

Fragmentation of a As_4Ph_4 -chain on a tetranuclear cobalt cluster induced by thermolysis or by reaction with $\text{Fe}_2(\text{CO})_9$

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Abstract

Thermolysis of the tetranuclear cobalt cluster $[\text{Co}_4(\mu_3\text{-AsPh})(\mu_4\text{-}\eta^2\text{:}\eta^2\text{:}\eta^1\text{-As}_4\text{Ph}_4)(\mu\text{-CO})_2(\text{CO})_8]$ (**1**) at 60°C in benzene for two days gives $[\text{Co}_4(\mu_3\text{-AsPh})_2(\mu_3\text{-}\eta^2\text{:}\eta^1\text{-As}_2\text{Ph}_2)(\mu\text{-CO})(\text{CO})_9]$ (**2**), in which the tetraarsine chain in **1** has been cleaved to give the bridging As_2Ph_2 unit in **2**. Similar fragmentation of the As_4Ph_4 chain occurs on treatment of **1** with $[\text{Fe}_2(\text{CO})_9]$ in benzene at room temperature for 3 days affording $[\text{Co}_4(\mu_3\text{-AsPh})_2\{(\mu_3\text{-}\eta^2\text{:}\eta^1\text{-As}_2\text{Ph}_2)\text{Fe}(\text{CO})_4\}(\mu\text{-CO})(\text{CO})_9]$ (**3**), in which one arsine atom of the As_2Ph_2 bridging ligand is additionally bound to an $\text{Fe}(\text{CO})_4$ unit. Conversely, reaction of **1** with excess $\text{P}(\text{OMe})_3$ at room temperature in benzene for 3 days gives the trisubstituted trimethylphosphite derivative $[\text{Co}_4(\mu_3\text{-AsPh})(\mu_4\text{-}\eta^2\text{:}\eta^2\text{:}\eta^1\text{-As}_4\text{Ph}_4)(\mu\text{-CO})_2(\text{CO})_5\{\text{P}(\text{OMe})_3\}_3]$ (**4**), in which the As_4Ph_4 unit remains intact. Single crystal X-ray diffraction studies have been performed on **2**, **3** and **4** and possible reaction pathways for the formation of the new complexes are proposed and discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cobalt; Arsine; Cluster; Chain; Fragmentation

1. Introduction

The cleavage and fragmentation of *cyclo*-polyarsanes (CPAs), *cyclo*-(RAs)_n (R = hydrocarbyl, n = 3–6), in the presence of transition metal carbonyl complexes to afford products containing arsine chains [e.g. (RAs)_n and As_n] and capping fragments (e.g. AsR or As) have been the subject of numerous reports [1–9]. Of particular note has been the reactions of cobalt carbonyl with CPAs which can result in low to high nuclearity clusters featuring both As and Co atoms [10–12]. For example, Dahl et al. reported the formation of the tetrahedrane complex $[\text{CoAs}_3(\text{CO})_3]$ from the reaction of $[\text{Co}_2(\text{CO})_8]$ with *cyclo*-(AsMe)₅ at 200°C in hexane under 110 atm of CO [10] while Rheingold and coworkers reported the synthesis of the remarkable Co₁₆ cluster $[\text{Co}_8(\mu_6\text{-As})(\mu_4\text{-As})(\mu_4\text{-AsPh})_2(\text{CO})_{16}]_2$ from the reaction of $[\text{Co}_2(\text{CO})_8]$ with *cyclo*-(AsPh)₆ in toluene in a sealed tube at 90°C [11]. More recently, we have re-investigated the latter reaction under less forcing conditions and have found

that the tetranuclear cobalt clusters $[\text{Co}_4(\mu_3\text{-AsPh})(\mu_4\text{-}\eta^2\text{:}\eta^2\text{:}\eta^1\text{-As}_4\text{Ph}_4)(\mu\text{-CO})_2(\text{CO})_8]$ **1** and $[\text{Co}_4(\mu_4\text{-AsPh})_2(\mu\text{-CO})_2(\text{CO})_8]$ are afforded in moderate yield when the reaction is performed at ambient temperature in toluene (Fig. 1) [12]. Herein we describe the results of a study of the reactivity of **1** towards thermolysis, $[\text{Fe}_2(\text{CO})_9]$ and $\text{P}(\text{OMe})_3$ with particular regard to further degradation of the tetraarsine unit in **1**.

