

Reactivity of $[\text{Cp}''_2\text{Zr}(\eta^{1:1}-\text{E}_4)]$ ($\text{E} = \text{P}, \text{As}$) towards Nucleophiles

Veronika Heinl,^[a] Michael Seidl,^[a] Gábor Balázs,^[a] and Manfred Scheer^{*[a]}

Dedicated to Professor Helmut Sitzmann on the occasion of his 65th birthday

Abstract: The functionalization of the polypnictogen ligand complexes $[\text{Cp}''_2\text{Zr}(\eta^{1:1}-\text{E}_4)]$ ($\text{E} = \text{P}$ (**1a**), As (**1b**); $\text{Cp}'' = 1,3$ -di-tert-butyl-cyclopentadienyl) is focused to modify the features of the polypnictogen unit to explore new synthetic pathways for further transformations. The reaction behavior of **1** towards main group nucleophiles is investigated. The reaction of **1a** with ${}^t\text{BuLi}$ leads to the ionic product $\text{Li}[\text{Cp}''_2\text{Zr}(\eta^{1:1}-\text{P}_4{}^t\text{Bu})]$ (**2**) where an organic group is attached to a bridge-

head phosphorus atom of the butterfly unit. Further reactions of **2** with quenching electrophilic reagents enable the introduction of other substituents. Moreover, a condensation of **2** to $[(\text{Cp}''_2\text{Zr})_2(\mu, \eta^{1:1:1:1}-\text{P}_8{}^t\text{Bu}_2)]$ (**3**), containing a novel P_8 -unit, has been observed. The reaction of **1** with LiNMe_2 and $\text{LiCH}_2\text{SiMe}_3$ leads to a partial fragmentation of the E_4 unit and the compounds $[\text{Cp}''_2\text{Zr}(\eta^2-\text{E}_3\text{Nu})]$ ($\text{Nu} = \text{NMe}_2$; $\text{E} = \text{P}$ (**6a**), As (**6b**); $\text{Nu} = \text{CH}_2\text{SiMe}_3$; $\text{E} = \text{P}$ (**7a**), As (**7b**)) are formed.

Introduction

Organophosphorus compounds represent essential reagents both in daily life and in industry.^[1,2,3] For their synthesis, usually white phosphorus (P_4) is the starting material, synthesized by the reduction of phosphate rocks. Ensuing chlorination to PCl_3 ^[4] and subsequent functionalization with, *inter alia*, alcohols, organolithium or Grignard reagents lead to the desired organophosphorus compounds.^[3–6] Because of the mostly multistep synthetic routes, this overall process has disadvantages, such as a low atom efficiency, the formation of stoichiometric amounts of waste and hazardous intermediates as well as a low selectivity.^[1,3,5,6] For these reasons, a direct functionalization of P_4 and ways to a selective P–C bond formation are active topics of current research.^[7a] Some progress could be made by using main group compounds^[7b–e] or transition metal complexes,^[7f] however the discovery of the stepwise degradation pathway is still a challenging topic in this field. The direct reaction of P_4 with main group metal organyls by using $\text{PhLi}/{}^t\text{BuLi}$ as nucleophiles in combination with some quenching reagents leading to a mixture of phosphines was described by *Rauhut* et al. in 1963.^[8] Reactions of P_4 with alkynyls also result in unselective product mixtures.^[9] However, *Fritz* et al. reported a

more selective and less harsh reaction to cyclotetraphosphines by the usage of ${}^t\text{BuLi}$ and Me_3SiCl as quenching agents to be attributed to the use of more bulky reagents.^[10] Using the sterically demanding Mes^*Li ($\text{Mes}^* = 2,4,6\text{-}{}^t\text{Bu}_3\text{C}_6\text{H}_2$) in combination with Mes^*Br , a single P–P bond cleavage of the phosphorus tetrahedron was observed and **1** was formed beside $\text{Mes}^*\text{P}=\text{PMes}^*$ (Figure 1).^[11] Another more selective P–P bond cleavage of P_4 was shown by *Tamm* et al. using frustrated carbene-borane Lewis pairs for the activation.^[12] This was also

