

Polyphosphorus Ligand Complexes of Coinage Metals for Multiple Capturing of Intact P₄ Tetrahedra

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Abstract: Two- and three-component self-assembly reactions of [Cp^RFe(η⁵-P₅)] (Cp^R = C₅(CH₃)₅ (Cp^{*}, **1a**), C₅(4-EtC₆H₄)₅ (Cp^{PEt}, **1b**)) with the coinage metal salts [Cu(CH₃CN)₄][SbF₆] or AgSbF₆ were investigated to study the prerequisites for the potential coordination of white phosphorus by using a sterically encumbered Cp^R ligand and noncoordinating anions. In the self-assembly reactions with white phosphorus, either 0D or 1D coordination complexes are formed, all of which feature coordinated intact P₄ tetrahedra and thus comprise an unprecedented class of mixed polyphosphorus ligand complexes capable of complete release of P₄ in solution confirmed by NMR studies. The bulkiness of the used Cp^R ligand and the correctly chosen solvent allowed for obtaining more beneficial structural motifs, the first discrete tetra- and penta-coordinated *cyclo*-P₅ ligand complexes, that provide the maximal content of coordinated P₄ molecules per species known so far. All products are characterized by single-crystal X-ray diffraction, NMR spectroscopy, and mass spectrometry.

Introduction

White phosphorus (P₄) is a demanded and demanding starting material as in industry as in academic research. In production, it is mainly used to obtain high-purity organophosphorus

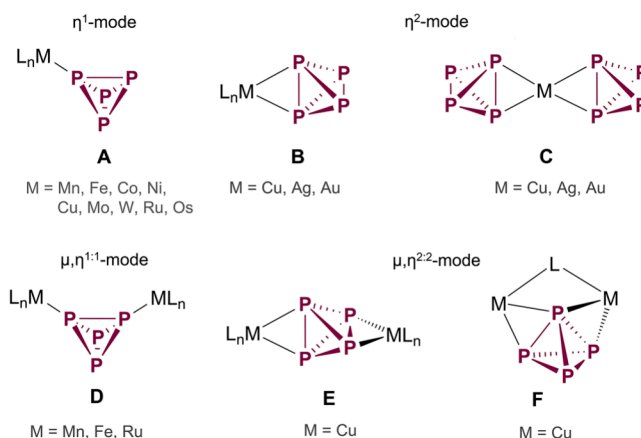
and inorganic phosphorus compounds^[1] whereas research focuses on the activation of the P₄ tetrahedron^[2–6] and thus the direct use of P₄ for commercial products.^[7–10] Due to the extreme reactivity of solid P₄, both its stabilization and storage are of great importance. Certain progress in the stabilization of P₄ molecules was made via their incorporation into porous materials,^[10,11,15] matrices of coordination polymers,^[13] cage compounds^[14] or discrete aggregates^[13,14] that can be used to store and release P₄ in subsequent reactions.^[11–15] These materials are either poorly soluble or often do not offer a convenient release of the captured P₄ in an atom-economical manner. All these approaches rest upon encapsulation^[11–15] that is less chemically advantageous than the coordination of the intact P₄ molecules to transition metals^[16–28] provided that the resulting carrier complex for *n*(P₄) is soluble and white phosphorus can be controllably released in full via complete decomplexation, e.g., by adding a convenient solvent. However, the coordination of the P₄ tetrahedron, extensively studied in the context of the activation of white phosphorus, often leads to breaking P–P bonds.^[2–6] Only a handful of metal complexes with slightly depleted or intact P–P bonds have been reported since Sacconi et al. discovered the first complex [(np₃)Ni(η¹-P₄)] (np₃ = tris(2-diphenylphosphinoethyl)amine) containing an intact P₄ tetrahedron in 1979.^[16] Besides η¹-(**A**)^[16–18] or η²-coordination (**B** and **C**),^[17–25] P₄ can also bridge two metal centers (Scheme 1). The metals can bind two P atoms in a μ,η^{1:1}-fashion (**D**)^[19,23,25,26] or two opposing (**E**)^[22,24,28] as well as adjacent (**F**)^[27] edges of the P₄ tetrahedron.

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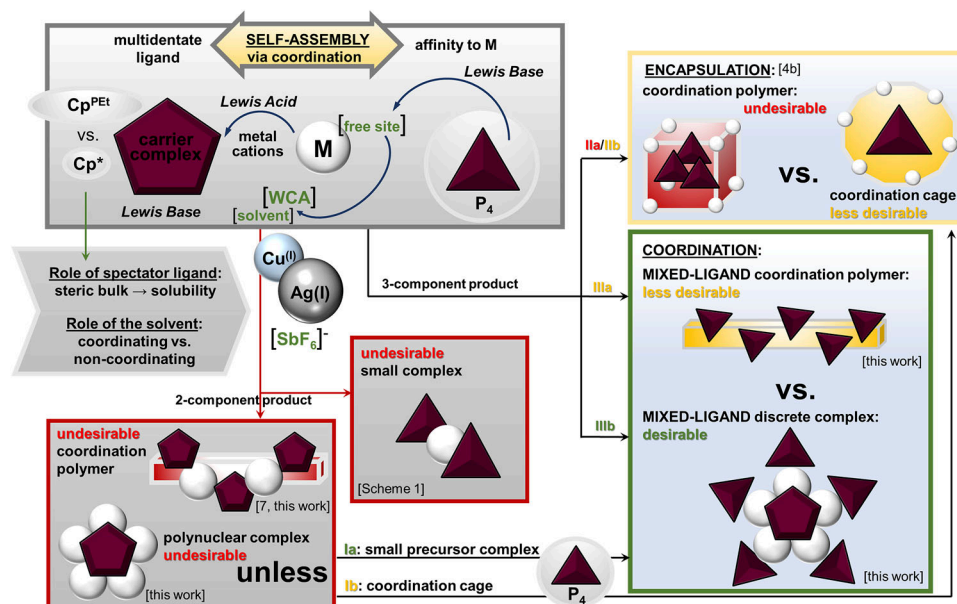
Dedicated to Professor Maurizio Peruzzini on the occasion of his 70th birthday

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Scheme 1. Different coordination types of intact P₄ tetrahedra to metal centers.



Scheme 2. Possible strategies to immobilize intact P_4 tetrahedra.

Notably, for the complex $[(LCu)_2(\mu, \eta^{2,2}-P_4)]$ ($L = [N(C_6H_3iPr_{2-2,6})C(Me)_2CH]^-$), a release of intact P_4 molecules was observed; $[Ag(\eta^2-P_4)_2][Al(OR_F)_4]$ ($R_F = OC(CF_3)_3$) is also reported as a suitable agent for the release of intact P_4 molecules under special reaction conditions.^[24,27] Analyzing these data, three crucial drawbacks are to be overcome: 1) Only one or two P_4 tetrahedra are bound in a discrete complex. Loading a complex with multiple P_4 molecules would be desirable and could be enabled by using polynuclear transition metal complexes. 2) The coordination of P_4 molecules must not compete with other ligands or counter anions as shown by complex **C** with weakly coordinating anions (WCAs), which assist in the coordination of two P_4 tetrahedra. 3) An appropriate type of metal complexes to serve as an efficient carrier of P_4 is still to be found.

Specific chemical environment supporting the realization of the coordination scenario (not excluding, however, less desirable encapsulation of P_4) can be provided by self-assembly systems containing pentaphosphaferrocene $[Cp^RFe(\eta^5-P_5)]$ (**1**, Cp^R : $Cp^* = C_5(CH_3)_5$ (**1a**), $Cp^{Bn} = C_5(CH_2Ph)_5$, $Cp^{BIG} = C_5(4-nBuC_6H_4)_5$)^[29–31] and coinage metal cations. The polydentate *cyclo*- P_5 ligand of **1** can coordinate transition metal centers adopting a full row from mono- to penta-coordination.^[32] This has made the *cyclo*- P_5 ligand complexes outstanding building blocks and gave rise to a variety of coordination polymers and discrete coordination cages over the past years.^[32–39] It was even possible to incorporate various guest molecules^[33–37] into both the polymeric matrices and giant cages of **1a** and CuX ($X = Cl, Br, \text{ and } I$), including, among others, the P_4 and As_4 tetrahedral molecules (Scheme 2).^[12] Building a discrete transition metal complex on the pentaphosphaferrocene platform could provide a suitable chemical and coordination environment for the targeted purpose.

