720000
1	-1.061758000	4.904444000	-2.039179000
1	-0.508149000	3.435070000	1.434780000
6	-0.318200000	-4.135945000	0.368266000
1	-0.280016000	-4.202550000	-1.778137000
6	0.074677000	-1.552491000	-3.201883000
6	-2.110104000	-2.793007000	-3.374539000
1	-1.806103000	-0.865459000	-2.465687000
1	-0.413600000	-3.781089000	2.484106000
6	-0.102076000	-0.925519000	3.378111000
6	-2.333962000	-2.063328000	3.651589000
1	-1.912820000	-0.363826000	2.403609000
1	-2.343909000	5.455506000	0.013259000
1	-0.617742000	5.672774000	0.334833000
1	0.113058000	-5.133925000	0.480190000
1	0.682030000	-2.469080000	-3.276829000
1	0.661362000	-0.798437000	-2.659870000
1	-0.093754000	-1.179112000	-4.225484000
1	-2.332708000	-2.335471000	-4.352218000
1	-3.064426000	-3.063643000	-2.899666000
1	-1.563466000	-3.728666000	-3.573334000
1	0.469109000	-1.819374000	3.676877000
1	-0.316569000	-0.346302000	4.291395000
1	0.541379000	-0.311982000	2.732516000
1	-3.268644000	-2.400075000	3.178368000
1	-2.598511000	-1.419043000	4.505742000
1	-1.834094000	-2.955786000	4.061052000
1	-1.753447000	2.517197000	-2.401191000
1	-1.753073000	4.425170000	2.207401000
33	0.494415000	1.248855000	-0.205810000
33	1.864715000	-0.814274000	0.103354000
33	3.784055000	0.209891000	-1.102530000
33	3.711126000	0.494701000	1.134803000

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6	0.963190000	-0.788112000	0.000000000
7	0.564139000	-2.087960000	0.000000000
6	2.496609000	-0.716443000	0.000000000
6	1.679861000	-3.107876000	0.000000000
6	-0.833571000	-2.483921000	0.000000000
6	2.940374000	-2.209118000	0.000000000
6	3.058150000	0.029257000	1.247952000
6	3.058150000	0.029257000	-1.247952000
6	1.629376000	-4.013500000	-1.239338000
6	1.629376000	-4.013500000	1.239338000
6	-1.516317000	-2.671773000	1.235220000
6	-1.516317000	-2.671773000	-1.235220000
1	2.848988000	-1.504137000	-2.811906000
6	-3.499045000	-3.375008000	0.000000000
1	-3.373669000	-3.285934000	2.141816000
6	-1.639873000	-1.137325000	3.246510000
6	-0.953117000	-3.539879000	3.575316000
1	0.123288000	-2.051018000	2.458877000
1	-3.373669000	-3.285934000	-2.141816000
6	-1.639873000	-1.137325000	-3.246510000
6	-0.953117000	-3.539879000	-3.575316000
1	0.123288000	-2.051018000	-2.458877000
1	-4.530823000	-3.735815000	0.000000000
1	-2.694408000	-1.369224000	3.468686000

1	3.562665000	-2.428535000	-0.878838000	1	-1.612734000	-0.259430000	2.585495000
1	3.562665000	-2.428535000	0.878838000	1	-1.152097000	-0.866702000	4.197630000
6	2.605347000	-0.445635000	2.626705000	1	-0.426711000	-3.285340000	4.509646000
1	2.819100000	1.099895000	1.151142000	1	-0.477309000	-4.436608000	3.152897000
6	2.605347000	-0.445635000	-2.626705000	1	-1.985195000	-3.810969000	3.849736000
1	2.819100000	1.099895000	-1.151142000	1	-2.694408000	-1.369224000	-3.468686000
1	4.158875000	-0.035853000	-1.180794000	1	-1.152097000	-0.866702000	-4.197630000
1	2.469498000	-4.724037000	-1.197587000	1	-1.612734000	-0.259430000	-2.585495000
1	1.716950000	-3.444532000	-2.173676000	1	-0.477309000	-4.436608000	-3.152897000
1	0.699651000	-4.599172000	-1.269560000	1	-0.426711000	-3.285340000	-4.509646000
1	0.699651000	-4.599172000	1.269560000	1	-1.985195000	-3.810969000	-3.849736000
1	1.716950000	-3.444532000	2.173676000	1	4.158875000	-0.035853000	1.180794000
1	2.469498000	-4.724037000	1.197587000	1	3.108001000	0.141438000	-3.411490000
6	-2.841669000	-3.130127000	1.200834000	1	1.521326000	-0.312606000	-2.760491000
6	-0.923176000	-2.343226000	2.606024000	1	1.521326000	-0.312606000	2.760491000
6	-2.841669000	-3.130127000	-1.200834000	33	-0.323764000	0.599468000	0.000000000
6	-0.923176000	-2.343226000	-2.606024000	33	0.949163000	2.732577000	0.000000000
1	2.848988000	-1.504137000	2.811906000	33	-0.881484000	3.967409000	-1.130181000
1	3.108001000	0.141438000	3.411490000	33	-0.881484000	3.967409000	1.130181000

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6	0.866671000	0.142258000	0.000000000	1	2.837456000	-0.237864000	-2.812897000
7	0.694146000	-1.203755000	0.000000000	6	-3.094596000	-3.155220000	0.000000000
6	2.364052000	0.476839000	0.000000000	1	-2.985927000	-3.046915000	2.141863000
6	1.968467000	-2.019236000	0.000000000	6	-1.633240000	-0.638236000	3.247111000
6	-0.616678000	-1.831296000	0.000000000	6	-0.556838000	-2.893995000	3.574738000
6	3.056441000	-0.918079000	0.000000000	1	0.256916000	-1.246718000	2.459132000
6	2.788331000	1.309220000	1.247939000	1	-2.985927000	-3.046915000	-2.141863000
6	2.788331000	1.309220000	-1.247939000	6	-1.633240000	-0.638236000	-3.247111000
6	2.071656000	-2.919933000	-1.239454000	6	-0.556838000	-2.893995000	-3.574738000
6	2.071656000	-2.919933000	1.239454000	1	0.256916000	-1.246718000	-2.459132000
6	-1.257359000	-2.130864000	1.235558000	1	-4.051754000	-3.683012000	0.000000000
6	-1.257359000	-2.130864000	-1.235558000	1	-2.634998000	-1.041438000	3.468649000
1	3.706877000	-1.027601000	-0.879001000	1	-1.751399000	0.232678000	2.586817000
1	3.706877000	-1.027601000	0.879001000	1	-1.197201000	-0.291439000	4.198574000
6	2.420467000	0.764985000	2.626454000	1	-0.080391000	-2.555807000	4.509306000
1	2.371379000	2.323221000	1.146923000	1	0.062086000	-3.698391000	3.151719000
6	2.420467000	0.764985000	-2.626454000	1	-1.529216000	-3.333773000	3.848685000
1	2.371379000	2.323221000	-1.146923000	1	-2.634998000	-1.041438000	-3.468649000
1	3.884470000	1.429531000	-1.181958000	1	-1.197201000	-0.291439000	-4.198574000
1	3.019931000	-3.477879000	-1.197388000	1	-1.751399000	0.232678000	-2.586817000
1	2.062101000	-2.344258000	-2.173712000	1	0.062086000	-3.698391000	-3.151719000
1	1.254514000	-3.654568000	-1.269988000	1	-0.080391000	-2.555807000	-4.509306000
1	1.254514000	-3.654568000	1.269988000	1	-1.529216000	-3.333773000	-3.848685000
1	2.062101000	-2.344258000	2.173712000	1	3.884470000	1.429531000	1.181958000
1	3.019931000	-3.477879000	1.197388000	1	2.817032000	1.428204000	-3.411373000
6	-2.487486000	-2.804209000	1.200964000	1	1.329394000	0.714781000	-2.760316000
6	-0.726620000	-1.708441000	2.606184000	1	1.329394000	0.714781000	2.760316000
6	-2.487486000	-2.804209000	-1.200964000	33	-0.640304000	1.291003000	0.000000000
6	-0.726620000	-1.708441000	-2.606184000	15	0.259388000	3.486233000	0.000000000
1	2.837456000	-0.237864000	2.812897000	15	-1.503573000	4.431842000	-1.019190000
1	2.817032000	1.428204000	3.411373000	15	-1.503573000	4.431842000	1.019190000

(CAAC-3)P-AsP_2

6	0.825531000	0.025135000	0.000000000	1	2.773963000	-0.356929000	-2.813882000
7	0.664310000	-1.333981000	0.000000000	6	-3.094038000	-3.340469000	0.000000000
6	2.327659000	0.361243000	0.000000000	1	-2.989587000	-3.225793000	2.142100000
6	1.938234000	-2.137785000	0.000000000	6	-1.681367000	-0.755232000	3.212066000
6	-0.639530000	-1.970994000	0.000000000	6	-0.582053000	-2.993681000	3.592166000
6	3.021962000	-1.032134000	0.000000000	1	0.220249000	-1.360693000	2.448708000
6	2.755863000	1.188530000	1.248941000	1	-2.989587000	-3.225793000	-2.142100000
6	2.755863000	1.188530000	-1.248941000	6	-1.681367000	-0.755232000	-3.212066000
6	2.050495000	-3.039142000	-1.239573000	6	-0.582053000	-2.993681000	-3.592166000
6	2.050495000	-3.039142000	1.239573000	1	0.220249000	-1.360693000	-2.448708000
6	-1.277884000	-2.278889000	1.234327000	1	-4.040287000	-3.887703000	0.000000000
6	-1.277884000	-2.278889000	-1.234327000	1	-2.679146000	-1.165865000	3.438253000
1	3.673335000	-1.139620000	-0.878668000	1	-1.807208000	0.096747000	2.528964000
1	3.673335000	-1.139620000	0.878668000	1	-1.254613000	-0.379955000	4.157079000
6	2.370717000	0.650806000	2.625161000	1	-0.118037000	-2.631886000	4.524241000
1	2.356575000	2.210248000	1.149366000	1	0.051778000	-3.796749000	3.188757000
6	2.370717000	0.650806000	-2.625161000	1	-1.550314000	-3.442204000	3.866721000
1	2.356575000	2.210248000	-1.149366000	1	-2.679146000	-1.165865000	-3.438253000
1	3.853729000	1.296015000	-1.190028000	1	-1.254613000	-0.379955000	-4.157079000
1	3.002348000	-3.591211000	-1.197953000	1	-1.807208000	0.096747000	-2.528964000
1	2.036346000	-2.463343000	-2.173853000	1	0.051778000	-3.796749000	-3.188757000
1	1.237683000	-3.778701000	-1.270948000	1	-0.118037000	-2.631886000	-4.524241000
1	1.237683000	-3.778701000	1.270948000	1	-1.550314000	-3.442204000	-3.866721000
1	2.036346000	-2.463343000	2.173853000	1	3.853729000	1.296015000	1.190028000
1	3.002348000	-3.591211000	1.197953000	1	2.768740000	1.309355000	-3.413256000
6	-2.494715000	-2.975838000	1.201080000	1	1.278012000	0.612542000	-2.747955000
6	-0.759277000	-1.829397000	2.600236000	1	1.278012000	0.612542000	2.747955000
6	-2.494715000	-2.975838000	-1.201080000	15	-0.589111000	1.062875000	0.000000000
6	-0.759277000	-1.829397000	-2.600236000	33	0.171976000	3.311433000	0.000000000
1	2.773963000	-0.356929000	2.813882000	15	-1.800546000	4.152846000	-1.016552000

1	2.768740000	1.309355000	3.413256000	15	-1.800546000	4.152846000	1.016552000

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6	-0.147628000	0.814568000	-0.461406000	1	-1.018847000	3.901662000	0.784686000
7	-1.466438000	0.471165000	-0.378744000	6	-2.993029000	-2.912392000	1.712127000
6	-0.001071000	2.097335000	-1.297915000	1	-2.697499000	-3.993813000	-0.119788000
6	-2.421037000	1.391738000	-1.096638000	6	-0.313229000	-3.139919000	-1.715234000
6	-1.935647000	-0.694844000	0.348175000	6	-2.622441000	-2.790158000	-2.668538000
6	-1.464403000	2.453007000	-1.692056000	1	-1.211037000	-1.252323000	-2.157426000
6	0.878352000	1.886187000	-2.567050000	1	-3.085704000	-1.625678000	3.429156000
6	0.653082000	3.262697000	-0.495774000	6	-0.896367000	0.408310000	3.600888000
6	-3.440458000	2.024028000	-0.136692000	6	-3.276637000	1.182686000	3.287378000
6	-3.208441000	0.659529000	-2.194117000	1	-1.657400000	1.456642000	1.901656000
6	-2.050569000	-1.946407000	-0.319509000	1	-3.419944000	-3.770332000	2.237965000
6	-2.274330000	-0.581515000	1.725864000	1	-0.578857000	-4.145314000	-1.349238000
1	-1.731398000	3.453250000	-1.323157000	1	0.478351000	-2.736634000	-1.067885000
1	-1.572212000	2.490552000	-2.785154000	1	0.096744000	-3.254087000	-2.732510000
6	0.517474000	0.732022000	-3.499575000	1	-2.233853000	-2.871527000	-3.696784000
1	1.925890000	1.766969000	-2.249750000	1	-3.529936000	-2.169793000	-2.698452000
6	0.044930000	3.623788000	0.857451000	1	-2.923672000	-3.802979000	-2.356269000
1	1.719756000	3.030693000	-0.351274000	1	-1.202157000	-0.346593000	4.343853000
1	0.627668000	4.146761000	-1.157745000	1	-0.661299000	1.336494000	4.147824000
1	-4.101409000	2.695249000	-0.706823000	1	0.022259000	0.055773000	3.110782000
1	-2.956783000	2.617351000	0.649854000	1	-4.111884000	1.358195000	2.593900000
1	-4.071713000	1.259182000	0.337812000	1	-3.058740000	2.132532000	3.802359000
1	-3.835043000	-0.139089000	-1.772051000	1	-3.626169000	0.472773000	4.054116000
1	-2.549918000	0.223305000	-2.956144000	1	0.844245000	2.836642000	-3.129082000
1	-3.876009000	1.377014000	-2.696126000	1	0.573758000	4.487491000	1.290603000
6	-2.595812000	-3.030294000	0.384330000	1	0.134492000	2.791644000	1.571790000
6	-1.542732000	-2.209201000	-1.737200000	1	0.621857000	-0.239705000	-2.993821000
6	-2.813432000	-1.702442000	2.374275000	15	1.057939000	-0.185303000	0.341743000
6	-2.015388000	0.665613000	2.571210000	15	3.055095000	0.761520000	-0.080752000
1	-0.509428000	0.807325000	-3.891957000	15	4.071983000	0.032519000	1.788867000
1	1.193565000	0.724203000	-4.369139000	33	4.332879000	-1.232395000	0.070533000

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15	2.152929000	-1.307005000	-0.018845000	1	1.912771000	0.772162000	2.614729000
15	0.902078000	0.517229000	-0.037557000	6	-3.853108000	0.895254000	-0.043641000
15	-0.902091000	-0.517158000	-0.037725000	6	-6.051602000	-0.122816000	-0.136005000
15	-2.152968000	1.307044000	-0.018756000	6	-6.162101000	1.369490000	-0.474393000
7	4.549386000	0.284951000	-0.104473000	1	-7.071809000	1.825517000	-0.056253000
7	-4.549394000	-0.284964000	-0.104450000	1	-6.215202000	1.480853000	-1.569420000
6	3.853082000	-0.895256000	-0.043672000	6	-4.875993000	2.066101000	0.029061000
6	6.051593000	0.122786000	-0.136072000	6	-5.053229000	2.579350000	1.496039000
6	6.162083000	-1.369542000	-0.474369000	1	-6.053059000	3.047637000	1.553882000
1	7.071769000	-1.825550000	-0.056159000	1	-5.068393000	1.729212000	2.194369000
1	6.215232000	-1.480985000	-1.569385000	6	-4.016056000	3.606276000	1.963218000
6	4.875949000	-2.066112000	0.029085000	1	-3.023082000	3.130327000	2.020791000
6	5.053152000	-2.579288000	1.496090000	6	-3.952207000	4.809261000	1.018496000
1	6.052985000	-3.047560000	1.553986000	1	-4.925318000	5.337220000	1.030584000
1	5.068288000	-1.729113000	2.194379000	1	-3.200005000	5.535529000	1.369553000
6	4.015986000	-3.606208000	1.963291000	6	-3.626510000	4.356243000	-0.407676000
1	3.023000000	-3.130278000	2.020807000	1	-2.597490000	3.966786000	-0.440600000
6	3.952195000	-4.809243000	1.018628000	1	-3.662681000	5.213643000	-1.101853000
1	3.200010000	-5.535521000	1.369702000	6	-4.603878000	3.283111000	-0.905110000
1	4.925324000	-5.337166000	1.030760000	1	-5.586161000	3.769525000	-1.055314000
6	3.626512000	-4.356301000	-0.407573000	6	-3.926641000	-1.586047000	-0.172154000
1	3.662725000	-5.213735000	-1.101708000	6	-3.585053000	-2.130284000	-1.441936000
1	2.597478000	-3.966886000	-0.440533000	6	-3.004054000	-3.405320000	-1.483713000
6	4.603854000	-3.283162000	-0.905044000	1	-2.732162000	-3.836088000	-2.449914000
1	5.586149000	-3.769562000	-1.055230000	6	-2.750283000	-4.128545000	-0.322445000
6	3.926665000	1.586041000	-0.172205000	1	-2.293323000	-5.119732000	-0.381126000
6	3.585042000	2.130240000	-1.441988000	6	-3.062007000	-3.573801000	0.914115000
6	3.004086000	3.405294000	-1.483788000	1	-2.834310000	-4.134929000	1.823193000
1	2.732164000	3.836031000	-2.449994000	6	-3.640950000	-2.300985000	1.022428000
6	2.750411000	4.128584000	-0.322536000	6	-6.722266000	-0.989912000	-1.209665000
1	2.293505000	5.119795000	-0.381234000	1	-6.379605000	-0.736945000	-2.219702000
6	3.062165000	3.573876000	0.914033000	1	-7.809394000	-0.818264000	-1.175071000
1	2.834545000	4.135051000	1.823101000	1	-6.547828000	-2.062044000	-1.035606000
6	3.641038000	2.301031000	1.022362000	6	-6.719227000	-0.469494000	1.208807000
6	6.722225000	0.989806000	-1.209802000	1	-6.607357000	-1.536711000	1.441870000
1	6.379494000	0.736798000	-2.219803000	1	-7.797704000	-0.258751000	1.137817000
1	7.809348000	0.818120000	-1.175266000	1	-6.320287000	0.113780000	2.047265000
1	6.547835000	2.061954000	-1.035789000	6	-3.774050000	-1.389559000	-2.768348000
6	6.719242000	0.469545000	1.208714000	1	-4.308872000	-0.453670000	-2.557079000
1	6.607264000	1.536748000	1.441786000	6	-4.609840000	-2.201337000	-3.777251000
1	7.797740000	0.258919000	1.137680000	1	-4.063510000	-3.092185000	-4.126427000
1	6.320397000	-0.113788000	2.047183000	1	-4.833915000	-1.590214000	-4.666926000
6	3.773951000	1.389445000	-2.768372000	1	-5.563524000	-2.546025000	-3.351627000
1	4.308766000	0.453557000	-2.557073000	6	-2.429426000	-0.996768000	-3.410499000
6	4.609700000	2.201137000	-3.777374000	1	-1.831903000	-0.360193000	-2.744138000
1	4.063382000	3.091985000	-4.126568000	1	-2.605682000	-0.441625000	-4.346830000
1	4.833684000	1.589949000	-4.667026000	1	-1.827183000	-1.886197000	-3.657568000

1	5.563429000	2.545811000	-3.351841000	6	-3.875627000	-1.742094000	2.426785000
6	2.429278000	0.996640000	-3.410419000	1	-4.381441000	-0.775042000	2.321251000
1	1.827044000	1.886070000	-3.657504000	6	-2.552968000	-1.471541000	3.169795000
1	1.831778000	0.360118000	-2.743986000	1	-1.979750000	-2.399927000	3.325403000
1	2.605461000	0.441437000	-4.346728000	1	-2.758292000	-1.035285000	4.161545000
6	3.875760000	1.742181000	2.426718000	1	-1.912618000	-0.772110000	2.614711000
1	4.381595000	0.775141000	2.321199000	6	-4.772990000	-2.659084000	3.279301000
6	4.773126000	2.659213000	3.279194000	1	-5.715679000	-2.913769000	2.771848000
1	5.715807000	2.913897000	2.771723000	1	-5.023059000	-2.170680000	4.235351000
1	5.023204000	2.170838000	4.235255000	1	-4.265084000	-3.606465000	3.521646000
1	4.265211000	3.606595000	3.521524000	1	4.272659000	-3.929784000	2.986688000
6	2.553123000	1.471626000	3.169765000	1	4.289727000	-2.910207000	-1.893637000
1	1.979890000	2.400005000	3.325340000	1	-4.289756000	2.910115000	-1.893690000
1	2.758478000	1.035411000	4.161529000	1	-4.272755000	3.929910000	2.986589000

***trans*-(CAAC-3)$_2$P$_4$**

15	2.053257000	-1.465156000	-0.083013000	6	-6.061135000	0.332515000	0.032430000
15	0.942927000	0.439740000	-0.063926000	6	-6.112940000	1.878797000	-0.010315000
15	-0.942951000	-0.439752000	-0.063671000	1	-6.646551000	2.264192000	0.869836000
15	-2.053280000	1.465141000	-0.083133000	1	-6.685649000	2.214572000	-0.886217000
7	4.573401000	-0.051364000	0.006891000	6	-4.663591000	2.430275000	-0.057938000
7	-4.573428000	0.051356000	0.006789000	6	-4.373606000	3.366740000	1.154057000
6	3.777162000	-1.158788000	-0.040732000	1	-3.364134000	3.786485000	1.019931000
6	6.061101000	-0.332517000	0.032749000	1	-5.075527000	4.216573000	1.073538000
6	6.112923000	-1.878795000	-0.010176000	6	-4.467285000	2.765063000	2.554447000
1	6.646701000	-2.264325000	0.869816000	1	-5.464616000	2.350294000	2.772876000
1	6.685477000	-2.214417000	-0.886234000	6	-4.582590000	2.614084000	-2.691329000
6	4.663572000	-2.430287000	-0.057696000	1	-5.588125000	2.188691000	-2.840950000
6	4.373551000	-3.366648000	1.154367000	1	-4.419333000	3.343193000	-3.500956000
1	3.364005000	-3.786246000	1.020325000	6	-4.427627000	3.294943000	-1.333286000
1	5.075338000	-4.216592000	1.073846000	1	-3.413417000	3.719601000	-1.267852000
6	4.467432000	-2.764922000	2.554723000	6	-4.068054000	-1.305801000	0.034200000
1	5.464871000	-2.350374000	2.773077000	6	-3.838520000	-1.999078000	-1.187159000
6	4.582479000	-2.614254000	-2.691061000	6	-3.381175000	-3.323169000	-1.125744000
1	4.419250000	-3.343414000	-3.500647000	1	-3.198702000	-3.866424000	-2.055522000
1	5.587967000	-2.188767000	-2.840754000	6	-3.134314000	-3.954001000	0.088713000
6	4.427659000	-3.295069000	-1.332978000	1	-2.773726000	-4.985607000	0.110017000
1	3.413517000	-3.719880000	-1.267488000	6	-3.326490000	-3.254470000	1.275117000
6	4.068025000	1.305798000	0.034074000	1	-3.101309000	-3.744014000	2.225161000
6	3.838627000	1.998887000	-1.187414000	6	-3.782295000	-1.928407000	1.281550000
6	3.381280000	3.322986000	-1.126257000	6	-6.789698000	-0.285943000	-1.170998000
1	3.198905000	3.866097000	-2.056138000	1	-6.421628000	0.104870000	-2.127981000
6	3.134301000	3.954015000	0.088076000	1	-7.861839000	-0.044931000	-1.100604000
1	2.773708000	4.985624000	0.109177000	1	-6.695242000	-1.380904000	-1.177580000
6	3.326376000	3.254678000	1.274609000	6	-6.733382000	-0.215727000	1.300880000
1	3.101121000	3.744374000	2.224556000	1	-6.637853000	-1.308750000	1.364965000
6	3.782172000	1.928609000	1.281295000	1	-7.807835000	0.022773000	1.266166000
6	6.789846000	0.286074000	-1.170500000	1	-6.322071000	0.227952000	2.216285000
1	6.421928000	-0.104664000	-2.127578000	6	-4.004602000	-1.372927000	-2.573325000
1	7.861981000	0.045077000	-1.099968000	1	-4.427956000	-0.371028000	-2.438710000
1	6.695365000	1.381035000	-1.176998000	6	-4.959819000	-2.176964000	-3.475847000
6	6.733145000	0.215586000	1.301368000	1	-4.531751000	-3.156247000	-3.744047000
1	6.637675000	1.308610000	1.365511000	1	-5.141080000	-1.634239000	-4.418044000
1	7.807589000	-0.022977000	1.266835000	1	-5.933502000	-2.361788000	-2.999391000
1	6.321635000	-0.228128000	2.216662000	6	-2.651894000	-1.189891000	-3.288710000
6	4.004897000	1.372520000	-2.573458000	1	-1.960726000	-0.572706000	-2.698560000
1	4.428316000	0.370676000	-2.438630000	1	-2.803854000	-0.698307000	-4.264053000
6	4.960151000	2.176472000	-3.476016000	1	-2.159962000	-2.158234000	-3.475880000
1	4.532050000	3.155684000	-3.744421000	6	-3.884752000	-1.223759000	2.635906000
1	5.141542000	1.633599000	-4.418104000	1	-4.313176000	-0.229691000	2.464214000
1	5.933773000	2.361434000	-2.999491000	6	-2.500566000	-1.004825000	3.277281000
6	2.652270000	1.189258000	-3.288943000	1	-2.001471000	-1.962802000	3.496275000
1	2.160275000	2.157531000	-3.476312000	1	-2.607521000	-0.458705000	4.229314000
1	1.961099000	0.572109000	-2.698760000	1	-1.836614000	-0.423809000	2.622551000
1	2.804362000	0.697536000	-4.264194000	6	-4.798141000	-1.972301000	3.625324000
6	3.884552000	1.224208000	2.635785000	1	-5.792518000	-2.181312000	3.204901000
1	4.313020000	0.230123000	2.464312000	1	-4.936260000	-1.376172000	4.542219000
6	4.797852000	1.972971000	3.625119000	1	-4.358492000	-2.935870000	3.929340000
1	5.792257000	2.181919000	3.204730000	1	4.269032000	-3.538926000	3.313217000
1	4.935912000	1.377039000	4.542151000	1	5.125902000	-4.149466000	-1.270712000
1	4.358155000	2.936595000	3.928894000	1	-5.125738000	4.149450000	-1.271051000
6	2.500340000	1.005345000	3.277124000	1	-4.269032000	3.539154000	3.312891000
1	2.001195000	1.963338000	3.495927000	1	3.722715000	-1.967508000	2.697060000
1	2.607271000	0.459396000	4.229258000	1	3.843562000	-1.809328000	-2.820645000
1	1.836447000	0.424181000	2.622464000	1	-3.843759000	1.809077000	-2.820921000
6	-3.777183000	1.158774000	-0.040866000	1	-3.722386000	1.967818000	2.696778000