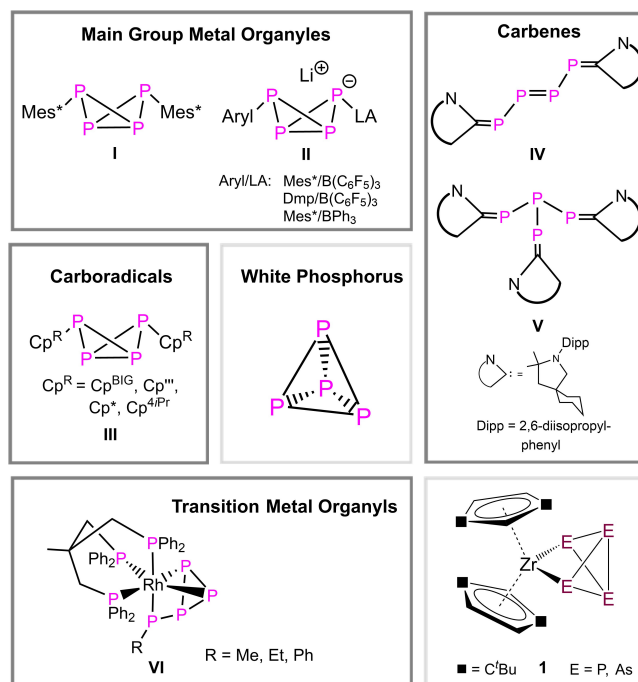


Figure 1. Selected examples of P–C bond formation by conversion of white phosphorus.

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demonstrated by Lammertsma et al. by the reaction of P_4 with ArLi in the presence of Lewis acids ($B(C_6F_5)_3$, BPh_3) leading to Lewis acid-stabilized bicyclo[1.1.0]tetraphosphabutane anions II (Figure 1) for which a subsequent functionalization of II was possible.^[13] Furthermore, our group was able to synthesize compound III (Figure 1) via metal-mediated functionalization of P_4 by Cp^R radicals.^[14] Also, it was shown that carbenes can functionalize P_4 . Thus, Bertrand et al. reported the usage of CAACs (cyclic-alkyl-amino-carbene) to form, for instance, the E- and Z-isomers of a linear tetraphosphorus chain (Figure 1, IV)^[15] or the tri-substituted P_4 derivative V. However, also aggregation to larger phosphorus units is observed, depending on the nature of the carbene.^[7] Another interesting approach was introduced by Peruzzini et al. who used rhodium alkyl or aryl complexes to form [(triphos)Rh(η^1 : η^2 - P_4R)] (VI, R=Me, Et, Ph, triphos = $MeC(CH_2PPH_2)_3$).^[16]

The use of transition metal complexes to convert white phosphorus and yellow arsenic, respectively, is widespread and a large variety of respective products are formed,^[17–21] which represents the first step of the P_4 conversion. The question arises if subsequent functionalizations of such initially formed products in the coordination sphere of transition metals lead to a more selective conversion and offer new insights into the reactivity of activated P_4 and As_4 moieties. Astonishingly, in this area, only few initial attempts were made. In 2016, Lammertsma et al. demonstrated a controlled P–C bond formation generated by the functionalization of P_4 in the coordination sphere of a gold cation. The reaction with ArLi leads to the formation of a Lewis acid-stabilized cationic Ar- P_4 unit in $[ArP_4(IPrAu)_2][Al(OC(CF_3)_3)_4]$ (Ar = mesityl, 2,6-di-mesityl-phenyl).^[22] Recently, our group showed that the reaction of polyphosphorus ligand complexes of tantalum and cobalt towards nucleophiles leads to a P–Nu bond formation with one M–P bond being cleaved.^[23a–d] However, no subsequent quenching with electrophiles was carried out.^[23e]

Other interesting transition metal complexes are the zirconium compounds $[Cp''_2Zr(\eta^{1-1}-E_4)]$ (**1**, $Cp'' = 1,3$ -diterbutylcyclopentadienyl; $E = P$ (**a**), As (**b**)) synthesized by the reaction of the corresponding carbonyl compounds with P_4 and As_4 , respectively. Here, one E–E bond is already cleaved and a “butterfly”-moiety is formed.^[24,25] Studies on their reaction behavior, inter alia towards Lewis acids and as transfer reagents, show a high potential in their reactivity.^[24,26] Since so far no reactions towards nucleophiles were carried out, the question arose if a nucleophilic attack on the polynictogen unit would lead to a second bond cleavage and, if so, can functional groups be selectively introduced that way?

