

Supramolecular Chemistry

Mixed Organometallic–Organic Hybrid Assemblies Based on the Diarsene Complex $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu, \eta^2\text{-As}_2)]$, Ag^{I} Salts and N-Donor Organic Molecules

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

Abstract: The reaction of the organometallic diarsene complex $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\eta^2\text{-As}_2)]$ (**1**) with $\text{Ag}[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ ($\text{Ag}[\text{TEF}]$) yielded the Ag^{I} monomer $[\text{Ag}(\eta^2\text{-1})_3][\text{TEF}]$ (**2**). This compound exhibits dynamic behavior in solution, which allows directed selective synthesis of unprecedented organometallic–organic hybrid assemblies upon its reaction with N-donor organic molecules by a stepwise pathway, which is supported by DFT calculations. Accordingly, the reaction of **2** with 2,2'-bipyrimidine (**L1**) yielded the dicationic molecular compound $[\{(\eta^2\text{-1})_2\text{Ag}\}_2(\mu\text{-L1})][\text{TEF}]_2$ (**3**) or the 1D

polymer $[\{(\eta^2\text{-1})\text{Ag}\}(\mu\text{-L1})_n][\text{TEF}]_n$ (**4**) depending on the ratio of the reactants. However, its reactions with the pyridine-based linkers 4,4'-bipyridine (**L2**), 1,2-bis(4-pyridyl)ethylene (**L3**) and 1,2-bis(4-pyridyl)ethyne (**L4**) allowed the formation of the 2D polymers $[\{(\eta^2\text{-1})\text{Ag}\}_2(\mu\text{-Lx})_3][\text{TEF}]_{2n}$ [**Lx** = **L2** (**5**), **L3** (**6**), **L4** (**7**), respectively]. Additionally, this concept was extended to step-by-step one-pot reactions of **1**, $[\text{Ag}(\text{CH}_3\text{CN})_3][\text{Al}\{\text{OC}(\text{CF}_3)_2(\text{CCl}_3)_3\}_4]$ ($[\text{Ag}(\text{CH}_3\text{CN})_3][\text{TEF}^{\text{Cl}}]$) and linkers **L2–L4** to produce the 2D polymers $[\{(\eta^2\text{-1})\text{Ag}\}_2(\mu, \text{Lx})_3][\text{TEF}^{\text{Cl}}]_{2n}$ [**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 increased remarkably 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 has been investigated only to a very limited extent.^[5] To close this gap, we developed the concept of using organometallic complexes bearing “naked” polyphosphorus (P_n) ligands to link metal ions.^[6] This 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 into the reactions between metal ions and P_n 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 than that of their P analogues.^[12a–c] In fact, coordination compounds of any polyarsenic ligand and Ag^{I} ions are very rare.^[7e, 12a, d, e] One of the simplest of such compounds is the tetrahedrane complex $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\eta^2\text{-As}_2)]$ (**1**). This compound was first reported by Rheingold et al. almost four decades ago,^[11a] but studies on its coordination chemistry were very limited^[11b, 13] until a short time ago. Recently,^[14] we started to investigate the coordination chemistry of **1** towards group 11 metal cations. Interestingly, this compound showed a different coordina-

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tion behavior towards Ag^{I} ions compared with 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 cyclic or catena compounds displaying short $\text{Ag}\cdots\text{Ag}$ interactions.^[14a] Because of these results, we became interested in studying the possibility of designing unprecedented mixed supramolecular aggregates in which the organometallic complex **1** and 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 σ/π coordination of the organometallic complex $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\eta^2\text{-As}_2)]$ (**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 assembly processes in solution to allow control of the final isolated solid-state products.

Herein, we report experimental and DFT studies on the stepwise assembly reaction of complex **1** with the Ag^{I} salt of the weakly coordinating anion $[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$ ($[\text{TEF}]^-$) and the N-donor organic linkers: 2,2'-bipyrimidine (**L1**), 4,4'-bipyridine (**L2**), 1,2-bis(4-pyridyl)ethylene (**L3**) and 1,2-bis(4-pyridyl)ethyne (**L4**). The first step led to the formation of a coordination compound of **1** and silver, namely $[\text{Ag}(\eta^2\text{-1})_3][\text{TEF}]$ (**2**), which is in equilibrium in solution with the less-saturated Ag^{I} monomer $[\text{Ag}(\eta^2\text{-1})_2][\text{TEF}]$ and free As_2 complex **1**. When this solution mixture reacts with **L1**, a dicationic molecular organometallic-organic hybrid compound or an unprecedented helix-like 1D hybrid polymer is accessible, depending on the ratio of starting materials. However, its reaction with the pyridine-based linkers **L2**, **L3** or **L4** allowed the selective formation of 2D or organometallic-organic hybrid polymers. Furthermore, this concept was extended to one-pot reactions of **1** with $[\text{Ag}(\text{CH}_3\text{CN})_3][\text{Al}\{\text{OC}(\text{CF}_3)_2(\text{CCl}_3)\}_4]$ ($[\text{Ag}(\text{CH}_3\text{CN})_3][\text{TEF}^{\text{Cl}}]$) and linkers **L2**–**L4**, which yielded solely 2D polymers. Although limited simple heteroleptic Ag^{I} coordination compounds having As- and N-donor ligands were previously reported,^[12e] 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