In our endeavor to develop the coordination chemistry of **1** and facilitate three-component self-assembly reactions with this building block, an approach to use coinage metal salts of WCAs proved successful.^[40–47] Noncoordinating behavior of WCAs leaves coordination sites at the coinage metal cation available for additional coordination.^[43–45] This approach allowed not only to circumvent the insolubility of the Ag halides and involve Ag^+ in the self-assembly reactions but also to use a series of organic dinitriles to access discrete supramolecular species lined in coordination networks.^[44] With this in mind and due to the proven ability of WCAs to stabilize charged species and weakly bound complexes,^[48,49] we considered multiple coordination of the very weak donor P_4 feasible, although no examples of mixed-ligand polyphosphorus complexes have been reported so far, except for $[Co(\eta^5-P_5)\{\eta^2-P_2H(Mes)\}]^{2-}$ obtained by chemical activation of the Zintl phase P_7^{3-} and possessing an organo-substituted phosphorus ligand in addition to the *cyclo*- P_5 ligand.^[50]

Based on our wide-ranging experience, the self-assembly system of **1**, WCA salts of coinage metal cations and P_4 can give different outcomes **I–III** (Scheme 2): Similar to the reactions of P_4 with $Ag[Al(OR_F)_4]$ ($OR_F = OC(CF_3)_3$, $OC(CH_3)(CF_3)_2$),^[20] it can facilitate the coordination of the P_4 tetrahedron as a weak ligand within discrete or polymeric complexes (**IIIa,b**), or P_4 is to be encapsulated as a guest in a hosting cage formed by *cyclo*- P_5 ligand complexes and metal ions similar to other host–guest compounds based on pentaphosphaferrocene (**Ib, II**).^[12,32] Both types of resulting products could be applied either as a storage material for P_4 or as starting material for further reactions involving white phosphorus. However, the most beneficial outcome of the self-assembly would be a compact, soluble, discrete complex of **1** bearing multiple metal centers loaded with intact P_4 molecules (**Ia**). However, known molecular or cationic

complexes of **1** are scarce and do not comply with these requirements.^[32]

Within our concept, different factors can be varied to tune the self-assembly: 1) The Lewis acidity of the metal cation can change the type of the resulting metal complex. Harder Cu⁺ or softer Ag⁺ should rather coordinate the *cyclo*-P₅ ligand or P₄, respectively, that can switch the self-assembly from molecular complexes or coordination cages, i.e., between coordination versus encapsulation scenarios. 2) Hexafluoroantimonates [Cu(CH₃CN)₄][SbF₆] or AgSbF₆ were chosen because an [SbF₆][−] anion can either act as a WCA or complete, if necessary, the coordination sphere of the metal ion by weak coordination preventing undesirable condensation to a polymeric product. 3) Based on previous experience, the solubility of pentaphosphaferrocene complexes can be tuned by the specific Cp^R ligand,^[33–37] therefore, using **1a** and the bulkier [Cp^{PEt}Fe(η⁵-P₅)] (Cp^{PEt} = C₅(4-EtC₆H₄)₅, **1b**)^[30] can reveal the role of this factor as well as of the steric bulk of Cp^R on the resulting polynuclear complex. Given numerous self-assembly routes, we considered it necessary first to explore the two-component self-assembly of **1a** and **1b** with [Cu(CH₃CN)₄][SbF₆] or AgSbF₆ depending on the stoichiometry and used solvent (Scheme 2). Afterward, three-component self-assembly reactions with white phosphorus were performed, resulting in first compounds containing two different polyphosphorus ligands, among them an unprecedented molecular complex in which a *cyclo*-P₅ ligand coordinates four very weakly bound intact P₄ units.

Results and Discussion

Preliminary Studies: Two-Component Self-Assembly of **1** and [Cu(CH₃CN)₄][SbF₆]

Two-component self-assembly of **1a** and similar [Cu(CH₃CN)₄][WCA] (WCA = BF₄[−], PF₆[−]) has been studied previously.^[32,47,51] In the reaction of **1b** with [Cu(CH₃CN)₄][SbF₆] different coordination products crystallize in moderate yields upon variation of the stoichiometry of the reactants (Scheme 3). After stirring **1b** and corresponding amounts of [Cu(CH₃CN)₄][SbF₆] in CH₂Cl₂ for 20 min, the brownish solutions are filtered into a Schlenk tube. The crystalline products **2–4** can be isolated by careful layering of the solutions with *n*-pentane (Scheme 3).

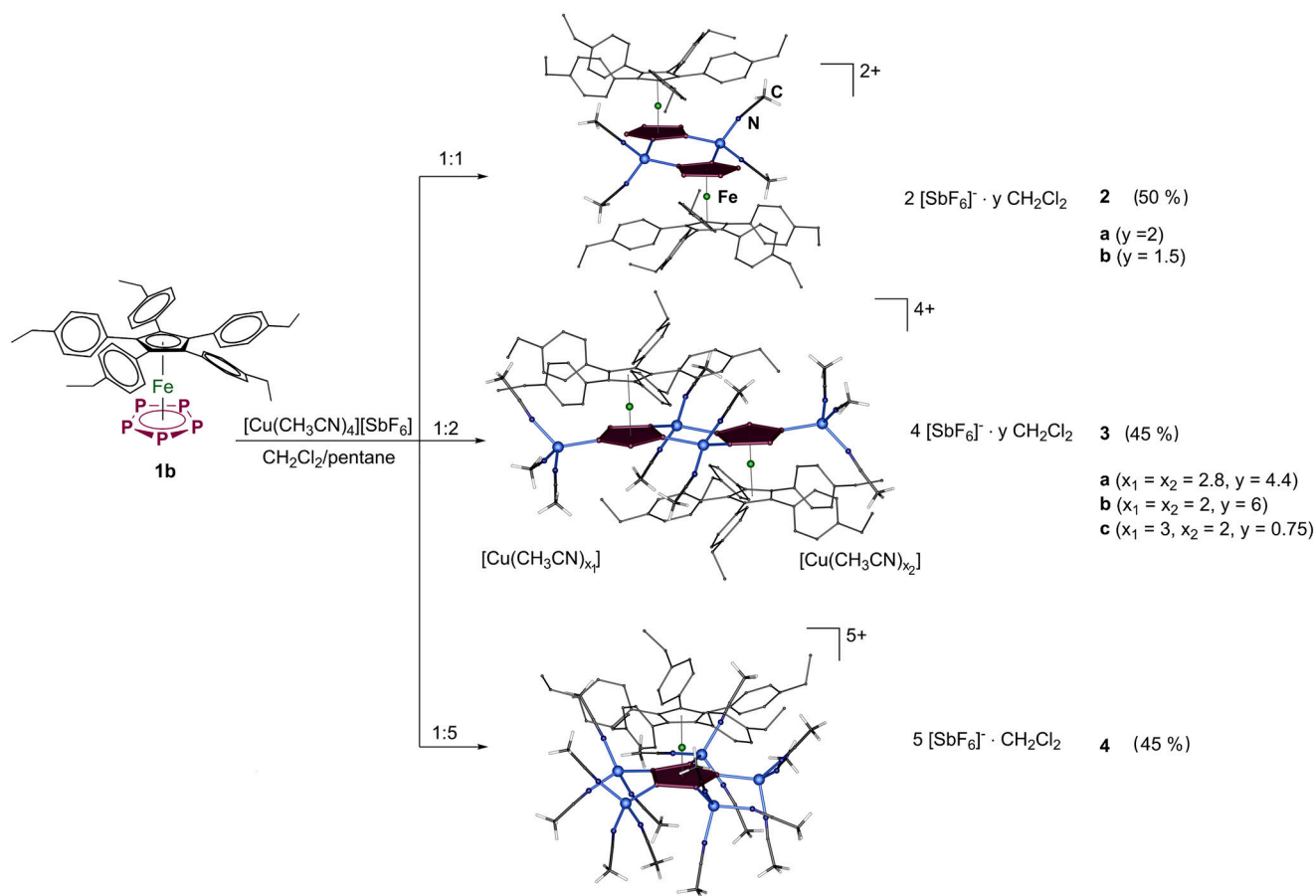
According to X-ray crystallography (SC-XRD),^[52] the dimeric cationic complexes of two triclinic phases [(**1b**)Cu(CH₃CN)₂]₂[SbF₆]₂ · *y* CH₂Cl₂ (bright green plates, **2a**: *y* = 2, **2b**: *y* = 1.5) consists of two units **1b** bridged by two Cu⁺ cations. Each unit **1b** is coordinated by Cu⁺ cations in a 1,2-coordination mode, forming a six-membered {Cu₂P₄} ring (Scheme 3). Each tetrahedral Cu⁺ cation is coordinatively saturated by two acetonitrile ligands. During sample handling, large green prisms of **3** were noticed to rapidly recrystallize in the mother solution. Hereby, the formation of at least three crystalline phases [(**1b**)₂Cu₄(CH₃CN)_{4+*x*}][SbF₆]₄ · *y* CH₂Cl₂ (**3a**: *x* = 5.6, *y* = 4.4; **3b**: *x* = 4, *y* = 6; **3c**: *x* = 5, *y* = 1) was identified by SC-XRD, all differing in the content of coordinated CH₃CN and CH₂Cl₂ solvent molecules. All

complexes **3** feature similar dimeric cations as in **2**; however, they contain two additional Cu⁺ cations resulting in a 1,2,4-coordination mode of each *cyclo*-P₅ ligand (Scheme 3). The different coordination geometries of copper(I), trigonal or tetrahedral, and therefore the various contents of acetonitrile ligands, highlight the differences in the compositions and molecular structures of the crystalline phases **3a–3c** (see Supporting Information).

