

Redox and Coordination Behavior of the Hexaphosphabenzene Ligand in $[(\text{Cp}^*\text{Mo})_2(\mu, \eta^6:\eta^6\text{-P}_6)]$ Towards the “Naked” Cations Cu^+ , Ag^+ , and Tl^+

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Dedicated to Professor Malcolm Chisholm on the occasion of his 70th birthday

Abstract: Although the cyclo- P_6 complex $[(\text{Cp}^*\text{Mo})_2(\mu, \eta^6:\eta^6\text{-P}_6)]$ (**1**) was reported 30 years ago, little is known about its chemistry. Herein, we report a high-yielding synthesis of **1**, the complex **2**, which contains an unprecedented cyclo- P_{10} ligand, and the reactivity of **1** towards the “naked” cations Cu^+ , Ag^+ , and Tl^+ . Besides the formation of the single oxidation products **3a, b** which have a bisallylic distorted cyclo- P_6 middle deck, the $[\text{M}(\text{1})_2]^+$ complexes are described which show distorted square-planar ($\text{M} = \text{Cu}$ (**4a**), Ag (**4b**)) or distorted tetrahedral coordinated ($\text{M} = \text{Cu}$ (**5**)) M^+ cations. The choice of solvent enabled control over the reaction outcome for Cu^+ , as proved by powder XRD and supported by DFT calculations. The reaction with Tl^+ affords a layered two-dimensional coordination network in the solid state.

In 1981, Nobel Laureate R. Hoffmann described how the isolobal analogy was building bridges between inorganic and organic chemistry.^[1] In this context, the isolation of the all-phosphorus analogue of one of the most prominent organic

molecules—benzene—stabilized in the complex $[(\text{Cp}^*\text{Mo})_2(\mu, \eta^6:\eta^6\text{-P}_6)]$ (**1**) in 1985 by Scherer et al. can be viewed as a milestone in inorganic chemistry.^[2] Cyclo- P_6 triple-decker complexes have also been described for Ti, V, Nb, and W.^[3–7] Over the last decade, inorganic supramolecules resembling fullerenes were isolated^[8–10] through coordination of the cyclo- P_5 complexes $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$ to Cu^+ halides. Intrigued by the idea of interconnecting cyclo- P_6 complexes **1** to build up a supramolecular inorganic analogue of graphene, we decided to investigate the coordination chemistry of **1**. The described yield of **1** after separation from several other products was only 1%, which is probably the reason why no studies on the reactivity of **1** have been carried out over the last 30 years.

Increasing the reaction temperature of the thermolysis of $[\text{Cp}^*\text{Mo}(\text{CO})_{2/3}]_2$ with P_4 to approximately 205 °C in boiling diisopropylbenzene gives **1** in analytically pure form in an astonishing 64% yield. Additionally, the novel phosphorus-rich complex $[(\text{Cp}^*\text{Mo})_2(\mu\text{-P}_{10})]$ (**2**) is obtained in trace amounts in a crystalline form during the isolation of **1**.^[11] The reaction energy calculated by DFT for the reaction $\mathbf{2} \rightarrow \mathbf{1} + \text{P}_4$ ($\Delta E = -19.6 \text{ kJ mol}^{-1}$) shows that **1** is the thermodynamic product.^[12] The molecular structure of **2** (Figure 1) displays a strongly folded cyclo- P_{10} ligand that has four shorter bonds between P1 and P2 as well as between P4 and

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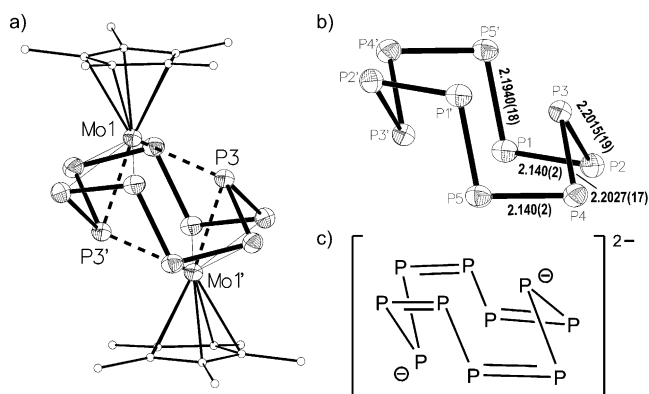