DFT calculations on **1a** show that the wing-tip phosphorus atoms carry the highest negative electrostatic potential (ESP), while the ESP on the bridge-head phosphorus atoms is more positive (Figure 2). Hence, a nucleophilic attack should occur on the bridgehead P atoms. Although the ESP on Zr is more positive than on the P_4 unit, it cannot be attacked by a nucleophile being sterically encased by the bulky Cp'' ligands. The LUMO of **1a**, is mainly localized on the P_4 core, with roughly equal contributions from the wing-tip and bridgehead phosphorus atoms (cf. Figure S33). This indicates that in the

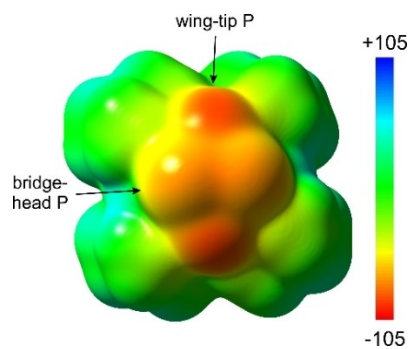


Figure 2. Electrostatic potential mapped on electron density (isovalue = 0.001) for **1a**, calculated at the D3(BJ)-TPSS/def2TZVP (CPM) level of theory. Color code (blue = positive, red = negative) in kJ mol^{-1} .

case of an orbital controlled reaction with a nucleophile the nucleophilic attack would occur with equal probability at the both sites. Therefore, the question arises at which position a nucleophilic attack would occur and if the reaction outcome can be influenced.

Herein, we report on the reaction behavior of **1** towards the main group nucleophiles $t\text{BuLi}$, $\text{LiCH}_2\text{SiMe}_3$ and LiNMe_2 , leading to novel functionalized polynictogen zirconium complexes. Moreover, further reactions with quenching electrophiles permit a selective subsequent functionalization for the first time. Moreover, an unprecedented dimerization of the polynictogen unit is achieved.

Results and Discussion

The reaction of $[Cp''_2Zr(\eta^{1-1}-P_4)]$ (**1a**) with $t\text{BuLi}$ in THF at -78°C yields the ionic product $\text{Li}[Cp''_2Zr(\eta^{1-1}-P_4)t\text{Bu}]$ (**2**). The nucleophilic attack of $t\text{Bu}^-$ at one of the bridgehead phosphorus atoms of the P_4 -butterfly unit leads to the cleavage of one P–P bond. This selective behavior was confirmed by NMR investigations (see below). An attack on wingtip phosphorus (P bound to Zr) atoms could not be observed, which agrees with the DFT calculations (see above).

Unfortunately, the structure of **2** can only be verified by NMR spectroscopy and mass spectrometry and **2** cannot be isolated as a solid, despite several attempts. But the anionic part of **2** can be clearly detected by ESI mass spectrometry as the only component in the reaction solution before workup. However, if the solvent of the reaction mixture is removed and the remaining solid extracted with *n*-pentane, the complex $[(Cp''_2Zr)_2(\mu_4\eta^{1:1:1:1}-P_8^t\text{Bu}_2)]$ (**3**) is obtained in 97% yield. **3** is probably formed by oxidation of **2** during the workup. Unfortunately, the nature of the oxidation agent is not clear.

$^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic measurements of a freshly prepared solution of **2** show four multiplets centered at $\delta = -180.1$ ppm, -37.1 ppm, -11.4 ppm and 110.0 ppm. They correspond to an AMNX spin system and can be assigned to the four inequivalent phosphorus atoms of **2** (Figure 3) beyond any doubt. The appropriate coupling constants were deter-

