

Silver Coordination Polymers

Strategies for the Construction of Supramolecular Dimers versus Homoleptic 1D Coordination Polymers Starting from the Diphosphorus $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\eta^2\text{-P}_2)]$ Complex and Silver(I) SaltsMehdi Elsayed Moussa,^[a] Martin Fleischmann,^[a] Eugenia V. Peresyphkina,^[a,b,c] Luis Dütsch,^[a] Michael Seidl,^[a] Gabor Balázs,^[a] and Manfred Scheer^{*,[a]}

Dedicated to Professor Dietrich Gudat on the occasion of his 60th birthday

Abstract: The reactions of the tetrahedral diphosphorus $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\eta^2\text{-P}_2)]$ (**1**; Cp = C₅H₅) complex with Ag[Al{OC(CF₃)₃}₄] (AgTEF) (**A**) and Ag[FAI{OC(C₆F₅)(C₆F₁₀)₃}] (AgFAI) (**B**) were studied. The first reaction led to the formation of the $[\text{Ag}_2(\eta^1\text{-1})_2(\eta^1\text{-1})_2][\text{TEF}]_2$ (**2**) dimer and the $[\text{Ag}_2(\eta^1\text{-1})_3]_n\text{-}[\text{TEF}]_{2n}$ (**3**) coordination polymer, whereas the second reaction

afforded the $[\text{Ag}_2(\eta^1\text{-1})_2(\eta^1\text{-CH}_2\text{Cl}_2)_2(\eta^2\text{-C}_7\text{H}_8)_2][\text{FAI}]_2$ (**4**) or the $[\text{Ag}_2(\eta^2\text{-1})_2(\eta^1\text{-1})_2][\text{FAI}]_2$ (**5**) dimer and the $[\text{Ag}_2(\eta^1\text{-1})_4]_n[\text{FAI}]_{2n}$ (**6**) coordination polymer. In each case, the products obtained depended on the ratio of the reactants and/or the synthetic procedure.

Introduction

In the past two decades, metal-directed self-assembly processes have been widely used to synthesize discrete supermolecules and extended polymeric frameworks.^[1] Those derivatives are usually obtained from the spontaneous association of organic multitopic ligands bearing N, O, or S donor atoms with a large variety of Lewis acidic metal cations.^[2] In fact, the directional but reversible coordinative bonds result in a typical equilibrium that exists between the involved molecular components and the various potential products. This feature is affected by the different reaction conditions applied and generally leads to the formation of the thermodynamically most stable product(s).^[3] In this field, our group developed an alternative approach by utilizing P-donating organometallic polyphosphorus (P_n) ligand complexes with flexible coordination modes as connectors between metal ions.^[4] Using this novel approach, it was possible to synthesize one- and two-dimensional coordination poly-

mers,^[5] vast fullerene-like supramolecular spherical aggregates,^[6] and organometallic nanosized capsules.^[7] Among the used P_n ligand complexes, the tetrahedral $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\eta^2\text{-P}_2)]$ (Cp = C₅H₅) (**1**) complex was extensively studied. The reaction of **1** with Cu^I halides led to one-dimensional $[\text{Cu}(\mu\text{-X})\{\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu,\eta^2\text{-}\eta^1\text{-P}_2)\}]_n$ (X = Cl, Br, I) polymers, and its reaction with AgNO₃ resulted in the undulated 1D $[\text{Ag}_2\{\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu,\eta^2\text{-}\eta^1\text{-P}_2)\}_3(\mu,\eta^1\text{-}\eta^1\text{-NO}_3)]_n[\text{NO}_3]_n$ polymer.^[8] The reactions of the AgX salts of weakly coordinating anions {X = BF₄, PF₆, ClO₄, SbF₆, Al[OC(CF₃)₃]₄} with **1** led to Ag^I dimers with the general formula $[\text{Ag}_2\{\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu,\eta^2\text{-}\eta^1\text{-P}_2)\}_2][\{\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu,\eta^2\text{-}\eta^1\text{-P}_2)\}_2][\text{X}]_2$.^[9] Some of these dimeric compounds were further treated with multitopic pyridine-based organic molecules, which in the solid state led to a large variety of unprecedented organometallic–organic hybrid coordination polymers.^[10] Although the coordination chemistry of **1** towards Ag^I has been extensively studied, no homoleptic polymeric compounds of **1** and Ag^I have yet been reported. We present herein a systematic study of the variation of the ratio of the reactants and the reaction procedure for the self-assembly processes of the P_2 ligand complex **1** and the Ag^I salts of the weakly coordinating anions $[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$ (TEF) and $[\text{FAI}\{\text{OC}(\text{C}_6\text{F}_5)(\text{C}_6\text{F}_{10})_3\}]^-$ (FAI). The found conditions allowed fine-tuning of the formation of either dimers or homoleptic one-dimensional coordination polymers.

