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# *cyclo*-Hexaphosphane versus *cyclo*-hexaarsane fragmentation on a sulphur-capped mixed-metal dicobalt–iron skeleton

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## Abstract

Reaction of the sulphur-capped dicobalt–iron complex [$Co_2Fe(\mu_3\text{-}S)(CO)_9$] with *cyclo*-$(PhAs)_6$ in toluene at 70 °C gives [$Co_2Fe(\mu_3\text{-}S)\{\mu\text{-}cyclo\text{-}(PhAs)_6\}(CO)_7$] (**1**) as the only product in good yield. Conversely, treatment of [$Co_2Fe(\mu_3\text{-}S)(CO)_9$] with *cyclo*-$(PhP)_6$ under the same reaction conditions gives two isomers [$Co_2Fe(\mu_3\text{-}S)\{\mu\text{-}cyclo\text{-}(PhP)_6\}(CO)_7$] (**2**) and [$Co_2Fe(\mu_3\text{-}S)\{\mu\text{-}cyclo\text{-}(PhP)_6\}(CO)_7$] (**3**) in ca. 1:1 ratio. Single crystal X-ray analysis shows **1** and **2** to be isostructural with the intact six-membered ring adopting a chair conformation and bridging a cobalt–cobalt edge via either two arsine (**1**) or two phosphorus (**2**) atoms in the 1,5 positions of the respective rings. Thermolysis of **2** or of **3** in toluene at 120 °C gives [$Co_2Fe(\mu_3\text{-}SPPh)(\mu\text{-}\eta^2{:}\eta^2{:}\eta^1\text{-}P_5Ph_5)(CO)_5$] (**4**) in moderate yield, while thermolysis of **1** under the same conditions leads to complete decomposition. A single crystal X-ray diffraction study performed on **4** reveals the *cyclo*-hexaphosphane rings in **2** or **3** to have cleaved to give a $P_5Ph_5$ chain and a PPh group, the latter of which has additionally undergone coupling with the sulphur cap. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Cobalt; Iron; *cyclo*-Hexaarsane; *cyclo*-Hexaphosphane; Fragmentation

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## 1. Introduction

The structural diversity exhibited by complexes obtained from the reactions of cyclic main group molecules of the pnictogen family, such as *cyclo*-polyarsanes (CPAs) [$(RAs)_n$, R = hydrocarbyl, $n = 4$–6] or *cyclo*-polyphosphanes (CPPs) [$(RP)_n$, $n = 3$–6], with transition metal carbonyl complexes, has been the focus for considerable research activity [1–3]. Often clusters are isolated that contain unprecedented transition metal/main group metal constructions in which the CPA or the CPP has ring opened and fragmented to give chains and capping groups (or mixtures of both) featuring RAs/RP units or the naked Group 15 elements.

Recently, we have been interested in the reactions of *cyclo*-$(PhX)_6$ (X = As, P) with the transverse alkyne–dicobalt complexes, [$Co_2(\mu\text{-}CRCR)(CO)_6$], and have found that following initial coordination of the intact CPA or CPP to afford [$Co_2(\mu\text{-}CRCR)\{\mu\text{-}cyclo\text{-}(PhX)_6\}(CO)_4$], the complexes decompose on further heating, without any evidence for products containing fragmented CPAs or CPPs nor species incorporating the organic fragment [4,5]. Notably, this is a particularly facile process for [$Co_2(\mu\text{-}CRCR)\{\mu\text{-}cyclo\text{-}(PhP)_6\}(CO)_4$], which decomposes even at room temperature [5]. In this report, we are concerned with replacing the acetylenic moiety in [$Co_2(\mu\text{-}CRCR)(CO)_6$] with a $(OC)_3FeS$ unit to form [$Co_2Fe(\mu_3\text{-}S)(CO)_9$] and examining its reactivity towards both *cyclo*-hexaphenylarsane and *cyclo*-hexaphenylphosphane. To the knowledge of the authors no studies of the reactivity of heterometallic complexes towards CPAs or CPPs have been reported.

## 2. Results and discussion

The reaction of [$Co_2Fe(\mu_3\text{-}S)(CO)_9$] with an equimolar amount of *cyclo*-$(PhAs)_6$ in toluene at 70 °C for 22 h gives [$Co_2Fe(\mu_3\text{-}S)\{\mu\text{-}cyclo\text{-}(PhAs)_6\}(CO)_7$] (**1**) as the

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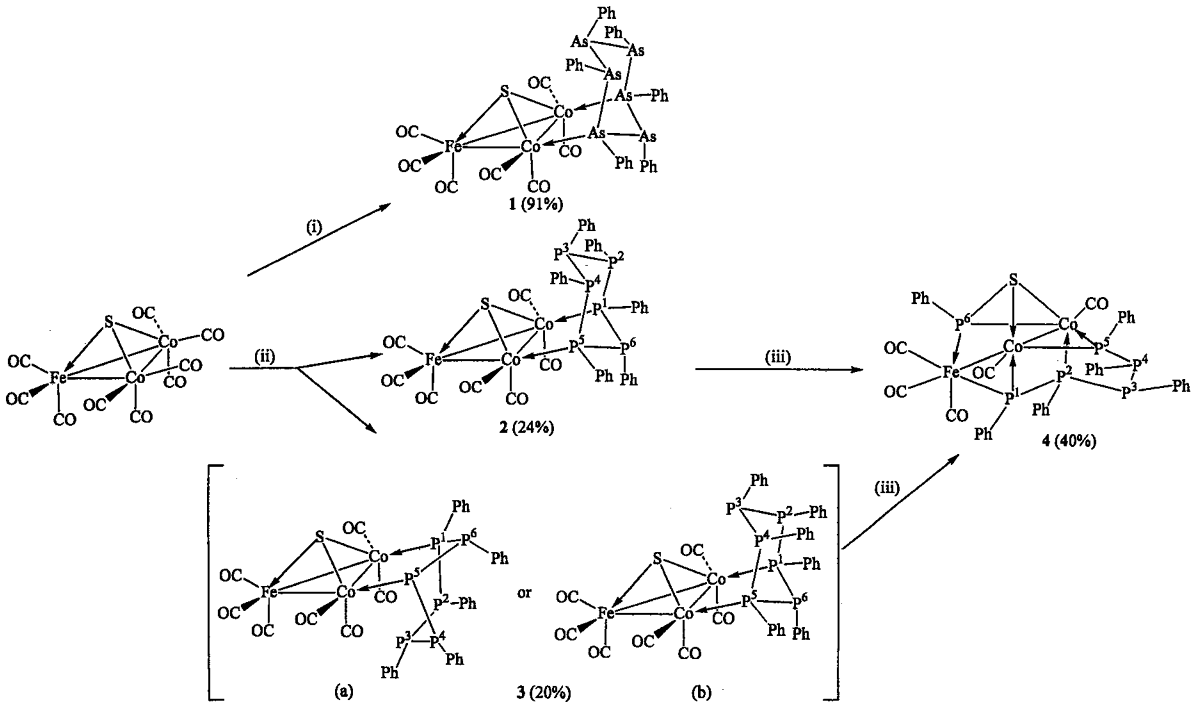

