Complexes of Yellow Arsenic

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Intact As_4 Tetrahedra Coordinated Side-On to Metal Cations**

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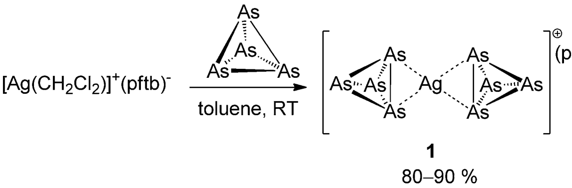
Dedicated to Professor Dieter Fenske on the occasion of his 70th birthday

In the last decades, the activation of white phosphorus by main-group elements[1] and transition metals[2] has become an area of ongoing interest in chemistry. Its heavier homologue, arsenic, is well-known for its toxicity and is mainly used as additive in metal alloys and in GaAs 13/15 semiconductors. Yellow arsenic is isostructural with white phosphorus and was first described by Bettendorff almost 150 years ago.[3] It consists of tetrahedral As_4 units, which was determined in the 1960s by electron diffraction.[4] Yellow arsenic is made in a time-consuming synthesis by heating gray arsenic to 750 °C. The emerging As_4 is removed in a constant flow of carrier gas, and it is discharged in a solvent to yield a diluted As_4 solution. Yellow arsenic is very unstable at ambient conditions. Especially when exposed to light, it immediately decomposes to gray arsenic. Moreover, smallest traces of gray arsenic accelerate the autodecomposition of As_4, even in solution. Therefore, As_4 is not storable as a solid or in solution as it is possible for the lighter homologue P_4 and a certain stoichiometry during reactions is hard to fulfill. Thus, only few results regarding the use of As_4 in main-group[5] and in transition-metal chemistry[6] have been published to date. Furthermore, no studies concerning the coordination behavior of the intact[7] As_4 tetrahedron are available. So far, the physical properties of As_4 could only be investigated under gas-phase conditions[4] or in thin films deposited on cooled substrates, which allowed spectroscopic and calorimetric investigations.[8]

To overcome all of these problems, we intended to develop an appropriate source of yellow arsenic. Herein we present the synthesis of $[Ag(\eta^2\text{-}As_4)_2]^+$ (**1**) as an unprecedented homoleptic complex possessing intact As_4 tetrahedra as ligands. It is light-stable and can be stored under inert conditions without decomposition. Moreover, this complex can be used as an effective source of intact As_4, as exemplified by the synthesis of $[(PPh_3)Au(\eta^2\text{-}As_4)]^+$ (**2**).

The reaction of freshly prepared As_4[9] with the weakly coordinated silver(I) salt $[Ag(CH_2Cl_2)][pftb]$ (pftb = $[Al\{OC(CF_3)_3\}_4]$)[10] leads to the formation of the first homoleptic metal–arsenic complex $[Ag(\eta^2\text{-}As_4)_2][pftb]$ (**1**) in excellent yields [Eq. (1)]. Compound **1** is obtained as an air- and moisture-sensitive colorless powder, which is interestingly stable to light and can be stored under an argon atmosphere at −30 °C without decomposition. It has good solubility in polar solvents, especially in dichloromethane, but is insoluble in hexane.



(1)

The ESI mass spectrum in the cation mode of **1** shows the molecular ion peak as well as a peak for the As_4 released fragment $[Ag(As_4)]^+$. In the anion mode, the complete $[Al\{OC(CF_3)_3\}_4]^-$ ion is detected. The Raman spectrum of **1** in solid state reveals three bands at 210, 265, and 343 cm^{-1}. Theoretical calculations predict six Raman-active vibrations for **1** in D_{2h} symmetry at 206, 208, 228, 260, 261, and 339 cm^{-1}, with that at 228 cm^{-1} being the least-intense. The measured vibrational frequencies for **1** also compare well to those of free As_4, which were obtained experimentally in the solid state (193 (two-fold degenerate), 250, and 341 cm^{-1})[8] and by theory in the gas phase (203 (two-fold degenerate), 259 (three-fold degenerate), and 349 cm^{-1}). The similar number and position of Raman active bands for **1** and free As_4 indicate a rather weak interaction between the Ag^+ cation and the two intact As_4 tetrahedra. However, it is strong enough to make **1** a light-stable and storable compound. The reason might be the positive charge of the complex, which prevents intermolecular contacts and therefore arsenic–arsenic interactions to form gray arsenic.

