As_4 Complexes

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An End-on-Coordinated As_4 Tetrahedron**

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

Almost 150 years ago, Bettendorff discovered yellow arsenic as an allotrope of the element but could not isolate it in pure form because of its high instability and fast decomposition into an amorphous form.[1] After 35 years of intense discussions on the existence or non-existence of As_4, Erdmann and Unruh were the first to report a large-scale synthesis of yellow arsenic along with its physical properties.[2] However, it took another 75 years until the groups of Sacconi and Scherer used this elusive arsenic allotrope[3] as well as P_4 for the synthesis of polyelement ligand complexes (E_n ligand complexes; E = P, As) to demonstrate well the analogy between the two Group 15 homologues. In particular the activation of white phosphorus by transition metals[4] and main-group elements[5] has become an active research field in inorganic chemistry. In contrast, the reactivity of As_4 has been much less explored,[3,6] which is due to its instability, poor solubility, time-consuming synthesis[3] and fast decomposition to grey arsenic, especially when exposed to light.

The coordination of the E_4 tetrahedron (E = P, As) to transition metals is of particular interest as it is the initial step of its activation. In the late 1970s, Sacconi et al. reported on the synthesis of $[(np_3)Ni(\eta^1\text{-}P_4)]$ (**I**) as the first complex containing an intact, end-on-coordinating P_4 tetrahedron as a ligand (Figure 1).[7] Thereafter, several other complexes were described in which white phosphorus acts as a monodentate ligand, including the neutral complexes $[M(CO)_3(PR_3)_2(\eta^1\text{-}P_4)]$ (**II**)[8] and also the cationic complexes $[(triphos)Re(CO)_2(\eta^1\text{-}P_4)][OTf]$[9] and $[Cp^RML_2(\eta^1\text{-}P_4)][OTf]$ (**III**).[10] Moreover, Peruzzini and co-workers reported on the bimetallic complex $[\{CpRu(PPh_3)_2\}_2(\mu,\eta^{1:1}\text{-}P_4)][OTf]_2$ (**IV**)[10c] in which the P_4 tetrahedron acts as a bridging end-on/end-on ligand that reacts with water to yield several products containing $-P(H)_x(OH)_y-$ units.[10c,11] This exemplifies well the activated stage of the P_4 tetrahedron induced by the coordinated complex cations, because white phosphorus itself can be stored under water without decomposition.

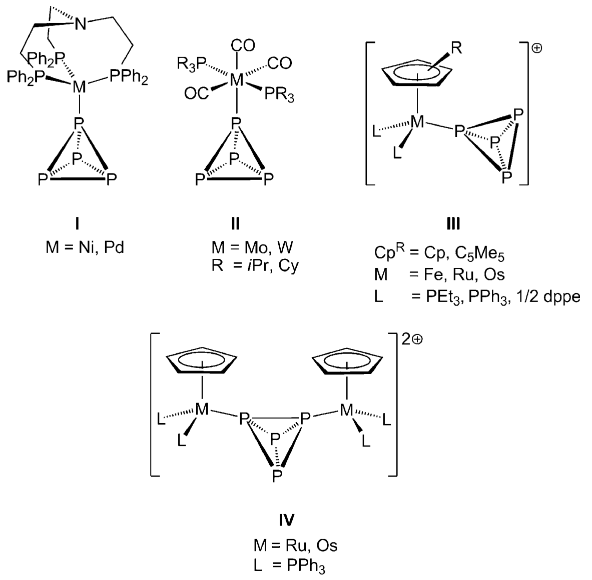

Figure 1. Examples of complexes with the P_4 tetrahedron as end-on coordinating ligand.

Contrary to the rich and well-explored coordination chemistry of P_4, little is known about the ligand properties of As_4. Recently, we reported the synthesis of $[Ag(\eta^2\text{-}As_4)_2][pftb]$ and $[(PPh_3)Au(\eta^2\text{-}As_4)][pftb]$ (pftb = $Al\{OC(CF_3)_3\}_4$) as the first complexes containing intact As_4 tetrahedra coordinated side-on to Lewis acidic Group 11 cations.[12] Interestingly, for these compounds, the arsenic derivatives are thermodynamically more stable than the analogous P_4 complexes. However, towards a targeted activation of As_4 (compare with the complexes **IV**), the more challenging vertex coordination of yellow arsenic by its lone pairs was of special interest. Herein we present the synthesis of $[Cp^*Ru(dppe)(\eta^1\text{-}As_4)][pftb]$ with an unprecedented intact, end-on-coordinated As_4 ligand. Moreover, it is shown that the addition of a second cationic ruthenium fragment does not lead to an expected second end-on coordination but to the insertion into an As–As bond.