Scheme 1. Reagents and conditions: (i) 70 °C, 22 h, *cyclo*-$(PhAs)_6$, $C_7H_8$; (ii) 70 °C, 22 h, *cyclo*-$(PhP)_6$, $C_7H_8$; (iii) 120 °C, 3 h, $C_7H_8$.

sole product in high yield (Scheme 1). Complex **1** has been characterised by IR, $^1$H-, $^{13}$C-NMR spectroscopies, mass spectrometry and by elemental analysis (see Table 1). In addition, its structure has been determined by single crystal X-ray diffraction. The molecular structure of **1** is shown in Fig. 1 while selected bond distances and angles are listed in Table 2.

Crystals suitable for the analysis were grown by slow diffusion of hexane into a dichloromethane solution of **1**. The structure of **1** consists of an inner $Co_2FeS$ core having a pseudo-tetrahedral structure in which the triangular $Co_2Fe$ moiety is capped by the triply bridging sulphido group in a manner that has been identified crystallographically for the parent complex $[Co_2Fe(\mu_3\text{-}S)(CO)_9]$ [6] and for a range of related structures [7,8]. Two equatorial carbonyl groups in the parent complex, one on each cobalt atom, are formally replaced in **1** by the two arsenic atoms in the 1,5 positions of the intact $(PhAs)_6$ ring. The average As–As–As angle of 94.79° in the arsenic ring is close to that in *cyclo*-$(PhAs)_6$ (91.03°) [9]. The As(1)–As(2)–As(3) angle of 84.51(5)° is smaller than any angle of the free ligand but comparable with the corresponding angles of 84.8(6) and 85.74(5)° observed for the complexes $[Co_2(\mu\text{-RCCR})\{\mu\text{-}cyclo\text{-}(PhAs)_6\}(CO)_4]$ (R = H, Ph) [4], respectively. This angle contraction allows the two arsenic atoms in the 1,5 positions in the ring to provide better matching to the Co–Co distance. The As(2)–As(3)–As(4), As(3)–As(4)–As(5) and As(1)–As(6)–As(5) angles of 97.20(6), 101.68(5) and 98.72(6)°, respectively, are larger than any As–As–As angles in the free ligand and this reflects the significant distortion of the six-membered arsenic ring on substitution. It appears that, on substitution, the molecule has undergone a structural

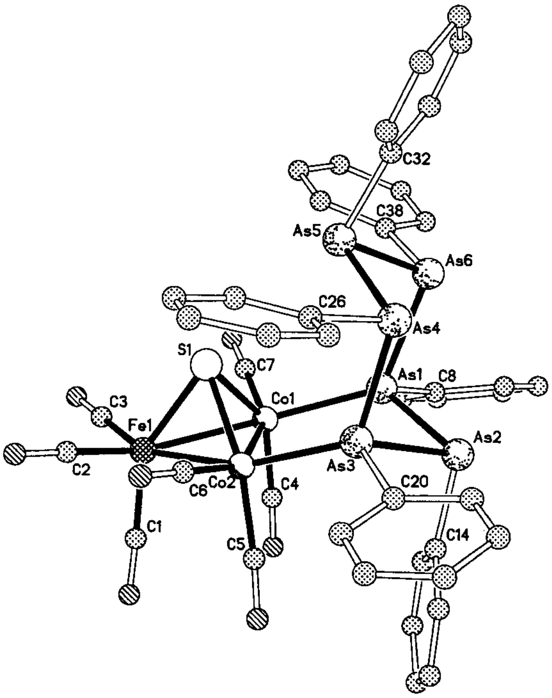

Fig. 1. Molecular structure of $[Co_2Fe(\mu_3\text{-}S)\{\mu\text{-}cyclo\text{-}(PhAs)_6\}(CO)_7]$ (**1**) including the atom numbering scheme. All hydrogen atoms have been omitted for clarity.

