Synthesis of arsenic-rich \( \text{As}_n \) ligand complexes from yellow arsenic†‡

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The reaction of \([\text{[\(\eta^5\text{-Cp}\)]\(\text{Co(\text{m}-\text{tol})}\)](2)}\) with yellow arsenic yields the arsenic-rich \( \text{As}_n \) ligand complexes \([\text{[\(\eta^5\text{-Cp}\)]\(\text{Co(\text{m}-\text{tol})}\)](1)}\), \([\text{[\(\eta^5\text{-Cp}\)]\(\text{Co(\text{m}-\text{tol})}\)](2)}\), and \([\text{[\(\eta^5\text{-Cp}\)]\(\text{Co(\text{m}-\text{tol})}\)](3)}\), which were comprehensively characterized. The molecular structure of 1 show a triple-decker complex with two \( \text{As}_2 \) units forming the middle-deck; compound 2 contains an all-arsenic \( \text{As}_{10} \) analogue of dihydrofulvalene in the molecular structure. The \( \text{As}_{12} \) ligand in 3 represents the largest \( \text{As}_n \) ligand complex reported so far.

Introduction

The synthesis of substituent-free \( \text{As}_n \) ligand complexes was established in the early 1980s. The first arsenic sources to be used for this purpose were cyclo-arsines such as \((\text{MeAs})_3\) and \((\text{PhAs})_3\), which formed the first triple-decker sandwich complex \( \text{A} \) with a distorted \( \text{As}_5\text{-As}_2 \) middle deck, revealing long \( \text{As}-\text{As} \) contacts of 2.726(3) and 2.752(3) \( \text{Å} \). Subsequently, poly-arsenides were introduced into this chemistry, for which the reaction of \( \text{As}^3^- \) with \([\text{Cr(\text{CO})_3(1,3,5-\text{Me}_3\text{C}_6\text{H}_3)}]\) was reported to yield a norbornadiene-like \( \text{As}_7 \) core in \( \text{B} \). A similar structural motif was obtained by Goicoechea et al. in \([\text{Ti(\text{η}^7\text{-As}_7)}]^- \) by the reaction of \( \text{As}^3^- \) with \( \text{TICl} \). The cobalt arsenic cluster \([\text{Co}_3\text{As}_2\{(\text{PEt}_2\text{Ph})_3\} \text{(C)} \text{, containing a cyclo-As}_6 \text{ unit, and } [\text{As@Ni}_{12@\text{As}_{10}}]^{13^-} \text{ were also synthesized using As}_7^- \text{ as the starting material}.\text{ Moreover, the neutral nortricyclane derivative, } [\text{As}_7\text{SiMe}_3]\text{, was used as the arsenic source by Fenske et al. in the reaction with } [\text{[\(\eta^5\text{-CoCl})_3\)}(\text{Cy}=\text{C}_5\text{Me}_5, \text{C}_5\text{Me}_5\text{-Bu})]\text{. Here, the cationic clusters } [\text{[\(\eta^5\text{-Co})_3(\text{µ}_3,\text{η}^1\text{-As}_3)\)}\text{]}^{2+} \text{ (D), } [\text{[\(\eta^5\text{-Co})_2(\text{µ}_3,\text{η}^4\text{-As}_4)\)}\text{]}^{2+} \text{ were obtained.} \text{ In contrast, the use of yellow arsenic (As}_4\text{, the unstable allotrope of arsenic, was introduced by cothermolysis reactions with cyclopentadienyl-containing carbonyl complexes, which led to a variety of cyclo-As}_3\text{, cyclo-As}_5\text{ and cyclo-As}_6\text{ complexes}}.\text{ For example, the reaction of As}_4\text{ with } [\text{[\(\eta^5\text{-Co(\text{CO})}_3\)}\text{]}(\text{Cp}^* = \text{C}_5\text{Me}_5) \text{ produced two binuclear complexes, } [\text{[\(\eta^5\text{-Co(\text{µ}_3\text{-As}_2)\)}\text{]}\text{ and } [\text{[\(\eta^5\text{-Co(\text{µ}_3\text{-As}_2)\)}\text{]}\text{, and one trinuclear complex, } [\text{[\(\eta^5\text{-Nb(\text{CO})}_3\)}\text{]}(\text{Cp}^* = 1,3\text{-Bu}_2\text{C}_5\text{H}_3)], \text{ Scherer et al. obtained } [\text{[\(\eta^5\text{-Nb}_2\text{As}_2\)}\text{]} (E), \text{ which contains the largest structurally characterized As}_n \text{ ligand known to date}.\text{ In the reaction of } [\text{[\(\eta^5\text{-Rh(\text{CO})}_3\)}\text{]}(\text{E} = \text{P, As}) \text{ the P}_{10} \text{ derivative of F was structurally characterized, whereas the As complex F was only characterized by mass spectrometry}.\text{ Larger structurally characterized arsenic scaffolds are present in the polyarsenide...}
anions (the Zintl ions: $\text{As}_4^{2-}$ and $\text{As}_6^{4-}$ and the cage compounds $\text{As}_2^{3-}$, $\text{As}_{11}^{3-}$, $\text{As}_{14}^{4-}$) derived from grey arsenic, with the largest reported polysubstituted anion hitherto being $\text{As}_{22}^{4-}$.$^{12}$ These ionic compounds confer thermodynamic stability through factors such as lattice enthalpy, which does not apply to analogous systems involving neutral $\text{As}_n$ ligands.

