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Synthesis of arsenic-rich As_n ligand complexes from yellow arsenic†‡

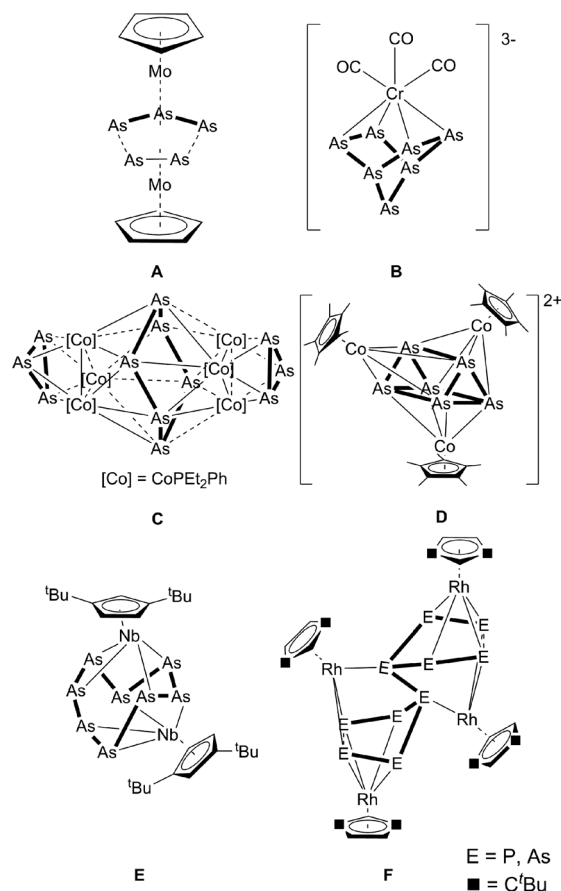
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The reaction of $[(\eta^5-Cp''Co)_2(\mu, \eta^{4:4}-toluene)]$ with yellow arsenic yields the arsenic-rich As_n ligand complexes $[(Cp''Co(\mu, \eta^{2:2}-As_2))_2]$ (**1**), $[(Cp''Co)_4(\mu_4, \eta^{4:4:2:2:1:1}-As_{10})]$ (**2**) and $[(Cp''Co)_3(\mu_3, \eta^{4:4:2:1}-As_{12})]$ (**3**), which were comprehensively characterized. The molecular structure of **1** shows a triple-decker complex with two As_2 units forming the middle-deck; compound **2** contains an all-arsenic As_{10} analogue of dihydrofulvalene in the molecular structure. The As_{12} ligand in **3** represents the largest As_n ligand complex reported so far.