Results and Discussion

In a first approach, P_2 ligand complex **1** was treated with Ag[TEF] (**A**), for which the dependence of the composition of the product on the stoichiometry of the reactants was studied by varying the **1/A** ratio. If the used reactant stoichiometry

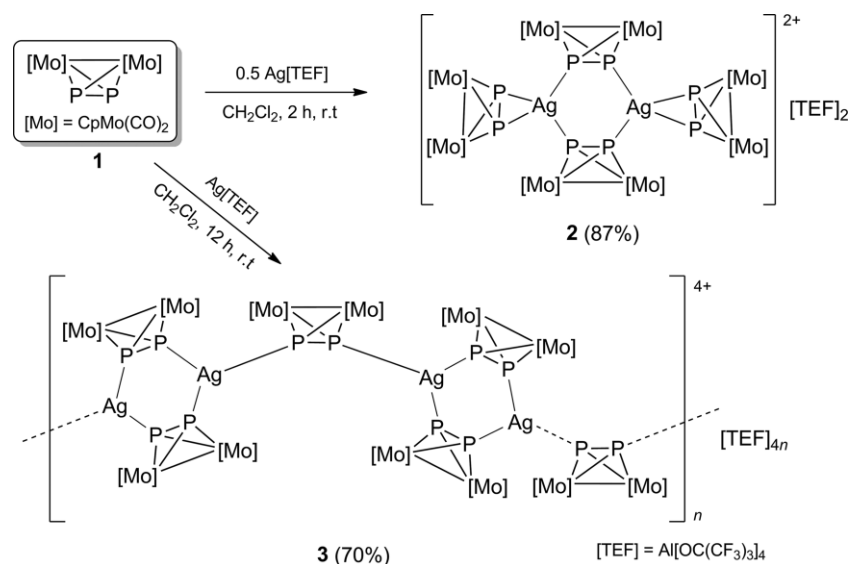
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Scheme 1. Reaction of **1** with Ag[Al(OC(CF₃)₃)₄] (**A**): synthesis of dimer **2** and one-dimensional coordination polymer **3**.

1/A was between 2:1 and 6:1, complex **2** was formed (87 % as the highest yield), which suggests that this product represents a thermodynamic minimum by using such an excess amount of P₂ ligand complex **1**. However, if the reactant stoichiometry **1/A** was between 2:1 and 1:1, compound **3** was obtained with very high selectivity (70 % as the highest yield). Interestingly, with these stoichiometric ratios, compound **2** was formed only if a CH₂Cl₂ solution of **A** was slowly added to a CH₂Cl₂ solution of **1** (if ligand **1** was in reasonable excess at the time of mixing the two reactants), whereas compound **3** was selectively isolated if a CH₂Cl₂ solution of **1** was added to a CH₂Cl₂ solution of **A** (if no excess amount of ligand **1** was present at the time of mixing the two reactants). This effect of the ratio of the reactants together with the reaction procedure on the product composition is clearly reflected in the solid-state structures of products **2** and **3**. Crystals of **2** and **3**, grown by layering CH₂Cl₂ solutions of the crude reaction mixtures with pentane (for **2**) and toluene (for **3**), were examined by X-ray structure analysis. Their crystal structures clearly reveal that the formed coordination compounds have different ratios of Ag^I/**1** in the solid state, 1:2 for **2** and 2:3 for **3**. Compound **2**·1.5CH₂Cl₂ turned out to be a solvatopolymorph of the silver [Ag₂(μ,η¹:η¹-**1**)₂(η²-**1**)₂]-[Al(OC(CF₃)₃)₄]₂·CH₂Cl₂ dimer previously reported by our group,^[9] whereas **3** is a unique homoleptic one-dimensional coordination polymer of the general formula [Ag₂(μ,η¹:η¹-**1**)₃]_n-[Al(OC(CF₃)₃)₄]_{2n} (Scheme 1, Figure 1b).