***trans*-(CAAC-2)$_2$As$_4$**

33	-0.426103000	2.718229000	0.088358000	1	1.352461000	1.769648000	-2.625847000
33	0.926650000	0.678205000	0.082715000	6	-0.680098000	-4.237215000	0.066564000
33	-0.926650000	-0.678205000	0.082715000	6	-2.480329000	-5.860837000	0.069911000
33	0.426103000	-2.718229000	0.088358000	6	-1.168579000	-6.548179000	0.468265000
7	2.036888000	4.413813000	0.067901000	1	-1.085949000	-7.562710000	0.050905000
7	-2.036888000	-4.413813000	0.067901000	1	-1.138329000	-6.643170000	1.565675000

6	0.680098000	4.237215000	0.066564000	6	-0.001279000	-5.635316000	0.021304000
6	2.480329000	5.860837000	0.069911000	6	0.470694000	-5.999213000	-1.425875000
6	1.168579000	6.548179000	0.468265000	1	0.506819000	-7.102638000	-1.483302000
1	1.085949000	7.562710000	0.050905000	1	-0.280688000	-5.674511000	-2.160915000
1	1.138329000	6.643170000	1.565675000	6	1.845842000	-5.455316000	-1.827307000
6	0.001279000	5.635316000	0.021304000	1	1.805668000	-4.354708000	-1.889667000
6	-0.470694000	5.999213000	-1.425875000	6	2.929182000	-5.872355000	-0.829395000
1	-0.506819000	7.102638000	-1.483302000	1	3.029979000	-6.974806000	-0.836550000
1	0.280688000	5.674511000	-2.160915000	1	3.909514000	-5.468429000	-1.133044000
6	-1.845842000	5.455316000	-1.827307000	6	2.572825000	-5.395638000	0.581551000
1	-1.805668000	4.354708000	-1.889667000	1	2.622610000	-4.296061000	0.619095000
6	-2.929182000	5.872355000	-0.829395000	1	3.311911000	-5.766611000	1.312452000
1	-3.909514000	5.468429000	-1.133044000	6	1.178884000	-5.869444000	1.011817000
1	-3.029979000	6.974806000	-0.836550000	1	1.231084000	-6.964506000	1.160112000
6	-2.572825000	5.395638000	0.581551000	6	-2.993613000	-3.332157000	0.099029000
1	-3.311911000	5.766611000	1.312452000	6	-3.425426000	-2.819147000	1.354732000
1	-2.622610000	4.296061000	0.619095000	6	-4.388549000	-1.799964000	1.360138000
6	-1.178884000	5.869444000	1.011817000	1	-4.729433000	-1.394338000	2.315211000
1	-1.231084000	6.964506000	1.160112000	6	-4.910377000	-1.283588000	0.178172000
6	2.993613000	3.332157000	0.099029000	1	-5.658960000	-0.487813000	0.209111000
6	3.425426000	2.819147000	1.354732000	6	-4.456142000	-1.770321000	-1.042787000
6	4.388549000	1.799964000	1.360138000	1	-4.848080000	-1.340970000	-1.967478000
1	4.729433000	1.394338000	2.315211000	6	-3.491872000	-2.786865000	-1.115720000
6	4.910377000	1.283588000	0.178172000	6	-3.591757000	-6.143773000	1.088552000
1	5.658960000	0.487813000	0.209111000	1	-3.274317000	-5.934148000	2.116484000
6	4.456142000	1.770321000	-1.042787000	1	-3.857434000	-7.211029000	1.034320000
1	4.848080000	1.340970000	-1.967478000	1	-4.500540000	-5.562400000	0.873403000
6	3.491872000	2.786865000	-1.115720000	6	-2.993613000	-6.330258000	-1.304743000
6	3.591757000	6.143773000	1.088552000	1	-3.921312000	-5.810837000	-1.578637000
1	3.274317000	5.934148000	2.116484000	1	-3.221489000	-7.406325000	-1.252516000
1	3.857434000	7.211029000	1.034320000	1	-2.261730000	-6.183237000	-2.107898000
1	4.500540000	5.562400000	0.873403000	6	-2.879412000	-3.289566000	2.705843000
6	2.993613000	6.330258000	-1.304743000	1	-2.209757000	-4.140180000	2.519692000
1	3.921312000	5.810837000	-1.578637000	6	-3.998734000	-3.758192000	3.656663000
1	3.221489000	7.406325000	-1.252516000	1	-4.623652000	-2.913355000	3.987850000
1	2.261730000	6.183237000	-2.107898000	1	-3.564558000	-4.212991000	4.562066000
6	2.879412000	3.289566000	2.705843000	1	-4.665761000	-4.497629000	3.190203000
1	2.209757000	4.140180000	2.519692000	6	-2.035543000	-2.204875000	3.402922000
6	3.998734000	3.758192000	3.656663000	1	-1.181525000	-1.895046000	2.785531000
1	4.623652000	2.913355000	3.987850000	1	-1.643121000	-2.589008000	4.359167000
1	3.564558000	4.212991000	4.562066000	1	-2.637095000	-1.308450000	3.625099000
1	4.665761000	4.497629000	3.190203000	6	-3.007972000	-3.210509000	-2.503913000
6	2.035543000	2.204875000	3.402922000	1	-2.311732000	-4.047551000	-2.374265000
1	2.637095000	1.308450000	3.625099000	6	-2.224933000	-2.088592000	-3.212907000
1	1.181525000	1.895046000	2.785531000	1	-2.856993000	-1.202753000	-3.387543000
1	1.643121000	2.589008000	4.359167000	1	-1.865524000	-2.440607000	-4.194197000
6	3.007972000	3.210509000	-2.503913000	1	-1.352461000	-1.769648000	-2.625847000
1	2.311732000	4.047551000	-2.374265000	6	-4.163720000	-3.684494000	-3.405852000
6	4.163720000	3.684494000	-3.405852000	1	-4.784292000	-4.455362000	-2.924696000
1	4.784292000	4.455362000	-2.924696000	1	-3.769550000	-4.103702000	-4.346015000
1	3.769550000	4.103702000	-4.346015000	1	-4.830181000	-2.849876000	-3.676864000
1	4.830181000	2.849876000	-3.676864000	1	-2.090016000	5.819555000	-2.839961000
6	2.224933000	2.088592000	-3.212907000	1	-0.913868000	5.437329000	1.990528000
1	2.856993000	1.202753000	-3.387543000	1	0.913868000	-5.437329000	1.990528000
1	1.865524000	2.440607000	-4.194197000	1	2.090016000	-5.819555000	-2.839961000

***trans*-(CAAC-3)$_2$As$_4$**

33	0.875887000	2.612080000	-0.127117000	6	1.457628000	-6.211683000	0.079646000
33	-0.791577000	0.833210000	-0.088447000	6	0.000100000	-6.726561000	0.012689000
33	0.791577000	-0.833210000	-0.088447000	1	-0.225361000	-7.341360000	0.895319000
33	-0.875887000	-2.612080000	-0.127117000	1	-0.130161000	-7.383275000	-0.858884000
7	-1.275798000	4.706428000	0.033225000	6	-0.959648000	-5.509122000	-0.068660000
7	1.275798000	-4.706428000	0.033225000	6	-1.966042000	-5.505123000	1.122896000
6	0.015482000	4.283710000	-0.045323000	1	-2.669991000	-4.672199000	0.967307000
6	-1.457628000	6.211683000	0.079646000	1	-2.561920000	-6.431930000	1.037072000
6	-0.000100000	6.726561000	0.012689000	6	-1.394828000	-5.401743000	2.535299000
1	0.225361000	7.341360000	0.895319000	1	-0.703794000	-6.226132000	2.774574000
1	0.130161000	7.383275000	-0.858884000	6	-1.106890000	-5.523532000	-2.707069000
6	0.959648000	5.509122000	-0.068660000	1	-0.394644000	-6.355282000	-2.830606000
6	1.966042000	5.505123000	1.122896000	1	-1.835281000	-5.600348000	-3.530014000
1	2.669991000	4.672199000	0.967307000	6	-1.829285000	-5.563106000	-1.362311000
1	2.561920000	6.431930000	1.037072000	1	-2.544242000	-4.725940000	-1.323602000
6	1.394828000	5.401743000	2.535299000	6	2.417170000	-3.814682000	0.072708000
1	0.703794000	6.226132000	2.774574000	6	3.036780000	-3.405928000	-1.141917000
6	1.106890000	5.523532000	-2.707069000	6	4.169251000	-2.581661000	-1.067195000
1	1.835281000	5.600348000	-3.530014000	1	4.654260000	-2.260191000	-1.991438000
1	0.394644000	6.355282000	-2.830606000	6	4.678288000	-2.149344000	0.152528000
6	1.829285000	5.563106000	-1.362311000	1	5.560605000	-1.505049000	0.183842000
1	2.544242000	4.725940000	-1.323602000	6	4.040725000	-2.522181000	1.330815000
6	-2.417170000	3.814682000	0.072708000	1	4.425340000	-2.154267000	2.284512000
6	-3.036780000	3.405928000	-1.141917000	6	2.904527000	-3.344732000	1.324991000
6	-4.169251000	2.581661000	-1.067195000	6	2.291391000	-6.732313000	-1.100986000
1	-4.654260000	2.260191000	-1.991438000	1	1.828537000	-6.508082000	-2.070220000
6	-4.678288000	2.149344000	0.152528000	1	2.381235000	-7.826628000	-1.017535000
1	-5.560605000	1.505049000	0.183842000	1	3.307648000	-6.314152000	-1.089939000

6	-4.040725000	2.522181000	1.330815000	6	2.156312000	-6.671790000	1.368180000
1	-4.425340000	2.154267000	2.284512000	1	3.169162000	-6.252738000	1.447177000
6	-2.904527000	3.344732000	1.324991000	1	2.250960000	-7.768709000	1.349050000
6	-2.291391000	6.732313000	-1.100986000	1	1.591627000	-6.400817000	2.269091000
1	-1.828537000	6.508082000	-2.070220000	6	2.519792000	-3.769174000	-2.535781000
1	-2.381235000	7.826628000	-1.017535000	1	1.683119000	-4.466001000	-2.411051000
1	-3.307648000	6.314152000	-1.089939000	6	3.591271000	-4.458094000	-3.402827000
6	-2.156312000	6.671790000	1.368180000	1	4.403222000	-3.761898000	-3.667698000
1	-3.169162000	6.252738000	1.447177000	1	3.146968000	-4.810854000	-4.347921000
1	-2.250960000	7.768709000	1.349050000	1	4.048788000	-5.322747000	-2.900788000
1	-1.591627000	6.400817000	2.269091000	6	1.966042000	-2.541537000	-3.284870000
6	-2.519792000	3.769174000	-2.535781000	1	1.150267000	-2.059903000	-2.728505000
1	-1.683119000	4.466001000	-2.411051000	1	1.574389000	-2.845762000	-4.269774000
6	-3.591271000	4.458094000	-3.402827000	1	2.749688000	-1.785784000	-3.456551000
1	-4.403222000	3.761898000	-3.667698000	6	2.240903000	-3.639843000	2.672147000
1	-3.146968000	4.810854000	-4.347921000	1	1.418900000	-4.342426000	2.493414000
1	-4.048788000	5.322747000	-2.900788000	6	1.616557000	-2.377422000	3.297817000
6	-1.966042000	2.541537000	-3.284870000	1	2.381430000	-1.614616000	3.516580000
1	-2.749688000	1.785784000	-3.456551000	1	1.119877000	-2.633840000	4.248383000
1	-1.150267000	2.059903000	-2.728505000	1	0.867996000	-1.922497000	2.634666000
1	-1.574389000	2.845762000	-4.269774000	6	3.211374000	-4.285142000	3.680286000
6	-2.240903000	3.639843000	2.672147000	1	3.715151000	-5.173202000	3.272180000
1	-1.418900000	4.342426000	2.493414000	1	2.667944000	-4.591387000	4.589105000
6	-3.211374000	4.285142000	3.680286000	1	3.994193000	-3.576555000	3.995313000
1	-3.715151000	5.173202000	3.272180000	1	2.209044000	5.440628000	3.276408000
1	-2.667944000	4.591387000	4.589105000	1	2.433028000	6.486674000	-1.299428000
1	-3.994193000	3.576555000	3.995313000	1	-2.433028000	-6.486674000	-1.299428000
6	-1.616557000	2.377422000	3.297817000	1	-2.209044000	-5.440628000	3.276408000
1	-2.381430000	1.614616000	3.516580000	1	0.862463000	4.449919000	2.681524000
1	-1.119877000	2.633840000	4.248383000	1	0.560802000	4.577444000	-2.838901000
1	-0.867996000	1.922497000	2.634666000	1	-0.560802000	-4.577444000	-2.838901000
6	-0.015482000	-4.283710000	-0.045323000	1	-0.862463000	-4.449919000	2.681524000

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6	1.535550000	-2.870635000	0.535882000	6	-5.212314000	-1.489285000	-4.024963000
6	0.989926000	-3.412072000	1.871559000	1	-5.404956000	-1.829818000	-5.045780000
6	1.448686000	-4.895278000	1.855376000	6	-5.144041000	-2.405930000	-2.981279000
1	1.732702000	-5.267677000	2.849167000	1	-5.268950000	-3.469691000	-3.196378000
1	0.616014000	-5.525321000	1.505626000	6	-4.899554000	-1.998962000	-1.660474000
6	2.617377000	-5.014109000	0.862107000	6	-4.480323000	1.821150000	-2.285050000
6	3.977479000	-4.956995000	1.583352000	1	-4.405717000	2.021274000	-1.207138000
1	4.809080000	-5.024147000	0.870000000	6	-5.597036000	2.714964000	-2.856632000
1	4.061202000	-5.813259000	2.271088000	1	-5.648672000	2.645366000	-3.955132000
1	4.098413000	-4.038460000	2.173392000	1	-5.403249000	3.771506000	-2.609020000
6	2.555438000	-6.330737000	0.077779000	1	-6.589974000	2.449340000	-2.463372000
1	1.580481000	-6.471779000	-0.404999000	6	-3.124700000	2.203109000	-2.911330000
1	2.710708000	-7.171099000	0.772459000	1	-2.307326000	1.597479000	-2.496061000
1	3.339093000	-6.383418000	-0.692867000	1	-2.895452000	3.262871000	-2.713152000
6	1.583687000	-2.613390000	3.067477000	1	-3.138634000	2.063069000	-4.005059000
1	2.683786000	-2.669319000	3.053180000	6	-4.741346000	-3.089321000	-0.601643000
1	1.323336000	-1.553854000	2.917404000	1	-4.586408000	-2.596499000	0.365947000
6	1.046122000	-3.072638000	4.430351000	6	-5.982404000	-3.994555000	-0.491064000
1	1.404337000	-4.092856000	4.658493000	1	-6.910305000	-3.420768000	-0.346322000
1	1.461518000	-2.425093000	5.221278000	1	-5.877661000	-4.690132000	0.357841000
6	-0.486077000	-3.050085000	4.475309000	1	-6.115862000	-4.606238000	-1.397965000
1	-0.832235000	-2.002693000	4.418048000	6	-3.489397000	-3.946396000	-0.870823000
1	-0.847952000	-3.447048000	5.439084000	1	-3.585398000	-4.512378000	-1.812124000
6	-1.090528000	-3.838679000	3.307182000	1	-3.346819000	-4.677965000	-0.057795000
1	-2.190143000	-3.750637000	3.316836000	1	-2.589617000	-3.318477000	-0.934235000
1	-0.870970000	-4.914544000	3.435910000	6	1.715577000	2.755477000	0.553882000
6	-0.554692000	-3.344176000	1.956634000	6	2.334882000	2.611859000	1.959369000
1	-0.882772000	-2.306827000	1.802868000	6	3.134663000	3.934148000	2.120002000
1	-0.992242000	-3.925309000	1.129197000	1	2.532607000	4.654737000	2.695612000
6	2.988609000	-3.677818000	-1.313577000	1	4.078036000	3.800553000	2.667015000
6	2.284319000	-4.149264000	-2.457745000	6	3.382473000	4.502614000	0.712888000
6	2.923479000	-4.101637000	-3.704677000	6	3.317732000	6.034686000	0.704244000
1	2.395352000	-4.467795000	-4.587850000	1	3.399270000	6.439768000	-0.315562000
6	4.209016000	-3.587921000	-3.845435000	1	4.160009000	6.432872000	1.291457000
1	4.690534000	-3.568345000	-4.826692000	1	2.390531000	6.408439000	1.156004000
6	4.864658000	-3.073683000	-2.731849000	6	4.762102000	4.084712000	0.168456000
1	5.857390000	-2.634281000	-2.853206000	1	4.884337000	2.993840000	0.137701000
6	4.274487000	-3.088872000	-1.458494000	1	5.551539000	4.496550000	0.816882000
6	0.839339000	-4.646892000	-2.420407000	1	4.925118000	4.479505000	-0.842829000
1	0.525904000	-4.693240000	-1.368061000	6	1.251184000	2.516065000	3.064003000
6	-0.099104000	-3.651136000	-3.130695000	1	0.609339000	3.411783000	3.022606000
1	0.140295000	-3.576800000	-4.204486000	1	0.605343000	1.651730000	2.849403000
1	-0.023895000	-2.647391000	-2.689712000	6	1.854741000	2.347310000	4.464858000
1	-1.146094000	-3.982818000	-3.044064000	1	2.440453000	3.242987000	4.741793000
6	0.674312000	-6.052124000	-3.029263000	1	1.042141000	2.275845000	5.207691000
1	0.863933000	-6.047378000	-4.114758000	6	2.750008000	1.105063000	4.537775000
1	-0.357712000	-6.410975000	-2.883632000	1	2.125069000	0.205036000	4.399369000
1	1.357443000	-6.788014000	-2.579343000	1	3.209722000	1.016527000	5.536894000
6	5.029105000	-2.395850000	-0.324412000	6	3.833187000	1.134578000	3.452889000
1	4.449051000	-2.530581000	0.597114000	1	4.406827000	0.192149000	3.459825000
6	6.438739000	-2.974275000	-0.100191000	1	4.561839000	1.931253000	3.689245000

1	6.430182000	-4.065835000	0.036977000	6	3.244193000	1.354961000	2.051586000
1	6.900913000	-2.524282000	0.793817000	1	2.647071000	0.475246000	1.765274000
1	7.102715000	-2.757285000	-0.952474000	1	4.053286000	1.418482000	1.308537000
6	5.123514000	-0.878037000	-0.576833000	6	1.818122000	4.365594000	-1.336870000
1	5.726390000	-0.658475000	-1.473430000	6	2.403974000	3.896483000	-2.544592000
1	5.609169000	-0.380094000	0.278913000	6	1.999495000	4.484517000	-3.753345000
1	4.125427000	-0.438250000	-0.713099000	1	2.448495000	4.139453000	-4.687368000
6	-3.337116000	0.081947000	0.523492000	6	1.029046000	5.479799000	-3.793788000
6	-3.534083000	0.775989000	1.886274000	1	0.734417000	5.923553000	-4.748487000
6	-5.048064000	1.123660000	1.881074000	6	0.416157000	5.886620000	-2.612132000
1	-5.514436000	1.025978000	2.870999000	1	-0.372520000	6.641465000	-2.651560000
1	-5.176147000	2.172575000	1.571148000	6	0.780949000	5.340008000	-1.374006000
6	-5.733092000	0.210775000	0.849818000	6	3.399344000	2.738868000	-2.622306000
6	-6.343205000	-1.033617000	1.524544000	1	3.617557000	2.413003000	-1.597440000
1	-6.825984000	-1.691082000	0.790223000	6	4.725151000	3.139826000	-3.296327000
1	-7.115787000	-0.715907000	2.242525000	1	5.450594000	2.312218000	-3.234584000
1	-5.593323000	-1.618349000	2.074550000	1	4.580116000	3.365141000	-4.365332000
6	-6.856413000	0.941324000	0.104247000	1	5.184052000	4.027328000	-2.835047000
1	-6.507599000	1.881548000	-0.340368000	6	2.786774000	1.529305000	-3.356449000
1	-7.661863000	1.184328000	0.814888000	1	3.482897000	0.675397000	-3.330498000
1	-7.288716000	0.317211000	-0.692316000	1	1.848089000	1.211178000	-2.882614000
6	-3.140456000	-0.172776000	3.054030000	1	2.583543000	1.763589000	-4.414571000
1	-3.739124000	-1.096405000	3.012213000	6	-0.009199000	5.776158000	-0.140037000
1	-2.092859000	-0.473098000	2.896407000	1	0.471911000	5.328414000	0.740633000
6	-3.269483000	0.481837000	4.436930000	6	-1.449687000	5.230218000	-0.194148000
1	-4.332037000	0.676230000	4.670069000	1	-2.012178000	5.676871000	-1.030957000
1	-2.917782000	-0.225064000	5.207663000	1	-1.988428000	5.473869000	0.736931000
6	-2.482395000	1.794646000	4.521462000	1	-1.452792000	4.138465000	-0.321650000
1	-2.645301000	2.277835000	5.499935000	6	-0.030361000	7.303542000	0.053525000
1	-1.402666000	1.571443000	4.457962000	1	0.980435000	7.737823000	0.059836000
6	-2.861428000	2.747270000	3.381088000	1	-0.518156000	7.561381000	1.008001000
1	-2.234772000	3.654467000	3.417778000	1	-0.599432000	7.805266000	-0.745607000
1	-3.902658000	3.092153000	3.519430000	7	2.379052000	-3.814708000	-0.009163000
6	-2.701647000	2.076214000	2.010050000	7	-4.576159000	-0.127570000	-0.044362000
1	-1.639461000	1.845363000	1.848732000	7	2.257372000	3.868819000	-0.052146000
1	-2.987583000	2.770652000	1.203932000	15	1.296030000	-1.363828000	-0.321146000
6	-4.750815000	-0.610906000	-1.395303000	15	-1.915463000	-0.453677000	-0.344463000
6	-4.767203000	0.330025000	-2.464079000	15	0.523484000	1.823814000	-0.324729000
6	-5.008817000	-0.137429000	-3.763295000	15	-0.061633000	-0.004013000	0.900054000
1	-5.029196000	0.575364000	-4.590714000				

