

How to cite: *Angew. Chem. Int. Ed.* **2023**, e202307696  
 doi.org/10.1002/anie.202307696

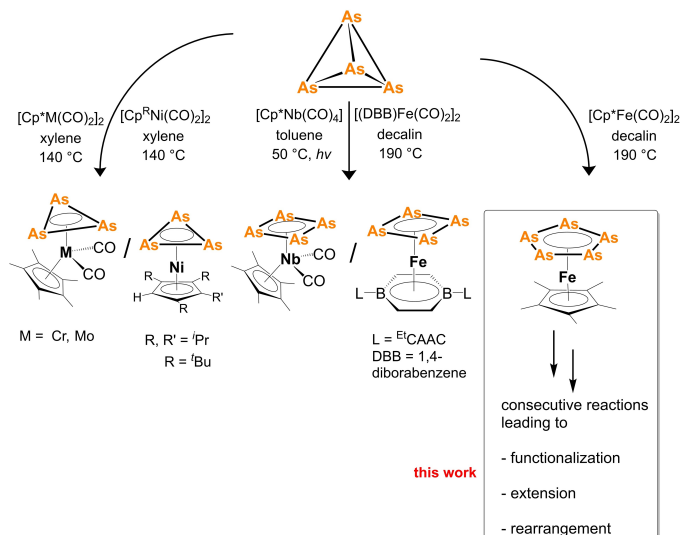
## Arsenic

# Nucleophilic Attack at Pentaarsaferrocene $[\text{Cp}^*\text{Fe}(\eta^5\text{-As}_5)]$ -The Way to Larger Polyarsenide Ligands

Stephan Reichl, Christoph Riesinger, and Manfred Scheer\*

Dedicated to Professor Lutz Gade on the occasion of his 60th birthday.

**Abstract:** By the reaction of  $[\text{Cp}^*\text{Fe}(\eta^5\text{-As}_5)]$  (**I**) ( $\text{Cp}^* = \text{C}_5\text{Me}_5$ ) with main group nucleophiles, unique functionalized products with  $\eta^4$ -coordinated polyarsenide ( $\text{As}_n$ ) units ( $n = 5, 6, 20$ ) are obtained. With carbon-based nucleophiles such as  $\text{MeLi}$  or  $\text{KBn}$  ( $\text{Bn} = \text{CH}_2\text{Ph}$ ), the anionic organo-substituted polyarsenide complexes,  $[\text{Li}(2.2.2\text{-cryptand})][\text{Cp}^*\text{Fe}(\eta^4\text{-As}_5\text{Me})]$  (**1a**) and  $[\text{K}(2.2.2\text{-cryptand})][\text{Cp}^*\text{Fe}(\eta^4\text{-As}_5(\text{CH}_2\text{Ph}))]$  (**1b**), are accessible. The use of  $\text{KAsPh}_2$  leads to a selective and controlled extension of the  $\text{As}_5$  unit and the formation of the monoanionic compound  $[\text{K}(2.2.2\text{-cryptand})][\text{Cp}^*\text{Fe}(\eta^4\text{-As}_6\text{Ph}_2)]$  (**2**). When **I** is reacted with  $[\text{M}]\text{As}(\text{SiMe}_3)_2$  ( $\text{M} = \text{Li}\cdot\text{THF}$ ;  $\text{K}$ ), the formation of the largest known anionic polyarsenide unit in  $[\text{M}'(2.2.2\text{-cryptand})]_2\text{-}[(\text{Cp}^*\text{Fe})_4(\mu_5\text{-}\eta^4\text{-}\eta^4\text{-}\eta^3\text{-}\eta^3\text{-}\eta^1\text{-}\eta^1\text{-}\text{As}_{20})]$  (**3**) occurred ( $\text{M}' = \text{Li}$  (**3a**),  $\text{K}$  (**3b**)).



## Introduction

The generation and handling of yellow arsenic ( $\text{As}_4$ ) is hardly possible due to its extreme light and air sensitivity.<sup>[1a,b]</sup> One approach to handle the metastable  $\text{As}_4$  is by its conversion with carbonyl-containing complexes under photolytic or thermolytic conditions to form polyarsenide transition metal complexes.<sup>[1a]</sup> The reaction of  $[\text{Cp}^*\text{Fe}(\text{CO})_2]$  with a freshly prepared solution of  $\text{As}_4$  in decalin at  $190^\circ\text{C}$  for 1.5 hours leads to  $[\text{Cp}^*\text{Fe}(\eta^5\text{-As}_5)]$  (**I**).<sup>[1,2]</sup> In contrast to yellow arsenic, complex **I** is stable towards light and oxygen.<sup>[2]</sup> Pentaarsaferrocene **I** is isostructural to ferrocene and represents with its  $\text{cyclo-As}_5$  ligand a true rarity as one of the very few end-on-coordinated-polyarsenide ligand complexes (Scheme 1).<sup>[1,3]</sup> Besides the donor