The molecular structure of **1**[11] shows the unique side-on coordination of two intact As_4 tetrahedra to the silver(I) cation in an almost coplanar way (Figure 1). The two $AgAs_2$ planes only deviate by 9° from perfect coplanarity, which compares well to the deviation of 10.9° in the phosphorus derivative $[Ag(\eta^2\text{-}P_4)_2][pftb]$.[12] The Ag−As bond distances in **1** vary from 2.611(1) Å to 2.626(2) Å. They are shorter than the Ag−As bond distances found in $[\{Cp^*Mo(CO)_2(As_3)\}_4Ag_2][pftb]_2$[13] (2.665–2.828 Å), which exhibits a side-on coordination of the *cyclo*-As_3 ring to a silver(I) cation. The

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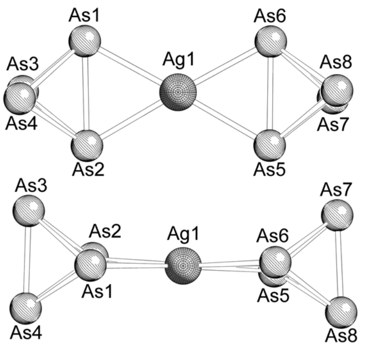


Figure 1. Top view and side view of the cationic part of **1** in the crystal (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ag1–As1 2.626(2), Ag1–As2 2.616(2), Ag1–As5 2.620(2), Ag1–As6 2.611(2), As1–As2 2.585(2), As1–As3 2.396(2), As1–As4 2.389(2), As2–As3 2.380(2), As2–As4 2.384(2), As3–As4 2.423(2), As5–As6 2.569(2), As5–As7 2.387(2), As5–As8 2.385(2), As6–As7 2.383(2), As6–As8 2.378 (2), As7–As8 2.419(2); As1-Ag1-As2 59.10(6), As5-Ag1-As6 58.83(5), As1-Ag1-As6 122.79(5), As2-Ag1-As5 119.61(5).

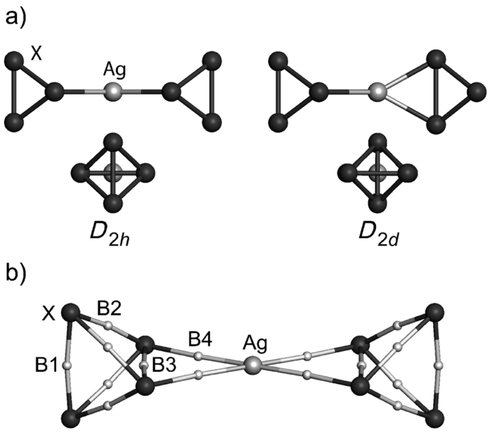


Figure 2. a) Conformational isomers of $[Ag(X_4)_2]^+$ (X = P, As) with corresponding point group symmetry. b) Bond critical points (gray spheres) in $[Ag(X_4)_2]^+$ (D_{2h} isomer) labeled as B1–B4.

Table 1: Relative energies for the conformational isomers of $[Ag(\eta^2\text{-}X_4)_2]^+$ [kJ mol^{-1}].

X	D_{2h}[a]	D_{2d}
As	0.00 (3.1*i*)	0.14
P	0.00 (8.8*i*)	−1.06

[a] The imaginary frequencies of first-order saddle points are given in parentheses.

Table 2: Calculated reaction Gibbs energies at 293.15 K in the gas phase and in CH_2Cl_2 solution (sol) [kJ mol^{-1}].

Reaction	$\Delta G_{(g)}$	$\Delta G_{(l)}$
$[Ag(As_4)_2]^+ \rightarrow [Ag(As_4)]^+ + As_4$	118.3	–
$[Ag(As_4)]^+ \rightarrow Ag^+ + As_4$	180.1	–
$[Ag(As_4)_2]^+ + \text{sol} \rightarrow [Ag(As_4)(\text{sol})]^+ + As_4$	47.9	39.5
$[Ag(As_4)(\text{sol})]^+ + \text{sol} \rightarrow [Ag(\text{sol})_2]^+ + As_4$	66.3	55.7
$[Ag(P_4)_2]^+ \rightarrow [Ag(P_4)]^+ + P_4$	107.5	–
$[Ag(P_4)]^+ \rightarrow Ag^+ + P_4$	149.5	–
$[Ag(P_4)_2]^+ + \text{sol} \rightarrow [Ag(P_4)(\text{sol})]^+ + P_4$	32.7	30.8
$[Ag(P_4)(\text{sol})]^+ + \text{sol} \rightarrow [Ag(\text{sol})_2]^+ + P_4$	40.0	37.9