2. Results and discussion

The thermolysis of $[\text{Co}_4(\mu_3\text{-AsPh})(\mu_4\text{-}\eta^2\text{:}\eta^2\text{:}\eta^1\text{-As}_4\text{Ph}_4)(\mu\text{-CO})_2(\text{CO})_8]$ (**1**) at 60°C in benzene for 48 h gives $[\text{Co}_4(\mu_3\text{-AsPh})_2(\mu_3\text{-}\eta^2\text{:}\eta^1\text{-As}_2\text{Ph}_2)(\mu\text{-CO})(\text{CO})_9]$ (**2**) as a red crystalline complex in moderate yield (Scheme 1).

The complex has been characterised by ¹H- and ¹³C-NMR spectroscopy, mass spectrometry and microanalysis (see Table 1). In addition, the structure of **2** has been determined by single crystal X-ray diffraction. Crystals suitable for such analysis were grown by diffusion of hexane into a dichloromethane solution of **2** at room temperature.

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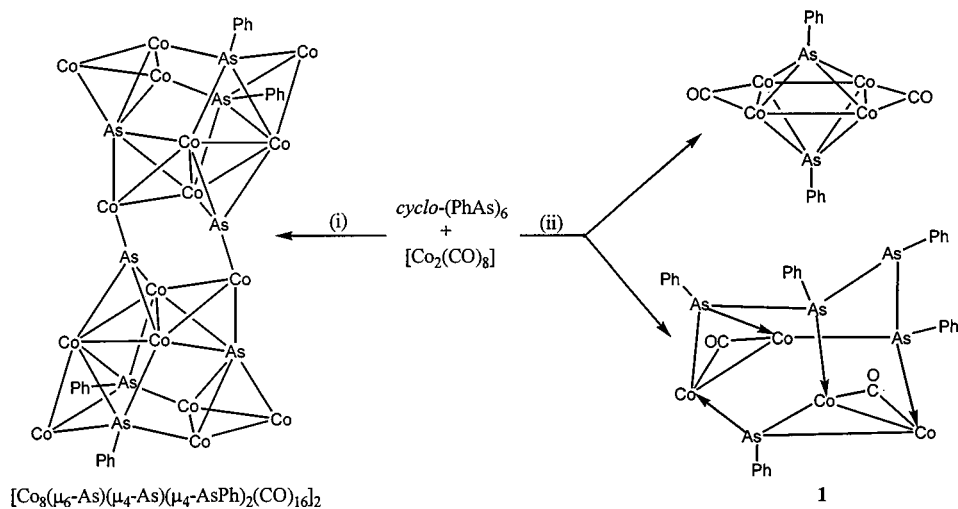
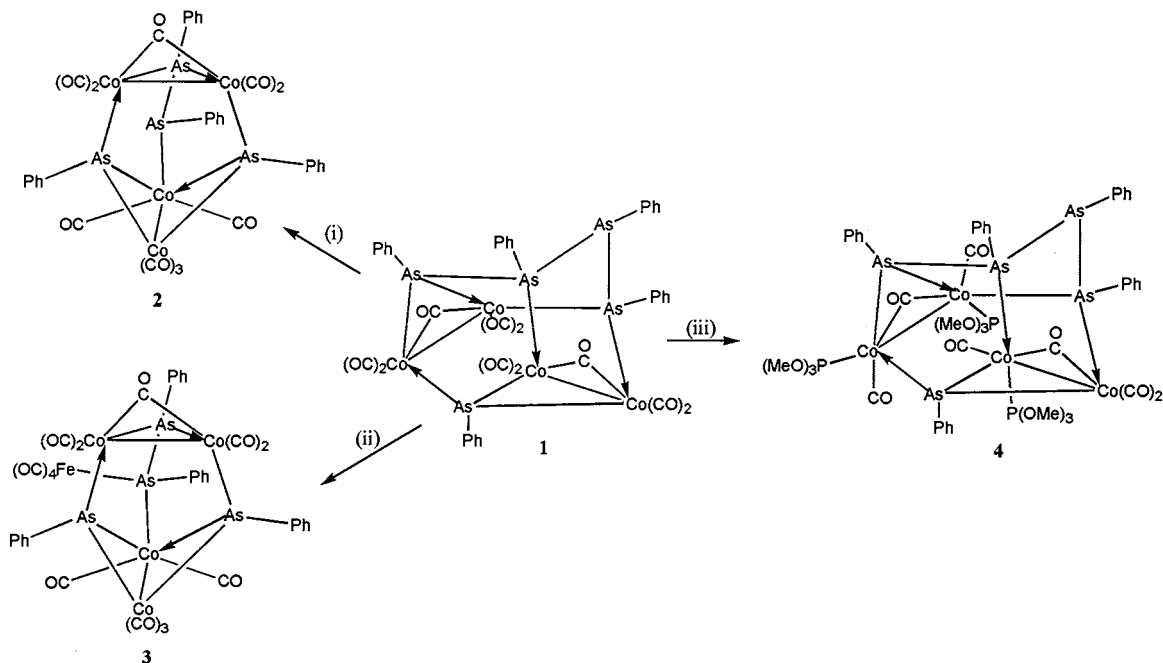