Table 1
Spectroscopic and microanalytical data for the new complexes **1**–**4**

| Compound | $\nu$(CO) ($cm^{-1}$) [a] | $^{1}$H-NMR ($\delta$) [b] | $^{13}$C-NMR ($\delta$) [c] | $^{31}$P-NMR ($\delta$) [d] | FABMS | Microanalysis (%) [e] | |
|---|---|---|---|---|---|---|---|
| | | | | | | C | H |
| **1** | 2051vs, 2015s, 2001s, 1948w | 8.1–6.4 [m, 30H, Ph] | 212.0 [s, CO], 209.0 [br, CO], 200.0 [br, CO], 137–127 [m, Ph] | | 1314 ([$M^{+}$] $n$CO, $n = 1$–7) | 40.23 (39.23) | 2.75 (2.30) |
| **2** | 2050vs, 2016s, 1997s, 1946w | 8.0–6.4 [m, 30H, Ph] | 213.6 [s, CO], 208.0 [br, CO], 199.0 [br, CO], 137–128 [m, Ph] | 19.2 [br, P(1), P(5)], 17.2 [m, P(6)], −6.8 [m, P(4), P(2)], −41.8 [m, P(3)] | 1050 ([$M^{+}$] $n$CO, $n = 1$–7) | 49.24 (49.13) | 3.07 (2.87) |
| **3** | 2050vs, 2017s, 1998s, 1945w | 8.2–6.4 [m, 30H, Ph] | 212.0 [s, CO], 210.0 [br, CO], 199.0 [br, CO], 135–127 [m, Ph] | 106.2 [m, P(6)], 16.2 [br, P(1), P(5)], 12.2 [m, P(4), P(2)], −40.8 [m, P(3)] | 1050 ([$M^{+}$] $n$CO, $n = 1$–7) | 49.16 (49.13) | 3.01 (2.87) |
| **4** | 2051w, 2028vs, 1976s | 8.1–6.7 [m, 30H, Ph] | 211.0 [s, CO], 206.0 [br, CO], 199.4 [br, CO], 190.6 [br, CO], 137–128 [m, Ph] | 185.2 [br, P(5), 144.0 [br, P(2)], 99.2 [br, P(1)], 94.2 [m, P(6)], 60.2 [m, P(4)], −2.8 [m, P(3)] | 994 ([$M^{+}$] $n$CO, $n = 1$–5) | 50.15 (49.53) | 3.30 (3.04) |

[a] Recorded in dichloromethane solution.

[b] $^{1}$H chemical shifts ($\delta$) in ppm relative to $SiMe_4$ (0.0 ppm), coupling constants in Hz in $CDCl_3$ at 293 K.

[c] Chemical shifts in ppm relative to $SiMe_4$ (0.0), in $CDCl_3$ at 293 K.

[d] $^{31}$P chemical shifts ($\delta$) in ppm relative to external 85% $H_3PO_4$ (0.0 ppm), {$^{1}$H}-gated decoupled, measured in $CDCl_3$ at 293 K.

[e] Calculated values in parentheses.

Table 2
Selected bond lengths (Å) and bond angles (°) for **1**

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Co(1)–Co(2) | 2.582(2) | Co(1)–Fe(1) | 2.532(2) |
| Co(2)–Fe(1) | 2.530(2) | Co(1)–S(1) | 2.171(3) |
| Co(2)–S(1) | 2.181(3) | Fe(1)–S(1) | 2.200(3) |
| Co(1)–As(1) | 2.355(2) | Co(2)–As(3) | 2.352(2) |
| As(1)–As(2) | 2.459(2) | As(1)–As(6) | 2.475(2) |
| As(2)–As(3) | 2.453(2) | As(3)–As(4) | 2.456(2) |
| As(4)–As(5) | 2.453(2) | As(5)–As(6) | 2.455(2) |
| *Mean* Co–C (carbonyl) | 1.788 | *Mean* Fe–C (carbonyl) | 1.78 |
| *Bond angles* | | | |
| Fe(1)–Co(1)–Co(2) | 59.29(6) | Fe(1)–Co(2)–Co(1) | 59.36(6) |
| Co(1)–Fe(1)–Co(2) | 61.35(6) | Co(1)–S(1)–Co(2) | 72.81(10) |
| Fe(1)–S(1)–Co(2) | 70.55(10) | Fe(1)–S(1)–Co(1) | 70.80(10) |
| S(1)–Fe(1)–Co(2) | 54.37(8) | S(1)–Fe(1)–Co(1) | 54.06(9) |
| Fe(1)–Co(1)–S(1) | 55.14(8) | Fe(1)–Co(2)–S(1) | 55.08(8) |
| As(1)–As(2)–As(3) | 84.51(5) | As(2)–As(1)–As(6) | 94.08(5) |
| As(2)–As(3)–As(4) | 97.20(6) | As(5)–As(4)–As(3) | 101.68(5) |
| As(4)–As(5)–As(6) | 92.55(6) | As(5)–As(6)–As(1) | 98.72(6) |
| *Mean* As–As–As | 94.79 | | |

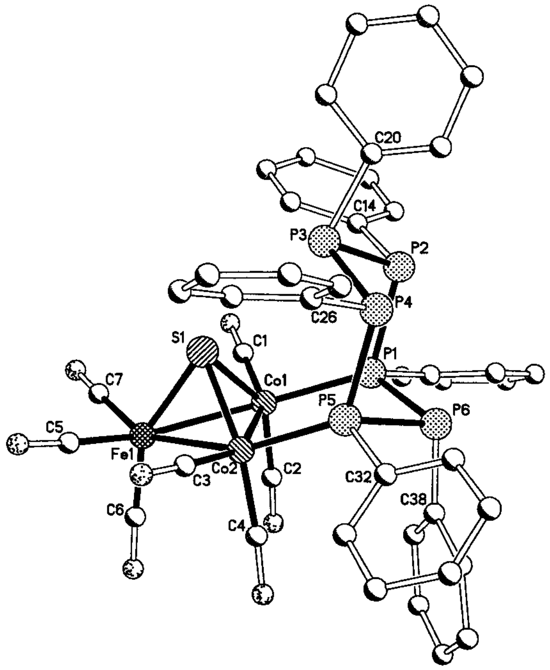

Fig. 2. Molecular structure of $[Co_2Fe(\mu_3\text{-}S)\{\mu\text{-}\mathit{cyclo}\text{-}(PhP)_6\}(CO)_7]$ (**2**) including the atom numbering scheme. All hydrogen atoms have been omitted for clarity.

change to minimise the intra-molecular interactions of the phenyl rings with the sulphur atom and the carbonyl groups. The average Co–As distance of 2.35 Å, agrees closely with the Co–As distances in the related species [10]. The replacement of the two equatorial carbonyl groups by two As atoms causes the following changes to the $Co_2FeS$ cluster core in the parent complex. The Co–Fe distances of 2.532(2) and 2.530(2) Å are shorter than in the parent molecule, which has an average value for the metal–metal bond lengths of 2.554 Å while the Co–Co bond length of 2.582(2) Å is slightly longer. The two Co–S bonds of 2.171(3) and 2.181(3) Å are shorter than in the parent complex [M–S 2.158 Å (av.)], whereas the Fe–S bond distance of 2.200(3) Å is longer. This lengthening of the Fe–S bond reflects the displacement of the apical sulphur atom towards the substituted cobalt atoms. A probable cause of the observed distortion is the build-up of electron density on the $Co_2FeS$ core as a result of the equatorial substitution of two cobalt carbonyl groups by *cyclo*-$(PhAs)_6$. Relief of the electron density accumulated on the cobalt–cobalt edge of the metal triangle is achieved by a more efficient overlap of the appropriate Co–Fe and Co–S orbitals. This would, therefore, result in the short Fe–Co distances and the displacement of the sulphur atom towards the substituted Co atoms. A similar effect has been reported for the complex $[Co_3(\mu\text{-}CCH_3)(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_7]$ [11], in which a displacement of the apical carbon atom towards the phosphine-substituted cobalt atoms is observed.