coordinating As1–As2 and As5–As6 bonds of **1** (2.585(2) Å and 2.569(2) Å) are elongated compared to the As–As bond lengths in As_4 (electron diffraction: 2.435 Å,[4] DFT calculations: 2.4372 Å[6d]), whereas the As3–As4 and As7–As8 bonds (2.423(2) Å and 2.419(2) Å) are slightly shorter. The shortest bonds are found between the coordinating and non-coordinating arsenic atoms and lie in the range from 2.379(2) Å to 2.396(2) Å. The As-As-As angles range from 57.11(5)° to 65.59(5)°, which further exemplifies the distortion of the As_4 tetrahedron induced by the coordination to the silver(I) cation. Similar tendencies for the bond lengths and angles have been reported for the P_4 derivative $[Ag(\eta^2\text{-}P_4)_2][pftb]$ and they are a result of the polarizing effect of the Lewis acid on the X_4 tetrahedron (X = P, As).

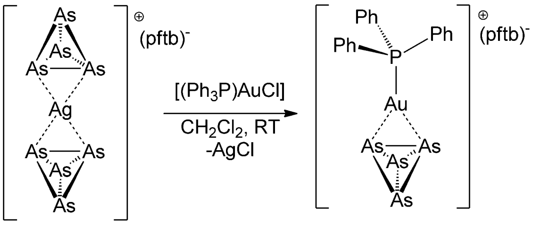
To gather a deeper insight in the bonding situation and the stability of $[Ag(\eta^2\text{-}As_4)_2]^+$ (**1**) compared to $[Ag(\eta^2\text{-}P_4)_2]^+$, detailed calculations regarding the electronic structure were carried out.[11] Structure optimizations of the complexes $[Ag(\eta^2\text{-}X_4)_2]^+$ (X = P, As) yield two conformational isomers with D_{2h} and D_{2d} symmetry (Figure 2). In case of **1** these conformers are virtually isoenergetic, while for the phosphorus analogue, slightly larger energy differences are predicted (Table 1).

For the assessment of the stability of **1**, the corresponding reaction Gibbs energies for the first and second dissociation of the complexes $[Ag(\eta^2\text{-}X_4)_2]^+$ (X = P, As) were calculated in the gas phase and also in CH_2Cl_2 solution at 293.15 K (Table 2). The dissociation of the $[Ag(X_4)_2]^+$ complexes is endergonic for phosphorus as well as for arsenic in the gas phase and in solution. The complexes $[Ag(As_4)_2]^+$ and $[Ag(As_4)]^+$ are more stable than the related phosphorus compounds by 10–20 kJ mol^{-1}, which may be explained by the larger polarizability of the As_4 tetrahedron compared to the P_4 tetrahedron.

Furthermore, bond critical points (BCP, Figure 2) were calculated to investigate the bonding situation in **1** and its phosphorus derivative.[11] Calculated properties of the electron density at the BCPs in $[Ag(\eta^2\text{-}X_4)_2]^+$ and free X_4 molecules are similar for both X = As and X = P. Upon coordination to Ag^+, only the bond between two X atoms involved in the coordination (B3, Figure 2b) shows appreciable depletion of electron density, while all of the other BCPs of the X_4 tetrahedron remain virtually unchanged. This demonstrates only a moderate change of the electronic structure of the X_4 tetrahedra.

As Raman spectroscopy together with the performed theoretical studies indicates intact As_4 tetrahedra in **1**, we decided to investigate its potential as an As_4 source. Interestingly, such reactions have never been performed with the P_4 compound $[Ag(\eta^2\text{-}P_4)_2][pftb]$,[12] because P_4 phosphorus itself is a stable starting material in phosphorus chemistry. The reaction of **1** with a soluble, halogenated substrate should lead to the formation of insoluble AgCl and a transfer of As_4 to the generated substrate cation in one step. During the reaction only small volumes of solvent are needed and the use of low boiling solvents is possible. Owing to its stability, **1** can be stored and weighed, which opens the way for stoichiometric reactions under daylight conditions with **1** as an As_4 synthon.