A more interesting structural motif is formed when using 5 equiv of [Cu(CH₃CN)₄][SbF₆] in the reaction with **1b** (Scheme 3), which results in the formation of triclinic khaki-green complex [(**1b**)Cu₅(CH₃CN)₁₅][SbF₆]₅ · CH₂Cl₂ (**4**). Every P atom of the *cyclo*-P₅ ligand of **1b** is coordinated to a Cu⁺ cation whose tetrahedral environment is completed by three CH₃CN ligands. As a result, the first discrete monomeric structure of a penta-coordinated *cyclo*-P₅ building block is formed, bearing five additional Cu⁺ centers, potentially for multiple coordination of P₄. Complex **4** is well-soluble and structurally beneficial precursor for this attempt.

Compounds **2**, **3**, and **4** are very well soluble in CH₂Cl₂ enabling their investigation by NMR spectroscopy in solution. The ¹H NMR spectra of **2** and **4** show the amount of CH₃CN that agrees with the X-ray data; the spectrum of **3** reveals an average number of 8.7 CH₃CN that is also confirmed by the elemental analysis. The ³¹P{¹H} NMR spectra show a correlation between the number of coordinated Cu⁺ cations in **2–4** and the shift of the signal of the P atoms of the *cyclo*-P₅ ligand: The ³¹P{¹H} NMR signal for **2** with a 1:1 ratio (**1b**: [Cu(CH₃CN)₄][SbF₆]) is detected at 140.4 ppm (rotation of the *cyclo*-P₅ ligand) and is considerably downfield shifted compared to the resonance signal found for free **1b** (172 ppm). When increasing the content of Cu(I) salt in compounds **3** and **4** to 1:2 and 1:5 ratios, the signal of the products shifts further downfield to 125.1 and 108.2 ppm, respectively. In each of the ESI MS spectra of compounds **2–4**, the highest peak at *m/z* = 900.11 was attributed to [(**1b**)Cu(CH₃CN)]⁺. The base peak at *m/z* = 144 corresponds to [Cu(CH₃CN)₂]⁺.

Using small precursor complexes **2–4** for the P₄ capture. The complexes **2–4** with labile CH₃CN ligands in the coordination sphere of copper were attempted as small precursor complexes for white phosphorus capture (Scheme 2, **1a**). These attempts have failed most probably due to the lower donor ability of P₄ in comparison to CH₃CN. An attempt to avoid this competition by starting from [Cu(mesitylene)₂][SbF₆]^[53] salt only led to the formation of poor-quality crystalline material and/or oily residues. Given these drawbacks, it seemed reasonable to abstain from using [Cu(CH₃CN)₄][SbF₆] and turn to AgSbF₆ instead, which does not necessarily need a stabilizing environment of coordinated solvents like CH₃CN. It was recently shown that in the self-assembly of **1a** and AgSbF₆, the Ag⁺ cations provide additional coordination sites that can be occupied by flexible aliphatic as well as rigid aromatic dinitriles as a third component.^[44,45] This encouraged us to introduce such a weak donor as white phosphorus in similar reactions after studying first corresponding two-component self-assembly systems to make sure that Ag(I) can form similar complexes with molecular structures supportive of multiple coordination of small molecules compared to copper.



Scheme 3. Self-assembly reactions of **1b** with $[Cu(CH_3CN)_4][SbF_6]$ resulting in discrete complexes **2–4**. Yields are given in parentheses.

Preliminary Studies: Two-Component Self-Assembly of $[(Cp^*Fe(\eta^5-P_5))] (1a)$ and $AgSbF_6$ in Noncoordinating Solvents

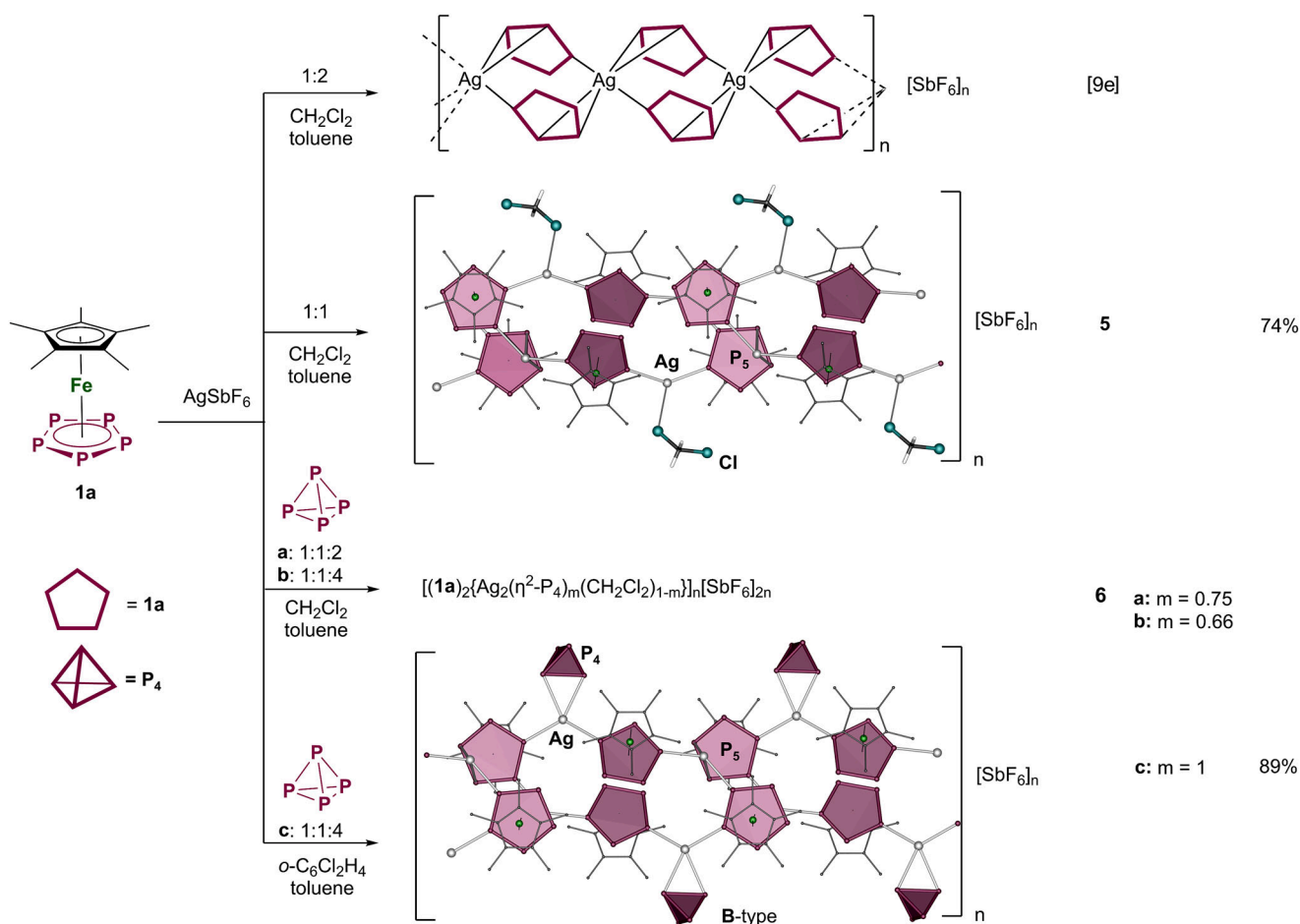
In the two-component self-assembly reaction of $AgSbF_6$ and **1a**, only a 1D polymer $[(1a)_2Ag]_n[SbF_6]_n$ has been isolated so far (Scheme 4).^[44] When reducing the ratio **1a**: $AgSbF_6$ of 1:2 to 1:1 ratio, another 1D polymer $[(1a)_2[Ag_2(CH_2Cl_2)]]_n[SbF_6]_{2n}$ (**5**) is observed to crystallize in the triclinic crystal system. The repeating unit of this double-stranded polymer is built up by two moieties **1a** and two Ag^+ cations (Scheme 4). Within this unit, one *cyclo*- P_5 ligand is coordinated to Ag^+ cations in a 1,3-mode, whereas the second moiety **1a**, displays a side-on and end-on coordination of three P atoms to two Ag^+ cations. Additionally, the side-on coordinated Ag^+ cation bridges two strands of **5** via additional end-on coordination of a P atom of an adjacent moiety **1a**. The Ag^+ cations weakly coordinate either $[SbF_6]^-$ anions or CH_2Cl_2 molecules displaying a pseudo-tetrahedral or trigonal environment.^[54–56] Crystals of **5** are insoluble in common solvents such as *n*-hexane, toluene, or CH_2Cl_2 . The addition of CH_3CN or pyridine to a suspension of **5** in CH_2Cl_2 gives an orange solution due to readily undergoing fragmentation. For the NMR spectroscopic investigations, the solvent was removed, and the residue was redissolved in CD_2Cl_2 . In the 1H NMR and $^{31}P\{^1H\}$ NMR spectra of solution of **5** in CD_2Cl_2 prepared in this way, only signals corresponding to the free