The spectroscopic properties of **1** are in accord with the solid-state structure being maintained in solution. Three strong $\nu$(CO) bands and one weak band are visible in the IR spectrum which is comparable with the spectra of the structurally related complexes $[Co_2Fe(\mu_3\text{-}S)(\mu\text{-}Ph_2PCH_2SR)(CO)_7]$ (R = Me, Ph) [7]. In the $^{13}C\{^1H\}$-NMR spectrum at 293 K, the iron-bonded carbonyl groups exchange rapidly at this temperature and give rise to a single sharp signal at $\delta$ 212.0 while the cobalt-bonded carbonyl groups are seen as two broad resonances at $\delta$ 209.0 and 200.0.

The reaction of $[Co_2Fe(\mu_3\text{-}S)(CO)_9]$ with an equimolar amount of *cyclo*-$(PhP)_6$ in toluene at 70 °C for 22 h, gives two isomers, $[Co_2Fe(\mu_3\text{-}S)\{\mu\text{-}\mathit{cyclo}\text{-}(PhP)_6\}(CO)_7]$ (**2**) and $[Co_2Fe(\mu_3\text{-}S)\{\mu\text{-}\mathit{cyclo}\text{-}(PhP)_6\}(CO)_7]$ (**3**), in ca. 1:1 yield (Scheme 1). The complexes have been characterised using IR, $^1H$-, $^{13}C$- and $^{31}P$-NMR spectroscopies, mass spectrometry and by elemental analysis (Table 1). In addition, complex **2** has been structurally characterised using X-ray crystallography. The structure of **2** is depicted in Fig. 2 and selected bond distances and angles are collected in Table 3.

Crystals suitable for the analysis were grown by slow evaporation of hexane into a dichloromethane solution of **2**. The structure of **2** is similar to that of **1** with two equatorial cobalt-bound carbonyl groups in $[Co_2Fe(\mu_3\text{-}S)(CO)_9]$ formally replaced by phosphorus atoms in the 1,5 positions of the intact *cyclo*-hexaphosphane ring. The average P–P–P angle of 96.6° in the phosphorus ring is close to the value of that found in free *cyclo*-$(PhP)_6$ (95.5°) [12]. The P(1)–P(2)–P(3) angle 90.5(3)°, is smaller than any angle of the free ligand, allowing the two phosphorus atoms in the 1,5 positions of the ring to efficiently bridge the Co–Co distance [2.570(4) Å].

The mean Co–P distance of 2.292 Å in **2** can be compared to the Co–P distances found in [$Co_3(\mu_3\text{-}S)(\mu\text{-}Ph_2PCH_2SPh)(CO)_7$] [2.207(3) Å] [7] and [$Co_3(\mu\text{-}CCH_3)(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_7$] [2.23 Å (av.)] [11]. As in **1**, the displacement of the apical sulphur atom towards the Co–Co bond is clear in the structure of **2**, from the presence of two Co–S [2.179(7), 2.176(7) Å] and one Fe–S [2.193(7) Å] bond of unequal length. Unlike in **1**, however, only the Co(1)–Fe(1) [2.553(4) Å] distance is significantly shorter than the Co(1)–Co(2) [2.570(4) Å] bond with the Co(2)–Fe(1) bond [2.574(4) Å] being, within experimental error, the same.

The spectroscopic properties of **2** are consistent with the solid-state structure being maintained in solution. Three strong $\nu$(CO) bands and one weak band are visible in the IR spectrum at frequencies similar to those for [$Co_2Fe(\mu_3\text{-}S)(\mu\text{-}Ph_2PCH_2SR)(CO)_7$] (R = Me, Ph) [7] and isostructural **1**. As with **1** the $^{13}C\{^1H\}$-NMR spectrum of **2** displays a sharp downfield signal ($\delta$ 212.0) and two more upfield broad signals ($\delta$ 210.0 and 199.0) in the carbonyl region implying that the three carbonyl ligands residing on the unsubstituted iron atom in **2** are fluxional at 293 K.

The $^{31}P\{^1H\}$-NMR spectrum of **2** shows four signals at $\delta$ 19.2, 17.2, $-6.8$, $-41.8$, with an integral ratio of 2:1:2:1, respectively, and consistent with **2** possessing an approximate mirror plane of symmetry passing through Fe, S, the midpoint of the Co–Co bond, P(3) and P(6) (see Fig. 2). The broad signal at $\delta$ 19.2 can be attributed to the two equivalent phosphorus atoms P(1) and P(5) coordinated to the quadrupolar cobalt atoms and the signal at $\delta$ $-6.8$, to the two non-coordinated equivalent phosphorus atoms P(2) and P(4). Through the use of two-dimensional COSY-90 $^{31}P\{^1H\}$-NMR spectroscopy, the signals at $\delta$ 17.2 and $-41.8$ have been assigned to P(6) and P(3), respectively.

