

Versatile Coordination of Ag^I and Cu^I Ions towards *cyclo*-As₅ Ligands

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Dedicated to Professor Werner Thiel on the occasion of his 60th birthday

Abstract: The reactions of the *cyclo*-As₅ complex [Cp*Fe(η⁵-As₅)] (**B**) with the Ag^I and Cu^I salts of the weakly coordinating anion (WCA) [FAI{OC₆F₁₀(C₆F₅)₃}][−] ([FAI][−]) are studied. These reactions allow the synthesis of the mono-nuclear complexes [M(η⁵:η²-B)₂][FAI] (M = Ag (**1**), Cu (**2**)) when a ratio of B/M(FAI) 2:1 is used. Compound **1** shows an unusual disorder of the central Ag^I cation between two π-coordinating *cyclo*-As₅ ligands, which is absent in **2** pointing to a weak interaction of the Ag center towards the *cyclo*-As₅ ligands in **B**. When the ratio of B/Ag(FAI) is changed to 3:1 or 1:1, the respective coordination compounds [Ag(η²-B)₃][FAI] (**3**) and [Ag₂(η²:η²-B)₂][FAI]₂ (**4**) are accessible. The coordination modes of the *cyclo*-As₅ units in **1**, **3** and **4** are all different, reflecting the adaptive coordination behavior of **B** towards Ag^I ions. The optimized geometries in the gas phase of **1–4** are determined by DFT calculations to support the bonding situation observed in their solid-state structures.

can be viewed as a benchmark.^[3] In the following decades, the reactivity of this compound towards strong oxidants and reductants,^[4] nucleophiles,^[5] metal centers^[6] and many more^[7] was thoroughly investigated. By far the most interesting research area involving the use of this compound is its supramolecular chemistry.^[8] This is due to its flexible coordination behavior towards metal centers which allowed for the formation of a large variety of supramolecular assemblies including coordination polymers (CPs), fullerene-like spherical aggregates, nano-bowls and nano-sized capsules. Although the all-arsenic analog [Cp*Fe(η⁵-As₅)] (**B**) was isolated only four years later, in 1990,^[9] its coordination chemistry compared to **A** has only been limitedly investigated so far. The Scherer group reported the reaction of **B** with the 16-valence-electron (VE) complex fragment [Cp*Rh(CO)]₂ and the 12 VE fragments [M(CO)₃] (M = Cr, Mo).^[10] The resulting products contain the ligand **B** possessing either an η⁵- or an η²-coordination. Our group also showed that the reaction of **B** with Cu(I) halides leads to the formation of 1D polymeric compounds.^[11] These polymers are built up by the π-coordination of the *cyclo*-As₅ ring to (Cu(halide))_n moieties forming discrete units, which are additionally linked by weak intermolecular As/Cu σ-interactions. Moreover, it was demonstrated that complex **B** can be forced to adopt a σ-coordination mode towards Cu(I) ions by sterical shielding of the metal center in the trinuclear complex [Cu₃(μ-Cl)₂(dpmp)]⁺ (dpmp = bis(diphenylphosphinomethyl) phenylphosphine).^[12] A while ago, we became further interested in investigating the donor ability of this compound towards monocations bearing weakly coordinating anions (WCAs) which mimic pseudo-gas phase conditions.^[13] Accordingly, we showed that compound **B** donates via a bridging η⁵:η¹-coordination mode with the very weak and soft Lewis acid Ti(I) bearing the WCA [Al{OC(CF₃)₃}][−].^[14] However, by only increasing the size of the anion to [FAI{OC₆F₁₀(C₆F₅)₃}][−] ([FAI][−]), a change of the coordination of **B** is observed and only the η⁵-coordination towards Ti(I) remains.