First, complex **1** was treated with $\text{Ag}[\text{TEF}]$ due to the very high solubility of the $[\text{TEF}]^-$ salts. This reaction was conducted with a 3:1 **1**: $\text{Ag}[\text{TEF}]$ ratio in CH_2Cl_2 at room temperature (Figure 1a).^[15] On layering the crude reaction mixture with *n*-pentane, red single crystals of compound **2** were obtained in 63% yields. The single-crystal X-ray structure analysis of **2** revealed an Ag^{I} monomer with the general formula $[\text{Ag}\{\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu_3, \eta^{2:2:2}\text{-As}_2)\}_3][\text{TEF}]$. Compound **2** crystallizes in the monoclinic space group $P2_1/c$. Its Ag^{I} core is surrounded by three Mo_2As_2 ligand complexes of **1**, each of which has an η^2 coordination mode; thus, the Ag^{I} center is sixfold coordinated to six As atoms. According to the CSD database,^[16] only one other coordination compound in which an Ag^{I} center is coordi-

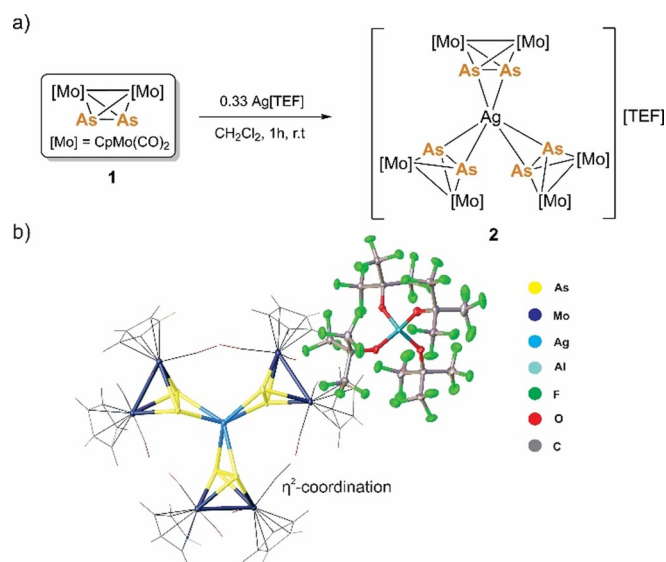


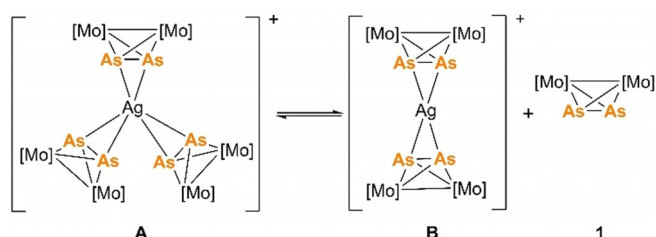
Figure 1. a) Reaction of **1** with $\text{Ag}[\text{TEF}]$ leading to complex **2**. b) Molecular structure of **2** in the solid state.

nated by six arsenic atoms has been previously reported, namely $[\text{Ag}_2(\text{Cp}^*\text{Mo}_2(\text{CO})_4(\mu_2, \eta^{3:2}\text{-As}_2)_2(\text{Cp}^*\text{Mo}_2(\text{CO})_4(\mu_2, \eta^{3:2}\text{-As}_2)_2)][\text{TEF}]_2$ ($\text{Cp}^* = \text{C}_5(\text{CH}_3)_5$)^[12c] and no Ag^{I} monomer stabilized by six As atoms is known to date. The As_2AgAs_2 plane-to-plane normal angles range from 71.77(3) to 108.77(3) $^\circ$. 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.

To gain further insight into the species present in solutions of **2**, variable-temperature ^1H NMR spectra were recorded. The spectrum of **2** in $[\text{D}_8]\text{THF}$ 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 ^1H NMR spectrum of diarsene complex **1** (5.25 ppm; $[\text{D}_8]\text{THF}$, room temperature), indicating that there is no full dissociation of compound **2** into free complex **1** and $\text{Ag}[\text{TEF}]$, otherwise the ^1H NMR spectra of **1** and **2** would show identical signals. On recording the ^1H NMR spectra of **2** at lower temperatures, the signal shifts to lower fields with decreasing temperature, but 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 Å³) and **2** (ca. 909 Å³) in $[\text{D}_8]\text{THF}$, estimated by diffusion-ordered spectroscopy (DOSY), differ significantly, and thus confirm 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**, $[\text{Ag}\{\text{Cp}_2\text{Mo}_2(\text{CO})_4(\eta^2\text{-As}_2)\}_3]^+$ (**A**, 1199 Å³), and larger than that calculated for $[\text{Ag}\{\text{Cp}_2\text{Mo}_2(\text{CO})_4(\eta^2\text{-As}_2)\}_2]^+$ (**B**, 806 Å³), which suggests that a dynamic equilibrium exists 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 $[D_8]THF$ and five more equivalents of **1** were added. The room-temperature 1H NMR spectrum of this mixture showed a single signal at 5.28 ppm. This observation is in agreement with our suggested equilibrium in solution and implies that the excess of As_2 complex **1** used did exchange 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} , 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_3CN , a major peak in the cation mode for the monocation $[Ag\{Cp_2Mo_2(CO)_4(\eta^2-As_2)\}_2]^+$ (**B**) and peaks for smaller fragments were detected (for further details, see Supporting Information).