Table 3
Selected bond lengths (Å) and bond angles (°) for **2**

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Co(1)–Co(2) | 2.570(4) | Co(1)–Fe(1) | 2.553(4) |
| Co(2)–Fe(1) | 2.574(4) | Co(1)–S(1) | 2.176(7) |
| Co(2)–S(1) | 2.179(7) | Fe(1)–S(1) | 2.193(7) |
| Co(1)–P(1) | 2.235(6) | Co(2)–P(5) | 2.249(7) |
| P(1)–P(2) | 2.250(8) | P(1)–P(6) | 2.225(8) |
| P(2)–P(3) | 2.225(8) | P(3)–P(4) | 2.243(8) |
| P(4)–P(5) | 2.250(8) | P(5)–P(6) | 2.237(8) |
| *Mean* Co–C (carbonyl) | 1.76 | *Mean* Fe–C (carbonyl) | 1.77 |
| *Bond angles* | | | |
| Fe(1)–Co(1)–Co(2) | 60.3(1) | Fe(1)–Co(2)–Co(1) | 59.51(1) |
| Co(1)–Fe(1)–Co(2) | 60.2(1) | Co(1)–S(1)–Co(2) | 72.3(2) |
| Fe(1)–S(1)–Co(2) | 72.1(2) | Fe(1)–S(1)–Co(1) | 71.5(2) |
| S(1)–Fe(1)–Co(2) | 53.7(2) | S(1)–Fe(1)–Co(1) | 53.9(2) |
| Fe(1)–Co(1)–S(1) | 54.6(2) | Fe(1)–Co(2)–S(1) | 54.2(2) |
| P(1)–P(2)–P(3) | 103.3(3) | P(2)–P(1)–P(6) | 94.1(3) |
| P(2)–P(3)–P(4) | 96.4(3) | P(5)–P(4)–P(3) | 100.7(3) |
| P(4)–P(5)–P(6) | 94.7(3) | P(5)–P(6)–P(1) | 90.5(3) |
| *Mean* P–P–P | 96.6 | | |

The spectroscopic properties of **3** are closely similar to those of **2**, suggesting that they have similar structures. This poses the question of how the structures of **2** and **3** differ from one another. The unequivocal identification of **3** by single crystal X-ray diffraction proved unsuccessful as crystals suitable for the analysis could not be obtained. However, the four terminal carbonyl IR bands observed for **3** are located at virtually identical wavenumbers to those in **2**, suggesting that the bridging of the six-membered ring across the dicobalt bond and the carbonyl arrangement around the metal atoms is similar in both cases. The mass spectrometric data along with the elemental analyses confirm that the two complexes have the same empirical formulae and it is clear from these data that they are isomers.

The $^{31}P\{^1H\}$-NMR spectrum of **3** resembles that of **2**, although it is noteworthy that one signal in **3** is considerably more downfield than any in **2**. Significantly, as for **2**, only four signals are observed for **3**, again implying a plane of symmetry passing through Fe, S, the midpoint of the Co–Co bond and two phosphorus atoms of the *cyclo*-hexaphosphane ring. However, the signals at $\delta$ 106.2, 16.2, 12.2, $-40.8$ have an integral ratio of 1:2:2:1, respectively, with the broad signal at $\delta$ 16.2 being attributed to the equivalent coordinated phosphorus atoms and the sharper signal at $\delta$ 12.2 to the equivalent non-coordinated phosphorus atoms. Two possible isomeric structures for **3** are shown in Scheme 1. Structure (a) differs from **2** in the orientation adopted by the $Co_2FeS$ core relative to the $(PhP)_6$ ring. In **2** the X-ray diffraction study shows that the sulphur atom is closest to that part of the $(PhP)_6$ ring which contains three uncoordinated phosphorus atoms. Therefore, it can be suggested that in **3**(a) the sulphur atom is directed towards that part of the $(PhP)_6$ ring which contains the one uncoordinated phosphorus atom. Alternatively, we cannot rule out isomer **3**(b) which differs from **2** in the orientations adopted by the phenyl groups and lone pairs attached to the uncoordinated P atoms. Only one of several such possible inversion isomers for **3** is depicted in Scheme 1. Notably, this type of inversion isomerism has been observed for *cyclo*-$(PhP)_5$ coordinated to a triosmium framework [13,14]. The spectroscopic data for **1** do not allow us to rule out the possibility that a similar set of isomers exists for **1** even though, in contrast to the analogous phosphorus species, only one product band is observed on the TLC plates. It is noteworthy that a related set of isomers has been proposed for [$Co_2(\mu\text{-}PhCCPh)\{\mu\text{-}$*cyclo*-$(PhAs)_6\}(CO)_4$] [4].

The thermolysis of **1**–**3**, containing intact rings of arsenic and phosphorus atoms, was carried out with the intention of breaking As–As and P–P bonds in order to

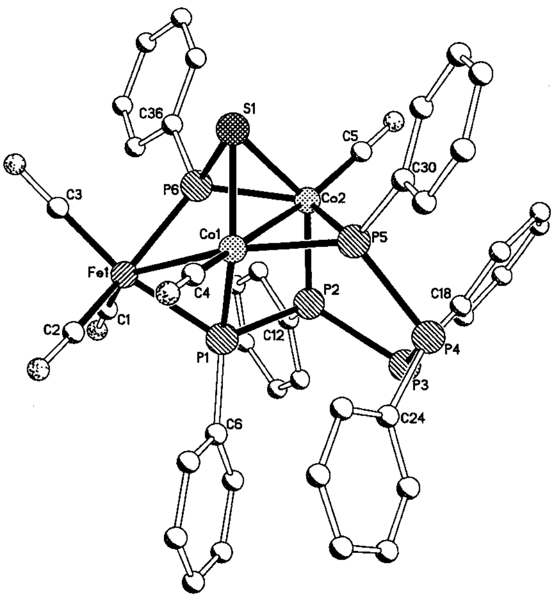

Fig. 3. Molecular structure of [$Co_2Fe(\mu_3\text{-}SPPh)(\mu\text{-}\eta^2{:}\eta^2{:}\eta^1\text{-}P_5Ph_5)(CO)_5$] (**4**) including the atom numbering scheme. All hydrogen atoms have been omitted for clarity.

examine the effect of having exchanged the acetylenic fragment in [$Co_2(\mu\text{-}CRCR)(CO)_6$] for the $(OC)_3FeS$ unit. Thermolysis of **2** and of **3** in toluene at 120 °C for 3 h gives [$Co_2Fe(\mu_3\text{-}SPPh)(\mu\text{-}\eta^2{:}\eta^2{:}\eta^1\text{-}P_5Ph_5)(CO)_5$] (**4**) as a brown crystalline complex in 40% yield (Scheme 1). However, the thermolysis of **1** under similar reaction conditions leads to complete decomposition of **1**. Complex **4** has been characterised by IR, $^1$H-, $^{13}$C-, $^{31}$P-NMR spectroscopies, mass spectrometry and elemental analysis. Complex **4** has also been the subject of a single crystal X-ray diffraction study. A view of the structure of **4** is illustrated in Fig. 3 and selected bond distances and angles are listed in Table 4.

