

# New organoarsino-bridged cobalt carbonyl complexes derived from reactions of $[\text{Co}_2(\text{CO})_8]$ or $[\text{Co}_2(\mu\text{-alkyne})(\text{CO})_6]$ with *cyclo*-(AsPh)<sub>6</sub>

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Reaction of hexaphenylcyclohexaarsane (PhAs)<sub>6</sub> with  $[\text{Co}_2(\text{CO})_8]$  in toluene at ambient temperature resulted in As–As bond cleavage and the new complexes  $[\text{Co}_4(\mu_4\text{-AsPh})_2(\text{CO})_{10}]$  **1** and  $[\text{Co}_4(\mu_3\text{-AsPh})(\mu_4\text{-}\eta^2\text{:}\eta^2\text{:}\eta^1\text{-As}_4\text{Ph}_4)(\text{CO})_{10}]$  **2**. In contrast, reaction of *cyclo*-(PhAs)<sub>6</sub> with the alkyne-bridged complexes  $[\text{Co}_2(\mu\text{-R}^1\text{C}\equiv\text{CR}^2)(\text{CO})_6]$  in toluene or in benzene at 65 °C afforded the new complexes  $[\text{Co}_2(\mu\text{-R}^1\text{C}\equiv\text{CR}^2)\{\mu\text{-cyclo}(\text{PhAs})_6\}(\text{CO})_4]$  ( $\text{R}^1 = \text{R}^2 = \text{H}$  **3**; or **Ph 4** and **5** (isomers);  $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{H}$  **6**;  $\text{R}^1 = \text{Me}$ ,  $\text{R}^2 = \text{H}$  **7**) in which the As<sub>6</sub> ring remains intact. All seven products have been characterised spectroscopically and, in addition, compounds **1–4** have been structurally characterised by X-ray diffraction analysis. The molecular structure of **1** comprises a rectangle of cobalt atoms capped above and below the plane by two quadruply bridging AsPh ligands, giving a pseudo-octahedral Co<sub>4</sub>As<sub>2</sub> core. The molecular structure of **2** consists of two discrete Co<sub>2</sub>(CO)<sub>5</sub> units linked by an As<sub>4</sub>Ph<sub>4</sub> chain and an AsPh unit. In complexes **3–7** the six-membered As<sub>6</sub> ring remains intact and acts as a bidentate bridging ligand replacing two equatorial carbonyl groups, one on each Co atom.

The reactions of transition-metal carbonyl complexes with cyclopolyarsines have attracted considerable attention due to the interesting bonding modes and structural features of the derived products. These include complexes with co-ordinated rings containing five to ten RAs units,<sup>1–6</sup> complexes with chains of two to eight RAs units<sup>7–10</sup> and complexes with naked As atoms obtained as a result of loss of the organic group R. These can contain naked As<sub>n</sub> units ranging from one,<sup>11</sup> two<sup>12</sup> and three As atom chains<sup>13</sup> to rings of five As atoms.<sup>14</sup> Another type of process involves the transfer of R groups between As atoms and this is exemplified by the reaction of hexaphenylcyclohexaarsane with metal carbonyl complexes, which leads to products containing AsPh,<sup>11,15</sup> AsPh<sub>2</sub><sup>16</sup> and As(Ph)AsPh<sub>2</sub><sup>16</sup> fragments.

Most of the above reactions were carried out using elevated temperatures and it seemed of interest to investigate reactions of this type at ambient temperature, or at temperatures lower than those used previously, in the hope of isolating new products which might provide an insight into the reaction

pathways involved in the formation of the products reported in earlier studies. Accordingly we now report (i) the reaction at ambient temperature of *cyclo*-(PhAs)<sub>6</sub> with  $[\text{Co}_2(\text{CO})_8]$ , which leads to the formation of two new tetracobalt complexes, one of which contains  $\mu_3\text{-AsPh}$ , and  $\mu_4\text{-As}_4\text{Ph}_4$  fragments, and (ii) the reactions at 65 °C between *cyclo*-(PhAs)<sub>6</sub> and the alkyne-bridged dicobalt complexes  $[\text{Co}_2(\mu\text{-R}^1\text{C}\equiv\text{CR}^2)(\text{CO})_6]$  ( $\text{R}^1 = \text{R}^2 = \text{H}$  or **Ph**;  $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{H}$ ; or  $\text{R}^1 = \text{Me}$ ,  $\text{R}^2 = \text{H}$ ), which afford new complexes containing an intact *cyclo*-(PhAs)<sub>6</sub> ring.

## Results and Discussion

The reaction of *cyclo*-(PhAs)<sub>6</sub> with  $[\text{Co}_2(\text{CO})_8]$  in a 1:4 molar ratio in toluene or in benzene at ambient temperature afforded, after 2 h, the red crystalline solid  $[\text{Co}_4(\mu_4\text{-AsPh})_2(\text{CO})_{10}]$  **1** and the brown crystalline solid  $[\text{Co}_4(\mu_3\text{-AsPh})(\mu_4\text{-}\eta^2\text{:}\eta^2\text{:}\eta^1\text{-As}_4\text{Ph}_4)(\text{CO})_{10}]$  **2** as the only isolable products. Compounds **1** and **2** have been characterised spectroscopically (Table 1) and their

**Table 1** Spectroscopic and microanalytical data for the new complexes **1–7**

IR ( $\tilde{\nu}_{\text{co}}/\text{cm}^{-1}$ )	<sup>1</sup> H NMR ( $\delta$ ) <sup>a</sup>	<sup>13</sup> C NMR ( $\delta$ ) <sup>b</sup>	FAB mass spectrum	Microanalysis (%) <sup>c</sup>	
				C	H
<b>1</b> 2033vs, 2023s, 2007s, 1864w	7.6–7.4 (m, 10 H, Ph)	133–128 (m, Ph), 209 (br, CO)	820 ( $M^+$ )	32.13 (32.33)	1.42 (1.22)
<b>2</b> 2058s, 2037vs, 2023vs, 2004m, 1995m, 1822w	8.2–6.8 (m, 25 H, Ph)	134–128 (m, Ph), 239 (s, CO), 235 (s, CO), 203 (br, CO), 202 (br, CO), 200 (br, CO), 198 (br, CO)	1249 ( $M^+ - \text{CO}$ )	37.67 (37.65)	2.25 (1.97)
<b>3</b> 2025s, 1996vs, 1969s	7.9–6.6 (m, 32 H, Ph + C <sub>2</sub> H <sub>2</sub> )	137–128 (m, Ph), 203 (br, CO), 202 (br, CO)	1168 ( $M^+ - n\text{CO}$ , $n = 1-4$ )	42.87 (43.18)	2.68 (2.76)
<b>4</b> 2021s, 1996vs, 1969s	8.1–6.6 (m, 40 H, Ph)	142–125 (m, Ph), 205 (br, CO), 201 (br, CO)	1320 ( $M^+ - n\text{CO}$ , $n = 1-4$ )	48.94 (49.1)	3.11 (3.0)
<b>5</b> 2022s, 1995vs, 1967s	7.5–7.0 (m, 40 H, Ph)	138–125 (m, Ph), 206 (br, CO), 203 (br, CO)	1320 ( $M^+ - n\text{CO}$ , $n = 1-4$ )	49.1 (49.1)	3.07 (3.0)
<b>6</b> 2023s, 1997vs, 1970s	7.9–6.4 (m, 36 H, Ph), 5.0 (s, H)	142–126 (m, Ph), 112 (s, CPh), 206 (br, CO), 201 (br, CO)	1226 ( $M^+ - n\text{CO}$ , $n = 1-4$ )	46.19 (46.33)	2.79 (2.92)
<b>7</b> 2020s, 1995vs, 1964s	7.9–6.6 (m, 30 H, Ph), 5.0 [q, <sup>4</sup> J <sub>HH</sub> 0.7, 1 H HCCMe]; 2.5 (d, 3 H, HCMe)	137–128 (m, Ph), 117 (s, CCH <sub>3</sub> ), 24 (s, CCH <sub>3</sub> ), 207 (br, CO), 202 (br, CO)	1154 ( $M^+ - n\text{CO}$ , $n = 1-4$ )	43.35 (43.69)	2.89 (2.89)

<sup>a</sup> Chemical shifts in ppm relative to SiMe<sub>4</sub> (0.0), coupling constants in Hz, in CDCl<sub>3</sub> at 293 K. <sup>b</sup> Chemical shifts in ppm relative to SiMe<sub>4</sub> (0.0), in CDCl<sub>3</sub> at 293 K. <sup>c</sup> Calculated values in parentheses.