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6	0.747459000	3.235766000	0.895827000	6	5.036175000	-2.062742000	-1.331649000
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6	1.770648000	4.775037000	2.499191000	1	1.592634000	-4.228448000	-0.937975000
1	1.202943000	5.286026000	3.288597000	6	1.905777000	-5.683874000	-2.490539000
1	2.823171000	4.809775000	2.811969000	1	2.069061000	-5.740189000	-3.578928000
6	1.583200000	5.512943000	1.153774000	1	0.942773000	-6.178430000	-2.283205000
6	0.732000000	6.778767000	1.336045000	1	2.698788000	-6.271716000	-2.006298000
1	0.543394000	7.280336000	0.376392000	6	0.764709000	-3.451754000	-2.753533000
1	1.278495000	7.486249000	1.979392000	1	0.689940000	-2.415248000	-2.397211000
1	-0.230760000	6.563536000	1.817424000	1	-0.213671000	-3.933383000	-2.600570000
6	2.928427000	5.945916000	0.547802000	1	0.961982000	-3.435177000	-3.838096000
1	3.616181000	5.100708000	0.421970000	6	5.708635000	-1.156149000	-0.302091000
1	3.408268000	6.677989000	1.216315000	1	5.243169000	-1.349929000	0.672328000
1	2.787046000	6.430194000	-0.429016000	6	7.224336000	-1.390439000	-0.167228000
6	0.181711000	2.980346000	3.388382000	1	7.472726000	-2.441259000	0.038910000
1	-0.093614000	1.921328000	3.270383000	1	7.631152000	-0.779161000	0.655032000
1	0.654115000	3.064150000	4.383694000	1	7.762248000	-1.096262000	-1.082797000
6	-1.081882000	3.836531000	3.360377000	6	5.439560000	0.320152000	-0.648966000
1	-1.588146000	3.767597000	2.386773000	1	5.896475000	0.589868000	-1.615242000
1	-1.792724000	3.493067000	4.128412000	1	5.870565000	0.982106000	0.119109000
6	3.699429000	2.462917000	1.738857000	1	4.360532000	0.516943000	-0.711789000
1	4.448597000	1.712638000	2.029290000	6	-3.175985000	-0.970564000	0.895827000
1	3.479037000	2.306776000	0.673655000	6	-3.506782000	-0.541268000	2.340691000
6	2.446574000	2.309269000	2.593265000	6	-5.020627000	-0.854092000	2.499191000
1	2.720145000	2.404190000	3.659662000	1	-5.179304000	-1.601234000	3.288597000
1	2.053295000	1.290025000	2.469191000	1	-5.576973000	0.040050000	2.811969000
6	0.526752000	4.783250000	-1.064111000	6	-5.565949000	-1.385380000	1.153774000
6	1.432586000	4.531973000	-2.134633000	6	-6.236585000	-2.755453000	1.336045000
6	1.096734000	4.986227000	-3.418863000	1	-6.576654000	-3.169575000	0.376392000
1	1.790947000	4.805104000	-4.242207000	1	-7.122530000	-2.635915000	1.979392000
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6	-1.008581000	5.827477000	-2.636529000	1	-6.225433000	0.581350000	0.421970000
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6	2.725218000	3.728300000	-2.000133000	6	-2.671911000	-1.332807000	3.388382000
1	2.865626000	3.493486000	-0.937975000	1	-1.617112000	-1.041736000	3.270383000
6	2.606952000	2.388135000	-2.753533000	1	-2.980689000	-0.965594000	4.383694000
1	2.493959000	2.550689000	-3.838096000	6	-2.781592000	-2.855203000	3.360377000
1	1.746696000	1.805129000	-2.397211000	1	-2.468761000	-3.259173000	2.386773000
1	3.513245000	1.781648000	-2.600570000	1	-2.128723000	-3.299078000	4.128412000
6	3.969491000	4.492388000	-2.490539000	6	-3.982663000	1.972341000	1.738857000
1	3.936619000	4.661953000	-3.578928000	1	-3.707487000	2.996279000	2.029290000

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1	4.082071000	5.473076000	-2.006298000
6	-1.853063000	5.521897000	-0.302091000
1	-1.452512000	5.215681000	0.672328000
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1	-1.622170000	7.692200000	0.038910000
1	-3.140803000	6.998352000	0.655032000
1	-2.931733000	7.270435000	-1.082797000
6	-2.997040000	4.550721000	-0.648966000
1	-3.459078000	4.811563000	-1.615242000
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1	-2.627952000	3.517861000	-0.711789000
6	2.428526000	-2.265201000	0.895827000
6	2.222143000	-2.766329000	2.340691000
6	3.249979000	-3.920944000	2.499191000
1	3.976361000	-3.684792000	3.288597000
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6	5.504585000	-4.023315000	1.336045000
1	6.033259000	-4.110762000	0.376392000
1	5.844034000	-4.850334000	1.979392000
1	5.799569000	-3.081924000	1.817424000
6	3.685101000	-5.509050000	0.547802000
1	2.609253000	-5.682059000	0.421970000
1	4.079174000	-6.290641000	1.216315000
1	4.175188000	-5.628749000	-0.429016000
6	2.490200000	-1.647539000	3.388382000
1	1.710726000	-0.879592000	3.270383000
1	2.326574000	-2.098556000	4.383694000
6	3.863474000	-0.981328000	3.360377000
1	4.056908000	-0.508423000	2.386773000
1	3.921447000	-0.193989000	4.128412000
6	0.283234000	-4.435258000	1.738857000
1	-0.741111000	-4.708917000	2.029290000
1	0.258208000	-4.166322000	0.673655000
6	0.776599000	-3.273429000	2.593265000
1	0.722018000	-3.557809000	3.659662000
1	0.090547000	-2.423218000	2.469191000
6	3.879040000	-2.847806000	-1.064111000
6	3.208511000	-3.506642000	-2.134633000
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1	3.265868000	-3.953558000	-4.242207000
6	4.941147000	-2.738239000	-3.672704000
1	5.363481000	-2.712547000	-4.680674000
6	5.551034000	-2.040282000	-2.636529000
1	6.445293000	-1.448999000	-2.845189000
1	-3.737245000	1.859546000	0.673655000
6	-3.223172000	0.964161000	2.593265000
1	-3.442162000	1.153619000	3.659662000
1	-2.143842000	1.133193000	2.469191000
6	-4.405792000	-1.935445000	-1.064111000
6	-4.641097000	-1.025331000	-2.134633000
6	-4.866567000	-1.543314000	-3.418863000
1	-5.056816000	-0.851546000	-4.242207000
6	-4.841958000	-2.910039000	-3.672704000
1	-5.030876000	-3.288637000	-4.680674000
6	-4.542453000	-3.787195000	-2.636529000
1	-4.477516000	-4.857288000	-2.845189000
6	-4.304474000	-3.330085000	-1.331649000
6	-4.591411000	0.495958000	-2.000133000
1	-4.458261000	0.734962000	-0.937975000
6	-5.875268000	1.191486000	-2.490539000
1	-5.822064000	2.272750000	-2.283205000
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1	-6.780859000	0.798639000	-2.006298000
6	-3.371661000	1.063619000	-2.753533000
1	-3.299575000	2.151736000	-2.600570000
1	-2.436636000	0.610118000	-2.397211000
1	-3.455941000	0.884488000	-3.838096000
6	-3.855572000	-4.365748000	-0.302091000
1	-3.790657000	-3.865753000	0.672328000
6	-2.442520000	-4.870873000	-0.648966000
1	-2.437397000	-5.401431000	-1.615242000
1	-2.084754000	-5.575112000	0.119109000
1	-1.732581000	-4.034803000	-0.711789000
6	-4.816323000	-5.561240000	-0.167228000
1	-5.850556000	-5.250941000	0.038910000
1	-4.490349000	-6.219191000	0.655032000
1	-4.830515000	-6.174173000	-1.082797000
7	0.900470000	4.471622000	0.304115000
7	3.422303000	-3.015641000	0.304115000
7	-4.322773000	-1.455981000	0.304115000
15	0.000000000	1.934106000	-0.014664000
15	1.674985000	-0.967053000	-0.014664000
15	-1.674985000	-0.967053000	-0.014664000
15	0.000000000	0.000000000	1.224558000
1	4.682741000	-1.689221000	3.564633000
1	0.899846000	-5.340037000	1.855039000
1	-5.074531000	1.890729000	1.855039000
1	-3.804279000	-3.210762000	3.564633000
1	-0.878462000	4.899983000	3.564633000
1	4.174684000	3.449308000	1.855039000

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6	1.331073000	-3.234791000	0.532176000
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1	1.245019000	-5.575095000	2.906048000
1	0.140824000	-5.766622000	1.540716000
6	2.195509000	-5.455829000	0.935592000
6	3.539656000	-5.471656000	1.688661000
1	4.379943000	-5.642592000	1.003703000
1	3.536564000	-6.294680000	2.420650000
1	3.721110000	-4.536175000	2.234935000
6	2.051792000	-6.790559000	0.195758000
1	1.076307000	-6.882283000	-0.297345000
1	2.139480000	-7.614806000	0.920791000
1	2.840386000	-6.923843000	-0.560149000
6	1.325064000	-2.916814000	3.063881000
1	2.412794000	-3.086862000	3.099654000
1	1.186397000	-1.840011000	2.878347000
6	0.686661000	-3.277721000	4.412920000
1	0.927034000	-4.322403000	4.682205000
1	1.134502000	-2.652765000	5.204273000
6	-0.835595000	-3.097547000	4.390099000
1	-1.070011000	-2.023106000	4.284278000
1	-1.275111000	-3.421972000	5.348759000
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1	-2.553232000	-3.668221000	3.180524000
1	-1.358923000	-4.949518000	3.389723000
6	-0.832627000	-3.465063000	1.882213000
1	-1.051660000	-2.405431000	1.685906000
1	-1.292484000	-4.026098000	1.052319000
6	2.664824000	-4.231051000	-1.299182000
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6	3.808139000	-4.273808000	-3.866679000
1	4.257545000	-4.302458000	-4.862815000
6	4.541268000	-3.809805000	-2.779943000
1	5.564545000	-3.460976000	-2.936679000
6	-5.647940000	-0.924198000	-3.973647000
1	-5.884249000	-1.251842000	-4.989469000
6	-5.650459000	-1.836856000	-2.924512000
1	-5.876563000	-2.885604000	-3.130274000
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6	-5.656170000	3.298928000	-2.818527000
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6	-3.236242000	2.588490000	-2.929109000
1	-2.461431000	1.918638000	-2.530764000
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6	-5.297752000	-2.542790000	-0.544490000
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6	-6.638167000	-3.288330000	-0.399860000
1	-7.485842000	-2.604472000	-0.242312000
1	-6.601405000	-3.985784000	0.453122000
1	-6.863969000	-3.884541000	-1.298749000
6	-4.168537000	-3.551949000	-0.831681000
1	-4.353925000	-4.109732000	-1.764484000
1	-4.100890000	-4.288492000	-0.013527000
1	-3.197366000	-3.044270000	-0.918348000
6	2.183054000	2.743747000	0.536890000
6	2.796358000	2.472947000	1.921832000
6	3.757609000	3.679386000	2.114467000
1	3.258179000	4.446489000	2.726937000
1	4.685496000	3.409839000	2.637505000
6	4.053507000	4.264864000	0.722622000
6	4.164625000	5.793402000	0.761753000
1	4.274667000	6.219161000	-0.247022000
1	5.056993000	6.073950000	1.342887000
1	3.294492000	6.255776000	1.243825000
6	5.369151000	3.708533000	0.145731000
1	5.363680000	2.612414000	0.079194000

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6	0.414436000	-5.056213000	-2.321662000	1	5.569806000	4.115835000	-0.853577000
1	0.133458000	-5.061500000	-1.259454000	6	1.723999000	2.470171000	3.042772000
6	-0.484889000	-4.018319000	-3.021661000	1	1.206010000	3.443735000	3.052236000
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1	-0.327171000	-3.011381000	-2.610491000	6	2.315351000	2.157494000	4.423879000
1	-1.547179000	-4.279129000	-2.885623000	1	3.015577000	2.955775000	4.731912000
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1	0.292809000	-6.489126000	-3.984316000	6	3.043516000	0.808265000	4.424385000
1	-0.906659000	-6.750017000	-2.705958000	1	2.307267000	0.003309000	4.250044000
1	0.791195000	-7.228579000	-2.450103000	1	3.495207000	0.612156000	5.411795000
6	4.852838000	-3.152038000	-0.381143000	6	4.113309000	0.754023000	3.327507000
1	4.279810000	-3.199240000	0.553302000	1	4.566061000	-0.251121000	3.283949000
6	6.178299000	-3.910965000	-0.178896000	1	4.936554000	1.444105000	3.588100000
1	6.027838000	-4.991025000	-0.031887000	6	3.541362000	1.107804000	1.947047000
1	6.715710000	-3.520296000	0.700824000	1	2.834299000	0.322557000	1.635970000
1	6.845263000	-3.790748000	-1.047878000	1	4.342741000	1.100255000	1.191935000
6	5.143455000	-1.662577000	-0.652440000	6	2.446576000	4.373160000	-1.306428000
1	5.757172000	-1.531007000	-1.558840000	6	2.953101000	3.877310000	-2.539416000
1	5.702394000	-1.225571000	0.191946000	6	2.574698000	4.527882000	-3.724335000
1	4.211096000	-1.093856000	-0.778387000	1	2.963092000	4.162245000	-4.677498000
6	-3.553047000	0.474761000	0.516307000	6	1.704626000	5.612665000	-3.716988000
6	-3.628133000	1.200035000	1.871360000	1	1.427121000	6.102505000	-4.654089000
6	-5.097621000	1.705437000	1.911096000	6	1.170928000	6.054424000	-2.509878000
1	-5.539414000	1.662795000	2.916215000	1	0.462372000	6.885841000	-2.511514000
1	-5.126509000	2.759951000	1.594923000	6	1.513639000	5.449135000	-1.292837000
6	-5.906378000	0.860121000	0.910954000	6	3.841906000	2.639977000	-2.668419000
6	-6.614350000	-0.312761000	1.616508000	1	4.044901000	2.264339000	-1.657772000
1	-7.187593000	-0.921358000	0.905564000	6	5.187767000	2.950817000	-3.350987000
1	-7.324023000	0.084987000	2.359066000	1	5.845323000	2.066628000	-3.321893000
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6	-6.972671000	1.693578000	0.191461000	1	5.721844000	3.786309000	-2.873872000
1	-6.547780000	2.595979000	-0.264944000	6	3.123143000	1.508272000	-3.429612000
1	-7.732621000	2.013313000	0.921518000	1	3.746024000	0.598872000	-3.435100000
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6	-3.297036000	0.232424000	3.044366000	1	2.930800000	1.787547000	-4.478743000
1	-4.001707000	-0.614271000	3.047679000	6	0.818467000	5.952696000	-0.026919000
1	-2.300679000	-0.195842000	2.852235000	1	1.262978000	5.428996000	0.830638000
6	-3.287932000	0.921086000	4.416712000	6	-0.682490000	5.601248000	-0.039981000
1	-4.309635000	1.242304000	4.689913000	1	-1.207413000	6.124629000	-0.856416000
1	-2.986587000	0.190563000	5.186745000	1	-1.154902000	5.906523000	0.908805000
6	-2.352147000	2.135197000	4.439560000	1	-0.834406000	4.520059000	-0.169203000
1	-2.410256000	2.646473000	5.415614000	6	1.001840000	7.466449000	0.191144000
1	-1.308951000	1.789203000	4.327204000	1	2.059772000	7.767131000	0.168485000
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1	-1.957061000	3.943129000	3.292132000	1	0.476336000	8.052383000	-0.580016000
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6	-2.655273000	2.405469000	1.937781000	7	-4.815689000	0.395033000	-0.014455000
1	-1.631406000	2.059334000	1.734931000	7	2.851536000	3.789392000	-0.046934000
1	-2.899209000	3.115227000	1.130451000	33	1.258418000	-1.603998000	-0.401891000
6	-5.070638000	-0.077224000	-1.356963000	33	-2.108804000	-0.270190000	-0.429249000
6	-5.017875000	0.856218000	-2.431781000	33	0.762841000	1.932229000	-0.391615000
6	-5.319979000	0.405251000	-3.724147000	33	-0.061653000	0.009087000	0.985336000
1	-5.288567000	1.112537000	-4.555923000				

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6	2.769170000	4.478953000	2.511810000	1	0.895680000	-4.856376000	-0.892878000
1	2.324998000	5.060679000	3.331444000	6	0.989773000	-6.377649000	-2.411373000
1	3.808181000	4.278878000	2.808213000	1	1.125121000	-6.479491000	-3.500250000
6	2.734902000	5.297095000	1.199321000	1	-0.025905000	-6.736548000	-2.177686000
6	2.092023000	6.675252000	1.416751000	1	1.707429000	-7.053531000	-1.924664000
1	2.012597000	7.234096000	0.473560000	6	0.145702000	-4.024238000	-2.715000000
1	2.725837000	7.262897000	2.099349000	1	0.216162000	-2.976273000	-2.392000000
1	1.093766000	6.600140000	1.866798000	1	-0.884139000	-4.368319000	-2.527485000
6	4.147299000	5.529642000	0.640513000	1	0.316933000	-4.064586000	-3.803390000
1	4.697810000	4.590291000	0.504471000	6	5.435902000	-2.423504000	-0.353380000
1	4.715680000	6.155849000	1.346018000	1	4.947057000	-2.513208000	0.624330000
1	4.114000000	6.059490000	-0.322182000	6	6.883796000	-2.929981000	-0.215665000
6	0.817565000	3.027725000	3.314952000	1	6.935611000	-4.004277000	0.011679000
1	0.346578000	2.042959000	3.173746000	1	7.400629000	-2.387738000	0.593109000
1	1.273375000	3.005792000	4.321403000	1	7.460932000	-2.758638000	-1.138584000
6	-0.263740000	4.104853000	3.276183000	6	5.443405000	-0.926504000	-0.719392000
1	-0.772696000	4.121973000	2.301068000	1	5.951983000	-0.754162000	-1.682255000
1	-1.027278000	3.904180000	4.044594000	1	5.981284000	-0.347181000	0.048663000
6	4.153341000	1.787274000	1.663996000	1	4.419960000	-0.532819000	-0.793989000
1	4.738356000	0.907496000	1.971205000	6	-3.545482000	-0.322526000	0.843902000
1	3.880758000	1.644771000	0.608458000	6	-3.722397000	0.148561000	2.297520000
6	2.913478000	1.922366000	2.542159000	6	-5.263472000	0.158695000	2.511810000
1	3.219572000	1.965127000	3.603239000	1	-5.545176000	-0.516832000	3.331444000
1	2.307233000	1.009827000	2.438290000	1	-5.609707000	1.158543000	2.808213000
6	1.629955000	4.811216000	-1.075166000	6	-5.954870000	-0.280053000	1.199321000
6	2.513358000	4.427659000	-2.125231000	6	-6.826950000	-1.525881000	1.416751000
6	2.273371000	4.920888000	-3.416396000	1	-7.271209000	-1.874088000	0.473560000

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1	1.029457000	6.124602000	-4.707958000	6	-6.862459000	0.826845000	0.640513000
6	0.298523000	6.065805000	-2.676618000	1	-6.324213000	1.773277000	0.504471000
1	-0.574231000	6.681420000	-2.905186000	1	-7.688961000	1.005974000	1.346018000
6	0.481786000	5.602048000	-1.365222000	1	-7.304672000	0.533084000	-0.322182000
6	3.680203000	3.454328000	-1.957622000	6	-3.030870000	-0.805830000	3.314952000
1	3.757905000	3.203870000	-0.892878000	1	-1.942543000	-0.721334000	3.173746000
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1	3.361568000	2.306765000	-3.803390000	6	-3.423037000	-2.280832000	3.276183000
1	2.469447000	1.675338000	-2.392000000	1	-3.183385000	-2.730161000	2.301068000
1	4.225145000	1.418472000	-2.527485000	1	-2.867481000	-2.841739000	4.044594000
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1	5.846974000	3.345839000	-2.177686000	1	-3.364793000	2.538450000	0.608458000
1	5.254823000	5.005443000	-1.924664000	6	-3.121557000	1.561963000	2.542159000
6	-0.619135000	5.919381000	-0.353380000	1	-3.311636000	1.805668000	3.603239000
1	-0.297026000	5.540882000	0.624330000	1	-2.028152000	1.493209000	2.438290000
6	-0.904460000	7.426533000	-0.215665000	6	-4.981613000	-0.994026000	-1.075166000
1	0.000000000	8.008553000	0.011679000	6	-5.091145000	-0.037197000	-2.125231000
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1	-1.341415000	7.840676000	-1.138584000	1	-5.492206000	0.235837000	-4.225540000
6	-1.919326000	5.177379000	-0.719392000	6	-5.572766000	-1.842832000	-3.694577000
1	-2.322868000	5.531649000	-1.682255000	1	-5.818789000	-2.170765000	-4.707958000
1	-2.689975000	5.353534000	0.048663000	6	-5.402402000	-2.774374000	-2.676618000
1	-1.748545000	4.094207000	-0.793989000	1	-5.499164000	-3.838009000	-2.905186000
6	2.052057000	-2.909215000	0.843902000	6	-5.092409000	-2.383785000	-1.365222000
6	1.732540000	-3.297971000	2.297520000	6	-4.831637000	1.459985000	-1.957622000
6	2.494302000	-4.637649000	2.511810000	1	-4.653585000	1.652506000	-0.892878000
1	3.220178000	-4.543847000	3.331444000	6	-6.018093000	2.331656000	-2.411373000
1	1.801526000	-5.437420000	2.808213000	1	-5.821069000	3.390708000	-2.177686000
6	3.219968000	-5.017043000	1.199321000	1	-6.173964000	2.265362000	-3.500250000
6	4.734927000	-5.149371000	1.416751000	1	-6.962252000	2.048089000	-1.924664000
1	5.258612000	-5.360008000	0.473560000	6	-3.557943000	1.885937000	-2.715000000
1	4.926935000	-5.992092000	2.099349000	1	-3.341006000	2.949847000	-2.527485000
1	5.169006000	-4.247299000	1.866798000	1	-2.685609000	1.300935000	-2.392000000
6	2.715161000	-6.356487000	0.640513000	1	-3.678501000	1.757821000	-3.803390000
1	1.626403000	-6.363568000	0.504471000	6	-4.816767000	-3.495877000	-0.353380000
1	2.973281000	-7.161823000	1.346018000	1	-4.650031000	-3.027673000	0.624330000
1	3.190672000	-6.592574000	-0.322182000	6	-3.524079000	-4.250875000	-0.719392000
6	2.213305000	-2.221895000	3.314952000	1	-3.629115000	-4.777487000	-1.682255000
1	1.595965000	-1.321625000	3.173746000	1	-3.291309000	-5.006354000	0.048663000
1	1.966404000	-2.605671000	4.321403000	1	-2.671414000	-3.561388000	-0.793989000
6	3.686777000	-1.824021000	3.276183000	6	-5.979336000	-4.496551000	-0.215665000
1	3.956081000	-1.391812000	2.301068000	1	-6.935611000	-4.004277000	0.011679000
1	3.894758000	-1.062442000	4.044594000	1	-5.768157000	-5.215264000	0.593109000
6	-0.528846000	-4.490536000	1.663996000	1	-6.119517000	-5.082037000	-1.138584000
1	-1.583264000	-4.557285000	1.971205000	7	1.910204000	4.416176000	0.293022000
1	-0.515966000	-4.183221000	0.608458000	7	2.869419000	-3.862373000	0.293022000
6	0.208079000	-3.484329000	2.542159000	7	-4.779622000	-0.553803000	0.293022000
1	0.092063000	-3.770795000	3.603239000	33	0.445536000	2.044052000	-0.175890000
1	-0.279081000	-2.503036000	2.438290000	33	1.547433000	-1.407872000	-0.175890000
6	3.351658000	-3.817190000	-1.075166000	33	-1.992969000	-0.636180000	-0.175890000
6	2.577786000	-4.390462000	-2.125231000	33	0.000000000	0.000000000	1.225218000
6	3.124929000	-4.429241000	-3.416396000	1	4.361619000	-2.672324000	3.474765000
1	2.541862000	-4.874309000	-4.225540000	1	-0.108431000	-5.506206000	1.736675000
6	4.382323000	-3.904741000	-3.694577000	1	-4.714298000	2.847007000	1.736675000
1	4.789333000	-3.953836000	-4.707958000	1	-4.495110000	-2.441111000	3.474765000
6	5.103879000	-3.291431000	-2.676618000	1	0.133491000	5.113435000	3.474765000
1	6.073395000	-2.843412000	-2.905186000	1	4.822730000	2.659199000	1.736675000