Because of their high Lewis acidity for the vertex coordination of As_4, we decided to use the complexes $[Cp^RML_2][A]$ (Cp^R = Cp and L = PPh_3; Cp^R = Cp* and L_2 = dppe; M = Fe, Ru, Os; A = weakly coordinating anion) . To evaluate the most promising candidate, the reaction energies of the above-mentioned complexes with white phosphorus and yellow arsenic in the gas phase were calculated at the B3LYP/def2-SVP level of theory (see the Supporting Infor-

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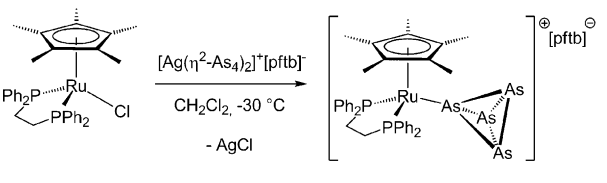
Supporting information for this article (full synthetic and spectroscopic details for **1** and **2**, crystallographic details, and full details and references for the DFT calculations) is available on the WWW under http://dx.doi.org/10.1002/anie.201302882.

mation). According to these calculations, the complex stability of $[Cp^RML_2(\eta^1\text{-}E_4)]^+$ (E = P, As) strongly depends on the metal used as well as the co-ligands, and it generally increases in the series Fe < Ru < Os, $2\,PPh_3$ < dppe, and Cp < Cp*. Whereas the formation of the P_4 complexes is predicted to be exothermic in the gas phase, the formation of the arsenic derivatives is endothermic. Thus, the ruthenium complex $[Cp^*Ru(dppe)]^+$ was chosen for the reaction with As_4, and more detailed calculations were carried out that account for the influence of solvent and temperature. Whereas for phosphorus the formation of $[Cp^*Ru(dppe)(\eta^1\text{-}P_4)]^+$ is exergonic in the gas phase ($-14.1\,kJ\,mol^{-1}$) as well as in solution ($-39.7\,kJ\,mol^{-1}$), the analogous reaction for arsenic is endergonic in the gas phase ($+8.8\,kJ\,mol^{-1}$) but slightly favored in solution ($-1.0\,kJ\,mol^{-1}$), which is due to the increased entropy. However, the corresponding equilibrium constant K_{298} of 1.5 is small and indicates a dissociation of the desired complex at ambient conditions. Thus, a considerable amount of unstable yellow arsenic is always present in solution, which shifts the equilibrium to the left side upon decomposition. This effect can be overcome by lowering the temperature to 243 K, which increases the equilibrium constant to 11.6 and promotes product formation. However, as yellow arsenic is only sparingly soluble in dichloromethane, especially at low temperatures, a direct synthesis by the reaction of $[Cp^*Ru(dppe)]^+$ with As_4 is not possible, and our efforts applying this method failed. Therefore, the soluble As_4 transfer reagent $[Ag(\eta^2\text{-}As_4)_2][pftb]$ was chosen as the arsenic source for the synthesis of the target molecule.

The reaction of $[Cp^*Ru(dppe)Cl]$ with one equivalent of $[Ag(\eta^2\text{-}As_4)_2][pftb]$ at $-30\,°C$ leads to a color change from orange to red and it was accompanied by the formation of a precipitate of AgCl [Eq. (1)]. The unique complex $[Cp^*Ru(dppe)(\eta^1\text{-}As_4)][pftb]$ (**1**) is obtained as dark red solid in good yields; this complex has excellent solubility in dichloromethane but is nearly insoluble in *n*-hexane.



(1)

1

63 %

In the ESI mass spectrum of **1** in cation mode, one peak is observed at *m/z* 635.1 that corresponds to the cationic fragment $[Cp^*Ru(dppe)]^+$. Any arsenic-containing fragments are not found, indicating the weak interaction between As_4 and the ruthenium cation. The $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2) of **1** reveals one singlet for the dppe ligand at $\delta = 69.9$ ppm, which is shifted upfield compared to the starting material $[Cp^*Ru(dppe)Cl]$ ($\delta = 76.3$ ppm).[13] The X-ray structure analysis of **1** reveals the unprecedented end-on coordination of an intact As_4 tetrahedron to the cationic complex fragment $[Cp^*Ru(dppe)]^+$ (Figure 2).

