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Hot Paper

Electrophilic Functionalization of a Hexaphosphabenzene Ligand in $[(Cp^*Mo)_2(\mu,\eta^{6:6}\text{-}P_6)]$

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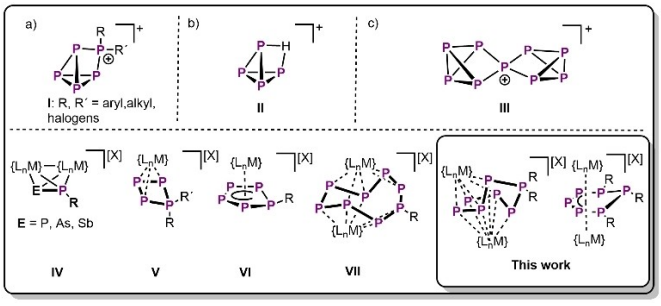
Dedicated to Professor M. Westerhausen on the occasion of his 65th birthday.

The electrophilic functionalization of the triple-decker sandwich complex $[\{Cp^*Mo\}_2(\mu,\eta^{6:6}\text{-}P_6)]$ (**A**) and its mono-oxidized counterpart $[\{Cp^*Mo\}_2(\mu,\eta^{6:6}\text{-}P_6)][SbF_6]$ (**B**) with reactive main-group electrophiles as well as radical scavengers is shown to be a reliable method for the selective functionalization of the hexaphosphabenzene ligand. Depending on the electrophile used, the regioselectivity of the functionalization can be adjusted. Using group 16 electrophiles, the trisubstituted compounds $[\{Cp^*Mo\}_2\{(\mu,\eta^{3:3}\text{-}P_3)(\mu,\eta^{1:1:1:1}\text{-}1,3\text{-}(SePh)_2\text{-}2\text{-}Br\text{-}P_3)\}][TEF]$ (**1**), $[\{Cp^*Mo\}_2(\mu,\eta^{3:3}\text{-}P_3)(\mu,\eta^{1:1:1:1}\text{-}1,2,3\text{-}(EPh)_3\text{-}P_3)][SbF_6]$ (E = S (**2**), Se (**3**)) as well as the side product $[\{Cp^*Mo\}_2(\mu,\eta^{4:4}\text{-}P_4)(\mu,\eta^{1:1}\text{-}P(SPh)_2)][SbF_6]$ (**4**) are obtained. By switching to phosphenium ions as group 15 electrophiles, the ring-inserted products $[\{Cp^*Mo\}_2(\mu,\eta^{3:3:2:2}\text{-}P_7R_2)][TEF]$ (R = Cy (**5**), ^{i}Pr (**6**)) are isolated, showing an unprecedented P_7R_2 structural motif. Furthermore, the reaction with MeOTf yields the dimeric $[\{Cp^*Mo\}_4(1,4\text{-}Me_2\text{-}\mu_4,\eta^{1:1:1:1:1:1}\text{-}P_6)(\mu,\eta^{3:3}\text{-}P_3)_2][TEF]_2$ (**7**) as the first example of a complex featuring two interconnected cyclo-P_6 middle deck ligands. Finally, by combination of the methylation step with Ph_2Se_2, the mixed group 14/16 complex $[\{Cp^*Mo\}_2\{(\mu,\eta^{3:3}\text{-}P_3)(\mu,\eta^{1:1:1:1}1,2\text{-}(SePh)_2\text{-}3\text{-}Me\text{-}P_3)\}][OTf]$ (**8**) is obtained.

Introduction

Carbon-based aromatic compounds with the general formula C_nH_n are an important class of compounds in organic chemistry. Electrophilic aromatic substitution reactions are one widely applied method for their functionalization using many different electrophiles such as H^+, halogens as well as alkyl and acyl cations.[1,2,3] However, after the first substitution, subsequent functionalizations become difficult in terms of regioselectivity and strongly depend on the nature of the incorporated substituents.[1,2] In contrast, the coordination to transition metals decreases the electron density of the arene ligand and therefore affects its reactivity.[4] As reported by *Graves* and *Lagowski*, the complexation of benzene in $[Cr(\eta^6\text{-arene})_2]$ significantly diminishes the overall π-electron density of the arene ligand, resulting in a greatly reduced tendency towards electrophilic aromatic substitution reactions as compared to free arene compounds.[5] Interestingly, aromatic hydrocarbons share a close relation to unsubstituted polyphosphorus (P_n) moieties. The isolobal principle between the CH and the P fragment[6] as well as the diagonal relationship between phosphorus and carbon[7] both suggest a similarity between these two elements and therefore comparable reactivity patterns. Typically, the electrophilic activation of P_4 leads to an insertion of the electrophiles into one P–P bond of the P_4 tetrahedron.[8,9] For this purpose, *in situ* generated phosphenium ions act as prototypical electrophiles which selectively enlarge the polyphosphorus framework.[8,9] By variation of the phosphenium ion precursors and the respective abstracting reagents, symmetrical or unymmetrical $[P_5RR']^+$ (R, R' = aryl, alkyl;[10] aryl/alkyl, halogen;[11] halogen[12,13]) cage compounds are generated (Scheme 1, **I**). However, despite phosphenium ions reacting readily with P_4, a variety of other electrophiles also reacted with