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6	0.727130000	3.325936000	0.861134000	6	5.085554000	-2.034332000	-1.387219000
6	1.254714000	3.419281000	2.308808000	6	1.953656000	-4.257246000	-2.034296000
6	1.731646000	4.892172000	2.450292000	1	1.696985000	-4.279596000	-0.968104000
1	1.161221000	5.407896000	3.235007000	6	2.018099000	-5.710013000	-2.541992000
1	2.784381000	4.936041000	2.761820000	1	2.166596000	-5.750460000	-3.633199000
6	1.539589000	5.614705000	1.096936000	1	1.069535000	-6.228390000	-2.326390000
6	0.672916000	6.872672000	1.262085000	1	2.831114000	-6.285316000	-2.076116000
1	0.478783000	7.358388000	0.295325000	6	0.822644000	-3.501701000	-2.760700000
1	1.209888000	7.595760000	1.896014000	1	0.731520000	-2.470472000	-2.392806000
1	-0.287832000	6.652589000	1.745255000	1	-0.142260000	-4.006326000	-2.595836000
6	2.881986000	6.057488000	0.491655000	1	1.000310000	-3.469679000	-3.848314000
1	3.580866000	5.219516000	0.378308000	6	5.754635000	-1.130762000	-0.352847000
1	3.349997000	6.803211000	1.153446000	1	5.307973000	-1.350981000	0.624432000
1	2.738670000	6.528398000	-0.491366000	6	7.276214000	-1.338764000	-0.244245000
6	0.147870000	3.103147000	3.356480000	1	7.546346000	-2.388240000	-0.059059000
1	-0.105285000	2.035035000	3.275146000	1	7.684268000	-0.733546000	0.581901000
1	0.609244000	3.230281000	4.352439000	1	7.794916000	-1.020230000	-1.162757000
6	-1.135961000	3.926312000	3.288239000	6	5.451518000	0.346513000	-0.666485000
1	-1.640559000	3.795101000	2.320089000	1	5.893512000	0.646374000	-1.630909000
1	-1.837193000	3.604652000	4.074605000	1	5.876120000	1.000935000	0.111870000
6	3.665718000	2.555015000	1.711528000	1	4.368032000	0.522530000	-0.714916000
1	4.423065000	1.823345000	2.028443000	6	-3.243910000	-1.033255000	0.861134000
1	3.433214000	2.347612000	0.657485000	6	-3.588541000	-0.623026000	2.308808000

6	2.423271000	2.434312000	2.586808000	6	-5.102568000	-0.946437000	2.450292000
1	2.707831000	2.572714000	3.645616000	1	-5.263986000	-1.698301000	3.235007000
1	2.035379000	1.407583000	2.511017000	1	-5.666927000	-0.056676000	2.761820000
6	0.491419000	4.844456000	-1.113525000	6	-5.632272000	-1.474029000	1.096936000
6	1.399818000	4.593247000	-2.181502000	6	-6.288367000	-2.853573000	1.262085000
6	1.050016000	5.015475000	-3.472951000	1	-6.611942000	-3.264555000	0.295325000
1	1.745427000	4.834511000	-4.295368000	1	-7.183066000	-2.750086000	1.896014000
6	-0.161993000	5.644439000	-3.734982000	1	-5.617395000	-3.575564000	1.745255000
1	-0.406866000	5.971684000	-4.748885000	6	-6.686931000	-0.532871000	0.491655000
6	-1.072101000	5.823712000	-2.699192000	1	-6.310667000	0.491363000	0.378308000
1	-2.042496000	6.276766000	-2.913668000	1	-7.566752000	-0.500423000	1.153446000
6	-0.780994000	5.421385000	-1.387219000	1	-7.023094000	-0.892441000	-0.491366000
6	2.710055000	3.820539000	-2.034296000	6	-2.761339000	-1.423514000	3.356480000
1	2.857746000	3.609430000	-0.968104000	1	-1.709749000	-1.108697000	3.275146000
6	2.621240000	2.463281000	-2.760700000	1	-3.102128000	-1.087520000	4.352439000
1	2.504675000	2.601133000	-3.848314000	6	-2.832306000	-2.946927000	3.288239000
1	1.773731000	1.868751000	-2.392806000	1	-2.466374000	-3.318316000	2.320089000
1	3.540710000	1.879962000	-2.595836000	1	-2.203123000	-3.393382000	4.074605000
6	3.935967000	4.602732000	-2.541992000	6	-4.045567000	1.897098000	1.711528000
1	3.896746000	4.751557000	-3.633199000	1	-3.790596000	2.918814000	2.028443000
1	4.859176000	4.040439000	-2.326390000	1	-3.749699000	1.799445000	0.657485000
1	4.027687000	5.594474000	-2.076116000	6	-3.319812000	0.881459000	2.586808000
6	-1.898049000	5.549042000	-0.352847000	1	-3.581951000	1.058693000	3.645616000
1	-1.484003000	5.272330000	0.624432000	1	-2.236692000	1.058899000	2.511017000
6	-2.478703000	6.970768000	-0.244245000	6	-4.441131000	-1.996646000	-1.113525000
1	-1.704897000	7.729447000	-0.059059000	6	-4.677778000	-1.084346000	-2.181502000
1	-3.206865000	7.021544000	0.581901000	6	-4.868536000	-1.598397000	-3.472951000
1	-3.013913000	7.260710000	-1.162757000	1	-5.059523000	-0.905671000	-4.295368000
6	-3.025848000	4.547897000	-0.666485000	6	-4.807231000	-2.962510000	-3.734982000
1	-3.506532000	4.780744000	-1.630909000	1	-4.968198000	-3.338198000	-4.748885000
1	-3.804895000	4.588402000	0.111870000	6	-4.507432000	-3.840323000	-2.699192000
1	-2.636540000	3.521561000	-0.714916000	1	-4.414591000	-4.907236000	-2.913668000
6	2.516780000	-2.292681000	0.861134000	6	-4.304561000	-3.387053000	-1.387219000
6	2.333827000	-2.796255000	2.308808000	6	-4.663711000	0.436707000	-2.034296000
6	3.370922000	-3.945735000	2.450292000	1	-4.554731000	0.670166000	-0.968104000
1	4.102765000	-3.709595000	3.235007000	6	-5.954066000	1.107281000	-2.541992000
1	2.882546000	-4.879365000	2.761820000	1	-5.928711000	2.187951000	-2.326390000
6	4.092683000	-4.140676000	1.096936000	1	-6.063342000	0.998903000	-3.633199000
6	5.615451000	-4.019099000	1.262085000	1	-6.858800000	0.690842000	-2.076116000
1	6.133159000	-4.093832000	0.295325000	6	-3.443884000	1.038420000	-2.760700000
1	5.973177000	-4.845674000	1.896014000	1	-3.398450000	2.126364000	-2.595836000
1	5.905227000	-3.077025000	1.745255000	1	-2.505252000	0.601721000	-2.392806000
6	3.804945000	-5.524616000	0.491655000	1	-3.504985000	0.868546000	-3.848314000
1	2.729801000	-5.710879000	0.378308000	6	-3.856587000	-4.418279000	-0.352847000
1	4.216755000	-6.302788000	1.153446000	1	-3.823970000	-3.921349000	0.624432000
1	4.284424000	-5.635957000	-0.491366000	6	-2.425670000	-4.894409000	-0.666485000
6	2.613469000	-1.679633000	3.356480000	1	-2.386979000	-5.427118000	-1.630909000
1	1.815034000	-0.926338000	3.275146000	1	-2.071225000	-5.589337000	0.111870000
1	2.492884000	-2.142761000	4.352439000	1	-1.731491000	-4.044091000	-0.714916000
6	3.968266000	-0.979385000	3.288239000	6	-4.797511000	-5.632004000	-0.244245000
1	4.106933000	-0.476784000	2.320089000	1	-5.841450000	-5.341207000	-0.059059000
1	4.040316000	-0.211270000	4.074605000	1	-4.477403000	-6.287998000	0.581901000
6	0.379848000	-4.452112000	1.711528000	1	-4.781003000	-6.240480000	-1.162757000
1	-0.632469000	-4.742159000	2.028443000	7	0.871901000	4.557142000	0.257423000
1	0.316485000	-4.147057000	0.657485000	7	3.510650000	-3.033659000	0.257423000
6	0.896540000	-3.315771000	2.586808000	7	-4.382551000	-1.523483000	0.257423000
1	0.874121000	-3.631407000	3.645616000	15	0.000000000	2.006561000	-0.035697000
1	0.201313000	-2.466482000	2.511017000	15	1.737733000	-1.003281000	-0.035697000
6	3.949712000	-2.847809000	-1.113525000	15	-1.737733000	-1.003281000	-0.035697000
6	3.277960000	-3.508901000	-2.181502000	33	0.000000000	0.000000000	1.307733000
6	3.818520000	-3.417078000	-3.472951000	1	4.811938000	-1.672149000	3.438017000
1	3.314096000	-3.928840000	-4.295368000	1	1.006090000	-5.355557000	1.775706000
6	4.969224000	-2.681929000	-3.734982000	1	-5.141093000	1.806479000	1.775706000
1	5.375063000	-2.633486000	-4.748885000	1	-3.854093000	-3.331186000	3.438017000
6	5.579533000	-1.983389000	-2.699192000	1	-0.957845000	5.003335000	3.438017000
1	6.457087000	-1.369529000	-2.913668000	1	4.135004000	3.549078000	1.775706000

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6	-3.360266000	-0.276620000	-0.889267000	6	1.421597000	-5.276948000	1.352707000
6	-3.464273000	-0.789892000	-2.335611000	6	4.078936000	-2.496065000	1.963041000
6	-4.982848000	-1.053869000	-2.541938000	1	4.109455000	-2.232583000	0.898728000
1	-5.376158000	-0.435739000	-3.360439000	6	5.520805000	-2.769783000	2.430547000
1	-5.163167000	-2.097126000	-2.835025000	1	5.568126000	-2.934586000	3.519132000
6	-5.729233000	-0.729852000	-1.226662000	1	6.161730000	-1.901064000	2.207975000
6	-6.806178000	0.342265000	-1.449194000	1	5.963800000	-3.650223000	1.943249000
1	-7.302581000	0.615061000	-0.507337000	6	3.508844000	-1.279197000	2.719089000
1	-7.576146000	-0.059761000	-2.126338000	1	2.492500000	-1.038792000	2.378201000
1	-6.396602000	1.251055000	-1.908723000	1	4.140873000	-0.393329000	2.550347000
6	-6.425522000	-1.971378000	-0.647882000	1	3.478419000	-1.464738000	3.805444000
1	-5.729364000	-2.807283000	-0.505601000	6	0.404701000	-5.800286000	0.339733000
1	-7.212619000	-2.300818000	-1.344192000	1	0.659179000	-5.379895000	-0.641046000
1	-6.906024000	-1.747181000	0.315187000	6	0.389758000	-7.334820000	0.216225000
6	-2.937351000	0.251621000	-3.364922000	1	1.384378000	-7.750491000	0.000509000
1	-1.856000000	0.370701000	-3.198209000	1	-0.289329000	-7.643819000	-0.595370000
1	-3.044304000	-0.206347000	-4.364778000	1	0.024521000	-7.811855000	1.139948000
6	-3.601361000	1.626156000	-3.370968000	6	-1.004467000	-5.292708000	0.698954000

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1	-3.123049000	2.277230000	-4.119590000	1	-1.735622000	-5.616154000	-0.059259000
6	-2.985823000	-3.297719000	-1.701884000	1	-1.024180000	-4.195484000	0.755164000
1	-2.364290000	-4.156981000	-1.992742000	6	1.528544000	2.996514000	-0.883545000
1	-2.792586000	-3.101989000	-0.637838000	6	1.131601000	3.385363000	-2.322459000
6	-2.639068000	-2.087073000	-2.561375000	6	1.648734000	4.842092000	-2.484640000
1	-2.753881000	-2.353358000	-3.627680000	1	2.403459000	4.896160000	-3.281053000
1	-1.576108000	-1.842353000	-2.420192000	1	0.836938000	5.516683000	-2.789375000
6	-4.888746000	0.160359000	1.035391000	6	2.263307000	5.307893000	-1.144594000
6	-4.825772000	-0.792611000	2.093345000	6	3.710393000	5.785600000	-1.339574000
6	-5.222532000	-0.394724000	3.378818000	1	4.176758000	6.060700000	-0.383021000
1	-5.184930000	-1.121834000	4.192718000	1	3.706889000	6.682825000	-1.978352000
6	-5.650495000	0.900829000	3.645572000	1	4.333662000	5.027382000	-1.830971000
1	-5.962803000	1.183085000	4.654406000	6	1.472991000	6.474226000	-0.528889000
6	-5.648663000	1.840657000	2.621424000	1	0.412388000	6.228923000	-0.394520000
1	-5.945010000	2.868717000	2.840630000	1	1.537991000	7.348499000	-1.195590000
6	-5.259865000	1.506552000	1.315256000	1	1.890615000	6.766766000	0.445091000
6	-4.291102000	-2.216829000	1.944590000	6	1.789141000	2.451074000	-3.379130000
1	-4.073677000	-2.385836000	0.883110000	1	1.350881000	1.448098000	-3.263960000
6	-2.966319000	-2.386274000	2.715145000	1	1.464065000	2.814896000	-4.370524000
1	-3.116328000	-2.255058000	3.799404000	6	3.311640000	2.339779000	-3.360130000
1	-2.211263000	-1.662020000	2.379016000	1	3.670543000	1.958263000	-2.393273000
1	-2.559525000	-3.397247000	2.556046000	1	3.652681000	1.640188000	-4.139587000
6	-5.296939000	-3.289735000	2.403914000	6	-1.289115000	4.189885000	-1.683805000
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1	-4.904915000	-4.295458000	2.180912000	1	-1.201577000	3.917288000	-0.622554000
1	-6.275283000	-3.191491000	1.912043000	6	-0.401401000	3.311648000	-2.558250000
6	-5.185212000	2.648394000	0.301785000	1	-0.570912000	3.566631000	-3.620059000
1	-4.924849000	2.218501000	-0.673451000	1	-0.714477000	2.263781000	-2.443035000
6	-6.508972000	3.420927000	0.150487000	6	2.674657000	4.072510000	1.065245000
1	-7.358487000	2.763417000	-0.082138000	6	1.819155000	4.425630000	2.148250000
1	-6.424486000	4.163754000	-0.659610000	6	2.377014000	4.556256000	3.428875000
1	-6.760517000	3.974145000	1.069609000	1	1.728942000	4.835280000	4.262486000
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1	-3.962324000	4.418801000	-0.075885000	6	4.542068000	3.917895000	2.616704000
1	-3.093711000	3.104242000	0.760612000	1	5.593311000	3.695194000	2.812197000
6	1.996048000	-2.749248000	-0.892602000	6	4.042591000	3.767383000	1.314364000
6	2.490533000	-2.631384000	-2.349170000	6	0.306128000	4.603386000	2.028581000
6	3.463514000	-3.830645000	-2.524145000	1	0.041005000	4.517623000	0.967804000
1	3.093508000	-4.516648000	-3.298257000	6	-0.186087000	5.971709000	2.536461000
1	4.450583000	-3.490776000	-2.866448000	1	-1.265289000	6.081868000	2.340989000
6	3.586981000	-4.576472000	-1.175502000	1	-0.043519000	6.073784000	3.624409000
6	3.247093000	-6.065906000	-1.337627000	1	0.332181000	6.813219000	2.054680000
1	3.271061000	-6.592635000	-0.373131000	6	-0.432190000	3.475095000	2.776347000
1	3.999210000	-6.534564000	-1.991667000	1	-1.519574000	3.562025000	2.623195000
1	2.262224000	-6.217352000	-1.798068000	1	-0.117823000	2.486246000	2.415329000
6	5.011299000	-4.488861000	-0.602996000	1	-0.243201000	3.526565000	3.861315000
1	5.348690000	-3.451007000	-0.492897000	6	4.992253000	3.191931000	0.264942000
1	5.708294000	-5.002738000	-1.283614000	1	4.477952000	3.215819000	-0.703692000
1	5.076944000	-4.983918000	0.376411000	6	5.294165000	1.715098000	0.580790000
6	1.319255000	-2.725152000	-3.369595000	1	5.832908000	1.615907000	1.537479000
1	0.692176000	-1.828813000	-3.248262000	1	5.927901000	1.274123000	-0.205380000
1	1.768474000	-2.650758000	-4.376407000	1	4.365360000	1.131880000	0.646381000
6	0.436485000	-3.969105000	-3.305093000	6	6.310061000	3.976272000	0.129396000
1	-0.045560000	-4.064002000	-2.321280000	1	6.146324000	5.047345000	-0.056668000
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6	4.457453000	-0.973063000	-1.802381000	1	6.928680000	3.888454000	1.037026000
1	4.877371000	-0.003304000	-2.106292000	7	-4.612500000	-0.246400000	-0.331462000
1	4.222581000	-0.903934000	-0.730869000	7	2.593906000	-3.845976000	-0.308787000
6	3.212778000	-1.284663000	-2.625890000	7	2.171670000	4.065412000	-0.296527000
1	3.477359000	-1.281248000	-3.698830000	33	-1.874718000	0.297547000	0.122041000
1	2.483149000	-0.473453000	-2.489378000	15	0.849829000	-1.799012000	0.036455000
6	2.379912000	-4.264353000	1.064749000	15	1.337487000	1.505295000	0.022958000
6	3.155223000	-3.703238000	2.119786000	15	0.133244000	-0.010347000	-1.202985000
6	3.020457000	-4.238716000	3.409612000	1	0.996059000	-4.897730000	-3.502077000
1	3.618482000	-3.819491000	4.221603000	1	5.253988000	-1.721412000	-1.936317000
6	2.137839000	-5.277553000	3.683333000	1	-1.061572000	5.262217000	-1.788508000
1	2.058419000	-5.683143000	4.695389000	1	3.810269000	3.303216000	-3.553613000
6	1.334676000	-5.772656000	2.662177000	1	-4.672494000	1.579014000	-3.625141000
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7	-3.745900000	3.634310000	2.509052000	7	-3.745900000	-3.634310000	-2.509052000
15	-1.130138000	1.116312000	-0.228575000	15	-1.130138000	-1.116312000	0.228575000
15	-1.987644000	1.724371000	1.761970000	15	-1.987644000	-1.724371000	-1.761970000
6	-3.826813000	3.006667000	3.809975000	6	-3.826813000	-3.006667000	-3.809975000
6	-0.430279000	3.627056000	4.742223000	6	-0.430279000	-3.627056000	-4.742223000
1	-0.382974000	2.783702000	4.038565000	1	-0.382974000	-2.783702000	-4.038565000
1	-0.282216000	3.234292000	5.761693000	1	-0.282216000	-3.234292000	-5.761693000
1	0.408838000	4.307300000	4.523411000	1	0.408838000	-4.307300000	-4.523411000
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6	-5.194817000	-0.116795000	2.715278000	6	-5.194817000	0.116795000	-2.715278000
1	-4.122856000	-0.166556000	2.477528000	1	-4.122856000	0.166556000	-2.477528000
1	-5.755663000	-0.548864000	1.870090000	1	-5.755663000	0.548864000	-1.870090000
1	-5.384169000	-0.747634000	3.599647000	1	-5.384169000	0.747634000	-3.599647000

6	-4.289965000	4.076682000	-2.099972000
1	-4.849367000	3.454201000	-2.818146000
1	-4.930639000	4.954283000	-1.896680000
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6	-2.117081000	5.312116000	-1.700127000
1	-1.145375000	5.585211000	-2.145054000
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6	-1.785992000	5.582819000	5.583119000
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6	-3.111743000	2.880249000	6.126719000
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6	-4.062785000	3.272629000	-0.812205000
1	-3.545956000	2.333698000	-1.062164000
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7	3.745900000	3.634310000	-2.509052000
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6	3.826813000	3.006667000	-3.809975000
6	0.430279000	3.627056000	-4.742223000
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1	0.282216000	3.234292000	-5.761693000
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6	2.977156000	3.144958000	-1.479637000
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1	4.122856000	-0.166556000	-2.477528000
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1	4.930639000	4.954283000	1.896680000
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1	7.508573000	2.396733000	-3.478596000
1	7.400360000	0.753198000	-4.139472000
1	7.721569000	0.987580000	-2.412160000
6	2.117081000	5.312116000	1.700127000
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1	2.740597000	6.128541000	-5.557199000
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1	1.271030000	5.041362000	-0.295274000
1	1.288548000	3.591344000	0.711468000

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1	-1.288548000	-3.591344000	0.711468000
6	-4.786374000	-1.984731000	-4.054022000
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1	-5.464580000	-1.886382000	-2.028237000
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6	-6.059446000	-4.524785000	-2.021361000
1	-6.482580000	-4.178448000	-2.974149000
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1	-3.196765000	-6.066615000	-1.007748000
1	-4.686302000	-5.678078000	-0.143747000
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1	5.384169000	0.747634000	3.599647000
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1	4.849367000	-3.454201000	-2.818146000
1	4.930639000	-4.954283000	-1.896680000
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1	1.288548000	-3.591344000	-0.711468000

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1	5.645797000	0.701617000	-5.560144000	1	5.645797000	-0.701617000	5.560144000
6	6.059446000	4.524785000	-2.021361000	6	6.059446000	-4.524785000	2.021361000
1	6.482580000	4.178448000	-2.974149000	1	6.482580000	-4.178448000	2.974149000
1	6.250698000	3.760734000	-1.256602000	1	6.250698000	-3.760734000	1.256602000
1	6.602004000	5.437390000	-1.729027000	1	6.602004000	-5.437390000	1.729027000
6	3.197401000	4.029923000	-0.238914000	6	3.197401000	-4.029923000	0.238914000
6	3.930629000	5.265859000	-0.826237000	6	3.930629000	-5.265859000	0.826237000
1	3.196765000	6.066615000	-1.007748000	1	3.196765000	-6.066615000	1.007748000
1	4.686302000	5.678078000	-0.143747000	1	4.686302000	-5.678078000	0.143747000
6	3.111743000	2.880249000	-6.126719000	6	3.111743000	-2.880249000	6.126719000
1	2.446144000	3.199543000	-6.931772000	1	2.446144000	-3.199543000	6.931772000
6	4.062785000	3.272629000	0.812205000	6	4.062785000	-3.272629000	-0.812205000
1	3.545956000	2.333698000	1.062164000	1	3.545956000	-2.333698000	-1.062164000
1	5.029261000	2.985099000	0.367999000	1	5.029261000	-2.985099000	-0.367999000
6	4.425486000	5.963452000	-3.213234000	6	4.425486000	-5.963452000	3.213234000
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15	2.102972000	1.034963000	-2.028695000	1	-2.873774000	-4.664836000	-3.575372000
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7	-3.293275000	4.442493000	1.274560000	1	-4.605450000	-6.979232000	0.678799000
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6	0.019752000	0.305582000	4.712788000	1	-1.815684000	6.619689000	-0.027828000
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1	-0.618562000	0.363202000	5.611436000	1	5.961059000	1.256054000	5.684708000
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6	0.846919000	-1.004639000	4.830750000	1	1.620327000	5.495318000	3.308676000
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7	4.186172000	4.010191000	-2.177187000	33	1.213817000	-1.196954000	-0.364877000
33	1.213817000	1.196954000	0.364877000	33	2.311550000	-1.950066000	1.731771000
33	2.311550000	1.950066000	-1.731771000	6	4.365248000	-3.472350000	3.508251000
6	4.365248000	3.472350000	-3.508251000	6	1.047305000	-4.251264000	4.645992000
6	1.047305000	4.251264000	-4.645992000	1	0.919558000	-3.365518000	4.007478000
1	0.919558000	3.365518000	-4.007478000	1	0.963641000	-3.933369000	5.698344000
1	0.963641000	3.933369000	-5.698344000	1	0.215467000	-4.945429000	4.441676000
1	0.215467000	4.945429000	-4.441676000	6	3.325383000	-3.465609000	1.261999000
6	3.325383000	3.465609000	-1.261999000	6	5.696416000	-0.258397000	2.539890000
6	5.696416000	0.258397000	-2.539890000	1	4.613426000	-0.165218000	2.376482000
1	4.613426000	0.165218000	-2.376482000	1	6.212904000	0.219490000	1.690861000
1	6.212904000	-0.219490000	-1.690861000	1	5.961345000	0.303917000	3.450583000
1	5.961345000	-0.303917000	-3.450583000	6	4.165987000	-4.224811000	-2.500028000
6	4.165987000	4.224811000	2.500028000	1	4.632803000	-3.570345000	-3.255235000
1	4.632803000	3.570345000	3.255235000	1	4.819047000	-5.113674000	-2.424899000
1	4.819047000	5.113674000	2.424899000	6	3.561019000	-3.968846000	4.572143000
6	3.561019000	3.968846000	-4.572143000	6	7.640799000	-1.829280000	2.854482000
6	7.640799000	1.829280000	-2.854482000	1	7.990341000	-2.865233000	2.974669000
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1	7.962056000	1.268705000	-3.747182000	1	8.168042000	-1.392624000	1.990455000
1	8.168042000	1.392624000	-1.990455000	6	2.055042000	-5.473259000	-1.877371000
6	2.055042000	5.473259000	1.877371000	1	1.031086000	-5.723359000	-2.201952000
1	1.031086000	5.723359000	2.201952000	1	2.575114000	-6.438654000	-1.734512000
1	2.575114000	6.438654000	1.734512000	6	2.523656000	-6.205098000	5.251227000
6	2.523656000	6.205098000	-5.251227000	1	3.490979000	-6.711924000	5.120933000
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1	1.725928000	6.923520000	-5.000754000	1	2.417839000	-5.965779000	6.321607000
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6	4.787169000	2.547701000	-6.127946000	1	4.962615000	-2.199102000	7.149091000
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6	2.769739000	4.658118000	2.961659000	1	2.838371000	-5.237304000	-3.898289000
1	2.838371000	5.237304000	3.898289000	1	2.168573000	-3.760383000	-3.190018000
1	2.168573000	3.760383000	3.190018000	6	2.398460000	-4.943251000	4.376733000
6	2.398460000	4.943251000	-4.376733000	1	2.394731000	-5.255363000	3.323163000
1	2.394731000	5.255363000	-3.323163000	6	1.990210000	-4.702242000	-0.552505000
6	1.990210000	4.702242000	0.552505000	1	1.478750000	-5.297283000	0.222513000
1	1.478750000	5.297283000	-0.222513000	1	1.378424000	-3.800705000	-0.703063000
1	1.378424000	3.800705000	0.703063000	6	5.327827000	-2.452337000	3.750555000
6	5.327827000	2.452337000	-3.750555000	6	4.972594000	-5.191835000	1.674941000
6	4.972594000	5.191835000	-1.674941000	6	6.116584000	-1.737876000	2.651959000
6	6.116584000	1.737876000	-2.651959000	1	5.866797000	-2.212187000	1.694696000
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6	5.525456000	2.023675000	-5.071763000	1	6.268005000	-1.248312000	5.273268000
1	6.268005000	1.248312000	-5.273268000	6	6.435284000	-4.825549000	1.364813000
6	6.435284000	4.825549000	-1.364813000	1	6.972911000	-4.536139000	2.277633000
1	6.972911000	4.536139000	-2.277633000	1	6.516516000	-4.006973000	0.637634000
1	6.516516000	4.006973000	-0.637634000	1	6.947656000	-5.704104000	0.942478000
1	6.947656000	5.704104000	-0.942478000	6	3.391747000	-4.287305000	-0.035459000
6	3.391747000	4.287305000	0.035459000	6	4.188938000	-5.548121000	0.398715000