Fig. 1. Products derived from the reactions of $[\text{Co}_2(\text{CO})_8]$ with $\text{cyclo}(\text{PhAs})_6$ at: (i) 90°C in a sealed tube, 12 h, C_7H_8 [11]; (ii) room temperature, 2 h, C_7H_8 [12]. Terminal carbonyls omitted for clarity.

The molecular structure of **2** is depicted in Fig. 2; selected bond distances and angles are listed in Table 2. The structure consists of a butterfly motif made up of Co(3) and Co(4) as the hinge and As(3) and As(4) as the wing-tips. This motif is further linked to a triangle of Co(1)–Co(2)–As(1) through both the wing-tips As(3) and As(4) to Co(2) and Co(1) respectively and by As(2) which connects Co(3) to As(1). Each Co atom possesses two terminal carbonyl ligands except for Co(4) where three terminally bonded carbonyl groups are present. In addition, Co(1) and Co(2) are bridged by a single carbonyl group. The unbridged Co(3)–

Co(4) bond is 0.09 \AA longer than the bridged Co(1)–Co(2) bond [$2.582(1) \text{ \AA}$ versus $2.491(1) \text{ \AA}$] and 0.063 \AA longer than the average Co–Co bond distance (2.519 \AA) present in **1**. The As–As bond distance of $2.427(1) \text{ \AA}$ is similar to that found in **1** [12] and to that found in $\text{cyclo}(\text{PhAs})_6$ [13]. The average Co–As bond distance of 2.35 \AA is within the range of values present in **1** and also comparable to the observed values in related structures [10–12,14,15]. The Co–As–Co angles are in the range $65\text{--}66^\circ$ for the arsenic atom bridging the two metal–metal bonded Co atoms from the same bimetal unit, and in the range $119\text{--}121^\circ$ for the arsenic atom



Scheme 1. Reagents and conditions: (i) 60°C , 48 h, C_6H_6 ; (ii) $[\text{Fe}_2(\text{CO})_9]$, room temperature, 48 h, C_6H_6 ; (iii) $x\text{s P}(\text{OMe})_3$, room temperature, 48 h, C_6H_6 .

Table 1
Spectroscopic and microanalytical data for the new complexes 2–4

Compound	$\nu(\text{CO})$ (cm^{-1}) ^a	¹ H-NMR (δ) ^b	C-NMR (δ) ^c	³¹ P-NMR (δ) ^d	FAB mass spectrum	Microanalysis (%) ^e	
						C	H
2	2075s, 2044vs, 2028s, 1998m, 1834w	7.8–6.9 [m, 20H, Ph]	200.0 [br, CO], 199.0 [br, CO], 197.0 [br, CO], 149–125 [m, Ph]	1123 (M^+), $M^+ - n\text{CO}$ ($n = 1-10$)	36.20 (36.33)	1.88 (1.79)	
3	2085m, 2055s, 2045vs, 2032sh, 2010w, 1964vw, 1938w, 1920w, 1846vw	7.8–6.6 [m, 20H, Ph]	214.0 [s, CO], 204.0 [br, CO], 203.0 [br, CO], 199.0 [br, CO], 197.0 [br, CO], 149–128 [m, Ph]	1291 (M^+), $M^+ - n\text{CO}$ ($n = 1-14$)	34.46 (34.07)	1.54 (1.47)	
4	2007m, 1974s, 1995vs, 1771m	8.2–6.8 [m, 25H, Ph], 3.40 [d, ³ J(PH) 10.7, 9H, P(OMe) ₃], 3.28 [d, ³ J(PH) 10.6, 9H, P(OMe) ₃], 3.26 [d, ³ J(PH) 11.5, 9H, P(OMe) ₃]	247.0 [br, CO], 211.0 [br, CO], 206.0 [br, CO], 205.0 [br, CO], 204.0 [br, CO], 150–127 [m, Ph], 53.0 [d, ² J(PC) 8, P(OCH ₃) ₃], 52.0 [d, ² J(PC) 8, P(OCH ₃) ₃], 51.0 [d, ² J(PC) 8, P(OCH ₃) ₃]	1508 ($M^+ - 2\text{CO}$), $M^+ - n\text{CO}$ ($n = 3-7$)	34.98 (35.32)	3.38 (3.35)	

^a Recorded in dichloromethane solution.

