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Synthesis and Redox Chemistry of a Homoleptic Iron Arsenic Prismane Cluster

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Dedicated to Professor Dieter Fenske on the occasion of his 80th birthday.

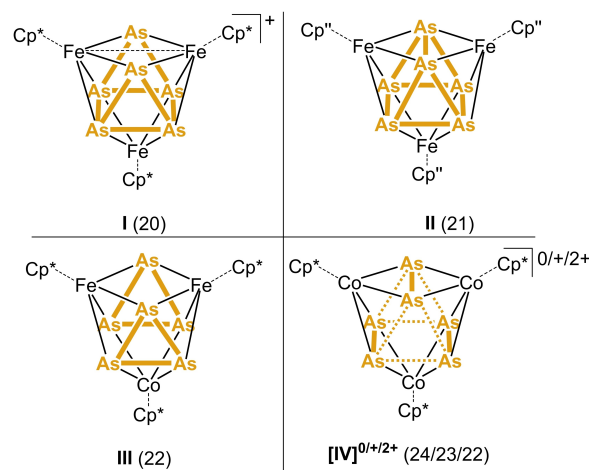
The redox chemistry of the homoleptic iron prismane cluster $[\{\text{Cp}^*\text{Fe}\}_3(\mu_3, \eta^{4:4:4}\text{-As}_6)]$ (**A**, $\text{Cp}^* = \text{C}_5\text{Me}_5$) is investigated both electrochemically and synthetically. While its first oxidation leads to the diamagnetic species $[\{\text{Cp}^*\text{Fe}\}_3(\mu_3, \eta^{4:4:4}\text{-As}_6)]\text{X}$ (**[1][TEF]**, **[1][FAI]**, $[\text{TEF}]^- = [\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$, $[\text{FAI}]^- = [\text{FAI}\{\text{O}(\text{C}_6\text{F}_5)_2\text{C}_6\text{F}_{10}\}_3]^-$), the second oxidation yields the paramagnetic $[\{\text{Cp}^*\text{Fe}\}_3(\mu_3, \eta^{4:4:4}\text{-As}_6)]\text{[TEF]}_2$ (**[2][TEF]**). The reduction of **A** leads

to the monoanionic compound $[\text{K}@\{2.2.2\text{-cryptand}\}][\{\text{Cp}^*\text{Fe}\}_3(\mu_3, \eta^{4:4:4}\text{-As}_6)]$ (**[K@crypt][3]**), while a second reduction could only be traced spectroscopically. All compounds were comprehensively characterized, revealing the structural changes accompanying the described redox processes. All findings are supported by spectroscopic as well as computational studies.

Molecular transition metal polyarsides (As_n ligand complexes) are a continually growing class of compounds, owing their attraction to their multifaceted structural chemistry.^[1] In general, the polyarsenic As_n units adopt a size and hapticity necessary to fulfill the 18 valence electron (VE) rule at the utilized transition metal fragment(s), often resembling aromatic hydrocarbon ligands.^[2] Thus, complexes featuring As_2 dumbbells,^[3] As_3 ,^[4] As_4 ,^[5] As_5 ,^[6] As_6 ^[7] and As_8 ^[8] rings have been described. Commonly, these species are obtained under thermolytic or photolytic conditions using transition metal carbonyl complexes and a suitable As source, such as yellow arsenic (As_4).^[1c] One of these very prominent thermolysis reactions is the one between $[\text{Cp}^*\text{Fe}(\text{CO})_2]_2$ and yellow arsenic, which affords $[\text{Cp}^*\text{Fe}(\eta^5\text{-As}_5)]$, a pentaarsolide (*cyclo*- As_5) derivative of the prototypical ferrocene.^[6b] However, we recently described two additional products arising from this reaction. The heteroleptic complex $[\{\text{Cp}^*\text{Fe}\}_2(\mu_3, \eta^{4:4:4}\text{-As}_6)\text{Fe}(\eta^3\text{-As}_3)]$ could be obtained as an analytically pure compound, while the homoleptic $[\{\text{Cp}^*\text{Fe}\}_3(\mu_3, \eta^{4:4:4}\text{-As}_6)]$ (**A**) was hypothesized but could not be structurally validated yet.^[9] Herein, we describe

the isolation as well as surprising structural features of **A**, allowing to further study its reactivity.