possibilities of the As atoms at the  $\text{cyclo-As}_5$  ring, DFT calculations show that the LUMO of **I** is mostly localized on the As atoms of the  $\text{cyclo-As}_5$ -ligand, which suggests potential inverted reactivity as an electron acceptor.<sup>[4]</sup> Indeed, this would mimic the reactivity of free  $\text{As}_4$ , which is, just as  $\text{P}_4$ , degradable by nucleophiles and would make **I** a model starting material to avoid the use of the difficult to handle  $\text{As}_4$ .<sup>[5]</sup> Over the years, a variety of  $\text{As}_n$  ligand complexes were reported, containing ligands of up to 18 arsenic atoms.<sup>[3,6,7]</sup> However, the pathways to arsenic-rich compounds have been much less studied as compared to those of the polyphosphorus ligand ones. Especially the synthesis of anionic organo-polyarsenide products is very challenging and of high interest, as they are starting materials for further functionalization. While a large number of polyarsenide ligand complexes was reported,<sup>[1a,c]</sup> almost no consecutive reactivity was communicated. Thus, due to its good accessibility, **I** represents a suitable starting material for further investigations in the described directions.

In 2016, P. W. Roesky and co-workers presented the reactivity of  $[\text{Cp}^*\text{Fe}(\eta^5\text{-As}_5)]$  (**I**) towards  $[\text{L}_2\text{Sm}(\text{thf})_2]$  ( $\text{L} = (2,6\text{-diisopropylphenyl-N})_2\text{CH}$ ), and our group investigated the versatile reduction chemistry of **I**.<sup>[7]</sup> The latter shows the different reaction behavior of pentaarsaferrocene in comparison to that of its lighter homolog  $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$  (**II**).<sup>[9]</sup> Notably, for **II**, the  $^{31}\text{P}$  NMR spectroscopy is a decisive tool

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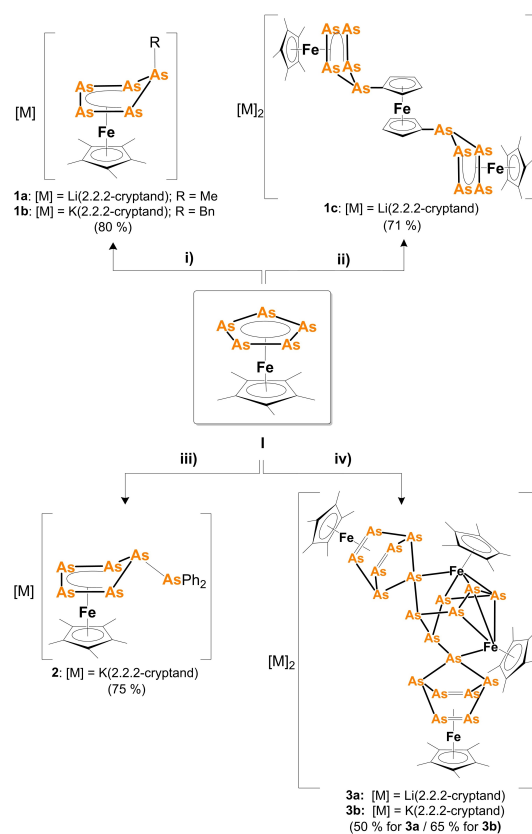
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to monitor the reactivity, which is, however, not possible for the arsenic derivative **I**. Thus, one is dependent on the isolation of single crystals to gain structural insight into the products. Since the reduction of **I** is not very selective and several mono- and dianionic  $As_n$  ligand complexes were obtained,<sup>[8]</sup> we were interested in whether it is possible to receive selective products by the reaction of **I** with nucleophiles, especially carbon- but also arsenic-based ones. In view of our reports on the reactivity of  $[Cp^*Fe(\eta^5-P_5)]$  (**II**) towards main group nucleophiles and the isolation of unprecedented functionalized products,<sup>[6b]</sup> the question arose of whether **I** follows the same pathway or offers the chance of ring expansion and rearrangement reactions.