Figure 1. a) Molecular structure of complex **2**. C atoms are depicted as small spheres and H atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths [Å]: Mo1-P3 2.4965(15), Mo1-P3' 2.5109(12). b) The cyclo- P_{10} ligand of **2**. c) P_{10}^{2-} .

P5 of 2.140(2) Å, while the remaining P–P bonds are longer, with an average length of 2.2 Å. Therefore, an adequate description of complex **2** would be a formal *cyclo*-decaphosphatetraenediide dianionic P₁₀ ligand (Figure 1c) stabilized by two [Cp*Mo]⁺ fragments.

The polyphosphido ligand binds to each Mo center through a η²:η² mode of the P–P double bonds and by additional η¹ coordination of P3 and P3'. This suggests an oxidation state of +2 for Mo. The Mo–Mo distance of 3.7018(8) Å is too long for any metal–metal interaction. DFT calculations show that Mo engages in a bonding interaction to P3 above and to its symmetry-equivalent P3' atom through the phosphorus ring with Wiberg bonding indexes (WBI) of 0.70 and 0.76, respectively. The intramolecular P–P distances P2–P4, P3–P1', and P3–P5' are below the sum of the van der Waals radii (3.13–3.17 Å). The respective WBIs of 0.05 and 0.06 indicate no bonding interactions. The molecular ion signal for [2]⁺ at *m/z* = 772.0 (g mol⁻¹) was clearly identified together with the signal for [1]⁺ at 647.9 (g mol⁻¹) by EIMS.

There is a substantial variety of polyphosphorus frameworks containing up to 24 P atoms^[13] described in the literature that are stabilized as Zintl anions,^[14] by main group substituents,^[15,16] or in the coordination sphere of transition metals.^[17,18] The unprecedented P₁₀²⁻ ligand of **2** represents the largest polyphosphorus cycle known so far. The isolobal dianion C₁₀H₁₀²⁻ has been studied exclusively by theoretical methods.^[19]

In addition to characterizing complex **2**, we were able to study the reactivity of **1** in detail and initiated these studies by the reaction of **1** with M⁺ salts (M = Ag, Cu) of the weakly coordinating anion (WCA) [Al{OC(CF₃)₃]₄⁻ ([TEF]).^[20–22] Addition of a solution of Ag[TEF] or Cu[TEF] in CH₂Cl₂ to a solution of **1** in CH₂Cl₂ results in oxidation taking place, which can easily be followed by an immediate color change from light brown to dark teal and the formation of a metal mirror or black precipitate (Scheme 1). The cyclic voltammogram of **1** shows a reversible oxidation at –0.24 V versus Cp₂Fe⁰/Cp₂Fe⁺ while the second oxidation at about +0.59 V is irreversible.^[23] The ¹H NMR spectrum of the paramagnetic complex **3a** in CD₂Cl₂ shows one broad singlet (ω_{1/2} = 16 Hz) at 4.08 ppm, while no signal can be resolved in the ³¹P NMR spectrum between –1200 and +1200 ppm. The ¹⁹F NMR spectrum shows the presence of [TEF]. The X-band EPR spectrum of [1]⁺ shows no signal at room temperature, but cooling to 77 K results in one broad signal being resolved

without any hyperfine coupling at *g*_{iso} = 2.024 (solid state) or *g*_{iso} = 2.019 (CD₂Cl₂).^[24] The magnetic moment of **3a** (μ_{eff} = 1.67 μ_B) was determined by the Evans NMR method and is consistent with one unpaired electron.^[24] In the ESI mass spectrum, [1]⁺ is detected. The dark teal crystals of **3a** were not suitable for an X-ray structure analysis.^[24] By exchanging the anion [TEF] for another WCA [FAI]{OC(CF₃)₃}₃⁻ ([FAI]),^[25] we were able to determine the crystal structure of the oxidized P₆ complex **3b** (Figure 2).