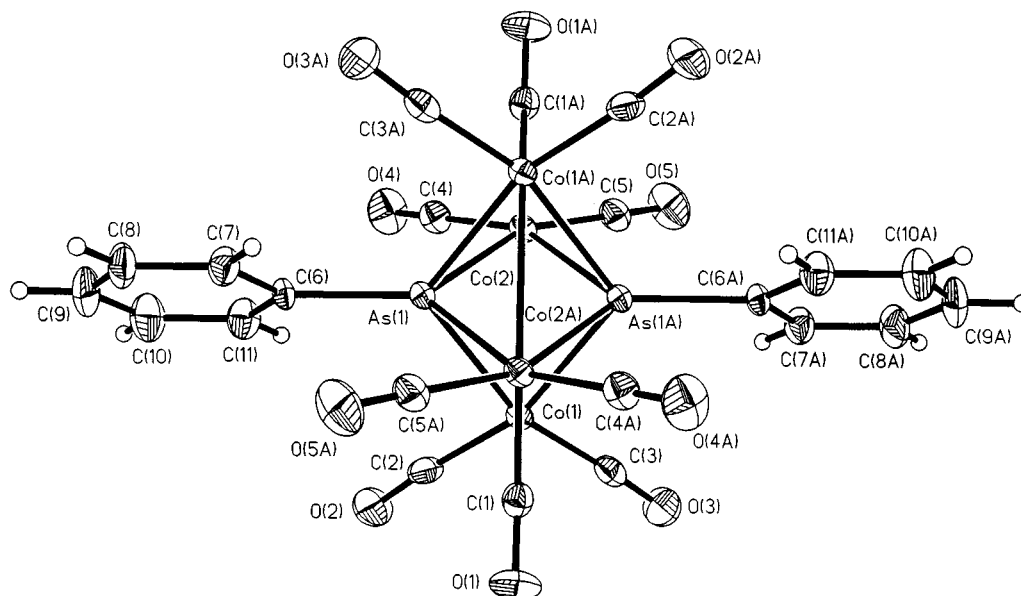


Fig. 1 Molecular structure of  $[\text{Co}_4(\mu_4\text{-AsPh})_2(\text{CO})_{10}]$  **1** including the atom numbering scheme. Hydrogen atoms have been omitted for clarity

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

As(1)–Co(1)	2.3551(9)	As(1)–Co(1A)	2.3572(9)
As(1)–Co(2)	2.360(2)	As(1)–Co(2A)	2.3635(12)
As(1)···As(1A)	2.7670(11)	Co(1)–C(1)	1.959(5)
Co(1)–As(1A)	2.3572(9)	Co(1)–Co(2A)	2.592(2)
Co(1)–Co(2)	2.8078(13)	Co(2)–C(1A)	1.949(4)
Co(2)–As(1A)	2.3636(12)	Co(2)–Co(1A)	2.592(2)
C(1)–Co(2A)	1.949(4)		
Co(1)–As(1)–Co(1A)	108.09(3)	Co(1)–As(1)–Co(2)	73.09(2)
Co(1A)–As(1)–Co(2)	66.67(2)	Co(1)–As(1)–Co(2A)	66.64(4)
Co(1A)–As(1)–Co(2A)	72.99(3)	Co(2)–As(1)–Co(2A)	108.28(5)
Co(1)–As(1)–As(1A)	54.08(3)	Co(2)–As(1)–As(1A)	54.20(2)
Co(1A)–As(1)–As(1A)	54.01(2)	Co(2A)–As(1)–As(1A)	54.08(5)
As(1)–Co(1)–As(1A)	71.91(3)	As(1)–Co(1)–Co(2A)	56.72(4)
As(1)–Co(1)–Co(2)	53.53(4)	As(1A)–Co(1)–Co(2)	53.61(2)
Co(2A)–Co(1)–Co(2)	90.21(6)	As(1)–Co(2)–As(1A)	71.72(5)
As(1)–Co(2)–Co(1A)	56.61(5)	As(1A)–Co(2)–Co(1A)	56.52(4)
As(1)–Co(2)–Co(1)	53.37(3)	As(1A)–Co(2)–Co(1)	53.40(3)
Co(1A)–Co(2)–Co(1)	89.79(6)		

Symmetry relation: A  $-x + 1, -y, -z + 2$ .

structures confirmed by X-ray crystallographic analysis. The synthesis of cluster **1** has been reported previously<sup>17</sup> but no details of the synthesis were given nor was it structurally characterised.

The molecular structure of compound **1** is shown in Fig. 1 together with the atomic numbering scheme. Selected bond lengths and angles are given in Table 2. The four Co atoms are coplanar and form a rectangle, with a crystallographic centre of symmetry as its centre, which is capped above and below the plane by quadruply bridging AsPh ligands, with the apical As atoms being situated 1.383(1) Å from the plane. The central pseudo-octahedral  $\text{Co}_4\text{As}_2$  core conforms closely to a  $D_{2h}$  symmetry and compound **1** is a member of the  $[\text{Co}_4(\text{CO})_{10}\text{E}_2]$  family where E = S,<sup>18</sup> Te,<sup>19</sup> PPh<sup>19,20</sup> or GeMe.<sup>21</sup> Each Co atom is bonded to the two As atoms and also to one bridging and two terminal CO ligands. The bridging CO groups span opposite sides of the cobalt rectangle and the bridged Co–Co bonds are 0.21 Å shorter than the unbridged Co–Co bonds [2.592(2) Å versus 2.8078(13) Å]. The unbridged Co–Co distances of 2.8078(13) Å can be compared to the corresponding distances of 2.88(2) Å in the tellurium analogue of **1**<sup>19</sup> and it is clear that Co–Co distances in the  $[\text{Co}_4(\text{CO})_{10}\text{E}_2]$  family increase with increasing covalent radius of the  $\mu_4$ -bridged hetero atom (covalent radii: As, 1.22; Te, 1.37 Å). The Co–As distances in **1**

range from 2.3551(9) Å to 2.3636(12) Å, with the mean value of 2.358 Å being comparable to the mean value of 2.39 Å for the corresponding  $\mu_4\text{-PhAsCo}_4$  distances in the  $\text{Co}_{16}$  cluster  $[\{\text{Co}_8(\mu_6\text{-As})(\mu_4\text{-As})(\mu_4\text{-AsPh})_2(\text{CO})_{16}\}_2]$ <sup>11</sup> and within the range (2.24–2.54 Å) of Co–E distances found in analogous  $\text{Co}_4\text{E}_2$  clusters.<sup>18,19,21</sup> The Co–As–Co bond angles are also comparable with Co–E–Co angles found in related  $\text{Co}_4\text{E}_2$  clusters. The As···As distance of 2.7670(11) Å is only 0.3 Å longer than a typical As–As single bond, a remarkable feature also found in other complexes of the type  $[\text{Co}_4(\text{CO})_{10}\text{E}_2]$ . Thus, for example, the P···P separation in the phosphorus analogue of **1** is 2.537(6) Å, only 0.3 Å greater than a P–P single bond.<sup>19</sup> It has been suggested that an attractive direct E···E interaction accounts for these short distances but the need to optimise the M–M and M–E distances is also acknowledged to be an important factor.<sup>19,20,22</sup> The cluster  $[\text{Fe}_3(\mu_3\text{-AsPh})_2(\text{CO})_9]$ <sup>23</sup> contains a similar short As···As separation of 2.789(2) Å.