Dimer **2** is surrounded by four P₂ ligands **1**, two of which possess a bridging μ,η¹:η¹-coordination mode and the other two of which show η²-side-on coordination (Scheme 1, Figure 1a). Hence, each Ag^I ion in **2** possesses a distorted tetrahedral coordination sphere consisting of four P atoms. The molecular geometry of this new solvatopolymorph of **2** is comparable to that of the initial structure. In addition, some Ag^I ions interact with CH₂Cl₂ solvent molecules [Ag–Cl 3.561(4)–3.647(8) Å], which is not the case in the earlier found structure. The structure of **3** exhibits a one-dimensional zigzag chain consisting of Ag₂(**1**)₂ repeating units interconnected by **1** as an additional

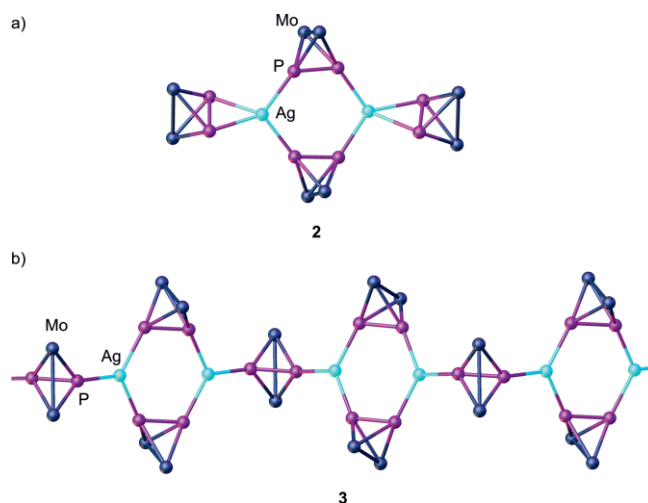


Figure 1. (a) Molecular structure of cationic dimer **2** in the solid state. (b) Section of 1D coordination polymer **3**. Cp and CO ligands, hydrogen atoms, counteranions, as well as minor disordered positions are omitted for clarity.

ligand. All the P₂ ligands **1** in **3** show a bridging μ,η¹:η¹-coordination mode. Each Ag^I ion in **3** possesses a distorted trigonal geometry consisting of three P atoms. The central Ag₂P₄ six-membered rings in **3** are nearly planar and show only a slight distortion towards a chair conformation [folding angle 12.5(1)°] as compared to the Ag₂P₄ six-membered ring in **2** [folding angle 18.4(1)°]. The P–P bond lengths in **3** [2.082(3)–2.097(2) Å] are comparable to those of noncoordinated ligand **1** [2.079(6) Å]^[11] and are slightly shortened relative to those of dimer **2** [2.087(2)–2.152(3) Å]. The Ag–P bond lengths inside [2.4464(14)–2.4642(15) Å] and outside [2.4425(16) Å] of the six-membered rings in **3** are almost identical and are slightly shortened relative to those of dimer **2** [2.4634(16)–2.6885(17) Å]. The Ag···Ag distances exceed 4.8 Å in **2** and 4.34 Å in **3**, which suggests no argentophilic interaction.^[12]

Compounds **2** and **3** are well soluble in CH₂Cl₂, THF, and CH₃CN; slightly soluble in toluene; and insoluble in *n*-pentane.

The room-temperature ^{31}P NMR spectra of **2** and **3** in CD_3CN each show a broad signal centered at $\delta = -86.1$ and -93.0 ppm, respectively, which is upfield shifted relative to that of free P_2 ligand complex **1** ($\delta = -43.2$ ppm).^[11] These observations suggest the presence of a dynamic behavior in solution, which was previously carefully studied for original solvatopolymorph **2**.^[9] Their room-temperature ^1H and ^{13}C NMR spectra show the expected signals attributable to the protons and carbon nuclei of ligand **1** and the TEF anions (for further details, see the Supporting Information).