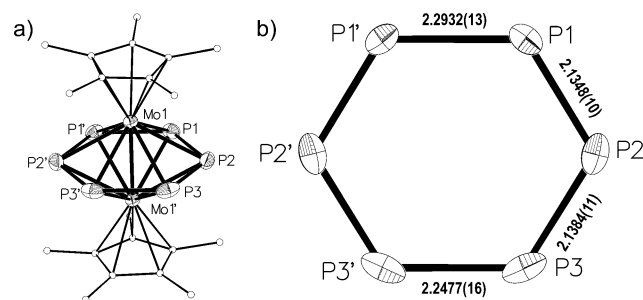
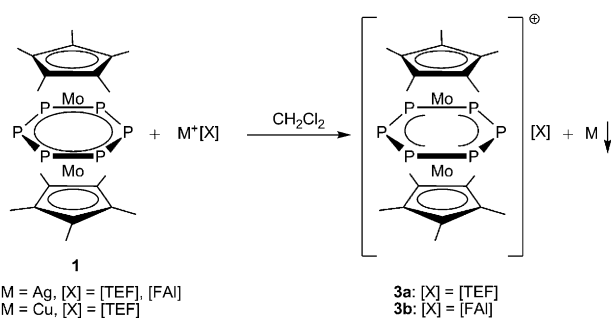


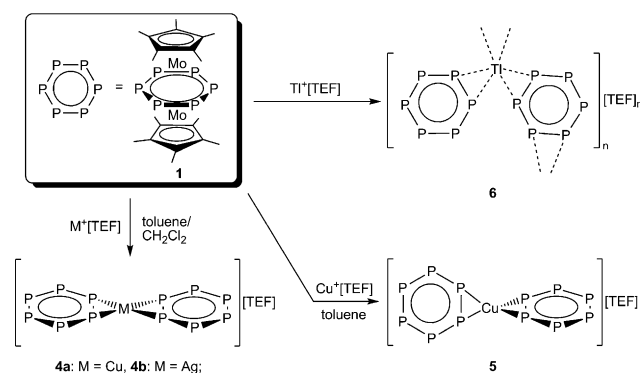
Figure 2. a) Molecular structure of the cation [1]⁺ in **3b**.^[26] Thermal ellipsoids are drawn at 50% probability. C atoms are depicted as small spheres, H atoms are omitted for clarity. Mo1–Mo1' 2.6617(4) Å. b) Bivalently distorted *cyclo*-P₆ ligand.

The structure of **3b** shows that the triple-decker geometry is retained during the one-electron oxidation of **1**. The Mo–Mo' bond length of the cation [1]⁺ is, at 2.6617(4) Å, almost identical to the 2.6463(3) Å of **1**.^[24] The P–P bond lengths on the other hand are strongly affected by the oxidation. While the bonds P1–P1' and P3–P3' are elongated, the remaining P–P bonds are shortened compared to the average P–P bond length of about 2.183 Å in the starting material. Therefore, the middle deck of [1]⁺ can best be described as a bivalently distorted *cyclo*-P₆ ligand. DFT calculations show that this distortion is due to depopulation of the P–P bonding orbitals in the oxidized complex cation [1]⁺.^[24]

To avoid oxidation of **1** by the M⁺[TEF] salts, we reduced the redox potential of the cations by the addition of toluene. Although with Ag we constantly obtained a mixture of the dark teal oxidation (**3a**) and bright orange coordination product (**4b**), with Cu we were able to completely avoid oxidation and only obtain bright orange **4a** (Scheme 2). The



Scheme 1. Oxidation of **1** by M⁺ salts.



