Supramolecular Chemistry

The Potential of the Diarsene Complex $[(C_5H_5)_2Mo_2(CO)_4(\mu,\eta^2\text{-}As_2)]$ as a Connector Between Silver Ions

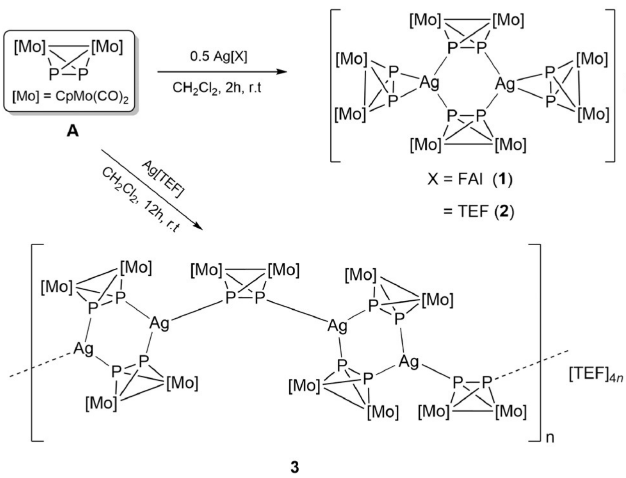
Mehdi Elsayed Moussa[+], Jana Schiller[+], Eugenia Peresypkina, Michael Seidl, Gábor Balázs, Pavel Shelyganov, and Manfred Scheer*[a]

Dedicated to Professor Christoph Janiak on the occasion of his 60th birthday

Abstract: The reaction of the organometallic diarsene complex $[Cp_2Mo_2(CO)_4(\mu,\eta^2\text{-}As_2)]$ (**B**) (Cp = C_5H_5) with $Ag[FAl\{OC_6F_{10}(C_6F_5)\}_3]$ (Ag[FAl]) and $Ag[Al\{OC(CF_3)_3\}_4]$ (Ag[TEF]), respectively, yields three unprecedented supramolecular assemblies $[(\eta^2\text{-}\mathbf{B})_4Ag_2][FAl]_2$ (**4**), $[(\mu,\eta^1:\eta^2\text{-}\mathbf{B})_3(\eta^2\text{-}\mathbf{B})_2Ag_3][TEF]_3$ (**5**) and $[(\mu,\eta^1:\eta^2\text{-}\mathbf{B})_4Ag_3][TEF]_3$ (**6**). These products are only composed of the complexes **B** and Ag^I. Moreover, compounds **5** and **6** are the only supramolecular assemblies featuring **B** as a linking unit, and the first examples of $[Ag^I]_3$ units stabilized by organometallic bichelating ligands. According to DFT calculations, complex **B** coordinates to metal centers through both the As lone pair and the As–As σ-bond thus showing this unique feature of this diarsene ligand.