starting material are detected. In the 1H NMR spectrum of **5** in CD_3CN , the signals of **1a** and CH_2Cl_2 present in the crystal lattice are visible in the expected ratio of 2:1. The $^{31}P\{^1H\}$ NMR spectrum shows only a broad signal at 138 ppm corresponding to **1a** coordinated to the Ag^+ cations in a dynamic equilibrium. In the ESI MS spectrum of **5** in CH_3CN/CH_2Cl_2 , peaks for oligomeric fragments are detected. The peak with the highest m/z at 2521.98 can be attributed to $[(1a)_4Ag_4(SbF_6)_3]^+$.

Formation of **5** did not provide an optimal precursor complex, but the fact that the silver cations in **5** coordinate either weakly bound $[SbF_6]^-$ anions or CH_2Cl_2 molecules, the coordination of P_4 molecules also seems feasible in this system.

Three-Component Self-Assembly of $[(Cp^*Fe(\eta^5-P_5))] (1a)$ with $AgSbF_6$ and White Phosphorus

By layering $AgSbF_6$ in CH_2Cl_2 or *ortho*-dichlorobenzene with a mixture of **1a** and P_4 in toluene in different stoichiometric ratios, crystals of $[(1a)_2\{Ag_2(\eta^2-P_4)_m(CH_2Cl_2)_{1-m}\}]_n[SbF_6]_{2n}$ (**6**; $m = 0.75$ (**6a**), 0.67 (**6b**), 1 (**6c**)) are isolated in good yields (Scheme 4). All three products are isostructural and possess similar double-stranded structures as in **5**, with the difference that the Ag^+ cations corresponding to those that coordinate



Scheme 4. Self-assembly reaction of **1a** with AgSbF₆. Yields are given in parentheses.

CH₂Cl₂ in **5** partly coordinate either a CH₂Cl₂ molecule or a P₄ tetrahedron, acting as η²-coordinating ligands. The P–P bond lengths in the coordinated P₄ tetrahedra in **6c** are in agreement with that reported in literature for an intact P₄ tetrahedron coordinated in an η²-mode to a coinage metal cation (Table 1).^[20–22,24,57,58] The P–P bond distances for adjacent and opposite to the coordinated bonds corroborate those found in the intact P₄ molecule (2.194(3)–2.2228(5) Å).^[57–60] The coordinated ones are slightly elongated. The single-point DFT computations using the experimental geometry of **6c** at the D3[61]-B3LYP[68,69]/def2-TZVPP[68,69] level of theory further confirm an elongated but intact nature of the coordinated P–P bond (see Supporting Information). The content of the coordinated P₄ depends on the relative amount of white phosphorus as well as on the solvents used (Scheme 4). In **6a**, a 1:1:2 ratio (1a:AgSbF₆:P₄) in CH₂Cl₂ leads to P₄ ligands and CH₂Cl₂ molecules sharing the same crystallographic position with an 0.75/0.25 occupancy. Counterintuitively, introducing a fourfold excess of white phosphorus in **6b** in CH₂Cl₂ slightly decreases the occupancy of P₄ to 67 %, which is why the pure P₄-containing compound **6c** cannot be obtained in a straightforward way. To avoid competitive coordination of CH₂Cl₂ and P₄, *ortho*-dichlorobenzene was used instead as a noncoordinating solvent for AgSbF₆. In this way, **6c**

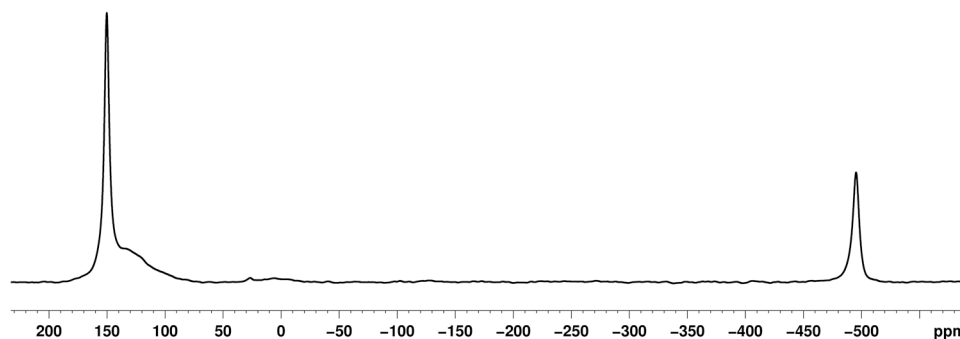
containing a maximum amount of P₄ was obtained selectively (Scheme 4). Surprisingly, **6a** can be stored as a crystalline solid at room temperature in air for weeks without decomposition as confirmed by SC-XRD (see Supporting Information), whereas **6c** has decomposed in air after 3 days. Therefore, a moderate content (25%–30%) of CH₂Cl₂ in the positions of P₄ seems to stabilize **6**.

The ³¹P{¹H} MAS NMR spectrum of crystalline **6** confirms coordination of the P₄ and agrees with the SC-XRD data (Figure 1): A sharp signal at 150.2 ppm and a small broad signal at 133.4 ppm are detected, which can most probably be attributed to the different coordination modes of the P atoms of the *cyclo*-P₅ units. Additionally, a singlet at –495.4 ppm is observed, which can be assigned to the coordinated intact P₄ tetrahedra, which is in agreement with the value of –497 ppm reported for [Ag(η²-P₄)₂][Al(OⁱPrF)₄].^[20] The Raman spectrum of solid **6** reveals bands similar to those found for free **1a** and for solid P₄, respectively (Table S1 and Figure S8). In the ESI MS spectrum of **6** in CH₃CN/CH₂Cl₂, the peak with the highest mass-to-charge ratio can be attributed to [(1a)₄Ag₄(SbF₆)₃]⁺ at *m/z* = 2521.98. White phosphorus is observed to get released from the polymer by grinding the crystals of **6** and readily reacts with oxygen when exposed to air.

Table 1: Selected bond lengths and angles for coordination products of P₄ and coinage metal cations.^{a)}

| Compound | M–P(P ₅) | M–(sp ² –C) | P–P(P ₅) | M–P(P ₄) | (P–P) _{coord} ^{b)} | (P–P) _{adj} | (P–P) _{opposite} | P(P ₄)–M–(P ₄) |
|--|--|------------------------|---------------------------|-------------------------|--------------------------------------|------------------------|---------------------------|--|
| 6c | 2.4606(17); 2.673(2)– 2.678(2) ^{c)} | – | 2.106(3)– 2.152(3) | 2.678(2)– 2.700(2) | 2.297(3) | 2.153(3)– 2.172(3) | 2.191(4) | 50.57(6) |
| 11 | 2.5051(8)– 2.5289(7) | 2.618(3)– 2.661(3) | 2.1098(11)– 2.1135(11) | 2.5825(9)– 2.6603(9) | 2.302(1)– 2.326(1) | 2.156(2)– 2.183(1) | 2.205(2)– 2.210(2) | 52.07(3)– 53.07(3) |
| 12a | 2.4938(15)– 2.5233(15) | 2.598(6)– 2.661(5) | 2.101(2)– 2.167(3) | 2.569(2)– 2.655(2) | 2.263(3)– 2.310(2) | 2.154(3)– 2.176(3) | 2.147(4)– 2.200(3) | 47.81(13)– 52.73(6) |
| 12b | 2.4939(14)– 2.664(8) | 2.114(2)– 2.700(10) | 2.107(2)– 2.114(2) | 2.53(2)– 2.75(2) | 2.266(3)– 2.348(9) | 2.020(2)– 2.248(14) | 2.152(7)– 2.200(6) | 50.4(5)– 54.9(5) |
| [LCu(η ² -P ₄)] ^{d)} | – | – | – | 2.2592(6)– 2.2707(6) | 2.386(4) | 2.180(4)– 2.280(4) | 2.141(6) | 63.10(12) |
| [Ag(η ² -P ₄)] [Al(OR _F) ₄] ^{e)} | – | – | – | 2.5262(8)– 2.5274(9) | 2.308(1) | 2.152(1)– 2.174(1) | 2.188(2) | 54.34(3) |
| [IPrAuP ₄][SbF ₆] ^{f)} | – | – | – | 2.4333(7)– 2.4352(6) | 2.357(1) | 2.164(1)– 2.170(1) | 2.194(1) | 57.79(7) |

^{a)} In Å and degrees, respectively. In **6c–12**, M = Ag. The distances with low occupied atoms are not listed (see Supporting Information for details). ^{b)} Bond lengths in the P₄ tetrahedra are given as (P–P)_{adj.} and (P–P)_{opposite} for adjacent and opposite bonds with respect to the coordinated (P–P)_{coord.} bond. ^{c)} Intervals for end-on and side-on coordination are shown. ^{d)} L is the β-diketiminato ligand [(N(C₆H₃iPr₂-2,6)C(Me))₂CH][–].^[24] ^{e)} OR_F = OC(CH₃)(CF₃)₂.^[20] ^{f)} IPr = 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene reported in Ref. [57].