Scheme 1. Top: Selected polyphosphorus cations **I**, **II** and **III**, generated by the electrophilic conversion of P_4 with *in situ* generated phosphenium moieties (**I**), by protonation (**II**) or by formal one-electron oxidation in the presence of an excess of P_4 (**III**). Bottom: Known E_n ligand complexes, functionalized with main group electrophiles (**IV–VI**; $\{L_nM\} = \{CpMo(CO)_2\}$; $\{Cp'''Ni\}$; $\{Cp^*Fe\}$), and, content of this work, ($\{L_nM\} = \{Cp^*Mo\}$).

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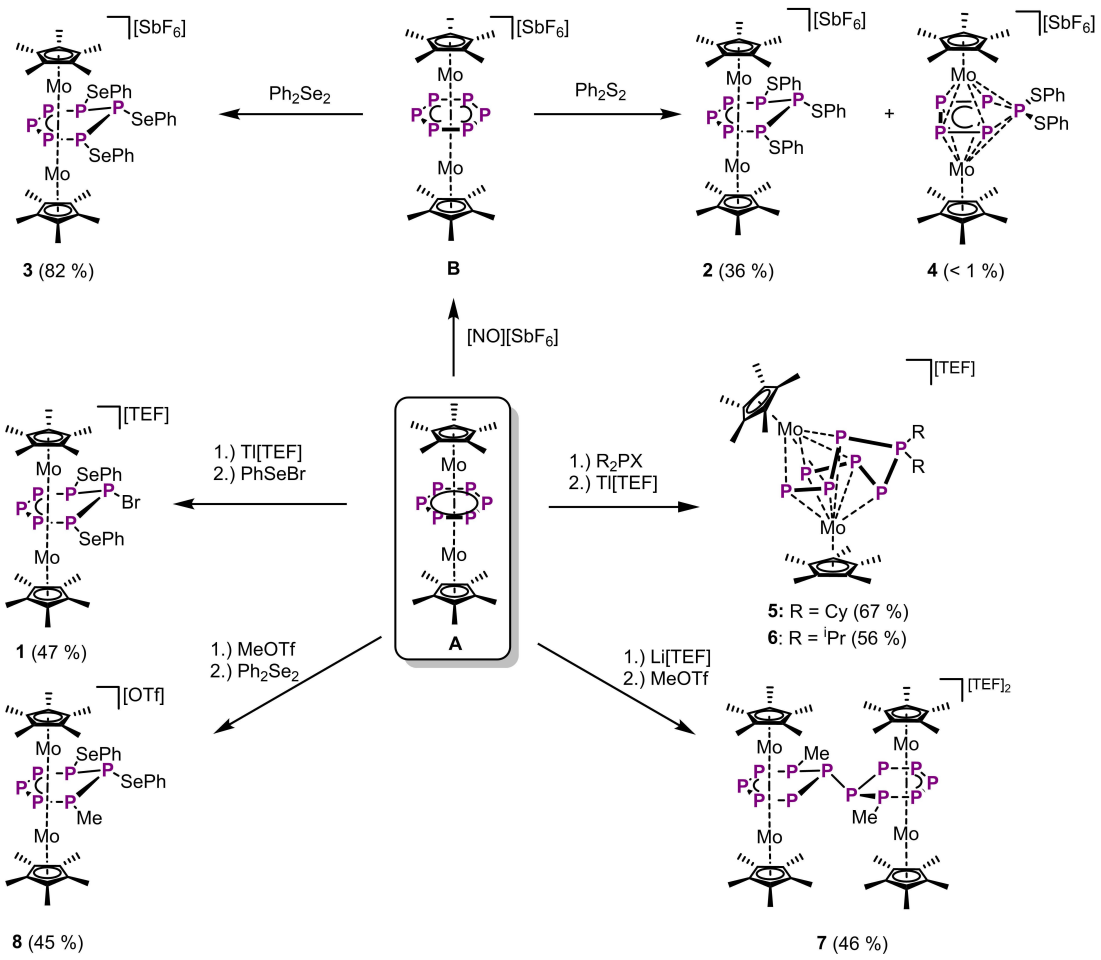
P_4. Examples range from the simplest known electrophile H^+, forming a three-center two-electron P–H–P bond (Scheme 1, **II**)[14] to one-electron oxidants such as $[NO]^+$,[15] forming together with an excess of P_4 the first homopolyatomic phosphorus cation (Scheme 1, **III**).[15,16] In contrast to phosphorus in its molecular form, polypnictogen (E_n) ligand complexes (E = P-Sb; n = 2–6) serve as useful starting materials to study the reactivity of unsubstituted E_n moieties. Some cyclic entities are isolobal to aromatic hydrocarbons. However, the reactivity of these species towards cationic electrophiles has only recently started to be explored. Depending on the electrophile used, different substitution patterns were achieved. This dependency was demonstrated by functionalizations of $[\{CpMo(CO)_2\}_2(\mu,\eta^{2:2}\text{-PE})]$ (E = P, As, Sb) with group 14 electrophiles (Scheme 1, **IV**), showing the selective substitution of the E_n ligand by the electrophile.[17] In contrast, the reaction of $[Cp'''Ni(\eta^3\text{-}P_3)]$ ($Cp''' = \eta^5\text{-}1,2,4\text{-}^tBu_3C_5H_2$) (Scheme 1, **V**) as well as $[Cp'''Ta(CO)_2(\eta^4\text{-}P_4)]$ with *in situ* generated phosphenium ions reveal an insertion into one P–P bond of the *cyclo*-P_3 and *cyclo*-P_4 ligand, respectively.[18,19] Interestingly, more extended polyphosphorus frameworks such as $[Cp^*Fe(\eta^5\text{-}P_5)]$ ($Cp^* = \eta^5\text{-}C_5Me_5$) (Scheme 1, **VI**)[20,21] or the very recently reported $[\{Cp'''Ta\}_2(\mu,\eta^{2:2:2:2:1:1}\text{-}P_8)]$ (**VII**)[22] exclusively show mono-substitution at the P_n ligand. Despite the previously reported examples of electrophilic functionalizations of E_n ligand complexes with main group electrophiles, no detailed investigations have so far been undertaken for the prototypical hexaphosphabenzene ligand in $[\{Cp^*Mo\}_2(\mu,\eta^{6:6}\text{-}P_6)]$[23] (**A**). Since the *cyclo*-P_6 ligand is isolobal with benzene and, in view of the low tendency of the benzene ligand to electrophilic substitutions, the question arose if electrophilic functionalization was also possible and, if so, whether they would give insertion reactions under ring expansion or substitution reactions. In contrast to the possible multi-substitution of uncoordinated carbon-based aromatic systems with electrophiles, reported examples of multi-substituted polypnictogen ligands featuring an intact E_n ring are still rare[24,25] and, in the case of **A**, only give rise to purely halogen-substituted complexes, as long as the *cyclo*-P_6 ligand stays intact.[25] Therefore, the question came up as to whether an electrophilic substitution principle could provide access to new cationic polypnictogen complexes featuring an intact and selectively functionalized *cyclo*-P_6 ligand. Herein, we report on the targeted and selective synthesis of novel cationic polyphosphorus complexes that bridge the gap between the reactivities of organic and inorganic aromatic systems. By the substitution reaction of the triple-decker sandwich complex **A** with chalcogenide-based electrophiles an allylic distortion is observed, whereas group 15 electrophiles insert into the *cyclo*-P_6 moiety leading to unprecedented P_7R_2 units.