Introduction

The synthesis of substituent-free 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 $(MeAs)_5$, and $(PhAs)_6$,¹ which formed the first triple-decker sandwich complex **A** with a distorted As_3-As_2 middle deck, revealing long As-As contacts of 2.726(3) and 2.752(3) Å.² Subsequently, polyarsenides were introduced into this chemistry, for which the reaction of As_7^{3-} with $[Cr(CO)_3(1,3,5-Me_3C_6H_3)]$ was reported to yield a norbornadiene-like As_7 core in **B**.³ A similar structural motif was obtained by Goicoechea *et al.* in $[Tl(\eta^2-As_7)]^{2-}$ by the reaction of As_7^{3-} with $TlCl$.⁴ The cobalt arsenic cluster $[Co_6As_{12}(PET_2Ph)_6]$ (**C**), containing a *cyclo*- As_6 unit, and $[As@Ni_{12}@As_{20}]^{3-}$ were also synthesized using As_7^{3-} as the starting material.^{5,6} Moreover, the neutral nortricyclane derivative, $[As_7(SiMe_3)_3]$, was used as the arsenic source by Fenske *et al.* in the reaction with $[(Cp^RCoCl)_2]$ ($Cp^R = C_5Me_5, C_5Me_4^tBu$). Here, the cationic clusters $[(Cp^RCo)_3(\mu_3, \eta^4-As_6)]^{2+}$ (**D**), $[(Cp^RCo)_3(\mu_3, \eta^4-As_6)]^+$ and $[(Cp^RCo)_2(\mu_2, \eta^4-As_4)]^{2+}$ were obtained.⁷ In contrast, the use of yellow arsenic (As_4), the unstable allotrope of arsenic, was introduced by cothermolysis reactions with cyclopentadienyl-containing carbonyl complexes, which led to a variety of *cyclo*- As_3 , *cyclo*- As_5 and *cyclo*- As_6 complexes.⁸ For example, the reaction of As_4 with $[Cp^*Co(CO)_2]$ ($Cp^* = C_5Me_5$) produced two binuclear complexes, $[Cp^*Co(\mu, \eta^{2:2}-As_2)]_2$ and $[Cp^*_2Co_2(\mu_2, \eta^{2:2}-As_6)]$, and one trinuclear complex, $[Cp^*Co(\mu, \eta^{2:2}-As_2)]_3$.⁹ By reacting As_4 with $[Cp''Nb(CO)_4]$ ($Cp'' = 1,3-tBu_2C_5H_3$), Scherer *et al.* obtained $[Cp''Nb_2As_8]$ (**E**), which contains the largest structurally

characterized As_n ligand known to date.¹⁰ In the reaction of $[Cp''Rh(CO)_2]$ with E_4 ($E = P, As$) the P_{10} derivative of **F** was structurally characterized, whereas the As complex **F** was only characterized by mass spectrometry.¹¹ Larger structurally characterized arsenic scaffolds are present in the polyarsenide



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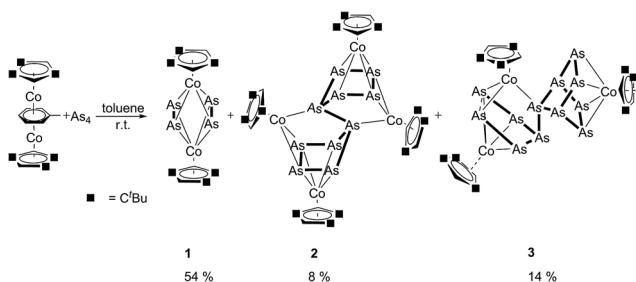
anions (the Zintl ions: As_4^{2-} and As_6^{4-} and the cage compounds As_7^{3-} , As_{11}^{3-} , As_{14}^{4-}) derived from grey arsenic, with the largest reported polyarsenide anion hitherto being As_{22}^{4-} .¹² These ionic compounds confer thermodynamic stability through factors such as lattice enthalpy, which does not apply to analogous systems involving neutral As_n ligands.

Thus, the question arises whether larger As_n units can be generated. Recently, we reported on the activation of white phosphorus by $[(Cp''Co)_2\{\mu,\eta^{4:4}\text{-toluene}\}]$ ($Cp'' = 1,3,5\text{-}t\text{-Bu}_3C_5H_2$),¹³ which led to the formation of extended polyphosphorus scaffolds. Since $[(Cp''Co)_2\{\mu,\eta^{4:4}\text{-toluene}\}]$ dissociates in solution into the unsaturated 14 VE complex $[Cp''Co]$, this reactive moiety allows one to work under mild reaction conditions at low temperatures, yielding complexes containing P_{16} and P_{24} ligands, respectively, by consuming 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 As_4 as an arsenic source at ambient temperature and below. Moreover, in the few reports where As_4 has been used in reactions with transition metal compounds at room temperature and below, conversions to relatively small As_1 or As_2 units¹⁵ or to a butterfly As_4^{2-} moiety¹⁶ were described. These observations raise important questions and challenges about whether solutions of As_4 be prepared in sufficiently high concentrations to form extended polyarsenic units that are larger than those currently known. Our findings on this topic are reported herein.