Suitable crystals of **4** were grown by the slow diffusion of hexane into a dichloromethane solution of **4**. The molecule is constructed around a distorted tetrahedral core, containing two cobalt atoms, a phosphorus atom and a sulphur atom. The edges Co(1)–P(6) and Co(1)–Co(2) of the tetrahedron, are bridged by a $Fe(CO)_3$ group and a phosphorus atom, P(5), respectively. Both cobalt atoms, Co(1) and Co(2), are coordinated by atoms S(1), P(5) and one carbonyl ligand. In addition, Co(1) is coordinated by the Fe(1) atom and P(1) while Co(2) is coordinated by P(2) and P(6). In this reaction the *cyclo*-$(PhP)_6$ ring has undergone ring opening and breaking to form a $P_5Ph_5$ chain and a PPh unit. The end phosphorus atoms of the P5 chain, P(1) and P(5), act as three-electron donors; P(1) bridges the Co(1) and Fe(1) atoms, while P(5) bridges Co(1) and Co(2). The PPh unit formed in the ring cleavage during thermolysis of **2** and **3** has undergone coupling with the sulphur cap to the bridging PhPS ligand in **4**. Related μ-RPS ligands have been structurally identified and the P–S bond distance [2.081(2) Å] in **4** lies in the mid-range [15]. The average P–P bond length of 2.208 Å within the chain, may be compared with the average P–P distance of 2.23 Å in free *cyclo*-$(PhP)_6$ [12]. The average Co–P distances for the bridging phosphorus atom P(5) are comparable with values obtained for other phosphido-bridged cobalt complexes [16]. The phosphorus atoms bridging the Fe–Co metal centres [P(6) and P(1)] also have metal–phosphorus distances similar to other phosphido-bridged Fe–Co complexes [17] with the Fe(1)–P(6)–Co(2) angle larger than Fe(1)–P(1)–Co(1) angle [115.34(9) vs. 76.09(7)°] and consistent with the absence of a metal–metal bond between Fe(1) and Co(2). Interestingly, the large Fe(1)–P(6)–Co(2) angle means the P(6) atom is 2.636 Å away from Co(1), suggesting there is a very weak interaction between the two atoms. The two Co–S bond distances of 2.288(3) and 2.261(3) Å fall at the top end of the range reported for Co–S distances [18] in SR-bridged dicobalt–carbonyl complexes. The average P–P–P bond angle of 103.45°, is larger than any of the

Table 4
Selected bond lengths (Å) and bond angles (°) for **4**

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Fe(1)–P(6) | 2.225(3) | Fe(1)–P(1) | 2.228(2) |
| Fe(1)–Co(1) | 2.706(1) | Co(1)–P(1) | 2.162(2) |
| Co(1)–P(5) | 2.200(2) | Co(1)–S(1) | 2.288(3) |
| Co(1)–Co(2) | 2.430(3) | Co(1)–P(6) | 2.636(3) |
| Co(2)–P(2) | 2.163(2) | Co(2)–P(6) | 2.177(2) |
| Co(2)–P(5) | 2.187(2) | Co(2)–S(1) | 2.261(3) |
| S(1)–P(6) | 2.081(2) | P(1)–P(2) | 2.190(3) |
| P(2)–P(3) | 2.225(2) | P(3)–P(4) | 2.201(3) |
| P(4)–P(5) | 2.457(3) | | |
| *Bond angles* | | | |
| P(6)–Fe(1)–P(1) | 87.81(9) | P(6)–Fe(1)–Co(1) | 63.75(7) |
| P(1)–Fe(1)–Co(1) | 50.86(5) | P(1)–Co(1)–P(5) | 100.40(8) |
| P(1)–Co(1)–S(1) | 127.88(8) | P(5)–Co(1)–S(1) | 87.36(9) |
| P(1)–Co(1)–Co(2) | 84.90(10) | P(5)–Co(1)–Co(2) | 56.11(8) |
| S(1)–Co(1)–Co(2) | 57.17(7) | P(1)–Co(1)–P(6) | 79.45(8) |
| P(5)–Co(1)–P(6) | 106.57(9) | S(1)–Co(1)–P(6) | 49.39(6) |
| Co(2)–Co(1)–P(6) | 50.72(6) | P(1)–Co(1)–Fe(1) | 53.05(5) |
| P(5)–Co(1)–Fe(1) | 142.99(6) | S(1)–Co(1)–Fe(1) | 91.25(7) |
| Co(2)–Co(1)–Fe(1) | 92.67(8) | P(6)–Co(1)–Fe(1) | 49.21(7) |
| P(2)–Co(1)–P(6) | 93.62(7) | P(2)–Co(2)–P(5) | 89.66(8) |
| P(6)–Co(2)–P(5) | 125.78(9) | P(2)–Co(2)–S(1) | 138.76(7) |
| P(6)–Co(2)–S(1) | 55.89(7) | P(5)–Co(2)–S(1) | 88.35(9) |
| P(2)–Co(2)–Co(1) | 86.89(10) | P(6)–Co(2)–Co(1) | 69.53(8) |
| P(5)–Co(2)–Co(1) | 56.62(7) | S(1)–Co(2)–Co(1) | 58.24(8) |
| P(6)–S(1)–Co(2) | 60.03(7) | P(6)–S(1)–Co(1) | 74.04(8) |
| Co(2)–S(1)–Co(1) | 64.59(8) | Co(1)–P(1)–P(2) | 93.29(10) |
| Co(1)–P(1)–Fe(1) | 76.09(7) | P(2)–P(1)–Fe(1) | 111.70(9) |
| Co(2)–P(2)–P(1) | 91.05(10) | Co(2)–P(2)–P(3) | 114.62(8) |
| P(1)–P(2)–P(3) | 108.98(10) | P(4)–P(3)–P(2) | 100.36(9) |
| P(3)–P(4)–P(5) | 101.03(9) | Co(2)–P(5)–Co(1) | 67.26(9) |
| Co(2)–P(5)–P(4) | 117.89(10) | Co(1)–P(5)–P(4) | 123.73(9) |
| S(1)–P(6)–Co(2) | 64.08(7) | S(1)–P(6)–Fe(1) | 112.49(10) |
| Co(2)–P(6)–Fe(1) | 115.34(9) | S(1)–P(6)–Co(1) | 56.57(7) |
| Co(2)–P(6)–Co(1) | 59.75(8) | Fe(1)–P(6)–Co(1) | 67.04(7) |