The spectroscopic properties of complex **1** are in accord with the solid-state structure being maintained in solution. The IR spectrum in  $\text{CH}_2\text{Cl}_2$  exhibits three carbonyl bands at 2033vs, 2023s and 2007s together with a band at 1864w  $\text{cm}^{-1}$  in the bridging carbonyl region. The <sup>13</sup>C NMR spectrum at 20 °C shows, in addition to the multiplet for the two phenyl groups, a single broad resonance at  $\delta$  209 due to the two bridging and eight terminal carbonyl groups. This is in good agreement with the observed value of  $\delta$  208 for the weighted average chemical shifts of the terminal and bridging carbonyl in studies of the temperature-dependent carbonyl spectra of related tetracobalt clusters.<sup>24</sup>

The molecular structure of complex **2** has also been determined by crystal structure analysis. Suitable crystals were grown by diffusion of hexane into a dichloromethane solution of **2**. The molecular structure together with the atom numbering scheme is shown in Fig. 2, selected bond distances and angles in Table 3. The structure consists of two discrete metal–metal bonded  $\text{Co}_2(\text{CO})_5$  units in each of which one of the CO ligands occupies a bridging position. The two units are linked by an AsPh<sub>4</sub> chain and by an AsPh group, both fragments being derived from opening and breaking of the *cyclo*-(PhAs)<sub>6</sub> ring. The end arsenic atoms of the As<sub>4</sub> chain, As(3) and As(4), act as three-electron donors; As(3) bridges the Co(1)–Co(3) edge in one of the dimetal units, while As(4) bridges Co(3) from this unit and Co(2) from the other dimetal unit. Additional coordination of one of the interior arsenic atoms in the chain, As(5), to Co(4) completes the linking of the two  $\text{Co}_2(\text{CO})_5$  units

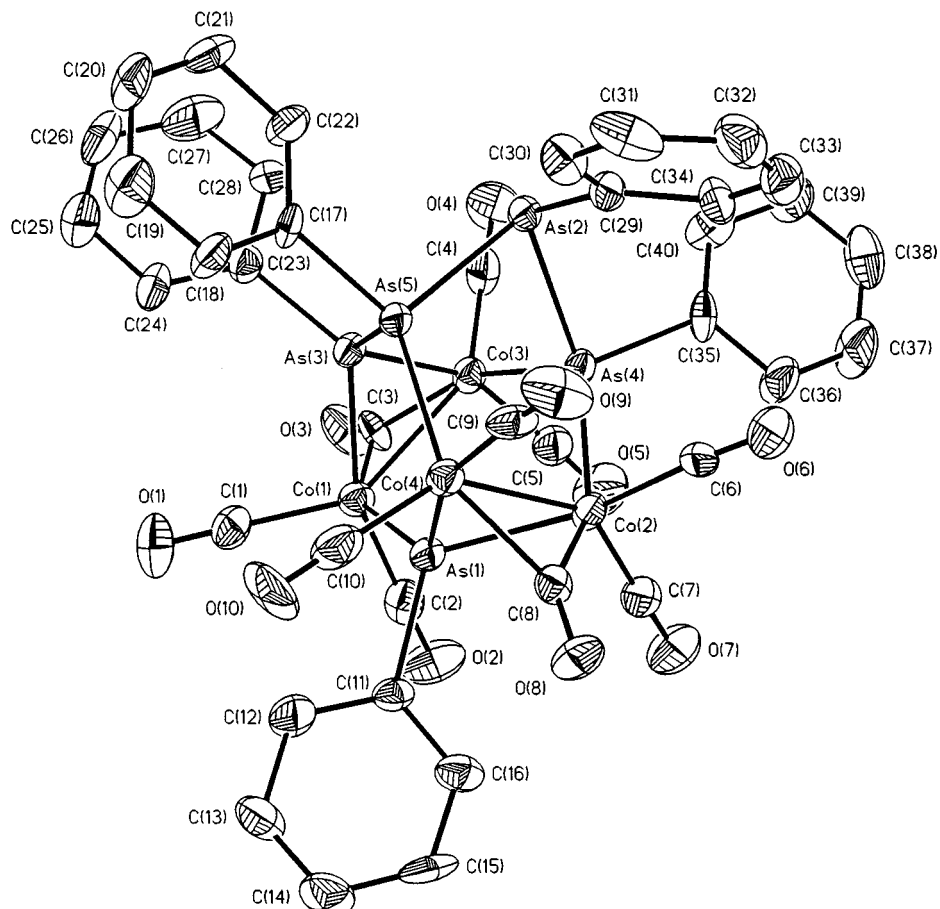


Fig. 2 Molecular structure of  $[\text{Co}_4(\mu_3\text{-AsPh})(\mu_4\text{-}\eta^2\text{:}\eta^2\text{:}\eta^1\text{-As}_4\text{Ph}_4)(\text{CO})_{10}]$  **2**. Details as in Fig. 1

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

As(1)–Co(2)	2.355(3)	As(1)–Co(1)	2.395(3)
As(1)–Co(4)	2.376(3)	As(2)–As(5)	2.436(2)
As(2)–As(4)	2.473(2)	As(3)–Co(1)	2.278(3)
As(3)–As(5)	2.450(2)	As(3)–Co(3)	2.307(3)
As(4)–Co(2)	2.429(3)	As(4)–Co(3)	2.431(3)
As(5)–Co(4)	2.388(3)	Co(1)–Co(3)	2.522(4)
Co(2)–Co(4)	2.516(3)	Co(1)–C(3)	1.97(2)
Co(3)–C(3)	1.92(2)	Co(2)–C(8)	1.91(2)
Co(4)–C(8)	1.97(2)	Co–C (terminal)	1.80 (av.)
Co(2)–As(1)–Co(4)	64.21(9)	Co(4)–As(1)–Co(1)	131.62(10)
Co(2)–As(1)–Co(1)	122.94(11)	As(5)–As(2)–As(4)	83.63(8)
Co(1)–As(3)–Co(3)	66.71(9)	Co(1)–As(3)–As(5)	117.86(10)
Co(3)–As(3)–As(5)	115.74(10)	Co(3)–As(4)–As(2)	99.75(9)
Co(2)–As(4)–Co(3)	116.54(10)	Co(2)–As(4)–As(2)	114.57(9)
As(2)–As(5)–As(3)	87.50(8)	Co(4)–As(5)–As(2)	117.66(9)
C(3)–Co(1)–Co(3)	48.7(5)	Co(4)–As(5)–As(3)	110.38(9)
As(3)–Co(1)–Co(3)	57.20(9)	As(3)–Co(1)–As(1)	88.49(10)
As(1)–Co(1)–Co(3)	98.95(11)	C(8)–Co(2)–As(1)	89.8(5)
C(8)–Co(2)–As(4)	149.7(5)	As(1)–Co(2)–As(4)	92.05(9)
C(8)–Co(2)–Co(4)	50.7(5)	As(1)–Co(2)–Co(4)	58.30(8)
As(4)–Co(2)–Co(4)	100.28(10)	C(3)–Co(3)–As(3)	82.0(6)
C(3)–Co(3)–As(4)	152.6(6)	As(3)–Co(3)–As(4)	87.44(10)
C(3)–Co(3)–Co(1)	50.5(6)	As(4)–Co(3)–Co(1)	102.93(11)
As(3)–Co(3)–Co(1)	56.09(8)	C(8)–Co(4)–As(1)	78.1(5)
C(8)–Co(4)–As(5)	145.4(5)	As(1)–Co(4)–As(5)	90.29(10)
C(8)–Co(4)–Co(2)	48.5(5)	As(1)–Co(4)–Co(2)	57.49(9)
As(5)–Co(4)–Co(2)	97.84(10)		