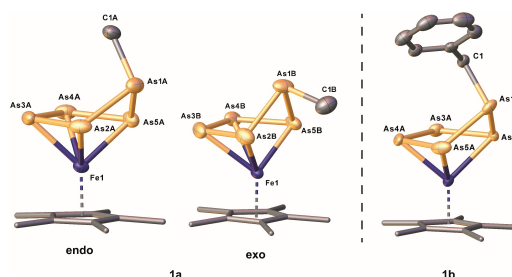
Herein, we report on the reactivity of the pentaarsaferrocene **I** with different organo- as well as arsenic-based nucleophiles ( $KAsPh_2$ ,  $[M]As(SiMe_3)_2$  ( $M=Li\cdot THF$ ;  $K$ ),  $KAsCO$  and  $KAsH_2$ ), bearing organo and/or labile substituents, to achieve a substitution but also a controlled extension of the polyarsenide ligand and induce a selective aggregation to obtain  $[(Cp^*Fe)_4\{\mu_4-\eta^4:\eta^4:\eta^3:\eta^3:\eta^1-As_{20}\}]^{2-}$  (**3a**, **3b**), the largest anionic polyarsenide complex known to date.

## Results and Discussion

In a first step, the reaction between  $[Cp^*Fe(\eta^5-As_5)]$  (**I**) and organo-based nucleophiles was investigated. The reaction of **I** with MeLi and KBn, respectively, and one equivalent of 2.2.2-cryptand at  $-80^\circ C$  leads to an immediate color change from green to brown. After workup, the complexes  $[Li(2.2.2-cryptand)][Cp^*Fe(\eta^4-As_5Me)]$  (**1a**) and  $[K(2.2.2-cryptand)][Cp^*Fe(\eta^4-As_5Bn)]$  (**1b**), respectively, can be isolated in crystalline yields of 80% and 75%, respectively (Scheme 2, i)). Notably, the use of cryptand at low temperature proved crucial, or else no crystals were obtained. This applies to all subsequent reactions, indicating that they are more selective and controlled when using cryptand and starting at  $-80^\circ C$ . Single crystal X-ray structure analyses of **1a** and **1b** reveal a novel  $\eta^4-As_5R$  moiety complexed at a  $Cp^*Fe$  center (**1a**:  $R=Me$ , **1b**:  $R=Bn$ ; Figure 1). Note that **1a** and **1b** represent the first anionic organo-substituted polyarsenide ligand complexes without the need of additional metal fragments to stabilize them.<sup>[8]</sup> The  $\eta^4-As_5R$  ligand exhibits an envelope geometry, featuring four arsenic atoms in the plane coordinating towards the  $Cp^*Fe$  fragment, whereas the arsenic atom bearing the organo substituent is out of the plane. The  $As-As$  bond lengths of 2.306(8)–2.401(4) Å are within the range of single and double bonds,<sup>[10,11]</sup> whereas the  $As-C$  distances (1.970(4) Å for **1a**; 1.994(4) Å for **1b**) correlate with an arsenic-carbon single bond.<sup>[10]</sup> The corresponding angles (see Table S4 and S6) indicate a nearly square planar geometry of the arsenic atoms in the plane. Contrary to the analogous phosphorus anion  $[Cp^*Fe(\eta^4-P_5Me)]$ <sup>[6]</sup> and all other P-based anions of this type,<sup>[6,9]</sup> the methyl group in **1a** is (disordered in the solid state structure) located in both an *endo* and an *exo* position (with respect to the envelope of the  $\eta^4-As_5$  moiety). Thus, **1a** is obtained in form of an isomeric mixture of a ratio of 86:14 (*endo:exo*, Figure 1). DFT calculations reveal



**Scheme 2.** Reactivity of **I** towards i) MeLi or KBn + 2.2.2-cryptand,  $-80^\circ C$  to r.t.; ii) 1,1'-dilithioferrocene + 2.2.2-cryptand,  $-80^\circ C$  to r.t.; iii)  $KAsPh_2$  + 2.2.2-cryptand,  $-80^\circ C$  to r.t.; iv)  $LiAs(SiMe_3)_2$  + 2.2.2-cryptand,  $-80^\circ C$  to r.t. for **3a**;  $KAs(SiMe_3)_2$  or  $KAsCO$  + 2.2.2-cryptand for **3b**,  $-80^\circ C$  to r.t.. Yields are given in parentheses.