bond angles in *cyclo*-$(PhP)_6$ reflecting a considerable strain in the $P_5$ chain.

The spectroscopic properties of **4** are consistent with the solid-state structure being maintained in solution. The IR spectrum shows two strong and broad carbonyl bands in the terminal carbonyl region which can be attributed to the three iron- and two cobalt-bound carbonyl groups. The $^{13}C\{^1H\}$-NMR spectrum shows, in addition to resonances corresponding to phenyl groups, four terminal carbonyl resonances. Two sharp peaks at $\delta$ 211.0 and 190.6 can be assigned to the three carbonyls bound to the iron and the two broad signals at $\delta$ 206.0 and 199.4 to the two carbonyls bound to the quadrupolar cobalt atoms. The $^{31}P\{^1H\}$-NMR spectrum of **4** displays six signals corresponding to the six unique environments for the phosphorus atoms. The three broad signals at low field ($\delta$ 185.2, 144.0, 99.2) can undoubtedly be assigned to the cobalt-bound phosphorus atoms. The assignment of the fourth cobalt-bound phosphorus atom was established using two-dimensional COSY-90 $^{31}P\{^1H\}$-NMR as P(6) ($\delta$ 94.2) while the uncoordinated phosphorus centres P(3) and P(4) correspond to the signals at $\delta$ $-2.8$ and 60.2, respectively.

In conclusion, the reaction of $[Co_2Fe(\mu_3\text{-}S)(CO)_9]$ with *cyclo*-$(PhX)_6$ (X = As, P) leads in the first instance to complexes **1**, **2** and **3**, in which an intact CPA or CPP ring bridges the dicobalt vector in a manner that has previously been observed for the transverse alkyne–dicobalt complexes $[Co_2(\mu\text{-}CRCR)\{\mu\text{-}cyclo\text{-}(PhX)_6\}(CO)_4]$. Unlike the thermolytic reactions of $[Co_2(\mu\text{-}CRCR)\{\mu\text{-}cyclo\text{-}(PhX)_6\}(CO)_4]$, the well characterised complex **4** is identified on thermolysis of **2** and **3**, resulting from fragmentation of the CPP to give a $P_5Ph_5$ chain and PPh unit (which additionally undergoes coupling with the sulphur cap). Notably, thermolysis of **1** yields only uncharacterised decomposition products.

## 3. Experimental

All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen, using standard Schlenk techniques. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use [19]. Infrared spectra were recorded in hexane solution in 0.5 mm NaCl cells, using a Perkin–Elmer 1710 Fourier-transform spectrometer. Fast atom bombardment mass spectra (FABMS) were recorded in a Kratos MS 890 instrument using 3-nitrobenzyl alcohol as a matrix. Proton (reference to $SiMe_4$), $^{31}P$-NMR and $^{13}C$-NMR spectra were recorded in either a Bruker WM250 or AM400 spectrometer; $^{31}P$-NMR chemical shifts are referenced to external 85% $H_3PO_4$. Preparative thin-layer chromatography (TLC) was carried out in commercial Merck plates with a 0.25 mm layer of silica, or in 1 mm silica plates prepared at the Department of Chemistry, Cambridge. Column chromatography was performed on Kieselgel 60 (70–230 or 230–400 mesh). Products are given in order of decreasing $R_f$ values. Elemental analyses were performed at the Department of Chemistry, Cambridge.

Unless otherwise stated all reagents were obtained from commercial suppliers and used without further purification. The syntheses of $[Co_2Fe(\mu_3\text{-}S)(CO)_9]$ [20], *cyclo*-$(PhAs)_6$ [9] and *cyclo*-$(PhP)_6$ [12] have been reported previously.

### 3.1. Reaction of $[Co_2Fe(\mu_3\text{-}S)(CO)_9]$ with *cyclo*-$(PhAs)_6$

The complex $[Co_2Fe(\mu_3\text{-}S)(CO)_9]$ (0.114 g, 0.25 mmol) and *cyclo*-$(PhAs)_6$ (0.228 g, 0.25 mmol) were dissolved in toluene (10 ml) in a Schlenk flask. The Schlenk flask was evacuated with three freeze-pump-thaw cycles and closed under vacuum. The mixture was stirred at 70 °C for 23 h. After cooling the reaction mixture was opened to the air and the solution filtered. The filtrate was then concentrated under reduced pressure and the residue dissolved in the minimum $CH_2Cl_2$, absorbed onto silica and added to the top of a chromatography column. Elution using hexane–$CH_2Cl_2$ (4:1) gave dark brown crystalline $[Co_2Fe(\mu_3\text{-}S)\{\mu\text{-}cyclo\text{-}(PhAs)_6\}(CO)_7]$ (**1**) (0.30 g, 91%).