by the  $\text{As}_4$  chain. The  $\mu_3$ -arsinidene group,  $\text{As}(1)\text{Ph}$ , caps  $\text{Co}(1)$ ,  $\text{Co}(2)$  and  $\text{Co}(4)$ , acting as a four-electron donor. The Co–Co distances within the dimetal units of 2.516(3) and 2.522(4) Å and the observed bond lengths of 2.278(3) and 2.307(3) Å for  $\text{As}(3)\text{--Co}(1)$  and  $\text{As}(3)\text{--Co}(3)$  respectively are similar to the lengths of corresponding bonds in related structurally

characterised clusters such as  $[\{\text{Co}_8(\mu_6\text{-As})(\mu_4\text{-As})(\mu_4\text{-AsPh})(\text{CO})_{16}\}_2]$ ,<sup>11</sup>  $[(\text{OC})_9\text{Co}_3(\mu_4\text{-As})\text{Co}_4(\text{CO})_{11}]$ <sup>25</sup> and  $[\{\text{Co}_3(\mu_4\text{-As})(\text{CO})_8\}_3]$ .<sup>26</sup> The  $\text{Co}(2)\text{--As}(4)$  and  $\text{Co}(3)\text{--As}(4)$  bond distances of 2.429(3) and 2.431(3) Å, respectively, are slightly longer than Co–As bonds in many other related complexes but comparable to the average Co–As distance of 2.439 Å recorded for  $[\text{CoAs}_3(\text{CO})_3]$ .<sup>27</sup> The cobalt–carbonyl carbon (terminal) bond lengths are almost equal (average = 1.819 Å) and comparable with previously reported values.<sup>27</sup> The average As–As distance  $[\text{As}(3)\text{--As}(5)\text{--As}(2)\text{--As}(4)]$  in the  $\text{As}_4$  chain of 2.45 Å is in accord with the average As–As distance of 2.456 Å for *cyclo*-(PhAs)<sub>6</sub>,<sup>28</sup> but the  $\text{As}(5)\text{--As}(2)\text{--As}(4)$  angle of 83.63(8)° is smaller than any angle in the free arsane, the distortion may be related to the general strain of the whole molecule caused by the close non-bonded approaches of the carbonyl and Ph groups. The Co–As–Co angles are in the range 64–66° for the arsenic atom bridging the two metal–metal bonded Co atoms from the same bimetal unit and in the range 116–131° for the arsenic atom which bridges the two non-bonded Co atoms from different units. These angle ranges are typical for correspondingly bonded As atoms in the related structures mentioned above. Complex **2** resembles  $[\{\text{Co}_8(\mu_6\text{-As})(\mu_4\text{-As})(\mu_4\text{-AsPh})_2(\text{CO})_{16}\}_2]$ <sup>11</sup> in having an  $\text{AsCo}_3$  unit of the type  $\text{As}(1)\text{--Co}(1)\text{--Co}(2)\text{--Co}(3)$  and an  $\text{As}_2\text{Co}_2$  of the type  $\text{As}(5)\text{--Co}(2)\text{--Co}(4)\text{--As}(4)$ .

The spectroscopic properties of complex **2** are in accord with the solid-state structure being maintained in solution. Five  $\nu(\text{CO})$  bands are visible in the IR spectrum including an absorption at 1822  $\text{cm}^{-1}$  corresponding to the presence of bridging CO groups in the molecule. The <sup>13</sup>C NMR spectrum displays two singlets at  $\delta$  239 and 235 for the two bridging carbonyls and four broad signals at  $\delta$  203, 202, 200 and 198 for the eight terminal carbonyl groups.

The reaction of *cyclo*-(PhAs)<sub>6</sub> with  $[\text{Co}_2(\mu\text{-R}^1\text{C}\equiv\text{CR}^2)(\text{CO})_6]$  in a 1:2 molar ratio in toluene or in benzene does not proceed

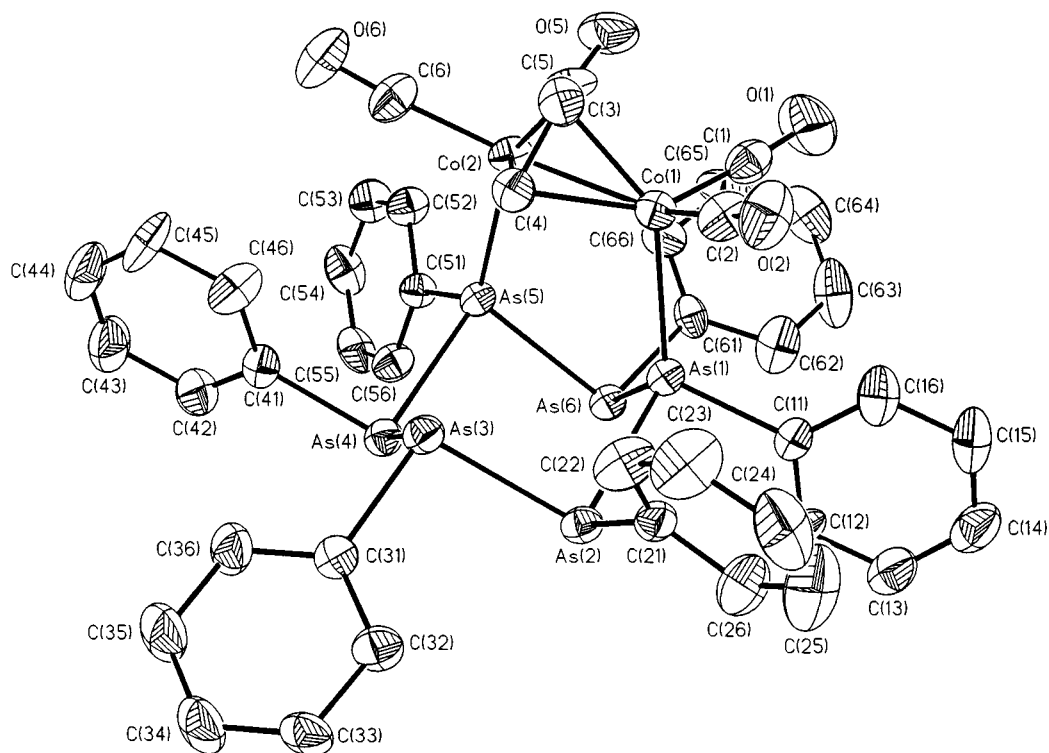


Fig. 3 Molecular structure of  $[\text{Co}_2(\mu\text{-HC}\equiv\text{CH})\{\mu\text{-cyclo-(PhAs)}_6\}(\text{CO})_4]$  **3**. Details as in Fig. 1