**Figure 1.** Molecular structure of the anions of **1a** (left) and **1b** (right) in the solid state.  $Cp^*$  ligands are drawn in a stick model. Cations and H atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

the energetic similarity of both isomers and thus provide reason for the formation of this mixture, which is in stark contrast to the respective phosphorus analog. Consistently, the methyl groups of both isomers are chemically inequivalent and show different chemical shifts in the  $^1H$  and  $^{13}C$  NMR spectra (Figures S1 and S8). Storing dissolved crystals of **1a** at room temperature or heating the solution for three hours at  $50^\circ C$ , does not change the ratio of the isomers in solution over a period of four days, indicating a kinetically controlled process during the formation of **1a** with regards

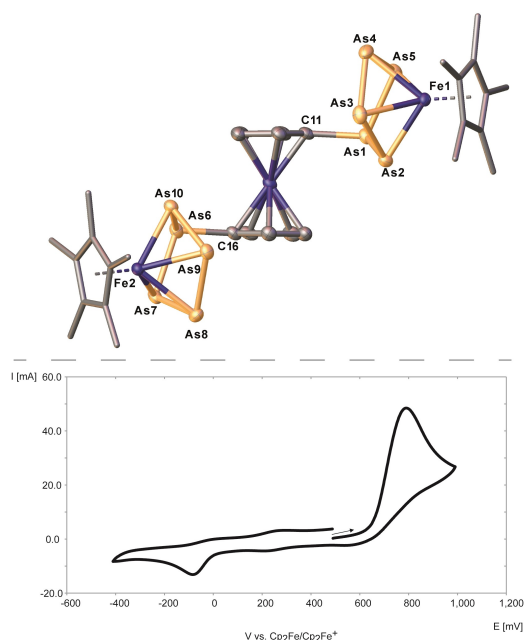
to the *endo/exo* products. Furthermore, this excludes thermodynamic equilibration of the isomeric ratio, which is supported by DFT calculations (*vide infra*). In contrast, **1b** is obtained solely as the *endo* isomer, which is attributed to the greater steric demand of the Bn-substituent.

Mixing a green solution of **1**, 1,1'-dilithioferrocene and 2.2.2-cryptand at  $-80^{\circ}\text{C}$  resulted in a dark green solution which turned brown-yellowish overnight. After workup (cf. SI), brown blocks of complex **1c** ( $[\text{Li}(2.2.2\text{-cryptand})]_2\{[\text{Cp}^*\text{Fe}(\eta^4\text{-As}_5)]_2(\eta^5\text{-C}_5\text{H}_4)_2\text{Fe}\}$ ) could be isolated (Scheme 1, ii)). XRD analysis revealed the formation of a dianionic species featuring two  $\eta^4\text{-As}_5$  moieties linked by a ferrocenyl unit (Figure 2). The As–As bond lengths are similar to complex **1a/1b**. The As–C bond lengths are 1.951(3) Å (As1–C11)/1.942(3) Å (As6–C16), respectively, indicating arsenic-carbon single bonds.<sup>[10]</sup>

Due to two iron fragments and the bridging ferrocene unit, complex **1c** is expected to exhibit interesting electrochemical properties. Hence, cyclic- (CV) and square wave voltammograms (SQV) of **1c** in THF were recorded. In accordance with initial expectations, the CV/SQV of **1c** show two oxidations at 0.878 V and 1.970 V (see Figure 2 and S23; vs.  $\text{Fc}/\text{Fc}^+$ ), respectively.

Hereby, the first oxidation is followed by an ECE-type process (electron transfer-chemical reaction-electron transfer), featuring the corresponding reduction at  $-0.814$  V (Figure 2, bottom). It should be noted that the second (irreversible) oxidation cannot be resolved properly by CV but can be detected by SQV (Figure S23).

Previous reports on the manifold reduction chemistry of **1**<sup>[7]</sup> showed its tendency to aggregate, forming arsenic-rich polyarsenides, stabilized by  $\text{Cp}^*\text{Fe}$  fragments e.g. in  $[\text{K}$

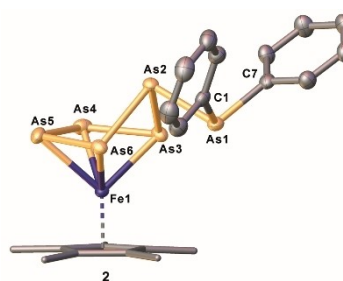


**Figure 2.** Molecular structure of the dianion of **1c** in the solid state (top;  $\text{Cp}^*$  ligands are drawn in a stick model. Cations and H atoms are omitted for clarity; thermal ellipsoids are drawn at 50% probability) and the corresponding cyclic voltammogram (bottom) of **1c**.