Results and Discussion

The *in situ* halide abstraction with suitable Tl^+ salts was assumed to be the most promising route[17–19,21,22] to generate reactive electrophiles. So far, however, this methodology has only yielded singly functionalized E_n ligand complexes.[17–19,21,22] Examples of multi- and regioselectively functionalized E_n ligand complexes generated by this method are still unknown. Therefore, the group 16 electrophile precursor PhSeBr in combination with **A** and the abstracting agent Tl[TEF] ($[TEF]^- = [Al\{OC(CF_3)_3\}_4]^-$)[26,27] was selected. After workup of the reaction mixture $[\{Cp^*Mo\}_2\{(\mu,\eta^{3:3}\text{-}P_3)(\mu,\eta^{1:1:1:1:1}\text{1,3-}(SePh)_2\text{-2-Br-}P_3)\}][TEF]$, (**1**) was isolated as the main product of this reaction (Scheme 2). NMR spectroscopic investigations revealed the formation of $[\{Cp^*Mo\}_2(\mu,\eta^{3:3}\text{-}P_3)(\mu,\eta^{1:1:1:1:1}\text{-1,2,3-}(SePh)_3\text{-}P_3)][TEF]$ (**3**) as a by-product. Numerous attempts of optimization failed to either reduce the amount of formed **3** or to completely suppress its formation, indicating that this side-reaction is an intrinsic feature of this reaction. Interestingly, a group 16 functionalization can also be achieved by reacting the mono-oxidized complex $[\{Cp^*Mo\}_2(\mu,\eta^{6:6}\text{-}P_6)]^+$ (**B**)[28,29] with the dichalcogenides Ph_2E_2 (E = S, Se) as classical radical scavenging agents. In these cases, the symmetrically substituted products $[\{Cp^*Mo\}_2(\mu,\eta^{3:3}\text{-}P_3)(\mu,\eta^{1:1:1:1:1}\text{-1,2,3-}(EPh)_3\text{-}P_3)][SbF_6]$ (E = S (**2**), Se (**3**)) were obtained (Scheme 2). In the case of the sulfur-containing derivative **2**, a higher reaction temperature of 80 °C is necessary to enable the homolytic cleavage of the stronger S–S bond and allow the isolation of **2**. Due to the significantly harsher reaction conditions, the formation of a side product $[\{Cp^*Mo\}_2(\mu,\eta^{4:4}\text{-}P_4)(\mu,\eta^{1:1}\text{-}P(SPh)_2)][SbF_6]$ (**4**) was observed in trace amounts, together with a diminished yield of **2** (36%) compared to **3**. Despite its paramagnetic nature, the formation of **4** could nevertheless be tracked by the detection of $P(SPh)_3$ as the extruded compound by ^{31}P NMR spectroscopy. This extrusion product explains the formation of **4** (cf. SI, Figure S13). To extend the scope of the cationic compound **B**, several anionic and neutral nucleophiles (OCP^-, N_3^-, OEt^-, etc.) were furthermore tested, however, due to the high redox activity of both **A** and **B**,[28] all attempts resulted in the quantitative back-formation of neutral **A**. As a by-product of the reaction yielding **1**, the symmetrically substituted cation of **3** could be identified by NMR spectroscopy, which suggests an oxidation reaction of **A** and a subsequent reaction with Ph_2Se_2 as the dominant side-reaction.

