A Square As_4 and a Prismatic As_6 Structure as Complex Ligands

Carsten von Hänisch, Dieter Fenske,* Florian Weigend and Reinhart Ahlrichs

Abstract: $[As_7(SiMe_3)_3]$ reacts with $[(Cp^*CoCl)_2]$ to give black crystals of the ionic compound $[(Cp^*Co)_3As_6][CoCl_4]$ (**1**). The cation $[(Cp^*Co)_3As_6]^{2+}$ consists of an As_6 prism, with squares capped by [Cp*Co] fragments. When $[(Cp^{tBu}CoCl)_2]$ is used instead of $[(Cp^*CoCl)_2]$ in the reaction, dark red crystals of $[(Cp^{tBu}Co)_3As_6][CoCl_3(thf)]_2$ (**2**) and green–black crystals of $[(Cp^{tBu}Co)_2As_4][Co_3Cl_8(thf)_2]$ (**3**) can be obtained. The cation in **2** shows a structure very similar to that of **1**. The $[(Cp^{tBu}Co)_2As_4]^{2+}$ cations in **3** can be described as a triple-decker sandwich complex with two $[Cp^{tBu}Co]^+$ fragments bridged by an As_4 ligand. Density functional calculations reproduce the experimental data of **1** and **3** and allow an interpretation of molecular electronic structure and bonding in these and related compounds with As replaced by P and Co by Fe.

Keywords
arsenic · cobalt · density functional calculations · structural elucidation · Zintl anions

Introduction

Over the past few years a number of authors[1–3] have reported on molecular and ionic compounds with As_n ligands. $(PhAs)_6$ and $(MeAs)_5$[1] as well as As_4[2, 3] usually served as the starting compounds. However, in comparison, only little is known about the chemical behaviour of intermetallic phases of the composition M_3As_7 (M = alkaline metal). Eichhorn et al. reported, for example, the reaction of $[Cr(CO)_3(C_6H_6)]$ with Rb_3As_7 in ethylenediamine which results in the formation of the anionic species $[As_7Cr(CO)_3]^{3-}$.[4] Recently, the synthesis of $[Co_6As_{12}(PEt_2Ph)_6]$ from K_3As_7 and $[CoCl_2(PEt_2Ph)_2]$ was successful.[5]

Here we report on the synthesis of the ionic compounds **1**, **2** and **3**, which were obtained through the reaction of

$[(Cp^*Co)_3As_6][CoCl_4]$ **1**
$[(Cp^{tBu}Co)_3As_6][CoCl_3(thf)]_2$ **2**
$[(Cp^{tBu}Co)_2As_4][Co_3Cl_8(thf)_2]$ **3**

$[As_7(SiMe_3)_3]$ with $[(Cp^*CoCl)_2]$ or $[(Cp^{tBu}CoCl)_2]$, respectively ($Cp^* = C_5Me_5$, $Cp^{tBu} = C_5Me_4tBu$).[6] We first present and discuss the structures of the new compounds. Molecular electronic structure calculations have been carried out for **1** and **3** and related compounds, to elucidate bonding in the central cages.

Results and Discussions

Synthesis of Complexes and Discussion of Structures: A suspension of $CoCl_2$ and Cp*Li in THF at −78 °C was treated with $[As_7(SiMe_3)_3]$, and the solution was slowly heated to 0 °C. Black, octahedral crystals of **1**[7] were obtained, which are composed of $[(Cp^*Co)_3As_6]^{2+}$ cations (Figure 1) and $[CoCl_4]^{2-}$ anions. According to the crystal structure analysis, the cation consists of an As_6 prism, the rectangular areas of which are capped by a Cp*Co fragment (Figure 1). The distances between As and Co are 236.3(1) and 241.1(1) pm, and the As–As distances in the As_3 rings are 256.4(1) pm. Owing to the coordination of the Cp*Co fragments, the As–As distance between the two As_3