To check whether such a proposed dissociation of **A** is thermodynamically feasible in dichloromethane solution (COSMO model),^[22] DFT calculations for this process were performed at the RI^[17]-/B3LYP^[18]/def2-TZVP^[19a,b] level of theory (ECP basis set



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

on Ag atoms)^[19c] with Turbomole^[20] software (Figure 2; for further information, see Supporting Information). 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 solutions of **2**. Moreover, further dissociation of **B** into smaller fragments such as $[Ag\{Cp_2Mo_2(CO)_4(\eta^2-As_2)\}(CH_2Cl_2)_2]^+$ (**C**) is not expected, because it is an endothermic process (47.1 $kJ\ mol^{-1}$, Figure 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 first focused on 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 attachment, the question arises whether it is possible to control mono-substitution of **L1** molecules in **A** or **B** by such chelating donors. DFT calculations at the B3LYP/def2-TZVP level of theory showed that the substitution of one As_2 ligand **1** in the preformed cationic complex **A** by one 2,2'-bipyrimidine molecule (**L1**) and the incorporation of one molecule of **L1** in **B** leading to **D** are both exothermic (-46.5 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 by a very careful choice of the amount of organic ligand **L1**.

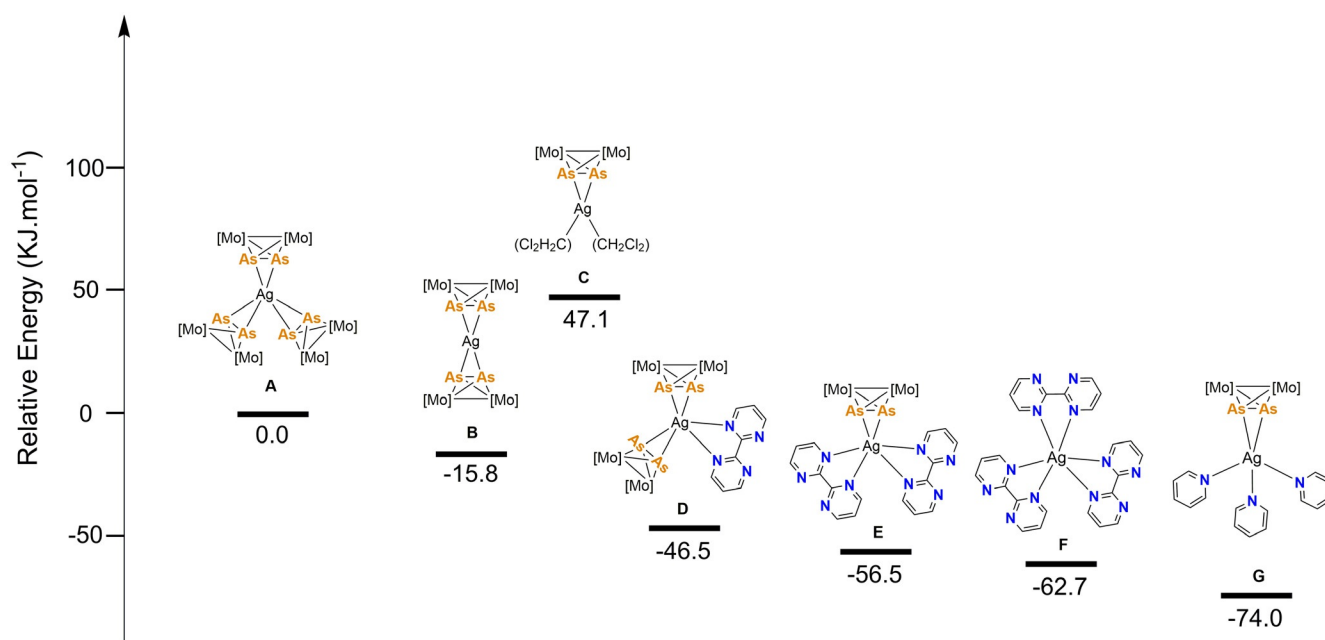


Figure 2. Energy diagram of the dissociation of complex **2** in CH_2Cl_2 and its reaction with 2,2'-bipyrimidine and pyridine, calculated at the B3LYP/def2-TZVP level of theory. For the reaction energies, COSMO-corrected total electronic energies were used. The positive charges are not depicted. $[Mo] = CpMo(CO)_2$