**Figure 1.** ³¹P{¹H} MAS NMR spectrum of **6c**.

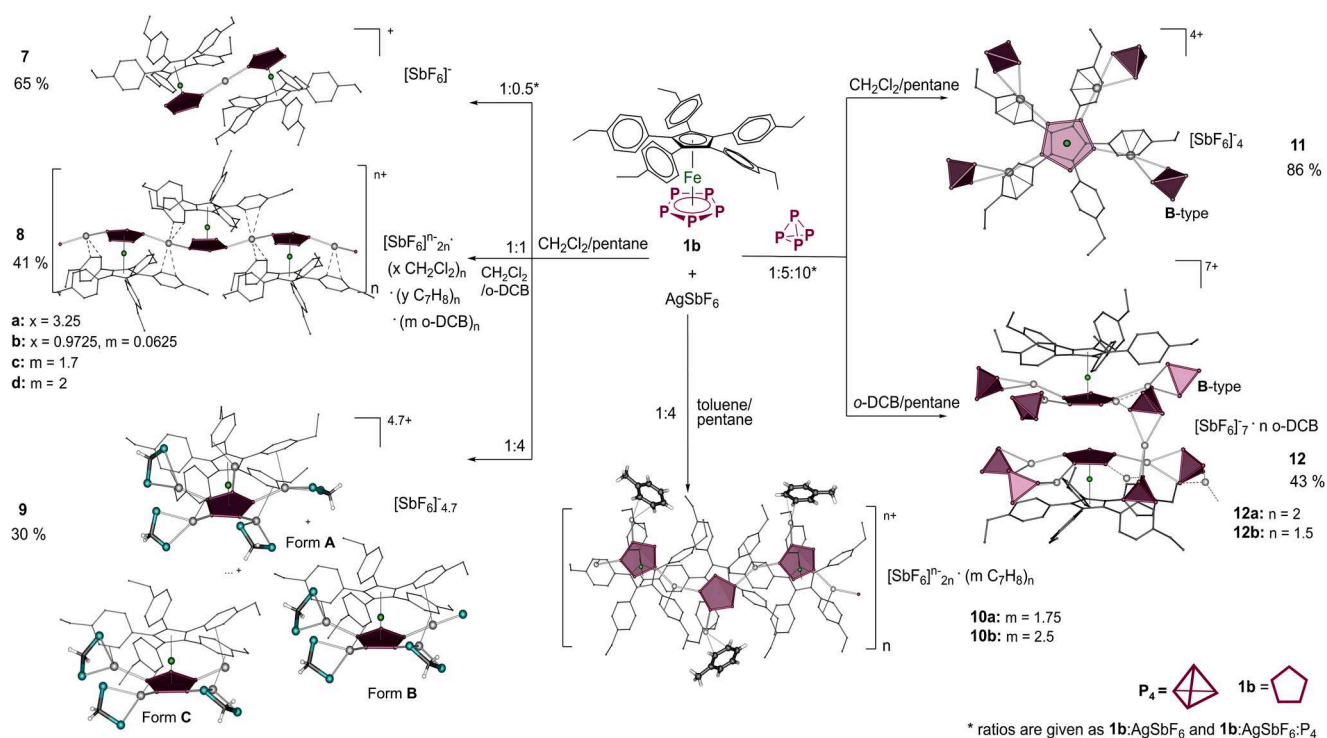
Using mixed-ligand polymer **6** for the P₄ release. Stable in air, crystalline **6** is insoluble in common solvents such as toluene or CH₂Cl₂ but can be dissolved in donor solvents under partial fragmentation of the polymeric structure, suggesting a convenient release of the coordinated P₄. To confirm this by NMR investigations in solution, crystals of **6** were directly dissolved in CD₃CN. In this case, a weak singlet at –525 ppm can be observed in the ³¹P{¹H} NMR spectrum, which is attributed to free P₄, in addition to a similar signal for **1a** at 136 ppm. When CH₃CN or pyridine was added to a suspension of **6** in CH₂Cl₂, the solvent mixture was removed, and the residue was redissolved in CD₂Cl₂. In the ¹H NMR and the ³¹P NMR spectra in CD₂Cl₂ of such solutions of **6**, only signals of free **1a** and P₄ are detected, confirming complete release of coordinated molecules.

Despite reaction of **1a** with AgSbF₆ and P₄ following the less desirable route **IIIa** (Scheme 2) toward complex **6** with relatively low content of P₄, novel mixed-ligand complexes that can coordinate multiple P₄ tetrahedra are obtained. However, further improvements can be made when using the starting complex **1b** instead of **1a** and avoiding competition between P₄ and weakly coordinating solvent.

Two-Component Self-Assembly of [(Cp^{PEt}Fe(η⁵-P₅))] (**1b**) and AgSbF₆ in Noncoordinating Solvents

Having succeeded in the synthesis of mixed P₄/P₅-ligand complexes of silver with **1a**, it was necessary to improve the solubility by introducing **1b** bearing the bulkier Cp^{PEt} ligand that also simultaneously changes the steric demand of the Cp^R spectator ligand at **1**. The influence of this factor on the reaction pathway and whether the prerequisites for the coordination of P₄ molecules still apply are the incentives for this section. The two-component self-assembly reaction of AgSbF₆ with **1b** afforded various products depending on the stoichiometry used (Scheme 5). According to the general procedure used for all these reactions, after stirring both components in CH₂Cl₂ for at least 30 min, the solution was filtered and layered with pentane or *o*-C₆H₄Cl₂, which led to the formation of crystalline products in moderate yields.

The SC-XRD^[52] of **7** reveals a discrete dimeric complex [(**1b**)₂Ag][SbF₆], in which two *cyclo*-P₅ ligands are bridged by an Ag⁺ cation. The two different monoclinic crystalline phases of [(**1b**)Ag]_n(SbF₆)_n (**8a** and **8b**) form with an equimolar stoichiometry. SC-XRD shows that in the 1D polymer **8a**,



Scheme 5. Two- and three-component self-assembly reactions of **1b** with AgSbF₆ and white phosphorus. Yields are given in parentheses.

cyclo-P₅ ligands are 1,3-coordinated to two Ag⁺ cations each and the Ag⁺ cations coordinate two molecules of **1b**. The distorted tetrahedral environment of Ag⁺ is completed by π -interaction with the phenyl groups of the Cp^{PEt} ligands so that Ag⁺ cations slightly deviate from the *cyclo*-P₅ planes.

Compound **8b** contains two isomeric entities: One entity and a major part of the disordered second one correspond to a 1D polymeric chain as in **8a**; the minor part (0.1) represents an overlay of discrete complexes $[(\mathbf{1b})Ag]^+$ formed with different positions of disordered Ag cations (see Supporting Information for detail). The connectivity of the cationic part of **8a** is comparable to the structure of $[(Cp^{BIG}Fe(\eta^5-P_5))Ag]_n[Al(OC(CF_3)_4)]_n$ that also contains a bulkier pentaphosphaferrocene and a weakly coordinating anion.^[41,48] The reactions of the less sterically demanding **1a** with Ag[Al(C(CF₃)₃)₄] or AgSbF₆ both lead to 1D cationic structures in which the Ag(I) coordination sphere is saturated not by π -interaction with bulky Cp^{PEt} ligands but by the P₅ ligands of two additional units of **1a**.^[40,44] Therefore, the bulkiness of the Cp^R ligand is more of an overwhelming factor for the nature of the resulting product than the steric demand of the anion. This factor can be used to tune the solubility of the products without impeding multiple coordination of silver cations.