The interest in using metal-directed self-assembly for the design of well-defined solid-state structures has remarkably increased over the past decades.[1] Specifically, Ag^I complexes present an attractive research area because of their rich structural diversity and wide range of applications.[2] This diversity is due on the one hand to the flexible coordination sphere of the Ag^I ion which can adopt various coordination geometries (linear, trigonal planar, tetrahedral, square-planar, trigonal bipyramidal, etc.)[3] and on the other hand to its ability to coordinate a variety of multitopic organic ligands bearing mainly N-, O-, S- or P- and, to a minor extent, Se, C, As or mixed-donor atoms.[2–4] Besides organic molecules, very few examples of organometallic building blocks were used as linking moieties to Ag^I centers.[5] Due to the lack of such compounds, our group developed the concept of using organometallic polyphosphorus (P_n) ligand complexes with flexible coordination modes as connectors between metal ions.[6] This new approach allowed for the synthesis of a large variety of unprecedented supramolecular aggregates including 1D, 2D, and 3D coordination polymers (CPs),[7] inorganic nanospheres,[8] nanosized bowls[9] and capsules.[10] One of the simplest of such P_n compounds is the diphosphorus complex $[Cp_2Mo_2(CO)_4(\mu,\eta^2\text{-}P_2)]$ (**A**) (Cp = $\eta^5\text{-}C_5H_5$).[11] Its reaction with a large number of Ag^I salts including those of the weakly coordinating anions $[Al\{OC(CF_3)_3\}_4]^-$ ($[TEF]^-$) and $[FAl\{OC_6F_{10})(C_6F_5)\}_3]^-$ ($[FAl]^-$) allowed for the isolation of Ag^I dimers of the general formula $[Ag_2(\eta^2\text{-}\mathbf{A})_2(\mu,\eta^1:\eta^1\text{-}\mathbf{A})_2][X]_2$ ($[X]^- = [FAl]^-$ (**1**), $[TEF]^-$ (**2**); Scheme 1).[7a] Notably, it is only possible to isolate these products selectively, if **A** is used in excess compared to the Ag^I salts. If, however, a stoichiometric reaction of for instance **A** and Ag[TEF] is conducted, the 1D polymer $[Ag_2(\mu,\eta^1:\eta^1\text{-}\mathbf{A})_3]_n[TEF]_{2n}$ (**3**) is formed instead. Interestingly, within the dimers **1** and **2**, due to the weaker coordination of the terminal η^2-coordinated ligands **A**, as compared to the $\eta^1:\eta^1$-coordinated ones, these can be easily substituted by for example, pyridyl functions upon the reaction of the Ag^I dimers with ditopic pyridine-based organic molecules to form a new class of hybrid CPs in which both organometallic and organic units link Ag^I centers.[12]

Just as P_n complexes, arsenic-based organometallic complexes have also been known for decades.[13] However, their co-



Scheme 1. Reaction of **A** with $Ag[FAl\{OC(C_6F_5)(C_6F_{10})\}_3]$ (AgFAl) and $Ag[Al\{OC(CF_3)_3\}_4]$ (AgTEF). Synthesis of the dimers **1** and **2** and the 1D CP **3**.

[a] Dr. M. E. Moussa,+ J. Schiller,+ Dr. E. Peresypkina, Dr. M. Seidl, Dr. G. Balázs, P. Shelyganov, Prof. Dr. M. Scheer
Institut für Anorganische Chemie der Universität Regensburg
93040 Regensburg (Germany)
E-mail: manfred.scheer@chemie.uni-regensburg.de
[+] These authors contributed equally to this work.
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ordination chemistry has so far been only very little investigated[14a–d] and their use as linkers in supramolecular chemistry is rare. Moreover, coordination compounds of any polyarsenic linker and silver ions are extremely scarce.[14a,c–e] Accordingly, we were keen to expand this research area by studying the supramolecular chemistry of polyarsenic As_n complexes and comparing it to that of their phosphorus analogues. In fact, because of the hindered accessibility of the lone pair on the heavier arsenic atoms, such As_n complexes were expected to have different coordination behaviors compared to their P_n analogues. Furthermore, due to the flexible coordination sphere of the Ag^I ion and its tendency to form Ag⋅⋅⋅Ag interactions,[15,3c] the question arose whether it is possible to stabilize short Ag–Ag distances by using a certain combination of the As_n complexes and Ag^I ions. Herein, we report that the reaction of the diarsene complex $[Cp_2Mo_2(CO)_4(\mu,\eta^2\text{-}As_2)]$ (**B**) with Ag[FAl] and Ag[TEF] using various ratios of starting materials allowed for the isolation of the first homoleptic coordination compounds of **B** and silver; $[(\eta^2\text{-}\mathbf{B})_4Ag_2][FAl]_2$ (**4**), $[(\mu,\eta^1:\eta^2\text{-}\mathbf{B})_3(\eta^2\text{-}\mathbf{B})_2Ag_3][TEF]_3$ (**5**) and $[(\mu,\eta^1:\eta^2\text{-}\mathbf{B})_4Ag_3][TEF]_3$ (**6**). Moreover, the assemblies **5** and **6** are the first supramolecular compounds featuring complex **B** as a connecter between metal ions and, to the best of our knowledge, the first examples of trinuclear $[Ag^I]_3$ units stabilized by organometallic bichelating ligands.

