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Mixed Organometallic-Organic Hybrid Assemblies Based on the Diarsene Complex [Cp₂Mo₂(CO)₄(μ,η²-As₂)], Ag(I) salts and N-Donor Organic molecules

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Dedicated to Professor Heinrich Lang on the occasion of his 65th birthday

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Abstract: *The reaction of the organometallic diarsene complex [Cp₂Mo₂(CO)₄(η²-As₂)] (1) (Cp = C₅H₅) with Ag[Al{OC(CF₃)₃}₄] (Ag[TEF]) yielded the Ag(I) monomer [Ag(η²-1)₃][TEF] (2). This compound exhibits a dynamic behaviour in solution, a feature that allows to direct a selective synthesis of unprecedented organometallic-organic hybrid assemblies upon its reaction with N-donor organic molecules possessing a stepwise pathway, which is supported by DFT calculations. Accordingly, the reaction of 2 with 2,2´-bipyrimidine (L1) yielded the dicationic molecular compound [{(η²-1)₂Ag}₂(μ,L1)][TEF]₂ (3) or the 1D polymer [{(η²-1)Ag}(μ,L1)]ₙ[TEF]ₙ (4) depending on the ratio of the used reactants. However, its reaction with the pyridine-based linkers 4,4´-bipyridine (L2), 1,2-di(4-pyridyl)ethylene (L3) and 1,2-di(4-pyridyl)ethyne (L4) allowed the formation of the 2D polymers [{(η²-1)Ag}₂(μ,Lx)₃]ₙ[TEF]₂ₙ (Lx = L2 (5), L3 (6), L4 (7)), respectively. Additionally, this concept was extended to step-by-step one-pot reactions of 1, [Ag(CH₃CN)₃][Al{OC(CF₃)₂(CCl₃)}₄] ([Ag(CH₃CN)₃][TEFCl]) and the linkers L2-L4, producing the 2D polymers [{(η²-1)Ag}₂(μ,Lx)₃]ₙ[TEFCl]₂ₙ (Lx = L2 (8), L3 (9), L4 (10)), respectively.*

Introduction

The interest in using metal-directed self-assembly for the design of well-defined solid-state structures has remarkably increased in the past decades.[1] The majority of these compounds are obtained from the association of multitopic organic linkers featuring N-, O- or S-donor atoms with Lewis-acidic metal cations.[2] In this field, considerable attention has been devoted to Ag(I)-based supramolecular assemblies owing to their rich structural diversity and wide range of applications.[3] However, due to the flexible coordination sphere of the Ag(I) ion (it has no strong geometric preferences) and the labile Ag(I)-ligand bond, many studies showed that the coordination of organic molecules to Ag(I) is hardly predictable and often leads to the unselective formation of diverse products.[3,4] Compared to

organic molecules, the potential of organometallic compounds as connectors in supramolecular chemistry was only very limitedly investigated.[5] To close this gap, our group developed the concept of using organometallic complexes bearing "naked" polyphosphorus (Pₙ) donor atoms to link metal ions.[6] This unique approach allowed for the synthesis of a large variety of supramolecular aggregates including 1D, 2D and 3D coordination polymers (CPs),[7] fullerene-like inorganic nanospheres[8] and nanosized capsules.[9] Furthermore, this concept was expanded by introducing N-donor multitopic organic molecules to the reactions between metal ions and Pₙ ligand complexes allowing the synthesis of unique organometallic-organic hybrid CPs.[10]

Besides polyphosphorus complexes, arsenic-based organometallic complexes have been known for decades.[11] However, their coordination chemistry has been studied much less compared to that of their P analogues.[12a-d] In fact, coordination compounds of any polyarsenic ligand and Ag(I) ions are very rare.[12a,c-e] One of the simplest of such compounds is the tetrahedrane complex [Cp₂Mo₂(CO)₄(η²-As₂)] (1) (Cp = C₅H₅). This compound was first reported by Rheingold et al. almost four decades ago,[11a] however, with its coordination chemistry having been very limitedly studied[11b,13] until a short time ago. Very recently,[14] we started to investigate the coordination chemistry of 1 towards group 11 metal cations. Interestingly, this compound showed a different coordination behavior towards Ag(I) ions compared to its P-analogue and allowed for the synthesis of unique discrete polymetallic solid-state aggregates in which four or five units of 1 stabilize Ag(I) dimers and trimers as cycles or catena compounds displaying short Ag···Ag interactions.[14a] Based on these results, we became interested in pushing this research area a decisive step further by studying the possibility of designing unprecedented mixed supramolecular aggregates in which the organometallic complex 1 together with organic N-donor molecules are involved in the coordination to metal centers. Here, the question arises whether the flexible coordination modes of Ag(I) complexes can be combined with the flexibility of a σ/π-

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coordination of the organometallic complex [Cp$_2$Mo$_2$(CO)$_4$(η^2-As$_2$)] (**1**), and, in view of both challenges, can the reaction outcome be controlled and directed if linkers are added? The main challenge is to understand the possible pathway of the assembling processes in solution which allows a control of the final isolated solid-state products.