6	4.188938000	5.548121000	-0.398715000	1	3.482187000	-6.361570000	0.625951000
1	3.482187000	6.361570000	-0.625951000	1	4.859987000	-5.921586000	-0.386887000
1	4.859987000	5.921586000	0.386887000	6	3.803982000	-3.497750000	5.870647000
6	3.803982000	3.497750000	-5.870647000	1	3.198942000	-3.877410000	6.697011000
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6	4.118904000	3.484183000	1.155833000	1	3.585222000	-2.530867000	-1.292025000
1	3.585222000	2.530867000	1.292025000	1	5.137979000	-3.221260000	-0.830126000
1	5.137979000	3.221260000	0.830126000	6	4.983240000	-6.359729000	2.669149000
6	4.983240000	6.359729000	-2.669149000	1	5.461983000	-6.080910000	3.619855000
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33	-1.129584000	1.306868000	-0.413376000	1	5.863769000	-1.285126000	-2.390225000
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33	-1.793364000	2.445369000	1.701097000	6	4.364471000	1.701976000	-6.656222000
33	-1.437200000	-1.032440000	0.478893000	1	4.358217000	1.339150000	-7.687388000
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33	-2.498858000	-1.989840000	-1.559136000	1	1.673578000	-5.546028000	3.374923000
33	1.897716000	-2.184439000	1.878589000	6	5.553291000	-2.134668000	3.275565000
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7	-3.207620000	4.841513000	2.165059000	1	6.490205000	-6.070844000	1.620030000
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1	3.199363000	4.910057000	1.102576000	1	3.868382000	6.013533000	-5.526268000
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6	3.080458000	-4.544549000	0.199315000	1	-2.765242000	-7.769462000	-2.863153000
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6	4.444875000	-5.515358000	2.065253000	1	6.301810000	6.144844000	-2.925244000
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1	1.438838000	4.533303000	-1.398443000	6	-5.938437000	-0.874047000	0.384177000
1	2.457458000	5.962102000	-1.088234000	1	-5.488201000	-0.515155000	-0.552921000
1	1.102062000	5.588347000	-0.010156000	1	-6.158637000	0.010419000	1.001142000
6	5.168677000	1.504241000	-4.361266000	1	-6.903879000	-1.348301000	0.144742000
6	5.144214000	3.213266000	1.961088000	6	3.747595000	-2.959887000	6.524926000
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1	5.682047000	2.455113000	2.551547000	6	7.444786000	0.503315000	-3.754269000
1	4.289355000	3.546356000	2.568558000	1	7.553401000	-0.102410000	-4.668358000
6	5.020012000	4.663098000	-0.895968000	1	7.997788000	-0.016104000	-2.954513000
1	4.519293000	5.638220000	-0.972819000	1	7.942676000	1.466556000	-3.937840000
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6	-3.949221000	3.492434000	-1.057281000	1	5.366228000	-1.694541000	5.901085000
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6	2.698325000	-4.315746000	4.791563000	6	-3.615684000	-3.872727000	1.390833000
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6	0.595900000	4.755714000	3.651838000	1	-6.676681000	4.797622000	4.275964000
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1	1.439020000	5.164970000	3.071523000	1	7.006148000	2.806472000	-1.519228000
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6	-4.168033000	-3.609460000	-6.107198000	1	7.264544000	3.293683000	-3.216203000
1	-4.035562000	-3.641450000	-7.191813000	6	0.710769000	-5.650170000	0.429615000
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6	1.741832000	-4.966081000	-0.467202000	1	0.167456000	-3.627364000	3.918713000
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1	1.995505000	-5.645178000	-1.298979000	1	-5.810514000	-4.964265000	0.746436000
6	5.135771000	1.061369000	-5.692238000	1	-6.774388000	-3.508403000	0.554099000
1	5.719652000	0.182399000	-5.974342000	6	-5.840305000	-1.301303000	-3.585867000
6	3.859027000	-5.804241000	0.669457000	1	-5.953481000	-1.434399000	-2.503483000
1	3.179236000	-6.665400000	0.732625000	6	1.532979000	-6.538148000	5.279022000
1	4.650278000	-6.083702000	-0.040102000	1	2.496483000	-7.068034000	5.257349000
6	-4.991283000	-1.809275000	1.130210000	1	0.756101000	-7.229561000	4.913365000
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6	5.202055000	-0.640076000	3.137954000	1	-7.387757000	-3.914749000	-2.980119000
1	4.157579000	-0.503832000	2.824066000	6	-7.243556000	-1.126795000	-4.196628000
1	5.851208000	-0.168485000	2.381717000	1	-7.189228000	-0.877022000	-5.268522000
1	5.352150000	-0.102518000	4.088764000	1	-7.774295000	-0.298753000	-3.698779000
6	2.606446000	4.424531000	-4.655262000	1	-7.861370000	-2.031013000	-4.098932000
1	2.772634000	4.720412000	-3.610892000	1	-2.776449000	-3.191103000	1.596970000
6	-4.607687000	-3.148321000	0.433917000	1	-4.143534000	-4.000155000	2.353111000
6	3.579059000	2.790585000	-6.290949000	6	-3.058208000	-5.219766000	0.939788000
1	2.944361000	3.266840000	-7.041537000	1	-3.845433000	-5.973472000	0.776655000
6	5.325322000	-0.724227000	-3.171930000	1	-2.379169000	-5.624251000	1.706613000
1	4.272420000	-0.639138000	-2.868118000	1	-2.478898000	-5.119064000	0.010112000

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Preface

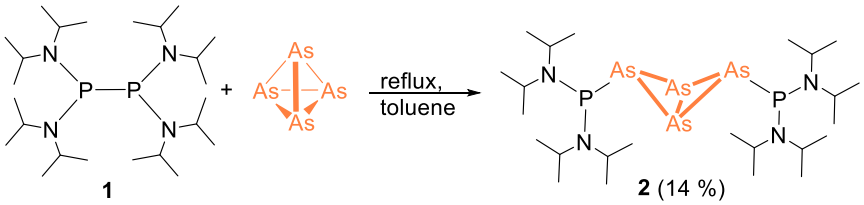
The following chapter includes unpublished results, which will be included in future publications or provide a basis for future research efforts. For the presented compounds, complete data of the single-crystal X-ray structural characterization are available, and the compounds are fully characterized by NMR spectroscopy, mass spectrometry and elemental analysis.

9. Thesis Treasury

9.1. Reactivity of [{(^{i}Pr$_2$N)$_2$P}$_2$] towards yellow arsenic

In 2004 *Lappert et al.* synthesized the diphosphine [P{N(SiMe$_3$)$_2$}$_2${N^{i}Pr$_2$}$_2$]$_2$, which reversibly dissociates in solution to the phosphinyl radical $^{\bullet}$[P{N(SiMe$_3$)}{N^{i}Pr$_2$}].[1] The reaction of such phosphinyl radicals with white phosphorus and the interpnictogen compound AsP$_3$ were already reported and led to the formation of [{(XX')$_2$P}$_2$(μ,η$^{1:1}$-E$_4$)] (X = X' = (^{i}Pr$_2$N); X = N(SiMe$_3$) and X' = (^{i}Pr$_2$N); or X/X' = [(H$_2$C)$_2$(NDipp)$_2$]; E = P, As), respectively.[1-2] Related complexes are accessible by the reaction of Cp^R (Cp^R = Cp'', Cp^{BIG}, …) with E$_4$, which undergoes also a radical reaction pathway.[3] Therefore it was of interest, which reactivity can be observed with yellow arsenic.

The reaction of [{(^{i}Pr$_2$N)$_2$P}$_2$][4] (**1**) with an excess of yellow arsenic in boiling toluene leads to the formation of [{(^{i}Pr$_2$N)$_2$P}$_2$(μ,η$^{1:1}$-As$_4$)] (**2**). Crystals of **2** were obtained as colourless plates in crystalline yield of 14 % (Scheme 9.1).



Scheme 9.1. Reaction of **1** with yellow arsenic.

The ^{31}P{^{1}H} NMR spectrum of **2** in C$_6$D$_6$ at room temperature shows one singlet at δ = 96.6 ppm. Compound **2** was also investigated by ^{1}H NMR spectroscopy at room temperature in C$_6$D$_6$, which shows only one shifted set of signals for the isopropyl groups. This indicates that both radical parts have the same chemical environment. The chemical composition was proofed by elemental analysis.

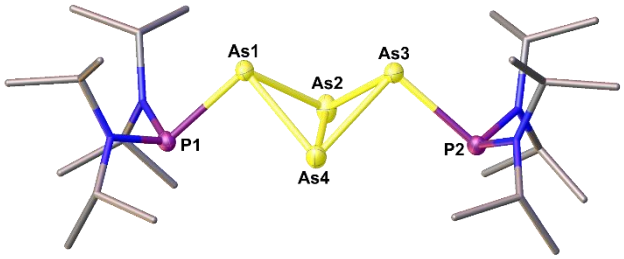


Figure 9.1. Molecular structure of **2** in the solid state. Thermal ellipsoids are shown at the 50 % probability level. Hydrogen atoms are omitted for clarity.

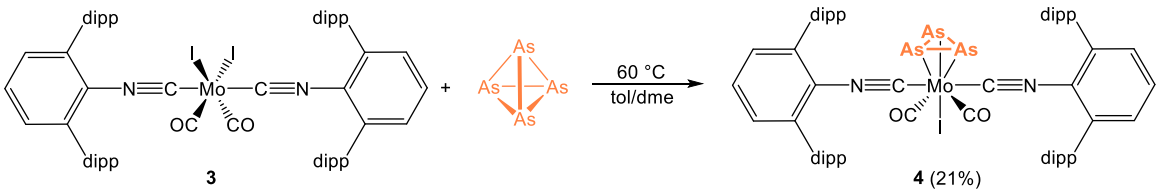
The molecular structure of **2** reveals a dinuclear compound bearing an As$_4$ butterfly ligand, which binds to both phosphorus fragments (Figure 9.1). The As-As bond distances vary from 2.4453(13) to 2.4493(13) Å, expect for the As2-As4 bond distance, which is

shortened to 2.3866(14) Å. This trend is comparable to other butterfly complexes.[5] The As1···As3 distance lies with 3.1707(12) Å in a non-bonding area. A similar compound was prepared by the group of *Goicoechea.* They investigated recently the reaction of a phosphenium salt with [Na(dioxane)$_{3.3}$][AsCO]. This reaction leads to the formation of [{(H$_2$C)$_2$(NDipp)$_2$P}$_2$(μ,η$^{1:1}$-As$_4$)][6] containing also an As$_4$ butterfly ligand. An interesting fact is the bonding between a nitrogen – phosphorus – arsenic atom.

9.2. Reactivity of [(CNAr^{dipp2})$_2$Mo(CO)$_2$(I)$_2$] towards yellow arsenic

The group of *J. S. Figueroa* are specialized in the preparation of highly reactive metal centers, stabilized by *m*-terphenyl isocyanides. Such complexes are the isolobal analogues to unsaturated metal carbonyls.[7] Due to the steric properties of these ligands, they are able to stabilize low-coordinated transition metal and main group complexes. Furthermore, these complexes show a high reactivity towards small molecules like N$_2$, H$_2$ and P$_4$.[8] Recently, they reported the synthesis of a mononuclear molybdenum complex containing a planar *cyclo*-P$_4$ unit by the reaction of [(CNAr^{dipp2})$_2$Mo(CO)$_2$(I)$_2$] (**3**, Ar^{dipp2} = 2,6-(2,6-(^{i}Pr)$_2$C$_6$H$_3$)$_2$C$_6$H$_3$) with P$_4$. The product [(CNAr^{dipp2})$_2$Mo(η^4-P$_4$)(CO)$_2$(I)$_2$] can release the P$_4$ unit by photo-elimination and can be reversible coordinated by reheating.[8e] Thereby the question arose if such an activation and release is also possible with yellow arsenic.

Treatment of [(CNAr^{dipp2})$_2$Mo(CO)$_2$(I)$_2$] (**3**) with an excess of yellow arsenic in a toluene/dme mixture at 60 °C leads to the formation of [(CNAr^{Dipp2})$_2$Mo(CO)$_2$(I)(η^3-As$_3$)] (**4**), which is isolated as yellow air sensitive solid in crystalline yield of 21 % (Scheme 9.2).



Scheme 9.2. Reaction of **3** with yellow arsenic.

Freshly dissolved **4** in C$_6$D$_6$ was investigated by ^{1}H NMR spectroscopy at room temperature, which shows one set of signals for the equivalent CNAr^{dipp2} ligands. The chemical composition was proofed by elemental analysis.

The molecular structure of **4** reveals a mononuclear molybdenum complex bearing a *cyclo*-As$_3$ ligand, coordinating in an η^3 fashion to the molybdenum atom (Figure 9.2). The As$_3$

cycle is disordered over three positions with occupancies for As2 and As3 of 46:36:18. In contrast to phosphorus no planar *cyclo*-As_4 unit could be obtained. The As-As distances are in the range between 2.167(8) and 2.412(9) Å, which lie between an As-As single[9] and double[10] bond. The As-As-As bond angles are around 60 °. The Mo-As bond distances are between 2.589(7) and 2.709(3) Å in **4**. A similar complex to **4** which also contains a *cyclo*-As_3 unit is [Cp*Mo(CO)$_2$(η^3-As_3)],[11] which exhibits As-As distances between 2.372(1) and 2.377(2) Å and Mo-As bond distances between 2.639(1) and 2.706(2) Å.

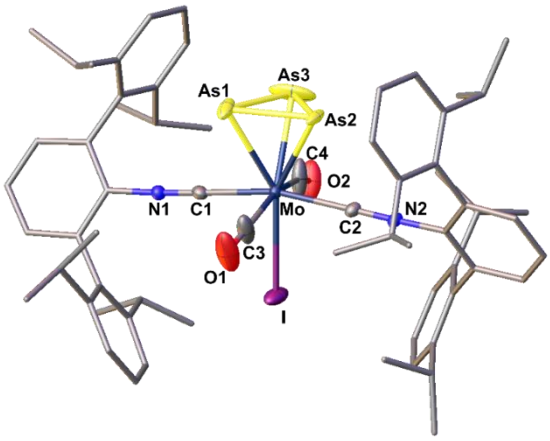


Figure 9.2. Molecular structure of **4** in the solid state. Thermal ellipsoids are shown at the 50 % probability level. Hydrogen atoms are omitted for clarity.

In the case of phosphorus, with the same reaction conditions a *cyclo*-P_4 unit could be obtained, changing the reaction conditions to 80 °C leads to the release of a phosphorus atom and to a *cyclo*-P_3 unit. With yellow arsenic, there couldn't be observed a formation of a *cyclo*-As_4 unit.

9.3. References

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9.4. Supporting Information

9.4.1. Synthesis and Characterization

General Remarks

All manipulations were performed with rigorous exclusion of oxygen and moisture using standard Schlenk techniques on a dual manifold Schlenk line with Argon or N_2 inert gas or glove box filled with nitrogen containing a high-capacity recirculator (<0.1 ppm O_2). Traces of oxygen and moisture in the inert gas were removed by passing it through a drying column filled with Cu/$MgSO_4$ catalyst as well as, concentrated H_2SO_4 and orange gel, respectively.

All solvents were degassed and purified by standard procedures. All NMR spectra have been recorded using deuterated d_6-benzene that was dried (over Na/K), refluxed for three hours and then distilled under inert atmosphere.

Characterization methods

Mass spectrometry was performed using a Jeol AccuTOF GCX LIFDI mass spectrometer or an Agilent Q-TOF 6540 UHD ES mass spectrometer by the MS department of the University of Regensburg. The compounds were dissolved in the corresponding solvent in a glove box under N_2 atmosphere. The observed fragments were assigned according to the mass/charge (m/z) ratio and the corresponding isotope pattern. Elemental analysis (CHN) were performed by the department of central analyses of the University of Regensburg on a Vario micro cube and a MT5 micro scale device. The compounds were filled in tin capsules in a glove box under N_2 atmosphere.

^{1}H and ^{31}P NMR spectra were recorded on a Bruker Avance III HD 400 (^{1}H: 400.130 MHz, ^{31}P: 161.976 MHz) spectrometer at the NMR department of the University of Regensburg. The chemical shifts are reported in ppm relative to external TMS (^{1}H) or 85 % H_3PO_4 (^{31}P). The chemical shifts δ are given in parts per million [ppm] and coupling constants J in [Hz].

Starting materials

The compounds [{(^{i}Pr$_2$N)$_2$P}$_2$][1] (**1**), [(CNAr^{dipp2})$_2$Mo(CO)$_2$(I)$_2$][2] (**3**), potassium graphite[3] and As_4[4] were prepared according to literature procedures.

9.4.1.1. Synthesis of [{(^{i}Pr$_2$N)$_2$P}$_2$(μ,η$^{1:1}$-As$_4$)] (**2**)

All manipulations were performed ***under exclusion of light***. [(^{i}Pr$_2$N)$_2$P)$_2$] (**1**) (100 mg, 0.2 mmol) was dissolved in 10 mL toluene and was added to a freshly prepared solution of As$_4$ in toluene (250 mL). The solution was refluxed for 2 hours. The solvent was removed in vacuum and the orange residue was stored at least over night to ensure the degradation of the excess of unreacted As$_4$ into As$_{grey}$. After dissolving the orange solid in 15 mL Et$_2$O, the solution was filtered over celite to remove the insoluble As$_{grey}$. 15 mL of ^{n}hexane were added. The solution was stored at -30 °C for a few days to yield crystals of **2**, suitable for X-ray analysis.

Crystallin Yield: 23 mg (14 %, 0.03 mmol)

^{1}H NMR (C$_6$D$_6$, 300 K): δ [ppm] = 3.35 (m, 8H, C***H***MeMe'), 1.26 (d, 24H, CH***Me***Me', $^{3}J_{HH}$ = 7 Hz), 1.06 (d, 24H, CHMe***Me'***, $^{3}J_{HH}$ = 7 Hz).

^{31}P{^{1}H} NMR (C$_6$D$_6$, 300 K): δ [ppm] = 96.6 (s, 2P).

EA calculated for C$_{24}$H$_{56}$As$_4$N$_4$P$_2$: C: 37.81, H: 7.40, N: 7.35; found [%]: C: 37.89, H: 7.07, N: 7.05.

LIFDI-MS (toluene): m/z (%) = 231 (100, [C$_{12}$H$_{28}$N$_2$P]$^{+}$). Compound **2** is very sensitive and is destroyed by the MS measurement.

9.4.1.2. Synthesis of [(CNAr^{dipp2})$_2$Mo(CO)$_2$I(η^3-As$_3$)] (**4**)

A 4:1 toluene/DME solution of [(CNAr^{dipp2})Mo(CO)$_2$(I)$_2$] (**3**, Ar^{dipp2} = 2,6-(2,6-(^{i}Pr)$_2$C$_6$H$_3$)$_2$C$_6$H$_3$)) (200 mg, 0.16 mmol, 12 mL) and an excess of yellow arsenic in CS$_2$ was stirred in a sealed 50 mL Schlenk ampoule at 60 °C for 2h. The colour changed from red to yellow. To the reaction mixture was added 4 mL of pentane, and the solution was chilled at - 30 °C for 30 minutes and then filtrated. The solution was taken to dryness, resolved in Et$_2$O, filtrated over diatomaceous earth and placed in the freezer at -30 °C to afford **4** as yellow blocks suitable for X-ray diffraction.

Crystalline Yield: 45 mg (21 %, 0.03 mmol)

^{1}H NMR (400 MHz C$_6$D$_6$, 25 °C) δ = 7.38 (t, $^{3}J_{HH}$ = 8 Hz, 4H), 7.22 (d, $^{3}J_{HH}$ = 8 Hz, 8H), 6.88 – 6.75 (m, 6H), 2.63 (sept, $^{3}J_{HH}$ = 7 Hz, 8H), 1.42 (d, $^{3}J_{HH}$ = 7 Hz, 24H), 1.01 (d, $^{3}J_{HH}$ = 7 Hz, 24H).

EA calculated for: C$_{64}$H$_{74}$N$_2$As$_3$IMoO$_2$: C: 56.90, H: 5.52, N: 2.07; found [%]: C: 56.45, H: 5.48, N: 1.98.

LIFDI-MS (toluene): m/z (%) = 1324.23 (100, [(CN^{Dipp2})$_2$Mo(I)(CO)(As$_3$)]), 1422.16 (46, [(CN^{Dipp2})$_2$Mo(I)$_2$(As$_3$)]).