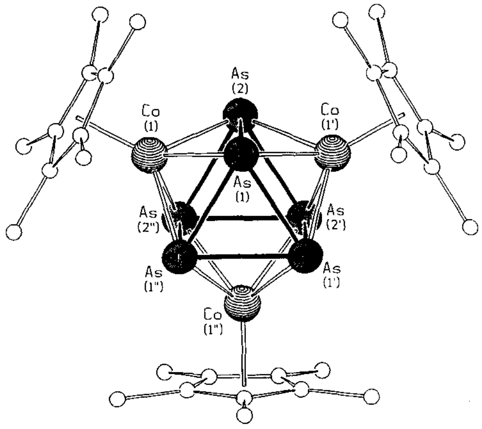

Figure 1. Molecular structure of the cation in **1**. Selected distances [±0.1 pm] and angles [±0.02°]: As(1)–As(1′), 256.3; As(1)–As(2), 285.4; As(2)–As(2′), 256.4; As(1)–Co(1), 236.3; As(2)–Co(1), 241.1; As(1)-As(1′)-As(1″), 60.00; As(1)-As(1′)-As(2′), 90.00; As(1)-Co(1)-As(2), 73.43; Co(1)-As(1)-As(1′), 104.44; Co(1)-As(2)-As(2′), 104.14; Co(1)-As(1)-As(1″), 57.15; Co(1)-As(2)-As(2″), 57.88; Co(1)-As(1)-Co(1′), 104.68; Co(1)-As(2)-Co(1′), 101.80.

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rings is significantly longer (285.4(1) pm) than the usual values (240–260 pm) for As single bonds.

The structure of the Co_3As_6 polyhedron is analogous to that of the Bi_9^{5+} cation in $[Bi_{10}Hf_3Cl_{18}]$.[8] Application of the Wade concept[9] to the Co_3As_6 cluster results in 22 valence electrons for the cluster core, which is equivalent to the valence electron number for Bi_9^{5+}.

The 22-valence-electron compound $[(Cp^*Fe)_2(Cp^*Co)As_6]$ (**4**)[10] published recently by Scherer et al. also shows a tricapped trigonal prismatic structure. However, the coordination of different transition metals leads to a slightly distorted As_6 prism.

To investigate steric effects on the reaction products $[(Cp^{tBu}CoCl)_2]$ was used instead of $[(Cp^*CoCl)_2]$ as the starting compound. In this reaction dark red crystals of **2** were formed initially, and then dark green–black crystals of **3** were obtained in the filtrate.[7]

$[(Cp^{tBu}Co)_3As_6]^{2+}$ cations, which show a structure very similar to that of the $[(Cp^*Co)_3As_6]^{2+}$ cations, can be found in **2**, but the asymmetrically substituted cyclopentadienyl ligand causes a slight distortion of the As_6 prism (Figure 2). The As–As distances between the As_3 rings are no longer identical; instead they have the following values: As(1)–As(4), 277.5(2) pm; As(2)–As(5), 279.3(2) pm; As(3)–As(6), 293.3(2) pm.

The $[(Cp^{tBu}Co)_2As_4]^{2+}$ cations in **3** form an octahedral cluster core with four arsenic and two cobalt atoms (Figure 3). The As_4 ring deviates only slightly from the geometry of a square, with As–As distances of As(1)–As(2) = 246.8(1) pm and As(1)–As(2′) = 245.5(1) pm, and angles of 90.07(3)° at As(1) and 89.93(3)° at As(2). The cation can therefore be described as a 34-VE triple-decker sandwich complex in which two $[Cp^{tBu}Co]^+$ fragments are bridged by a neutral $(\mu_2,\eta^4\text{-}As_4)$ ligand.