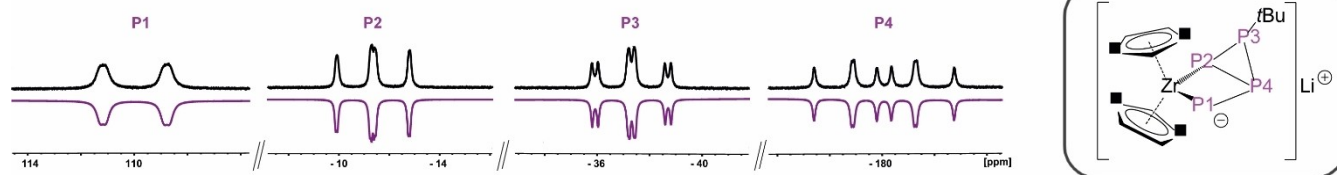


Figure 3. Sections of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** in THF (CD_2Cl_2 capillary). Top: experimental, bottom: simulated.

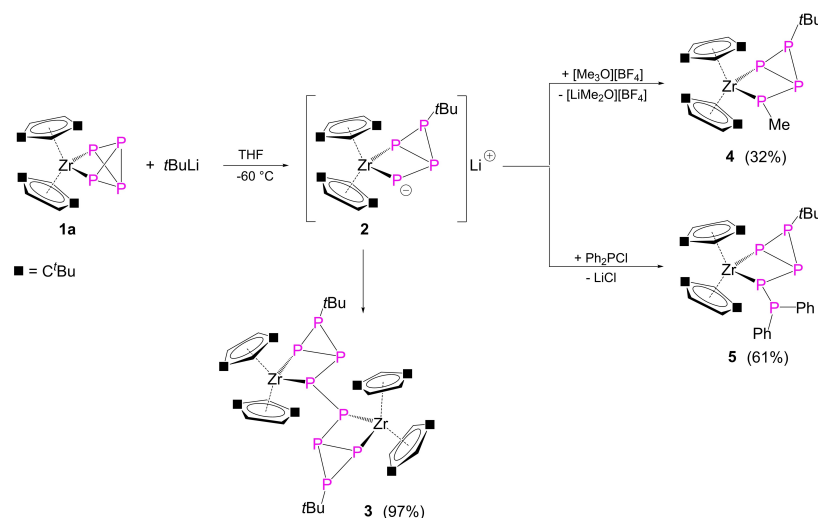
mined via simulation (cf. Figure S10). The proposed structure of **2** in solution is proved by DFT calculations which show that the structure of **2** based on NMR spectroscopy is a true minimum structure (cf. Supporting Information). Since crystals of **2** could not be obtained, ingredients such as crown ethers and different solvents were used to induce crystallization. Unfortunately, this leads to a more unspecific reaction and several side products are formed. Interestingly, in the NMR spectra of these reactions, a strong shift to higher ppm values for the phosphanide type atom P1 is observed (Figure S12). Surprisingly, in solution, compound **2** seems to be stable, and even after five days no decomposition or conversion can be observed (Figure S11). For this reason, we propose that the conversion of **2** to **3** occurs during the purification process. The high sensitivity toward oxidation of **2** is based on the energetically high-lying Highest Occupied Molecular Orbital (HOMO) which represents a lone pair of electrons of the phosphanide-type P1 atom (cf. Supporting Information).

To obtain further proof of the existence of compound **2**, subsequent reactions with the quenching reagents $[\text{Me}_3\text{O}][\text{BF}_4]$ and Ph_2PCl , respectively, were carried out. These reactions at -78°C in THF lead to $[\text{Cp}''_2\text{Zr}(\eta^{1-1}\text{-P}_4^t\text{BuMe})]$ (**4**) and $[\text{Cp}''_2\text{Zr}(\eta^{1-1}\text{-P}_4^t\text{BuPPh}_2)]$ (**5**), respectively, in which an Me and a Ph_2P group are attached to a former wing-tip phosphorus atom. That way, the identity of **2** (Scheme 1) was proven. Compounds **3**, **4** and **5** were comprehensively characterized by NMR spectroscopy,

single crystal X-ray diffraction analysis, mass spectrometry and elemental analysis.