Herein, we report, experimentally and by DFT calculations, the stepwise assembling reaction of complex **1** with the Ag(I) salt of the weakly coordinating anion [Al{OC(CF$_3$)$_3$}$_4$]$^-$ ([TEF]$^-$) and the N-donor organic linkers: 2,2′-bipyrimidine (**L1**), 4,4′-bipyridine (**L2**), 1,2-di(4-pyridyl)ethylene (**L3**) and 1,2-di(4-pyridyl)ethyne (**L4**). The first step leads to the formation of a novel coordination compound of **1** and silver: [Ag(η^2-**1**)$_3$][TEF] (**2**) which is found in equilibrium in solution with the less saturated Ag(I) monomer [Ag(η^2-**1**)$_2$][TEF] and a free As$_2$ complex **1**. When this solution mixture is reacted with **L1**, a dicationic molecular organometallic-organic hybrid compound or an unprecedented helix-like one-dimensional (1D) hybrid polymer are accessible depending on the used ratio of educts. However, its reaction with the pyridine-based linkers **L2**, **L3** or **L4** allowed the selective formation of the 2D organometallic-organic hybrid polymers Furthermore, this concept was extended to a one-pot reaction of **1** with [Ag(CH$_3$CN)$_3$][Al{OC(CF$_3$)$_2$(CCl$_3$)}$_4$] ([Ag(CH$_3$CN)$_3$][TEF^{Cl}]) and the linkers **L2-L4**, yielding solely 2D polymers. Although limited simple heteroleptic Ag(I) coordination compounds possessing As- and N-donor ligands were previously reported,[12f] the obtained products are, to the best of our knowledge, the only supramolecular assemblies unifying organometallic compounds with As-donor atoms and organic N-donor linkers to coordinate at Lewis acidic metal centers.

Results and Discussion

In a first approach, complex **1** was treated with Ag[TEF] due to the very high solubility of the [TEF]$^-$ salts. This reaction was conducted using a 3:1 ratio of **1**:Ag[TEF] in CH$_2$Cl$_2$ at room temperature (Figure 1a).[15] Upon layering the crude reaction mixture with *n*-pentane, red single crystals of compound **2** were
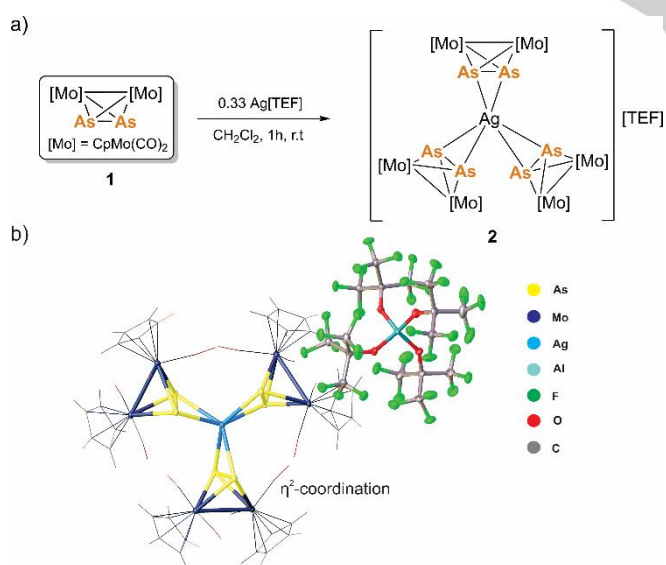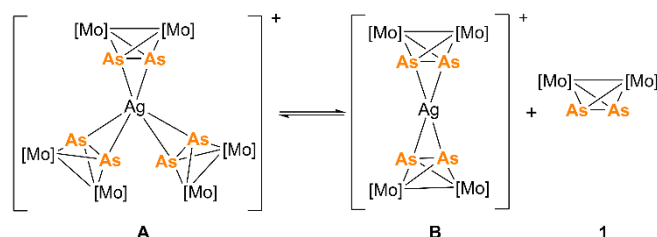
[Ag{Cp$_2$Mo$_2$(CO)$_4$(μ_3,$\eta^{2:2:2}$-As$_2$)}$_3$][TEF]. Compound **2** crystallizes in the monoclinic space group *P*2$_1$/*c*. Its Ag(I) core is surrounded by three Mo$_2$As$_2$ ligand complexes of **1** each possessing an η^2-coordination mode, thus the Ag(I) center is hexacoordinated to six As atoms. According to the CSD database,[16] only one other coordination compound in which an Ag(I) center is coordinated by six arsenic atoms has been previously reported, [Ag$_2$(Cp$^*_2$Mo$_2$(CO)$_4$(μ_2,$\eta^{3:2}$-As$_3$)$_2$(Cp$^*_2$Mo$_2$(CO)$_4$(μ_2,$\eta^{3:2:2}$-As$_3$)$_2$][TEF]$_2$ (Cp*= C$_5$(CH$_3$)$_5$),[12d] and no Ag(I) monomer stabilized by six As atoms is known to date. The As$_2$AgAs$_2$ plane-to-plane normal angles range from 71.77(3) to 108.77(3)°. As a consequence, the Ag(I) center adopts a distorted trigonal prismatic coordination sphere. The As-As bond lengths in **2** (2.3572(4)-2.3734(3) Å) are slightly elongated compared to those in the non-coordinated ligand complex **1** (2.312(3) Å).[11a] The Ag-As bond lengths in **2** range between 2.7337(3) and 2.9186(3) Å.