9.4.2. NMR studies

9.4.2.1. [((^{i}Pr$_2$N)$_2$P)$_2$(μ,η$^{1:1}$-As$_4$)] (**2**)

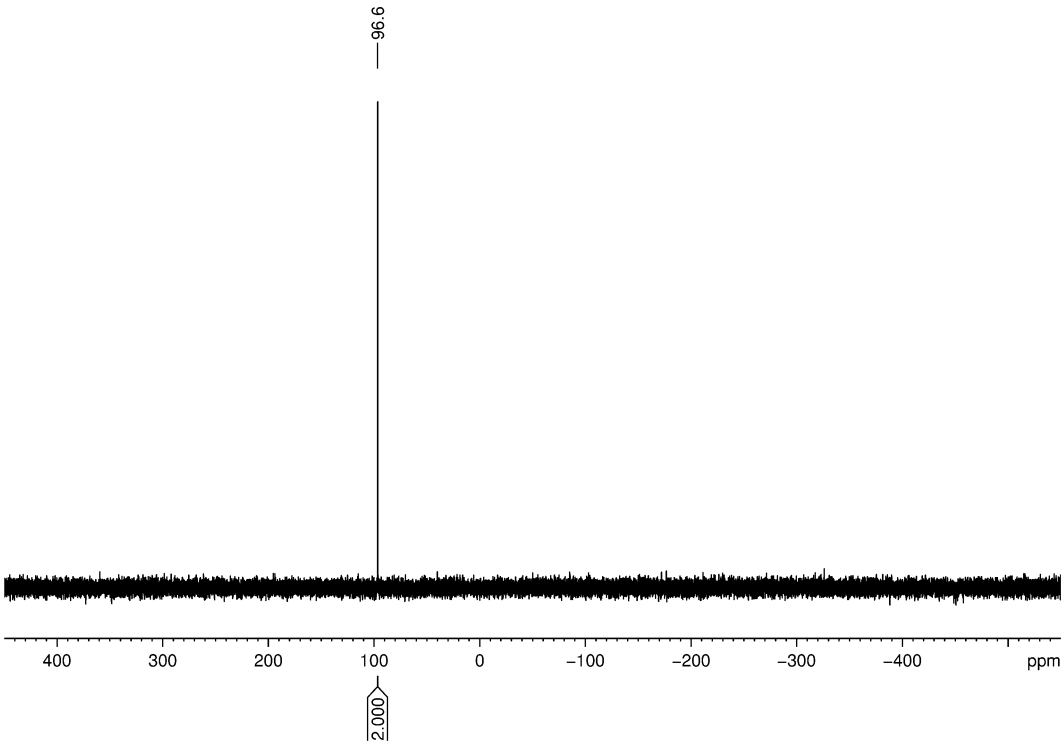

Figure S9.1. ^{31}P{^{1}H} NMR spectrum of **2** in C$_6$D$_6$ at room temperature.

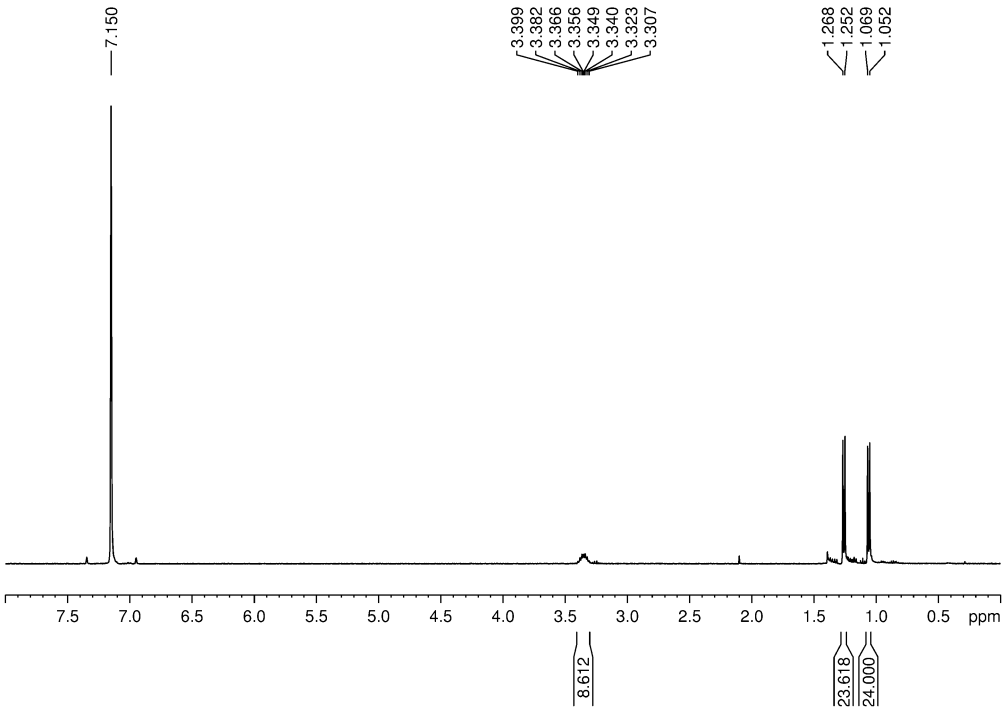

Figure S9.2. ^{1}H NMR spectrum of **2** in C_6D_6 at room temperature.

9.4.2.2. [(CNAr^{dipp2})$_2$Mo(CO)$_2$I(η^3-As$_3$)] (**4**)

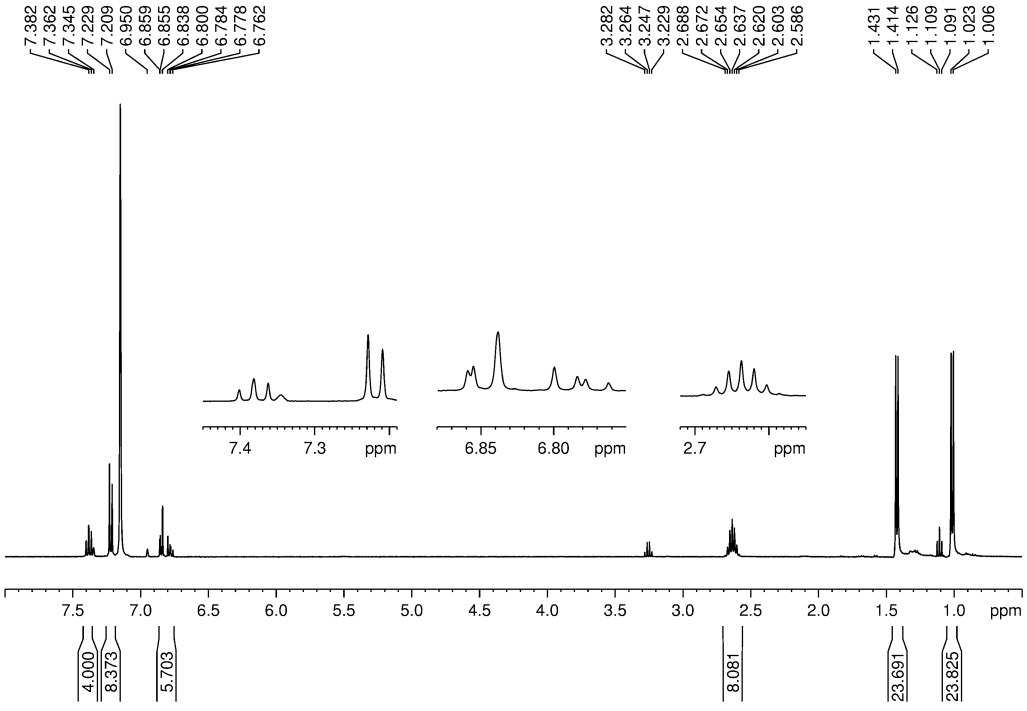

Figure S9.3. ^{1}H NMR spectrum of **4** in C_6D_6 at room temperature.

9.4.3. Details on single crystal X-ray structure analysis

The X-ray diffraction experiments were performed on a SuperNova diffractometer (Rigaku, formerly Agilent Technologies) with an Atlas CCD detector applying Cu-K_α radiation (λ = 1.54178 Å) (**2**, **4**). All measurements were performed at 123 K, respectively. Data collection and reduction were performed with CrysAlisPro[5] (Version 171.41.21a, 2019 (**4**), 171.41.76a, 2020 (**2**)). For the compound **4** a gaussian absorption correction based on gaussian integration over a multifaceted crystal model was applied. For compound **2** an analytical numeric absorption correction[6] using a multifaceted crystal model was applied. Using Olex2, were the structures solved by direct methods with ShelXT[7] and refined by full-matrix least-squares method against F^2 in anisotropic approximation using ShelXL.[8] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined in calculated positions using riding on pivot atom model.

Figures were created with Olex2.[9]

9.4.3.1. $[(({}^{i}Pr_2N)_2P)_2(\mu,\eta^{1:1}\text{-}As_4)]$ (**2**)

Compound **2** crystallizes from a ^{n}hexane:diethyl ether (1:1) solution at -30 °C in the orthorhombic space group *Pbca* as slightly yellow plate. The asymmetric unit contains one molecule of **2**. The structure in solid state is given in Figure S9.4.

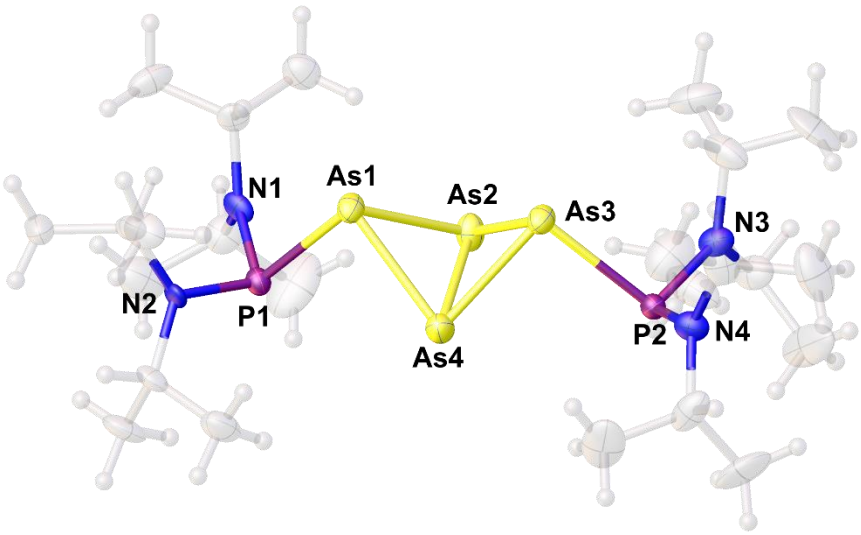

Figure S9.4. Molecular structure of **2** in solid state. Selected bond lengths [Å] and angles [°]: As1-As2 2.4493(13), As1-As4 2.4453(13), As2-As3 2.4489(13), As3-As4 2.4462(13), As2-As4 2.3866(14), As1-P1 2.371(2), As3-P2 2.363(2), P1-N1 1.697(7), P1-N2 1.695(7), P2-N3 1.690(7), P2-N4 1.682(7), As4-As1-As2 58.37(4), As4-As3-As2 58.36(4), As3-As2-As1 80.68(4), As4-As2-As1 60.73(4), As4-As2-As3 60.76(4), As1-As4-As3 80.81(4), As2-As4-As1 60.90(4), As2-As4-As3 60.88(4).

9.4.3.2. $[(CNAr^{Dipp2})_2Mo(CO)_2I(\eta^3\text{-}As_3)]$ (**4**)

Compound **4** crystallizes from a concentrated diethyl ether solution at -30 °C in the monoclinic space group $P2_1/c$ as yellow blocks. The asymmetric unit contains one molecule of **4** and half a molecule of Et_2O. The arsenic atoms As2 and As3 are disordered over three positions in a ratio of 46:36:18 (A:B:C, see Figure S9.5, right). Additionally, are both CO ligands and the iodine disordered over two positions in a ratio of 75:25. Furthermore, one dipp group is disordered over all positions in a ratio of 59:41 and one isopropyl group is disordered in a ratio of 75:25. The structure in solid state is given in Figure S9.5.

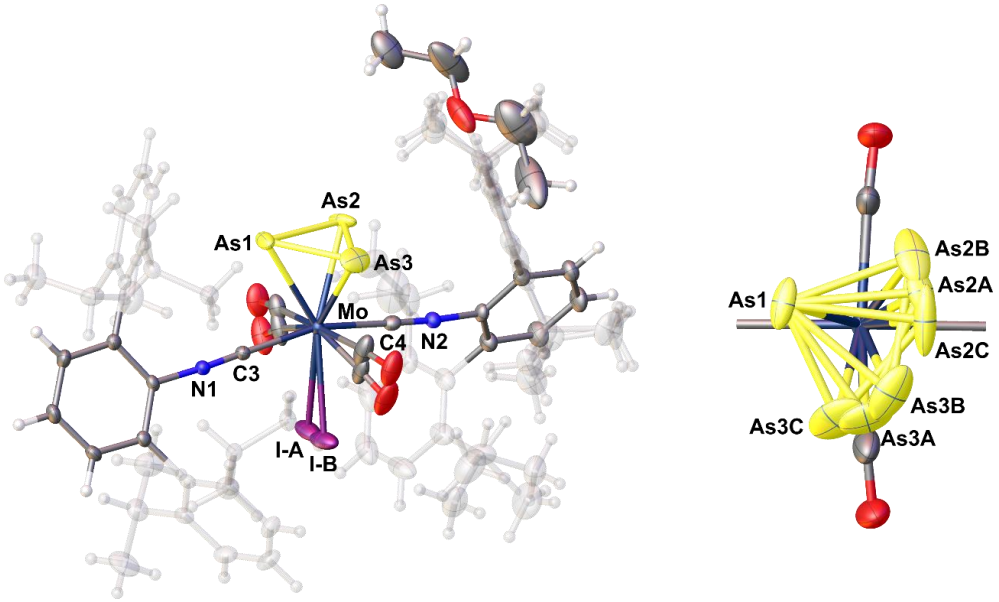

Figure S9.5. Left: Molecular structure of compound **4**, thermal ellipsoids are drawn at the 50 % probability level. Solvent molecules are omitted for clarity. Right: disordered As_3 unit. Selected bond lengths [Å] and angles [°]: Mo1-As1 2.6771(3), Mo1-As2A 2.666(2), Mo1-As2B 2.636(3), Mo1-As3A 2.672(3), Mo1-As3B 2.709(3), Mo1-As2C 2.666(8), Mo1-As3C 2.589(7), As2A-As3A: 2.334(4), As2A- As1 2.329(3), As3A-As1 2.385(3), As1-As3B 2.358(3), As1-As2B 2.320(3), As3B-As2B 2.338(3), As1-As2C 2.412(9), As1-As3C 2.167(8), As3C-As2C 2.274(11), Mo1-IA 2.8008(3), Mo1-IB 2.7935(8), Mo1-C3 2.123(2), Mo1-C4 2.122(2), Mo1-C1A 2.089(7), Mo1-C2A 2.036(7), Mo1-C2B 2.05(3), Mo1-C1B 2.01(2), N1-C3 1.157(3), N2-C4 1.158(3), O2A-C2A 1.122(7), O2B-C2B 1.16(3).

9.4.3.3. Crystallographic Information

Table S9.1. Crystallographic data and details of diffraction experiments for **2** and **4**.

Compound	**2**	**4**·0.5 Et_2O
Formula	$C_{24}H_{56}As_4N_4P_2$	$C_{66}H_{79}As_3IMoN_2O_{2.5}$
$D_{calc.}$/ g cm^{-3}	1.466	1.473
μ/mm^{-1}	5.536	7.687
Formula Weight	762.34	1387.91
Colour	clear colourless	clear yellow
Shape	plate	block
Size/mm^3	0.18×0.17×0.03	0.11×0.08×0.06
T/K	122.9(2)	122.97(12)
Crystal System	orthorhombic	monoclinic
Space Group	*Pbca*	$P2_1/c$
a/Å	21.0349(5)	19.2625(3)
b/Å	12.8250(3)	17.0451(2)
c/Å	25.6097(7)	20.8112(2)
α/°	90	90
β/°	90	113.667(2)
γ/°	90	90
V/Å^3	6908.8(3)	6258.27(16)
Z	8	4
Z'	1	1
Wavelength/Å	1.54184	1.54184
Radiation type	Cu K$_\alpha$	Cu K$_\alpha$
Θ_{min}/°	3.452	3.479
Θ_{max}/°	73.753	74.210
Measured Refl's.	18984	30773
Indep't Refl's	6441	12311
Refl's I≥2 σ(I)	5579	11145
R_{int}	0.0556	0.0268
Parameters	323	925
Restraints	0	155
Largest Peak	2.210	0.970
Deepest Hole	-0.832	-0.768
GooF	1.121	1.012
wR_2 (all data)	0.1907	0.0728
wR_2	0.1866	0.0703
R_1 (all data)	0.0838	0.0337
R_1	0.0750	0.295

9.5. References

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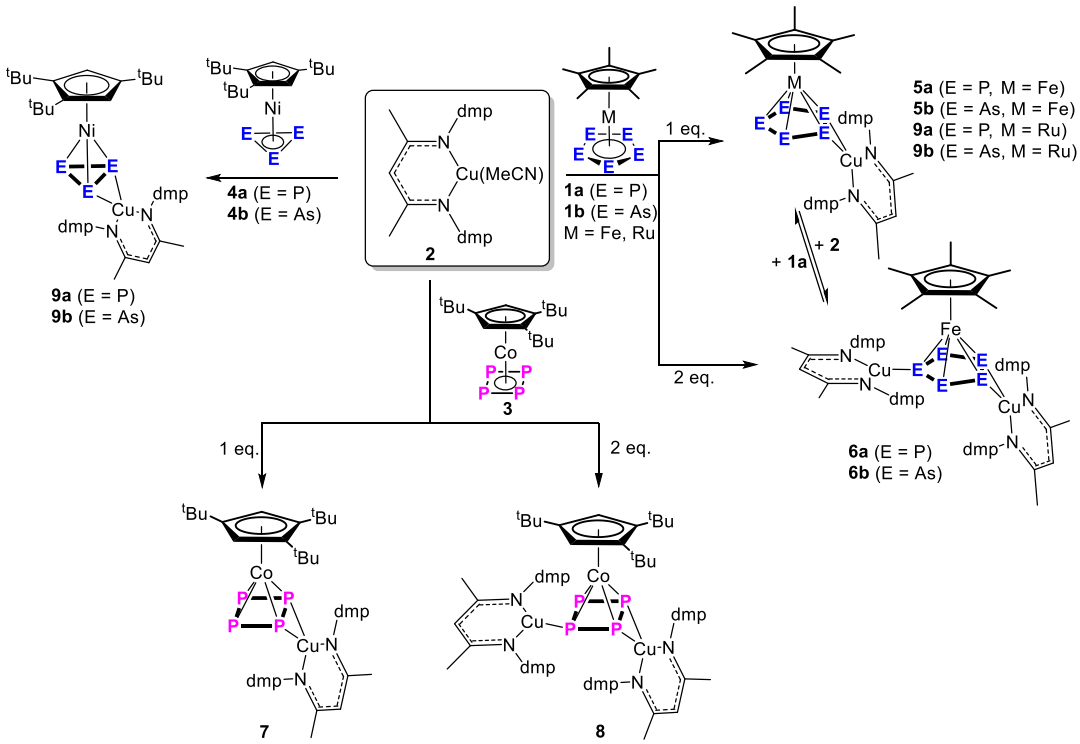
10. Conclusion

This work provides a detailed insight into the reactivity of M(I) (M = Cu, Ni, Ga) *β*-diketiminato complexes towards E_n (E = P, As; n = 3-5) ligand compounds and the reactivity of late transition metal (Ni, Cu) complexes and main group (Al, Ga, cyclic alkyl amino carbenes) compounds towards white phosphorus, yellow arsenic and the interpnictogen compound AsP_3. Of particular interest are the use of *β*-diketiminato ligand systems (nacnac, L^1 = [{N($C_6H_3Me_2$-2,6)C(Me)}$_2$CH]$^-$); L^3 = [{N($C_6H_3{}^iPr_2$-2,6)C(Me)}$_2$CH]$^-$)) and cyclic alkyl amino carbenes (CAACs). The numeration of compounds in the individual subchapters are independent from each other and similar to the numeration in the chapters of the thesis (except of chapter 3 and 7 which is connected in chapter 10.1).

10.1. Reactivity of Cu(I) Nacnac Complexes Towards Polypnictogen Compounds

The reactivity of [L^3Cu(MeCN)] towards white phosphorus and yellow arsenic was studied in our group. These reactions lead to the formation of molecular and neutral copper complexes containing an intact E_4 tetrahedron.[1] Similar observations about the integrity of the copper coordinated E-E bonds in [(L^3Cu)$_2$(μ,η$^{2:2}$-E_4)] (E = P, As) were made in this dissertation based on the studied reactivity of [L^1Cu(MeCN)] towards polypnictogen ligand complexes.



Scheme 10.1. Summary of the coordination compounds obtained from **2** with selected polypnictogen ligand complexes. (eq. based on **2**, dmp = 2,6-dimethylphenyl)

The reaction of [L^1Cu(NCMe)] (**2**) with [Cp*M(η^5-E_5)] (M = Fe, E = P (**1a**), As (**1b**); M = Ru, E = P (**1a-Ru**), As (**1b-Ru**)) leads to the formation of the heterometallic complexes [(Cp*M)(μ,$\eta^{5:2}$-E_5)(L^1Cu)] (M = Fe, E = P (**5a**), As (**5b**); M = Ru, E = P (**9a**), As (**9b**), Scheme 10.1) and [(Cp*Fe)(μ_3,$\eta^{5:2:1}$-E_5)($L^1Cu)_2$] (E = P (**6a**), As (**6b**), Scheme 10.1). The molecular structure of **6a** and **6b** reveals a trinuclear heterobimetallic complex in which the E_5 ligand coordinates in a side-on η^2 coordination mode to one {L^1Cu} fragment and in an end-on η^1 coordination mode to the second {L^1Cu} fragment. The side-on coordinated {L^1Cu} fragment is nearly perpendicular to the E_5 ring while the η^1-coordinated {L^1Cu} fragment is nearly coplanar with the *cyclo*-E_5 ring. We were able to show experimentally and by DFT calculations that a side-on coordination is preferred to the end-on coordination.

The dynamic behavior of **6a** was investigated by variable-temperature $^{31}P\{^1H\}$ NMR spectroscopy. While at room temperature only one broad singlet could be observed, at 193 K **6a** shows three sharp multiplets with an integral ratio of 1:2:2 displaying an AMM'XX' spin system. The coupling pattern observed at low temperature indicates that the geometry of **6a** determined by single-crystal X-ray diffractions, is retained in solution at that temperature. Further, we investigated a crystalline sample of **6a** by $^{31}P\{^1H\}$ MAS NMR spectroscopy which also exhibits three multiplets at similar chemical shifts. There are two possibilities for the dynamic process of **6a** in solution, either a fast dissociation-reassociation of the L^1Cu moiety or an $\eta^1 \rightarrow \eta^2 \rightarrow \eta^1$ walk of the two {L^1Cu} units along the P_5 ring. With a $^{31}P\{^1H\}$ EXSY experiment at 233 K we were able to identify the dynamic process as an $\eta^1 \rightarrow \eta^2 \rightarrow \eta^1$ walk of the two {L^1Cu} units along the P_5 ring. DFT calculations suggest that the copper coordinated E-E bonds in **5a**, **5b**, **6a** and **6b** are still intact.

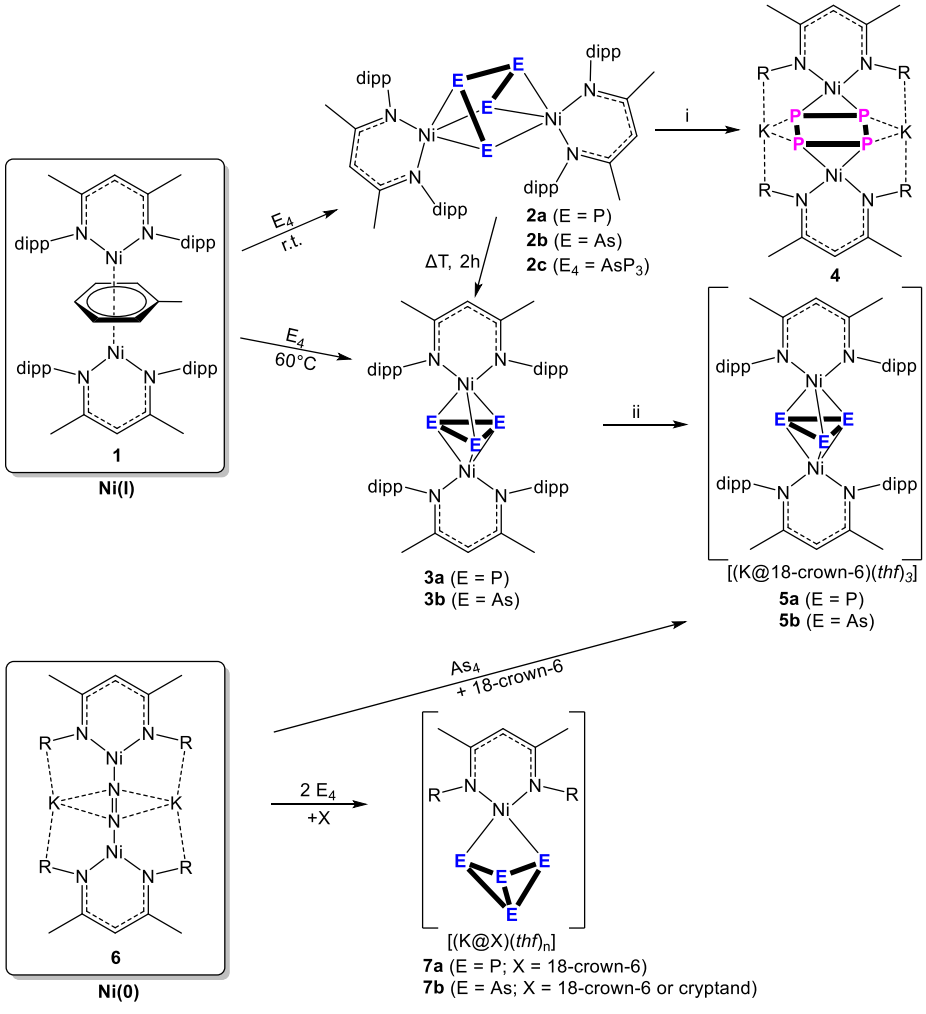
In order to investigate, if this reactivity can also be extended to other *cyclo*-E_n ligand complexes, we reacted **2** with [Cp'''Co(η^4-P_4)] (**3**, Cp''' = η^5-$C_5H_2{}^tBu_3$) and [Cp'''Ni(η^3-E_3)] (E = P (**4a**), As (**4b**), Scheme 10.1). The 1:1 reactions of **2** with **3**, **4a** and **4b** lead to the formation of [(Cp'''Co)(μ,$\eta^{4:2}$-P_4)(L^1Cu)] (**7**) and [(Cp'''Ni)(μ,$\eta^{3:2}$-E_3)(L^1Cu)] (E = P (**9a**), As (**9b**)). By the reaction of **3** with an excess of **2** the trinuclear compound [(Cp'''Co)(μ_3,$\eta^{4:2:1}$-P_4)($L^1Cu)_2$] (**8**) could be obtained. As in the case of [Cp*Fe(η^5-E_5)], first a side-on coordination to the *cyclo*-P_4 ring occurs.