Scheme 2. Reactivity of **1** towards the cations Cu⁺, Ag⁺, and TI⁺.

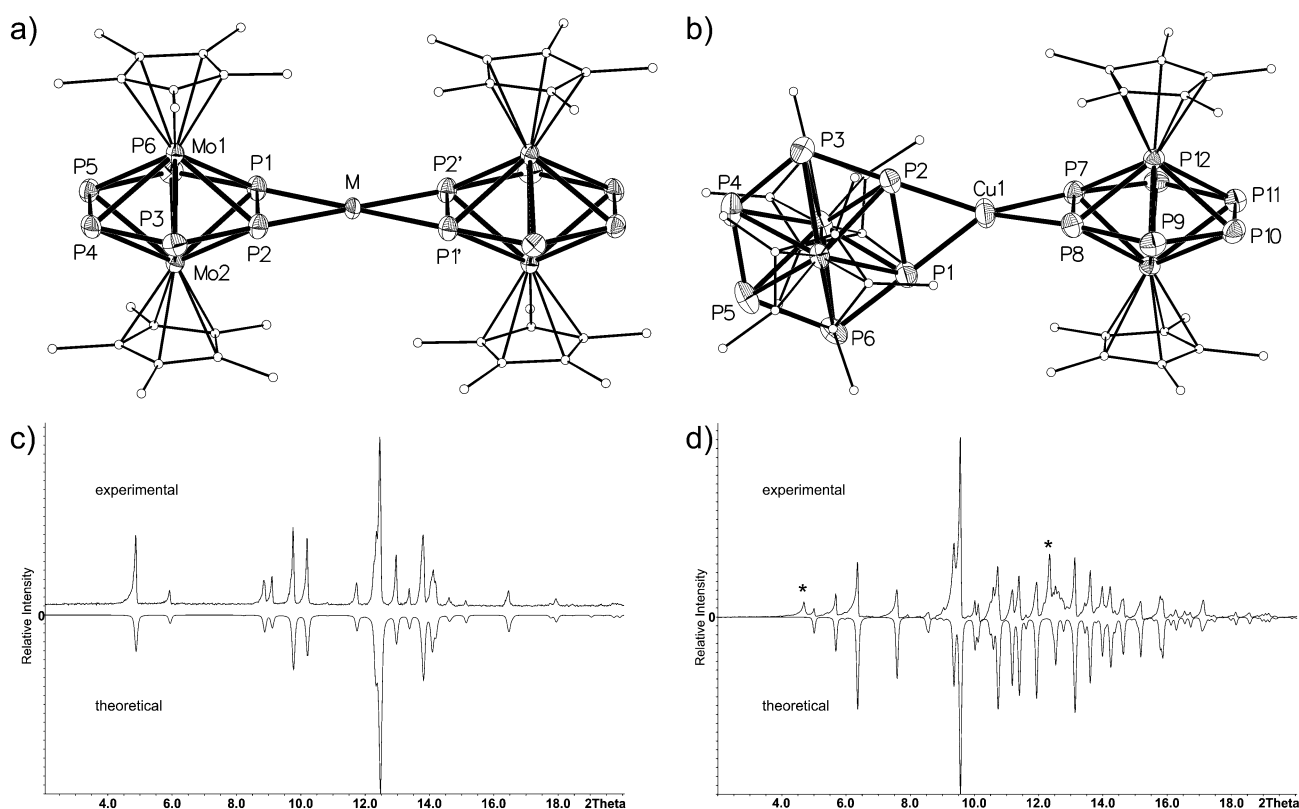


Figure 3. Solid-state structure of a) the cations of **4a** ($M = \text{Cu}$) and **4b** ($M = \text{Ag}$) and b) the cation of **5**. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths [\AA]: **4a**: Cu1-P1 2.4354(12), Cu1-P2 2.3927(12), P1-P2 2.2694(16); **4b**: Ag1-P1 2.5793(10), Ag1-P2 2.6196(10), P1-P2 2.2915(14); **5**: Cu1-P1 2.3546(16), Cu1-P2 2.3343(16), Cu1-P7 2.3483(16), Cu1-P8 2.3383(16), P1-P2 2.286(2), P7-P8 2.2876(19). Angle between the planes P1P2Cu1 and P7P8Cu1 93.5°; C atoms are depicted as small spheres and H atoms are omitted for clarity. XRD pattern (positive intensities: measured, negative intensities: simulated) of c) **4a** and d) **5** (measured diagram of **5** is background-corrected). * Peaks arising from unknown impurities.