Amongst others, the group of Fenske succeeded in obtaining several hetero- and homometallic As_6 prismane clusters $[\{\text{Cp}^R\text{M}\}_3(\mu_3, \eta^{4:4:4}\text{-As}_6)]^{+n}$ (**I–IV**; $\text{Cp}^R = \text{Cp}^*$, Cp^+ , Cp' , Cp'' ; $\text{M} = \text{Fe}$, Co ; $n = 0, 1, 2$, Scheme 1) as well as their lighter P-derivatives $[\{\text{Cp}^R\text{M}\}_3(\mu_3, \eta^{4:4:4}\text{-P}_6)]^{+n}$ ($\text{M} = \text{Fe}$, Co ; $n = 0, 1$) from co-thermolysis as well as salt metathesis reactions.^[10] However, studies on their reactivity are scarce and limited to “Aufbau”-reactions leading to extended heterotetranuclear clusters.^[11] Yet, the redox chemistry of these compounds remains completely unstudied and no anionic arsenic prismane clusters could be isolated so far, which becomes even more of a target against the background of the wide range of skeletal electron numbers observed in the complexes mentioned above (Scheme 1).



Scheme 1. Known arsenic prismane clusters and their respective skeletal electron counts in brackets; $\text{Cp}^* = \text{C}_5\text{Me}_5$, $\text{Cp}'' = 1,3\text{-}i\text{-Bu-C}_5\text{H}_3$.

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A was synthesized by the co-thermolysis of $[\text{Cp}^*\text{Fe}(\text{CO})_2]_2$ with As_4 and could be isolated in an improved 39% yield by a more elaborate chromatographic workup involving toluene/hexane mixtures as eluents (see SI).^[6b,9]

With **A** in hand, we investigated its electrochemical properties by means of cyclic voltammetric measurements that reveal four distinct and reversible redox processes at -1.76 V, -1.16 V, 0.10 V and 0.75 V versus the Fc/Fc^+ couple (Figure 1, $\text{Fc} = \text{ferrocene}$). Accordingly, **A** should be doubly reducible as well as doubly oxidizable. Therefore, the thianthrenium radical cation $[\text{Thia}]^{\bullet+}$ should be a suitable oxidant for both oxidative processes.^[12] When **A** is reacted with one equivalent of $[\text{Thia}][\text{X}]$ ($[\text{X}]^- = [\text{TEF}]^-$ or $[\text{FAI}]^-$, $[\text{TEF}]^- = [\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$, $[\text{FAI}]^- = [\text{FAI}\{\text{O}(1-\text{C}_6\text{F}_5)\text{C}_6\text{F}_{10}\}_3]^-$)^[13] in CH_2Cl_2 or *o*-DFB (*ortho*-difluorobenzene), a

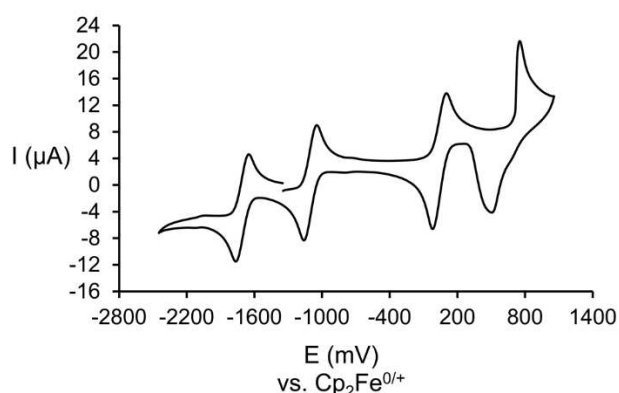
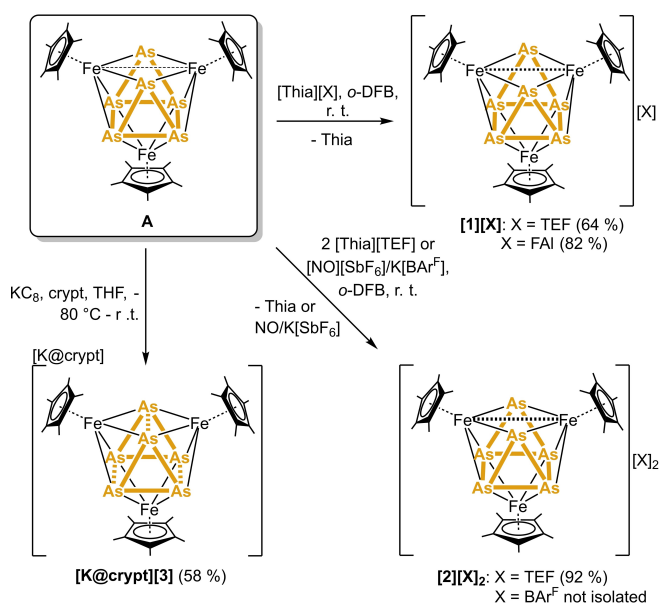