These results reveal the adaptive coordination behavior of complex **B** towards metal ions and raise the question as to which solid state structures can be obtained by reacting it with the Ag(I) ion, which is known to have a more flexible coordination sphere compared to Ti(I).^[15] Furthermore, the comparison to the Cu(I) coordination might be desirable because these coinage metals frequently yielded different supramolecular assemblies when reacted with organometallic

Since the first general introduction of the isolobal analogy as a bridge between organometallic and organic chemistry by Hoffmann,^[1] this concept has had a great impact on the development of many areas of inorganic, organometallic and coordination chemistry.^[2] In this context, the preparation of the all-phosphorus analog of the well-known Cp ligand in the complex [Cp*Fe(η⁵-P₅)] (**A**) by Scherer and co-workers in 1986

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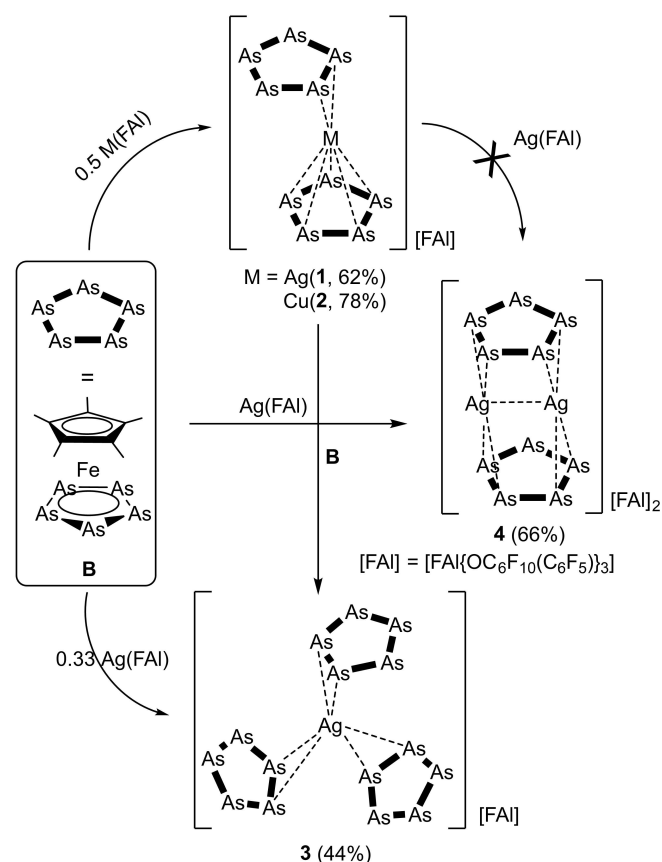
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polyphosphorus and polyarsenic complexes. Herein we report on the reaction of **B** with Ag[FAl] using different molar ratios experimentally and by DFT calculations. Depending on the ratio of Ag[FAl]:**B** used (1:2, 1:3, 1:1), different coordination compounds $[\text{Ag}(\eta^5\text{-}\mathbf{B})_2][\text{FAl}]$ (**1**), $[\text{Ag}(\eta^2\text{-}\mathbf{B})_3][\text{FAl}]$ (**3**) and $[\text{Ag}_2(\eta^2\text{-}\mathbf{B})_2][\text{FAl}]_2$ (**4**), respectively, with various coordination modes of the cyclo- As_5 units are obtained. The weak metal-to-ligand interaction allows for an unique notably shifted position of the central Ag atom located in between the cyclo- As_5 ligands in the solid-state structure of **1**, which is absent in the isomorphous compound $[\text{Cu}(\eta^5\text{-}\mathbf{B})_2][\text{FAl}]$ (**2**) obtained from the reaction of **B** with $[\text{Cu}(\text{CH}_3\text{CN})_{3.5}][\text{FAl}]$. The behavior in **1** is reminiscent of a remarkable ion mobility only known so far for extended solids. Interestingly, the optimized geometry of the compounds **1**–**4** in the gas phase are found to be similar to those observed in their solid-state structures.