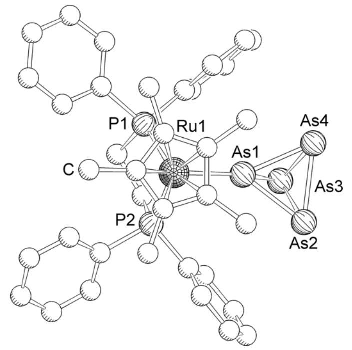


Figure 2. Molecular structure of the cation of **1** in the crystal. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1–As1 2.4023(8), Ru1–P1 2.316(1), Ru1–P2 2.329(1), As1–As2 2.376(2), As1–As3 2.386(1), As1–As4 2.380(1), As2–As3 2.438(2), As2–As4 2.431(2), As3–As4 2.431(2); As2-As1-As3 61.60(5), As2-As1-As4 61.48(5), As3-As1-As4 61.34(3).

The Ru1–As1 bond length of 2.4023(8) Å is shorter than Ru–As distances in complexes of the strong σ-donor and weak π-acceptor ligand $AsPh_3$ (2.412(1) Å in $[CpRu(CO)(AsPh_3)Cl]$,[14] 2.442(1) Å and 2.449(1) Å in $[Cp^*Ru(AsPh_3)_2Cl]$,[15] and 2.435(1) Å in $[CpRu(MeCN)_2(AsPh_3)]^{+}$[16]). The As_4 tetrahedron in **1** is sterically shielded by the Cp* ligand as well as by two of the four phenyl substituents of the dppe ligand. Together, these moieties form a tetrahedral shaped binding pocket in which the As_4 tetrahedron is embedded. However, the distances between the planes defined by the atoms As1, As2, and As3 as well as As1, As3, and As4 and the corresponding phenyl planes are in the range of 3.197(1) Å and 3.936(1) Å, indicating only minor interactions ($\Sigma_{vdWradii}$(C and As) = 3.55 Å).

The As–As bonds between the coordinating arsenic atom As1 and the three non-coordinating As atoms vary from 2.376(2) Å to 2.386(1) Å and are shortened compared to the As–As bonds in yellow arsenic (2.435(4) Å determined by electron diffraction[17] and 2.4372 Å specified by DFT calculations[6f]). In contrast, the bond lengths between the basal arsenic atoms (2.431(2) Å–2.438(2) Å) compare well to those in free As_4. A similar trend has been found for the P_4 derivative.[10a]

To evaluate the nature of bonding in the cationic part of **1**, detailed DFT calculations were performed. The Wiberg Bond Index (WBI) of 0.606 for the Ru1–As1 bond indicates a dative single bond between the As_4 tetrahedron and the cationic ruthenium fragment. Upon coordination, the spherical aromaticity of the As_4 tetrahedron is only slightly decreased. The calculated nucleus-independent chemical shift (NICS) increases from −52.9 (for free As_4) to −46.2 in **1**. The same tendency is observed for the P_4 derivative (the NICS increases from −55.2 to −48.5), emphasizing the analogy between $[Cp^*Ru(dppe)(\eta^1\text{-}As_4)]^+$ and $[Cp^*Ru(dppe)(\eta^1\text{-}P_4)]^+$. The molecular orbital distribution of the complex cation $[Cp^*Ru(dppe)(\eta^1\text{-}As_4)]^+$ provides a deeper insight in the bonding situation. The isosurfaces of the molecular orbitals characterize the As_4 ligand as a σ-donor (Figure 3a) and π-donor/π-acceptor ligand (Figure 3b and c). A similar orbital distribution is also found in the P_4 derivative (see the Supporting Information). In case of the π-type MOs, the respective orbitals are distributed over the whole As_4