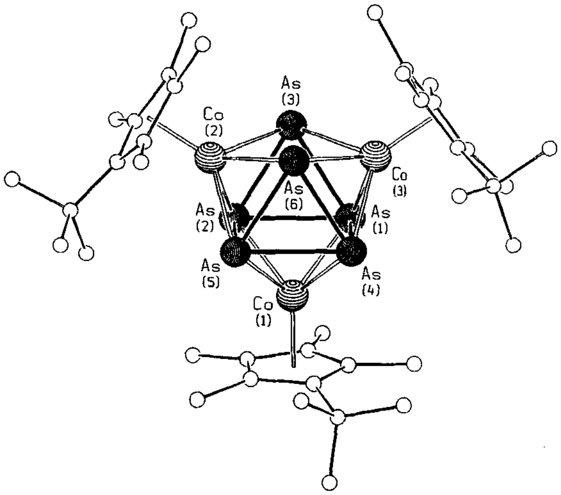

Figure 2. Molecular structure of the cation in **2**. Selected distances [±0.2 pm] and angles [±0.08°]: As(1)–As(2), 260.2; As(1)–As(3), 256.2; As(2)–As(3), 253.2; As(1)–As(4), 277.5; As(2)–As(5), 279.3; As(4)–As(5), 260.0; As(5)–As(6), 255.1; As(6)–As(4), 253.9; Co(1)–As(1), 239.2; Co(1)–As(2), 239.1; Co(1)–As(4), 239.4; Co(1)–As(5), 238.7; Co(2)–As(2), 238.5; Co(2)–As(3), 237.7; Co(2)–As(5), 237.7; Co(2)–As(6), 238.8; Co(3)–As(1), 238.2; Co(3)–As(3), 238.9; Co(3)–As(4), 239.3; Co(3)–As(6), 239.2; As(1)-As(2)-As(3), 59.85; As(2)-As(3)-As(1), 61.44; As(3)-As(1)-As(2), 58.71; As(3)-As(1)-As(4), 91.48; As(4)-As(5)-As(6), 59.02; As(5)-As(6)-As(4), 61.43; As(6)-As(4)-As(5), 59.50; As(1)-Co(1)-As(4), 70.89; As(2)-Co(1)-As(5), 71.56; As(3)-Co(2)-As(6), 75.99; As(3)-Co(3)-As(6), 75.68; Co(2)-As(3)-Co(3), 102.11; Co(2)-As(6)-Co(3), 101.66.

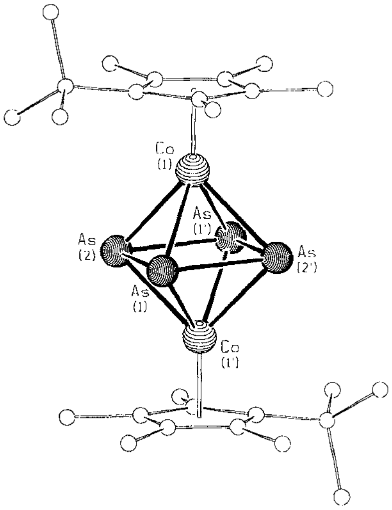

Figure 3. Molecular structure of the cation in **3**. Selected distances [±0.1 pm] and angles [±0.03°]: As(1)–As(2), 246.8; As(1)–As(2′), 245.5; Co(1)–As(1), 243.3; Co(1)–As(1′), 242.0; Co(1)–As(2), 242.8; Co(1)–As(2′), 242.9; As(2)-As(1)-As(2′), 90.07; As(1)-As(2)-As(1′), 89.93; Co(1)-As(1)-Co(1′), 88.40; Co(1)-As(2)-Co(1′), 88.34; Co(1)-As(1)-As(2), 59.38; As(1)-Co(1)-As(2), 61.03.