The dynamic behavior of **7**, **8** and **9a** was investigated by VT $^{31}P\{^1H\}$ NMR spectroscopy. All spectra show broad signals at room temperature. For compound **7** and **9a**, the dynamic processes are not even slowed down at 193 K. Compound **8** shows a splitting into four broad singlets at 193K with an integral ratio of 1:1:1:1. However, no fine splitting pattern can be observed, which indicates its highly dynamic behavior in solution. Further, DFT calculations show that all copper coordinated E-E bonds are still intact, even if they are elongated.

All in all, the synthesized compounds represent molecular and neutral examples of group 11 element complexes coordinated to intact *cyclo*-E_5, *cyclo*-P_4 and *cyclo*-E_3 ligands, respectively.

10.2. Conversion of E_4 (E_4 = P_4, As_4, AsP_3) by Ni(0) and Ni(I) Synthons – A Comparative Study

In 2010, *Driess et al.* reported the reaction of [(L^3Ni)$_2$tol] (**1**) towards white phosphorus, which leads to [(L^3Ni)$_2$(μ-η^2,κ^1:η^2,κ^1-P_4)] (**2a**).[2] The central core is a Ni_2P_4 unit in form of a prism. We were interested in the reactivity of **1** towards E_4 (E_4 = P_4, As_4, AsP_3) and also in the comparative reaction with an electron richer nickel(0) precursor. Parts of this chapter were already described in the Ph.D. thesis of Dr. C. Graßl.[3]



Scheme 10.2. Summary of the compounds obtained by the conversion of E_4 (E_4 = P_4, As_4, AsP_3) with Ni(I) and Ni(0) synthons. i) potassium graphite, ii) potassium graphite, 18-crown-6. (R = dipp = 2,6-diisopropylphenyl, X = 18-crown-6 or cryptand)

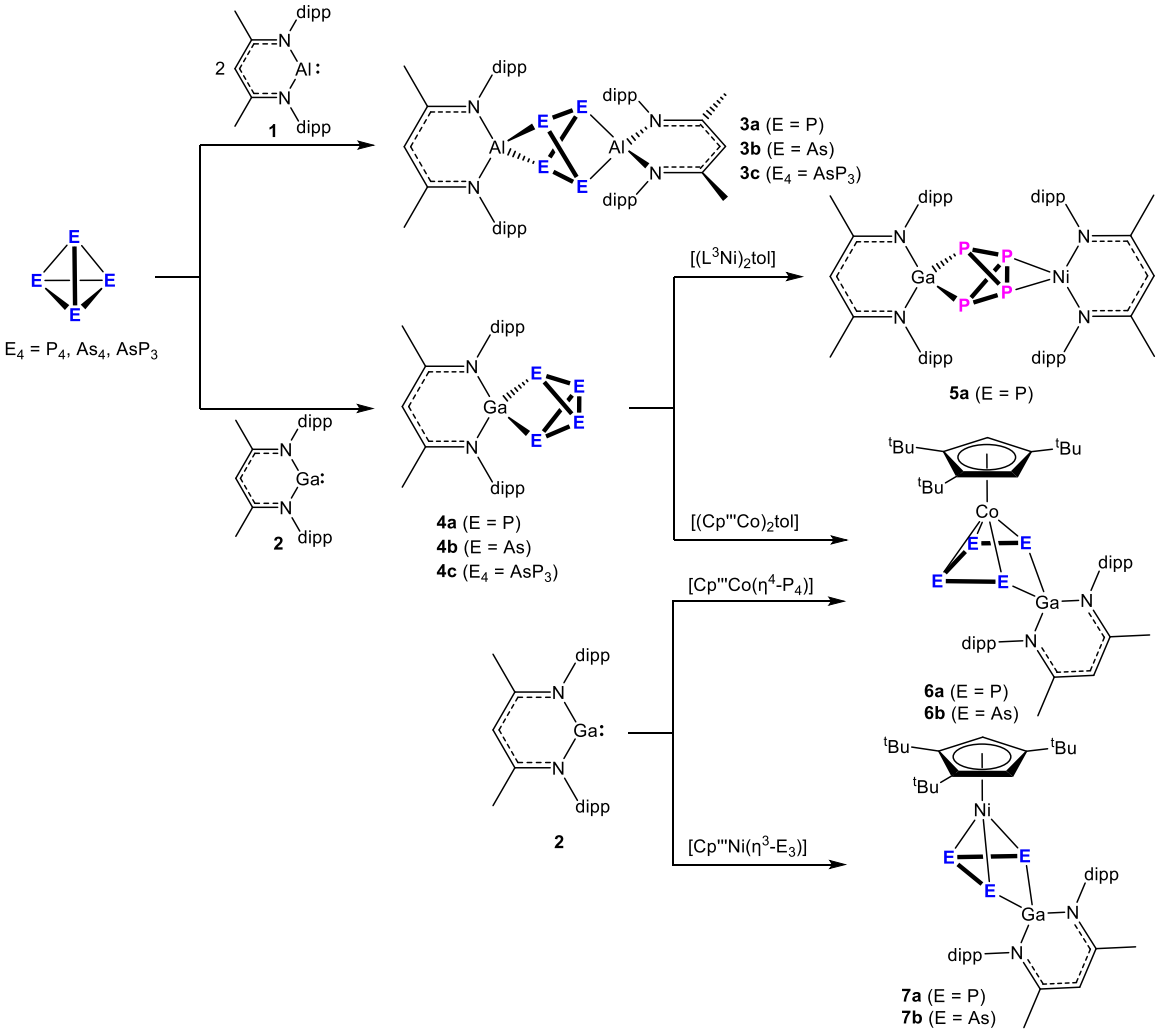
The reaction of **1** with E_4 (E_4 = P_4, As_4, AsP_3) leads depending on the temperature to the formation of the homobimetallic complexes $[(L^3Ni)_2(\mu\text{-}\eta^2,\kappa^1\text{:}\eta^2,\kappa^1\text{-}E_4)]$ (E = P (**2a**), As (**2b**), AsP_3 (**2c**), Scheme 10.2) and $[(L^3Ni)_2(\mu,\eta^{3:3}\text{-}E_3)]$ (E = P (**3a**), As (**3b**), Scheme 10.2). Compound **3a** and **3b** can also be obtained by stirring **2a**, **2b** or **2c**[4] in boiling toluene for 2h. Compound **2c** is a rare example of AsP_3 conversion. The molecular structure of **2c** in the solid state shows disorder of the arsenic atom over all four pnictogen positions. Compound **3a** and **3b** are paramagnetic, their ^{1}H NMR spectra show broad and shifted signals. The effective magnetic moment was determined by the Evans method and corresponds to approximately one unpaired electron. The paramagnetic nature of **3a** and **3b** was confirmed by X-band EPR spectroscopy at room temperature and 77 K. The EPR spectrum of **3a** at 77 K shows a hyperfine coupling to two phosphorus nuclei. In accordance with that, the performed DFT calculations show that the spin density is delocalized over both nickel atoms and two phosphorus atoms. To evaluate the redox reactivity of **3a** and **3b,** cyclic voltammetry measurements were performed, which shows that a reversible reduction and also an irreversible oxidation take place. The reduction was performed chemically with potassium graphite, which leads to the formation of $[K@18\text{-}c\text{-}6(thf)_3][(L^3Ni)_2(\mu,\eta^{3:3}\text{-}E_3)]$ (E = P (**5a**), As (**5b**), Scheme 10.2). The molecular structures of **5a** and **5b** are very similar to the structures of **3a** and **3b**. The only noteworthy structural difference is the orientation of the ligands. The chemical reduction of **2a** with potassium graphite leads to the formation of $[K_2][(L^3Ni)_2(\mu,\eta^{2:2}\text{-}P_4)]$ (**4**, Scheme 10.2). This compound contains a novel planar *cyclo*-P_4 unit.

Further, we synthesized and characterized the Ni(0) synthon $[K_2][(L^3Ni)_2(\mu,\eta^{1:1}\text{-}N_2)]$ (**6**) and investigated their reactivity towards white phosphorus and yellow arsenic. This leads to the formation of the anionic compounds $[K@X(thf)_2][L^3Ni(\eta^{1:1}\text{-}E_4)]$ (E = P (**7a**, X = 18-c-6), As (**7b**, X = 18-c-6 or cryptand), Scheme 10.2), which contains an E_4 butterfly ligand coordinating in an $\eta^{1:1}$ fashion. Additionally, an alternative synthetic route for **5b** was found by using **6** as starting material.

In conclusion, we have shown the different reactivity of Ni(I) and Ni(0) complexes stabilized by *β*-diketiminato ligands, which leads to a broad variety of complexes containing different E_n units.

10.3. Reactivity of E_4 (E_4 = P_4, As_4, AsP_3) towards low valent Al(I) and Ga(I) compounds

Up to now, there are no known examples of the activation of yellow arsenic or the interpnictogen compound AsP_3 with main group metals stabilized by *β*-diiminato ligands. The activation of white phosphorus with [L^3Al] (**1**) and [L^3Ga] (**2**) were already reported by the groups of *H. W. Roesky*, *R. A. Fischer and J. J. Weigand*.[5] These reactions lead to the formation of [$(L^3Al)_2(\mu,\eta^{1:1:1:1}\text{-}P_4)$] (**3a**), [$L^3Ga(\eta^{1:1}\text{-}P_4)$] (**4a**) and polyphosphanes stabilized by two {L^3Ga} fragments. The question arose if there are differences or similarities when reacting **1** and **2** with As_4 and AsP_3.



Scheme 10.3. Overview over the reactivity of E_4 towards main group complexes and their further reactivity. (dipp = 2,6-diisopropylphenyl.)

The reaction of [L^3Al] (**1**) and [L^3Ga] (**2**) with E_4 (E_4 = P_4, As_4, AsP_3) yields [$(L^3Al)_2(\mu,\eta^{1:1:1:1}\text{-}E_4)$] ($E_4$ = P_4 (**3a**), As_4 (**3b**), AsP_3 (**3c**), Scheme 10.3) and [$L^3Ga(\eta^{1:1}\text{-}E_4)$] ($E_4$ = P_4 (**4a**), As_4 (**4b**), AsP_3 (**4c**), Scheme 10.3), the first examples of the conversion of As_4 and AsP_3 with group 13 metal complexes stabilized by *β*-diiminato ligands. They possess the same

structure motifs than the corresponding phosphorus complexes **3a** and **4a**. Also, the change of the reaction conditions did not lead to the formation of dinuclear gallium compounds as in the case of phosphorus. In the solid state structure of **3c** and **4c** the arsenic atoms are disordered over all four pnictogen positions. In the $^{31}P\{^{1}H\}$ NMR spectrum of **4c** two isomers are visible. Also, the $^{31}P\{^{1}H\}$ NMR spectrum of the crude reaction solution of [L^3Al] with AsP_3 shows two different isomers of a probably mononuclear compound which could not be crystallized. Dissolving crystals of [$(L^3Al)_2(\mu,\eta^{1:1:1:1}\text{-}AsP_3)$] (**3c**) show a doublet and a triplet in the $^{31}P\{^{1}H\}$ NMR spectrum.

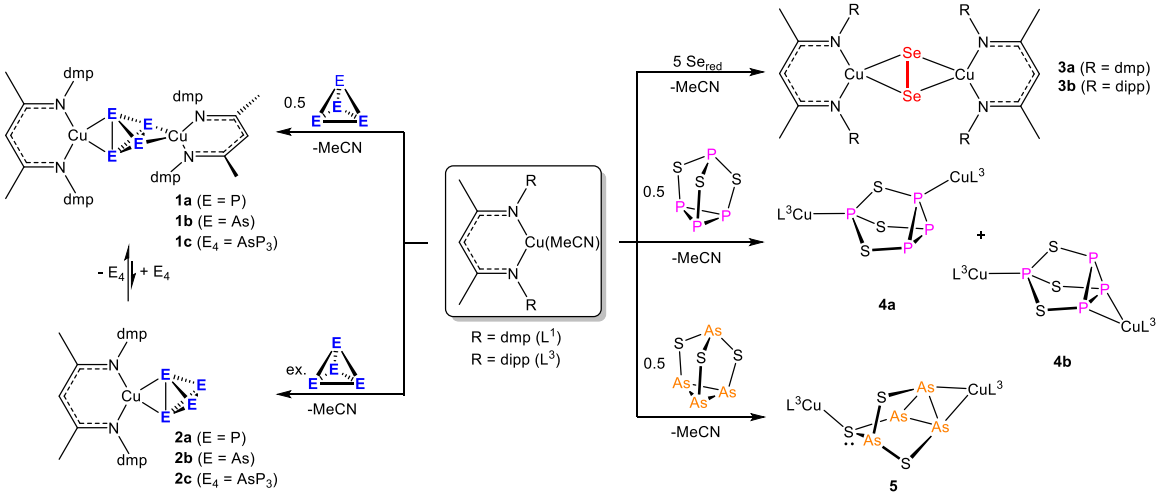
Furthermore, we reacted **4a** and **4b** with unsaturated metal fragments. Treatment of **4a** with [$(L^3Ni)_2$tol] leads to the formation of [$(L^3Ga)(\mu,\eta^{2:1:1}\text{-}P_4)(L^3Ni)$] (**5a**, Scheme 10.3). The reaction of **4a** and **4b** with [$(Cp'''Co)_2$tol] lead to the formation of the heterobimetallic complexes [$(Cp'''Co)(\mu,\eta^{4:1:1}\text{-}E_4)(L^3Ga)$] (E = P (**6a**), As (**6b**), Scheme 10.3). Compound **5a** is paramagnetic. The ^{1}H NMR spectrum show broad and shifted signals. The effective magnetic moment was determined by the Evans method and corresponds to approximately one unpaired electron. The paramagnetic nature of **5a** was confirmed by X-band EPR spectroscopy and shows a hyperfine coupling to the phosphorus atoms at 77 K. In accordance with that, the performed DFT calculations show that the spin density is delocalized over the nickel and all four phosphorus atoms. The reaction of [$(Cp'''Co)_2$tol] with **4a** was investigated by $^{31}P\{^{1}H\}$ NMR spectroscopy and shows besides the formation of **6a** also the formation of [$(Cp'''Co)_2(\mu,\eta^{2:2}\text{-}P_2)_2$]. For **6b**, the reaction is selective and gives good crystalline yields. The molecular structure of **6b** show a cleavage of two further As-As bonds in comparison to **4b**.

The reaction of [L^3Ga] with [$Cp'''Co(\eta^4\text{-}P_4)$] and [$Cp'''Ni(\eta^3\text{-}E_3)$] leads to the formation of [$(Cp'''Co)(\mu,\eta^{4:1:1}\text{-}P_4)(L^3Ga)$] (**6a**) and [$(Cp'''Ni)(\eta^{3:1:1}\text{-}E_3)(L^3Ga)$] (E = P (**7a**), As (**7b**), Scheme 10.3). In contrast to the reaction of [$(Cp'''Co)_2$tol] with **4a**, the formation of **6a** is selective in the alternative reaction pathway, as shown by NMR studies. The $^{31}P\{^{1}H\}$ NMR spectrum reveals two multiplets with an integral ratio of 1:1 displaying an AA'XX' spin system. The molecular structure of **7b** shows the insertion of a {L^3Ga} fragment into an As-As bond.

In conclusion, the results show no structural difference for compound **3** and **4** for white phosphorus, yellow arsenic or AsP_3. Furthermore, **5a** is a rare example for a mixed metal nacnac compound and **6a**, **6b**, **7a** and **7b** are examples for mixed metal (main group and transition metal) and ligand (Cp and nacnac) compounds. These complexes also show the difference between the reactivity of Cu nacnac and Ga nacnac. While the {L^1Cu} just coordinates to *cyclo*-E_n units, the {L^3Ga} fragment opens one E-E bond. This is due to the fact that the E-E bond cleavage by the reaction with [L^3Ga] can be considered as oxidative addition, with the gallium atom in the oxidation state +III while in the case of copper such an oxidation state is less favored.

10.4. Reactivity of Cu(I) Nacnac Complexes Towards E_4, E_4S_3 (E = P, As) and red selenium

In the case of iron(I) and cobalt(I) nacnac complexes a systematic investigation of the ligand design towards the resulting E_n unit was done by *Driess et al.* and *Scheer et al.*.[6] These results show the possible effect of the ligand design towards the E_n unit. We already reported the reactivity of $[L^3Cu(MeCN)]$ towards P_4 and As_4, which results in the formation of $[(L^3Cu)_2(\mu,\eta^{2:2}\text{-}E_4)]$ and $[L^3Cu(\eta^2\text{-}P_4)]$, the first, neutral and molecular complexes containing an side-on coordinated intact E_4 tetrahedron stabilized by *β*-diiminato ligands.[1] Motivated by the impact of the ligand design in the case of iron and cobalt, the question arose if the resulting E_n structure motif can also be affected in the case of copper. Parts of this chapter were already described in the Ph.D. thesis of Dr. F. Spitzer[7] and my master thesis.[8]



Scheme 10.4. Overview over the reactivity of $[LCu(MeCN)]$ (L = L^1, L^3) towards E_4 (E_4 = P_4, As_4, AsP_3), red selenium and the cage compounds E_4S_3 (E = P, As). (dmp = 2,6-dimethylphenyl; dipp = 2,6-diisopropylphenyl)

The reaction of $[L^1Cu(NCMe)]$ with E_4 leads to the formation of the mono- or dinuclear compounds $[(L^1Cu)_2(\mu,\eta^{2:2}\text{-}E_4)]$ (E_4 = P_4 (**1a**), As_4 (**1b**), AsP_3 (**1c**), Scheme 10.4) and $[L^1Cu(\eta^2\text{-}E_4)]$ (E = P (**2a**), As (**2b**), AsP_3 (**2c**), Scheme 10.4) containing intact E_4 tetrahedra. In the case of copper(I) there are no effects of the ligand design towards the resulting E_n unit (L^1 to L^3). Complex **2b** is the first mononuclear, neutral copper complex containing an intact As_4 tetrahedron that could be characterized by X-ray. Further **1c** and **2c** are rare example of the conversion of AsP_3 with transition metal complexes. In the solid state structure of **1c** the arsenic is disordered over all four pnictogen positions. In solution a highly dynamic behavior was observed. While at room temperature only one broad singlet could be obtained, at 193 K **1c** shows a triplet and a doublet with an integral ratio of 1:2. The same behavior is obtained for **2c**.

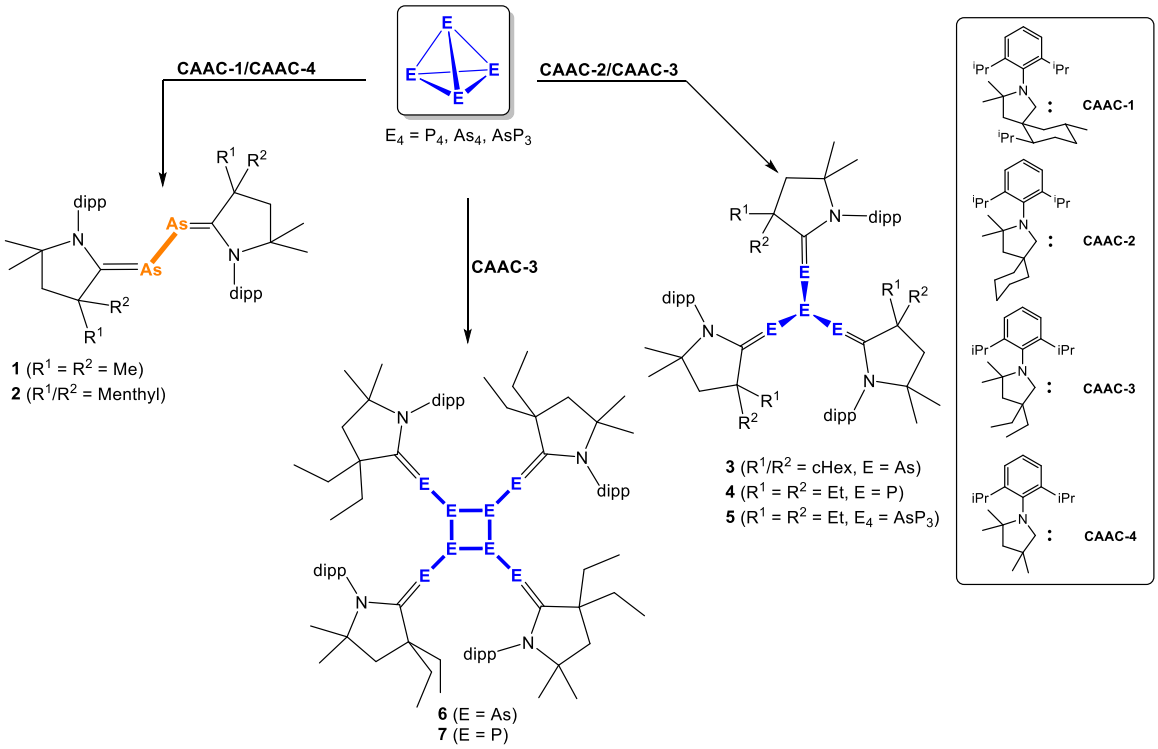
The reactivity of [LCu(NCMe)] (L = L^1, L^3) towards red selenium and the cage compounds E_4S_3 (E = P, As) was also investigated. This leads to the formation of the diselenium compounds [$(LCu)_2(\mu,\eta^{2:2}\text{-}Se_2)$] (L = L^1 (**3a**), L^3 (**3b**), Scheme 10.4) and the cage compounds [$(L^3Cu)_2(E_4S_3)$] (E = P (**4**), As (**5**), Scheme 10.4). The latter complexes show a coordination of the {L^3Cu} fragments towards intact E_4S_3 cage units. For compound **4a**, the {L^3Cu} fragments are η^1 coordinated to one basal and one apical phosphorus atom. The molecular structure also shows a minor isomer (**4b**) in which one {L^3Cu} fragment is η^2 coordinated to two basal phosphorus atoms. In the case of As_4S_3 the {L^3Cu} fragments are η^2-coordinated to two basal arsenic atoms and η^1-coordinated to the sulfur atom while the basal arsenic atom is not coordinating to a {L^3Cu} fragment, due to the fact that sulfur is more electronegative than arsenic.

These products represent examples of group 11 complexes coordinating to E_4, chalcogens and mixed cage compounds.

10.5. Reactivity of yellow arsenic towards Cyclic Alkyl Amino Carbenes (CAACs)

Since their discovery in 2005, cyclic alkyl amino carbenes (CAACs) gained increased attention. They were able to activate small molecules like H_2, N_2 or O_2 and most interestingly P_4. *Bertrand et al.* already reported a few reactions of different CAACs with P_4.[9] Up to now, there are no examples of the conversion of yellow arsenic with CAACs. Parts of this chapter were already described in the Ph.D. thesis of Dr. C. Schwarzmaier.[10] The nomenclature is adopted according to inorganic complexes to ensure clarity.