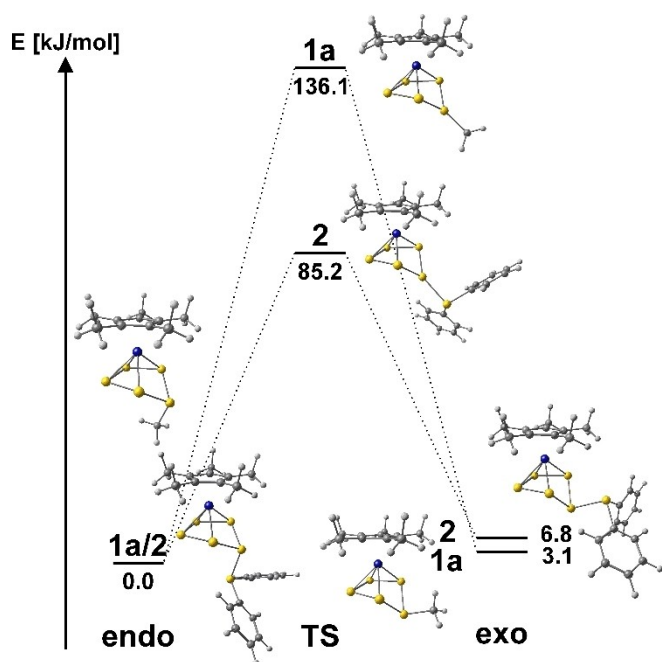
( $\text{dme}$ )<sub>3</sub>]<sub>2</sub>[( $\text{Cp}^*\text{Fe}$ )<sub>4</sub>{ $\mu_4\eta^4\text{-}\eta^3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^1\text{-}\eta^1\text{-As}_{18}$ }] as a main product, in a rather unselective way under formation of additional products.<sup>[7]</sup> In contrast to the redox properties of **1**, which show two quasi reversible oxidations and one irreversible reduction,<sup>[7]</sup> compound **1c** shows two irreversible oxidations. Whereas in **1**, a reduction leads to dimerization,<sup>[7]</sup> the ferrocene linker prevents a further reduction of **1c**. Surprisingly, the ferrocene linker in **1c** does not stabilize a one oxidation step and a following reduction can be observed after the oxidation (according to the CV).

To realize As–As aggregation processes in a more controlled manner, **1** was reacted with  $\text{KAsPh}_2$  as an arsenic-containing nucleophile. Indeed, this reaction gave single crystals of pure  $[\text{K}(2.2.2\text{-cryptand})][\text{Cp}^*\text{Fe}(\eta^4\text{-As}_6\text{Ph}_2)]$  (**2**) in 75% yield (Scheme 2, iii)). The anion of **2** features an unusual  $\eta^4\text{-As}_6\text{Ph}_2$  ligand (Figure 3 and S18), proving that an extension of the polyarsenide ligand is possible in a selective manner. The newly formed As1–As2 bond possesses a distance of 2.4440(3) Å, which is in agreement with an arsenic single bond.<sup>[10]</sup> Interestingly, **2** crystallizes as the *exo* isomer exclusively (Figure 3), which is attributed to beneficial packing effects, as DFT calculations reveal only a minor energy difference between both isomers (*vide infra*). This is of particular interest, as the *endo* isomer appears to be preferred for simple organic substitution in **1a-c**.

The *endo/exo* isomerism within the nucleophilically functionalized polyarsenide derivatives **1** and **2** is unprecedented for such *cyclo-E*<sub>3</sub>R polypnictide species, especially for  $\text{E}=\text{P}$ . Thus, to gain insight into this intriguing isomerization behavior of **1** and **2**, DFT calculations (B3LYP/def2-TZVP) were performed to elucidate the energetic relationship between the *endo* and the *exo* isomers of these compounds. Exemplary, the Me-substituted derivative **1a** was chosen for its simplicity to be compared against the more complicated  $\text{Ph}_2\text{As}$ -substituted **2** (Figure 4). Surprisingly, the energetic difference between the *endo* and the *exo* isomer is marginal in both cases (**1a**: 3.1 kJ/mol, **2**: 6.8 kJ/mol). Thus, thermodynamically, an equilibrium between both isomers is expected in both cases, yet a mixture of isomers is only experimentally observed in the case of **1a**. An explanation for this phenomenon can be found in the transition states (TS) connecting the *endo* and *exo* isomers for **1a** and **2**, respectively. In both cases the TS effectively revolves around the inversion of As1. However, the TS for



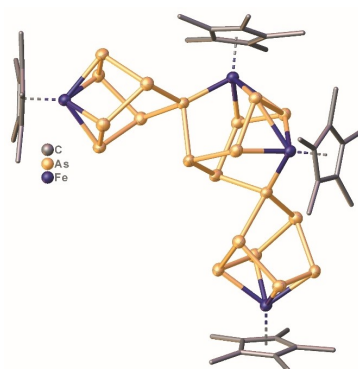
**Figure 3.** Molecular structure of the anion of **2** in the solid state;  $\text{Cp}^*$  ligand is drawn in a stick model. Cations and H atoms are omitted for clarity; thermal ellipsoids are drawn at 50% probability.