$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4a** in CD_2Cl_2 shows a broad singlet at -290.4 ppm ($\omega_{1/2} = 126$ Hz) at room temperature, which is shifted 24 ppm to lower field compared to that of **1**. At 193 K, the signal gets sharper ($\omega_{1/2} = 71$ Hz) and moves slightly to -293.4 ppm, but no splitting of this singlet could be resolved. The $^{31}\text{P}\{^1\text{H}\}$ MAS NMR spectrum (293 K, $f = 30$ kHz) shows only one broad singlet at -288.8 ppm ($\omega_{1/2} = 937$ Hz). The characterization of crystalline **4b** in solution by NMR spectroscopy proved to be challenging because of its low solubility in CD_2Cl_2 and fast decomposition. Nevertheless, a broad signal ($\omega_{1/2} = 155$ Hz) at -294.0 ppm could be resolved in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 253 K when warming a crystalline sample in CD_2Cl_2 . This suggests a highly dynamic coordination behavior of **1** towards Cu^+ and Ag^+ .

Single-crystal X-ray analysis reveals that **4a** and **4b** are isostructural, showing a distorted square-planar coordination environment around the central cation through two side-on coordinating P–P bonds (Figure 3a). The Ag–P distances of **4b** (ca. 2.6 \AA) are shorter than the Ag–P distances observed with η^2 -coordination in $[\text{Cp}^*\text{Fe}(\eta^3\text{-P}_3)]$ (ca. 2.8 \AA)^[27] or $[\text{Cp}^*\text{Mo}(\text{CO})_2(\eta^3\text{-P}_3)]$ (ca. 2.7 \AA).^[28] The Cu–P distances of **4a** (ca. 2.4 \AA) are a little longer than for the η^2 -coordination in $[\text{Cp}_2\text{Mo}_2(\mu, \eta^2\text{:}\eta^2\text{-P}_2)]$ (ca. 2.35 \AA), but compare well to $[\text{CpMo}(\text{CO})_2(\eta^3\text{-P}_3)]$ (ca. 2.4 \AA).^[29] The P–P bonds are elon-

gated to 2.2694(16) \AA (**4a**) and 2.2915(14) \AA (**4b**) upon coordination, while the remaining P–P bonds are not affected. Examination of the crystal packing reveals that **4a** and **4b** are layered compounds that crystallize in the monoclinic space group $C2/c$ with alternating negatively charged layers of the [TEF] anions and positively charged layers of isolated $[\text{M}(\mathbf{1})_2]^+$ complexes.^[24] The layers lie inside the bc plane and alternate along the a axis (Figure 4a,c). When $\text{Cu}[\text{TEF}]$ is treated with **1** in pure toluene, the solution shows the bright orange color of the complex cation $[\text{Cu}(\mathbf{1})_2]^+$. To our surprise, analysis of crystals of **5** from this solution reveals a distorted tetrahedral coordination environment around Cu (Figure 3b). The resulting Cu–P distances of **5** are somewhat shorter than their counterparts in **4a**, while the coordinating P–P bonds are a little longer. This can be explained by less steric crowding in the tetrahedral coordination geometry around the Cu center in **5**. To gain further insight into the equilibrium between the “tetrahedral” and “square-planar” coordination of **1** towards Cu^+ and Ag^+ , DFT calculations were performed for different media. The results are presented in Table 1 and show that the enthalpy for the tetrahedral \rightarrow square-planar isomerization is positive for both metals, which means that the tetrahedral coordination should be favored. When the entropy is taken into account by calculating the Gibbs energy, small positive values for Cu^+