The reaction of **1** with $[(PPh_3)AuCl]$[14] in dichloromethane [Eq. (2)] leads to an immediate formation of a beige-colored precipitate of AgCl together with the ionic complex



1 **2**
70 %

(2)

$[(PPh_3)Au(\eta^2\text{-}As_4)][pftb]$ (**2**), which is obtained as an air- and moisture-sensitive yellowish powder in good yields.

In the ESI mass spectrum of **2**, the fragment $[(PPh_3)_2Au]^+$ can be detected in cation mode, whereas the counterion $[pftb]^-$ is found in anion mode. In the $^{31}P\{^1H\}$ NMR one singlet at $\delta = 54.6$ ppm for the PPh_3 ligand was found. Compared to the halogenated starting material $[(PPh_3)AuCl]$, the signal is shifted downfield by 21 ppm.

X-ray structure analysis of **2**[11] confirms the coordination of an intact As_4 tetrahedron to a gold(I) cation. This is also confirmed by the topological analysis of the electron density of $[(PPh_3)Au(As_4)]^+$, which shows very similar properties at the BCPs as in case of $[Ag(\eta^2\text{-}As_4)_2]^+$.[11]

The molecular structure of **2** shows a linear coordinated Au^I cation with one coordination site occupied by a PPh_3 ligand and the other by a side-on coordinated As_4 tetrahedron (Figure 3). The Au–As bonds (2.536(1) Å and 2.551(1) Å) are slightly shorter than the corresponding Ag–As bonds in **1**. The coordinating As1–As2 bond is 2.616(1) Å and is a little longer than those in **1** but can still be regarded as an intact bond. The bond lengths between the coordinating and non-coordinating arsenic atoms range from 2.3953(7) Å to 2.4093(9) Å, which compares well to the corresponding bond lengths in **1**. As3–As4 (2.421(1) Å) is slightly longer and is reminiscent of the As–As bond length of 2.435 Å found in yellow arsenic. As a result of the shorter Au–As bonds, the As1-Au1-As2 angle of 61.90(2) is larger than the As-Ag-As angles in **1**. The As1-Au1-P1 angle of 138.69(3)° is smaller than the As2-Au1-P1 angle (159.34(3)°). Thus, the As_4 tetrahedron is slightly tilted and the gold(I) cation is coordinated in a distorted linear way.

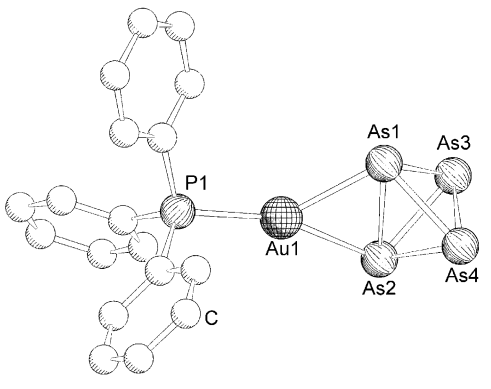


Figure 3. Molecular structure of the cationic part of **2** in the crystal (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Au1–As1 2.5358(6), Au1–As2 2.5514(5), Au1–P1 2.3136(9), As1–As2 2.6162(8), As1–As3 2.4072(7), As1–As4 2.4093(9), As2–As3 2.4009 (8), As2–As4 2.3935(7), As3–As4 2.421(1); As1-Au1-As2 61.90(2), As1-Au1-P1 138.69(3), As2-Au1-P1 159.34(3).

In conclusion, by the reaction of yellow arsenic with a weakly coordinated silver(I) complex, it was possible to synthesize $[Ag(\eta^2\text{-}As_4)_2][pftb]$ (**1**) as an unprecedented homoleptic As_4 metal complex in excellent yield. X-ray structure analysis reveals a central silver cation that is coordinated by two As_4 tetrahedra in a side-on coordination mode. Raman spectroscopy together with detailed theoretical calculations clearly indicates the presence of two intact As_4 tetrahedra. Thus, complex **1** is the first known coordination compound of yellow arsenic. As **1** is light-stable, storable, and has good solubility, it can be used as a unique, stoichiometric As_4 equivalent in preparative chemistry. This was shown by reacting it with $[(PPh_3)AuCl]$ to afford $[(PPh_3)Au(\eta^2\text{-}As_4)][pftb]$ (**2**) in good yields. Future research will target on the liberation of yellow arsenic to gain further information about its reactivity and coordination chemistry.

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