In the anions in **3** (Figure 4), there are two cobalt atoms with a distorted tetrahedral environment of four chlorine atoms. One cobalt atom is surrounded by four chlorine atoms and two oxygen atoms of the THF ligands in a nearly octahedral configuration. A trinuclear cobalt chloride anion of this type has not yet been described in the literature. The distances between the cobalt and chlorine atoms for the terminal chlorine ligands are 223.9(2)–224.3(2) pm. For the bridging atoms the Co–Cl distances range from 230.6(2) to 231.0(2) pm in the tetrahedron and from 241.2(1) to 248.7(1) pm for the octahedrally coordinated cobalt atom.

The neutral compounds $[(Cp^*Co)_3As_6]$ (**5**) and $[(Cp^{Et}Co)_2As_4]$ ($Cp^{Et} = C_5Me_4Et$), which are analogous to the cations $[(Cp^*Co)_3As_6]^{2+}$ and $[(Cp^{tBu}Co)_2As_4]^{2+}$, have been known for some years now.[11] In those cases, however, the As_n polyhedrons do not have the highly symmetrical form of a prism

Abstract in German: *$[As_7(SiMe_3)_3]$ reagiert mit $[(Cp^*CoCl)_2]$ unter Bildung von schwarzen Kristallen der ionischen Verbindung $[(Cp^*Co)_3As_6][CoCl_4]$* **1**. *Das $[(Cp^*Co)_3As_6]^{2+}$-Ion besteht aus einem As_6-Prisma, dessen Rechtecksflächen von $[Cp^*Co]$-Fragmenten überkappt sind. Setzt man statt $[(Cp^*CoCl)_2]$ $[(Cp^{tBu}CoCl)_2]$ mit $[As_7(SiMe_3)_3]$ um, so erhält man dunkelrote Kristalle von $[(Cp^{tBu}Co)_3As_6][CoCl_3(thf)]_2$* **2** *und grün-schwarze von $[(Cp^{tBu}Co)_2As_4][Co_3Cl_8(thf)_2]$* **3**. *Die Struktur des Kations in* **2** *ist der des Kations in* **1** *sehr ähnlich. Das $[(Cp^{tBu}Co)_2As_4]^{2+}$-Ion in* **3** *kann als Tripeldecker-Sandwichkomplex beschrieben werden, in dem zwei $[Cp^{tBu}Co]^+$-Fragmente über einen neutralen As_4-Liganden verbrückt sind. Durch Dichtefunktionalrechnungen können die experimentell bestimmten Strukturen der Kationen in* **1** *und* **3** *nachvollzogen werden. Die elektronischen Strukturen dieser und verwandter Verbindungen werden beschrieben und interpretiert.*

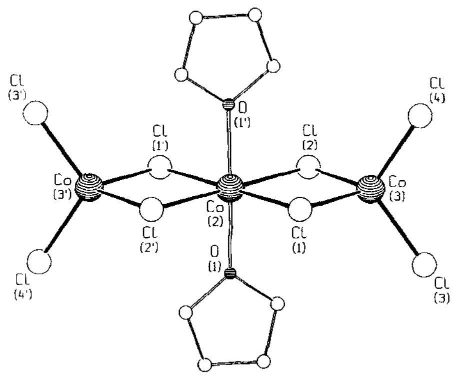

Figure 4. Molecular structure of the anion in **3**. Selected distances [±0.2 pm] and angles [±0.07°]: Co(2)–Cl(1), 241.2; Co(2)–Cl(2), 248.7; Co(2)–O(1), 212.8; Co(3)–Cl(1), 230.6; Co(3)–Cl(2), 231.0; Co(3)–Cl(3), 224.3; Co(3)–Cl(4), 223.9; Cl(1)-Co(2)-Cl(2), 85.96; Cl(1)-Co(2)-Cl(2′), 94.04; Cl(1)-Co(2)-O(1), 89.62; Cl(2)-Co(2)-O(1), 89.67; Cl(1′)-Co(2)-O(1), 90.38; Cl(2′)-Co(2)-O(1), 90.33; Cl(1)-Co(3)-Cl(2), 92.71; Cl(1)-Co(3)-Cl(3), 110.19; Cl(1)-Co(3)-Cl(4), 111.40; Cl(2)-Co(3)-Cl(3), 116.65; Cl(2)-Co(3)-Cl(4), 111.89; Cl(3)-Co(3)-Cl(4), 112.33.

or a square; instead, they are distorted and therefore have to be described as being constructed of three or two As_2 units, respectively.