In a second step, P_2 ligand complex **1** was treated with $\text{Ag}[\text{FAI}]$ (**B**) in various stoichiometric ratios. The 1:1 reaction in CH_2Cl_2 and subsequent layering with toluene gave **4** as an orange crystalline solid in moderate yield (39%; Scheme 2, Figure 2a). However, if the 2:1 stoichiometry was used, compound **5** or **6** was formed depending on the order in which one reactant was added to the other. Product **5** was formed selectively (76% yield) only if a CH_2Cl_2 solution of **B** was slowly added to a CH_2Cl_2 solution of **1** (in other words, if there was an excess of ligand **1** present). On the contrary, compound **6** was isolated (89% yield) if the reaction order was reversed, that is, if ligand **1** was the limiting reactant at the time of mixing the two reactants. Single-crystal X-ray structure analysis of **4**, **5** and **6** reveals composition ratios of 1:1 (for **4**) and 1:2 (for **5** and **6**) of $\text{Ag}^I/\text{1}$ in the solid state. Among these, compounds **4** and **5** represent dimers with general formulas of $[\text{Ag}_2(\mu, \eta^1: \eta^1\text{-1})_2(\eta^1\text{-CH}_2\text{Cl}_2)_2]$

$(\eta^2\text{-C}_7\text{H}_8)_2][\text{FAI}]_2$ and $[\text{Ag}_2(\mu, \eta^1: \eta^1\text{-1})_2(\eta^2\text{-1})_2][\text{FAI}]_2$, respectively, whereas derivative **6** is a homoleptic one-dimensional coordination polymer with the formula $[\text{Ag}_2(\mu, \eta^1: \eta^1\text{-1})_4]_n[\text{FAI}]_{2n}$

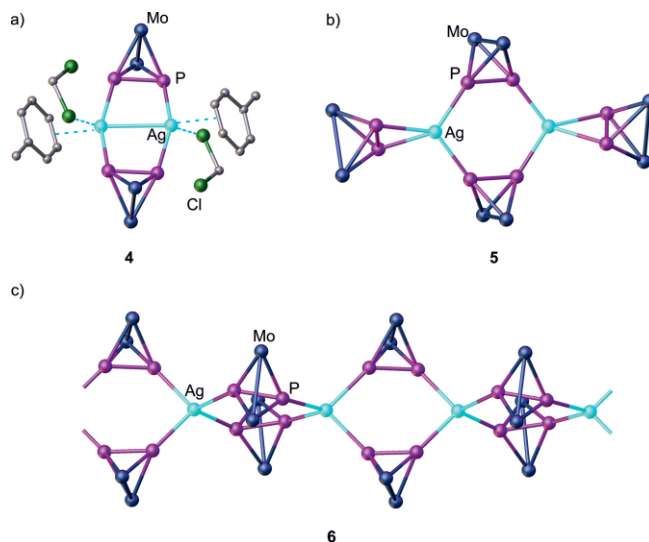
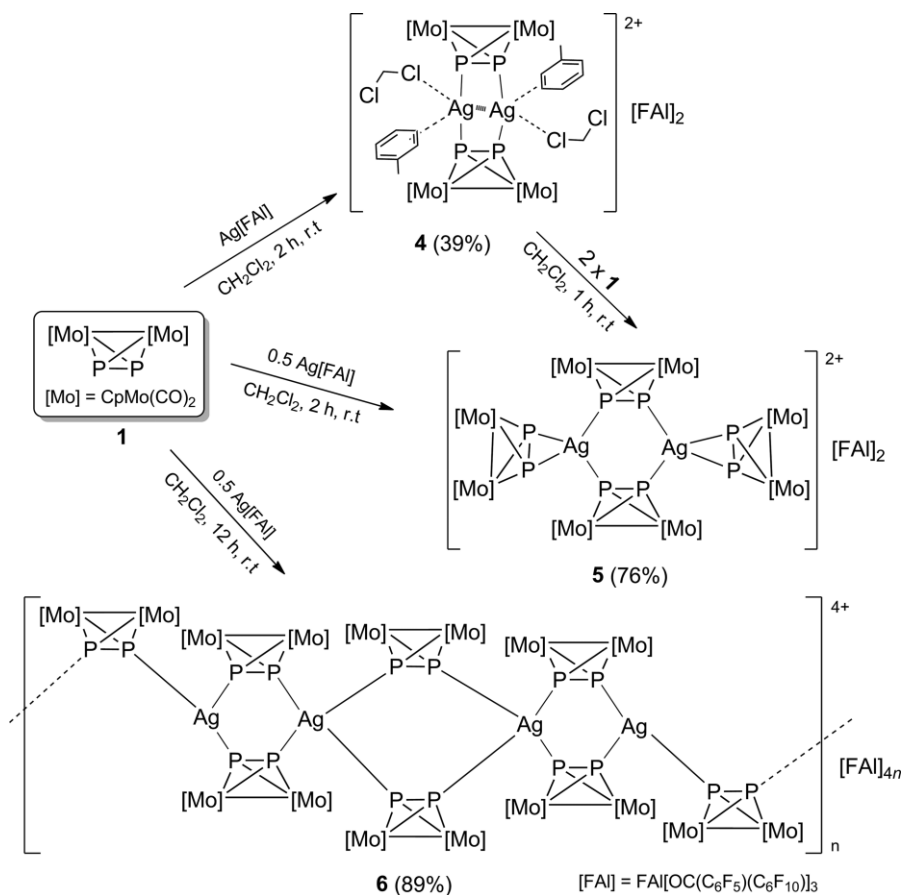
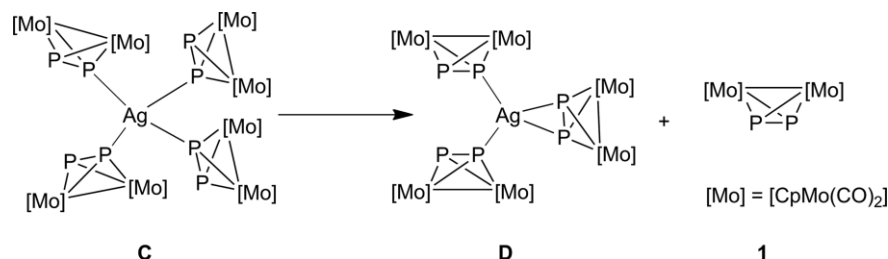