In accordance with the predictions of the DFT calculations, compound **2** was initially prepared by the reaction of the As₂ ligand complex **1** and Ag[TEF] and was further treated with 2,2'-bipyrimidine (**L1**) with two different ratios of **2**:**L1**, 2:1 and 1:1. These reactions were performed under similar conditions (CH₂Cl₂, room temperature; Figure 3). The first reaction resulted in the formation of the coordination compound $[\{\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu_3, \eta^{2,2,2}\text{-As}_2)\}_4(\mu, \eta^{1:1:1:1}\text{-L1})\text{Ag}_2][\text{TEF}]_2$ (**3**), while the second reaction afforded the 1D organometallic-organic CP $[\{\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu_3, \eta^{2,2,2}\text{-As}_2)\}(\mu_2, \eta^{1:1:1:1}\text{-L1})\text{Ag}]_n[\text{TEF}]_n$ (**4**) in yields of 68 and 42%, respectively. Orange crystals of **3** and **4** were obtained at room temperature by diffusion of *n*-pentane into CH₂Cl₂ solutions of **3** and **4** 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 **D** with one molecule of **L1** as bridging unit, as a result of two species **B** having been formed initially in solution. The X-ray structure analysis of **4** revealed a 1D CP with organometallic Ag(1) nodes of type **E** linked to the polycationic chain through 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, and 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 groups from four N-donor organic molecules on Ag(1) units in the 1D hybrid CP **4** would open prospects for the formation of 2D and 3D hybrid CPs. Thus, reactions of **2** with 1.5 or 2.0 equiv of the ditopic pyridyl-based linkers **L2**–**L4** were carried out under 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 $[\{\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu_3, \eta^{2,2,2}\text{-As}_2)\}_2(\mu, \eta^{1:1}\text{-Lx})_3\text{Ag}_2]_n[\text{TEF}]_{2n}$ (**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 by three pyridyl groups 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 to 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 longer than those of the free ligand **1** and complex **2**, whereas the Ag–As bond lengths in **5**–**7** (2.614(1)–2.660(1) Å) are shorter than 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 honeycomb network. In the crystal packing, the interstitial space between the layers of networks is occupied by anions and solvent molecules, and the dimensions of the meshes of maximum diameters are approximately, 1.80 (**5**), 2.62 (**6**) and 2.71 nm (**7**).^[21]

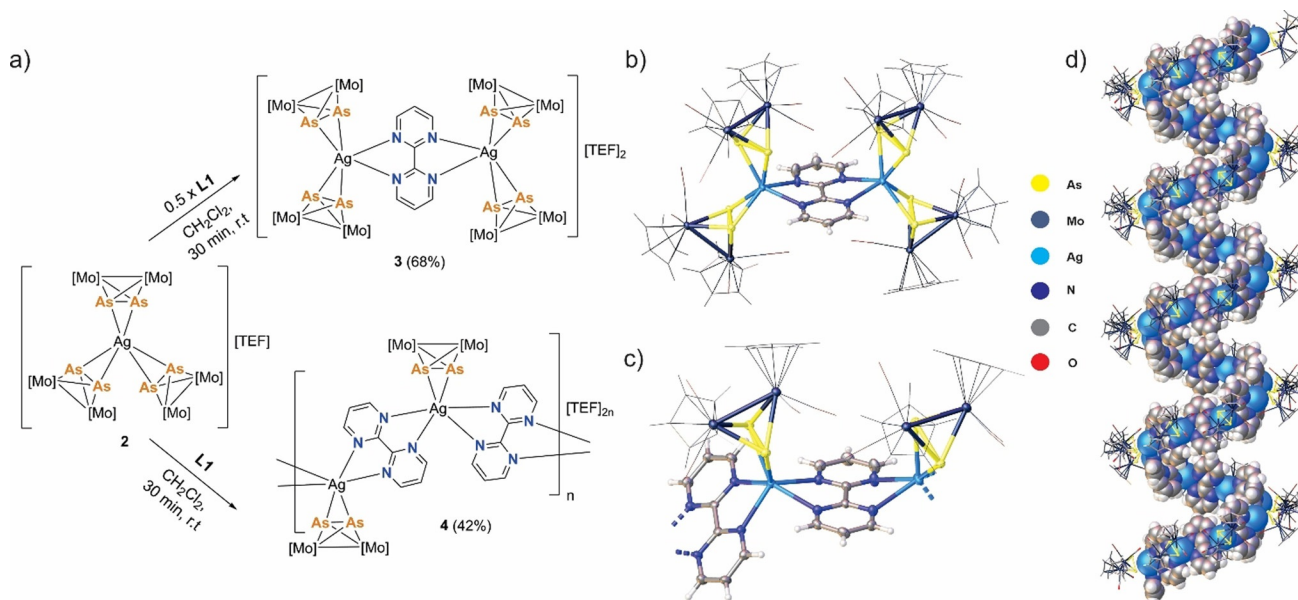


Figure 3. a) Reaction of complex **2** with 2,2'-bipyrimidine (**L1**). Synthesis of supramolecular compounds **3** and **4**. Yields are shown in parentheses. b) X-ray structure of the dicationic molecular complex **3**. c) Section of the 1D CP **4** in the solid state. Cp and CO ligands are shown as a wireframes; counteranions are omitted for clarity. d) View perpendicular to the *b* axis of the 1D polymer **4** with Ag⁺ ions and 2,2'-bipyrimidine molecules shown in CPK style; counteranions have been omitted for clarity.

