Polyarsenides

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Molecular Polyarsenides of the Rare-Earth Elements

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Abstract: *Reduction of [Cp*Fe(η^5-As_5)] with [Cp″$_2$Sm(thf)] (Cp″ = η^5-1,3-(tBu)$_2$C$_5$H$_3$) under various conditions led to [(Cp″$_2$Sm)(μ,η^4:η^4-As_4)(Cp*Fe)] and [(Cp″$_2$Sm)$_2$$As_7$-(Cp*Fe)]. Both compounds are the first polyarsenides of the rare-earth metals. [(Cp″$_2$Sm)(μ,η^4:η^4-As_4)(Cp*Fe)] is also the first d/f-triple decker sandwich complex with a purely inorganic planar middle deck. The central As_4^{2-} unit is isolobal with the 6π-aromatic cyclobutadiene dianion $(CH)_4^{2-}$. [(Cp″$_2$Sm)$_2$$As_7$(Cp*Fe)] contains an As_7^{3-} cage, which has a norbornadiene-like structure with two short As–As bonds in the scaffold. DFT calculations confirm all the structural observations. The As–As bond order inside the cyclo As_4 ligand in [(Cp″$_2$Sm)(μ,η^4:η^4-As_4)(Cp*Fe)] was estimated to be in between an As–As single bond and a formally aromatic As_4^{2-} system.*

Rare-earth arsenides[1] are known to show semimetallic and interesting magnetic properties.[2] Recently, they have been utilized as epitaxial nanoparticles[3] and nanostructures[4] in combination with the well-established III-V semiconductor GaAs.[2a,5] Rare-earth arsenides can also be epitaxially grown as single crystals on III-V substrates.[6] Proposed applications include multijunction solar cells,[7] transparent electrical contacts,[8] and thermoelectric devices.[9] Although the solid-state chemistry of rare-earth arsenides is rich,[10] the number of structurally characterized molecular rare-earth arsenides is surprisingly low. To the best of our knowledge, only six structurally characterized compounds with Ln–As bonds, namely Ln–AsR$_2$[11] and Ln–As(R)–Ln,[12] are known. Although the solid-state and coordination chemistry of polyarsenides has been extensively explored,[10,13] no molecular rare-earth polyarsenide has ever been reported.[10b,14] In contrast, very recently a few U–As compounds were published.[15]

Herein, we report the synthesis and structural characterization of two mixed Fe/Sm polyarsenides obtained from reactions of [Cp*Fe(η^5-As_5)] with [Cp″$_2$Sm(thf)]. The products are the first rare-earth polyarsenides. By exchanging the solvent the reaction either yields a trinuclear complex containing a norbornadiene-like As_7^{3-} anionic ligand or the first d- and f-metal triple-decker sandwich complex containing a planar As_4^{2-} ring as the middle deck.

Recently, we reported the reactions of divalent samarium compounds with white phosphorus[16] or transition-metal-coordinated polyphosphides.[17] In this context, the first P–P bond formation between two [Cp*Fe(η^5-P_5)] (Cp* = η^5-C_5Me_5) molecules was induced by divalent lanthanide complexes.[17b] Inspired by these findings, we have been interested to compare this reaction behavior of [Cp*Fe(η^5-P_5)] towards the corresponding *cyclo*-As_5 analogue [Cp*Fe(η^5-As_5)],[18] since it is known for different behavior.[19] The treatment of the arsenic compound [Cp*Fe(η^5-As_5)][18] with [Cp″$_2$Sm(thf)] (Cp″ = η^5-1,3-(tBu)$_2$C$_5$H$_3$)[20] in toluene in a 1:1 stoichiometric ratio leads to the isolation of the sandwich compound [(Cp″$_2$Sm)(μ,η^4:η^4-As_4)(Cp*Fe)] (**1**) as black crystals in moderate yields (Scheme 1). Single-crystal X-ray structure determination of **1** revealed a triple decker complex containing a planar As_4 middle deck (Figure 1). The bond distances within the As_4^{2-} dianion can be considered as equal with an average length of 2.410 Å. The angles within the As_4^{2-} dianion are close to 90°. These structural parameters are in agreement with [{K(18-crown-6)}$_2$(As_4)] (av. As–As 2.39 Å).[21] The average Sm–As bond distance (3.273 Å) is longer than Sm–As single bonds, for example, [Cp*$_2$SmAsPh$_2$] (2.973(3) Å).[11c] Thus, the distance of the samarium atom to the ring centroid of the As_4 plane is relatively short (2.7957(14) Å). The Fe–Sm distance of 4.518(2) Å is longer than in the polyphosphide [Cp*Fe(μ-P_5)Sm(DIP$_2$pyr)(thf)$_2$] (4.303(2) Å; DIP$_2$pyr = 2,5-bis{*N*-(2,6-diisopropylphenyl)iminomethyl}pyrrolyl).[17b] The Sm–Cg(As_4)–Fe angle (Cg = ring centroid) is linear with 179.5(4)° and the three aromatic rings around the samarium atom afford an almost perfect trigonal coordination geometry (359.9°).