Figure 1. Cyclic voltammogram of **A** in CH_2Cl_2 referenced to the Fc/Fc^+ couple with $[\text{Bu}_4\text{N}][\text{PF}_6]$ as conducting salt.



Scheme 2. Synthesis of ionic iron-arsenic prismane clusters **1–3** starting from **A**. Isolated yields are given in parentheses. Thia = thianthrene ($\text{C}_{12}\text{H}_8\text{S}_2$), $[\text{TEF}]^- = [\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$, $[\text{FAI}]^- = [\text{FAI}\{\text{O}(1-\text{C}_6\text{F}_5)\text{C}_6\text{F}_{10}\}_3]^-$, $[\text{BArF}]^- = [\text{B}(\text{C}_6\text{F}_5)_4]^-$, crypt = [2.2.2]-cryptand ($\text{C}_{18}\text{H}_{36}\text{O}_6\text{N}_2$).

rapid reaction affords the respective diamagnetic monocationic species $[\{\text{Cp}^*\text{Fe}\}_3(\mu_3, \eta^{4:4:4}\text{-As}_6)][\text{X}]$ (**[1][TEF]** (64%), **[1][FAI]** (82%)) (Scheme 2). The doubly oxidized species $[\{\text{Cp}^*\text{Fe}\}_3(\mu_3, \eta^{4:4:4}\text{-As}_6)][\text{TEF}]_2$ (**[2][TEF]**) is obtained in even better yields of 92% when two equivalents of $[\text{Thia}][\text{TEF}]$ are employed. The paramagnetic dication $[\mathbf{2}]^{2+}$ is highly reactive, preventing the isolation of its salts with less innocent anions. Thus, samples of $[\mathbf{2}][\text{BArF}]_2$, which we prepared to obtain better crystallographic data, are highly contaminated with a range of oxidized polyarsenic complexes. The reduction of **A** can be achieved by reacting it with one equivalent of KC_8 in THF (Scheme 2). The product $[\text{K@crypt}][\{\text{Cp}^*\text{Fe}\}_3(\mu_3, \eta^{4:4:4}\text{-As}_6)]$ (**[K@crypt][3]**, 58%, crypt = [2.2.2]-cryptand) was obtained after the addition of crypt to the reaction solution and careful workup. The second reduction of **A** could not be achieved, which we attribute to the high sensitivity of the proposed dianionic species $[\{\text{Cp}^*\text{Fe}\}_3(\mu_3, \eta^{4:4:4}\text{-As}_6)]^{2-}$, which appears to decompose upon workup. EPR spectroscopic data (see SI), however, points towards the presence of this paramagnetic compound in the reaction mixture.