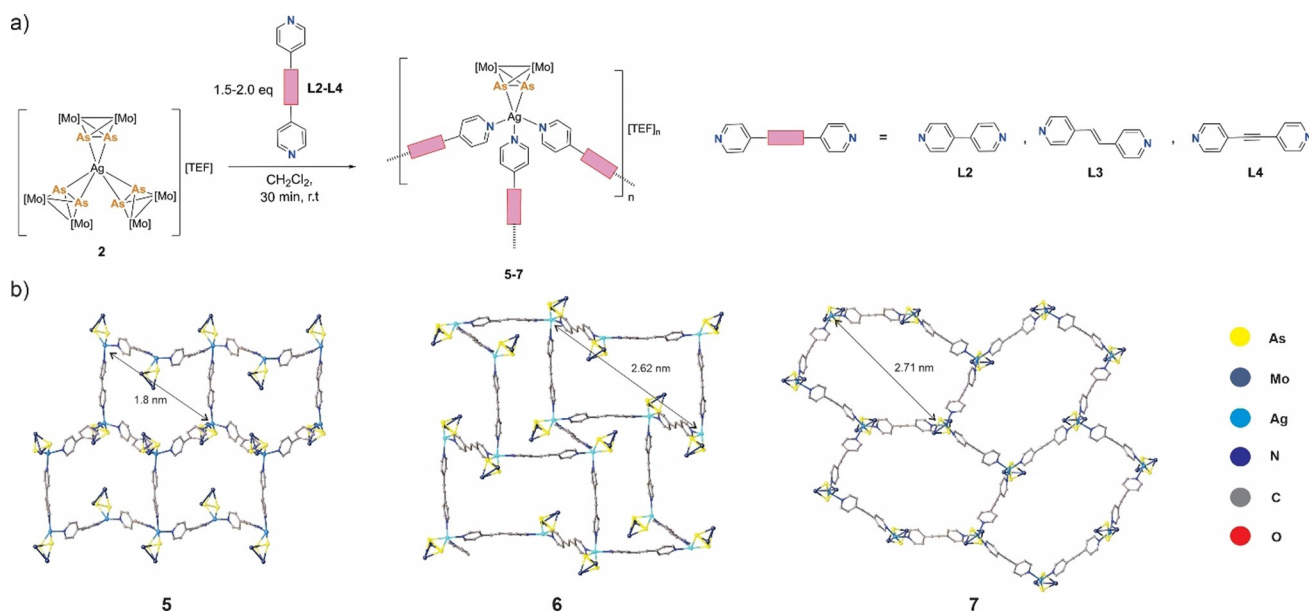


Figure 4. a) Reaction of **2** with pyridyl-based organic linkers **L2–L4**. Synthesis of the 2D organometallic-organic hybrid CPs **5–7**. b) Sections of the 2D cationic polymeric networks of **5–7**.^[21] Counterions, Cp and CO ligands as well as H atoms are omitted for clarity.

To check whether selective formation of 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 were performed by first treating complex **1** with Ag[TEF] with stirring for 10 mins and then adding to this mixture the corresponding ligand **L_x** (for further details, see Supporting Information). Indeed, all these reactions led to the selective for-

matation of CPs **5–7**. Moreover, a similar reaction of complex **1** with the more-soluble salt [Ag(CH₃CN)₃][Al{OC(CF₃)₂(CCl₃)₃}₄] ([Ag(CH₃CN)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 general formula $[\{\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu_3, \eta^{2,2,2}\text{-As}_2)\}_2(\eta^{1,1}\text{-L}_x)_3\text{Ag}_2]_n[\text{TEF}^{\text{Cl}}]_{2n}$ (**L_x** = **L2–L4**) were obtained as orange crystalline products suitable for X-ray diffraction experiments (Figure 5a). Their crystal structures show that **8–10** are 2D CPs with node-to-linker ratios similar to those in CPs **5–7** (Figure 5b).