In order to evaluate the bonding situation in complex **B** towards unsaturated Ag^I centers, DFT calculations were performed at the B3LYP/def2TZVP level of theory. The results show that the lone pairs of the As atoms in **B** are lower in energy compared to those of the P atoms in **A** (Figure 1). Additionally, the energy of the As–As σ bond is higher compared to the P–P σ bond, which allows for a more effective overlap of these orbitals with the unoccupied orbitals of Ag instead of those of a lone pair. As for the As_2 complex **B**, the As–As σ bond can therefore be assumed to be involved in the bonding with unsaturated transition metal fragments, rather than the lone pair. Moreover, the energy difference between the lone pairs and the E–E σ bond is considerably higher for the arsenic derivative **B** than for the phosphorus derivative **A** (0.55 eV and 2.85 eV for **A** and **B**, respectively). This indicates that **A** can easily participate in the bonding to transition metals with both orbitals (lone pair and E–E σ bond), while for **B** a considerably higher preference for the coordination via the As–As σ bond is expected. This preference is in line with the experimental results (vide infra).

Inspired by these calculations, complex **B**[13a] was reacted with the Ag^I salt Ag[FAl]. This reaction was conducted using a 2:1 ratio of **B**:Ag[FAl] in CH_2Cl_2 at room temperature (Scheme 2). This specific ratio of the reactants was studied in order to compare the formed product to that obtained from a similar reaction of the P-donor analog **A** affording the Ag^I dimer **1** (Scheme 1). From this reaction, however, compound **4** was isolated as red prisms in 36% yield suitable for X-ray structure analysis. In the solid state, **4** is air- and light-stable for several hours while it decomposes gradually after one hour in solvents such as CH_3CN or CH_2Cl_2 under air. Compound **4** crystallizes in the orthorhombic space group *Pccn*. Its molecular structure (Figure 2a) reveals a unique Ag^I dimer stabilized by four As_2 ligands **B**. The entire molecular complex lies on the twofold axis along the *z* direction and is additionally disordered over two positions lying closely together with occupancies of 0.75 and 0.25, respectively. As regards the interpretation of the structure, this type of disorder is ambiguous and allows for three possible individual cores for **4**, with two of them, core **4a** and core **4b**, possessing twofold rotational symmetry and core **4c** being asymmetric (Figure 2b; for further details see the Supporting Information). The said disorder implies that the crystal structure of **4** is always a mixture of complexes with different cores. If the cores **4a** and **4b** co-crystallize, they

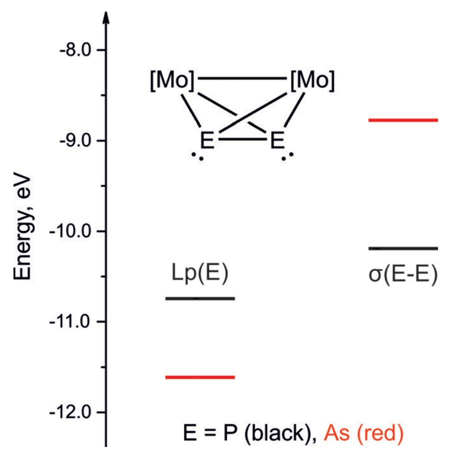
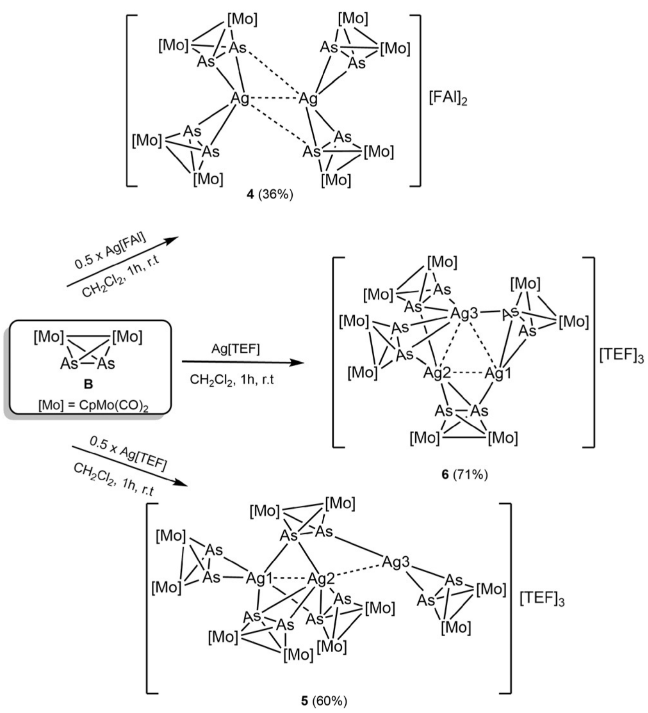