^b ¹H chemical shifts (δ) in ppm relative to SiMe₄ (0.0 ppm), coupling constants in Hz in CDCl₃ at 293 K.

^c Chemical shifts in ppm relative to SiMe₄ (0.0), in CDCl₃ at 293 K.

^d ³¹P chemical shifts (δ) in ppm relative to external 85% H₃PO₄ (0.0 ppm), ¹H-gated decoupled, measured in CDCl₃ at 293 K. Deduct 140.2 from tabulated values in order to reference relative to external P(OMe)₃.

^e Calculated values in parentheses.

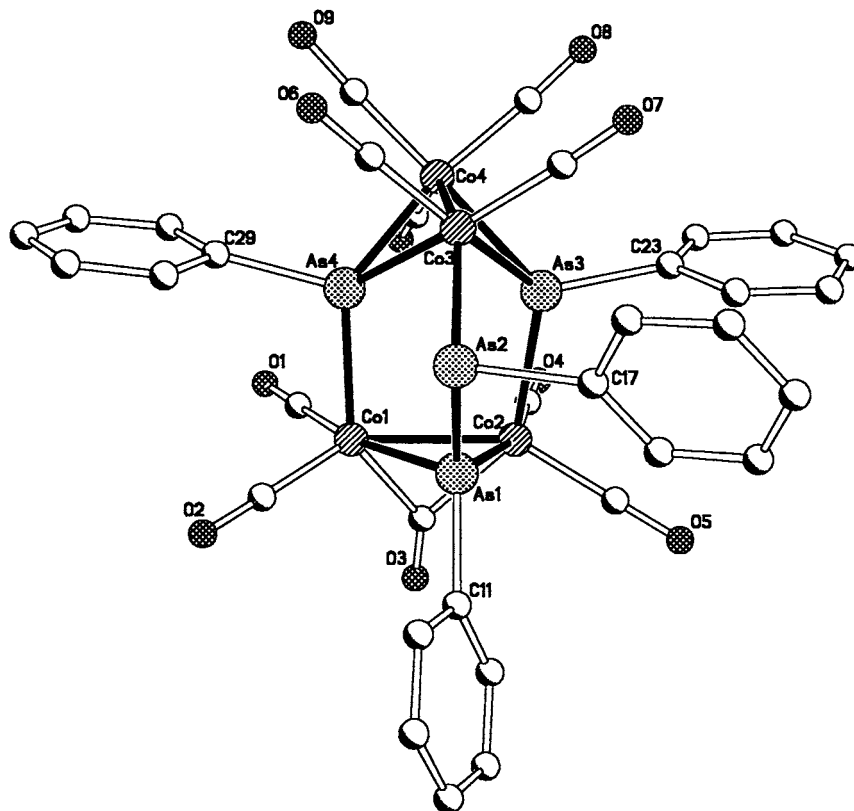


Fig. 2. Molecular structure of $[\text{Co}_4(\mu_3\text{-AsPh})_2(\mu_3\text{-}\eta^2\text{:}\eta^1\text{-As}_2\text{Ph}_2)(\mu\text{-CO})(\text{CO})_9]$ (**2**) including the atom numbering scheme. All hydrogen atoms have been omitted for clarity.

which bridges the two non-bonded Co atoms from different units. These angle ranges are typical for correspondingly bonded As atoms in related structures [11,12,14,15]. It may be that **2** is an intermediate in the formation of the cluster $[\text{Co}_8(\mu_6\text{-As})(\mu_4\text{-As})(\mu_4\text{-AsPh})_2(\text{CO})_{16}]_2$ [11] although the formation of this latter complex was not observed in the thermolysis of **1** under the conditions used to obtain **2**. Complex **2** and $[\text{Co}_8(\mu_6\text{-As})(\mu_4\text{-As})(\mu_4\text{-AsPh})_2(\text{CO})_{16}]_2$ do, however, share one notable structural feature in common that is a distorted Co_2As_2 tetrahedral unit linked to a Co–Co–As unit via phenyl arsenidene groups. In **2** these phenyl arsenidene groups bridge three metal centres while in and $[\text{Co}_8(\mu_6\text{-As})(\mu_4\text{-As})(\mu_4\text{-AsPh})_2(\text{CO})_{16}]_2$ four metal centres are bridged.

