Three-component reactions of the organometallic diarsene complex \([\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu_2-\text{As}_2)]\) (B) (\(\text{Cp} = \text{C}_5\text{H}_5\)) with AgPF\(_6\) in the presence of different N-donor linkers are presented. Depending on the organic linker used, discrete \([[\text{Ag}_2(\text{L})_2(\text{L})_2]]\)PF\(_6\) (1) and \([[\text{Ag}_2(\text{L})_2(\text{L})_2]]\)PF\(_6\) (2) organometallic-organic hybrid assemblies and polymeric \([[\text{Ag}_2(\text{L})_2(\text{L})_2]]\)PF\(_6\) (3), \([[\text{Ag}_2(\text{L})_2(\text{L})_2]]\)PF\(_6\) (4), \([[\text{Ag}_2(\text{L})_2(\text{L})_2]]\)PF\(_6\) (5) and \([[\text{Ag}_2(\text{L})_2(\text{L})_2]]\)PF\(_6\) (6) ones are obtained. 4–6 possess unique structures in which Ag:Ag interactions occur.

The design and study of Ag(i) complexes represent an interesting research area because of their rich structural diversity and wide range of applications especially in anti-cancer activities.\(^1\) This diversity is, on the one hand, due 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.),\(^1,2\) and, on the other hand, to its ability to coordinate a variety of multitiopic organic ligands bearing mainly N-, O-, S- or P- and, to a lesser extent, Se-, C-, As- or mixed-donor atoms.\(^3\) However, only few examples of organometallic building blocks have been used as ligands to stabilize Ag(i) and other coinage metal ions.\(^4\) Due to the lack of such investigations, our group focused on studying the potential of organometallic polyphosphorus (P\(_n\)) and polyarsenic (As\(_n\)) complexes with flexible coordination modes as connectors between metal ions.\(^5\) This novel approach allowed for the synthesis of a large variety of discrete and extended supramolecular aggregates including 1D, 2D and 3D coordination polymers (CPs),\(^6\) inorganic nanospheres,\(^7\) and nanosized capsules.\(^8\) Furthermore, we investigated the possibility of conducting reactions in which both organic molecules and organometallic complexes are used together to link metal centers.\(^9,10\) Within this field, the most studied compound is the diphosphorus complex \([\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu_2-P_2)]\) (\(\text{Cp} = \text{C}_5\text{H}_5, \text{A}\)).\(^10\) Its reactions with Ag(i) or Cu(i) salts in the presence of a variety of ditopic N-donor linkers allowed for the formation of unprecedented solid-state organometallic-organic hybrid polymers.\(^11\) Interestingly, such reactions with Ag(i) ions can be performed in two ways: (i) either in one-step three-component reactions by mixing all starting materials under certain experimental conditions\(^11\) or (ii) in two-step reactions in which the first step involves the preparation of a preorganized precursor composed of Ag(i) ions and the P\(_2\) ligand complex and the second step comprises the reaction of this precursor with the N-donor organic molecules.\(^11,12\)

More recently, we became interested in studying the supramolecular chemistry of similar molybdenum complexes bearing unsubstituted heavier homo- and heterodiatomic group 15 elements as connectors between metal ions.\(^12\) For example, the diarsene complex \([\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu_2-\text{As}_2)]\) (B)\(^13\) was reacted with the Ag(i) salt of the weakly coordinating anion \([\text{Al}2\text{OC(CF}_3)_3\text{]}_2\)]\(^-\) ([TETF])\(^2-\) allowing the synthesis of first coordination compounds \([\mu_2-\text{As}_2][\text{Al}2\text{OC(CF}_3)_3\text{]}(\text{TETF})\] and \((\mu_2-\text{As}_2)[\text{Al}2\text{OC(CF}_3)_3\text{]}(\text{TETF})\), containing \([\text{Ag}(\text{Al}2\text{OC(CF}_3)_3\text{]}(\text{TETF})\] units stabilized by organometallic bichelating ligands.\(^12\) Within these compounds, complex B was found to possess either an \(\eta^2\)- or an \(\eta^1\)-coordination mode. These results were particularly interesting considering the fact that similar reactions from the P\(_2\) analogue complex A and Ag(TETF) yield totally different products: the Ag(i) dimers of the general formula \([\text{Ag}_2(\text{Al}2\text{OC(CF}_3)_3\text{]})(\eta^2-\text{P}_2)](\text{TETF})\] or the 1D polymer \([\text{Ag}_2(\mu_1-\text{As})_2(\eta^1-\text{As}_2)](\text{TETF})\).\(^14\) The accessibility of these products from two-component reactions raises the question whether it would be possible to execute three-component reactions of complex B with Ag(i) ions in the presence of N-donor organic molecules. In fact, the adaptive coordination sphere of Ag(i) includes both an \(\eta^1\)- and an \(\eta^2\)-coordination mode. Hence, it would be possible to execute three-component reactions of complex B with Ag(i) ions, which allows for the formation of unprecedented solid-state organometallic-organic hybrid polymers.\(^11\)
(L1), 1,2-di(4-pyridyl)ethyne (L2), 2,2'-bipyrimidine (L3), 1,3-di(4-pyridyl)propane (L4) and 4,4'-bipyridine (L5) (by following the approach (i)) allows for the synthesis of the novel dicatonic molecular organometallic-organic hybrid complexes \([(\eta^3-B)AgL_2]\) (L1)\([PF_6]_2\) (1) and \([(\eta^3-B)AgL_2][PF_6]_2\) (2), the new one-dimensional (1D) organometallic-organic hybrid polymer \([(\eta^3-B)AgL_3][PF_6]_2\) (3) as well as the unique 1D organometallic-organic hybrid polymers \([(\eta^3-B)AgL_4][PF_6]_2\) (4), \([(\eta^3-B)AgL_5][PF_6]_2\) (5) and \([(\eta^3-B)AgL_6][PF_6]_2\) (6). Compounds 4–6 are, to the best of our knowledge, the first supramolecular assemblies containing ditopic As- and N-donor ligands to connect Ag(1) centers.