Crystals of **3**, **4** and **5** suitable for single crystal X-ray diffraction analysis were obtained by storing a concentrated solution in *n*-pentane (**3**, **5**) at -30°C or in hexamethyldisiloxane (**4**) at -78°C . Their molecular structures are depicted in figure 4. In all three compounds, one P–P bond of the original P₄ butterfly unit is cleaved and a C–P bond is formed by the introduction of a ^tBu group on P2. Due to the steric repulsion of the introduced units, the Zr–P distances are slightly elongated compared to the ones in **1a**.^[27] All P–P distances are in the range of normal single bonds (**3**: 2.1965(6) Å to 2.2270(6) Å; **4**: 2.186(5) Å to 2.235(3) Å; **5**: 2.2021(8) Å to 2.2376(8) Å) in which the bond between P1 and P2 represents the shortest one.^[17,18,20]

LIFDI (**3**, **4**) and FD (**5**) mass spectrometric measurements show the corresponding molecular ion peaks. ^1H NMR investigations for **3** and **4** reveal the expected signals for the magnetically inequivalent Cp'' ligands and the introduced substituents. Similar to the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2**, four multiplets can be observed in the spectra of **3** and **4** (cf. Supporting Information). The ^1H NMR spectrum of **5** shows four signals ($\delta = 0.97$ ppm, 1.04 ppm, 1.19 ppm, 1.47 ppm) for four magnetically inequivalent ^tBu groups located on the Cp'' rings and six signals for the hydrogen atoms directly bound to the ring in the region of $\delta = 5.5$ to 6.1 ppm. Moreover, the signals at



Scheme 1. Overview of the reactions of $[\text{Cp}''_2\text{Zr}(\eta^{1-1}\text{-P}_4)]$ (**1a**) with ^tBuLi. All reactions were performed in THF at -78°C . Isolated yields are given in parentheses.

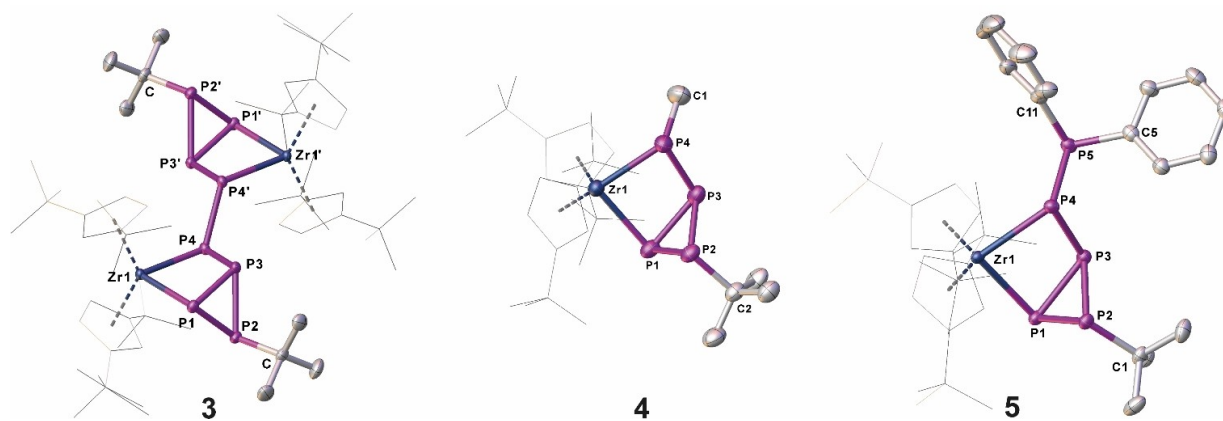


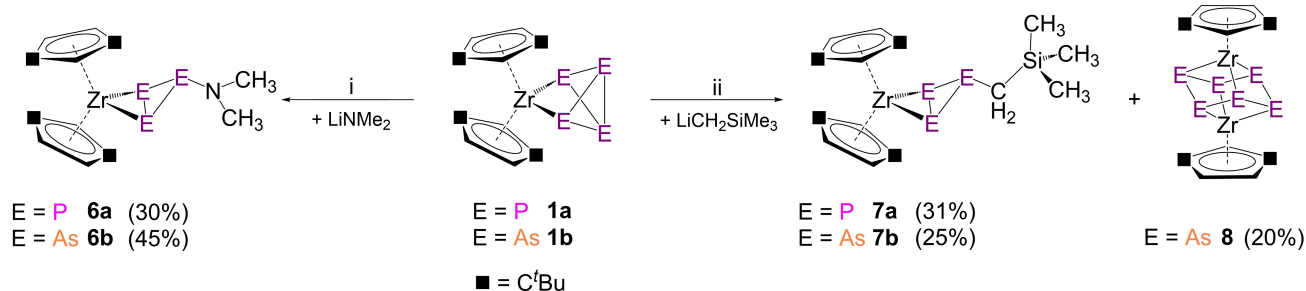
Figure 4. Molecular structure of **3**, **4** and **5** in the solid state with thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted and the Cp'' ligands are drawn in the wire frame model for clarity.