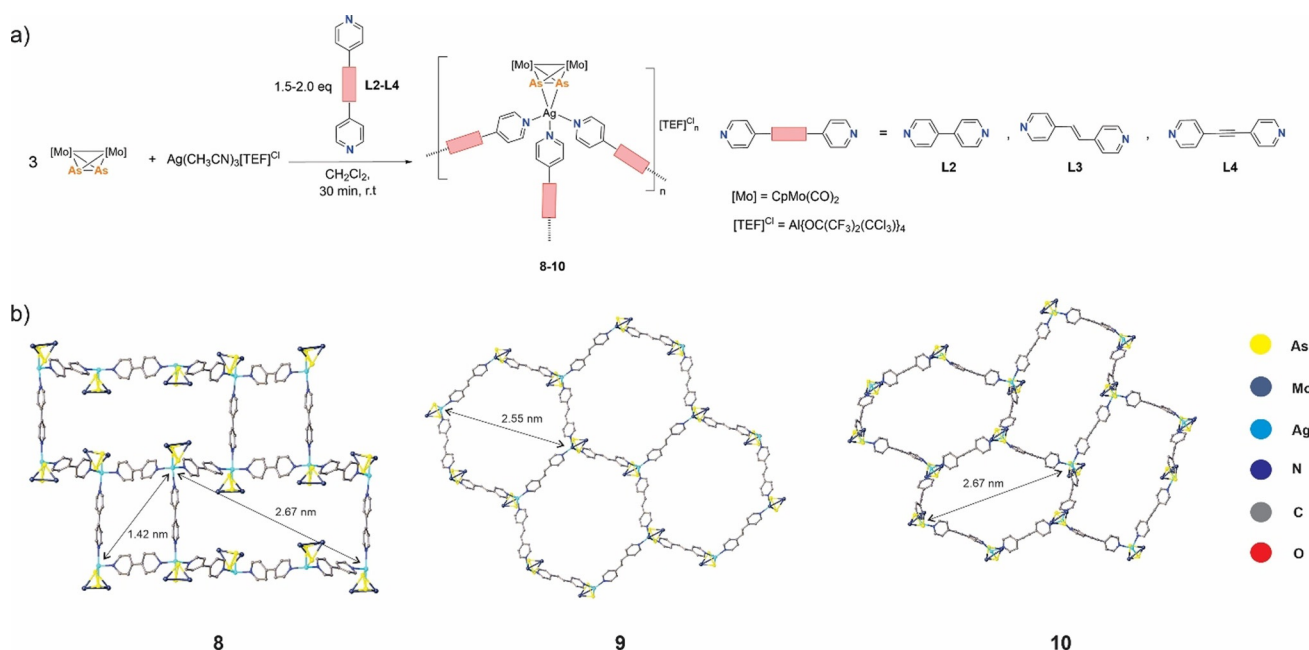


Figure 5. a) Reaction of **1** with Ag[TEF^{Cl}] and pyridyl-based organic linkers **L2–L4**. Synthesis of the 2D organometallic-organic hybrids CPs **8–10**. b) Sections of the 2D cationic polymeric networks of **8–10**.^[21] Counterions, Cp and CO ligands as well as H atoms are omitted for clarity.

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 longer than those of 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 honeycomb networks with meshes of a maximum dimension of 2.55 (**9**) and 2.67 nm (**10**).^[21] Interestingly, CPs **5–10** are obtained from the one-pot synthetic procedure regardless of whether a 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 CH₂Cl₂ 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 polymers **5–10** is independent of the applied reaction procedure (isolation of **2** or 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 active precursor that reacts with ligands **L1–L4**. Finally, DFT calculations performed on model complex **G** mimicking the silver nodes of the 2D CPs **5–10** indicated that its formation from precursor **A** or **B** is slightly more exothermic (–74.0 and –58.2 kJ mol^{–1}, respectively) than that of complexes **D–F** (Figure 2).

Compounds **3–10** are soluble in common organic solvents such as CH₂Cl₂ and CH₃CN, slightly soluble in THF and insoluble in *n*-pentane. Their ¹H and ¹³C{¹H} NMR spectra in CD₃CN 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 approximately 1920 and approximately 2000 cm^{–1}, attributable to the stretching vibrations of the CO ligands in the coordinated units **1**. These vibrations appear at higher energies than those reported for the free complex **1** (1900 and 1949 cm^{–1}).

Conclusion

We have shown that the reaction of the diarsene complex [Cp₂Mo₂(CO)₄(η²-As₂)] (**1**) with Ag[TEF] affords Ag^I monomeric complex [Ag(η²-1)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 all suggest that **2** exhibits a dynamic behavior in solution in which both cationic species [Ag(1)₃]⁺ (**A**) and [Ag(1)₂]⁺ (**B**) are present. Intermediate **B** plays a decisive role in directing selective synthesis of organometallic–organic hybrid aggregates **3–7** upon reaction of **2** with multitopic N-donor organic compounds 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(CH₃CN)₃][Al{OC(CF₃)₂(CCl₃)₄}] ([Ag(CH₃CN)₃][TEF^{Cl}]) with ditopic pyridine-based organic molecules to produce 2D hybrid polymers. Compounds **3–10** represent an unprecedented family of supramolecular aggregates in which mixed organo-

metallic 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 As₂ ligand complex **1** as a building block. The aim of these studies is to investigate whether 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 [Cp₂Mo₂(CO)₄(η²-E₂)] featuring the heavier homologues Sb and Bi.

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Conflict of interest

The authors declare no conflict of interest.