Table 4 Selected bond distances (Å) and angles (°) for complex **3**

Co(1)–C(3)	1.927(14)	Co(1)–C(4)	1.971(13)
Co(1)–Co(2)	2.496(2)	Co(1)–As(1)	2.362(2)
Co(2)–C(3)	1.927(14)	Co(2)–C(4)	1.947(13)
Co(2)–As(5)	2.371(2)	As(1)–As(2)	2.466(2)
As(1)–As(6)	2.459(2)	As(2)–As(3)	2.455(2)
As(3)–As(4)	2.462(2)	As(4)–As(5)	2.476(2)
As(5)–As(6)	2.452(2)	Co–C (mean)	1.780
C–O (mean)	1.140	As–C (mean)	1.957
C(3)–Co(1)–C(4)	39.8(5)	C(4)–Co(1)–As(1)	106.0(4)
C(3)–Co(1)–As(1)	143.3(4)	C(4)–Co(1)–Co(2)	50.0(4)
C(3)–Co(1)–Co(2)	49.6(4)	As(1)–Co(1)–Co(2)	101.48(8)
C(3)–Co(2)–C(4)	40.1(5)	C(3)–Co(2)–As(5)	140.4(4)
C(4)–Co(2)–As(5)	103.6(4)	C(3)–Co(2)–Co(1)	49.6(4)
C(4)–Co(2)–Co(1)	50.8(4)	As(5)–Co(2)–Co(1)	98.36(7)
Co(1)–As(1)–As(6)	116.30(7)	Co(1)–As(1)–As(2)	124.71(8)
As(3)–As(2)–As(1)	95.16(6)	As(6)–As(1)–As(2)	96.65(6)
As(3)–As(4)–As(5)	98.61(6)	As(2)–As(3)–As(4)	91.13(7)
As(6)–As(5)–As(4)	90.52(6)	Co(2)–As(5)–As(6)	117.97(7)
Co(2)–As(5)–As(4)	125.72(8)	As(5)–As(6)–As(1)	84.8(6)

Table 5 Selected distances (Å) and angles (°) for complex **4**

Co(1)–C(3)	1.930(7)	Co(1)–C(4)	1.995(7)
Co(1)–Co(2)	2.486(2)	Co(1)–As(1)	2.395(2)
Co(2)–C(3)	1.953(7)	Co(2)–C(4)	1.963(7)
Co(2)–As(5)	2.373(2)	As(1)–As(2)	2.4739(13)
As(1)–As(6)	2.4504(13)	As(2)–As(3)	2.451(2)
As(3)–As(4)	2.4422(13)	As(4)–As(5)	2.611(13)
As(5)–As(6)	2.468(2)	Co–C (mean)	1.784
C–O (mean)	1.144	As–C (mean)	1.962
C(3)–Co(1)–As(1)	147.0(2)	C(3)–Co(1)–C(4)	40.3(3)
C(3)–Co(1)–Co(2)	50.6(2)	C(4)–Co(1)–As(1)	111.6(2)
As(1)–Co(1)–Co(2)	100.28(5)	C(4)–Co(1)–Co(2)	50.5(2)
C(3)–Co(2)–C(4)	40.4(3)	C(3)–Co(2)–As(5)	143.9(2)
C(4)–Co(2)–As(5)	107.4(2)	C(3)–Co(2)–Co(1)	49.8(2)
C(4)–Co(2)–Co(1)	51.7(2)	As(5)–Co(2)–Co(1)	100.32(5)
Co(1)–As(1)–As(6)	116.92(5)	As(6)–As(1)–As(2)	88.51(4)
Co(1)–As(1)–As(2)	129.88(4)	As(4)–As(3)–As(2)	93.67(5)
As(3)–As(2)–As(1)	94.22(4)	Co(2)–As(5)–As(6)	115.16(5)
Co(3)–As(4)–As(5)	97.24(4)	Co(2)–As(5)–As(4)	128.61(5)
As(4)–As(5)–As(6)	93.64(5)	As(5)–As(6)–As(1)	85.74(5)

at ambient temperature but at 65 °C afforded the complexes  $[\text{Co}_2(\mu\text{-R}^1\text{C}\equiv\text{CR}^2)\{\mu\text{-cyclo-(PhAs)}_6\}(\text{CO})_4]$  ( $\text{R}^1 = \text{R}^2 = \text{H}$  **3**; or Ph **4** and **5** (isomers);  $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{H}$  **6**;  $\text{R}^1 = \text{Me}$ ,  $\text{R}^2 = \text{H}$  **7**). The structures of **3** and **4** have been determined by single-crystal X-ray analysis. Suitable crystals were grown by diffusion of hexane into dichloromethane solutions of **3** and **4**. The molecular structures are illustrated in Figs. 3 and 4 and selected bond lengths and angles are given in Tables 4 and 5. In both **3** and **4** the  $(\text{PhAs})_6$  moiety acts as a bidentate ligand through the two arsenic atoms in 1,5 positions in the ring, replacing two equatorial carbonyls, one on each cobalt atom, and bridging the Co–Co vector. The six-membered ring of arsenic atoms remains intact and the geometry of this ring is close to that of the free arsane. The solid-state structures of **3** and **4** are similar, both in the orientations adopted by the aromatic rings attached to the unco-ordinated arsenic atoms and in the orientation of the alkyne bridge. The average As–As–As angle of 92.82° in the arsenic ring in **3** is almost equal to the average angle 92.16° in **4**

and close to the value of that in free *cyclo-(PhAs)*<sub>6</sub> (91.03°).<sup>28</sup> However the As(5)–As(6)–As(1) angle of 84.8(6)° in **3** and the corresponding angle of 85.74(5)° in **4** are smaller than any of the As–As–As angles in the free arsane. This allows the two arsenic donor atoms in the 1,5 positions in the arsenic rings to approach each other more closely, providing a better match to the Co–Co distances. The Co–Co distances of 2.496(2) and 2.486(2) Å in **3** and **4**, respectively, are identical within experimental error with the observed values for other bis-equatorially and bis-pseudo-equatorially substituted alkyne-bridged dicobalt complexes.<sup>29,30</sup> The mean cobalt to carbonyl carbon distance of 1.78 Å in both compounds is comparable to the corresponding distance of 1.77 Å in  $[\text{Co}_2(\mu\text{-PhC}_2\text{Ph})(\text{dpmm})(\text{CO})_4]$  (dpmm =  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ),<sup>29</sup> 1.75 Å in  $[\text{Co}_2(\mu\text{-PhC}_2\text{Ph})(\text{dpam})_2(\text{CO})_2]$  (dpam =  $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2$ )<sup>29</sup> and 1.78 Å in  $[\text{Co}_2(\mu\text{-HC}\equiv\text{H})(\text{PPh}_3)_2(\text{CO})_4]$ .<sup>30</sup> The cobalt to arsenic average bond lengths of 2.36 and 2.38 Å, respectively, for complexes **3** and **4** agree closely with Co–As distances in related species.<sup>29</sup>

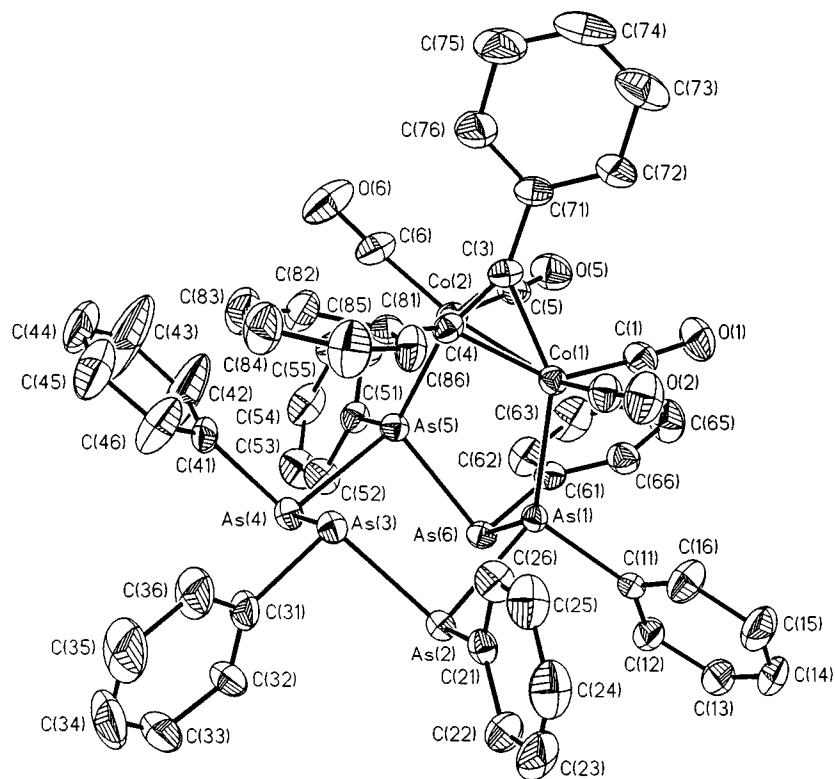


Fig. 4 Molecular structure of  $[\text{Co}_2(\mu\text{-PhC}\equiv\text{CPh})\{\mu\text{-cyclo-(PhAs)}_6\}(\text{CO})_4]$  **4**. Details as in Fig. 1