### 3.2. Reaction of $[Co_2Fe(\mu_3\text{-}S)(CO)_9]$ with *cyclo*-$(PhP)_6$

The complex $[Co_2Fe(\mu_3\text{-}S)(CO)_9]$ (0.114 g, 0.25 mmol) and *cyclo*-$(PhP)_6$ (0.162 g, 0.25 mmol) were dissolved in toluene (10 ml) in a Schlenk flask. The Schlenk flask was evacuated with three freeze-pump-thaw cycles and closed under vacuum. The mixture was stirred at 70 °C for 23 h. After cooling the reaction mixture was opened to the air and the solution filtered. The filtrate was then concentrated under reduced pressure, the residue dissolved in the minimum $CH_2Cl_2$ and the solution applied to the base of silica TLC plates. Elution with hexane–$CH_2Cl_2$ (4:1) gave the green solid $[Co_2Fe(\mu_3\text{-}S)\{\mu\text{-}cyclo\text{-}(PhP)_6\}(CO)_7]$ (**2**) (0.05 g, 20%) followed by dark green crystalline $[Co_2Fe(\mu_3\text{-}S)\{\mu\text{-}cyclo\text{-}(PhP)_6\}(CO)_7]$ (**3**) (0.06 g, 24%).

### 3.3. Thermolysis of complexes **1–3**

(i) Thermolysis of a solution of $[Co_2Fe(\mu_3\text{-}S)\{\mu\text{-}cyclo\text{-}(PhAs)_6\}(CO)_7]$ (**1**) (0.10 g, 0.076 mmol) in toluene (50 ml) at 120 °C for 3 h led to complete decomposition as indicated by TLC.

(ii) A solution of $[Co_2Fe(\mu_3\text{-}S)\{\mu\text{-}cyclo\text{-}(PhP)_6\}(CO)_7]$ (**2**) or $[Co_2Fe(\mu_3\text{-}S)\{\mu\text{-}cyclo\text{-}(PhP)_6\}(CO)_7]$ (**3**) (0.05 g, 0.05 mmol) in toluene (25 ml) was thermolysed at 120 °C for 3 h. The solvent was removed under re-

Table 5
Crystal data and structure refinement parameters for complexes **1**, **2** and **4**

| Complex | **1** | **2** | **4** |
|---|---|---|---|
| Empirical formula | $C_{43}H_{30}As_6Co_2FeSO_7$ | $C_{43}H_{30}P_6Co_2FeSO_7$ | $C_{41}H_{30}P_6Co_2FeSO_5$ |
| Formula weight | 1313.96 | 1050.26 | 994.24 |
| Temperature (K) | 150(2) | 293(2) | 180(2) |
| Crystal system | Monoclinic | Orthorhombic | Triclinic |
| Space group | $P2_1/n$ | $Pna2_1$ | $P\bar{1}$ |
| Unit cell dimensions | | | |
| $a$ (Å) | 15.089(4) | 21.326(6) | 11.830(9) |
| $b$ (Å) | 16.322(5) | 17.569(4) | 18.423(7) |
| $c$ (Å) | 18.613(7) | 13.678(6) | 10.701(12) |
| $\alpha$ (°) | 90 | 90 | 97.35(6) |
| $\beta$ (°) | 96.97(3) | 90 | 116.01(6) |
| $\gamma$ (°) | 90 | 90 | 94.83(5) |
| $V$ (Å$^3$) | 4550(3) | 5125(3) | 2053(3) |
| $Z$ | 4 | 4 | 2 |
| $D_{calc}$ (mg m$^{-3}$) | 1.918 | 1.361 | 1.608 |
| $F$(000) | 2552 | 2120 | 1004 |
| Crystal size (mm) | 0.30 × 0.30 × 0.18 | 0.20 × 0.20 × 0.15 | 0.30 × 0.20 × 0.20 |
| $\mu$ (Mo–K$_\alpha$) (mm$^{-1}$) | 5.459 | 1.190 | 1.476 |
| Reflections collected | 20 337 | 7009 | 11 486 |
| Independent reflections | 7276 | 4995 | 9422 |
| $R_{int}$ | 0.0862 | 0.0996 | 0.0674 |
| Parameters/restraints | 541/0 | 327/1 | 505/0 |
| Final $R$ indices [$I>2\sigma(I)$] | $R_1 = 0.0856$, $wR_2 = 0.1267$ | $R_1 = 0.1195$, $wR_2 = 0.2454$ | $R_1 = 0.0596$, $wR_2 = 0.1422$ |
| All data | $R_1 = 0.1079$, $wR_2 = 0.1664$ | $R_1 = 0.1421$, $wR_2 = 0.2795$ | $R_1 = 0.1010$, $wR_2 = 0.1664$ |

Data in common: graphite-monochromated Mo–K$_\alpha$ radiation, $\lambda = 0.71073$ Å; $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$, $w^{-1} = [\sigma^2(F_o)^2+(aP)^2]$, $P = [\max(F_o^2,0)+2(F_c^2)]/3$, where $a$ is a constant adjusted by the program; goodness-of-fit $= [\Sigma(F_o^2-F_c^2)2/(n-p)]^{1/2}$ where $n$ is the number of reflections and $p$ the number of parameters.

duced pressure, the residue dissolved in the minimum quantity of $CH_2Cl_2$ and the solution applied to the base of preparative TLC plates. Elution using hexane–$CH_2Cl_2$ (4:1) gave brown crystalline [$Co_2Fe(\mu_3$-SPPh)($\mu$-$\eta^2$:$\eta^2$:$\eta^1$-$P_5Ph_5$)$(CO)_5$] (**4**) (0.02 g, 40%).

### *3.4. Crystallography*

X-ray intensity data was collected using Rigaku RAXIS-IIC image plate (**1** and **2**) and AFC7R diffractometers (**4**). Both systems were equipped with an Oxford Cryosystems Cryostream. Details of data collection, refinement and crystal data are listed in Table 5. Semiempirical absorption corrections based on $\varphi$-scan data were applied [21,22] to the data for **4**; no absorption correction was applied to the data for **1** and **2**. The structures were solved by direct methods (SHELXS 86 [23]) and subsequent Fourier-difference syntheses and refined anisotropically on all ordered non-hydrogen atoms by full-matrix least-squares on $F^2$ (SHELXL 93 [24]). Hydrogen atoms were placed in geometrically idealised positions and refined using a riding model. In the final cycles of refinement a weighting scheme was introduced which produced a flat analysis of variance.

## 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 167868–167870 for compounds **1**, **2**, **3** and **4**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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