The reaction of the As2 ligand complex B with 0.5 equivalents of AgPF6 and 0.5 equivalents of 1,2-di(4-pyridyl)ethylene (L1) in a 1:1 mixture of CH2Cl2:CH3CN at room temperature, followed by a slow diffusion of pentane, leads to the selective formation of compound 1 as dark red crystals in excellent yields (74%) suitable for X-ray diffraction studies (Scheme 1 and Fig. 1a). By using 1,2-di(4-pyridyl)ethyne (L2) instead, product 2 becomes accessible as red crystals in 66% yield. Compounds 1 and 2 crystallize in the triclinic space group P1. Both compounds consist of two \([AgB_2]^{2+}\) fragments that are connected to each other with one molecule of the linkers L1 or L2, respectively, via the free coordination sites at the Ag(i) ions. Within the \([AgB_2]^{2+}\) units, the two As2 ligand complexes B are coordinated in an \(\eta^3\)-coordination mode to the Ag(i) atoms. This coordination mode of B has recently been found to be attributable to a donation through the As–As \(\sigma\) bond.12 The coordination sphere of each of the two Ag(i) atoms in 1 and 2 is completed by an N atom from one bridging ligand L1 and L2, respectively. The As–As bond lengths in 1 and 2 range between 2.373(1) and 2.386(1) Å, thus being slightly elongated compared to those in the non-coordinated complex B (2.312(3) Å).13 Their Ag–As bond lengths are in the range of 2.676(5)–2.764(6) Å. Interestingly, compounds 1 and 2 are the only isolated products regardless of how much excess of the ligand complex B or of the linkers L1 and L2 is used in the reactions.

The reaction of the As2 ligand complex B with AgPF6 and 2,2'-bipyrimidine (L3) under similar reaction conditions resulted in the 1D coordination polymer (CP) 3 (Scheme 1 and Fig. 1b). Compound 3 crystallizes in the monoclinic space group P21/c as red blocks in a good yield (40%). The 1D chain structure of 3 consists of \([AgB]^{+}\) organometallic nodes instead of \([AgB_2]^{2+}\) moieties as observed in compounds 1 and 2. This ratio of Ag(i):B is also different from that of the used starting materials (1:2). Surprisingly, more free sites are available on the Ag(i) centers in 3 which allow to coordinate two organic spacers L3 instead of one as in 1 and 2. Within each organometallic node to each Ag(i) atom, the As2 ligand complex B is coordinated through an \(\eta^3\)-coordination mode. In addition,

**Scheme 1** Reaction of B with AgPF6 and the linkers L1–L5. Synthesis of the coordination compounds 1–6. (i) Used solvent ratio of CH2Cl2:CH3CN = 1:1; (ii) used solvent ratio of CH2Cl2:CH3CN = 8:2; yields are given in parentheses.
four N atoms are also coordinated, resulting in a distorted trigonal prismatic coordination environment of the Ag(I) centers (The NAgN plane to plane angle is 83°). Moreover, compounds 4 and 5 were obtained by reacting complex B and AgPF6 with the linkers 1,3-di(4-pyridyl)propane (L4) and 4,4′-bipyridine (L5) respectively, as orange crystals in moderate yields (35%(4), 22%(5)). Both compounds crystallize in the triclinic space group P1. Their X-ray structures present 1D CPs interestingly composed of similar organometallic nodes (Fig. 1f). These nodes consist each of two Ag(I) atoms in close contact to each other with intrametallic Ag···Ag distances in 4 (2.97(4) Å) and 5 (2.98(4) Å). These distances are significantly shortened compared to the sum of the van der Waals radii for two Ag(I) atoms (3.44 Å), demonstrating the possible existence of argentophilic interactions.15 These two Ag(I) atoms are connected to each other by two bridging As2 ligands, each possessing an η1:η1-coordination mode. Such a coordination mode is attributed to two types of donations from each ligand B: (i) one donation via the As-As σ bond (η1), and (ii) another donation through the lone pair of one As atom (η1).12 Each Ag(I) atom is additionally coordinated by one CH3CN solvent molecule and one molecule of the linkers L4 (in 4) and L5 (in 5) through one of its pyridyl functions. Thus, unique organometallic [Ag2B(CH3CN)3]+ units are found to be linked to each other via the organic linkers L4 (in 4) and L5 (in 5), respectively (Fig. 1c and d). Compound 4 shows a cis arrangement of the CH3CN molecules coordinated to the Ag(I) centers, while compound 6 shows a trans arrangement. Upon using an excess of L4 and L5 in reactions leading to 4 and 5, respectively, no further substitution of the CH3CN ligands by L4 (in 4) or L5 (in 5) is observed and only the initially obtained polymers 4 and 5 were isolated. Thus, a further extension of the polymers to a higher dimensionality was not possible.