The spectroscopic properties of complexes **3** and **4** are in accord with the solid-state structures being maintained in solution. Three strong  $\nu(\text{CO})$  bands are visible in the terminal carbonyl region of the IR spectrum similar to that observed for other equatorially disubstituted alkyne-bridged dicobalt derivatives.<sup>29</sup> The  $^1\text{H}$  NMR spectrum of **3** shows a complex multiplet at  $\delta$  7.94–6.60 which can be assigned as being due to the thirty aromatic protons in the six phenyl rings. There are no separate identifiable peaks corresponding to the two acetylenic protons and the resonances for these two protons are presumably masked by the aromatic protons. For the compound  $[\text{Co}_2(\text{PPh}_3)_2\{\mu\text{-HC}_2\text{C}(\text{Me})\text{Ph}(\text{OH})\}(\text{CO})_4]$ <sup>31</sup> the corresponding  $^1\text{H}$  signal is at  $\delta$  6.62.

The spectroscopic properties of complexes **5–7** are closely similar to those of **3** and **4**, suggesting that they have analogous structures. The question then arises as to how the structures of **4** and **5** differ from each other. Unfortunately it did not prove possible to obtain crystals of **5** suitable for a single-crystal X-ray diffraction study. However, the IR spectrum of **5** is identical to that of complex **4**, suggesting that the bridging of the ligand across the metal centres and the carbonyl arrangement around the metal atoms is similar in both cases. The mass spectroscopic data and elemental analyses confirm that the two complexes have the same empirical formulae and it is clear from these data that they are isomers. A possible isomeric structure for **5** is shown in Scheme 1(b). It differs from **4** in the orientation adopted by the alkyne bridge relative to the co-ordinated  $(\text{PhAs})_6$  ring. In **4** the X-ray diffraction study shows that the alkyne bridge leans towards that part of the  $(\text{PhAs})_6$  ring which contains the three unco-ordinated arsenic atoms. It is suggested that in **5** the alkyne bridge leans towards that part of the  $(\text{PhAs})_6$  which contains the one unco-ordinated arsenic atom. An alternative possibility, which we cannot exclude, is that **5** is related to **4** by inversion of the phenyl group and the lone pair at one or more of the unco-ordinated As atoms. One such possible inversion is shown in Scheme 1(c). This type of inversion isomerism has been observed previously for  $\text{cyclo-(PhP)}_5$  co-ordinated to a triosmium framework in the complex  $[\text{Os}_3\{\text{cyclo-(PhP)}_5\}(\text{CO})_{10}]$ .<sup>32,33</sup>

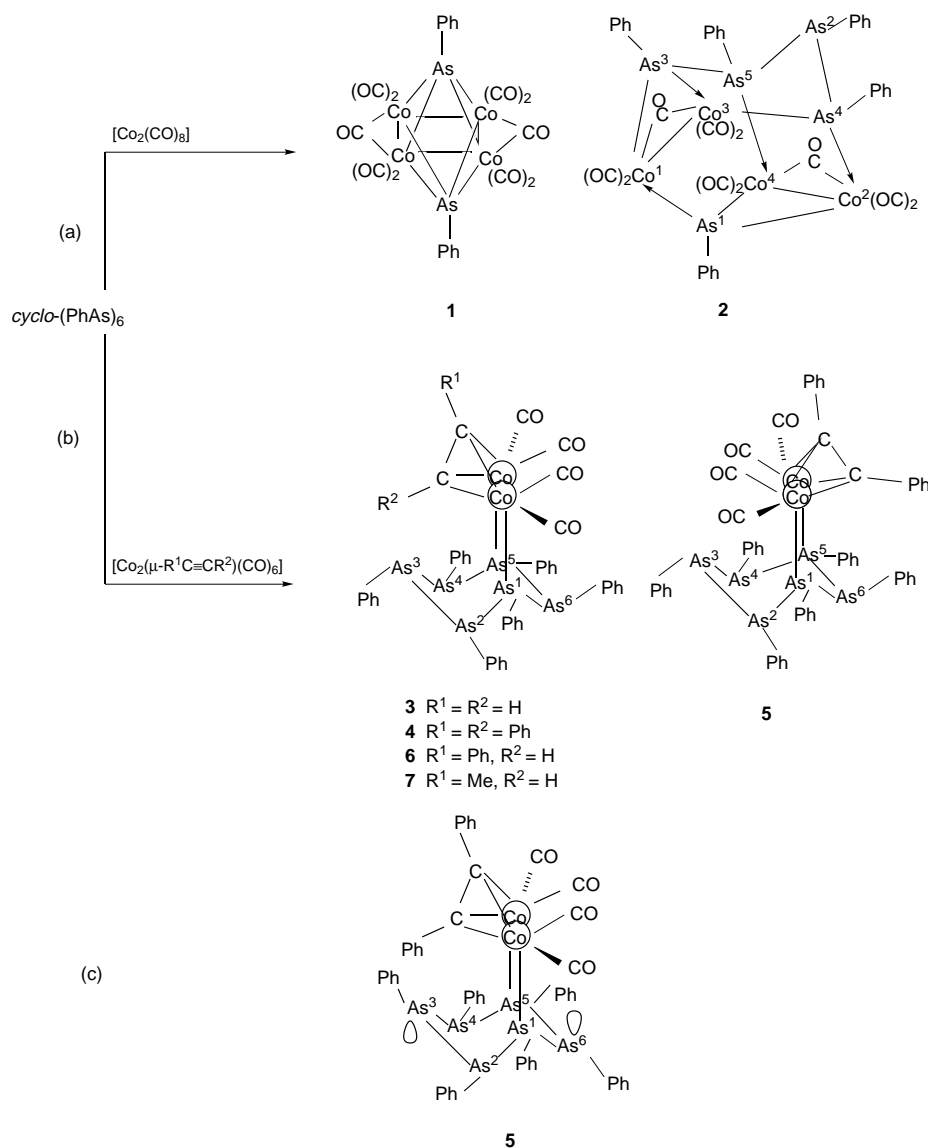
Attempts *via* thermolysis to convert **1** and **2** into any of the complexes obtained previously in the reaction of  $\text{cyclo-(PhAs)}_6$  with  $[\text{Co}_2(\text{CO})_8]$  in a sealed tube at higher temperatures and pressures, such as  $[\{\text{Co}_8(\mu_6\text{-As})(\mu_4\text{-As})(\mu_4\text{-AsPh})_2(\text{CO})_{16}\}_2]$ ,<sup>11</sup> were not successful, and we were unable to demonstrate that **1** or **2** is present as an intermediate in this earlier reaction.