Furthermore, halogenophosphines were chosen as group 15 electrophiles. Despite the high tendency of halogenophosphines to form phosphino-phosphonium cations under Lewis-acidic conditions,[13,30] the ring-inserted products $[\{Cp^*Mo\}_2(\mu,\eta^{3:3:2:2}\text{-}P_7R_2)][TEF]$ (R = Cy (**5**), ^{i}Pr (**6**)) were obtained in 67% (**5**) and 56% yields (**6**), respectively, by the reaction of *in situ* generated phosphenium ions with **A**. Note that analogous experiments with the heavier arsenium ions lead to the oxidation of **A**. Despite recent reports on enlarged oligophosphorus ligands,[31] this is nevertheless a surprising result, since for a *cyclo*-P_5 aromatic system, a substitution by group 15 electrophiles was observed,[21] similar to the COT-like P_8 ligand in **VII**.[22] To demonstrate the transferability of the reaction to group 14 electrophiles, MeOTf was envisioned to react with **A**. For reasons of solubility, a salt metathesis with Li[TEF][26,27,32] was performed giving $[\{Cp^*Mo\}_4(1,4\text{-}Me_2\text{-}\mu_4,\eta^{1:1:1:1:1:1}\text{-}P_6)(\mu,\eta^{3:3}\text{-}P_3)_2][TEF]_2$ (**7**) in 46% yield as the first complex featuring two interconnected *cyclo*-P_6 middle deck ligands. This dication is thermally unstable in solution and decomposes quantitatively



Scheme 2. Reactivity of [{Cp*Mo}$_2$(μ,η$^{6:6}$-P$_6$)] (**A**) towards different cationic main group electrophiles; reactions were carried out in o-DFB or CH_2Cl_2 and stirred for 2 h at room temperature (for details see SI). While all compounds shown were fully characterized with their depicted counterions, **1**, **5** and **7** were crystallized with the $[OTf]^-$ (**1**) or the $[B(C_6F_5)_4]^-$ (**5**, **7**) counterion, but for reasons of solubility were characterized with the $[TEF]^-$ counteranion.