Therefore, compound **1** is the first d/f-triple decker sandwich complex with a purely aromatic inorganic middle deck. Compound **1** can also be considered as the first polyarsenide complex of the rare-earth elements. The charge of the As_4^{2-} dianion is balanced by a $(Cp''_2Sm)^+$ cation and a $(Cp^*Fe)^+$ cation. Since the As_4^{2-} dianion is a 6π-aromatic system, the {(η^4-As_4)(Cp*Fe)}$^-$ unit characterizes an 18 VE fragment.

Divalent organometallic lanthanide compounds usually initiate reactions via a single-electron transfer (SET) from the metal to a bonded substrate.[22] In contrast to the reaction of the analogous phosphorus compound [Cp*Fe(η^5-P_5)], the As_5

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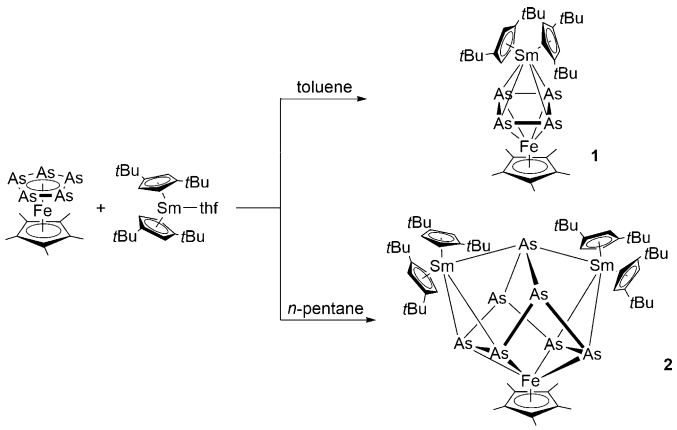


Scheme 1. Synthesis of the first polyarsenides of the rare-earth elements.

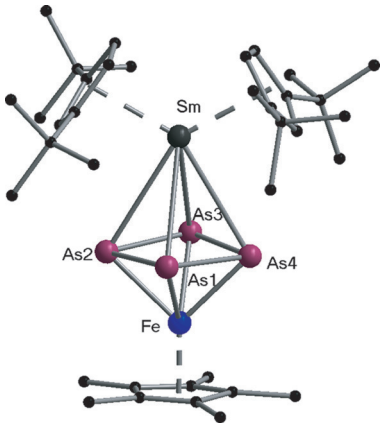
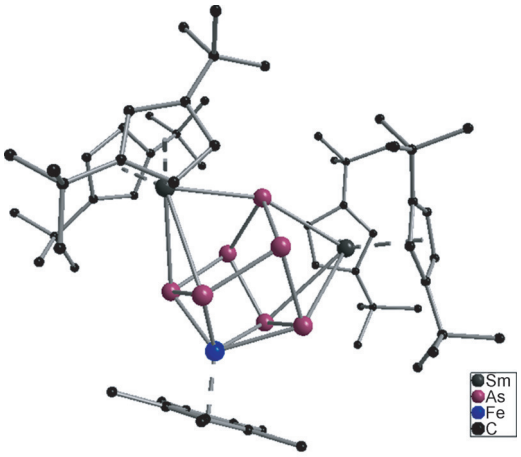


Figure 1. Solid-state structure of **1**.[32] Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sm–As1 3.213(4), Sm–As2 3.348(4), Sm–As3 3.239(4), Sm–As4 3.294(4), Sm–Cg(As_4) 2.7957(14), Sm–Cg(Cp″1) 2.465(10), Sm–Cg(Cp″1) 2.488(11), Fe–As1 2.437(5), Fe–As2 2.402(5), Fe–As3 2.470(5), Fe–As4 2.378(5), Fe–Cg(As_4) 1.723(3), Fe–Cg(Cp*) 1.674(9), As1–As2 2.414(4), As1–As4 2.396(5), As2–As3 2.415(5), As3–As4 2.414(3); As1-As2-As3 89.2(2), As2-As1-As4 90.6(2), As2-As3-As4 90.2(2), As1-As4-As3 89.7(2); Cg(As_4)-Sm-Cg(Cp″1) 120.4(3), Cg(As_4)-Sm-Cg(Cp″2), 119.5(3), Cg(Cp″1)-Sm-Cg(Cp″1) 120.0(4), Sm-Cg(As_4)-Fe 179.5(4) (Cg = ring centroid).