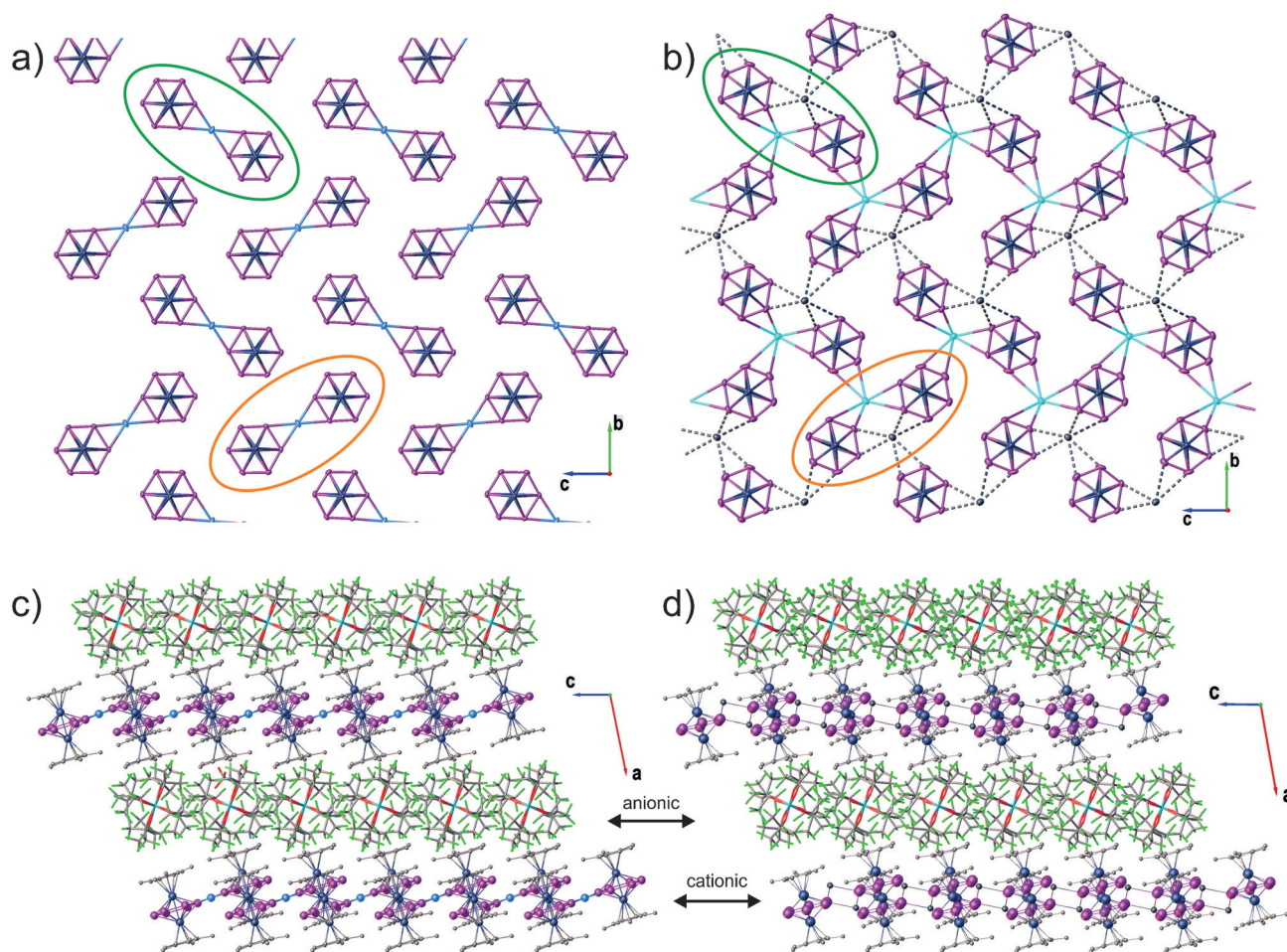


Figure 4. Cationic layers inside the bc plane of a) **4b** and b) **6**. Ti^+ positions (light and dark) in (b) are half-occupied. For (a) and (b), the anions as well as C and H atoms are omitted for clarity. c,d) Crystal packing of c) **4b** and d) **6** with the viewing direction along the b axis showing the alternation of cationic and anionic layers along the a axis. The P_6 planes include a tilt angle of 16.3° (**4a**), 16.3° (**4b**), and 13.8° (**6**) to the bc plane.

Table 1: Standard enthalpies ΔH_{298}° and Gibbs energies ΔG_{298}° (kJ mol^{-1}), standard entropies ΔS_{298}° ($\text{J mol}^{-1} \text{K}^{-1}$), and equilibrium constants K_{298} for the tetrahedral \rightarrow square-planar isomerization process in different media.

Metal	Medium	ΔH_{298}°	ΔS_{298}°	ΔG_{298}°	K_{298}
Cu	gas phase	22.5	57.5	5.34	0.12
	toluene	20.7	57.5	3.55	0.24
	CH_2Cl_2	19.5	57.5	2.39	0.38
Ag	gas phase	8.3	43.9	-4.8	7.0
	toluene	4.8	43.9	-8.3	28.3
	CH_2Cl_2	3.0	43.9	-10.1	59.1

and larger, but negative, values for Ag^+ are observed. This means that the tetrahedral geometry is predominant for Cu^+ , but a significant percentage of the complexes adopt a square-planar geometry in solution. For Ag^+ , the equilibrium is shifted significantly to the right side (ca. 98% for CH_2Cl_2 solution), which is probably the reason why a tetrahedral coordination of **1** and Ag^+ has not yet been observed. With the help of the powder XRD analysis shown in Figure 3c,d we were able to prove that we can isolate the cation $[\text{Cu}(\mathbf{1})_2]^+$