Quantum-chemical Calculations: Density functional methods were applied to investigate the electronic structure of the complexes. The calculations were performed with the TURBOMOLE program system[12] employing the B–P functional.[13] The molecular structures were optimized on the basis of analytical gradients by means of a relaxation procedure. During the optimization the RI (resolution of identity) approximation[14] was used for energies and gradients. Finally the electronic structure was calculated again without this approximation. To reduce computational effort, methyl groups were substituted by hydrogen atoms throughout. SVP (split valence plus polarization) basis sets[15] were used in all calculations.

For $[(Cp'Co)_2As_4]^{2+}$ (**3′**) (Cp′ = C_5H_4Me), C_i symmetry was assumed. The lowest energy was found for a diamagnetic state ($S = 0$) with the occupancy $68a_g67a_u$. The calculated structure parameters for this state are in good agreement with experimental results (in parentheses): As–As, 250–251 pm (246–247 pm); As–Co, 245–246 pm (243 pm). The larger deviations for the As–As distances are expected, since DFT methods always overestimate the covalent radius of As by about 1.5 pm (tetrahedral As_4: As–As, 247 pm (244 pm)). For the bonding in the Co_2As_4 cage in **3**, 14 electrons have to be considered. This agrees with Wade's $(2n+2)$ rule.[9] The d_{zx} and d_{zy} AOs of the metal play the role of the p_x and p_y AOs of the boron atoms (in *closo*-$B_6H_6^{2-}$), where the z axis is identical with the C_4 axis of the Co_2As_4 cage.

To obtain a more detailed picture, let us first consider a planar As_4 ring, capped by two Co atoms. The d_{xy}, $d_{x^2-y^2}$ and d_{z^2} AOs of the cobalt atom interact only weakly with the MOs of the As_4 ring, whereas there is pronounced overlap between the d_{zx} and d_{zy} AOs of Co and the $4p_\pi$ MOs of the As_4 ring. These interactions lead to a bonding e_g MO (in D_{4h} symmetry) which is occupied. Figure 5 then shows the nature of the bonding in the cage. This picture is confirmed by a Mulliken population analysis.[16] For the Co 3d AOs we obtain $d_{z^2}^{1.9}d_{x^2-y^2}^{1.7}d_{zy}^{1.7}d_{xz}^{1.1}\ d_{yz}^{1.1}$, which shows a well-localized d^6 configuration (almost double

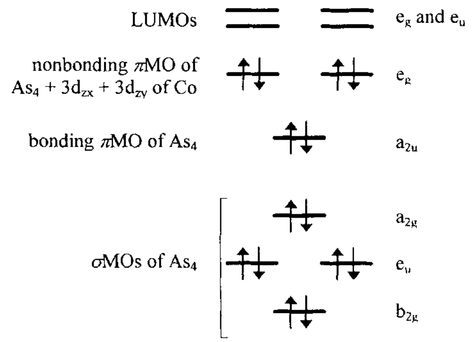

Figure 5. MOs relevant for cage bonding in Co_2As_4.

occupation of d_{z^2}, d_{xy}, $d_{x^2-y^2}$) and one electron in each of d_{zx} and d_{zy}, which are available for bonding to the As_4 plane.