In a first step, complex $[\text{Cp}^*\text{Fe}(\eta^5\text{-}\text{As}_5)]$ (**B**) was reacted with Ag(FAl) in CH_2Cl_2 at room temperature using a 2:1 ratio. The room temperature ^1H and $^{19}\text{F}\{^1\text{H}\}$ NMR spectra recorded from the crude reaction mixture show the presence of the Cp^* ligands of **B** and the anion $[\text{FAl}]^-$, respectively, but are not conclusive regarding the species present in solution. Upon layering the reaction mixture with *n*-pentane, dark red single crystals of compound **1** were obtained in good yield (62%, Scheme 1). The single-crystal X-ray structure analysis of **1**



Scheme 1. Reaction of complex **B** with $\text{M}(\text{FAl})$, $\text{M} = \text{Ag}, \text{Cu}$; Synthesis of the coordination compounds **1**–**4**.

(measurement at 123 K, $\text{Cu}_{\text{K}\alpha}$ radiation)^[16] revealed an Ag(I) monomer with the general formula $[\text{Ag}(\eta^5\text{-}\mathbf{B})_2][\text{FAl}]$. Compound **1** crystallizes in the triclinic space group $P\bar{1}$. The unit cell contains two independent $[\text{Ag}(\eta^5\text{-}\mathbf{B})_2][\text{FAl}]$ formula units, in which Ag is situated between two π -coordinating As_5 rings, as well as CH_2Cl_2 and *n*-pentane solvent molecules and two $[\text{FAl}]^-$ anions. Interestingly, while all light atoms of the anions as well as the solvent molecules show small ellipsoids, the central Ag atoms show pronounced oblate a.d.p. ellipsoids parallel to the As_5 planes. In order to minimize the influences of possible thermal motion, series termination effects on the residual density map next to heavy atoms and X-ray absorption, the data collection was repeated at 90 K with $\text{Mo}_{\text{K}\alpha}$ radiation.^[17] The low-temperature high-angle diffraction experiment revealed a disorder of Ag(I) cations similar to that found in several thiophosphates as for instance $\text{Ag}_7\text{Pb}(\text{PS}_4)_3$, $\text{Ag}_2\text{Ti}_2\text{P}_2\text{S}_{11}$ and $\text{Ag}_2\text{MnP}_2\text{S}_6$,^[18] minerals,^[19] and fast ionic conductors such as Ag_8SiTe_6 , $\gamma\text{-Ag}_8\text{GeTe}_6$, $\text{Ag}_7\text{Fe}_3(\text{X}_2\text{O}_7)_4$ ($\text{X} = \text{P}, \text{As}$) or Ag_7PSe_6 .^[20] Two crystallographically unique Ag atoms are located near to inversion centers between parallel $\eta^5\text{-}\text{As}_5$ rings (Figure 1a and Figure S2, for further information see Supporting Information). The anisotropic refinement of a single Ag position reveals a large positive residual density peak directly on the center of inversion while both Ag positions (symmetry equivalent) show a negative residual density (Figure 1b), which suggests a possible disorder of the Ag center. In order to describe the electron density near to the disordered Ag(I) atom, we have chosen four approaches: split atom model (Ag is split over six close positions) and anisotropic as well as first- and second-order anharmonic approximation for one (non-split) crystallographically unique Ag position. Therefore, a total of six structural models for **1** were generated^[21] (for further information see Supporting Information). The best description of the determined electron density around Ag was achieved by split positions of isotropic Ag atoms (see below). The refinement resulted in the quite satisfactory residuals of $R_1 = 0.0394$, $wR_2 = 0.0925$. Both Ag atoms were split into six independent positions until no significant residual electron density was left. The resulting complexes are shown in Figure 1c and Figure S2. It has to be emphasized that the rest of the structure determination including the *n*-pentane solvent molecule could be refined without any difficulties.