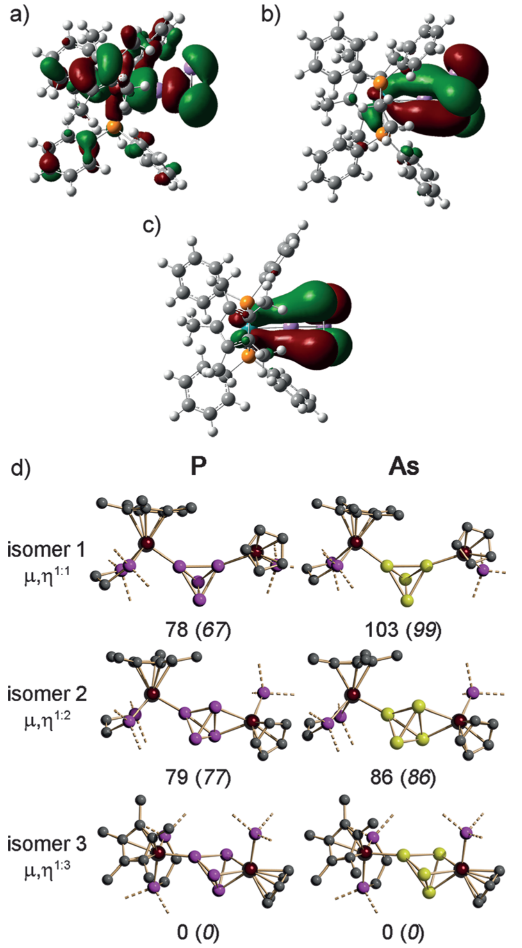


Figure 3. a–c) Selected molecular orbitals of the complex cation of **1**: a) σ-type interaction; b),c) π-type interactions between the As_4 tetrahedron and $[Cp^*Ru(dppe)]^+$. d) Three different coordination isomers of $[\{Cp^*Ru(dppe)\}(\mu\text{-}E_4)\{CpRu(PPh_3)\}]^{2+}$ (E = P, As) with their relative energies (polarizable continuum model (PCM) corrected values in parentheses) in $kJ\,mol^{-1}$. Phenyl substituents are omitted for clarity.

ligand and are bonding with respect to the coordinating atom As1 and the basal atoms As2, As3, and As4, respectively. Referring to the bonds between the basal arsenic atoms, the π-MOs show an antibonding character. This is in good agreement with the shortened bond lengths between As1 and As2/As3/As4, as well as the unchanged bonds lengths between the basal arsenic atoms. The MO distribution is also in good agreement with the short Ru1−As1 bond. Owing to the additional π-interactions, the Ru−As bond in **1** is shortened compared to the corresponding bonds in $AsPh_3$ ruthenium complexes, which are mainly characterized by σ-donor interactions.

To further investigate the coordination behavior of the intact As_4 tetrahedron, the reactivity of **1** towards a second cationic ruthenium fragment was investigated. Surprisingly, the reaction of **1** with one equivalent of $[CpRu(PPh_3)_2][pftb]$, generated in situ, does not lead to the expected η^1:η^1 coordination of an intact As_4 tetrahedron (known for P_4) but to a bond cleavage of one As−As bond to afford the binuclear complex $[\{Cp^*Ru(dppe)\}(\mu,\eta^{1:3}\text{-}As_4)\{CpRu(PPh_3)\}][pftb]_2$ (**2**) in good yields.

The positive-ion ESI mass spectrum of **2** shows two peaks at m/z 710.1 and 1450.4 that can be assigned to the cationic fragments $[\{Cp^*Ru(dppe)\}As_4\{CpRu(PPh_3)\}]^{2+}$ and $[\{Cp^*Ru(dppe)\}As_4\{CpRu(PPh_3)\}]^{+}$. The $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2) of the crude reaction mixture shows two sharp singlets at $\delta = 72.7$ ppm and $\delta = 32.9$ ppm as well as a broad signal at $\delta = 12.4$ ppm with an integral intensity ratio of 2:1:1. While the singlet at $\delta = 72.7$ ppm can be assigned to the dppe ligand in **2** ($\delta = 69.9$ ppm for **1**), the signal at $\delta = 32.9$ ppm corresponds to a ruthenium bound PPh_3 ligand (compare for $[\{CpRu(PPh_3)_2\}_2(\mu,\eta^{1:1}\text{-}P_4)]^{2+}$ with $\delta = 38.3$ ppm).[10c] The broad signal at $\delta = 12.4$ ppm originates from free PPh_3, indicating the loss of one phosphine ligand from the starting material $[CpRu(PPh_3)_2]^+$. This PPh_3 abstraction has already been stated for the ruthenium-catalyzed formation of α,β-unsaturated ketones.[18]

The X-ray structure of **2** reveals the coordination of the basal As_3 unit of the η^1-As_4 ligand at a $[CpRu(PPh_3)]$ fragment and the cleavage of one basal As−As bond (Figure 4).

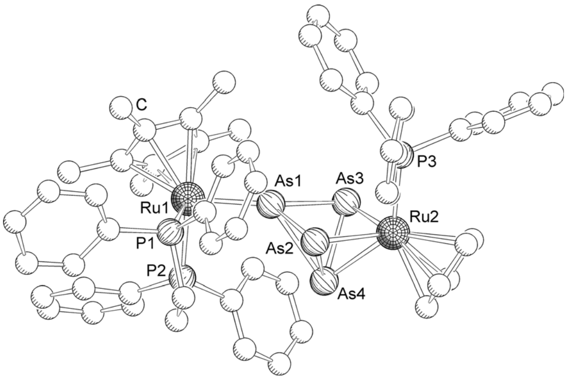


Figure 4. Molecular structure of the dication of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1–As1 2.356(1), Ru2–As2 2.458(1), Ru2–As3 2.459(1), Ru2–As4 2.549(1), As1–As2 2.403(1), As1–As3 2.443(1), As1–As4 2.621(1), As2–As4 2.459(2), As3–As4 2.424(1); As2-As1-As3 87.74(4), As1-As3-Ru2 92.32(4), As1-As2-Ru2 93.29(4), As2-Ru2-As3 86.16(3), As1-As4-Ru2 86.27(4), As2-As4-As3 86.91(5).