In discussing the neutral $[(Cp^{Et}Co)_2As_4]$ molecule, which has 16 electrons for the cage bonding, it is most important to point out that the lowest unoccupied MOs are of type e_g (and e_u) and that they have nearly identical orbital energies. For a diamagnetic state, a Jahn–Teller distortion is expected. This distortion was calculated by first taking the structure parameters of the dication, then adding two electrons to obtain a $68a_g68a_u$ state, and finally optimizing the geometric structure. The calculated structure parameters are again in relatively good agreement with experiment: As–As (short), 232 pm (227 pm); As–As (long), 293 pm (284 pm); As–Co, 245 pm (242 pm).

Unlike structures with six atoms in the cage, those with nine atoms sometimes show exceptions to the $(2n+2)$ rule: in B_9Cl_9, a capped trigonal prism (D_{3h}), there are 18 electrons, whereas in **1** with an approximately D_{3h} cage structure and in $[(Cp^*Fe)_2(Cp^*Co)As_6]$ (**4**), which was published recently by Scherer and co-workers,[10] there are 22 electrons in the cage. Systems with 20 electrons, the Wade case, tend to assume a distorted D_{3h} structure. A detailed discussion of the bonding in molecules of this type is rather complicated,[17] but the As–Co bonding is quite similar to that of **3**: there are weak interactions between the d_{xy}, $d_{x^2-y^2}$ and d_{z^2} AOs of the metal atom and the arsenic atoms, but the interactions of the cobalt d_{xz} and d_{yz} AOs with those p MOs of the underlying As_4 plane that point approximately to the cobalt atoms are strong. This is confirmed by a Mulliken population analysis for **1′** which shows the following values for the 3d AOs of Co: $d_z^{1.9}d_{xy}^{1.6}d_{x^2-y^2}^{1.8}d_{xz}^{1.2}d_{yz}^{1.2}$. The calculated structure parameters agree well with the experimental ones: As–As (As_3 ring), 261 pm (256 pm); As–As (between rings), 285–286 pm (285–286 pm); As–Co, 240–241 pm (236–241 pm).

The distortion of the neutral molecule **5′** (Figure 6) is again rationalized by a Jahn–Teller effect. The two LUMOs, both e representations in the assumed C_{3v} symmetry, are nearly degenerate (energies −0.3642 and −0.3588 hartree). By reducing the symmetry to C_1, by occupying one of the LUMOs and optimizing the geometric structure, the calculation of this distortion leads to good agreement with experiment: As(1)–As(2), 232 pm (229 pm); As(3)–As(5), 246 pm (241 pm); As(1)–As(3), 305 pm (301 pm); Co(1)–As (mean), 242 pm (240 pm); Co(3)–As(1), 246 pm (242 pm); Co(3)–As(3), 239 pm (237 pm).

The calculated structures for compounds **1′** (Figure 7) and (**4′**) (Figure 8) indicate that electron-deficient cases with nine

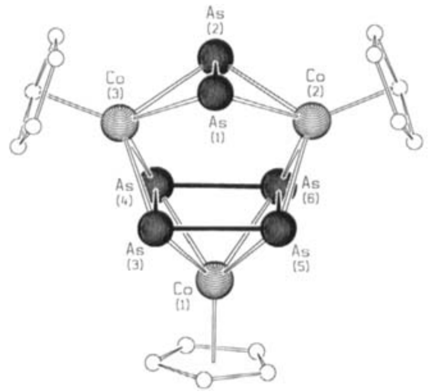

Figure 6. Calculated molecular structure of $[(CpCo)_3As_6]$ (**5′**).

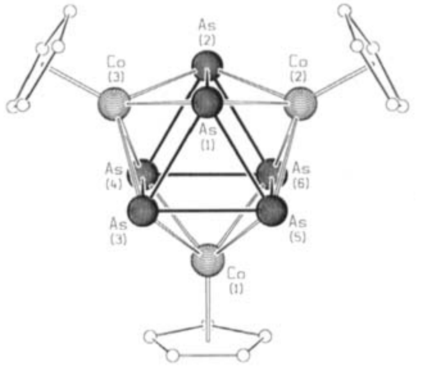

Figure 7. Calculated molecular structure of $[(CpCo)_3As_6]^{2+}$ (**1′**).