**Figure 4.** Calculated (B3LYP/def2-TZVP) energetic profile for the isomerization of **1a** and **2**; Energies are provided in kJ/mol and given aside or below each molecular structure.

**1a** has an energetic barrier of 136.1 kJ/mol and is thus inaccessible under standard conditions. In contrast, the respective TS for **2** is only 85.2 kJ/mol in energy and thus accessible even at room temperature. This decrease in the energetic barrier is attributed to the electronically stabilizing effect of the  $\text{AsPh}_2$  substituent. Consequently, the formation of isomers for **1a** is most probably caused by kinetic control during its synthesis, while **2** can slowly equilibrate and forms the single *exo* isomer due to packing effects in the crystal.

Another interesting arsenic-containing nucleophile is  $\text{As}(\text{SiMe}_3)_2^-$ , which is known to react as an  $\text{As}^-$  synthon by the release of the weakly bound TMS (trimethylsilyl) groups.<sup>[12]</sup> When mixing complex **I**,  $\text{LiAs}(\text{SiMe}_3)_2 \cdot \text{THF}$  and 2.2.2-cryptand at  $-80^\circ\text{C}$ , a color change to brown was observed. After workup (cf. SI), green/brownish block-shaped single crystals were obtained. XRD analysis revealed the formation of an unprecedented  $\text{As}_{20}$  ligand complex, stabilized by four  $\text{Cp}^*\text{Fe}$  fragments (Scheme 2, iv). Compound **3a** ( $[\text{Li}(2.2.2\text{-cryptand})]_2[(\text{Cp}^*\text{Fe})_4\{\mu_4\text{-}\eta^4\text{-}\eta^4\text{-}\eta^3\text{-}\eta^1\text{-}\eta^1\text{-}\text{As}_{20}\}]$ ) is obtained in 50% yield and represents the largest molecular anionic polyarsenide ( $\text{As}_n$ ) ligand complex ( $n=20$ ). Despite being formally a tetramerization product of **I**, the molecular structure of the anion of **3a** comprises two norbornadiene-like  $\text{As}_7^{3-}$  moieties and one *cyclo*-hexane-like  $\text{As}_6$  unit in a chair configuration (Figure 5). The As–As bond lengths (Table S11) are similar to those of other  $\text{As}_n$  ligand complexes.<sup>[6]</sup> The alternating As–As bond lengths of 2.3903(7)–2.567(1) Å in the chair-like *cyclo*- $\text{As}_6$  moiety are within the range of arsenic single and double bonds.<sup>[10,11]</sup> The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3a** in  $\text{THF-d}_8$  at r.t. exhibit the equivalence of the  $\text{Cp}^*$  groups (cf. Figure S5 and S12). The analogous potassium compound **3b** ( $[\text{K}(2.2.2\text{-cryptand})]_2$ -



**Figure 5.** Molecular structure of the dianion of **3a/3b** in the solid state.  $\text{Cp}^*$  ligands are drawn in a stick model. The cation and H atoms are omitted for clarity. thermal ellipsoids are drawn at 50% probability.