$\delta = 7.16$ – 7.29 ppm, 7.74 ppm and 7.93 ppm can be assigned to phenyl groups. The t -Bu group bound to P5 appears as a doublet at $\delta = 0.95$ ppm with a $^3J_{P-H}$ coupling constant of 11 Hz. The $^1H\{^{31}P\}$ NMR confirms the coupling to the phosphorus atom (cf. Figure S19). The $^{31}P\{^1H\}$ NMR spectrum of **5** shows five multiplets for the magnetically inequivalent phosphorus atoms. The corresponding coupling constants were obtained by simulation (Figure S22). Hence, a coupling constant of $^2J_{P3-P5} = 190$ Hz between the atoms P3 and P5 that are not directly bound indicates a through-space coupling, probably enabled by the geometry and the rather short distance of 3.179 Å, found in the solid-state structure. Similar observations of such a through-space coupling are reported in the literature.^[28] However, there is a second set of signals in the $^{31}P\{^1H\}$ NMR spectrum of at least a tenth of the intensity observed for the signals corresponding to **5**, even at low temperatures (Figure S21). Associated signals can also be observed in the 1H NMR spectra (Figure S17). These low-intensity signals can be tentatively assigned to a possible isomer of **5**, present in solution. However, the relative ratio of the signals in the NMR spectrum does not change over time, neither at room temperature nor at low temperatures nor if crystals of **5** are dissolved at -78 °C.

Due to the fact that **2** cannot be isolated and a full conversion to **3** is observed during the work-up of the reaction solution, the reaction behavior of **1** toward other main group

nucleophiles was investigated to trap ionic intermediates related to **2** (Scheme 2). Surprisingly, the reaction with the nucleophiles $LiNMe_2$ and $LiCH_2SiMe_3$, respectively, in DME leads to different products. Here the neutral compounds $[Cp''_2Zr(\eta^2-E_3Nu)]$ (Nu = NMe_2 : **6a**; As (**6b**); Nu = CH_2SiMe_3 : P (**7a**); As (**7b**)) containing a *cyclo-E*₃ unit are isolated (Scheme 2). In the case of the reaction of **1b** with $LiCH_2SiMe_3$, also the so far unknown triple-decker complex $[(Cp''Zr)_2(\mu, \eta^{1:1:1:1:1}-As_6)]$ (**8**) was isolated as a second product. However, it is not unambiguously clear in which form the abstracted phosphorus or arsenic atom is converted. We assume the formation of polyphosphides/arsenides due to a formation of a porous beige solid during the reactions and the workup. Furthermore, a singlet at 469.7 ppm in the $^{31}P\{^1H\}$ NMR spectrum of the reaction solution of **6a** indicates the formation of LiP_5 .^[29] Compounds **6a/b**, **7a/b** and **8** were comprehensively characterized by NMR spectroscopy, single crystal X-ray diffraction analysis, mass spectrometry and elemental analysis.

Crystals suitable for single crystal X-ray diffraction analysis were obtained by storing a concentrated solution of *n*-pentane (**6a**, **6b**), *n*-hexane (**7a**, **7b**) or Et_2O (**8**) at -78 °C. Figure 5 exemplifies the molecular structures of **6a**, **7b** and **8** (**6b** and **7a** are depicted in the Supporting Information). Compounds **6a/b** and **7a/b** consist of an E₃ ring, attached to a $[Cp''_2Zr]$ fragment (η^2 -coordinated) and the introduced nucleophilic part.