## Conclusion

The dependence of the products on the reaction temperature indicates that there must be more than one reaction pathway involved in the reaction between  $\text{cyclo-(PhAs)}_6$  and  $[\text{Co}_2(\text{CO})_8]$ . It is clear that As–As bond cleavage in  $\text{cyclo-(PhAs)}_6$  is such a facile process that it is promoted by  $[\text{Co}_2(\text{CO})_8]$  even at ambient temperature. It is then at first sight surprising that the reaction between  $\text{cyclo-(PhAs)}_6$  and  $[\text{Co}_2(\mu\text{-R}^1\text{C}\equiv\text{CR}^2)(\text{CO})_6]$  does not also lead to products derived from As–As bond cleavage, since the cleavage of P–P and P–S bonds in the ligands  $\text{PhPPPPh}_2$ <sup>34</sup> and  $\text{Ph}_2\text{PSPPh}$ <sup>35</sup> in substituted dinuclear complexes of the type  $[\text{Co}_2(\mu\text{-R}^1\text{C}\equiv\text{CR}^2)(\mu\text{-Ph}_2\text{PXR}_n)(\text{CO})_4]$  ( $\text{XR}_n = \text{PPh}_2$  or  $\text{SR}$ ) occurs under relatively mild conditions (and As–As bonds are in general weaker than P–P bonds). Thus the complex  $[\text{Co}_2(\mu\text{-PhC}\equiv\text{CPh})(\mu\text{-Ph}_2\text{PPPPh}_2)(\text{CO})_4]$  is readily converted into  $[\text{Co}_2\{\mu\text{-PPh}_2\text{C}(\text{Ph})\text{C}(\text{Ph})\text{CO}\}(\mu\text{-PPh}_2)(\text{CO})_4]$  on thermolysis at  $55^\circ\text{C}$  in toluene.<sup>34</sup> Complexes **3–7** are, however, stable to thermolysis at temperatures up to  $100^\circ\text{C}$  and thermolysis of **3** and **4** at  $120^\circ\text{C}$  resulted in complete decomposition. This difference in thermolytic stability may be due to the fact that *e.g.* in  $[\text{Co}_2(\mu\text{-PhC}\equiv\text{CPh})(\mu\text{-Ph}_2\text{PPPPh}_2)(\text{CO})_4]$  there is considerably more strain in the four-membered  $\text{Co}_2\text{P}_2$  dimetallic ring than in the corresponding five-membered  $\text{Co}_2\text{As}_3$  ring present in  $[\text{Co}_2(\mu\text{-R}^1\text{C}\equiv\text{CR}^2)\{\mu\text{-cyclo-(PhAs)}_6\}(\text{CO})_4]$ .

## Experimental

Unless otherwise stated, all reactions were performed under an atmosphere of dry oxygen-free nitrogen, using solvents which had been freshly distilled from the appropriate drying agent. Infrared spectra were recorded in dichloromethane solution 0.5



**Scheme 1** Products derived from the reaction of *cyclo*-(PhAs)<sub>6</sub> with (a) [Co<sub>2</sub>(CO)<sub>8</sub>] and (b) [Co<sub>2</sub>(μ-R<sup>1</sup>C≡CR<sup>2</sup>)(CO)<sub>6</sub>]. (c) An alternative structure for complex 5, an isomer of 4

mm NaCl cells, using a Perkin-Elmer 1710 Fourier-transform spectrometer, fast atom bombardment (FAB) mass spectra on a Kratos MS890 instrument using 3-nitrobenzyl alcohol as a matrix and <sup>1</sup>H and <sup>13</sup>C NMR spectra on either a Bruker WM250 or AM-400 spectrometer. Microanalyses were performed by the microanalytical department, University of Cambridge. Preparative TLC was carried out on 1 mm silica plates prepared at the University of Cambridge. Products are given in order of decreasing R<sub>f</sub> values. All reagents were obtained from commercial suppliers and used without further purification. The compounds [Co<sub>2</sub>(μ-R<sup>1</sup>CCR<sup>2</sup>)(CO)<sub>6</sub>] (R<sup>1</sup> = R<sup>2</sup> = H or Ph; R<sup>1</sup> = Ph, R<sup>2</sup> = H; R<sup>1</sup> = Me, R<sup>2</sup> = H)<sup>36–38</sup> and *cyclo*-(PhAs)<sub>6</sub><sup>39</sup> were prepared by published procedures.

#### Reaction of *cyclo*-(PhAs)<sub>6</sub> with [Co<sub>2</sub>(CO)<sub>8</sub>]

To a solution of [Co<sub>2</sub>(CO)<sub>8</sub>] (0.171 g, 0.5 mmol) in toluene (25 cm<sup>3</sup>) was added *cyclo*-(PhAs)<sub>6</sub> (0.114 g, 0.125 mmol) and the resulting solution stirred at ambient temperature for 2 h then filtered. After removal of solvent at reduced pressure, the residue was dissolved in the minimum volume of CH<sub>2</sub>Cl<sub>2</sub> and separated by preparative TLC. Elution using hexane–CH<sub>2</sub>Cl<sub>2</sub> (4:1) gave red crystalline [Co<sub>4</sub>(μ<sub>4</sub>-AsPh)<sub>2</sub>(CO)<sub>10</sub>] **1** (0.021 g, 20%), a green solid (decomposed, uncharacterised) and brown crystalline [Co<sub>4</sub>(μ<sub>3</sub>-AsPh)(μ<sub>4</sub>-η<sup>2</sup>:η<sup>2</sup>:η<sup>1</sup>-As<sub>4</sub>Ph<sub>4</sub>)(CO)<sub>10</sub>] **2** (0.038 g, 23%).

#### Reaction of *cyclo*-(PhAs)<sub>6</sub> with [Co<sub>2</sub>(μ-R<sup>1</sup>C≡CR<sup>2</sup>)(CO)<sub>6</sub>]

(a) [Co<sub>2</sub>(μ-HC≡CH){μ-*cyclo*-(PhAs)<sub>6</sub>}(CO)<sub>4</sub>] **3**. To a solution of [Co<sub>2</sub>(μ-HC≡CH)(CO)<sub>6</sub>] (0.312 g, 1 mmol) in toluene or in benzene (50 cm<sup>3</sup>) was added *cyclo*-(PhAs)<sub>6</sub> (0.456 g, 0.5 mmol) and the resulting solution heated at 65 °C for 20 h. The solution was then cooled to room temperature and filtered. After removal of solvent at reduced pressure, the residue was redissolved in CH<sub>2</sub>Cl<sub>2</sub>, silica added and the mixture pumped dry. The solid was added to the top of a silica chromatography column. Elution with hexane–CH<sub>2</sub>Cl<sub>2</sub> (4:1) gave red crystalline [Co<sub>2</sub>(μ-HC≡CH){μ-*cyclo*-(PhAs)<sub>6</sub>}(CO)<sub>4</sub>] **3** (0.335 g, 57%).

(b) [Co<sub>2</sub>(μ-PhC≡CPh){μ-*cyclo*-(PhAs)<sub>6</sub>}(CO)<sub>6</sub>] **4** and **5**. To a solution of [Co<sub>2</sub>(μ-PhC≡CPh)(CO)<sub>6</sub>] (0.464 g, 1 mmol) in toluene or in benzene (50 cm<sup>3</sup>) was added *cyclo*-(PhAs)<sub>6</sub> (0.912 g, 1.0 mmol) and the resulting solution heated at 65 °C for 24 h. The solvent was then removed under reduced pressure, the residue dissolved in the minimum volume of CH<sub>2</sub>Cl<sub>2</sub> and applied to the base of TLC plates. Elution with hexane–CH<sub>2</sub>Cl<sub>2</sub> (3:1) gave green crystalline [Co<sub>2</sub>(μ-PhC≡CPh){μ-*cyclo*-(PhAs)<sub>6</sub>}(CO)<sub>4</sub>] **4** (0.297 g, 45%) followed by red solid [Co<sub>2</sub>(μ-PhC≡CPh){μ-*cyclo*-(PhAs)<sub>6</sub>}(CO)<sub>6</sub>] **5** (0.23 g, 35%).