Figure 1. Frontier orbital energy diagram of $[Cp_2Mo_2(CO)_4(\mu,\eta^2\text{-}E_2)]$ (E = P, As), calculated at the B3LYP/def2-TZVP level of theory.



Scheme 2. Reaction of **B** with $Ag[FAl\{OC(C_6F_5)(C_6F_{10})\}_3]$ (Ag[FAl]) and $Ag[Al\{OC(CF_3)_3\}_4]$ (Ag[TEF]). Synthesis of the supramolecular compounds **4**–**6**. Yields are shown in parentheses.

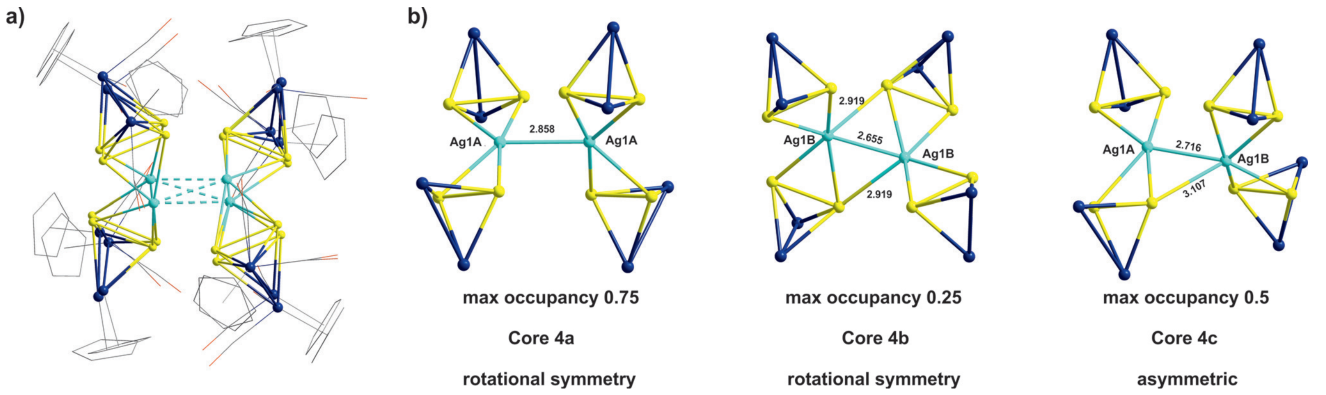


Figure 2. a) The disordered complex **4** (2_z axis is directed vertically to the plane of the picture). b) Possible individual cores of **4** in the disordered structure.

should form the mixture of 75% of **4a** and 25% of **4b**. The cores **4c** and **4a** can co-exist in a 1:1 ratio. In principle, any mixture of all three complexes **4a**–**4c** is possible with a ratio that does not contradict the crystallographic occupancies of the atoms, for example, the mixture of **4a**, **4b**, and **4c** in a ratio of 0.25:0.25:0.5. Thus, the question as to which of these alternatives do really exist cannot be answered by means of the X-ray structural data.