either as its tetrahedral isomer in **5** or as its square-planar isomer in **4a**.

Although **4a** and **4b** can be described as consisting of alternating layers, the $[\text{M}(\mathbf{1})_2]^+$ ($\text{M} = \text{Cu}, \text{Ag}$) cations as well as the $[\text{TEF}]^-$ anions do not form a two-dimensional network. Prior studies have demonstrated an abundance of coordination compounds formed from Ti^+ and polyphosphorus and polyarsenic ligands; therefore, we treated **1** with $\text{Ti}[\text{TEF}]$.^[30–32] An immediate color change from light brown (**1**) to the deep red color of compound **6** occurs when $\text{Ti}[\text{TEF}]$ is added to a solution of **1** in CH_2Cl_2 . No signal can be resolved in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **6** in CD_2Cl_2 solution at room temperature. Upon cooling the solution to 193 K, a very broad signal ($\omega_{1/2} = 1303$ Hz) appears at -305.5 ppm, shifted approximately 8 ppm to lower field compared with that of **1**. The $^{31}\text{P}\{^1\text{H}\}$ MAS NMR spectrum of **6** at 293 K ($f = 27$ kHz) shows one broad singlet at -291.1 ppm ($\omega_{1/2} = 1530$ Hz), while at 343 K ($f = 25$ kHz) two broad signals at -289.6 ($\omega_{1/2} = 300$ Hz) and -309.2 ($\omega_{1/2} = 260$ Hz) can be resolved in a ratio of about 1:12.^[24] Elemental analysis is consistent with the molar ratio of the P_6 complex **1** and Ti^+ being 2:1, while the crystal structure reveals a trigonal