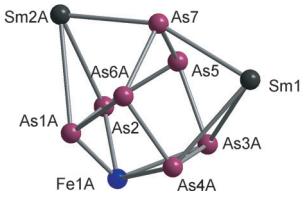


Figure 2. Solid-state structure of **2** (top) and the central core of the solid-state structure of **2** showing the norbornadiene-like As_7^{3-} cage (bottom). For details of the disorder, see the Supporting Information, Figure S7.

ring in [Cp*Fe(η^5-As_5)] is rearranged upon SET, and the sandwich compound **1** is formed (Scheme 1). Formation of the aromatic cyclotetraarsenide As_4^{2-} dianion from various arsenic sources is known; for example, the $[(Cp'Co)_2As_4]^+$ cation (Cp′ = η^5-(*t*Bu)C_5H_4)) was obtained by degradation of $[As_7(SiMe_3)_3]$ in the presence of $[Cp'CoCl]_2$.[23] As_4^{2-}, which is isolobal with the 6π-aromatic cyclobutadiene dianion $(CH)_4^{2-}$, has previously been described as a 6π-lone pair aromatic system.[21]

By changing the solvent from toluene to *n*-pentane, the reaction of [Cp*Fe(η^5-As_5)][18] with [Cp″$_2$Sm(thf)] in a 1:1 stoichiometric ratio afforded the trinuclear complex [(Cp″$_2$Sm)$_2$$As_7$(Cp*Fe)] (**2**) as red-brown crystals in 41% yield. Single-crystal X-ray diffraction analysis revealed compound **2** (Figure 2, top) containing a norbornadiene-like As_7^{3-} cage as the central structural motif (Figure 2, bottom). Since there is some disorder, the bonding parameters are not discussed in detail (Figure S7 in the Supporting Information shows the disorder in detail). The {η^4-As_7(Cp*Fe)}$^{2-}$ scaffold can be compared with similar transition metal complexes such as $[(en)(CO)_3W(\mu,\eta^1,\eta^4\text{-}P_7)M(CO)_3]^{3-}$[24] (en = ethylenediamine, M = Cr, W) or $[K(2,2,2\text{-crypt})]_3[E_7M(CO)_3]$ (E = P, As, Sb and M = Cr, Mo, W).[25] As observed in **2**, the norbornadiene-like E_7^{3-} anion in $[E_7M(CO)_3]^{3-}$ binds in an η^4-mode to the transition-metal fragment. As shown by detailed experimental and theoretical studies, there is significant charge transfer from the π-type orbitals of the E_7^{3-} fragment to the transition metal, in analogy to [(butadiene)Fe$(CO)_3$].[25] In a similar way, the As_7^{3-} cage in **2** acts as a six-electron donor in the {η^4-As_7(Cp*Fe)}$^{2-}$ scaffold, resulting in an 18 VE iron complex. The norbornadiene-like structure of **2** is in contrast to the recently reported P_7^{3-} cages in $[\{(NN^{fc})Ln(THF)_n\}_3P_7]$ (Ln = Sc, n = 0; Ln = Y, La, Lu n = 1; NN^{fc} = 1,1′-fc(NSi*t*BuMe$_2$)$_2$, fc = ferrocenediyl), which show a nortricyclane-like structure.[26]

To verify the trivalent oxidation state for Sm, NIR spectra for **1** and **2** were recorded. In general, Sm^{3+} complexes exhibit a characteristic absorption pattern in the NIR even in the presence of a strong visible absorption.[27] The NIR spectra of **1** and **2** (Supporting Information, Figures S2 and S5) compare very well with Sm^{3+}/$POCl_3$/$ZrCl_4$[28] and Sm^{3+}/$SeOCl_2$/$SnCl_4$,[29] which confirms that the Sm atoms in **1** and **2** are in the trivalent oxidation state.

The nature of the bonding in **1** and **2** was investigated by quantum-chemical RI-DFT calculations on the model com-