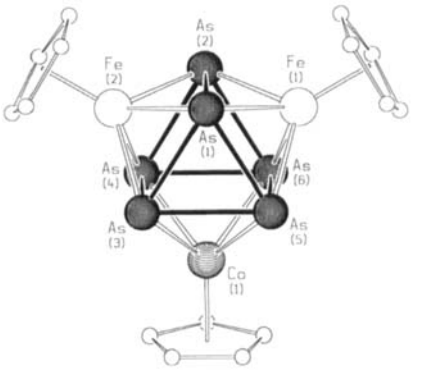

Figure 8. calculated molecular structure of $[(CpFe)_2(CpCo)As_6]$ (**4′**).

atoms in the cage prefer a threefold-capped trigonal prism with D_{3h} symmetry if there are 22 electrons. The structures may be slightly distorted if the ligands are bulky and cause a reduction in symmetry. The compound $[(Cp^*Fe)_2(Cp^*Co)P_6]$ (**6**), recently synthesized by Scherer and co-workers,[10] could be an exception: although **6** is analogous to **1** and **4** (i.e., it has 22 electrons for cage bonding), the structure is remarkably different. The published structure parameters are in fact virtually identical to those previously obtained for $[(Cp^*Co)_3P_6]$ (**7**)[5] (**6** and **7** differ only in the replacement of the two Fe by two Co atoms). This would be an unusual coincidence, and we have performed DFT calculations to investigate the case in more detail. The structures computed for **4′** and **7′** (Figures 8 and 9) are in close agreement with those deduced from X-ray diffraction (in parentheses) for **4** and **7**:

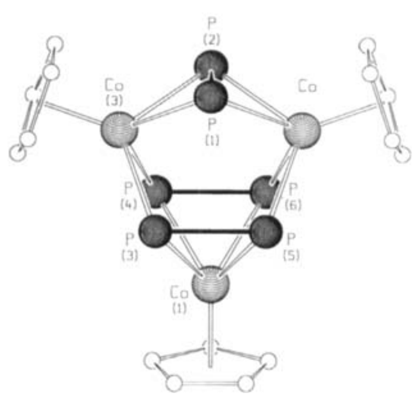

Figure 9. Calculated molecular structure of $[(CpCo)_3P_6]$ (**7′**).

4: As (between rings), 284–288 pm (280–287 pm); Co–As, 242 pm (239 pm); Fe–As, 238–242 pm (238–239 pm).

7: P(3)–P(5), 221 pm (217 pm); P(3)–P(4), 264 pm (255 pm); P(1)–P(2), 208 pm (205 pm); Co–P, 229–234 pm (227–231 pm).

The stucture predicted for **6′** (Figure 10) is analogous to that of **4′** (Figure 8) and **1′** (Figure 7), and it is incompatible with the experimental results of Scherer et al.[10] Calculated distances for **6′** are: P–P (P_3 rings), 236–241 pm; P–P (between rings), 269–274 pm. These incompatibilities would be most easily resolved if the structure assigned previously[10] to **6** belonged to **7**. This suggestion has in fact been confirmed.[18]

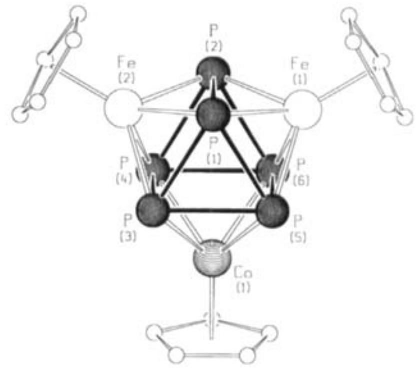

Figure 10. Calculated molecular structure of $[(CpFe)_2(CpCo)P_6]$ (**6′**).