The reaction of different CAACs (see Scheme 10.5, **CAAC-1** – **CAAC-4**) with white phosphorus, yellow arsenic and the interpnictogen compound AsP_3 leads to the formation of different di-, tri- or tetracarbene substituted compounds with E_2, E_4 or E_8 cores. The reaction of **CAAC-1** and **CAAC-4** with yellow arsenic leads to the formation of the 2,3-diarsabutadiene-derivates [$(CAAC\text{-}4)_2(\mu,\eta^{1:1}\text{-}As_2)$] (**1**, Scheme 10.5) and [$(CAAC\text{-}1)_2(\mu,\eta^{1:1}\text{-}As_2)$] (**2**, Scheme 10.5). In the case of phosphorus, the reaction leads to the formation of a P_4 chain stabilized by two carbenes.[9a] To have a deeper insight into the formation processes we carried out DFT computations. According to this, the formation of an E_4 chain is exergonic for phosphorus and arsenic but a subsequent fragmentation to [$(CAAC)_2E_2$] is endergonic for phosphorus and exergonic for arsenic. These computations can explain the formation of the different E_n unit for phosphorus and arsenic. We also performed cyclic voltammetry measurements in thf, which show a first reversible oxidation and a second irreversible oxidation for **2**.



Scheme 10.5. Overview over the reaction of CAAC-n (n = 1-4) with E_4 (E_4 = P_4, As_4, AsP_3).

Treating of **CAAC-2** with yellow arsenic leads to the formation of the isotetraarsan adduct stabilized by three CAAC molecules [(CAAC-2)$_3$(μ_3,$\eta^{1:1:1}$-As_4)] (**3**, Scheme 10.5). A compound containing a similar structure could be obtained by *Bertrand et al.* by the reaction of **CAAC-2** with P_4. One significant difference is the bending of the CAAC molecules towards the E_4 unit. In the case of arsenic derivative, the carbenes are bent counterclockwise, while in the phosphorus derivative they are bent clockwise.

The reaction of **CAAC-3** with AsP_3 or P_4 leads also to the formation of such compounds [(CAAC-3)$_3$(μ_3,$\eta^{1:1:1}$-E_4)] (E_4 = P_4 (**4**), AsP_3 (**5**), Scheme 10.5). The molecular structure of **5** shows disorder of the arsenic atom over all four pnictogen positions, leading to two isomers: the major isomer **5a**, with a carbene coordinated arsenic atom and the minor isomer **5b**, with an arsenic atom in the centre of the E_4 unit. The molecular structure of **5** shows a clockwise bending of the CAAC molecules towards the E_4 unit. The reaction of **CAAC-3** with E_4 (E_4 = P_4, As_4) in a 1:0.5 stoichiometry leads to the formation of an E_8 tetracarbene [(CAAC-3)$_4$(μ_4,$\eta^{1:1:1:1}$-E_8)] (E = As (**6**), P (**7**), Scheme 10.5), which contains a four membered E_4 ring where every pnictogen atom is connected to a further pnictogen atom and stabilized by four CAAC fragments. While in the case of phosphorus the P_4 ring is nearly planar, the As_4 cycle in **6** is folded. For phosphorus a different stoichiometry leads to different products (**4** and **7**), changing the reaction conditions in the case of arsenic leads to the sole formation of **6**. To get a deeper insight into the formation of **4**, **6** and **7**, we performed DFT computations and proposed different reaction pathways, which can explain the sole formation of **6**.

In summary, the reaction of different CAACs with E_4 (E_4 = P_4, As_4, AsP_3) leads to the aggregation, fragmentation and rearrangement of the E_4 unit. Different CAACs stabilize different As_n (n = 2, 4, 8) units. These are the first examples of the reactivity of yellow arsenic and AsP_3 towards CAACs. We have shown some similarities and also differences between the conversion of white phosphorus, yellow arsenic and AsP_3.

10.6. References

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[4] Stirring **2c** in boiling toluene for 2 hours leads to the formation of **3a**, the reaction was tracked by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy.

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11. Appendix

11.1. Thematic List of Abbreviations

NMR spectroscopy

NMR	Nuclear Magnetic Resonance
δ	chemical shift
ppm	part per million
Hz	Hertz, s^{-1}
K	Kelvin
J	coupling constant, Hz
s	singlet
d	doublet
t	triplet
sept	septet
q	quartet
m	multiplet
br	broad
$\omega_{½}$	half width at full maximum, Hz
VT	variable temperature
EXSY	exchange spectroscopy
MAS	Magic Angle Spinning

Cyclic Voltammetry

CV	Cyclic Voltammetry
$E_{1/2}$	half potential, V

Solvents

thf	tetrahydrofuran, C_4H_8O
tol	toluene, C_7H_8
dib	1,3-diisopropylbenzene, $C_{12}H_{18}$
dme	1,2-dimethoxyethane, $C_4H_{10}O_2$
CH_2Cl_2	dichloromethane
MeCN	acetonitrile, CH_3CN
Et_2O	diethylether, $C_4H_{10}O$

Other

Å	Angstroem, 1 Å = $1 \cdot 10^{-10}$ m
T	temperature, K or °C
c	concentration, mol · L^{-1}
M	metal, specified in text
d	distance, Å
$\sphericalangle$	Angle, °
r.t.	room temperature
E	group 15 element

Mass spectroscopy

MS	mass spectrometry
$[M]^+$	molecular ion peak
m/z	mass to charge ratio
LIFDI	liquid injection field desorption ionization
FD	field desorption
ESI	electro spray ionization
EI	electron impact

Evans Method and EPR spectroscopy

χ_M	molar measured magnetic susceptibility
χ_P	molar paramagnetic susceptibility
χ_D	molar diamagnetic susceptibility
$\Delta\nu$	chemical shift difference, [Hz]
ν_0	measuring frequency, [Hz]
μ_{eff}	effective magnetic moment
n	number of unpaired electrons
μ_B	Bohr magneton
EPR	electron paramagnetic resonance
g	gyromagnetic factor
iso	isotropic

Theoretical computations

DFT	density functional theory
HOMO	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital
SOMO	single occupied molecular orbital
WBI	Wiberg Bond Indices
NBO	Natural Bond Orbital
BCP	Bond Critical Point
AIM	Atoms In Molecules
RCP	Ring Critical Point

Ligands

L	Ligand, specified in text
acac	acetylaceton
nacnac	*β*-diketiminato, substituents specified in text
Ph	Phenyl, -C_6H_5
Ph*	aromatic substituent, specified in text
dipp	2,6-diisopropylphenyl
dmp	2,6-dimethylphenyl
R	organic substituent, specified in text
Me	Methyl, -CH_3
Et	Ethyl, -C_2H_5
^{i}Pr	*iso*-Propyl, -C_3H_7
^{t}Bu	*tert*-Butyl, -C_4H_9
^{n}Bu	*n*-Butyl, -C_4H_9
Cp	cyclopentadienyl, η^5-C_5H_5
Cp*	η^5-C_5Me_5
Cp^4	η^5-C_5*i*Pr_4H
Cp'''	1,2,4-tris-*tert*-butylcyclopentadienyl, η^5-C_5H_2*t*Bu_3
Cp^{Benz}	pentabenzylcyclopentadienyl, η^5-$C_5(CH_2Ph)_5$
Cp^{PET}	η^5-$C_5(4\text{-}EtC_6H_4)_5$
pftb	$[Al\{OC(CF_3)_3\}_4]$
Pz	pyrazolate
triphos	1,1,1-tris(diphenylphosphinomethyl)ethane)
etriphos	(1,1,1-tris(diethylphosphinomethyl)ethane)
dppe	1,2-bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$
dppm	bis(diphenylphosphinomethane)
np_3	tris(2-diphenylphosphinoethyl)amine
L^0	$[\{N(C_6H_3{}^{i}Pr_2\text{-}2,6)C(H)\}_2CH]^-$
L^1	$[\{N(C_6H_3Me_2\text{-}2,6)C(Me)\}_2CH]^-$
L^2	$[\{N(C_6H_3Me_2\text{-}2,6)C(H)\}_2CH]^-$
L^3	$[\{N(C_6H_3{}^{i}Pr_2\text{-}2,6)C(Me)\}_2CH]^-$
$L^{Me,mes}$	$[\{N(C_6H_2Me_3\text{-}2,4,6)C(Me)\}_2CH]^-$
CAAC-1	^{Menthyl}CAAC
CAAC-2	^{Cyclohexyl}CAAC
CAAC-3	^{Et}CAAC
CAAC-4	^{Me}CAAC

11.2. List of numbered compounds

11.2.1. Introduction

I $[L_2RhCl(\eta^{1:1}\text{-}P_4)]$

II $[(CO)_3Co(\eta^3\text{-}As_3)]$

III $[Cp^*Fe(\eta^5\text{-}E_5)]$

IV $[(L^3Al)_2(\mu,\eta^{1:1:1:1}\text{-}P_4)]$

V $[L^3Ga(\eta^{1:1}\text{-}P_4)]$

VI $[(L^{Me,mes}Mg)_3(\mu,\eta^{1:1:1:1:1:1}\text{-}P_7)]$

VII $[(L^3V(N(tolyl_2))_2(\mu,\eta^{3:2}\text{-}P_3)]$

VIII $[(L^3(N^tBu)Nb)_2(\mu,\eta^{3:3}\text{-}P_4)]$

IX $[(L^3(N^tBu)Ta)_2(\mu,\eta^{3:3}\text{-}P_4)]$

X $[(L^3NbN^tBu)_3(\mu_3,\eta^{3:3:1:1}\text{-}P_{12})]$

XIa $[(L^0Fe)_2(\mu,\eta^{2:2}\text{-}P_2)_2]$

XIb $[(L^0Fe)_2(\mu,\eta^{2:2}\text{-}As_2)_2]$

XIIa $[(L^1Fe)_4(\mu,\eta^{1:1:1:1:1:1:1:1}\text{-}P_8)]$

XIIb $[(L^1Fe)_4(\mu,\eta^{1:1:1:1:1:1:1:1}\text{-}As_8)]$

XIIc $[(L^2Fe)_4(\mu,\eta^{1:1:1:1:1:1:1:1}\text{-}P_8)]$

XIId $[(L^2Fe)_4(\mu,\eta^{1:1:1:1:1:1:1:1}\text{-}As_8)]$

XIIIa $[(L^3Fe)_2(\mu,\eta^{4:4}\text{-}P_4)]$

XIIIb $[(L^3Fe)_2(\mu,\eta^{4:4}\text{-}As_4)]$

XIVa $[(L^{0\text{-}3}Co)_2(\mu,\eta^{4:4}\text{-}P_4)]$

XIVb $[(L^0Co)_2(\mu,\eta^{4:4}\text{-}As_4)]$

XV $[(L^3Ni)_2(\mu\text{-}\eta^2,\kappa^1\text{:}\eta^2,\kappa^1\text{-}P_4)]$

XVIa $[(L^3Cu)_2(\mu,\eta^{2:2}\text{-}P_4)]$

XVIb $[(L^3Cu)_2(\mu,\eta^{2:2}\text{-}As_4)]$

XVII $[L^3Cu(\mu,\eta^{2:2}\text{-}P_4)]$

XVIII $[(Cp^*Fe)(\mu,\eta^{5:3}\text{-}P_5)(L^3Al)]$

XIX $[(CAAC\text{-}1)_2(\mu,\eta^{1:1}\text{-}P_4)]$

XX $[(CAAC\text{-}2)_2(\mu,\eta^{1:1}\text{-}P_2)]$

XXI $[(CAAC\text{-}2)_3(\mu_3,\eta^{1:1:1}\text{-}P_4)]$

XXII $[(CAAC\text{-}2)_3(\mu_4,\eta^{1:1:1:1}\text{-}P_8)]$

XXIII $[(P^iPr_3)_2Mo(CO)_3(\eta^1\text{-}AsP_3)]$

XXIV $[\{(^iPr_2N)(SiMe_3)P\}_2(\mu,\eta^{1:1}\text{-}AsP_3)]$

XXVa $[(Cp'''Fe(CO)_2)_2(\mu^1,\eta^{1:1}\text{-}AsP_3)]$

XXVb $[(Cp^*Cr(CO)_3)_2(\mu^1,\eta^{1:1}\text{-}AsP_3)]$

11.2.2. Reactivity of Cu(I) Nacnac Complexes Towards Polypnictogen Compounds

A $[Cu(\eta^2\text{-}P_4)_2][pftb]$

B $[P_4CuGaCl_4]_n$

C $[IPrM(\eta^2\text{-}P_4)][Al(pftb)_4]$ (M = Cu, Ag)

D1 $[(L^3Cu)_2(\mu_2,\eta^{2:2}\text{-}P_4)]$

D2 $[(L^3Cu)_2(\mu_2,\eta^{2:2}\text{-}As_4)]$

E $[(L^3Cu)(\eta^2\text{-}P_4)]$

F $[(Cp^*Fe)(\mu_3,\eta^{5:2:2}\text{-}P_5)(Cu(3,5\text{-}(CF_3)_2Pz))_3]$

G $[(Cp^*Fe)(\mu,\eta^{5:2}\text{-}P_5)(Cp^*Ir(CO))]$

H $[(Cp^*Fe)(\mu,\eta^{5:2}\text{-}As_5)(Cp^*Rh(CO))]$

1a $[Cp^*Fe(\eta^5\text{-}P_5)]$

1b $[Cp^*Fe(\eta^5\text{-}As_5)]$

2 $[L^1Cu(MeCN)]$

2a $[L^2Cu(MeCN)]$

3 $[Cp'''Co(\eta^4\text{-}P_4)]$

4a $[Cp'''Ni(\eta^3\text{-}P_3)]$

4b $[Cp'''Ni(\eta^3\text{-}As_3)]$

5a $[(Cp^*Fe)(\mu,\eta^{5:2}\text{-}P_5)(L^1Cu)]$

5b $[(Cp^*Fe)(\mu,\eta^{5:2}\text{-}As_5)(L^1Cu)]$

6a $[(Cp^*Fe)(\mu_3,\eta^{5:2:1}\text{-}P_5)(L^1Cu)_2]$

6b $[(Cp^*Fe)(\mu_3,\eta^{5:2:1}\text{-}As_5)(L^1Cu)_2]$

7 $[(Cp'''Co)(\mu,\eta^{4:2}\text{-}P_4)(L^1Cu)]$

8 $[(Cp'''Co)(\mu_3,\eta^{4:2:1}\text{-}P_4)(L^1Cu)_2]$

9a $[(Cp'''Ni)(\mu,\eta^{3:2}\text{-}P_3)(L^1Cu)]$

9b $[(Cp'''Ni)(\mu,\eta^{3:2}\text{-}As_3)(L^1Cu)]$

S1 $[(Cp^{Benz}Fe)(\mu,\eta^{5:2}\text{-}P_5)(L^1Cu)]$

S2 $[(Cp^{Benz}Fe)(\mu_3,\eta^{5:2:1}\text{-}P_5)(L^1Cu)_2]$

S3 $[(Cp^*Fe)(\mu,\eta^{5:2}\text{-}P_5)(L^2Cu)]$

S4 $[(Cp^*Fe)(\mu,\eta^{5:2}\text{-}As_5)(L^2Cu)]$

S5 $[(Cp^*Fe)(\mu_3,\eta^{5:2:1}\text{-}P_5)(L^2Cu)_2]$

11.2.3. Conversion of E_4 (E_4 = P_4, As_4, AsP_3) by Ni(0) and Ni(I) Synthons – A Comparative Study

A	$[(L^3Al)_2(\mu,\eta^{1:1:1:1}\text{-}P_4)]$
B	$[(L^3V(Ntolyl_2))_2(\mu,\eta^{3:2}\text{-}P_3)]$
C	$[(L^0Fe)_2(\mu,\eta^{2:2}\text{-}P_2)_2]$
D1	$[(L^1Fe)_4(\mu,\eta^{2:2:2:2}\text{-}P_8)]$
D2	$[(L^1Fe)_4(\mu,\eta^{2:2:2:2}\text{-}As_8)]$
D3	$[(L^2Fe)_4(\mu,\eta^{2:2:2:2}\text{-}P_8)]$
D4	$[(L^2Fe)_4(\mu,\eta^{2:2:2:2}\text{-}As_8)]$
E1	$[(L^3Cu)_2(\mu,\eta^{2:2}\text{-}P_4)]$
E2	$[(L^3Cu)_2(\mu,\eta^{2:2}\text{-}As_4)]$
F	$[(Cp^4Ni)_2(\mu\text{-}\eta^2,\kappa^1\text{:}\eta^2,\kappa^1\text{-}As_4)]$
G	$[\{(^iPr)_2NCP_2\}_2]$

1	$[(L^3Ni)_2tol]$
2a	$[(L^3Ni)_2(\mu\text{-}\eta^2,\kappa^1\text{:}\eta^2,\kappa^1\text{-}P_4)]$
2b	$[(L^3Ni)_2(\mu\text{-}\eta^2,\kappa^1\text{:}\eta^2,\kappa^1\text{-}As_4)]$
2c	$[(L^3Ni)_2(\mu\text{-}\eta^2,\kappa^1\text{:}\eta^2,\kappa^1\text{-}AsP_3)]$
3a	$[(L^3Ni)_2(\mu,\eta^{3:3}\text{-}P_3)]$
3b	$[(L^3Ni)_2(\mu,\eta^{3:3}\text{-}As_3)]$
4	$[K_2][(L^3Ni)_2(\mu,\eta^{2:2}\text{-}P_4)]$
5a	$[(K@18\text{-}c\text{-}6)thf)_3][(L^3Ni)_2(\mu,\eta^{3:3}\text{-}P_3)]$
5b	$[(K@18\text{-}c\text{-}6)thf)_3][(L^3Ni)_2(\mu,\eta^{3:3}\text{-}As_3)]$
6	$[K_2][(L^3Ni)_2(\mu,\eta^{1:1}\text{-}N_2)]$
7a	$[(K@X)(thf)_2][L^3Ni(\eta^{1:1}\text{-}P_4)]$
7b	$[(K@X)(thf)_2][L^3Ni(\eta^{1:1}\text{-}As_4)]$

11.2.4. Reactivity of E_4 (E_4 = P_4, As_4, AsP_3) towards low valent Al(I) and Ga(I) compounds

A	$[((Mes_2Si)_2)_2As_4]$
B	$[\{mes\}_2SiAs]_2$
C	$[Cp^*\{(SiMe_3)_2N\}SiAs]_2$
D	$[((PhC(N^tBu)_2)SiN(SiMe_3)_2)_3As_{10}]$
E	$[Cp^{PET}{}_2As_4]$
F	$[(Cp^*Co(CO))_2(\mu,\eta^{1:1:1:1}\text{-}As_4)]$
G	$[(Cp'''Co)(\mu,\eta^{2:2}\text{-}P_2)_2]$
H	$[Cp'''Co(\eta^4\text{-}P_4)]$
I	$[Cp'''Ni(\eta^3\text{-}E_3)]$

1	$[L^3Al]$
2	$[L^3Ga]$
3a	$[(L^3Al)_2(\mu,\eta^{1:1:1:1}\text{-}P_4)]$
3b	$[(L^3Al)_2(\mu,\eta^{1:1:1:1}\text{-}As_4)]$
3c	$[(L^3Al)_2(\mu,\eta^{1:1:1:1}\text{-}AsP_3)]$
4a	$[L^3Ga(\eta^{1:1}\text{-}P_4)]$
4b	$[L^3Ga(\eta^{1:1}\text{-}As_4)]$
4c	$[L^3Ga(\eta^{1:1}\text{-}AsP_3)]$
5a	$[(LGa)(\mu,\eta^{2:1:1}\text{-}P_4)(L^3Ni)]$
6a	$[(Cp'''Co)(\mu,\eta^{4:1:1}\text{-}P_4)(L^3Ga)]$
6b	$[(Cp'''Co)(\mu,\eta^{4:1:1}\text{-}As_4)(L^3Ga)]$
7a	$[(Cp'''Ni)(\eta^{3:1:1}\text{-}P_3)(L^3Ga)]$
7b	$[(Cp'''Ni)(\eta^{3:1:1}\text{-}As_3)(L^3Ga)]$

11.2.5. Reactivity of Cu(I) Nacnac Complexes Towards E_4, E_4S_3 (E = P, As) and red selenium

A	$[(L^0Fe)_2(\mu,\eta^{2:2}\text{-}P_2)_2]$
B1	$[(L^1Fe)_4(\mu,\eta^{2:2:2:2}\text{-}E_8)]$
B2	$[(L^2Fe)_4(\mu,\eta^{2:2:2:2}\text{-}E_8)]$
C	$[(L^3Fe)_2(\mu,\eta^{4:4}\text{-}E_4)]$
D	$[(LCo)_2(\mu,\eta^{4:4}\text{-}P_4)]$
E	$[(L^1Co)_2(\mu,\eta^{3:3}\text{-}As_4)]$
F	$[(L^2Co)_2(\mu,\eta^{3:3}\text{-}As_4)]$
G	$[(L^3Co)_2(\mu,\eta^{1:1:1:1}\text{-}As_4)]$

1a	$[(L^1Cu)_2(\mu,\eta^{2:2}\text{-}P_4)]$
1b	$[(L^1Cu)_2(\mu,\eta^{2:2}\text{-}As_4)]$
1c	$[(L^1Cu)_2(\mu,\eta^{2:2}\text{-}AsP_3)]$
2a	$[L^1Cu(\eta^2\text{-}P_4)]$
2b	$[L^1Cu(\eta^2\text{-}As_4)]$
2c	$[L^1Cu(\eta^2\text{-}AsP_3)]$
3a	$[(L^1Cu)_2(\mu,\eta^{2:2}\text{-}Se_2)]$
3b	$[(L^3Cu)_2(\mu,\eta^{2:2}\text{-}Se_2)]$
4	$[(L^3Cu)_2(P_4S_3)]$
5	$[(L^3Cu)_2(As_4S_3)]$

11.2.6. Reactivity of Cu(I) Nacnac Complexes Towards [Cp*Ru(η^5-E_5)] (E = P, As)

A	$[Cp^*RuP_6I_6][I]$
B	$[(Cp^*Ru)_2(As_4I_4)]$
C	$[(Cp^*Fe)(\mu,\eta^{5:3}\text{-}P_5)(L^3Al)]$

1a-Ru	$[Cp^*Ru(\eta^5\text{-}P_5)]$
1b-Ru	$[Cp^*Ru(\eta^5\text{-}As_5)]$
1a-Fe	$[Cp^*Fe(\eta^5\text{-}P_5)]$
1b-Fe	$[Cp^*Fe(\eta^5\text{-}As_5)]$
2	$[L^1Cu(MeCN)]$
3a	$[(Cp^*Ru)(\mu,\eta^{5:2}\text{-}P_5)(L^1Cu)]$
3b	$[(Cp^*Ru)(\mu,\eta^{5:2}\text{-}As_5)(L^1Cu)]$
3a-Fe	$[(Cp^*Fe)(\mu,\eta^{5:2}\text{-}P_5)(L^1Cu)]$
3b-Fe	$[(Cp^*Fe)(\mu,\eta^{5:2}\text{-}As_5)(L^1Cu)]$

11.2.7. Reactivity of yellow arsenic towards Cyclic Alkyl Amino Carbenes (CAACs)

A	$[(CAAC\text{-}1)_2P_4]$
B	$[(CAAC\text{-}2)_2P_2]$
C	$[(CAAC\text{-}2)_3P_4]$
D	$[(CAAC\text{-}2)_4P_8]$
E	$[(CAAC\text{-}3)_2As_2]$

1	$[(CAAC\text{-}4)_2(\mu,\eta^{1:1}\text{-}As_2)]$
2	$[(CAAC\text{-}1)_2(\mu,\eta^{1:1}\text{-}As_2)]$
3	$[(CAAC\text{-}2)_3(\mu_3,\eta^{1:1:1}\text{-}As_4)]$
4	$[(CAAC\text{-}3)_3(\mu_3,\eta^{1:1:1}\text{-}P_4)]$
5	$[(CAAC\text{-}3)_3(\mu_3,\eta^{1:1:1}\text{-}AsP_3)]$
6	$[(CAAC\text{-}3)_4(\mu_4,\eta^{1:1:1:1}\text{-}As_8)]$
7	$[(CAAC\text{-}3)_4(\mu_4,\eta^{1:1:1:1}\text{-}P_8)]$

11.2.8. Treasury

1	$[\{(^iPr_2N)_2P\}_2]$
2	$[\{(^iPr_2N)_2P\}_2(\mu,\eta^{1:1}\text{-}As_4)]$

3	$[(CNAr^{dipp2})_2Mo(CO)_2(I)_2]$
4	$[(CNAr^{Dipp2})_2Mo(CO)_2(I)(\eta^3\text{-}As_3)]$

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