The analysis of the crystal structure of **1** suggests that the observed atomic displacement parameters of the Ag atoms are due to the contribution of various factors: *i*) the adaptive coordination mode of the cyclo- As_5 ligands in **B**, *ii*) the flexible coordination sphere of the Ag(I) ion and *iii*) the weak η^5 -coordination of ligand **B** towards the Ag(I) ion. Thus, the exchange of Ag against Cu should lead to a compound without such atomic displacements. Based on this assumption, we performed the reaction of **B** with $[\text{Cu}(\text{CH}_3\text{CN})_{3.5}][\text{FAl}]$ using similar reaction conditions as utilized for the Ag(FAl) reaction. From this reaction, single crystals of compound **2** were isolated in excellent yields (78%, Scheme 1). Compound **2** crystallizes in the triclinic space group $P\bar{1}$. Similar to what was observed for compound **1**, the unit cell in **2** contains two independent $[\text{Cu}(\eta^5\text{-}\mathbf{B})_2][\text{FAl}]$ units in which each of the Cu atoms is located

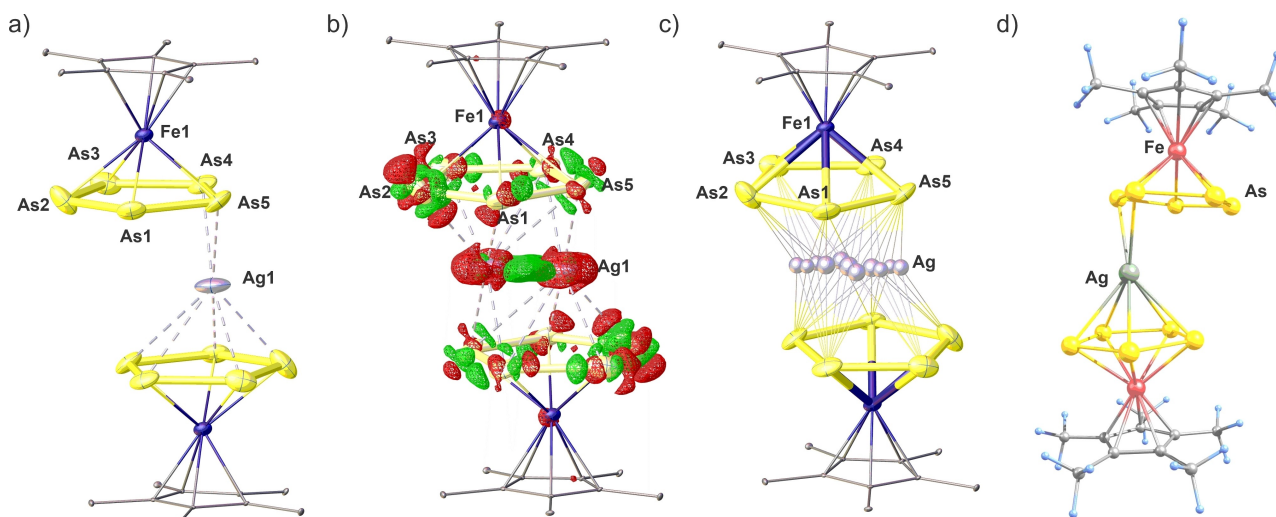


Figure 1. a) Illustration of one of the two $[\text{Ag}(\text{B})_2]^+$ complex cations showing the coordination environment of Ag1 (one of the two Ag positions is removed); b) Representation of the residual electron density map of the same complex cation. Green: positive residual density, red: negative residual density; c) Illustration of the complex cation found in the solid-state structure of compound **1** (from the same measurement as in Figure 1a, but with the refinement of the Ag atoms on split positions in an isotropic approximation). H atoms are omitted and C atoms are represented by small spheres for clarity. d) Gas-phase-optimized geometry of **1'** at the $\omega\text{B97XD}/\text{def2TZVP}$ level of theory.

between two π -coordinating As_5 rings. In contrast to the Ag compound **1**, the Cu atoms in **2** do not show ellipsoids indicative of multiple crystallographic disorder or thermal motion, but rather each Cu is clearly split over only two positions (Figure 2a). The DFT calculations performed in the gas phase at the $\omega\text{B97XD}/\text{def2TZVP}$ level of theory show that the geometry optimization of the cations $[\text{Ag}(\eta^5\text{:}\eta^2\text{-B})_2]^+$ (**1'**) and $[\text{Cu}(\eta^5\text{:}\eta^2\text{-B})_2]^+$ (**2'**) leads to a geometry in which the *cyclo*- As_5 ligands possess in each case an $\eta^5\text{:}\eta^2$ -coordination mode which is similar to that observed in the solid states of **1** and **2**