$[(\text{Cp}^*\text{Fe})_4\{\mu_4\text{-}\eta^4\text{-}\eta^4\text{-}\eta^3\text{-}\eta^1\text{-}\eta^1\text{-}\text{As}_{20}\}]$ ) can be obtained when reacting **I** with  $\text{KAs}(\text{SiMe}_3)_3$  (Scheme 2, iv) under the formation of inter alia  $(\text{As}\{\text{SiMe}_3\}_2)^{[13]}$  as a side product according to NMR findings (Figures S24 and S25). Furthermore, a LIFDI-mass spectrum of the washing solution (cf. SI) indicates the formation of  $[(\text{Cp}^*\text{Fe})_2(\text{As}_5)]^+$ , traces of **I** and  $[\text{As}_2\text{Si}_4\text{C}_{10}\text{H}_{33}]^+$ , the latter of which can be assigned to a fragmentation product of  $(\text{As}\{\text{SiMe}_3\}_2)_2$ . This agrees with the tendency of polyarsenide ligand complexes to exhibit aggregation. Since the obtained crystals of **3a/3b** also contain starting material ( $[\text{M}]\text{As}(\text{SiMe}_3)_2$ ;  $\text{M}=\text{Li}$  (**3a**),  $\text{K}$  (**3b**)), 0.5 equivalents of the corresponding nucleophile were used to see if a full conversion of **I** can be achieved. Indeed, this led to the quantitative conversion and formation of complexes **3a/3b** in 50 and 42% yields, respectively. A better yield of 65% of **3b** can be achieved when using 0.5 equivalents of  $\text{KAsCO}$  as a nucleophile. Here, the formation of grey arsenic ( $\text{As}_{\text{gr}}$ ) can be observed. It should be noted that crystals of **3a** are hardly soluble and crystals of **3b** are not soluble at all in  $\text{THF-d}_8$ . Using  $\text{CD}_3\text{CN}$  leads to decomposition of **3** which was detected by monitoring additional peaks in the  $^1\text{H}$  NMR spectrum, which could unfortunately not be assigned (see Figure S6). Therefore, **3b** was not characterized in solution, but its composition was proven by elemental analysis (cf. SI).

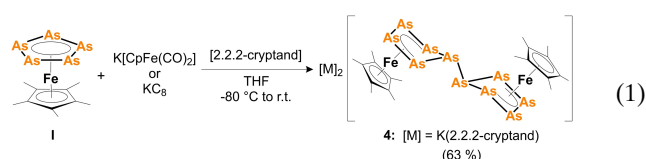
It is interesting to see that the arsenic nucleophile seems not to be present in the final product, but instead activates complex **I** which leads to the aggregation/tetramerization and release of  $(\text{As}\{\text{SiMe}_3\}_3)^{[13]}$  or  $\text{As}_{\text{gr}}$ , respectively. To verify this assumption, **I** was reacted with  $\text{LiP}(\text{SiMe}_3)_2 \cdot 1.8 \text{ THF}/\text{NaOCP}$  and 2.2.2-cryptand, respectively. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the reaction mixture of the latter shows exclusively traces of the starting material NaOCP. The crystals obtained from the reaction of **I** with  $\text{LiP}(\text{SiMe}_3)_2 \cdot 1.8 \text{ THF}$  are identical to complex **3a** and its  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum shows no signals, indicating that no P atom is incorporated in the polyarsenide scaffold and, thus, an activation of the  $\text{As}_5$  unit of **I** followed by a rearrangement and aggregation occurs.

Surprisingly, when reacting complex **I** with  $\text{KAsH}_2$  in the presence of 2.2.2-cryptand, the formation of two different



anionic polyarsenide ligand complexes was observed. In line with previous reactions, **3b** can be identified by XRD analysis, alongside with  $[(K(2.2.2\text{-cryptand}))_2[(Cp^*Fe)_2\{\mu-\eta^2:\eta^2:\eta^2-As_{14}\}]]$ . Unfortunately, the crystals of  $[(K(2.2.2\text{-cryptand}))_2[(Cp^*Fe)_2\{\mu-\eta^2:\eta^2:\eta^2-As_{14}\}]]$  are highly twinned and, therefore, their crystal structure cannot be discussed in detail. However, the connectivity and composition are clearly confirmed (Figure S22) and the same dianion was already reported by our group (see CCDC 1535410).<sup>[7]</sup> Since the latter complex can be also obtained by the reduction of **I** with KH, it may be proposed that  $KAsH_2$  reacts as a nucleophile giving the  $As_{20}$  ligand complex as well as a reducing agent towards **I** to result in a ligand complex containing an  $As_{14}$  moiety.

The question arose whether the formation of **3a/3b** is caused by reduction and consecutive aggregation. Thus,  $K[CpFe(CO)_2]$  was used as a molecular and soluble reducing agent. The reaction of **I** with  $K[CpFe(CO)_2]$  and 2.2.2-cryptand did not yield complex **3b**. However, yellow crystals of  $[K(2.2.2\text{-cryptand})_2]_2[(Cp^*Fe)_2\{\mu-\eta^4:\eta^4-As_{10}\}]$  (**4**) were obtained after crystallization from mixtures of acetonitrile and toluene at  $-30^\circ\text{C}$  (Equation 1). As an alternative route, complex **4** can be obtained spectroscopically pure in 63% yield when changing the reducing agent to potassium graphite ( $KC_8$ ) (Equation 1). Contrary to previous observations in the reduction chemistry of **I**,<sup>[7]</sup> the combination of  $KC_8$  and 2.2.2-cryptand leads to a highly selective reduction of **I**.