Figure 2. Molecular structures of cationic dimers (a) **4** and (b) **5** in the solid state. (c) Section of 1D coordination polymer **6**. Cp and CO ligands, hydrogen atoms, counterions, as well as minor disordered positions are omitted for clarity.



Scheme 2. Reaction of **1** with $\text{Ag}[\text{FAI}\{\text{OC}(\text{C}_6\text{F}_5)(\text{C}_6\text{F}_{10})\}_3]$ (**B**): synthesis of dimers **4** and **5** and one-dimensional coordination polymer **6**.



Scheme 3. Dissociation of hypothetical intermediate **C** into **D** and **1**.

(Scheme 2, Figure 2). Dimer **4** is composed of two Ag^I ions with a short Ag...Ag contact of 3.0532(10) Å and is capped by two bridging $\mu, \eta^1: \eta^1$ -coordinating P₂ ligands of **1** to form a central P₂Ag₂P₂ ladder-shaped structural motif with nearly identical P–Ag bond lengths [2.4523(14)–2.4550(13) Å]. Additionally, each Ag^I ion is η^2 -coordinated by a toluene molecule [Ag–(C=C) 3.010(6) Å] and η^1 -coordinated by a CH₂Cl₂ molecule [Ag–Cl 3.402(3) Å]. Interestingly, these labile ligands can be easily substituted by the addition of another equivalent of **1**, which leads to dimer **5**. The cationic part of dimer **5** is very similar to that of dimer **2**, which was isolated from a similar reaction with the use of Ag^I salt **A**. In this case, the central Ag₂P₄ six-membered ring shows a slight distortion towards a chair conformation [fold angle 20.53(10)°], and no Ag–Ag interaction is observed in **5** [*d*(Ag...Ag) > 4.85 Å]. The Ag–P distances inside the six-membered Ag₂P₄ ring [2.4871(11) and 2.4834(11) Å] are significantly shorter than the Ag–P distances to the end-on coordinated ligands **1** [2.7112(11) and 2.5988(11) Å]. The η^2 -coordinating P–P bond [2.1395(16) Å] is slightly elongated, and the $\eta^1: \eta^1$ -coordinating P–P bonds [2.091(2) Å] are almost unchanged relative to those of free ligand **1** [2.079(2) Å]. The structure of **6** exhibits a one-dimensional coordination polymer of infinite interconnected Ag₂P₄ six-membered ring repeating units. Most probably, as a result of the steric hindrance of the Cp and CO groups on the Mo centers, two consecutive Ag₂P₄ repeating units along the polymeric chain of **6** are oriented in an angle of 85.82(6)° towards each other. The Ag₂P₄ rings themselves are almost planar and show only a slight distortion towards a chair conformation [fold angles 10.50(6)–11.00(6)°]. The P–P distances in **6** [2.1004(12)–2.1005(12) Å] are elongated relative to those of free ligand **1** [2.079(6) Å], and the Ag–P distances [2.5775(8)–2.6086(8) Å] are also elongated relative to those of dimers **4** and **5**.