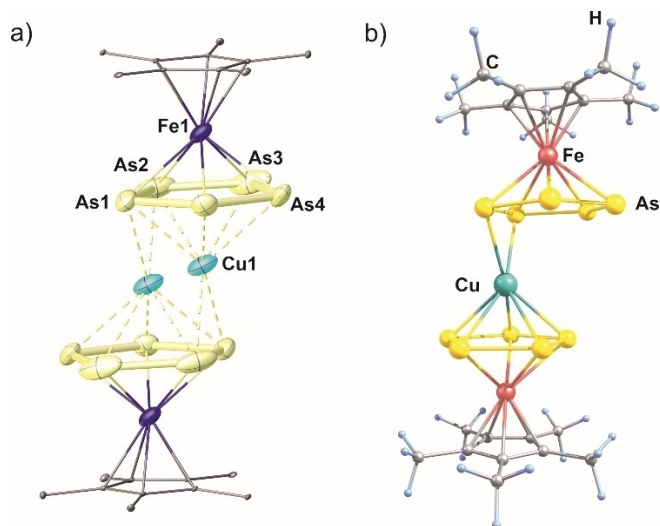


Figure 2. a) Solid-state structure of the first $[\text{Cu}(\text{B})_2]^+$ complex cation. H atoms are omitted and C atoms are represented by small spheres for clarity; b) Gas-phase-optimized geometry of **2'** at the $\omega\text{B97XD}/\text{def2TZVP}$ level of theory.

(Figures 1d and 2b) and, in some way, reminiscent of the slipped sandwich of beryllocene (Cp_2Be).

These observations raised the issue whether the synthesis of compounds with different composition ratios of **B**:Ag(FAI) might lead to other coordination modes of the *cyclo*- As_5 ligands and, as a consequence, if it is possible to achieve a stable coordination sphere around the Ag(I) center. Accordingly, we calculated the relative energies of the reaction of **B** with the Ag(I) ion leading to the cationic species $[\text{Ag}_2(\text{B})_2]^{2+}$ (**4'**), $[\text{Ag}(\text{B})_2]^+$ (**1'**) and $[\text{Ag}(\text{B})_3]$ (**3'**) comprising variable ratios of **B** and Ag(I); 1:1, 2:1 and 3:1, respectively, in order to check if such reactions are thermodynamically feasible (Figure 3).

Indeed, these reactions are calculated to be increasingly exothermic upon addition of more equivalents of **B**. This means that all processes leading to the species **4'**, **1'** and **3'** should be attainable. Interestingly, the geometry optimization of the formed species leads to geometries showing in each case *cyclo*- As_5 ligands possessing different coordination modes ($\eta^5\text{:}\eta^2$ -coordination in **1'**, η^2 -coordination in **3'** and $\eta^2\text{:}\eta^2$ -coordination in **4'**). Thus, the reaction of compound **1** with one equivalent of **B** leading to the monomeric compound **3** is exothermic ($-87.1 \text{ kJ mol}^{-1}$) in the gas phase with a subtle change of the coordination mode of the *cyclo*- As_5 ligands from $\eta^5\text{:}\eta^2$ -coordination to solely η^2 -coordination (Scheme 1, Figures 3, 1d and 4a). However, the reaction of **1** with one equivalent of Ag(FAI) leading to the dimeric complex **4** $[\text{Ag}_2(\eta^5\text{:}\eta^2\text{-B})_2][\text{FAI}]_2$ (**4**) in which the *cyclo*- As_5 ligands possess a bridging $\eta^2\text{:}\eta^2$ -coordination mode is highly endothermic ($348.3 \text{ kJ mol}^{-1}$) and therefore not accessible (Scheme 1, Figures 3, and 5a).