Results and discussion

In contrast to the situation with P_4 solutions (*vide supra*), the concentration of As_4 in solution is too low at $-30\text{ }^\circ\text{C}$. Therefore, the reaction of $[(Cp''Co)_2\{\mu,\eta^{4:4}\text{-toluene}\}]$ ¹³ 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 As_{12} complex **3** (14%) and the As_{10} complex **2** (8%) (Scheme 1). Complex **1** can be formed selectively when the reaction takes place at $70\text{ }^\circ\text{C}$ in good yields (82%) with



Scheme 1 Synthesis of compounds 1–3.

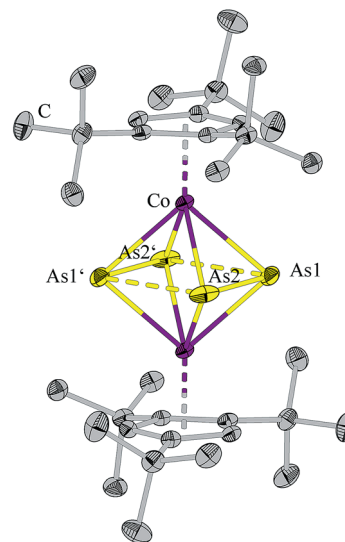


Fig. 1 Molecular structure of **1**. H atoms are omitted for clarity. Anisotropic displacement parameters are depicted at 50% probability level. Selected bond lengths [Å] and angles [°]: As1–As2 2.2795(5), As1⋯As2' 2.8209(4), Co–As1 2.4355(5), Co–As2 2.4211(5), Co–Ccentr. 2.092(3); As2–As1–As2' 89.747(13).

no evidence for **2** and **3**. Similar complexes of **1** have been reported as minor products of the cothermolysis between $[Cp^RCo(CO)_2]$ ($Cp^R = C_5Me_5$ (Cp^*), C_5Me_4Et (Cp^t)) and yellow arsenic at $190\text{ }^\circ\text{C}$ (for $[Cp^*CoAs_2]_2$ 6% and for $[Cp^tCoAs_2]_2$ 2% yield).⁹

The 1H NMR spectra of **1–3** show the corresponding signals for the t Bu groups and the signals for the aromatic protons. Due to the rotation of the cyclopentadienyl ligands in **2** only broad signals for the t Bu groups as well as the aromatic protons are observed in the 1H 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, $[(Cp''Co)_2As_6]^+$ and $[(Cp''Co)_2As_4]^+$, and in addition for

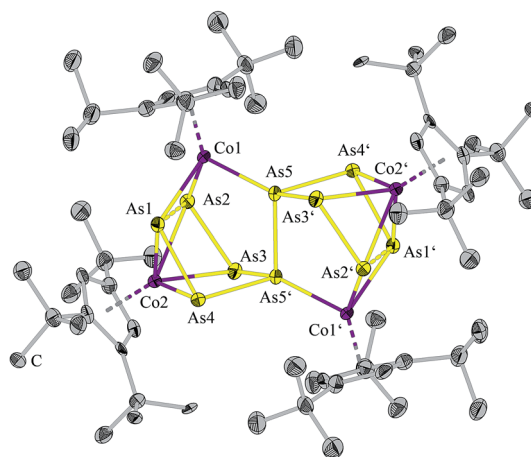


Fig. 2 Molecular structure of **2**·4CH₂Cl₂. The H atoms and the solvent molecules are omitted for clarity. Anisotropic displacement parameters are depicted at 50% probability level.