All structures discussed above with a composition $[(CpM)_3E_6]^{n+}$ (E = P, As; $n = 0$, 2) form a regular threefold-capped trigonal prism, if 22 electrons are available for the cage bonding, and are Jahn–Teller-distorted if there are two more electrons in the cage.

Experimental Procedure

1: A suspension of $CoCl_2$ (0.09 g, 0.67 mmol) and Cp*Li (0.10 g, 0.67 mmol) in THF (25 mL) was stirred for 30 min at room temperature, then cooled to −78 °C. $[As_7(SiMe_3)_3]$ (0.5 g, 0.67 mmol) was added in solid form. This solution was heated to 0 °C over a period of 10 h, with continuous stirring. The dark brown solution was filtered at 0 °C and then stored at −25 °C. Black crystals of **1** (0.1 g, 30%) were formed within three weeks.

2, 3: $[As_7(SiMe_3)_3]$ (0.5 g, 0.67 mmol) in solid form was added to a suspension of $CoCl_2$ (0.26 g, 2.01 mmol) and $Cp^{tBu}K$ (0.44 g, 2.01 mmol) in THF (25 mL), which had been cooled to −78 °C. This solution was heated to room temperature over a period of 10 h while being stirred constantly. The dark brown solution was decanted from the dark brown precipitate and cooled to −25 °C; during the cooling pocess, red needle-shaped crystals of **2** (18%, 0.2 g) were formed. These were recrystallized from 10 mL of THF. After **2** had been separated, the filtrate was concentrated to a small volume. Dark green–black crystals of **3** (36%, 0.2 g) were formed over a period of two weeks.

Crystal structure analysis: A STOE IPDS diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) was used at $T = -73$ °C. Data collection, structure solution (SHSLXS-86) and refinement (SHELXL-93) parameters of **1**–**3** are described below.

1·2THF: $a = 1376.0(2)$, $b = 1376.0(2)$, $c = 2224.2(4)$ pm, $V = 3647.3(10) \times 10^6$ pm^3; trigonal, $R3m$, $Z = 3$, $\mu(Mo_{K\alpha}) = 5.643$ mm^{-1}, $2\theta_{max} = 56°$; 4554 reflections, 1775 independent reflections, 1590 $[I > 2\sigma(I)]$ reflections observed, 88 parameters (Co, As, Cl, C anisotropically refined, H calculated for idealized positions, the two disordered THF solvent molecules isotropically refined); $R_1 = 0.033$.

2·0.5THF: $a = 1317.6(3)$, $b = 1964.7(8)$, $c = 2579.4(5)$ pm, $\alpha = 104.90(3)°$, $\beta = 102.39(2)°$, $\gamma = 94.89(3)°$, $V = 6232(3) \times 10^6$ pm^3; triclinic, $P\bar{1}$, $Z = 2$, $\mu(Mo_{K\alpha}) = 4.757$ mm^{-1}, $2\theta_{max} = 45°$, 15287 reflections, 15287 independent reflections, 10458 $[I > 2\sigma(I)]$ reflections observed, 1183 parameters (Co, As, Cl, C anisotropically refined, H calculated for idealized positions, the disordered THF solvent molecule and one disordered anion molecule isotropically refined); $R_1 = 0.071$.

3: $a = 1327.8(3)$, $b = 1122.5(2)$, $c = 1685.9(3)$, $\beta = 106.05(3)°$, $V = 2414.8(8) \times 10^6$ pm^3; monoclinic, $P2_1/c$, $Z = 2$, $\mu(Mo_{K\alpha}) = 4.874$ mm^{-1}, $2\theta_{max} = 52°$; 10285 reflections, 4351 independent reflections, 3072 $[I > 2\sigma(I)]$ reflections observed, 248 parameters (Co, As, Cl, O, C anisotropically refined, H calculated for idealized positions); $R_1 = 0.044$.

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