When using *ortho*-dichlorobenzene as solvent instead of CH₂Cl₂ in the reaction of **1b** with AgSbF₆ in a ratio of 1:1, two different crystalline phases were isolated revealing the 1D polymers $[(\mathbf{1b})Ag]_n[SbF_6]_n \cdot m \text{ oDCB}$ ($m = 1.7n$ (**8c**), $2n$ (**8d**)) with similar structural motifs as observed for **8a** but with a different packing of the chains (see Figure S29). Due to no

change in the structural behavior, no further investigations were attempted in this media.

Increasing the relative amount of AgSbF₆ to 4 equiv (Scheme 5) leads to the discrete complex $[(\mathbf{1b})_2Ag_{7.5}Cl_{0.6}(CH_2Cl_2)_{5.7}][SbF_6]_{6.9} \cdot 2 CH_2Cl_2$ (**9**) crystallizing in the monoclinic space group $P2_1/n$. The SC-XRD shows that **9** contains two opposing units of **1b** with two slightly off-set and almost parallel *cyclo*-P₅ ligands suggesting a certain stabilization by weak π - π interactions (Figure 2). The overall composition of **9** amounts to a noninteger number (7.5) of AgSbF₆ per formula unit implying that **9** consists of structurally similar complexes of different composition that cocrystallize in the solid state (Scheme 5). Formally, the average amount of the Ag⁺ cations coordinated to one moiety of **1b** and disordered over four positions is 3.95, reflecting a mixture of tri- and tetra-coordinated *cyclo*-P₅ ligands in a ratio of 0.05:0.95. The other moiety of **1b** is coordinated by an average amount of 3.55 Ag⁺ ions at all five possible positions allowing penta-, tetra-, and mono-coordinated complexes of Ag(I) (Figure S31). Due to this disordering, the structure of individual cations cannot be unambiguously derived. However, the structural motif of **9** seems beneficial for making good carrier complex for multiple coordination of P₄ molecules.

Interestingly, two of the Ag⁺ cations in **9** (Figure 2a) are coordinated by Cl⁻ anions (Table S30) formed most likely by abstraction of Cl⁻ from dichloromethane.^[70–73] These partly occupied Cl⁻ anions balance the positive charge in **9**. Several SC-XRD experiments show that a similar content of the coordinated Cl⁻ is always present in different crystalline samples.

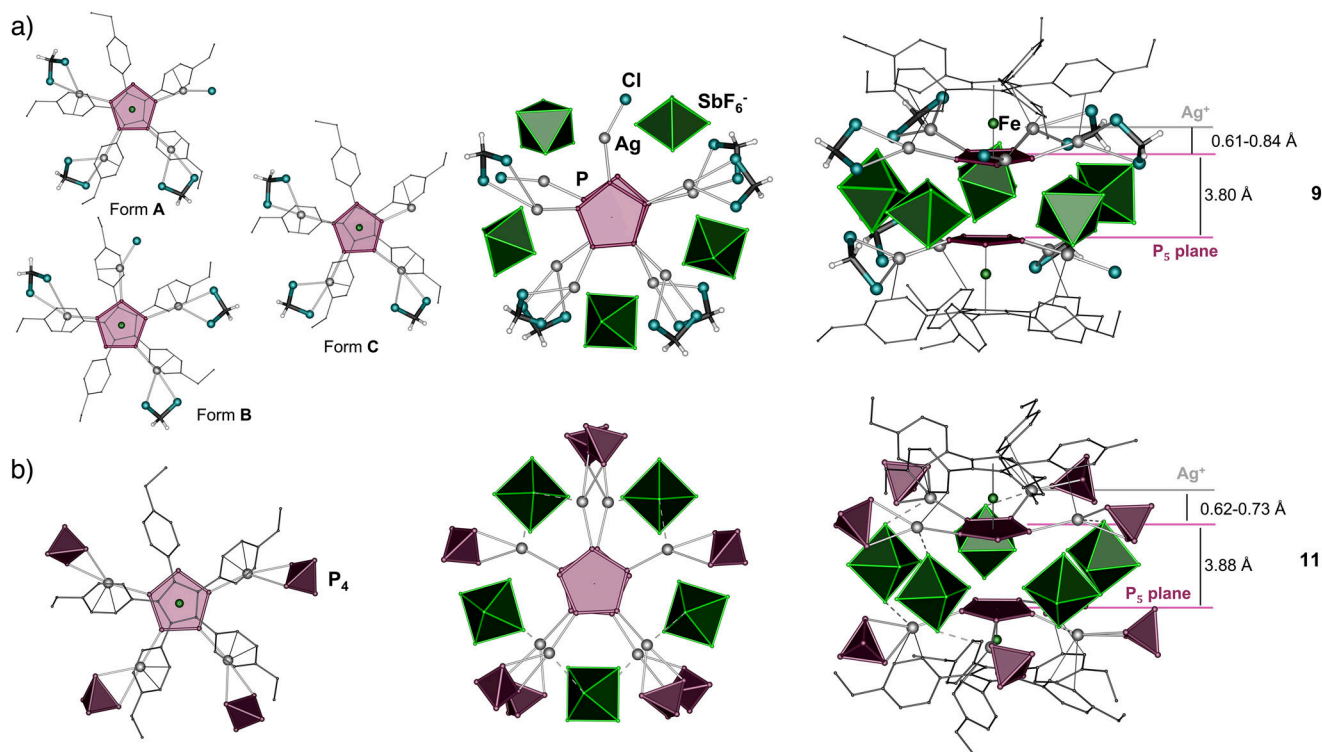


Figure 2. Comparison of complexes a) **9** (major forms) and b) **11**. $[\text{SbF}_6]^-$ are shown as octahedra; disorder and outer sphere $[\text{SbF}_6]^-$ and CH_2Cl_2 are not shown.

The remaining Ag^+ cations coordinate CH_2Cl_2 molecules in an asymmetric η^2 -mode. The coordination sphere of the Ag^+ cations is completed by π -interactions via aromatic bonds of the Cp^{PEt} ligand, which causes a deviation of the Ag^+ cations from the *cyclo*- P_5 plane. Furthermore, 4.85 $[\text{SbF}_6]^-$ anions are distributed over five positions in the cavity between the Ag^+ cations of the $\{(\mathbf{1b})\text{Ag}\}_x$ fragments (Figures 2a and S32); two of the $[\text{SbF}_6]^-$ anions are terminally coordinated to Ag^+ cations and another two bridge Ag^+ cations of different complexes. An excess of AgSbF_6 in the reaction allows neither to saturate partly occupied positions of Ag^+ nor to change the composition of **9**.

Crystals of **7**, **8a**, and **9** are poorly soluble in CH_2Cl_2 but dissolve in a mixture of CH_2Cl_2 and CH_3CN undergoing partial fragmentation. As a result, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **7** and **8a** in $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$ show sharp singlets at 161 and 156 ppm, respectively, which are highfield shifted compared to the signal typical of the free pentaphosphaferrocene **1b** (172 ppm), whereas the observed singlet at 152.2 ppm for **9** is slightly downfield shifted. This fragmentation can also be detected in the ESI MS spectra of compounds **7–9**, all of them with the highest peak at $m/z = 905.06$, which can be attributed to a $[(\mathbf{1b})\text{Ag}]^+$ moiety.

Using toluene instead of CH_2Cl_2 in a similar reaction, crystal formation can be observed after layering the reaction mixture of **1b** and AgSbF_6 (ratio 1:4) with *n*-pentane. SC-XRD reveals another 1D polymer with the general formula $[(\mathbf{1b})\text{Ag}_2]_n[\text{SbF}_6]_{2n} \cdot m \text{C}_7\text{H}_8$ ($m = 1.75n$ (**10a**), $2.5n$ (**10b**)). However, the synthesis of **10** is accompanied by the formation of unavoidable oily residues as well as

by undergoing redox processes making the isolation of analytically pure compounds in good yield problematic (see Supporting Information for detail).

Due to the weak coordination of the CH_2Cl_2 molecules exemplified by compounds **5** and **9** as well as the π -coordination to the aromatic moieties of the Cp^{PEt} ligands, the prerequisites for the coordination of white phosphorus to $\text{Ag}(\text{I})$ seem feasible under similar conditions (Scheme 2). Complex **5** exemplifies the less desirable route **IIIa** to give a polymeric matrix for P_4 coordination, whereas complex **9** resembling copper complex **4**, promises to be an effective carrier for higher P_4 load.