to **B** within a period of 12 hours. This decomposition could not be prevented by different counterions such as $[BAr^F]^-$ ($[BAr^F]^- = [B(C_6F_5)_4]^-$)[33] or the $[TEF]^-$ anion. However, performing the reaction at −80 °C followed by slow warming to room temperature over a period of 90 minutes enabled the isolation of **7**. **7** is nevertheless stable in the solid state. After isolation of **7**, the question arose as to the underlying mechanism involved and if the supposed mono-functionalized intermediate [{Cp*Mo}$_2$(μ,η$^{6:6}$-P$_6$Me)]$^+$ could be trapped. Therefore, Ph_2Se_2 was used together with MeOTf at a slightly higher reaction temperature of 80 °C. Hereby, the selective formation of [{Cp*Mo}$_2${(μ,η$^{3:3}$-P$_3$)(μ,η$^{1:1:1:1}$1,2-(SePh)$_2$-3-Me-P$_3$)}][OTf] (**8**) in 45 % yield occurred representing a novel mixed group 14/15/16 compound. The X-ray structural characterization of the compounds **1**, **2**, **3**, **7** and **8**, respectively, showed a triple-decker sandwich complex with a distorted but still intact *cyclo*-P$_6$ middle deck for which elongated P3-P4 and P6-P1 bonds were observed (Figure 1). These P–P distances (**1**: 2.662(2) Å, 2.645(3) Å; **2**: 2.680(3) Å, 2.681(3) Å; **3**: 2.684(3) Å, 2.682(2) Å; **7**: 2.667(3) Å, 2.678(3) Å; **8**: 2.662(3) Å, 2.664(3) Å) significantly exceed the sum of the covalent radii for a P–P single bond (2.22 Å)[34–36] but still are within the sum of the van-der-Waals radii (r(P) = 1.80 Å).[37] This enlargement points to an only weak interaction between the unsubstituted P_3 and the substituted $P_3R_{2/3}$ moieties (Figure 1). Additional NBO analyses[38] of the exemplified compound **1** prove this classification by decreased Wiberg Bond Indices (WBI) between these two fragments (**1**: WBI(P1-P6) = 0.19; WBI(P3-P4) = 0.21). Such a distortion was only observed in an iodine-substituted complex, reported in the halogenation protocol of **A** (d(P–P) = 2.652(5) Å, 2.665(5) Å).[25] Furthermore, all compounds with an intact yet distorted *cyclo*-P$_6$ middle deck ligand show a non-planar geometry where the P2 atom is slightly bent out of the plane spanned by the other P atoms (**1**: 153.21(1)°; **2**: 155.08(12)°; **3**: 152.92(8)°; **7**: 154.6(1)°; **8**: 153.62(12)°). In addition, its substitution with heteroelements leads to a slight enlargement of the P–P bonds in the $P_3R_{2/3}$ moiety (**1**: 2.210(3) Å, 2.208(3) Å; **2**: 2.216(3) Å, 2.243(3) Å; **3**: 2.218(2) Å, 2.226(2) Å; **7**: 2.207(3) Å, 2.212(3) Å; **8**: 2.233(4) Å, 2.245(4) Å) as compared to the unsubstituted P_3 moiety which shows P–P distances in-between single and double bonds (**1**: 2.138(3) Å, 2.145(3) Å; **2**: 2.150(5) Å, 2.106(5) Å; **3**: 2.2133(3) Å, 2.145(3) Å; **7**: 2.135(4) Å, 2.140(3) Å; **8**: 2.135(2) Å, 2.132(3) Å) (P–P = 2.22 Å; P=P: 2.04 Å) reminiscent of the allylic nature of this P_3 ligand[34–36] and also supported by DFT calculations (*vide*