Generally, the structural chemistry of the described iron arsenic prismane clusters is governed by the number of skeletal electrons.^[10] Thus, it is even more surprising that, in contrast to its Cp'' analog, the As_6 core in **A** does not adopt a regular prismatic structure.^[9] Instead, the As1-As2 edge is opened ($3.5012(4)$ Å), which goes in hand with a shortening of the Fe1-Fe2 distance ($3.2504(4)$ Å). The edges of the distorted prismane show As-As distances of $2.683(3)$ – $2.706(7)$ Å, while those within the triangular faces are in between $2.512(2)$ Å and $2.636(8)$ Å and thus above the sum of the covalent radii.^[14] Interestingly, the distortion of the prismane core is even more accentuated in the monocation, which was already reported.^[10e] In the monocationic **[1][FAI]** synthesized here, the elongation of the As1-As2 distance ($3.797(13)$ Å) increases (Figure 2). Accordingly, the respective Fe1-Fe2 distance is even shorter ($2.8956(9)$ Å) compared to **A**. The second oxidation, however, seems to have less structural influence on the As_6 core, as the As1-As2 ($3.689(4)$ Å) as well as the Fe1-Fe2 distances ($2.8993(6)$ Å) in **[2][BArF]**₂ are similar to those in **[1][FAI]**. Furthermore, the prismane edges ($2.698(4)$ – $2.721(3)$ Å) as well as the As-As distances in the triangular faces ($2.5047(7)$ – $2.6199(11)$ Å) remain similar to those found in **A**. The reduction of **A** to **[K@crypt][3]** is accompanied by an equalization within the prismane core, as found in the Fe_2Co analog **III** (Scheme 1). The As-As distances along the edges amount to $2.795(10)$ – $2.847(1)$ Å, while the triangular faces share As-As distances of $2.543(9)$ – $2.5833(15)$ Å. Accordingly, the Fe-Fe distance is elongated to a nonbonding interaction of $3.7832(8)$ Å. Conclusively, the stepwise oxidation from **[3]**[−] to **[2]**²⁺ primarily results in a gradual distortion of the central Fe_2As_2 square. While this is dominated by a closer As1-As2 distance in the reduced **[3]**[−], the oxidized **[2]**²⁺ reveals a significantly closer Fe1-Fe2 and an elongated As1-As2 distance.

The diamagnetic species **[1][X]** ($[\text{X}]^- = [\text{TEF}]^-$ or $[\text{FAI}]^-$) and **[K@crypt][3]** only show the expected signal for chemically equivalent Cp^* ligands in their respective ^1H NMR spectra (see SI). In contrast, **A** in CD_2Cl_2 reveals a broad resonance at $\delta =$

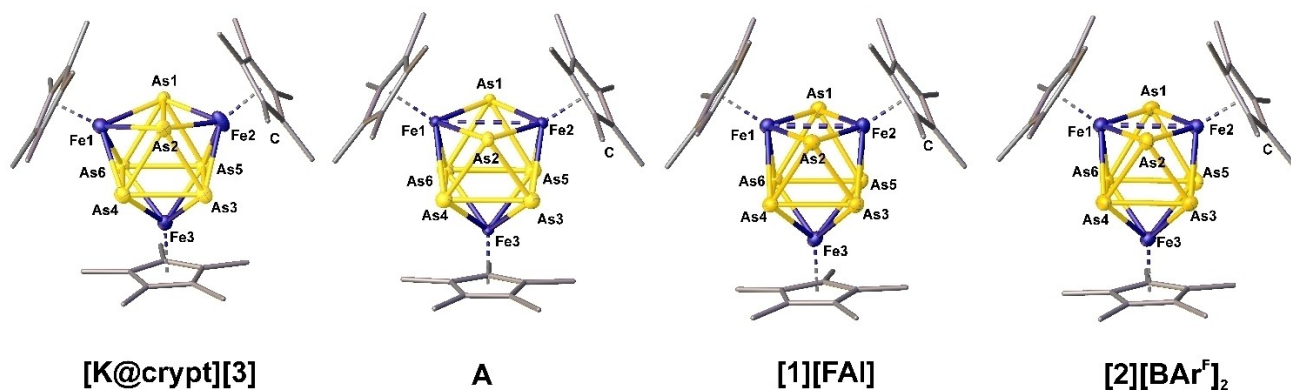


Figure 2. Molecular structures of the $[(\text{Cp}^*\text{Fe})_3(\mu_3, \eta^{4:4'}\text{-As}_6)]^{-/0/+2+}$ core within the compounds **A**, **1[FAI]**, **2[BAr^F]₂** and **[K@crypt][3]** in order of decreasing electron count for the central prismane cluster.