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- a) J.-Ke. Sun, X.-D. Yang, G.-Y. Yang, J. Zhang, *Coord. Chem. Rev.* **2019**, *378*, 533–560; b) J.-W. Cui, S.-X. Hou, K. V. Hecke, G.-H. Cui, *Dalton Trans.* **2017**, 46, 2892–2903; c) X.-Y. Dong, C.-D. Si, Y. Fan, D.-C. Hu, X.-Q. Yao, Y.-X. Yang, J.-C. Liu, *Cryst. Growth Des.* **2016**, *16*, 2062–2073; d) X. Zhang, W. Wang, Z. Hu, G. Wang, K. Uvdal, *Coord. Chem. Rev.* **2015**, *284*, 206–235; e) C. He, D. Liu, W. Lin, *Chem. Rev.* **2015**, *115*, 11079–11108; f) J. Heine, K.-M. Buschbaum, *Chem. Soc. Rev.* **2013**, *42*, 9232–9242; g) W. L. Leong, J. J. Vittal, *Chem. Rev.* **2011**, *111*, 688–764.
- a) T. R. Cook, Y.-R. Zheng, P. J. Stang, *Chem. Rev.* **2013**, *113*, 734–777; b) S. Park, S. Y. Lee, K.-M. Park, S. S. Lee, *Acc. Chem. Res.* **2012**, *45*, 391–403; c) R. Chakrabarty, P. S. Mukherjee, P. J. Stang, *Chem. Rev.* **2011**, *111*, 6810–6918; d) F. A. Cotton, E. V. Dikarev, M. A. Petrukina, *Angew. Chem. Int. Ed.* **2001**, *40*, 1521–1523; *Angew. Chem.* **2001**, *113*, 1569–1571.
- a) M. I. Rogovoy, D. G. Samsonenko, M. I. Rakhmanova, A. V. Artem'ev, *Inorg. Chim. Acta* **2019**, *489*, 19–26; b) C. S. Rocha, L. F. O. B. Filho, A. E. De Souza, R. Diniz, A. M. L. Denadai, H. Beraldo, L. R. Teixeira, *Polyhedron* **2019**, *170*, 723–730; c) M. Dosen, Y. Kawada, S. Shibata, K. Tsuge, Y. Sasaki, A. Kobayashi, M. Kato, S. Ishizaka, N. Kitamura, *Inorg. Chem.* **2019**, *58*, 8419–8431; d) J. P. Carpenter, C. T. McTernan, T. K. Ronson, J. R. Nitschke, *J. Am. Chem. Soc.* **2019**, *141*, 11409–11413; e) J. M. Alderson, J. R. Corbin, J. M. Schomaker, *Acc. Chem. Res.* **2017**, *50*, 2147–2158; f) S. Medici, M. Peana, G. Crisponi, V. M. Nurchi, J. I. Lachowicz, M. Remelli, M. A. Zoroddu, *Coord. Chem. Rev.* **2016**, *327*, 349–359; g) T. Zhang, H.-Q. Huang, H.-X. Mei, D.-F. Wang, X.-X. Wang, R.-B. Huang, L.-S. Zheng, *J. Mol. Struct.* **2015**, *1100*, 237–244; h) N. Kishi, M. Akita, M. Kamiya, S. Hayashi, H.-F. Hsu, *J. Am. Chem. Soc.* **2013**, *135*, 12976–12979; i) H.-Y. Bai, J. Yang, B. Liu, J.-F. Ma, W.-Q. Kan, Y.-Y. Liu, Y.-Y. Liu, *CrystEngComm* **2011**, *13*, 5877–5884; j) R. Lin, J. H. K. Yip, *Inorg. Chem.* **2006**, *45*, 4423–4430; k) S. Hiraoka, K. Harano, M. Shiro, M. Shionoya, *Angew. Chem. Int. Ed.* **2005**, *44*, 2727–2731; *Angew. Chem.* **2005**, *117*, 2787–2791.
- A. N. Khlobystov, A. J. Blake, N. R. Champness, D. A. Lemenovskii, A. G. Majouga, N. V. Zyk, M. Schröder, *Coord. Chem. Rev.* **2001**, *222*, 155–192.
- a) L. A. Wilkinson, T. T. C. Yue, E. Masey, A. J. P. White, N. J. Long, *Dalton Trans.* **2019**, 48, 72–78; b) K. Škoch, I. Císařová, J. Schulz, U. Siemeling, P. Štěpnička, *Dalton Trans.* **2017**, 46, 10339–10354; c) K. Škoch, I. Císařová, P. Štěpnička, *Inorg. Chem. Commun.* **2017**, *84*, 234–236; d) K.