In order to elucidate which of the above-mentioned cores represents an energy minimum in the gas phase, we performed DFT calculations using the range-separated hybrid functional ωB97XD,[15] which also incorporates dispersion corrections together with the def2SVP basis set. Starting from the experimental geometry of the core **4b**, the geometry optimization in the gas phase leads to a geometry that is very similar to that of the core **4a**. The Ag···Ag distance in the optimized geometry is with 3.188 Å longer than the one found experimentally for core **4a** (Figure 3, left). Interestingly, the geometry optimization of a $[(\{CpMo(CO)_2\}_2As_2)_2Ag]^+$ unit, starting from the experimental coordinates of half a core of **4a**, leads to a more symmetric geometry containing a distorted tetrahedrally coordinated Ag^I center (Figure 3, right structure), which indicates that attraction forces should be present between the two $[(\{CpMo(CO)_2\}_2As_2)_2Ag]^+$ units in the solid state. This is also reflected by the gas phase "dimerization" energy of two $[(\{CpMo(CO)_2\}_2As_2)_2Ag]^+$ units to the gas-phase-optimized geometry of **4** of $-9.90\ kJ\,mol^{-1}$ (for further details see ESI).

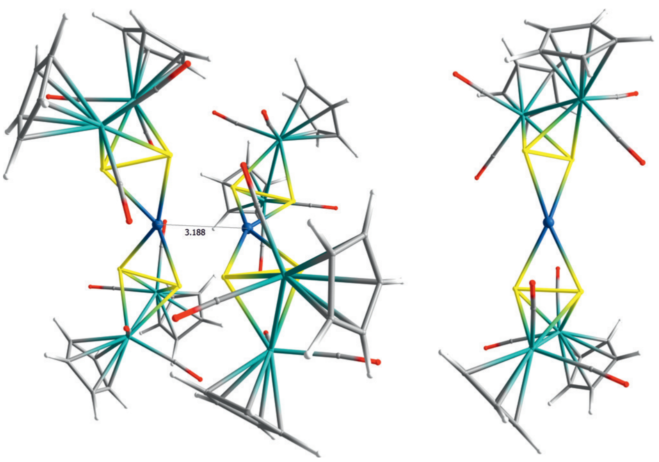


Figure 3. Gas-phase-optimized geometry of **4** at the ωB97XD/def2SVP level of theory.

Irrespective of which structures are adopted by **4** in the solid state, its composition (a Ag^I dimer stabilized by four As_2 ligands **B**) is only slightly related to the Ag^I dimer **2**, obtained from a similar reaction with the phosphorus analog **A** (Scheme 1). Still, two main differences are perceived between the two dimers **2** and **4**. First, although two of the E_2 units (E = P, As) in both dimers possess an η^2-coordination mode each, the remaining ones each possess a bridging $\mu,\eta^1:\eta^1$-coordination in **2** and a bridging $\mu,\eta^1:\eta^2$-coordination or an η^2-coordination in **4**. Additionally, the distances between the metal centers in **2** [d(Ag···Ag) > 4.85 Å] are much larger than those in **4** [2.65 Å > d(Ag···Ag) > 2.86 Å]. Therefore, there is no argentophilic interaction in **2**, while there is a possible metal–metal interaction in **4** (the sum of the van der Waals radii for silver (3.44 Å)).[16] The As–As (2.331(1)-2.414(2) Å) bond lengths in **4** are slightly elongated compared to those in the non-coordinated ligand complex **B** (As–As = 2.312(3) Å).[13a] The As–Ag bond lengths are in the range of 2.613(1)–2.919(6) Å. As expected, these lengths are longer than the P–Ag bond lengths (2.442(5)–2.688(5) Å) found in the Ag^I dimer based on the lighter analog $[Cp_2Mo_2(CO)_4(\mu,\eta^2\text{-}P_2)]$.[7a]