2.93 ppm with $\omega_{1/2} = 40$ Hz indicating its paramagnetic character. The corresponding X-band EPR spectrum of **A** in frozen CH_2Cl_2 solution at 77 K shows a rhombic signal with $g_1 = 2.20$, $g_2 = 2.13$ and $g_3 = 2.04$ and additional hyperfine coupling to the arsenic nuclei. Similarly, a solution of the dicationic **[2][TEF]₂** in CD_2Cl_2 shows a broad signal at $\delta = 7.84$ ppm with $\omega_{1/2} = 126$ Hz in the ^1H NMR spectrum. The X-band EPR spectrum of **[2][TEF]₂** in frozen CH_2Cl_2 solution at 77 K again reveals a rhombic signal with $g_1 = 2.42$, $g_2 = 2.00$, $g_3 = 1.96$ and coupling to the arsenic nuclei (see SI).

To better understand the bonding and electronic situation within **A** and **1–3**, we conducted DFT computations at the B3LYP^[15]/def2SVP^[16] level of theory. As expected, the Wiberg bond indices (WBI) obtained from NBO analyses^[17] for the central Fe_3As_6 core are all below 1 which is indicative of the cluster nature of these compounds. However, the WBIs for the As1–As2 interactions decrease from the reduced **[3]⁻** (0.283) to the neutral **A** (0.095) to the cationic **[1]⁺** and dicationic species **[2]²⁺** (0.078/0.080). Accordingly, the WBIs for the Fe1–Fe2 interaction increase from 0.089 (**[3]⁻**) to 0.1 (**A**) to 0.207 (**[1]⁺**)/0.219 (**[2]²⁺**). This is in line with a decreased As1–As2 contribution and an increased Fe1–Fe2 contribution to the multi center bonding interaction within the Fe_2As_2 square upon oxidation. Furthermore, the spin density distribution was calculated for the neutral **A** and the dicationic **[2]²⁺** (Figure 3).

While the unpaired electron in **A** seems to be located mainly at the two iron atoms close to each other (Fe1 and Fe2), the spin density within **[2]²⁺** in a doublet ground state should solely be located at the Fe3 atom. In a hypothetical quartet ground state of **[2]²⁺**, however, the spin density would be smeared out across all three iron atoms.

In summary, we report the isolation and characterization of a side product that had long been unclarified, formed during the co-thermolysis of $[\text{Cp}^*\text{Fe}(\text{CO})_2]_2$ and yellow arsenic (As_4), which is the prismatic cluster $[(\text{Cp}^*\text{Fe})_3(\mu_3, \eta^{4:4'}\text{-As}_6)]$ (**A**). For the first time, we shed light on the redox chemistry and the accompanying structural changes of arsenic prismane complexes, utilizing **A** as starting material. It was possible to oxidize **A** once to form **[1][X]** ($[\text{X}]^- = [\text{TEF}]^-$ or $[\text{FAI}]^-$) and twice to give **[2][TEF]₂**. While **A** should be doubly reducible, we could only experimentally realize selectively its monoreduction to give **[K@crypt][3]** which represents the first anionic cluster of this type. Structural characterization of these compounds revealed Fe–Fe bond formation as well as As–As bond splitting upon oxidation. Reduction on the other hand leads to additional As–As interaction formation and Fe–Fe bond breaking. DFT calculations elucidated the electronic structures of **A** and **1–3**. These results display a starting point in the study of the electrochemical properties of polyarsenide prismane clusters and give insight into the influence of redox processes on As–As bond formation/splitting processes.

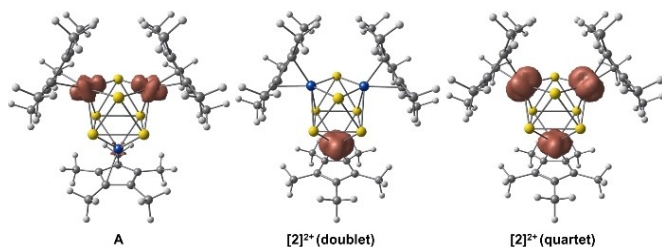


Figure 3. Computed spin densities for **A** and **[2]²⁺** in a doublet and a hypothetical quartet ground state obtained at the B3LYP/def2SVP level of theory.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: arsenic · iron cluster · redox chemistry

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- [18] Supplementary crystallographic informations on compounds **A**, **[1][TEF]**, **[1][FAI]**, **[2][BAr^F]₂** and **[K@crypt][3]** are available from the Cambridge Crystallographic Data Center under the reference numbers 2157447–2157451.

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