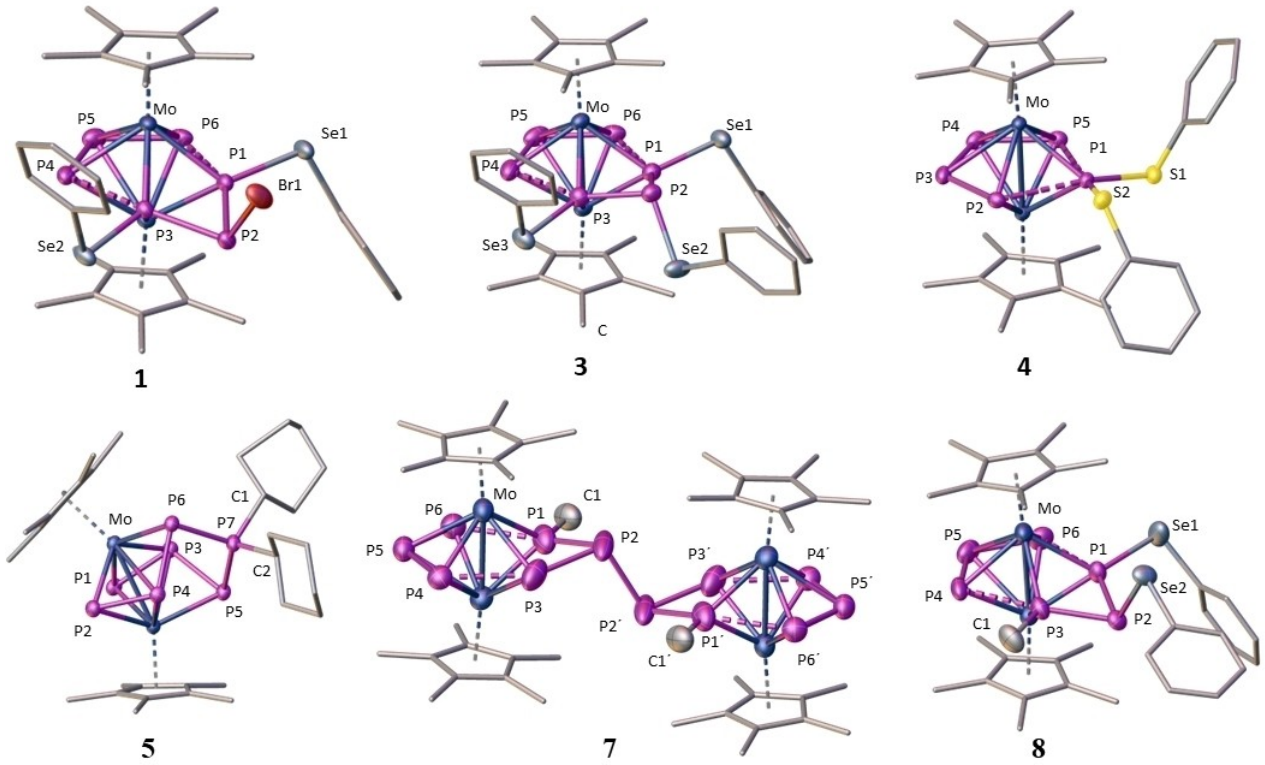


Figure 1. Molecular structures of the cations **1**, **3**, **4**, **5**, **7** and **8** in the solid state. Structural models for the cations **2** and **6** as well as a list of selected structural parameters (bond lengths) for all compounds can be found in the SI.

infra). Compound **4** shows a distorted *cyclo*-P_5 middle deck ligand, and a significant bond elongation is also observed between the P1-P2 as well as the P1-P5 bonds (2.6797(9) Å, 2.6639(8) Å), respectively, which also indicates an only weak interaction between the P_4 and the P_1R_2 moieties. The calculated P–E bond lengths (see SI) represent P–E single bonds and deviate only very little from the reported values (d(P–Se) = 2.26 Å; d(P–S) = 2.14 Å; d(P–Br) = 2.25 Å; d(P–C) = 1.86 Å).[34–6] When switching to phosphenium cations as classical group 15 electrophiles, the insertion of the electrophile into one P–P bond of **A** leads to a significant distortion of the originally planar middle deck ligand. However, the respective P–P bond lengths of both compounds **5** and **6** as well as the P–C bonds show no significant enlargement and strongly correlate with the sum of the covalent radii for P–P and P–C single bonds (d(P–P) = 2.22 Å; d(P–C) = 1.86 Å), respectively.[34–36] In all cases, the functionalization of the *cyclo*-P_6 middle deck ligand leads to an enlargement of the Mo-Mo distance (see SI) compared to **A**[23] but correlates with previously reported threefold substituted P_6R_3 species.[25] To further elaborate the structure of **1**–**8** in solution, the complexes were investigated by multinuclear NMR spectroscopy. In the ^{1}H NMR spectra, all compounds show the expected sharp signals for the Cp* ligands and the corresponding signals of the substituents. Furthermore, the Me substituents of both **7** and **8** show a significant broadening of the signal, caused by the coupling to the adjacent P atoms (**8**: $^2J_{P\text{-}H}$ = 10.6 Hz; **7**: the coupling constant could not be determined by simulation, compare SI). The ^{31}P{^{1}H} NMR spectra of **1**, **2** and **3**, respectively, show an ADD'MM'X spin system which could be analyzed by simulation (Figure 2). For **7** and **8**, the asymmetric substitution pattern leads to the more complicated ADMQRX (**7**) and ADEMQX (**8**) spin systems. When comparing the ^{31}P NMR spectra of the respective compounds, all compounds with a substituted *cyclo*-P_6 middle deck show similar spectra due to their similar chemical environment. Nevertheless, minor changes in the coupling constants and chemical shifts for

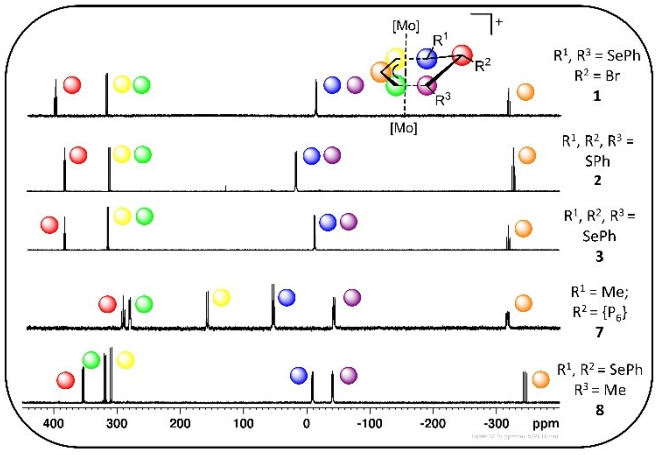
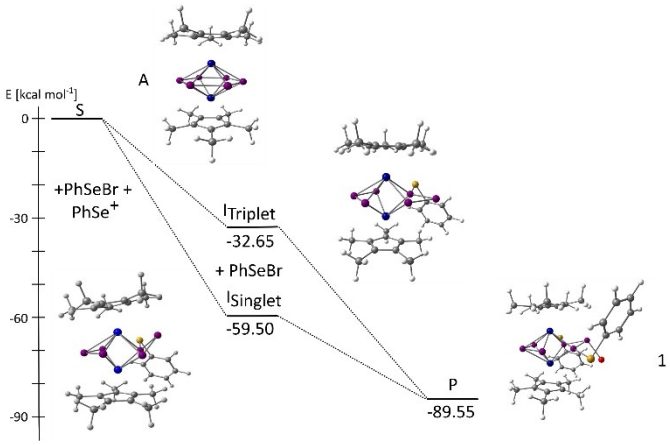