The crystallographic features of **4**, including the flexible coordination mode of the As_2 ligand complex **B** and the short Ag···Ag contacts, prompted us to further study the effect of the change in the stoichiometry of the reactants and the used counteranion on the outcome of the reaction. Obviously, a higher amount of Ag^I salts would lead to a higher number of Ag^I ions with a possible metal-metal interaction in the formed products in the solid-state. Thus, the reaction of **B** with the Ag^I salt $Ag[Al\{OC(CF_3)_3\}_4]$ (Ag[TEF]) was studied, due to the very high solubility of the [TEF] salts. In this case, two **B**:Ag[TEF] ratios (2:1 and 1:1) were used to be able to compare the outcome of these reactions to similar ones based on the diphosphorus analogue **A** (Scheme 1). These reactions were performed in CH_2Cl_2 and subsequently layered with *n*-pentane. The 2:1 ratio reaction afforded compound **5** and the 1:1 reaction produced compound **6** in yields of 60 and 71 %, respectively. Compounds **5** and **6** were selectively isolated from their corresponding crude reaction mixtures as red crystals, showing air and light stability in the solid state. Their single-crystal X-ray structure analysis reveals composition ratios of 5:3 (for **5**) and 4:3 (for **6**) of **B**:Ag[TEF]. In contrast, such reactions with the complex **A** yielded the dimer **2** and the one-dimensional coordination polymer (**3**). Both compounds, **5** and **6**, represent unprecedented Ag^{I} trimers with the formulas $[Ag_3(\mu,\eta^2$-**B**$)_2(\mu,\eta^1{:}\eta^2$-**B**$)_3][TEF]_3$ and $[Ag_3(\mu,\eta^1{:}\eta^2$-**B**$)_4][TEF]_3$, respectively.

Compounds **5** and **6** crystallize in the monoclinic space groups $P2_1/n$ and $P2_1/c$, respectively. The central structural motif of **5** consists of a bent trinuclear Ag_3 chain while it shows an almost equilateral Ag_3 triangle in **6** (Figure 4). In **5**, these Ag^{I} ions are stabilized by five Mo_2As_2 ligands **B** with two of them showing an η^2-coordination mode and three others a $\mu,\eta^2{:}\eta^1$-coordination. Interestingly, one of these bridging ligands **B** connects all the three Ag^{I} ions, Ag1, Ag2 and Ag3, while the other two ligands **B** connect each only the Ag1 and Ag2 ions. Additionally, the intermetallic Ag···Ag distances in **5** (2.8376(3)–2.9053(3) Å) are significantly shorter than the sum of the van der Waals radii for two silver atoms (3.44 Å), indicating the possible existence of argentophilic interactions.[16] As a consequence, all the Ag^{I} ions in **5** show different coordination environments: Ag1 is hexacoordinated to five As atoms and one Ag^{I} ion, Ag2 is heptacoordinated to five As atoms and two Ag^{I} ions and Ag3 is tetracoordinated to three As atoms and one Ag^{I} ion. The Ag_3 core in **6** is stabilized by four bridging Mo_2As_2 ligands **B**, each showing an $\eta^2{:}\eta^1$-coordination. All Ag^{I} ions in **6** show different coordination spheres: Ag3 is heptacoordinated to five As atoms and two Ag^{I} ions, Ag2 is hexacoordinated to four As atoms and two Ag^{I} ions and Ag1 is pentacoordinated to three As atoms and two Ag^{I} ions. The intermetallic Ag···Ag distances in **6** range between 2.858(2) and 2.980(1) Å and are also within the range of argentophilic interactions.[16] The As—As bond lengths in **5** (2.321(1)–2.458(3) Å) and **6** (2.378(5)–2.409(5) Å) are elongated compared to those in the non-coordinated complex **B** (2.312(3) Å).[13a] The Ag—As bond lengths are in the range of (2.438(1)–3.123(1) Å) and (2.573(8)–2.989(8) Å), respectively.