In an attempt to gain further insight into the species present in solutions of **2**, variable temperature ^{1}H NMR spectra were recorded. The spectrum of **2** in THF-d$_8$ at room temperature displays one sharp signal centered at 5.39 ppm, which is attributable to the protons of the Cp ligands on molybdenum. This signal is slightly downfield shifted compared to that observed in the ^{1}H NMR spectrum of the diarsene complex **1** (5.25 ppm; THF-d$_8$, room temperature), indicating that there is no full dissociation of compound **2** into the free complex **1** and Ag[TEF], otherwise both ^{1}H NMR spectra of **1** and **2** would show identical signals. By recording the ^{1}H NMR spectra of **2** at lower temperatures, the signal shifts to lower fields as the temperature is reduced, nevertheless no splitting or broadening is detected even at 180 K. This observation indicates that the signal corresponds either to an individual compound in solution (non-dissociated complex **2**) or to several species that are in a fast equilibrium even at 180 K, which could, however, not be detected within the NMR timescale. Molecular volumes of **1** (ca. 435 Å^3) and **2** (ca. 909 Å^3) in THF-d$_8$, estimated from diffusion-ordered spectroscopy (DOSY), differ significantly, thus confirming the incomplete dissociation of **2**. Moreover, the volume estimated from solutions of **2** is smaller than that obtained from DFT calculations for the cation of **2** [Ag{Cp$_2$Mo$_2$(CO)$_4$(η^2-As$_2$)}$_3$]$^+$ (**A**, 1199 Å^3) and larger than that calculated for [Ag{Cp$_2$Mo$_2$(CO)$_4$(η^2-As$_2$)}$_2$]$^+$ (**B**, 806 Å^3), which suggests that there exists a dynamic equilibrium in solutions of **2**, arising from a partial dissociation of the cations of **2** (**A**) into the cationic species **B** and **1** (Scheme 1). Furthermore, compound **2** was dissolved in THF-d$_8$ to which five more equivalents of **1** were added. The recorded room temperature ^{1}H NMR spectrum of this mixture showed one single signal at 5.28 ppm. This observation is in agreement with our suggested equilibrium in solution and implies that the excess of the As$_2$ complex **1** used did exchange

Figure 1. a) Reaction of **1** with Ag[TEF] leading to the complex **2**; b) Molecular structure of **2** in the solid state.

obtained in good yields (63%). The single-crystal X-ray structure analysis of **2** revealed an Ag(I) monomer with the general formula

Scheme 1. Proposed equilibrium for the cations of **2** in solution.

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with coordinated As$_2$ units in **B**. The recorded IR spectrum of **1** in THF shows two strong absorptions and one medium one at 1900, 1953 and 1973 cm^{-1} respectively, attributable to the stretching vibrations of the CO ligands. However, the IR spectrum of **2** in THF shows, in addition to the two strong absorptions at 1900 and 1953 cm^{-1}, an enlargement of the band at 1973 cm^{-1} and an additional strong band at 1927 cm^{-1}. In the ESI-mass spectrum of **2** in CH$_3$CN, a major peak in the cation mode for the monocation [Ag{Cp$_2$Mo$_2$(CO)$_4$(η^2-As$_2$)}$_2$]$^+$ (**B**) as well as peaks for smaller fragments were detected (for further details see ESI).

In order to check if such a proposed dissociation of **A** is thermodynamically feasible in dichloromethane solution (COSMO model)[22], DFT calculations for this process were performed on the RI[17]-/B3LYP[18]/def2-TZVP[19a-b] level of theory (ECP basis set on Ag atoms)[19c] using Turbomole[20] software (Figure 2, for further information see ESI). The calculated energy of dissociation of **A** into **B** and **1** is exothermic (-15.8 kJ·mol^{-1}). This, partially in contrast to our experimental studies, suggests nearly complete dissociation of **A** into **B** and **1** in solution of **2**. Moreover, further dissociation of **B** into smaller fragments such as [Ag{Cp$_2$Mo$_2$(CO)$_4$(η^2-As$_2$)}(CH$_2$Cl$_2$)$_2$]$^+$ (**C**) is not expected because it is an endothermic process (47.1 kJ·mol^{-1}, Scheme 2). Thus, taking into account these DFT calculations in addition to all the above described experimental observations, we suggest that

A and **B** are the only cationic species present in solutions of **2** (Scheme 1).