Figure 2. ^{31}P{^{1}H} NMR spectra of the compounds **1**, **2**, **3**, **7** and **8** (from top to bottom), measured in CD_2Cl_2 at room temperature, representing different substituents in different positions with the signals being assigned according to the color code; [Mo] = Cp*Mo.

the respective signals were detected (Figure 2). Interestingly, the significantly diminished $^{1}J_{P-P}$ coupling constants (**1**: 23.7 Hz, 6.1 Hz, **2**: 33.2 Hz, 48.4 Hz, **3**: 24.1 Hz, 21.7 Hz) between the unsubstituted P_3 and the substituted P_3R_3 moieties indicate an only weak bonding interaction between the adjacent nuclei. This is in line with the long distances between the corresponding P atoms observed in the solid-state structures of the corresponding compounds **1**, **2**, and **3**, respectively (cf. Figure 1). By switching to group 15 electrophiles, the insertion of the phosphenium ion into one P–P bond of the *cyclo*-P_6 middle deck ligand in **5** and **6** results in an AA'DD'EXX' spin system. Furthermore, in the ^{31}P NMR spectra of compounds **5** and **6**, a characteristic broadening of the signal corresponding to the nucleus P_E (compare SI) clearly indicates a $^{n}J_{P\text{-}H}$ coupling (**5**: 35.0 Hz; **6**: 14.7 Hz), which proves the connectivity to the alkyl groups. In addition, the chemical shifts of these two compounds show only very small differences and thus also support their isostructural character in solution.

In order to obtain better insight into the energetic pathway of the electrophilic activation, theoretical calculations at the B3LYP-D4/def2-TZVP[39–43] level of theory were performed for the formation of **1** as a representative reaction (Scheme 3). Employing solvent correction,[44] the calculated and optimized geometries agree very well with the molecular solid-state structures obtained by single crystal X-ray diffraction. Even though the proposed singly substituted intermediate $[\{Cp^*Mo\}_2(P_6R)]^+$ (**I**) could not be experimentally detected, its formation is assumed to be the crucial step in the formation of the observed trisubstituted products. The first step in the formation of **1** is the reaction of **A** with the *in situ* generated $[PhSe]^+$ cation, formally yielding the mono-functionalized intermediate **I** in a strongly exergonic process. To determine the spin state of **I**, further calculations were conducted which revealed a significant energetic preference for the singlet ($\mathbf{I}_{Singlet}$) spin state over the triplet ($\mathbf{I}_{Triplet}$) state ($\Delta G_{298K} = -26.8$ kcal mol^{-1}) which is therefore considered to be the more likely spin state of **I**. Both the $\mathbf{I}_{Singlet}$ and the $\mathbf{I}_{Triplet}$ show a distorted middle deck, which, in the case of the singlet state, deviates from planarity much stronger than in the energetically higher lying triplet state ($\measuredangle$(singlet) = 83°; $\measuredangle$(triplet) = 55°). The second also strongly exergonic step is the addition of an equivalent of PhSeBr to $\mathbf{I}_{singlet}$, leading to **1**. The overall conversion of **A** to **1** was calculated to be a strongly exergonic reaction with $\Delta G_{298K} = -89.55$ kcal mol^{-1}. Similar calculations regarding the energetic difference between the ring-inserted product **5** and its suspected formal isomer $[\{Cp^*Mo\}_2(\mu,\eta^{6:6}\text{-}P_6\text{-}PCy_2)]^+$, featuring a still planar *cyclo*-P_6 middle deck ligand substituted with a PCy_2 moiety, showed a notable energetic preference for the inserted complex **5** of $\Delta G_{298K} = -18.4$ kcal mol^{-1}. This supports the selectivity of this insertion reaction further. Additional NBO analyses[38] of the suggested intermediate $\mathbf{I}_{singlet}$ show significantly decreased Wiberg Bond Indices (WBI) between the substituted $P_3R_{1,2,3}$ and the unsubstituted P_3 moieties that are similar to **1**, indicating a very weak interaction between the two moieties caused by the attack of the electrophile on the unsubstituted *cyclo*-P_6 middle-deck ligand ($\mathbf{I}_{Singlet}$: WBI(P1-P6) = 0.53; WBI(P3-P4) = 0.17). The WBI's of the residual P–P bonds are located in the range of regular single bonds ($\mathbf{I}_{Singlet}$: WBI (P1-P2) = 1.03; WBI (P2-P3) = 1.04; WBI (P4-P5) = 0.995; WBI (P5-P6) = 0.78); **1**: WBI (P1-P2) = 0.87, WBI (P2-P3) = 0.86; WBI (P4-P5) = 0.92; WBI (P5-P6) = 0.92). Thus, the observation of significantly longer distances between the two P_3 units which emerged from the X-ray crystallographic experiments is also clearly supported by theoretical computations.