Thus, the question arises whether larger $\text{As}_n$ units can be generated. Recently, we reported on the activation of white phosphorus by $[(\text{Cp}''\text{R})\text{Co}(\text{CO})_2]_2[\mu_3,\eta^4\text{-toluene}]] (\text{Cp}'' = 1,3,5$-$\text{Bu}_3\text{C}_5\text{H}_2)^{13}$, which led to the formation of extended polyphosphorus scaffolds. Since $[(\text{Cp}''\text{R})\text{Co}(\text{CO})_2][\mu_3,\eta^4\text{-toluene}]]$ dissociates in solution into the unsaturated 14 VE complex $[\text{Cp}''\text{R}\text{Co}]$, this reactive moiety allows one to work under mild reaction conditions at low temperatures, yielding complexes containing $\text{P}_{16}$ and $\text{P}_{24}$ ligands, respectively, by consuming $\text{P}_4$ moieties for aggregation.$^{14}$

This success with phosphorus raised the question of approaching As-rich ligand complexes by a similar methodology using yellow arsenic. However, the poor solubility of yellow arsenic in common solvents combined with its extreme light sensitivity with respect to the formation of grey arsenic, are in strong contrast to the properties of white phosphorus. This complicates the use of $\text{As}_4$ as an arsenic source at ambient temperature and below. Moreover, in the few reports where $\text{As}_4$ has been used in reactions with transition metal compounds at room temperature and below, conversions to relatively small $\text{As}_3$ or $\text{As}_5$ units$^{15}$ or to a butterfly $\text{As}_4^{2-}$ moiety$^{16}$ were described. These observations raise important questions and challenges about whether solutions of $\text{As}_4$ be prepared in suitable solvents, where $\text{As}_n$ units can be

no evidence for 2 and 3. Similar complexes of 1 have been reported as minor products of the cothermolysis between $[\text{Cp}''\text{R}\text{Co}(\text{CO})_2]$ ($\text{Cp}'' = \text{C}_5\text{Me}_5\text{C}_5\text{Me}_5$, $\text{C}_5\text{Me}_4\text{Et}$) and yellow arsenic at 190 °C (for $[\text{Cp}''\text{R}\text{Co}(\text{CO})_2]$, 6% and for $[\text{Cp}''\text{R}\text{Co}(\text{CO})_2]$, 2% yield),$^*$

The $^1\text{H}$ NMR spectra of 1–3 show the corresponding signals for the $^1\text{H}$ groups as well as the aromatic protons. Due to the rotation of the cyclopentadienyl ligands in 2 only broad signals for the $^1\text{H}$ groups as well as the aromatic protons are observed in the $^1\text{H}$ NMR spectra. In the FDI mass spectra the molecular ion peaks of 1–3 are observed, and in the case of 1 further fragmentation was not detected. For 2 and 3 two fragments, $[(\text{Cp}''\text{R})\text{Co}\text{As}_n]^+$ and $[(\text{Cp}''\text{R})\text{As}_n]^+$, and in addition for

Results and discussion

In contrast to the situation with $\text{P}_4$ solutions (vide supra), the concentration of $\text{As}_4$ in solution is too low at $-30$ °C. Therefore, the reaction of $[(\text{Cp}''\text{R})\text{Co}(\text{CO})_2][\mu_3,\eta^4\text{-toluene}]]$ was performed at room temperature, with a saturated arsenic solution in toluene yielding three products (Scheme 1). After column chromatographic workup, 1 was isolated in 54% yield as the main product, followed by the $\text{As}_{12}$ complex 3 (14%) and the $\text{As}_{10}$ complex 2 (8%) (Scheme 1). Complex 1 can be formed selectively when the reaction takes place at 70 °C in good yields (82%) with

![Scheme 1](image1)

Scheme 1 Synthesis of compounds 1–3.

![Fig. 1](image2)

Fig. 1 Molecular structure of 1. H atoms are omitted for clarity. Anisotropic displacement parameters are depicted at 50% probability level. Selected bond lengths [Å] and angles [°]: As1–As2 2.2795(5), As1–As2 2.7029(4), Co–As1 2.4355(5), Co–As2 2.4211(5), Co–C centr. 2.092(3); As2–As1–As2 89.747(13).