The central structural motif in **2** is a five-membered As_4Ru cluster core with an additional η^1-coordinated $[Cp^*Ru(dppe)]^+$ fragment. The cluster is formally derived by an insertion of the 14 VE fragment $[CpRu(PPh_3)]^+$ into the As2−As3 bond together with an additional coordination of As4 to Ru2. The cluster core itself may best be described as an As_4Ru nido cluster (according to the Wade–Mingos rules). Thus it is formally derived from an octahedral core with one vacant vertex. The As1−As2, As1−As3, As3−As4, and As2−As4 bond lengths (2.403(1) Å, 2.443(1) Å, 2.424(1) Å, and 2.459(1) Å, respectively) compare well to the As−As bond lengths in As_4 (2.437(2)–2.435(4) Å).[6f,17] In contrast, the As1−As4 bond (2.621(1) Å) is elongated. A similar tendency can be observed for the Ru−As bonds in the cluster core. While the Ru2−As2 and Ru2−As3 bond lengths (2.458(1) Å and 2.459(1) Å) are almost the same, the Ru2−As4 bond (2.549(1) Å) is elongated. The angles between opposing atoms (for example, As2 and As3) of the cluster core vary from 86.16(3)° to 93.29(4)° and are reminiscent of the native octahedral arrangement. The Ru1−As1 bond (2.356(1) Å) is shortened compared to the Ru−As bond in the starting material **1** (2.4023(8) Å).

To explain the different reactivity of $[Cp^*Ru(dppe)(\eta^1\text{-}E_4)]^+$ towards a second Lewis acid, three different coordination isomers were calculated for the cationic complexes $[\{Cp^*Ru(dppe)\}(\mu\text{-}E_4)\{CpRu(PPh_3)\}]^{2+}$ (E = P, As) at the B3LYP/def2-SVP level of theory (Figure 3d). The structure of isomer 3 ($\mu,\eta^{1:3}$-E_4 coordination mode) with one broken, basal E−E bond is predicted to be the thermodynamically most stable form for phosphorus as well as arsenic by more than 70 kJ mol^{-1}. However, the formation of isomer 3 is predicted to be endothermic in gas phase (by 160–150 kJ mol^{-1}) as well as in solution (55 kJ mol^{-1} for P_4 and 33 kJ mol^{-1} for As_4), indicating that other factors (such as ion-pair formation or kinetic reasons) play an important role for the final formation of the different isomers. Obviously, the first step of the reaction involves the coordination of the Lewis acidic $[CpRu(PPh_3)]^+$ complex fragment (isomers 1 and 2). Whereas the end-on/end-on coordination mode (isomer 1) is more stable for phosphorus than the end-on/side-on coordination mode (isomer 2), isomer 2 is energetically favored for arsenic. The side-on coordination weakens the As−As bond and leads finally to its cleavage. Furthermore, the bond energy is lower for an As−As bond (36 kcal mol^{-1}) compared to a P−P bond (47 kcal mol^{-1}),[19] which favors the bond breaking reaction in the case of As_4. Thus, $[\{Cp^*Ru(dppe)\}(\mu,\eta^{1:2}\text{-}As_4)\{CpRu(PPh_3)\}]^{2+}$ (isomer 2) may be regarded as an intermediate product on the way to complex **2** (isomer 3).

In conclusion, we were able to isolate and fully characterize $[Cp^*Ru(dppe)(\eta^1\text{-}As_4)][pftb]$ as the first complex possessing an intact coordinating As_4 tetrahedron in a monohapto coordination mode. The ideal complex system for this purpose was identified by using extended DFT calculations. Detailed bonding analyses reveal that the coordinated As_4 tetrahedron not only serves as a σ-donor but also as a π-donor/π-acceptor ligand. The reaction of a second cationic ruthenium complex does not lead to the expected twofold end-on coordination found for P_4 complexes. Instead an insertion into an As−As bond occurs, which is caused by the low As−As bond energy and the energetically preferred side-on coordination mode of As_4. This enhanced reactivity of the As_4 tetrahedron in comparison to P_4 will open novel paths for its targeted activation.

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