Due to the fact that these CH3CN molecules were captured from the CH3CN solvent used, we performed the reaction leading to compound 5 by using, however, a different solvent mixture CH3CN : CH2Cl2 (2 : 8) in order to decrease the amount of available CH3CN molecules in the reaction medium.16 In this case, compound 6 is formed instead as red single crystals (57% yield). The organometallic fragment in 6 consists of [Ag2B]+ units instead of [Ag2B2]+ units that are present in 5 (Fig. 1g). Within these units, two As2 ligands are found to each adopt an η1:η1-coordination mode (similar to 5), while the third one adopts a unique η1:η1-coordination. Just as observed in compound 5, either two neighboring organometallic nodes are connected to each other via one molecule L5. However, unlike 5, no CH3CN molecules are found to be coordinated to Ag(I) centers in 6. Interestingly, the Ag···Ag distance in 6 (2.787(6) Å) is found to be shorter than in 5, also proposing possible argentophilic interactions. Considering the structural features of 1–6, and also previously published coordination aggregates built only of B and Ag(i), it becomes evident that bridging As2 ligands towards Ag(i) ions has a high potential to stabilize short Ag···Ag distances by bringing the Ag(i) centers in close proximity to each other. These distances are found to decrease with an increased number of As2 ligands B around the Ag(i) centers.

Compounds 1–6 are well soluble in CH3CN, weakly soluble in CH2Cl2 and THF and insoluble in toluene and n-pentane.
Their room temperature $^1$H and $^{13}$C{H} NMR spectra show signals attributed to the proton and carbon nuclei of the ligand complex B and the corresponding organic molecules. The ESI mass spectra in CH$_3$CN show mainly peaks in the positive ion mode for the monocations [Ag$B$]$,^+$, [AgB(CH$_3$CN)]$,^+$ and [Ag$[B]^+$, revealing no complete dissociation of assemblies 1–6 in solution. The solid-state IR spectra of 1–6 exhibit two or three CO bands between 1905 and 1983 cm$^{-1}$, which are shifted to higher wavenumbers as compared to the uncoordinated ligand complex B (1900, 1949 cm$^{-1}$).$^{13}$

Conclusions

In summary, we presented the first three-component reactions of the diarsene complex [Cp$_2$Mo$_2$(CO)$_4$($\eta^1$-$\eta^3$-$\eta^1$-$\eta^1$)-As$_2$] [B] and the monovalent Ag(I) salt AgPF$_6$ in the presence of the organic N-donor linkers L1–L5. These reactions lead to the synthesis of unprecedented discrete (1,2) and polymeric (3–6) organometallic-organic supramolecular aggregates. The derivatives 4–6 are the only known infinite assemblies built from a mixture of polytopic As- and N-donor linkers to coordinate Ag(I) centers. In addition, the organometallic nodes in compounds 4–6 are each composed of two Ag(I) atoms in close contact revealing argentophilic interactions. The flexible coordination modes of the As$_2$ ligand complex B ($\eta^1$-$\eta^3$-$\eta^1$-$\eta^1$) and $\eta^1$-coordination modes observed in these compounds leads to such variety of organometallic nodes within the formed complexes. Current investigations in this field focus on reactions of tri- and tetratopic N-donor molecules with complex B and Ag(I) salts, attempting to build unique 3D assemblies as a new class of organometallic-organic MOF-like materials. Another direction in our efforts to obtain 2D and 3D aggregates involves the usage of the highly soluble Ag(I) salts Ag[Al(O$_6$C$_3$)$_4$]$_3$ and Ag[Al(O$_6$C$_5$)$_3$(C$_6$F$_3$)$_3$]$_3$, respectively. Based on our knowledge for the respective P$_2$ ligand complex A, these salts tend to result in higher dimensional structures.

Conflicts of interest

There are no conflicts to declare.

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Notes and references


16 Excluding the use of CH$_3$CN is not possible due to the limited solubility of the formed product in CH$_2$Cl$_2$.