pounds $[(Cp_2Sm)(\mu,\eta^4{:}\eta^4\text{-}As_4)(CpFe)]$ (**1′**) and $[(Cp_2Sm)_2As_7(CpFe)]$ (**2′**). The calculated geometry of **1′** and **2′** is in good agreement with the determined structural parameters of **1** and **2**. For both molecules, population analyses based on occupation numbers were performed (Roby–Davidson–Ahlrichs–Heinzmann population analysis).[30] Partial charges (Q) to interpret the ionicity of the bonds were obtained. Shared electron numbers (SENs) served as a measure of the covalent bond strength. The analysis confirmed the ionic nature of compound **1′** with regard to both Sm and Fe ($Q(Sm) = +0.41$, $Q(Fe) = +0.35$, $Q(As) = -0.09$). We compared the As–As bond in **1′** with that in $[(CpCo)_2(\mu,\eta^4{:}\eta^4\text{-}As_4)]^{2+}$ and $(Na^+)_2(As_4)^{2-}$: in $[(CpCo)_2(\mu,\eta^4{:}\eta^4\text{-}As_4)]^{2+}$, the As–As bond was interpreted as part of a Co_2As_4 *closo* Wade cluster.[23] This finding was confirmed by recalculation of the SENs (SEN(As–As) = 0.99) and partial charges ($Q(As) = +0.03$). In the model compound $(Na^+)_2(As_4)^{2-}$, an As_4^{2-} ligand with a SEN(As–As) of about 1.18 is realized.[31] Since aromaticity, indicated by a significant decrease in bond lengths comparable to that in organic compounds, was not detectable for As_4 scaffolds, so-called "lone pair aromaticity"[21] was proposed. According to the SEN(As–As) value calculated for **1′** (1.08), we assume a bond order between that of a single bond and that of a formally aromatic As_4^{2-} system. The part of the MO diagram of $[(Cp_2Sm)(\mu,\eta^4{:}\eta^4\text{-}As_4)(CpFe)]$ (**1′**) related to the As_4 unit differs from that of $(Na^+)_2(As_4)^{2-}$ by a splitting of the π-type MO $5e_g$ due to interaction with Fe of the molecule (MO 72a). Still, a Jahn–Teller distortion could not be observed (Supporting Information, Figure S8).

For **2′**, similar behavior of a hypothetical As_7^{3-} ligand showing covalent interaction with the metal centers is observed: The SENs of the short As–As bonds of the ionic model compound $(Na^+)_3(As_7)^{3-}$ (symmetry C_{2v}) were calculated to be 1.23 (As1A–As2 and As3A–As4A, **2′**: 1.08), while the longer ones were calculated to be 0.99 (As1A–As6A, **2′**: 0.94) and 1.08 (As5–As7, **2′**: 1.02). Electron transfer is indicated by the reduced partial charges Q(As) going from the purely ionic model compound $(Na^+)_3(As_7)^{3-}$ to the complex **2′**: −0.38 (As7, **2′**: −0.21), 0.06 (As5, **2′**: 0.00), and −0.20 (As1A, **2a**: 0.02).

In conclusion, the reactions of $[Cp^*Fe(\eta^5\text{-}As_5)]$ with the divalent samarium compound $[Cp''_2Sm(thf)]$ result in an unprecedented reduction of the *cyclo*-As_5 ligand including its rearrangement and the isolation of the first polyarsenides containing rare-earth metal complexes. By adjusting the reaction conditions either the triple decker complex $[(Cp''_2Sm)(\mu,\eta^4{:}\eta^4\text{-}As_4)(Cp^*Fe)]$ (**1**) containing a 6π-aromatic As_4^{2-} ligand or the As-rich complex $[(Cp''_2Sm)_2As_7(Cp^*Fe)]$ (**2**) can be obtained as crystalline products. Single-crystal X-ray structure determination reveals that **2** contains a central norbornadiene-like As_7^{3-} scaffold while **1** is the first mixed d/f triple decker complex containing a purely inorganic aromatic middle deck. The negative charges of the anionic As_7^{3-} and As_4^{2-} ligands in **1** and **2** are balanced by $(Cp^*Fe)^+$ and $(Cp''_2Sm)^+$ complex fragments. The oxidation state III of Sm^{III} was confirmed by NIR spectroscopy. Supporting DFT calculations reveal the ionic nature of the compounds **1** and **2** showing significant interaction of the anionic polyarsenide ligands to the bonded metals. The As–As bond order inside the *cyclo*-As_4 ligand in **1** is estimated to be in between an As–As single bond and a formally aromatic As_4^{2-} system.

The observed reactivity of $[Cp^*Fe(\eta^5\text{-}As_5)]$ towards $[Cp''_2Sm(thf)]$ differs significantly from previously described reactions including the analogous phosphorus complex $[Cp^*Fe(\eta^5\text{-}P_5)]$. While reduction of the *cyclo*-P_5 ligand afforded a P–P bond formation the analogous *cyclo*-As_5 ligand was degraded and rearranged to afford the first polyarsenide complexes of the rare-earth elements.

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[31] Such a perfectly comparable behavior is found after comparison of $[(SmCp)_4P_8]$ with $(Na)_4(P_8)$: see Ref. [16].
[32] CCDC 1426212 (**1**), and 1426213 (**2**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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