With the intention of studying **2** as a suitable precursor for the synthesis of organometallic-organic hybrid CPs, we focused, in a first attempt, its reaction with 2,2´-bipyrimidine (**L1**). This ligand was chosen from bis-chelating ligands due to its small size and rigidity. Considering that the η^2-coordinated units of **1** in **2** can be viewed as bis-chelating ligands (because they coordinate to one metal ion with two points of attachments), the question arises whether it is possible to control a mono-substitution of **L1** molecules in **A** or **B** by such chelating donors. DFT calculations performed at the B3LYP/def2-TZVP level of theory show that the substitution of one As$_2$ ligand **1** in the preformed cationic complex **A** by one 2,2'-bipyrimidine molecule (**L1**) or the incorporation of one molecule **L1** in **B** leading to **D** are both exothermic (-46.5 kJ.mol^{-1} and -30.7 kJ.mol^{-1}, respectively) in solution (Figure 2). However, the substitution of a second ligand **1** by **L1** leading to **E** and the full substitution of all three ligands **1** by three molecules of **L1** leading to **F** are only slightly exothermic (-10.0 and -6.2 kJ.mol^{-1} relative to **D** and **E**, respectively). Therefore, all three processes from **A** or **B** leading to **D**, **E** and **F** might be accessible, however by a very careful choice of the used stoichiometry of the organic ligand **L1**.
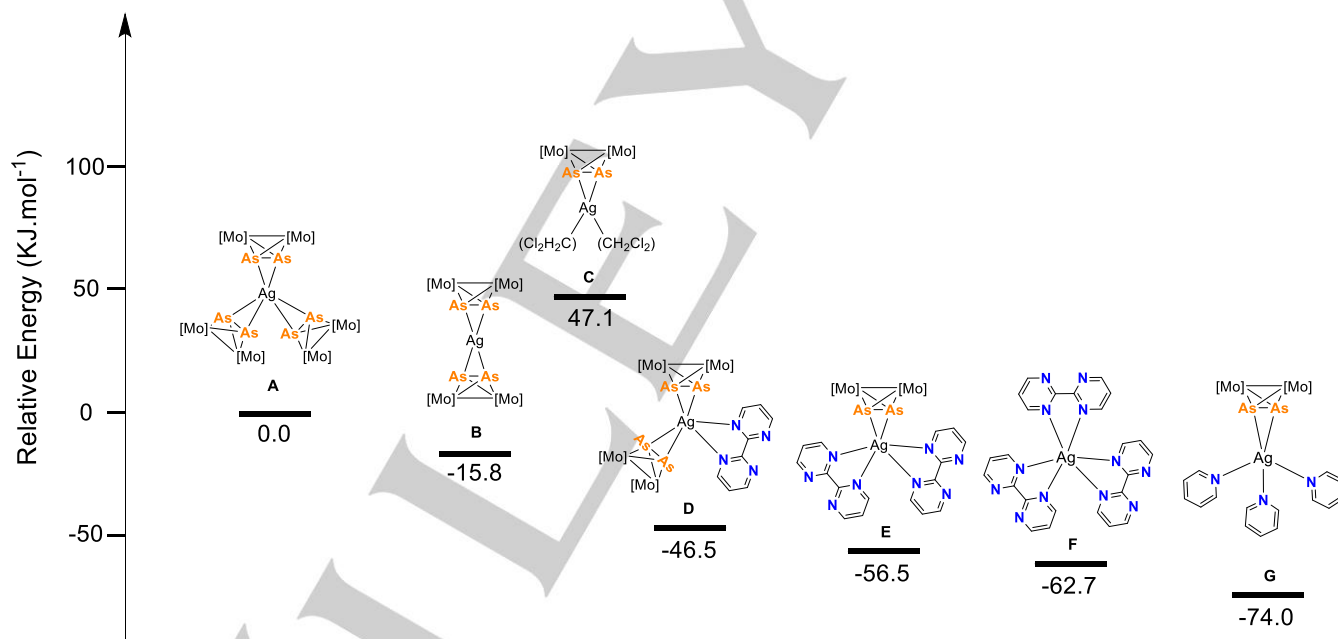
Figure 2. Energy diagram of the dissociation of complex **2** in CH$_2$Cl$_2$ and its reaction with 2,2´-bipyrimidine and pyridine calculated at the B3LYP/def2-TZVP level of theory. For the reaction energies COSMO-corrected total electronic energies were used. The positive charges are not depicted. [Mo] = CpMo(CO)$_2$.

Trusting the predictions of the DFT calculations, compound **2** was initially prepared by the reaction of the As$_2$ ligand complex **1** and Ag[TEF] and was further treated with 2,2' bipyrimidine (**L1**) using two different ratios of **2**:**L1**, 2:1 and 1:1. These reactions were performed under similar conditions (CH$_2$Cl$_2$, room temperature; Figure 3). The first reaction resulted in the formation of the coordination compound [{Cp$_2$Mo$_2$(CO)$_4$(μ$_3$,η$^{2:2:2}$-As$_2$)}$_4$(μ,η$^{1:1:1}$-**L1**)Ag$_2$][TEF]$_2$ (**3**), while the second reaction afforded the 1D organometallic-organic CP [{Cp$_2$Mo$_2$(CO)$_4$(μ$_3$,η$^{2:2:2}$-As$_2$)}(μ$_2$,η$^{1:1:1:1}$-**L1**)Ag]$_n$[TEF]$_n$ (**4**) in