(c) [Co<sub>2</sub>(μ-PhC≡CH){μ-*cyclo*-(PhAs)<sub>6</sub>}(CO)<sub>6</sub>] **6**. To a solution of [Co<sub>2</sub>(μ-PhC≡CH)(CO)<sub>6</sub>] (0.388 g, 1 mmol) in benzene (50

**Table 6** Crystal data\* for complexes 1–4

	1	2	3	4
Molecular formula	C <sub>22</sub> H <sub>10</sub> As <sub>2</sub> Co <sub>4</sub> O <sub>10</sub>	C <sub>40</sub> H <sub>25</sub> As <sub>5</sub> Co <sub>4</sub> O <sub>10</sub>	C <sub>42</sub> H <sub>32</sub> As <sub>6</sub> Co <sub>2</sub> O <sub>4</sub>	C <sub>54</sub> H <sub>40</sub> As <sub>6</sub> Co <sub>2</sub> O <sub>4</sub>
<i>M</i>	819.86	1275.92	1168.06	1320.24
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>Pc</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>Pc</i>
<i>a</i> /Å	9.713(3)	13.418(3)	13.231(3)	14.277(6)
<i>b</i> /Å	12.649(12)	16.443(3)	24.380(5)	14.720(4)
<i>c</i> /Å	10.649(3)	12.751(3)	13.278(3)	13.607(5)
<i>α</i> /°		110.22(3)		105.41(3)
<i>β</i> /°	96.74(2)	107.31(3)	100.76(3)	111.12(3)
<i>γ</i> /°		89.04(3)		89.04(3)
<i>U</i> /Å <sup>3</sup>	1299.3(13)	2508.7(9)	4207.8(16)	2561.7(16)
<i>Z</i>	2	2	4	2
<i>D<sub>c</sub></i> /Mg m <sup>-3</sup>	2.096	1.689	1.844	1.712
Crystal size/mm	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.24 × 0.22 × 0.18	0.30 × 0.25 × 0.15
Crystal habit	Red block	Brown block	Red block	Green block
<i>F</i> (000)	792	1236	2272	1296
<i>μ</i> /mm <sup>-1</sup>	5.090	4.619	5.511	4.537
Maximum, minimum relative transmission	0.761, 1.000	0.808, 0.999	0.343, 0.260	1.000, 0.810
Data collection range/°	5.02 < 2θ < 49.98	5.16 < 2θ < 45.0	7.08 < 2θ < 47.0	5.02 < 2θ < 55.0
Index ranges	−10 ≤ <i>h</i> ≤ 12, 0 ≤ <i>k</i> ≤ 16, −13 ≤ <i>l</i> ≤ 13	0 ≤ <i>h</i> ≤ 14, −17 ≤ <i>k</i> ≤ 17, −13 ≤ <i>l</i> ≤ 13	−14 ≤ <i>h</i> ≤ 14, 0 ≤ <i>k</i> ≤ 27, −3 ≤ <i>l</i> ≤ 14	0 ≤ <i>h</i> ≤ 18, −19 ≤ <i>k</i> ≤ 19, −17 ≤ <i>l</i> ≤ 16
Reflections measured	4360	7039	6238	12 220
Independent reflection ( <i>R<sub>int</sub></i> )	2986 (0.0467)	6559 (0.066)	6198 (0.038)	11 748 (0.037)
Parameters	172	532	487	595
<i>wR</i> 2 (all data)	0.190	0.2658	0.1662	0.1790
<i>x</i> , <i>y</i>	0.0255, 0.0129	0.1568	0.0756, 7.838	0.100, 0.871
<i>R</i> 1 [ <i>I</i> > 2σ( <i>I</i> )]	0.0325	0.0653	0.0649	0.0656
Observed reflections [ <i>I</i> > 2σ( <i>I</i> )]	2098	4028	3829	7533
Goodness of fit on <i>F</i> <sup>2</sup> (all data)	1.025	1.024	1.051	1.009
Maximum shift/σ	−0.001	0.001	0.004	0.001
Peak, hole in final difference map/e Å <sup>-3</sup>	0.666, −0.785	1.586, −1.044	0.610, −0.755	1.197, −1.040
Decay (%)	−2	12	0	0

\* Data in common: graphite-monochromated Mo-*K*α radiation, λ = 0.710 73 Å; *T* = 293(2) K; *R*1 = Σ||*F<sub>o</sub>*|| − |*F<sub>c</sub>*||/Σ|*F<sub>o</sub>*||, *wR*2 = [Σ*w*(*F<sub>o</sub>*<sup>2</sup> − *F<sub>c</sub>*<sup>2</sup>)<sup>2</sup>/Σ*wF<sub>o</sub>*<sup>4</sup>]<sup>1/2</sup>, *w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*)<sup>2</sup> + (*xP*)<sup>2</sup> + *yP*], *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3, where *x* and *y* are constants adjusted by the program; goodness of fit = [Σ*w*(*F<sub>o</sub>*<sup>2</sup> − *F<sub>c</sub>*<sup>2</sup>)<sup>2</sup>/(*n* − *p*)]<sup>1/2</sup> where *n* is the number of reflections and *p* the number of parameters.

cm<sup>3</sup>) was added *cyclo*-(PhAs)<sub>6</sub> (0.912 g, 1.0 mmol) and the resulting solution heated at 65 °C for 24 h. The solution was then cooled to room temperature and filtered. After removal of the solvent at reduced pressure, the residue was redissolved in CH<sub>2</sub>Cl<sub>2</sub>, silica added and the mixture pumped dry. The solid was then added to the top of a silica chromatography column and elution using hexane–CH<sub>2</sub>Cl<sub>2</sub> (4:1) gave traces of starting material followed by uncharacterised unstable products. Further elution with CH<sub>2</sub>Cl<sub>2</sub> gave red crystalline [Co<sub>2</sub>-(μ-PhC≡CH){μ-*cyclo*-(PhAs)<sub>6</sub>}(CO)<sub>4</sub>] **6** (0.650 g, 52%).

(*d*) [Co<sub>2</sub>(μ-MeC≡CH){μ-*cyclo*-(PhAs)<sub>6</sub>}(CO)<sub>4</sub>] **7**. To a solution of [Co<sub>2</sub>(μ-MeC≡CH)(CO)<sub>6</sub>] (0.326 g, 1 mmol) in toluene (50 cm<sup>3</sup>) was added *cyclo*-(PhAs)<sub>6</sub> (0.456 g, 0.5 mmol) and the resulting solution heated at 65 °C for 24 h. The procedure as in (*c*) was then followed. Elution with hexane–CH<sub>2</sub>Cl<sub>2</sub> (4:1) gave [Co<sub>2</sub>(μ-MeC≡CH){μ-*cyclo*-(PhAs)<sub>6</sub>}(CO)<sub>4</sub>] **7** (0.42 g, 70%) as a dark brown-red crystalline solid.

### Crystallography

Diffraction data were collected by the ω–2θ scan method on a Rigaku AFC5R (complexes **1**, **2**), AFC7R (**4**) and ω–θ scan method on a Stoe-Siemens four-circle diffractometer (**3**). Three standard reflections were monitored at intervals of 200 reflections (**1**, **4**, **2**) or 60 min (**3**) and a decay correction applied for **2**. Cell parameters were obtained by least-squares refinement on diffractometer angles from 25 centred reflections (15 < θ < 20°). Semiempirical absorption corrections based on ψ-scan data were applied.<sup>40,41</sup> The structures were solved by direct methods (SHELXL PLUS,<sup>42</sup> SIR 92<sup>43</sup>) and subsequent Fourier-difference syntheses and refined anisotropically on all ordered

non-hydrogen atoms by full-matrix least squares on *F*<sup>2</sup> (SHELXL 93<sup>44</sup>). 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. Crystal data are given in Table 6.

CCDC reference number 186/796.

### Acknowledgements

We gratefully acknowledge the financial support of the Cambridge Commonwealth Trust and the United Kingdom Committee of Vice Chancellors and Principals (to R. M. D. S.).

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*Received 9th September 1997; Paper 7/06576K*