Scheme 3. Calculated (B3LYP/def2TZVP, CPCM (CH_2Cl_2)) relative energies of the reaction of **A** with $[PhSe]^+$ as well as PhSeBr, leading to **1**. Energies are given in kcal mol^{-1}. The sum of the Gibbs free energy of **A**, $[PhSe]^+$ and PhSeBr were set arbitrarily to 0 kcal mol^{-1}.

Conclusions

In summary, a method to selectively functionalize a benzene-analogous hexaphosphabenzene ligand with various main group electrophiles was discovered, resulting in unprecedented products adjustable by selecting the appropriate main group electrophile. The reaction with PhSeBr yields the symmetrically substituted $[\{Cp^*Mo\}_2\{(\mu,\eta^{3:3}\text{-}P_3)(\mu,\eta^{1:1:1:1}1,3\text{-}(SePh)_2\text{-}2\text{-}Br\text{-}P_3)\}][TEF]$ (**1**). The functionalization of the mono-oxidized complex $[(Cp^*Mo)_2(\mu,\eta^{6:6}\text{-}P_6)][SbF_6]$ (**B**) with the dichalcogenide compounds Ph_2E_2 (E = S, Se) yields the related trisubstituted products $[\{Cp^*Mo\}_2(\mu,\eta^{3:3}\text{-}P_3)(\mu,\eta^{1:1:1:1}\text{-}1,2,3\text{-}(EPh)_3\text{-}P_3)][SbF_6]$ (E = S (**2**), Se (**3**)) as well as $[\{Cp^*Mo\}_2(\mu,\eta^{4:4}\text{-}P_4)(\mu,\eta^{1:1}\text{-}P(SPh)_2)][SbF_6]$ (**4**). In contrast, the reaction of **A** with phosphenium ions leads to the formation of the inserted, ring-expanded products $[\{Cp^*Mo\}_2(\mu,\eta^{3:3:2:2}\text{-}P_7R_2)][TEF]$ (R = Cy (**5**), ^{i}Pr (**6**)). By switching to MeOTf as a group 14 electrophile, the formation of the dimeric complex $[\{Cp^*Mo\}_4(1,4\text{-}Me_2\text{-}\mu_4,\eta^{1:1:1:1:1:1}\text{-}P_6)(\mu,\eta^{3:3}\text{-}P_3)_2][TEF]_2$ (**7**) is observed representing the first complex featuring two interconnected *cyclo*-P_6 middle deck ligands. By performing the reaction in the presence of a radical scavenging agent, *i.e.* Ph_2Se_2, the dimerization can be prevented, yielding the asymmetrically substituted compound $[\{Cp^*Mo\}_2\{(\mu,\eta^{3:3}\text{-}P_3)(\mu,\eta^{1:1:1:1}1,2\text{-}(SePh)_2\text{-}3\text{-}Me\text{-}P_3)\}][OTf]$ (**8**). DFT calculations show that the reaction proceeds via a cationic singlet state intermediate, which could not be isolated and immediately reacts further to the stable endproduct. Therefore, **A** was shown to be a versatile platform for the generation of novel, selectively

functionalized polypnictogen ligand complexes featuring a diversity of main group substituents.

Experimental Section

Experimental procedures for the synthesis of all compounds, analytical data, quantum chemical calculations and X-ray crystallographic details are summarized in the Supporting Information. The authors have cited additional references within the Supporting Information (Ref. [27–29,39–43,45]). Deposition Numbers 2310024 (for **1**), CCDC-2310025 (for **2**), CCDC-2310026 (for **3**), CCDC-2310027 (for **4**), CCDC-2310028 (for **5**), CCDC-2310029 (for **6**), CCDC-2310030 (for **7**), and CCDC-2310031 (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

There are no conflicts to declare.

Data Availability Statement

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

Keywords: chalcogens · electrophilic substitution · molybdenum · phosphorus · triple decker complexes

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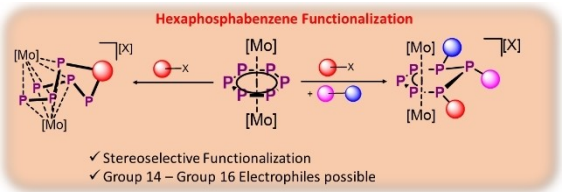

The reactivity of the triple-decker sandwich complex [{Cp*Mo}$_2$(μ,η$^{6:6}$-P$_6$)] with main group electrophiles as well as radical scavengers is explored. These studies yield novel cationic derivatives of the isolobal P homolog of the ubiquitous benzene ligand, featuring group 14, 15, and 16 as well as mixed group 14/16 element substituents.

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Electrophilic Functionalization of a Hexaphosphabenzene Ligand in [(Cp*Mo)$_2$(μ,η$^{6:6}$-P$_6$)]