moderate to good yields (68% (**3**) and 42% (**4**)). Orange crystals of **3** and **4** were obtained at room temperature from diffusion of *n*-pentane into a CH$_2$Cl$_2$ solution of **3** and **4**, respectively, and were examined by single-crystal X-ray structure analysis. The crystal structure of **3** shows a bimetallic supramolecular complex consisting of two Ag(**1**)$_2$ organometallic nodes connected to each other by one molecule of **L1** (Figure 3b). Taking into account that solutions of **2** contain both cationic species **A** and **B**. The construction of **3** corresponds to a species of **D**, with one molecule of **L1** as a bridging unit, as a result that two species of **B** have
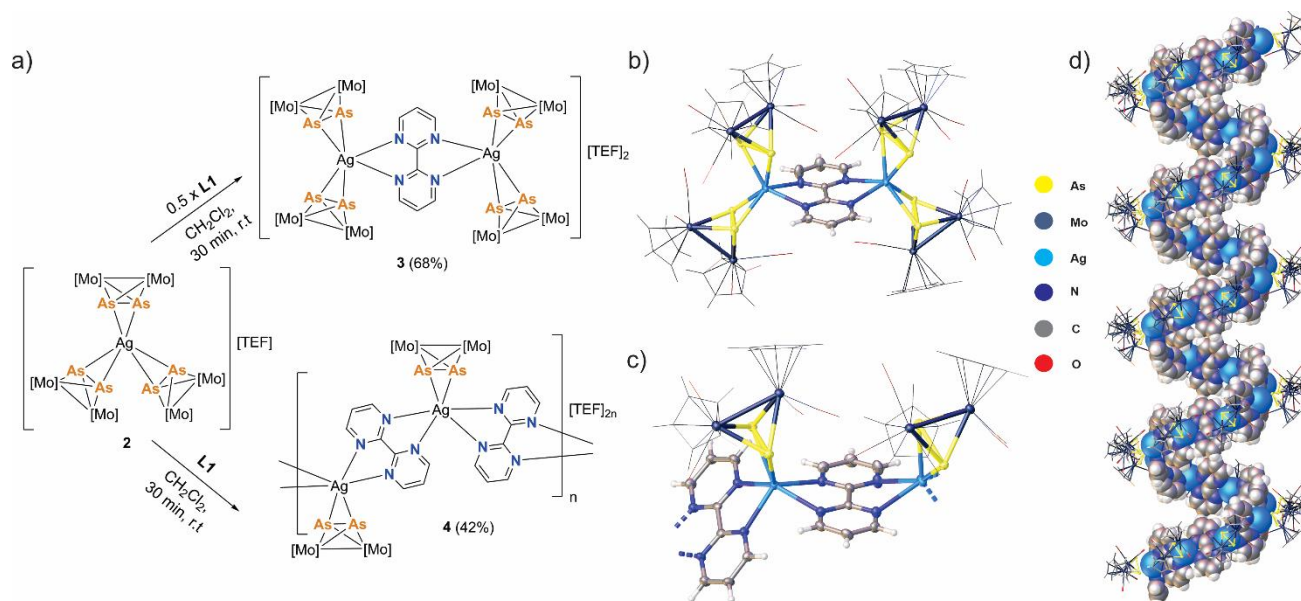
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Figure 3. a) Reaction of complex **2** with 2,2'-bipyrimidine (**L1**). Synthesis of the supramolecular compounds **3** and **4**. Yields are shown in parentheses; b) X-ray structure of the dicationic molecular complex **3**; c) Section of the 1D CP **4** in the solid state. Cp and CO ligands are shown as a wireframe; Counteranions are omitted for clarity, d) view perpendicular to the *b* axis of the 1D polymer **4** with Ag(I) ions and 2,2'-bipyrimidine molecules being shown in CPK style, counteranions have been omitted for clarity.

been formed initially in solution. The X-ray structure analysis of **4** revealed a 1D CP with organometallic Ag(**1**) nodes of **E**-type linked to the polycationic chain via the organic connectors **L1** (Figure 3c). Similarly to compounds **2** and **3**, each Ag atom in **4** has a distorted trigonal prismatic environment. Interestingly, chains of **4** are rolled into a helix, however, the unit cell contains both types of helicity (P and M helices, Figure 3d). This helical topology observed for **4** is unique in the family of organometallic-organic hybrid CPs. The As-As bond lengths in **3** (2.369(1)-2.381(1) Å) and **4** (2.381(1)-2.390(1) Å) are slightly elongated

compared to those in the non-coordinated complex **1** (As-As = 2.312(3) Å)[11a] and comparable to those in the parent complex **2** (2.3572(4)-2.3734(3) Å). The Ag-As bond lengths in **3** (2.649(1)-2.857(1) Å) and **4** (2.669(1)-2.751(1) Å) are shortened compared to those in **2** (2.7337(3)-2.9186(3) Å).