Scheme 2. Overview of the reactions of $[Cp''_2Zr(\eta^{1-1}-E_4)]$ (E = P: **1a**; E = As: **1b**) with the nucleophiles $LiNMe_2$ (i) and $LiCH_2SiMe_3$ (ii) in DME at -60 °C. Isolated yields are given in parentheses.

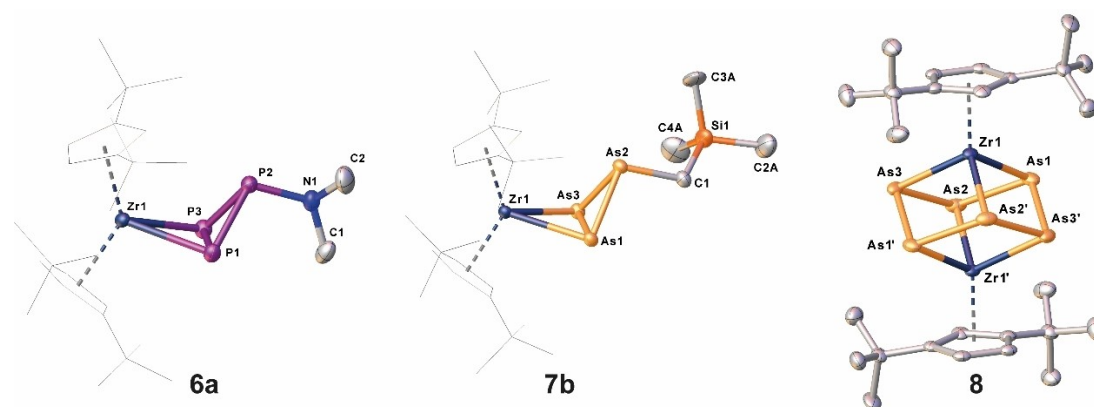


Figure 5. Molecular structure of **6a** (left), **7b** (middle) and **8** (right) in the solid state with thermal ellipsoids at 50% probability level. **6a**, **6b**: Hydrogen atoms are omitted and the Cp* ligands are drawn in the wire frame model for clarity. **8a**: Hydrogen atoms are omitted for clarity.

All E–E distances are in the range of a single bond.^[17,18,20,21] The central structural core of **8** can best be described as a chair-type As₆ unit stabilized by two [Cp*Zr] fragments. Due to the η^{1:1:1:1:1:1} coordination mode, the triple decker complex can also be described as a Zr₂As₆ cube. The As–As distances of 2.4908(7) Å to 2.5147(7) Å are in the range of single bonds and in good agreement with other polyarsenic transition metal complexes.^[21] Transition metal complexes containing an As₆ unit are known and usually represent a prismane core.^[30] Therefore, **8** represents the first complex containing a chair-like As₆ unit. Otherwise, only organo-substituted chair-like (RAs)₆ units were reported.^[31] Recently, the synthesis of the isostructural antimony complex [(Cp*Zr)₂(μ,η^{1:1:1:1:1:1}-Sb₆)] by the reaction of [Cp*ZrCl₂] with K₂Sb(SiMe₃)₂ was reported.^[32] Furthermore, besides the starting material **1b** and the complex [(Cp*Zr)(Cp*Zr)(μ,η^{2:2:1}-As₅)] which is formed as by-product of the synthesis of **1b**, **8** represents a rare example of a polyarsenic-containing zirconium complex.^[24]

The ¹H NMR spectra of **6a/b** and **7a/b** and **8** reveal the expected signals. For **6a/b** and **7a/b**, two sets of signals for the Cp* ligands in an asymmetric environment are detected. In comparison, the spectrum of **8** contains only one set of signals. Furthermore, also the methyl groups of the amide ligand in **6a** and **6b** are not equivalent and two signals are observed, because the rotation along the P2–N axis is hindered. In the ³¹P {¹H} NMR spectra of **6a** and **7a**, a triplet (**6a**: –16.7 ppm; **7a**: –105.9 ppm) and a doublet (**6a**: 67.2 ppm; **7a**: 103.8 ppm) arise with ¹J_{P,P} coupling constants of 263 Hz (**6b**) and 224 Hz (**7a**) consistent with the symmetric P₃ unit.