Experimentally, the reaction of **B** with Ag(FAI) using a 3:1 ratio of **B**:Ag(FAI) allowed for the isolation of the solid-state compound **3** in moderate yield (44%, Scheme 1, Figure 4b). Compound **3** can also be obtained from the reaction of

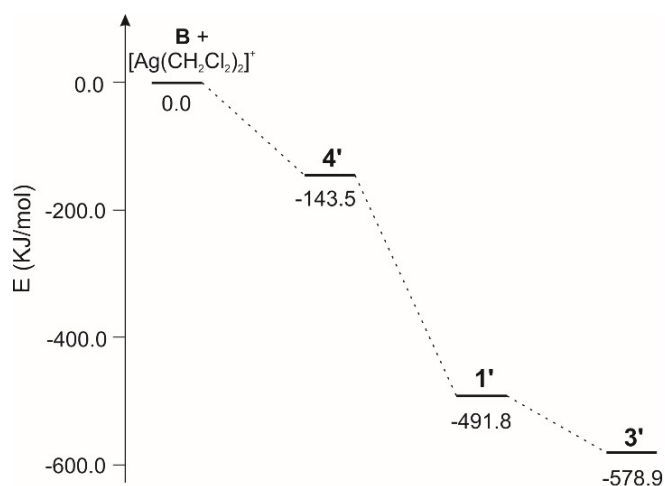


Figure 3. Energy diagram of the reaction of **B** with Ag^{I} ions.

complex **1** with one equivalent of **B**, which is in agreement with the DFT calculations in the gas phase. The X-ray diffraction study reveals that **3** crystallizes in the trigonal space group $P\bar{3}$. The cationic part of **3** shows an Ag atom stabilized by three ligands **B** each coordinating through an η^2 -coordination to form the paddle-wheel complex cations $[\text{Ag}(\eta^2\text{-B})_3]^+$. The atomic displacement parameters of the Ag atom show no peculiarities and its environment can be best described as a trigonal planar geometry created by three side-on coordinating As–As bonds. The resulting Ag–As bonds in compound **3** show very similar lengths of Ag1–As1 2.8183(6) Å and Ag1–As2 2.7719(5) Å, respectively. The π -coordinating As1–As2 bond is marginally elongated with 2.3718(7) Å compared to the remaining As–As bonds which show uniform lengths close to 2.327(6) Å, the average As–As bond length of the free ligand **B**.

Finally, compound **B** was reacted with $\text{Ag}(\text{FAI})$ in a 1:1 ratio. This reaction performed in CH_2Cl_2 at room temperature

followed by layering the crude reaction mixture with *n*-pentane allowed the isolation of compound $[\text{Ag}_2(\text{B})_2][\text{FAI}]$ (**4**) as dark red crystals in good yield (66 %, Scheme 1, Figure 5b). Compound **4** crystallizes in the triclinic space group $P\bar{1}$. The cationic part of **4** consists of an Ag(I) dimer which is stabilized by two ligand complexes **B** adopting each an unprecedented bridging $\eta^2:\eta^2$ -coordination mode of the *cyclo*-As₅ ligands. Within **4**, each Ag(I) ion is stabilized by two side-on coordinating As–As bonds. Additionally, a weak interaction probably exists between the two Ag centers due to the short Ag...Ag distance (2.88 Å) which is below the sum of their van der Waals radii.^[22] The Ag–As bonds in **4** are shorter than those found in **3** and range between 2.6477(7) and 2.7057(8) Å. The As–As bond distances (2.3334(9)–2.3951(9) Å) in **4** are comparable to those found in **3**. The geometry optimization in the gas phase of $[\text{Ag}_2(\eta^2:\eta^2\text{-B})_2]$ (**4'**) shows that the most stable geometry is the one in which the *cyclo*-As₅ ligands each possess an $\eta^2:\eta^2$ -coordination mode to Ag(I) (Figure 5a), which is in agreement with the solid state observations. The calculated Ag...Ag distance in **4'** is, however, with 2.974 Å, longer than that observed in the solid state. Attempts to synthesize compound **4** by the reaction of complex **1** with $\text{Ag}(\text{FAI})$ failed. This can probably be explained by the endothermic process in the gas phase from $[\text{Ag}(\eta^5:\eta^2\text{-B})_2]$ (**1'**) to $[\text{Ag}_2(\eta^2:\eta^2\text{-B})_2]$ (**4'**) predicted by DFT calculations. The analysis of the structural characteristics of compounds **2–4** matches well with the hypothesis that Ag(I) is weakly bound by the *cyclo*-As₅ ligands of complex **B** in compound **1**. The replacement of the Ag(I) ions by Cu(I) ions or the introduction of another equivalent of **B** or an Ag atom to **1** result in the saturation of the coordination environment of the metal center accompanied by its better localization between *cyclo*-As₅ ligands, which is evidenced by lower values of the atomic displacement parameters in comparison to those observed in **1**.