These first results prompted us to further investigate what can be modified in the reactions of **2** and N-donor ligands in order to design hybrid CPs of higher dimensionalities. The exchange of two 2,2'-bipyrimidine molecules (**L1**) by four pyridyl functions from four N-donor organic molecules on Ag(**1**) units in the 1D hybrid
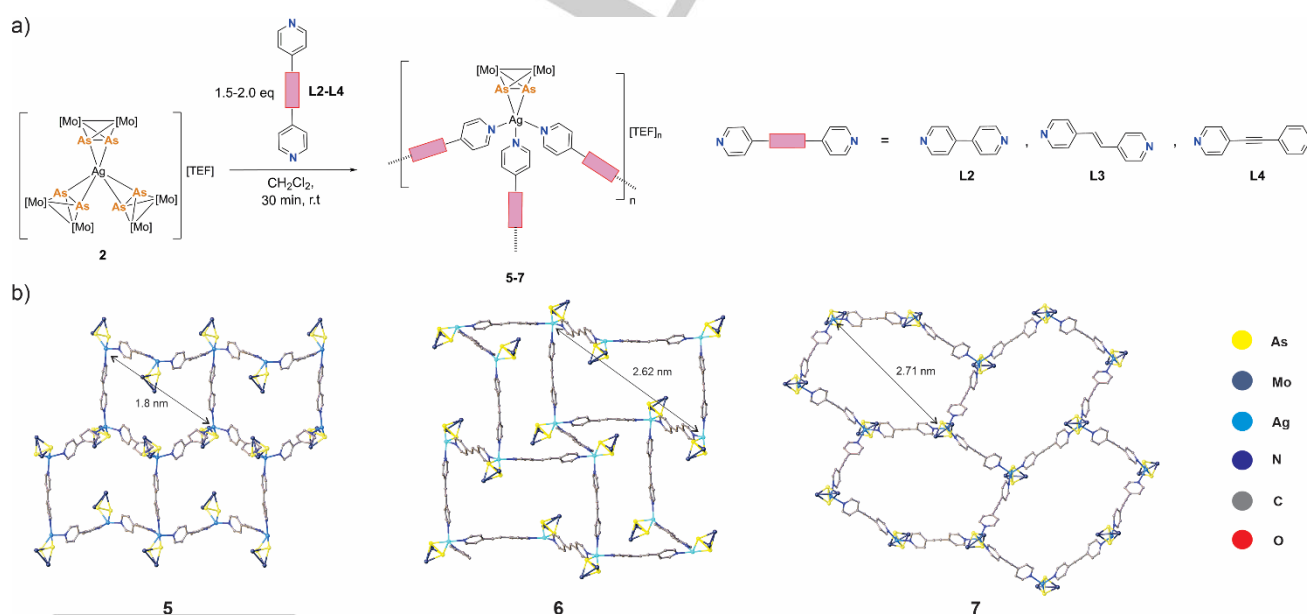

Figure 4. a) Reaction of **2** with the pyridyl-based organic linkers (**L2-L4**). Synthesis of the 2D organometallic-organic hybrid CPs **5-7**; b) Sections of the 2D cationic polymeric networks of **5-7**.[21] Counterions, Cp and CO ligands as well as H atoms are omitted for clarity.

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CP **4** would open prospects of the formation of 2D and 3D hybrid CPs. Thus, reactions of **2** with 1.5 or 2.0 equivalents of the ditopic pyridyl-based linkers **L2-L4** were carried out using reaction conditions similar to the previously mentioned ones (Figure 4a). These reactions allowed the selective formation of the complexes **5-7** of the general formula [{Cp$_2$Mo$_2$(CO)$_4$(μ_3,$\eta^{2:2:2}$-As$_2$)}$_2$(μ,$\eta^{1:1}$-**Lx**)$_3$Ag$_2$]$_n$[TEF]$_{2n}$ (**Lx = L2-L4**). Single-crystal X-ray diffraction studies revealed that compounds **5-7** are 2D organometallic-organic hybrid CPs with Ag(**1**) organometallic nodes linked to one another via three pyridyl functions from three different pyridyl-based linkers (Figure 4b). Interestingly, each Ag cation in **5-7** is coordinated to only three N atoms instead of four. The most probable rationalization of this fact is the steric clash between the backbones of the linkers preventing a fourth linker molecule from coordinating. Similar as in compounds **3** and **4**, the As-As bond lengths in **5** (2.377(1)-2.378(1) Å), **6** (2.377(1)-2.382(1) Å) and **7** (2.393(1)-2.418(1) Å) are slightly elongated compared to those of the free ligand **1** and complex **2**, whereas Ag-As bond lengths in **5-7** (2.614(1)-2.660(1) Å) are shortened compared to those in complex **2** (2.7337(3)-2.9186(3) Å). In each of the CPs **5-7**, organometallic Ag(**1**) units form the vertices of the 2D honey-comb network. In the crystal packing, the interstitial space between the layers of networks is occupied by anions and solvent molecules with the dimensions of the meshes of maximum diameters being approx. 1.80 nm (**5**), 2.62 nm (**6**) and 2.71 nm (**7**).[21]