Three-Component Self-Assembly of $[(\text{Cp}^{\text{PEt}}\text{Fe}(\eta^5\text{-P}_5))] (\mathbf{1b})$ with AgSbF_6 and White Phosphorus

To introduce P_4 into the self-assembly of **1b** and AgSbF_6 , the pentaphosphaferrocene **1b**, AgSbF_6 , and P_4 in a 1:5:10 ratio are stirred together in CH_2Cl_2 for 1 h at most. The turbid brown solution is filtered and layered with *n*-pentane. After complete diffusion, brown prisms of the monomeric complex $[(\mathbf{1b})\{\text{Ag}(\text{P}_4)\}_4][\text{SbF}_6]_4 \cdot \text{CH}_2\text{Cl}_2$ (**11**) crystallizing in the monoclinic space group $P2_1/n$ are obtained (Scheme 5). The cationic part of **11** consists of one unit of **1b** that is coordinated to four Ag^+ cations bearing a P_4 tetrahedron as an η^2 -coordinating ligand each (type **B**, Table 1), thus representing a unique molecular complex of a tetra-coordinated *cyclo*- P_5 building block with a remarkably high content of P_4 .^[16–28,32] Additional π -interaction between the phenyl groups of the

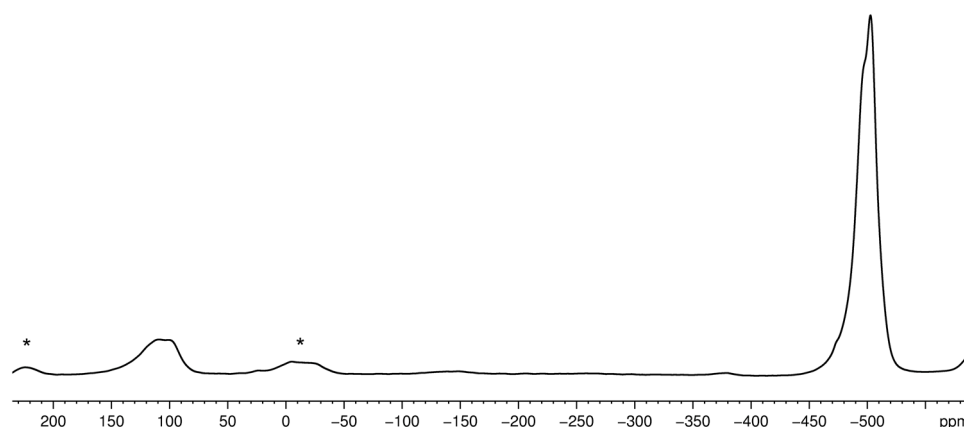


Figure 3. $^{31}\text{P}\{^1\text{H}\}$ MAS NMR spectrum of **11**. Rotational sidebands are marked with asterisks.

Cp^{PEt} ligand completes the distorted tetrahedral environment of the Ag^+ cations and leads to a deviation of Ag^+ from the *cyclo*- P_5 plane. In the solid state, two units of **11** are stacked with slightly slipped but almost parallel *cyclo*- P_5 ligands at an interplanar distance of 3.87 Å that suggests some stabilization via weak π - π interactions (Figure 2b). Five $[\text{SbF}_6]^-$ anions occupy the concave cavities between the $[\text{AgP}_4]$ units of the two complexes of **11**. Interestingly, the cavity at the free coordination site at the *cyclo*- P_5 ligand is only screened by a solvate molecule of CH_2Cl_2 (Figure S35), but all attempts to increase the amount of the $[\text{AgP}_4]$ units to a maximum of five by using a higher excess of AgSbF_6 and P_4 in the reaction failed.

The $^{31}\text{P}\{^1\text{H}\}$ MAS NMR spectrum of crystalline **11** displays a broad signal with a shoulder at -502 ppm for the intact coordinated P_4 tetrahedra (Figure 3). The appearance of this shoulder can be explained by the position of the P_4 units in the solid-state structure of **11** leading to a chemically slightly different environment of the P_4 units (cf. Figure S35). Furthermore, a broad signal with a shoulder at 103 ppm is observed corresponding to the different coordination modes of the P atoms of the *cyclo*- P_5 ligand.

To increase the amount of the $[\text{AgP}_4]$ units in compound **11**, *ortho*-dichlorobenzene was used as a solvent instead of CH_2Cl_2 as in the case of compound **6** and in the expectation that larger solvent molecule will not fit into the cavity suited for the fifth silver cation. After stirring a 1:5:10 mixture of **1b**, AgSbF_6 , and P_4 and layering it with *n*-pentane, brown plates of **12** crystallize in the monoclinic space group $P2_1/n$ (Scheme 5). The asymmetric unit consists of $[(\text{1b})_2(\text{Ag}_{6.25}(\text{P}_4)_8)\text{Ag}_{0.75}][\text{SbF}_6]_7 \cdot 2 \text{C}_6\text{H}_4\text{Cl}_2$ (**12a**) with overall 10 Ag positions. In an idealized structure with all Ag positions fully occupied, a tetrameric structure would be built up by two pairs of opposed units of **1b** connected via silver cations. In fact, six Ag positions are fully occupied, while the remaining Ag^+ cation is disordered over four positions (Figure S41) leading to different isomeric structures (see Supporting Information). Since other potential positions for the Ag^+ cations are geometrically available in the crystal structure of **12**, it is not surprising that also crystals of $[(\text{1b})_2(\text{Ag}_{6.265}(\text{P}_4)_8)\text{Ag}_{0.735}][\text{SbF}_6]_7 \cdot 1.5 \text{C}_6\text{H}_4\text{Cl}_2$ (**12b**) with

the same composition but with another distribution of the Ag^+ cations were found in the course of our multiple attempts to obtain high-quality single-crystal X-ray data (see Supporting Information). In **12**, the $\text{Ag}-\text{P}(\text{P}_4)$ bond lengths of the fully occupied Ag^+ cations as well as the P-P distances of the P_4 units agree with those found in **6c**, **11**, and in literature (Table 1).^[14,57,58]

Using mixed-ligand complexes **11** and **12** for the release of P_4 . Since **11** is insoluble in common solvents and slightly soluble in CH_2Cl_2 , it is convenient to use donor solvents to release the weakly bound P_4 molecules. Crystals of **11** and **12** were redissolved in a mixture of $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$ where partial decomplexation occurs in both cases. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of such solutions for **11** shows two sharp singlets at 136.8 ppm and -522.6 ppm corresponding to **1b** coordinated to Ag^+ cations and to P_4 , respectively (Figure 4a). The shift of the latter signal corresponds to the one of free P_4 ($\delta = -522$ ppm). For comparison, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction solution in CD_2Cl_2 shows two singlets at 122.4 and -515.0 ppm (Figure 4b). Here, the signals for both the *cyclo*- P_5 ligand and the P_4 molecules are shifted compared to the free compounds, indicating a coordination of both polyphosphorus ligands to Ag^+ cations. Interestingly, singlets at -513 ppm and -515 ppm were observed for $[\text{P}_4\text{Ag}(\text{GaCl}_4)]_n$ and $[\text{Ag}(\eta^2\text{-P}_4)][\text{Al}(\text{OC}(\text{CH}_3)(\text{CF}_3)_2)_4]$, respectively, in their $^{31}\text{P}\{^1\text{H}\}$ NMR spectra in CD_2Cl_2 .^[20,22] This suggests that $[\text{Ag}(\eta^2\text{-P}_4)]^+$ units are present in the reaction solution.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **12** redissolved in a mixture of CD_2Cl_2 and CD_3CN shows singlets at 151.9 and -520.7 ppm for the *cyclo*- P_5 moiety and free P_4 units, respectively, for which the former signal is slightly shifted in comparison to the free ligand **1b**.

The partial decomplexation of compounds **11** or **12** in solutions of $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ can also be observed in the ESI-MS spectrum in which the highest peak corresponding to $[(\text{1b})\text{Ag}]^+$ is centered at an m/z ratio of 905.06 (**11**) or 905.07 Da (**12**). Although the same crystals **11** used for the NMR study in solution were dissolved for the ESI-MS measurement in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$, no fragments containing P_4 were detected, which is most probably due to the nonpolar

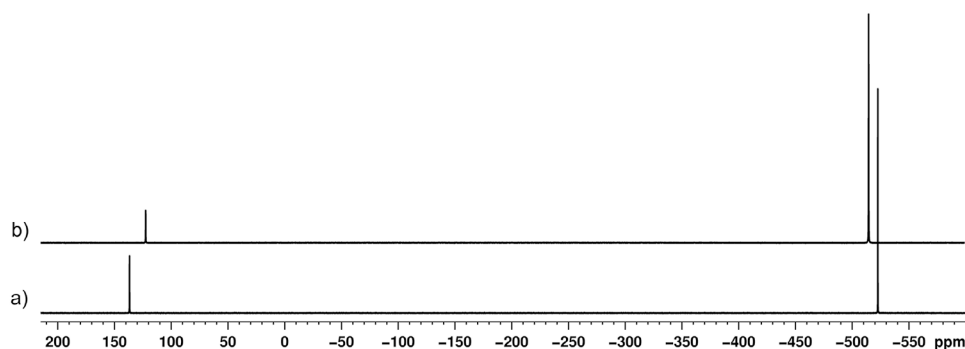


Figure 4. $^{31}\text{P}\{^1\text{H}\}$ NMR of a) crystals of **11** in $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$ and b) reaction solution of **11** in CD_2Cl_2 .

nature of P_4 , which does not ionize under the conditions of ESI-MS. No P_4 -containing fragments were detected also for **12**.