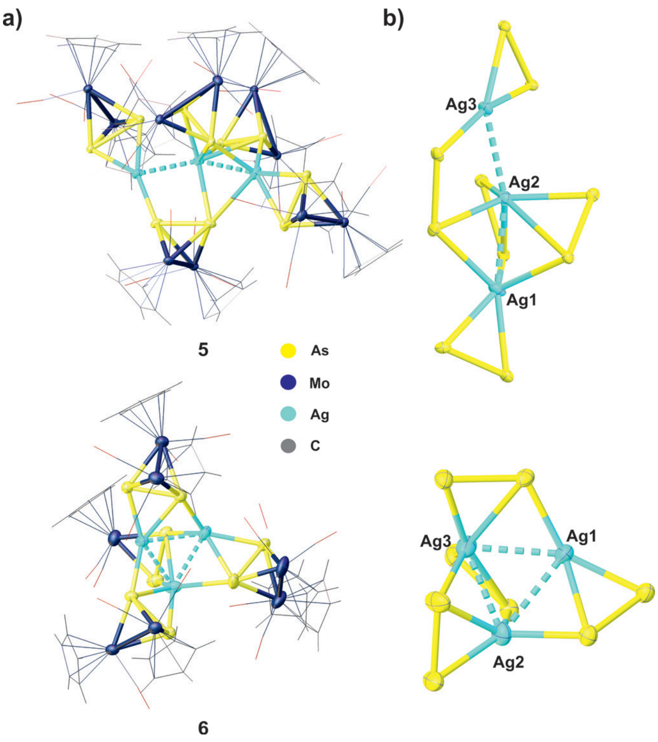


Figure 4. a) Molecular structures of the supramolecular assemblies **5** and **6** in the solid state. Counter anions are omitted for clarity. b) Structures of the cationic fragments in **5** and **6** showing the Ag—As cores.

Compounds **4**–**6** are well soluble in common organic solvents such as CH_2Cl_2 and CH_3CN, little soluble in THF and insoluble in *n*-pentane. Their ^{1}H and ^{13}C{^{1}H} NMR spectra in CD_3CN at room temperature show signals typical for Cp and CO ligands. In the ESI mass spectra in CH_3CN, peaks for the cations $[Ag(\mathbf{B})_2]^+$ and $[Ag(\mathbf{B})(CH_3CN)]^+$ are mainly detected in the positive ion mode and a peak for the [TEF] or the [FAl] anions in the negative ion mode. These data indicate that only a partial dissociation of the assemblies **4**–**6** occurs in solutions of CH_3CN. The solid state IR spectra of **4** show each three strong broad absorptions between 1921 and 2048 cm^{-1}, while those of **5** and **6** show each two absorptions between 1942 and 1980 cm^{-1}, attributable to the stretching vibrations of the CO ligands in the coordinated ligand units **B**. These vibrations appear at lower energies as compared to those reported for the free complex **B** (1900 and 1949 cm^{-1}).[13a]

In summary, we synthesized the first homoleptic complexes (**4**–**6**) of the tetrahedral diarsene complex Mo_2As_2 (**B**) and Ag^{I} ions. In so doing, the potential of **B** as a connector in supramolecular chemistry stabilizing short Ag···Ag distances was demonstrated for the first time. By using various stoichiometric ratios of the starting materials and changing the counteranion, a variety of solid-state Ag^{I} coordination compounds stabilized by four or five of these ligand complexes is selectively accessible. The solid-state structures of these products allow for a comparison to corresponding P-containing derivatives obtained from similar reactions using the lighter analogue P_2 complex **A** as a building block. The 2:1 stoichiometric ratio reactions of the Mo_2P_2 ligand complex (**A**) and Ag[FAl] or Ag[TEF] afforded the Ag^{I} dimers **1** and **2**, whereas a 1:1 reaction with Ag[TEF] gave the 1D polymer **3**. Similar reactions of the Mo_2As_2 ligand complex (**B**) using similar ratios afforded products with entirely different structures (**4**–**6**). According to DFT calculations, the reactivity difference of the complexes **A** and **B** towards Ag^{I} salts originates from the difference in the donor nature of both complexes. Specifically, the As—As σ bond is better accessible for coordination to metal centers than the P—P σ bond. This σ-donation towards Ag^{I} offers the As_2 units more flexibility and promotes the formation of unprecedented dimers (**4**) and trimers as cycle (**6**) or catena (**5**) compounds showing remarkable Ag···Ag interactions. Current investigations in this field focus on three-component reactions of the complex **B** with Ag^{I} salts and N-donor organic molecules to build unprecedented supramolecular architectures with (As,N) mixed-donor ligands.

Experimental Section

Crystallographic data:

Deposition numbers 1985242, 1985244, and 1985245 (**4**, **5**, and **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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Conflict of interest

The authors declare no conflict of interest.

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