To check whether a selective formation of the 2D CPs **5-7** is attainable without a pre-isolation of compound **2** as a solid intermediate, and to investigate if the presence of species **B** alone is enough to direct such synthesis, we performed one pot step-by-step self-assembly reactions using the initial building blocks (complex **1**, Ag[TEF] and linkers **L2-L4**). These reactions are performed by first reacting complex **1** with Ag[TEF] upon stirring for ten minutes and then adding to this mixture the corresponding ligand **Lx** (for further details see SI). Indeed, all these reactions lead to the selective formation of the CPs **5-7**. Moreover, a similar reaction of complex **1** with the more soluble salt [Ag(CH$_3$CN)$_3$][Al{OC(CF$_3$)$_2$(CCl$_3$)}$_4$] ([Ag(CH$_3$CN)$_3$][TEF^{Cl}]) in the presence of the organic linkers **L2-L4** yielded related polymers. Thus, the 2D organometallic-organic hybrid CPs **8-10** of the general formula [{Cp$_2$Mo$_2$(CO)$_4$(μ_3,$\eta^{2:2:2}$-As$_2$)}$_2$($\eta^{1:1}$-**Lx**)$_3$Ag$_2$]$_n$[TEF^{Cl}]$_{2n}$ (**Lx = L2-L4**) are obtained as orange crystalline products suitable for X-ray diffraction experiments (Figure 5a). Their crystal structures show that compounds **8-10** are 2D CPs with node-to-linkers ratios similar to those in CPs **5-7** (Scheme 5b).
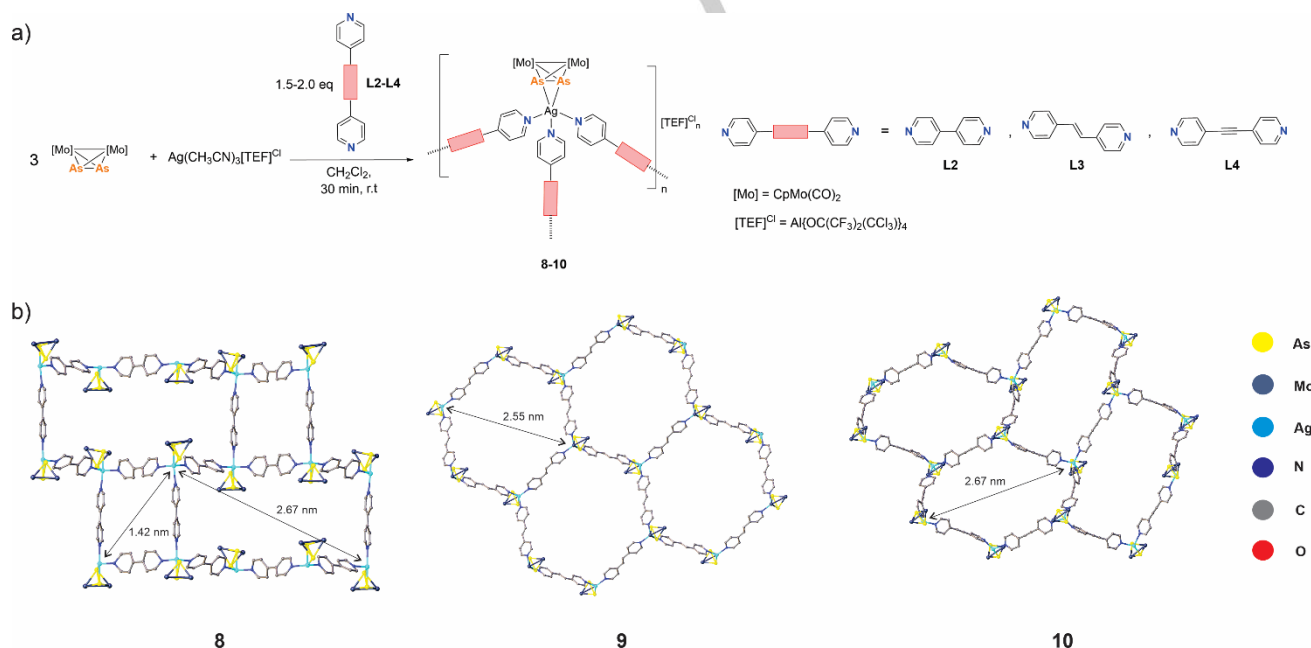

Figure 5. a) Reaction of **1** with Ag[TEF^{Cl}] and the pyridyl-based organic linkers (**L2-L4**). Synthesis of the 2D organometallic-organic hybrid CPs **8-10**; b) Sections of the 2D cationic polymeric networks of **8-10**.[21] Counterions, Cp and CO ligands as well as H atoms are omitted for clarity.