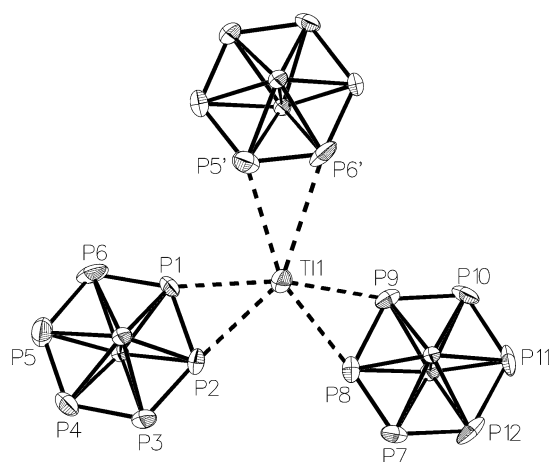


Figure 5. Coordination environment of Tl^+ in **6**. Thermal ellipsoids are drawn at 50% probability. Cp^* ligands are omitted. Sum of coordination angles: 343.5° .

pyramidal coordination of Tl^+ by three side-on coordinating P–P bonds of the *cyclo-P*₆ ligands (Figure 5).

The atoms P1, P2, P8, and P9 show shorter and uniform Tl–P distances of 3.2–3.3 Å, which are shorter than the Tl–P distances observed for the η^5 -coordination of $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$ to Tl^+ (ca. 3.5–3.9 Å).^[30,31] This coordination results in a slight elongation of these P–P bonds to about 2.22 Å, while the third molecule of **1** (P5'–P6') shows an unsymmetrical coordination with long Tl–P distances of approximately 3.42 and 3.69 Å and no P–P bond elongation. Although the environment of Tl^+ in **6** is distinctly different from that of Cu^+ and Ag^+ in **4a** and **4b**, their structures are related.^[33] Figure 4a shows the isolated $[\text{M}(\mathbf{1})_2]^+$ complex cations of **4a** and **4b**, and Figure 4b shows the two-dimensional coordination network that propagates inside the *bc* plane of **6**. The green and orange ellipses directly correspond to each other. Please note that the Tl cations depicted in light blue and dark gray are symmetry-equivalent positions and only half-occupied. Indeed, there is a statistical distribution of the Tl^+ cations inside the two-dimensional coordination network with the restriction that one of the ellipses can only be occupied by one Tl^+ cation. Here structural similarities to graphene-like structures occur. Figure 4c,d illustrate the equal crystal packing with alternating positively charged “coordination” layers and negatively charged “anion” layers along the crystallographic *a* axis.

In summary, we have presented a facile synthesis of the *cyclo-P*₆ complex **1** which enabled us to study its reactivity for the first time. Additionally, the by-product $[(\text{Cp}^*\text{Mo})_2(\mu\text{-P}_{10})]$ (**2**), which contains the largest known cyclic polyphosphorus ligand, has been structurally characterized. We have demonstrated that the bisallylic distortion of the *cyclo-P*₆ middle deck occurs upon one-electron oxidation of **1**. The highly dynamic coordination behavior of the cations was monitored in solution by treating **1** with Cu^+ , Ag^+ , and Tl^+ salts of the weakly coordinating anion [TEF]. The product distribution of the reaction of **1** with Cu^+ can be controlled by changing the solvent and, surprisingly, two isomers with either distorted square-planar or distorted tetrahedral coordination geometry around Cu^+ were selectively obtained. The results further

demonstrate the potential of the *cyclo-P*₆ complex **1** to act as a multidentate ligand in supramolecular chemistry for the formation of layered coordination compounds (**4a**, **4b**, and **6**). While Cu^+ and Ag^+ (**4a**, **4b**) form layered structures with isolated $[\text{M}(\mathbf{1})_2]^+$ complex cations, Tl^+ shows further interconnection of the *cyclo-P*₆ ligands to form an extended 2D network that can be regarded as a supramolecular analogue of graphene.

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Keywords: hexaphosphabenzene · inorganic graphene · polyphosphorus complexes · solvent-controlled reactivity · weakly coordinating anions

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- [33] The compounds **4a**, **4b**, and **6** crystallize in the same space group C2/c with similar unit cells. see Supporting Information for details.

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