Interestingly, a similar reaction of the P-analog $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$ (**A**) with $\text{M}(\text{FAI})$ in a 2:1 ratio yields the tetranuclear $[\text{Ag}_4(\text{B})_8][\text{FAI}]_4$ and the dinuclear $[\text{Cu}_2(\text{B})_2(\text{CH}_3\text{CN})_2][\text{FAI}]_2$ complexes respectively.^[21,23] These results reveal the difference in

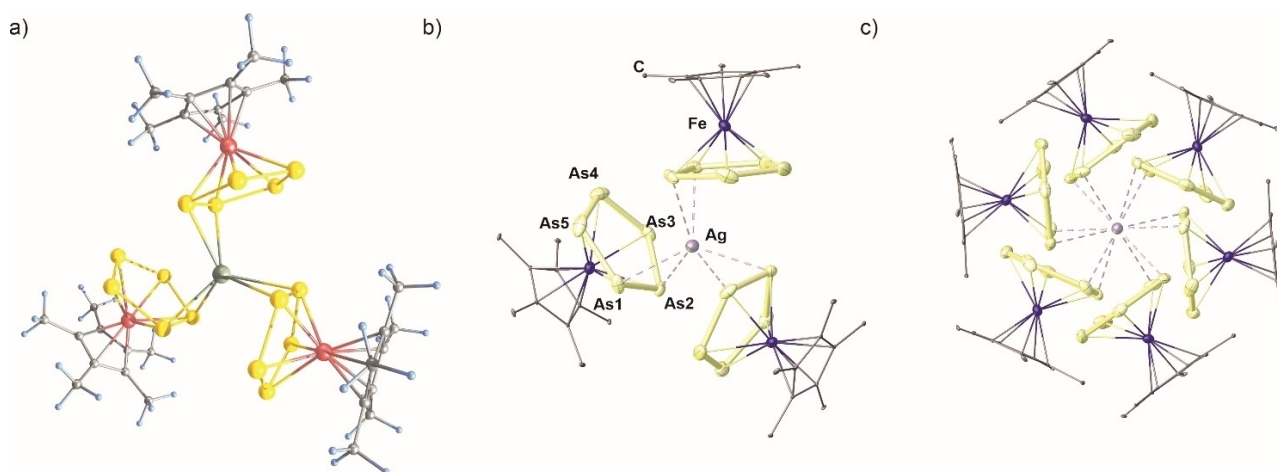


Figure 4. a) Gas-phase optimized geometry of **3'**; b) Molecular structure of the complex cation of **3** in the solid state; c) Viewing direction along the crystallographic *c*-axis of the trigonal crystal system showing the staggered arrangement of two consecutive $[\text{Ag}(\eta^2\text{-B})_3]^+$ complexes. H atoms are omitted and C atoms are represented by small spheres for clarity.