![Fig. 2](image3)

Fig. 2 Molecular structure of 2·$4\text{CH}_2\text{Cl}_2$. The H atoms and the solvent molecules are omitted for clarity. Anisotropic displacement parameters are depicted at 50% probability level.
Compound 1 crystallizes from a saturated hexane solution as dark green blocks. The solid state structure (Fig. 1) shows a triple decker complex with two As₂ units as middle deck. The bond length As₁–As₂ of 2.2795(5) Å is shorter as a single bond determined for As₅ by electron diffraction in the gas phase (2.44 Å [ref. 17] and 2.435(4) Å [ref. 18]) and by DFT calculations (2.437 Å [ref. 15b]), respectively. The As₁–As₂ distance can be compared with the distance in the diarsene (((Me₃Si)₃CAs)₂), which contains an arsenic–arsenic double bond of 2.245(1) Å."  

In contrast, the distance between the two As₂ units of 2.8209(4) Å is beyond what can reasonably be considered a bond, however it is closer than the sum of the van-der-Waals-radii (3.7 Å). The distance between the two As₂ units in [Cp’CoAs₂]⁺ was found to be 2.844(1) Å, which is comparable to the distance in 1.

Compound 2 crystallizes from a saturated dichloromethane solution and constitutes the all-pnictogen analogue As₁₀ of dihydrofulvalene, which acts formally as a 16-electron donor ligand. The main feature of the structure of 2 (Fig. 2) is an As₁₀ ligand consisting of two As₅ units bonded by an As–As bond. In each of the As₅ rings four arsenic atoms coordinate to a [Cp’’Co] fragment whereas a second [Cp’’Co] fragment is coordinated by two arsenic atoms of one As₅ ring and one arsenic atom of the second As₅ ring. Accordingly, there are two types of [Cp’’Co] fragments, one coordinates via π bonds to four As atoms (av. As–Co 2.456(2) Å) and the other [Cp’’Co] fragment is coordinated formally by its lone pair to the atom Co1 (As₅–Co1 2.273(2) Å), and side-on to an As–As bond (As₁–As₁ 2.350(3) Å). Viewing the bond distance alternations, the shorter lone pair donation leads obviously to a longer π-type bond inclusive of the longer As–As bond of the linking As atoms (vide infra). However, formal coordination of the arsenic lone pair to cobalt occurs in the range of 2.326(1)–2.350(2) Å in compounds such as [Co₃([µ–(C₅H₅)₂CO₂Me]₂)(µ–(AsMe₂)₂S)](CO)₄ and [Co₂(RCCR’)(µ–AsPh₂)₂S]²⁻(CO)₄] (R’, R” = CO₂Me, Ph). The As–As bond lengths of 2 are in the range characteristic of single bonds (for details see ESI†), and only two distances between As₁–As₂ (As₁’–As₁”) are longer 2.705(2) Å (Fig. 2). However, these elongated distances are shorter than the As–As distances found in [(Cp’’Fe)₂(Cp’’Co)As₅], where two As₅ triangles are connected by As–As bonds with distances of 2.800(2) to 2.871(1) Å. In the triple-decker sandwich complex A there are As–As distances in the range of 2.726(3) and 2.752(3) Å which are regarded as being bonds with the bond order of 0.5. Therefore, one can speculate of a weak interaction between the atoms As₁ and As₂.

Single crystals of 3 were obtained from a saturated hexane solution as black needles. The structure of 3 (Fig. 3) can be derived from that of 2 in which one As₅(CoCp’’Co)₂ unit is replaced by a norbornane-like As₅Cp’’CoCp’’ fragment. All bond lengths are in the range of As–As single bonds, with the exception of the linking distance of the two As₅ moieties at the atoms As₁–As₂ (2.6684(5) Å). This distance is comparable with the corresponding bond length in 2 (2.705(2) Å). The elongation of the As–As bond through the coordination of two [Cp’’Co] fragments is comparable with the phosphorus analogue of 3, where a similar behavior is observed."  

Also in 3 the formal lone-pair coordination of Co to As (Co₂–As₅ 2.6286(6) Å) is slightly shorter than the other Co–As distances (average 2.4314(6) Å). The As₁₂ ligand, which is the largest yet obtained, can be described as a 12-electron donor.

**Conclusions**

In summary, it has been shown that the use of the Co complex [(Cp’’Co)₂(μ,η⁴-toluenel)] can initiate mild activation of yellow arsenic. Using this method, arsenic-rich As₅ ligand complexes could be synthesized. Complexes 2 and 3 contain As₁₀ and As₁₂ ligands, which are the largest substituent-free polyarsenic ligands yet observed in transition metal complexes, and have been unambiguously characterized by X-ray crystallography for the first time.

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**Notes and references**