- Škoch, F. Uhlík, I. Císařová, P. Štěpnička, *Dalton Trans.* **2016**, *45*, 10655–10671.
- [6] a) K. H. Whitmire, *Coord. Chem. Rev.* **2018**, *376*, 114–195; b) M. Scheer, *Dalton Trans.* **2008**, 4372–4386.
- [7] a) M. Elsayed Moussa, M. Fleischmann, E. V. Peresyphkina, L. Dütsch, M. Seidl, G. Balázs, M. Scheer, *Eur. J. Inorg. Chem.* **2017**, 3222–3226; b) C. Heindl, E. Peresyphkina, D. Lüdeker, G. Brunklaus, A. V. Virovets, M. Scheer, *Chem. Eur. J.* **2016**, *22*, 2599–2604; c) M. Fleischmann, S. Welsch, E. V. Peresyphkina, A. V. Virovets, M. Scheer, *Chem. Eur. J.* **2015**, *21*, 14332–14336; d) F. Dielmann, C. Heindl, F. Hastreiter, E. V. Peresyphkina, A. V. Virovets, R. M. Gschwind, M. Scheer, *Angew. Chem. Int. Ed.* **2014**, *53*, 13605–13608; *Angew. Chem.* **2014**, *126*, 13823–13827; e) M. Scheer, L. J. Gregoriades, A. V. Virovets, W. Kunz, R. Neueder, I. Krossing, *Angew. Chem. Int. Ed.* **2006**, *45*, 5689–5693; *Angew. Chem.* **2006**, *118*, 5818–5822; f) J. Bai, A. V. Virovets, M. Scheer, *Angew. Chem. Int. Ed.* **2002**, *41*, 1737–1740; *Angew. Chem.* **2002**, *114*, 1808–1811.
- [8] a) C. Heindl, E. Peresyphkina, A. V. Virovets, I. S. Bushmarinov, M. G. Medvedev, B. Krämer, B. Dittrich, M. Scheer, *Angew. Chem. Int. Ed.* **2017**, *56*, 13237–13243; *Angew. Chem.* **2017**, *129*, 13420–13426; b) C. Heindl, E. V. Peresyphkina, A. V. Virovets, W. Kremer, M. Scheer, *J. Am. Chem. Soc.* **2015**, *137*, 10938–10941; c) M. Scheer, A. Schindler, R. Merkle, B. P. Johnson, M. Linseis, R. Winter, C. E. Anson, A. V. Virovets, *J. Am. Chem. Soc.* **2007**, *129*, 13386–13387; d) J. Bai, A. V. Virovets, M. Scheer, *Science* **2003**, *300*, 781–783.
- [9] S. Welsch, C. Gröger, M. Sierka, M. Scheer, *Angew. Chem. Int. Ed.* **2011**, *50*, 1435–1438; *Angew. Chem.* **2011**, *123*, 1471–1474.
- [10] a) M. Elsayed Moussa, E. Peresyphkina, A. V. Virovets, D. Venus, G. Balázs, M. Scheer, *CrystEngComm* **2018**, *20*, 7417–7422; b) M. Elsayed Moussa, S. Welsch, L. J. Gregoriades, G. Balázs, M. Seidl, M. Scheer, *Eur. J. Inorg. Chem.* **2018**, 1683–1687; c) M. Elsayed Moussa, S. Welsch, M. Lochner, E. V. Peresyphkina, A. V. Virovets, M. Scheer, *Eur. J. Inorg. Chem.* **2018**, 2689–2694; d) M. Elsayed Moussa, B. Attenberger, E. V. Peresyphkina, M. Scheer, *Dalton Trans.* **2018**, *47*, 1014–1017; e) M. Elsayed Moussa, M. Seidl, G. Balázs, M. Zabel, A. V. Virovets, B. Attenberger, A. Schreiner, M. Scheer, *Chem. Eur. J.* **2017**, *23*, 16199–16203; f) M. Elsayed Moussa, B. Attenberger, M. Seidl, A. Schreiner, M. Scheer, *Eur. J. Inorg. Chem.* **2017**, 5616–5620; g) M. Elsayed Moussa, B. Attenberger, M. Fleischmann, A. Schreiner, M. Scheer, *Eur. J. Inorg. Chem.* **2016**, 4538–4541; h) M. Elsayed Moussa, B. Attenberger, E. V. Peresyphkina, M. Fleischmann, G. Balázs, M. Scheer, *Chem. Commun.* **2016**, *52*, 10004–10007; i) B. Attenberger, E. V. Peresyphkina, M. Scheer, *Inorg. Chem.* **2015**, *54*, 7021–7029; j) B. Attenberger, S. Welsch, M. Zabel, E. Peresyphkina, M. Scheer, *Angew. Chem. Int. Ed.* **2011**, *50*, 11516–11519; *Angew. Chem.* **2011**, *123*, 11718–11722.
- [11] a) P. J. Sullivan, A. L. Rheingold, *Organometallics* **1982**, *1*, 1547–1549; b) K. Blechschmitt, H. Pfisterer, T. Zahn, M. Ziegler, *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 66–67; *Angew. Chem.* **1985**, *97*, 73–74.
- [12] a) C. Schwarzmaier, M. Sierka, M. Scheer, *Angew. Chem. Int. Ed.* **2013**, *52*, 858–861; *Angew. Chem.* **2013**, *125*, 891–894; b) H. Krauss, G. Balázs, M. Bodensteiner, M. Scheer, *Chem. Sci.* **2010**, *1*, 337–342; c) L. J. Gregoriades, H. Krauss, J. Wachter, A. V. Virovets, M. Sierka, M. Scheer, *Angew. Chem. Int. Ed.* **2006**, *45*, 4189–4192; *Angew. Chem.* **2006**, *118*, 4295–4298; d) D. Fenske, F. Simon, *Z. Anorg. Allg. Chem.* **1996**, *622*, 45–52; e) Effendy, F. Marchetti, C. Pettinari, R. Pettinari, B. W. Skelton, A. H. White, *Inorg. Chim. Acta* **2007**, *360*, 1388–1413.
- [13] a) M. Fleischmann, L. Dütsch, M. Elsayed Moussa, A. Schindler, G. Balázs, C. Lescop, M. Scheer, *Chem. Commun.* **2015**, *51*, 2893–2895; b) M. L. Ziegler, K. Blechschmitt, B. Nuber, T. Zahn, *Chem. Ber.* **1988**, *121*, 159–171.
- [14] a) M. Elsayed Moussa, J. Schiller, E. Peresyphkina, M. Seidl, G. Balázs, P. Shelyganov, M. Scheer, *Chem. Eur. J.* **2020**, *26*, 14315–14319; b) J. Schiller, A. Schreiner, M. Seidl, G. Balázs, M. Scheer, *Chem. Eur. J.* **2020**, *26*, 14570–14574.
- [15] The reaction of **1** with Ag[TEF] with different 1:Ag[TEF] ratios has been recently reported (ref. [14a]).
- [16] C. R. Groom, I. J. Bruno, M. P. Lightfoot, S. C. Ward, *Acta Crystallogr.* **2016**, *B72*, 171–179.
- [17] a) K. Eichkorn, O. Treutler, H. Oehm, M. Haeser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *242*, 652–660; b) K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, *97*, 119.
- [18] a) P. A. M. Dirac, *Proc. R. Soc. London Ser. A* **1929**, *123*, 714–733; b) J. C. Slater, *Phys. Rev.* **1951**, *81*, 385; c) S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200; d) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098; e) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785; f) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
- [19] a) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305; b) F. Weigend, M. Häser, H. Patzelt, R. Ahlrichs, *Chem. Phys. Lett.* **1998**, *294*, 143–152; c) D. Andrae, U. Häussermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta* **1990**, *77*, 123–141.
- [20] a) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165–169; b) O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346–354.
- [21] The diagonal distances (calculated between the Ag⁺ ions minus twice the ionic radius of Ag⁺ ions for coordination number four) do not represent the size of the cavities, but the span of the network, which is used for the comparison between the networks and for their description (different sizes and shapes of the meshes).
- [22] A. Klamt, G. Schürmann, *J. Chem. Soc. Perkin. Trans. 2* **1993**, 799–805.

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