**Equation 1.** Reaction of **I** with  $K[CpFe(CO)_2]$  or  $KC_8$  and 2.2.2-cryptand starting at  $-80^\circ\text{C}$  to r.t.. Yield is given in parentheses.

The anion of **4** was already reported, however alongside different side products which could not be separated.<sup>[7]</sup> Thus, this new method represents a much more selective way to isolate pure **4** in an easy way. It has to be noted that an excess of  $KC_8$  does not lead to the formation of the dianion  $[Cp^*Fe(\eta^4-As_5)]^{2-}$ , which is known for the phosphorus analog.<sup>[9]</sup>

## Conclusion

In summary, a selective way was presented to functionalize the polyarsenide ligand in **I** with organo-based nucleophiles, as for instance Me (**1a**) and Bn (**1b**), yielding unprecedented  $As_5R$  moieties. By using  $KAsPh_2$ , the  $As_5$  unit can be extended in a controlled way to obtain the  $As_5AsPh_2$  entity in **2** (Scheme 2). The unprecedented tendency towards formation of both *endo* as well as *exo* (with regard to the bent  $As_5$  ring) functionalized isomers was elaborated computationally. Furthermore, it was possible to link two arsenic ligand complexes with a ferrocenyl unit (**1c**), featuring interesting electrochemical properties. Surpris-

ingly, the reaction of **I** with arsenic-based nucleophiles, bearing labile substituents such as  $SiMe_3$  or CO groups, triggers the aggregation of complex **I** as a formal tetramer and leads to the selective formation of the largest anionic molecular  $As_n$  ligand complexes so far  $[(Cp^*Fe)_4\{\mu_4-\eta^4:\eta^4:\eta^3:\eta^3:\eta^1:\eta^1-As_{20}\}]^{2-}$  (**3a**, **3b**) containing unprecedented  $As_{20}$  dianions. Furthermore, a selective reduction of **I** was found when using  $KC_8$  and 2.2.2-cryptand to form dianionic  $[(Cp^*Fe)_2\{\mu-\eta^2:\eta^2:\eta^2-As_{10}\}]^{2-}$ . Thus, the reduction of **I** leads, under As–As bond formation, to the  $As_{10}$  containing dianionic species **4**, whereas the reaction of **I** with special nucleophiles, possibly involving covalent interactions, leads to a more complex activation, rearrangement, and aggregation process, forming an  $As_{20}$  unit stabilized by  $Cp^*Fe$  moieties in **3**. Current studies focus on the selective reduction of **I** to a possible  $[Cp^*Fe(\eta^4-As_5)]^{2-}$  species and to shed light into the aggregation process to form **3**, which might help for an even better understanding of its complex reactivity. But in any case, **I** was shown to be a suitable starting material for the selective preparation of novel polyarsenide compounds. Having been consigned to the shadows so far, it can now be used as an alternative kind of  $As_n$  source in coordination chemistry.

## Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft within the project Sche 384/38-3. SR and CR are grateful to the Studienstiftung des Deutschen Volkes for PhD fellowships. Open Access funding enabled and organized by Projekt DEAL.

## 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 • Functionalization • Iron • Nucleophiles • Polyarsenide Units

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Manuscript received: June 1, 2023

Accepted manuscript online: July 5, 2023

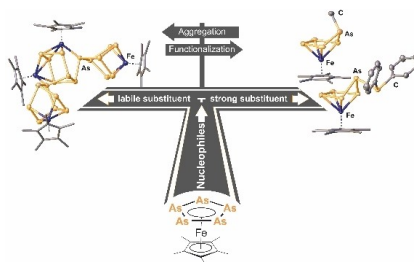
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## Research Articles

## Arsenic

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Nucleophilic Attack at Pentaarsaferrocene  
[Cp\*Fe( $\eta^5$ -As<sub>5</sub>)]-The Way to Larger Polyarsenide  
Ligands



A selective way for the nucleophilic substitution of the *cyclo*-As<sub>5</sub> ligand in [Cp\*Fe( $\eta^5$ -As<sub>5</sub>)] (**1**) was found, resulting in first As<sub>5</sub>R entities. By the reduction of **1**, an access to the dianionic compound [(Cp\*Fe)<sub>2</sub>{ $\mu$ - $\eta^4$ : $\eta^4$ -As<sub>10</sub>}]<sup>2-</sup> (**4**), and by using As-based nucleophiles, the straightforward formation of tetramers representing the largest polyarsenide-containing (As<sub>20</sub>) molecular complexes could be achieved.