Compounds **4–6** are well soluble in polar solvents such as CH₃CN, are slightly soluble in CH₂Cl₂, and are insoluble in other common organic solvents such as THF and *n*-pentane. Their room-temperature ³¹P NMR spectra in CD₃CN show signals varying significantly between $\delta = -74.6$ and -92.6 ppm, which are upfield shifted relative to those of free P₂ ligand complex **1** ($\delta = -43.2$ ppm). The room-temperature ¹H and ¹³C NMR spectra of **4–6** reveal the expected signals corresponding to the protons and carbon nuclei of ligand **1** and the FAI anion (for further details, see the Supporting Information).

Experimentally, the effect of the reaction procedure on the formation of compounds **5** and **6** (which contain the same ratio of ligand **1**/Ag^I) is not clear. Structurally, the differences be-

tween **5** and **6** are the coordination modes of terminal ligands **1** (η^2 -coordination mode in **5** and $\eta^1: \eta^1$ -coordination mode in **6**). To better understand the reaction mechanism with respect to the difference in product formation, DFT calculations were performed at the B3LYP/def2-TZVP level of theory. The calculations show that by adding the Ag^I salt to **1**, species **D** is present in solution, as the dissociation of the expected species **C** (local excess of **1**) to **D** and **1** is thermodynamically favored by -13.9 kJ mol⁻¹ (Scheme 3). Additionally, the reaction in Scheme 3 shows that if P₂ ligand **1** is in excess relative to Ag^I, the η^2 -coordination mode of “terminal” P₂ ligand **1** is preferred over the η^1 -coordination mode.

On the basis of these DFT calculations and the experimental observations, we assume that, in both cases, the Ag₂P₄ six-membered ring motif is formed first, for example, compound **4**. In the case of a local excess of P₂ ligand **1**, upon adding Ag[FAI] to **1**, dimer **5** is formed as a result of the preference of **1** for the η^2 -coordination mode under these conditions. While as long as an excess amount of Ag^I salt is present, upon adding **1** to Ag[FAI], possibly by preformation of oligomers containing linear P–Ag–P scaffolds with bridging ligand **1**, these intermediates can probably be further transformed into the coordination polymer **6** as long as more ligand **1** is added.

Conclusions

The obtained results present a smooth strategy for the construction of either dimers (i.e., **2**, **4**, and **5**) or homoleptic one-dimensional coordination polymers (i.e., **3** and **6**) on the basis of a diphosphorus ligand complex, [Cp₂Mo₂(CO)₄(η^2 -P₂)] (**1**), and Ag^I metal ions. The coordination polymers are the first homoleptic polymeric compounds of **1** and Ag^I. The variation in product formation was discovered to be due to the flexible coordination modes of ligand complex **1**, which could adopt either an η^2 - or $\eta^1: \eta^1$ -coordination mode according to the ratio of ligand **1**/Ag^I present in solution at the time the reaction was initiated. These results, in addition to the large variety of assemblies based on ligand **1**,^[8,9] show the advantage of our approach, in which P-donating ligand complexes are used in metal-directed self-assembly, as it can lead to a very rich library of supramolecular compounds with large structural diversity. Current investigations involve reactions based on heavier analogues [Cp₂Mo₂(CO)₄(η^2 -E₂)] (E = As, Sb, Bi) to study the possibility of utilizing these rarely used ligands as connectors between metal ions in addition to the well-established study of using P₂ ligand **1**.

CCDC 1551486 (for **2**), 1551487 (for **3**), 1551488 (for **4**), 1551489 (for **5**), and 1551490 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Supporting Information (see footnote on the first page of this article): NMR spectroscopy data, elemental analysis, mass spectrometry, as well as crystal-structure refinement data for compounds **2–6**.

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Keywords: Phosphorus · Coordination polymers · Coordinating anions · Silver · Synthetic methods

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