Conclusion

The comprehensive study of the reactions of the pentaphosphaferrocenes **1a** or **1b** with coinage $\text{M}(\text{I})$ salts ($\text{M} = \text{Cu}, \text{Ag}$) of WCAs in the presence of white phosphorus sheds light onto self-assembly processes that lead to coordination rather than to encapsulation of tetrahedral P_4 molecules (cf. Scheme 1). By variation of the stoichiometry in the two-component self-assembly reactions of $[(\text{Cp}^{\text{PEt}}\text{Fe}(\eta^5\text{-P}_5))](\text{1b})$ with $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{SbF}_6]$, different coordination products were obtained. Besides the dimeric compounds **2** and **3**, the pentanuclear $[(\text{1b})\text{Cu}_5(\text{CH}_3\text{CN})_{15}][\text{SbF}_6]_5 \cdot \text{CH}_2\text{Cl}_2$ (**4**) was isolated, which represents the first discrete monomeric complex of a penta-coordinated *cyclo*- P_5 building block that could be used as a precursor for efficient P_4 coordination. However, such attempts proved fruitless due to competition between acetonitrile ligands and the weak donor P_4 , as well as the attempts to use acetonitrile-free copper source. To replace $\text{Cu}(\text{I})$ by more Lewis acidic $\text{Ag}(\text{I})$ offered better perspectives since AgSbF_6 is available in coordinated ligand-free form. The two-component self-assembly reactions of $[(\text{Cp}^{\text{R}}\text{Fe}(\eta^5\text{-P}_5))](\text{Cp}^{\text{R}} = \text{Cp}^* (\text{1a}), \text{Cp}^{\text{PEt}} (\text{1b}))$ with AgSbF_6 in different stoichiometric ratios lead to a series of coordination compounds **5**, **7–9**. Compounds **5** and **8** exemplify weakly coordinating CH_2Cl_2 molecules at the Ag^+ ions suggesting that they can easily be removed to give space for P_4 in subsequent three-component self-assembly reactions. Indeed, the CH_2Cl_2 ligands are thus partly or completely replaced by P_4 in case of the reactions of **1a** with AgSbF_6 and P_4 depending on the stoichiometry and the solvent used, leading to the novel 1D polymeric compounds $[(\text{1a})_2\{\text{Ag}_2(\eta^2\text{-P}_4)_m(\text{CH}_2\text{Cl}_2)_{1-m}\}]_n[\text{SbF}_6]_{2n}$ (**6**; $m = 0.75$ (**6a**), 0.67 (**6b**), 1 (**6c**)). However, the derivatives of **1a** form polymeric structures that render them completely insoluble, and the content of the coordinated P_4 molecules is not very high (max. one P_4 per unit **1a**). In contrast, using **1b** with the larger steric demand of its Cp^{PEt} ligand hinders the coordination of one or more **1b** units to the same $\text{Ag}(\text{I})$ cation. Moreover, the silver cations are additionally stabilized only by weak interactions with the aromatic substituents at the

Cp^{PEt} ligand. Therefore, if the weak donor P_4 is present, the self-assembly does not proceed to the formation of polymers like **7–8** and multiple coordination of P_4 becomes beneficial. Thus, the way to discrete monomeric complexes $[(\text{1b})\{\text{Ag}(\eta^2\text{-P}_4)_4\}][\text{SbF}_6]_4 \cdot \text{CH}_2\text{Cl}_2$ (**11**) carrying the unprecedented content of four intact P_4 moieties as ligands is enabled. The formation of this first complex of a tetra-coordinated *cyclo*- P_5 ligand shows that a spectator Cp^{R} ligand can not only drive the reaction toward a molecular product but can also enhance the solubility of the resulting P_4 -rich assembly. If the reaction is performed in *ortho*-dichlorobenzene instead of CH_2Cl_2 , molecular complexes **12** with the general formula $[(\text{1b})_2(\text{Ag}_7(\text{P}_4)_8)][\text{SbF}_6]_7 \cdot n \text{C}_6\text{H}_4\text{Cl}_2$ ($n = 2, 1.5$) with a more complex structure are built up with as high content of P_4 tetrahedra as in **11**. The disorder of one Ag atom in **12a** ($n = 2$) over alternative positions leads to different forms of the cocrystallizing P_4 -rich complexes. These forms differ by the coordination of P_4 in multiple positions and suggest the possibility of further increase of the P_4 content provided that all partly occupied positions available for P_4 coordination are filled.

Compounds **6**, **11**, and **12** are the first examples of P_4 -rich mixed P_n -ligand complexes of coinage metals, a groundbreaking new type of product in this chemistry, capable of P_4 coordination with controlled decomplexation. NMR spectroscopy studies in solution reveal that it is possible to release P_4 by the addition of CH_3CN to a suspension of the crystals of **6**, **11**, or **12** in CH_2Cl_2 under fragmentation of the coordination compounds. Furthermore, it was proven that crystals of the polymeric complex **6a** show no decomposition in air at room temperature for weeks.

The access to different naked polyphosphorus ligands in a mix-ligand molecular complex opens an unexplored area of coordination of small molecules to coinage metal ions bound to a *cyclo*- P_5 building block. The possibility of using the obtained products for storage and transport of the intact P_4 molecules for subsequent reactions will be further investigated. Additionally, other small molecules, especially air- or light-sensitive molecules such as As_4 , that are capable of coordinating to metal ions, come into the focus of research, including studies for storage purposes or additional reactions after the release of the coordinated molecules. Aside from this, the novel mixed ligand metal complexes of naked polyphosphorus ligands may act as promising precursors and

create new avenues in P₄ transformation chemistry, thereby offering fresh insights into related research fields.

Supporting Information

The authors have cited additional references within the Supporting Information.^[1–52]

Acknowledgements

The Deutsche Forschungsgemeinschaft is acknowledged for the support within the project Sche 384/44-1. E.P. is grateful for a postdoc research scholarship for female early career researchers within the framework of the Free State of Bavaria's 'Programme to Realise Equal Opportunities for Women in Research and Teaching' at the University of Regensburg. Parts of this research (Projects I-20180646, I-20190225, I-20190914, I-20191087, and II-20180579) were carried out at PETRA III at DESY, a member of the Helmholtz Association (HGF). The authors thank Dr. E. Crosas for her assistance regarding the use of the beamline P11, Dr. L. Noohinejad and Dr. M. Tolkiehn for their assistance when using the beamline P24, and Dr. Mathias Meyer (Rigaku Oxford Diffraction) for his unceasing support with the implementation of *CrysAlisPro* software to the synchrotron data. The authors are grateful to Prof. Dr. W. Kremer (University of Regensburg) for measuring the MAS NMR spectra.

Open access funding enabled and organized by Projekt DEAL.

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 Supporting Information of this article.

Keywords: Coinage metal • Mixed-ligand polyphosphorus complexes • Pentaphosphaferrocene • Supramolecular chemistry • White phosphorus

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- [52] If not otherwise indicated, hereinafter the $[\text{SbF}_6]^-$ counter anions are located in the outer sphere of the corresponding cations. Deposition numbers CCDC-2376066 (**2a**), CCDC-2376067 (**2b**), CCDC-2376068 (**3a**), CCDC-2376069 (**3b**), CCDC-2376070 (**3c**), CCDC-2376071 (**4**), CCDC-2376072 (**5**), CCDC-2376073 (**6a**), CCDC-2376074 (**6a_{air}**), CCDC-2376075 (**6b**), CCDC-2376076 (**6c**), CCDC-2376077 (**7**), CCDC-2376078 (**8a**), CCDC-2376079 (**8b**), CCDC-2376080 (**8c**), CCDC-2376081 (**8d**), CCDC-2376082 (**9**), CCDC-2376083 (**10a**), CCDC-2376084 (**10b**), CCDC-2376085 (**11**), CCDC-2376086 (**12a**), CCDC-2376087 (**12b**), and CCDC-2376087 ($[\text{Ag}(\text{P}_4)_2][\text{SbF}_6]$) 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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Manuscript received: February 13, 2025

Revised manuscript received: March 27, 2025

Accepted manuscript online: April 15, 2025

Version of record online: May 05, 2025