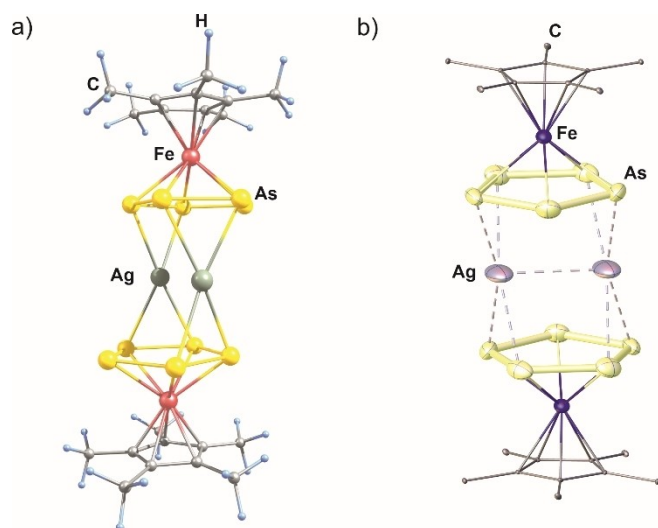


Figure 5. a) Gas-phase optimized geometry of **4**⁺; b) Molecular structure of the complex cation of **4** in the solid state. H atoms are omitted and C atoms are represented by small spheres for clarity.

the reactivity between complexes **A** and **B** and motivates the persistence of our investigations of their supramolecular chemistry for the design and characterization of new unprecedented solid-state structures.

In summary, we showed that the reaction of the *cyclo*-As₅ ligand complex **B** with Ag(FAl) or Cu(FAl) allowed for the formation of four novel homoleptic complexes of **B** and metal ions. The formation of either **1**, **3** or **4** can be controlled by using the appropriate stoichiometric ratio of **B**:Ag(FAl). Due to the flexible coordination sphere of Ag(I) and its weak coordination towards **B**, the Ag(I) center in **1** shows an unprecedented disorder between two parallel *cyclo*-As₅ ligands, which is reminiscent with the ion conducting behaviour of Ag in ion conductor solids. This phenomenon is not observed in the similar Cu(I) coordination compound **2** probably due to the stronger coordination of Cu towards **B** and the less flexible coordination sphere of Cu(I) compared to Ag(I). Additionally, within the compounds **1**, **3** and **4**, different coordination modes of the *cyclo*-As₅ units are observed revealing the adaptive coordination behavior of **B** towards Ag(I) ions. Finally, all experimental results are in line with DFT calculations performed in the gas phase. Current investigations in this field focus on performing three-component reactions of **B** with Ag(I) salts and N-donor organic linkers aiming to synthesize unprecedented supramolecular assemblies and to understand their aggregation pathways by DFT calculation.

Deposition numbers 2066857–2066859 (**1**), 2070510 (**2**), 2070511 (**3**) and 2070512 (**4**) 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.

Keywords: adaptive coordination • arsenic • copper • silver • weakly coordinating anions

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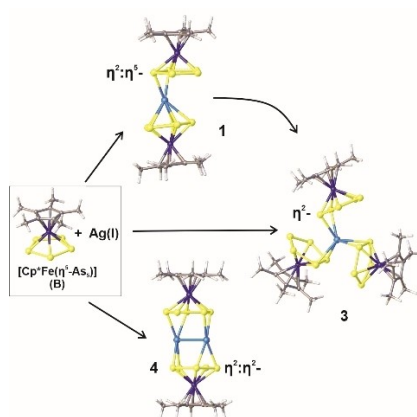
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COMMUNICATION

The first homoleptic Ag^{I} and Cu^{I} coordination compounds of the *cyclo*- As_5 complex $[(\text{Cp}^*\text{Fe}(\eta^5\text{-As}_5))]$ (**B**) are obtained from its reaction with the $\text{M}[\text{FAl}\{\text{OC}_6\text{F}_{10}(\text{C}_6\text{F}_5)_3\}_3]$ ($\text{M}(\text{FAl})$; $\text{M} = \text{Ag}, \text{Cu}$) salts. Varying the ratio of the starting materials is reflected in a diversity of the isolated supramolecular assemblies (**1**, **3**, **4**) as products. The coordination mode of the *cyclo*- As_5 units in each of **1**, **3** and **4** is different revealing the pronounced adaptive coordination of **B** towards Ag^{I} ions.



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Versatile Coordination of Ag^{I} and Cu^{I} Ions towards *cyclo*- As_5 Ligands