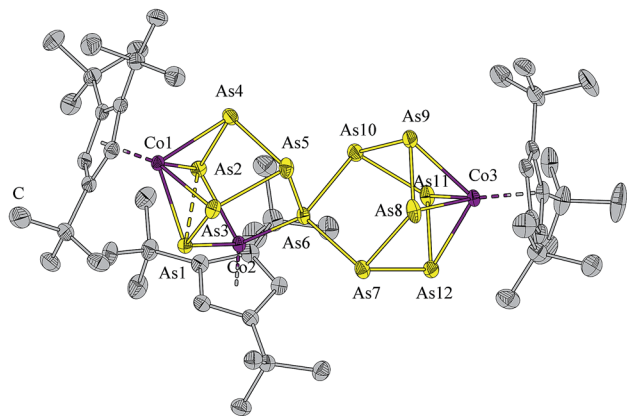


Fig. 3 Molecular structure of **3**. H atoms are omitted for clarity. Anisotropic displacement parameters are depicted at 50% probability level.

3 the fragment $[(\text{Cp}^{\text{III}}\text{Co})_2\text{As}_5]^+$ can be further found in the mass spectra (FDI-MS).

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 As_2 units as middle deck. The bond length As1–As2 of 2.2795(5) Å is shorter as a single bond determined for As_4 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 $[(\text{Me}_3\text{Si})_3\text{CAs}]_2$, which contains an arsenic–arsenic double bond of 2.245(1) Å.¹⁹ In contrast, the distance between the two As_2 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 As_2 units in $[\text{Cp}^{\text{I}}\text{CoAs}_2]_2$ 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 As_{10} of dihydrofulvalene, which acts formally as a 16-electron donor ligand. The main feature of the structure of **2** (Fig. 2) is an As_{10} ligand consisting of two As_5 units bonded by an As–As bond. In each of the As_5 rings four arsenic atoms coordinate to a $[\text{Cp}^{\text{III}}\text{Co}]$ fragment whereas a second $[\text{Cp}^{\text{III}}\text{Co}]$ fragment is coordinated by two arsenic atoms of one As_5 ring and one arsenic atom of the second As_5 ring. Accordingly, there are two types of $[\text{Cp}^{\text{III}}\text{Co}]$ fragments, one coordinates *via* π bonds to four As atoms (av. As–Co 2.456(2) Å) and the other $[\text{Cp}^{\text{III}}\text{Co}]$ 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–Co1, As2–Co1 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 $[\text{Co}_2\{\mu\text{-(C}_2\text{(CO}_2\text{Me)}_2)\}\{\mu\text{-(AsMe}_2)_2\text{S}\}(\text{CO})_4]$ and $[\text{Co}_2(\text{R}'\text{CCR}'')\{\mu\text{-(AsPh}_2)_2\text{S}\}(\text{CO})_4]$ ($\text{R}', \text{R}'' = \text{CO}_2\text{Me, Ph}$).²⁰ 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'–As2') are longer 2.705(2) Å (Fig. 2). However, these elongated distances are shorter than the As–As distances found in $[(\text{Cp}^*\text{Fe})_2(\text{Cp}^*\text{Co})\text{As}_6]$, where two As_3 triangles are connected by As–As bonds with distances of 2.800(2) to 2.871(1) Å.²¹ 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 0.5.² 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 $\text{As}_5(\text{CoCp}^{\text{III}})_2$ unit is replaced by a norbornane-like $\text{As}_7\text{CoCp}^{\text{III}}$ fragment. All bond lengths are in the range of As–As single bonds, with the exception of the linking distance of the two As_n 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 $[\text{Cp}^{\text{III}}\text{Co}]$ fragments is comparable with the phosphorus analogue of **3**, where a similar behavior is observed.¹⁶ Also in **3** the formal lone-pair coordination of Co to As (Co2–As6 2.2628(6) Å) is slightly shorter than the other Co–As distances (average 2.4314(6) Å). The As_{12} 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 $[(\text{Cp}^{\text{III}}\text{Co})_2\{\mu, \eta^{4,4}\text{-toluene}\}]$ can initiate mild activation of yellow arsenic. Using this method, arsenic-rich As_n ligand complexes could be synthesized. Complexes **2** and **3** contain As_{10} and As_{12} 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.

Acknowledgements

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