The As-As bond lengths in **8** (2.388(1)-2.403(1) Å), **9** (2.378(1) Å) and **10** (2.390(6)-2.427(6) Å) are elongated compared to the free complex **1** (As-As = 2.312(3) Å).[11a] The Ag-As bond lengths in **8** (2.590(6)-2.748(4) Å), **9** (2.659(1)-2.6783(4) Å) and **10** (2.490(4)-2.820(4) Å) are comparable to those in **5-7** (2.614(1)-2.660(1) Å). Similarly to CPs **5-7**, the organometallic nodes of CPs **8-10** form 2D honey-comb networks with meshes of a maximum dimension of 2.55 nm (**9**) and 2.67 nm (**10**).[21] Interestingly, the CPs **5-10** are obtained from the one-pot synthetic procedure regardless of whether 3:1 or 2:1 ratio of **1**: Ag[TEF] is used. The ESI mass spectra of the crude mixtures containing **1** and the Ag(I) salts as well as those of all polymers **5-10** in CH$_2$Cl$_2$ show in each case a peak in the positive ion mode for the monocation [Ag**1**$_2$]$^+$. This indicates the presence of the species **B** not only in solutions of **2**, but also in the crude solutions containing **1** and the Ag(I) salts. This reveals that the formation of the polymers **5-10** is independent of the applied reaction procedure (whether via isolation of **2** or via one-pot synthesis) as long as **B** is present as a starting material in solution. These observations may suggest that in all reactions leading to assemblies **3-10**, species **B** is the

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active precursor to react with ligands **L1**-**L4**. Finally, DFT calculations performed on a model complex **G** mimicking the silver nodes of the 2D CPs **5**-**10** indicate that its formation from the precursors **A or B** are slightly more exothermic (-74.0 kJ/mol and -58.2 kJ/mol, respectively) than that of the complexes **D**-**F** (Figure 2).

Compounds **3**-**10** 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 ^1H and $^{13}C\{^1H\}$ NMR spectra in CD_3CN at room temperature show signals typical for Cp and CO ligands as well as for the organic molecules **L1**-**L4**. The solid-state IR spectra of **3**-**10** show two to four strong broad absorptions between approx. 1920 and ca. 2000 cm^{-1}, attributable to the stretching vibrations of the CO ligands in the coordinated units **1**. These vibrations appear at higher energies as compared to those reported for the free complex **1** (1900 and 1949 cm^{-1}).

Conclusion

In conclusion, we have shown that the reaction of the diarsene complex [Cp$_2$Mo$_2$(CO)$_4$(η^2-As$_2$)] (**1**) with Ag[TEF] afforded the Ag(I) monomeric complex [Ag(η^2-**1**)$_3$][TEF] (**2**), which is the first Ag(I) monomer stabilized by six arsenic atoms. Variable temperature ^1H NMR studies, DOSY experiments, solution IR spectroscopy and ESI-MS spectrometry all suggest that **2** exhibits a dynamic behaviour in solution in which both cationic species [Ag(**1**)$_3$]$^+$ (**A**) and [Ag(**1**)$_2$]$^+$ (**B**) are present. Intermediate **B** play a decisive role in directing a selective synthesis of organometallic-organic hybrid aggregates (**3**-**7**) upon the reaction of **2** with multitopic N-donor organic molecules via a stepwise pathway, which is supported by DFT calculations. Additionally, this concept was extended to the one-pot reactions of **1**, Ag[TEF] (without isolating **2**) or [Ag(CH$_3$CN)$_3$][Al{OC(CF$_3$)$_2$(CCl$_3$)}$_4$] ([Ag(CH$_3$CN)$_3$][TEF^{Cl}]) with ditopic pyridine-based organic molecules producing 2D hybrid polymers Compounds **3**-**10** present an unprecedented family of supramolecular aggregates in which mixed organometallic As- and organic N-donor molecules are used as building blocks in combination with metal ions to build complex supramolecular structures. Current investigations in this field focus on the synthesis of neutral 2D and 3D hybrid polymers with the As$_2$ ligand complex **1** as a building block. The aim of these studies is to investigate if potential unusual properties of these compounds arise due to the presence of organometallic fragments in the formed networks. Extensive studies also involve extending this new supramolecular approach to complexes [Cp$_2$Mo$_2$(CO)$_4$($\eta^{2:2}$-E$_2$)] featuring the heavier homologs Sb and Bi.

Acknowledgements

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Organometallic-organic aggregates
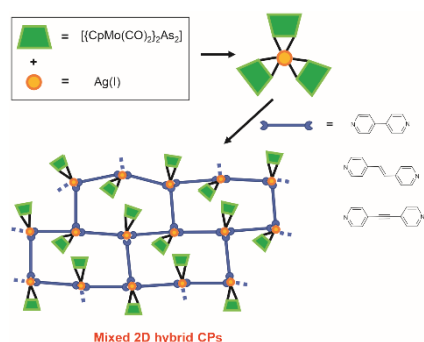
The Ag(I) monomer [Ag{[Cp$_2$Mo$_2$(CO)$_4$(η^2-As$_2$)]}$_3$][TEF] ([TEF] = [Al{OC(CF$_3$)$_3$}$_4$]) is obtained from the reaction of the organometallic diarsene complex {[Cp$_2$Mo$_2$(CO)$_4$(η^2-As$_2$)]} with Ag[TEF]. In solution, this compound is found to be in an equilibrium with another monomeric species [Ag{[Cp$_2$Mo$_2$(CO)$_4$(η^2-As$_2$)]}$_2$][TEF] exhibiting a less saturated Ag(I) center. This solution mixture reacts with a variety of ditopic pyridine-based organic linkers to afford selectively unprecedented 2D organometallic-organic hybrid assemblies, among them a helix-like 1D structure.