Conclusion

In summary, the reaction behavior of **1** towards main group nucleophiles was investigated and the synthesis and characterization of a variety of substituted polypnictogen ligand complexes as well as the isolation of a new polyarsenic triple-decker complex [(Cp*Zr)₂(μ,η^{1:1:1:1:1:1}-As₆)] (**8**) were reported. By using the nucleophile ^tBuLi, the introduction of a single organo

group on a bridgehead phosphorus atom of **1a** is achieved and the product Li[(Cp*Zr)(η^{1:1}-P₄^tBu)] (**2**) is formed. However, during workup, an oxidative dimerization occurs and leads to the exclusive isolation of the dimeric zirconium complex [(Cp*Zr)₂(μ,η^{1:1:1:1}-P₈^tBu₂)] (**3**), bearing a novel P₈ unit. Even if it was not possible to crystallize **2**, further reactions with the quenching reagents [Me₃O][BF₄] and Ph₂P₂Cl enable the introduction of an electrophilic group and the complexes [Cp*Zr(η^{1:1}-P₄^tBu(FG))] (FG=Me (**4**), PPh₂ (**5**)) were isolated confirming the initial formation of **2**. This underlines the potential of the presented approach of multiple functionalizations of a coordinated P₄ unit. Furthermore, the reaction behavior of **1** towards other main group nucleophiles like LiNMe₂ and LiCH₂SiMe₃, respectively, was investigated. Here, a more exclusive way to the formation of organo-substituted E₃ units was discovered. The size of the initial E₄ unit is reduced by the elimination of one pnictogen atom. Therefore, E₃-rings are formed and the neutral compounds [Cp*Zr(η^{1:1}-E₃Nu)] (Nu=NMe₂: E=P (**6a**), As (**6b**); Nu=CH₂SiMe₃: E=P (**7a**), As (**7b**)) were isolated. Due to the properties of the formed polypnictogen complexes with organic and main group element substituents, these products might offer interesting applications by their usage in transfer reactions and ring closure reactions. Nonetheless, the presented approach shows the potential to selectively diversify a fixed E₄ unit by reaction with nucleophilic and electrophilic reagents.

Experimental Section

Experimental procedures for the synthesis of all compounds, analytical data, quantum chemical calculations and X-ray crystallography are described in the Supporting Information.

Deposition Numbers 2162104 (for **3**), 2162105 (for **4**), 2162106 (for **5**), 2162107 (for **6a**), 2162108 (for **6b**), 2162109 (for **7a**), 2162110 (for **7b**) and 2162111 (for **8**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

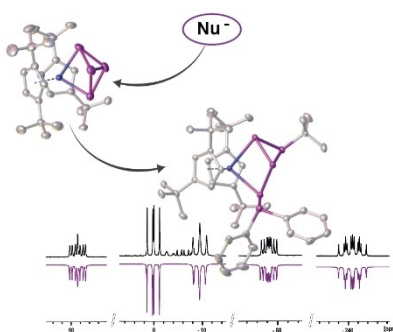
Keywords: arsenic · nucleophile · phosphorus · polypnictogen complexes · triple decker complex

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RESEARCH ARTICLE

The reactivity of $[\text{Cp}''_2\text{Zr}(\eta^{1:1}\text{-E}_4)]$ ($\text{E}=\text{P}, \text{As}$) towards main group nucleophiles is investigated to functionalize the polypnictogen unit. With $t\text{BuLi}$ as nucleophile, a single organic group is attached to a bridgehead phosphorus atom. The framework can be extended by further reactions with the quenching reagents $[\text{Me}_3\text{O}][\text{BF}_4]$ and Ph_2PCI . Furthermore, a condensation of two initially formed molecules occurs and a complex bearing a P_8 unit is obtained. In contrast, reactions with the nucleophiles LiNMe_2 and $\text{LiCH}_2\text{SiMe}_3$ lead to an abstraction of one pnictogen atom and the formation of a substituted *cyclo*- E_3 unit on a neutral $\text{Cp}''_2\text{Zr}$ complex.



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Reactivity of $[\text{Cp}''_2\text{Zr}(\eta^{1:1}\text{-E}_4)]$ ($\text{E}=\text{P}, \text{As}$) towards Nucleophiles