The spectroscopic properties of **2** are consistent with the solid state structure being maintained in solution. Five ν_{CO} bands are visible in the IR spectrum including an absorption at 1834 cm^{-1} corresponding to the presence of a bridging carbonyl group in the molecule. The $^{13}\text{C}\text{-}\{^1\text{H}\}\text{-NMR}$ spectrum at 293 K displays, in addition to the multiplet at δ 149–125 for the phenyl carbon atoms, three broad signals at chemical shifts (δ 200.0, 199.0 and 197.0) typical of terminal cobalt carbonyl groups. At this temperature it would appear that the bridging carbonyl in **2** is involved in an exchange process with the terminal carbonyl ligands on one or

more metal centres. The FAB mass spectrum displays a molecular ion consistent with the proposed formula along with fragmentation peaks corresponding to the loss of up to ten carbonyl groups.

The reaction of **1** with $[\text{Fe}_2(\text{CO})_9]$ in a 1:4 ratio in benzene at ambient temperature for 2 days gives the complex $[\text{Co}_4(\mu_3\text{-AsPh})_2\{(\mu_3\text{-}\eta^2\text{:}\eta^1\text{-As}_2\text{Ph}_2)\text{Fe}(\text{CO})_4\}(\mu\text{-CO})(\text{CO})_9]$ (**3**) as the major product in addition to other uncharacterised unstable products (Scheme 1). Complex **3** has been characterised by ^1H , ^{13}C and IR spectroscopy, mass spectrometry and microanalysis (Table 1). In addition, a crystal of **3** has been the subject of a single-crystal X-ray diffraction study. Crystals suitable for the study were grown by slow diffusion of hexane into a dichloromethane solution of **3** at 0°C .

The molecular structure of **3** is illustrated in Fig. 3 and selected bond distances and angles are shown in Table 3. The structure of **3** resembles that of **2** with one of the arsine atoms of the As_2 chain [As(2)] being bound to an $\text{Fe}(\text{CO})_4$ unit. The effect of this addition on the Co–As core causes only minor changes in the molecular structure when compared with **2**. For example, the bond angles for Co(4)–As(3)–Co(3), Co(4)–As(4)–Co(1) and Co(1)–As(1)–As(2) of $118.9(1)$, $119.6(1)$ and $118.3(1)^\circ$ in **3**, respectively, are reduced when compared with the corresponding angles of $120.5(1)$, $121.8(1)$ and $125.4(1)^\circ$ in **2**. This observation

can be rationalised as being necessary to reduce intramolecular interactions between the Co–As core and the Fe(CO)₄ unit. The Fe–As distance, 2.366(3) Å, is comparable to that in other iron complexes in which As functions as a two-electron donor [16,17]. The coordination of the As(2) atom to the Fe(CO)₄ occurs at an axial site within the trigonal bipyramidal iron coordination sphere.

The spectroscopic properties of **3** are in accord with the solid state structure being maintained in solution. The IR spectrum displays a number of additional peaks in the terminal carbonyl region when compared to the parent structure **2** which can be assigned as arising from the Fe(CO)₄ unit. Furthermore, there is an absorption at 1846 cm⁻¹ corresponding to the presence of a bridging CO group in the molecule. The ¹³C-¹H-NMR spectrum shows a sharp singlet at δ 214.0 corresponding to carbonyl groups bound to the Fe atom, suggesting that the four carbonyl groups residing on the iron atom are fluxional at 293 K [18]. The four broad peaks between δ 204.0 and δ 197.0 can be assigned to the cobalt-bound carbonyl groups, while phenyl carbon resonances are observed at δ 149–128. The FAB mass spectrum indicates a molecular ion and fragmentation peaks corresponding to up to fourteen carbonyl losses.

The mechanism by which **3** is obtained from **1** is not obvious but a plausible pathway is given in Scheme 2. This pathway initially involves Fe–Fe bond cleavage and attack of the resultant Fe(CO)₄ fragment at the uncoordinated arsenic atom in **1**, As⁵, to produce an intermediate **A**. This may weaken the As–As bonds between As⁵–As³ and As⁵–As² in the adduct **A** as compared to the parent complex **1**, resulting in subse-

quent cleavage of these bonds. Formation of a bond between As³ and Co³ could then occur, with the cleavage of the Co³–CO(bridging) bond to give complex **2**. Attack of the lone pair of electrons on As² of the As₂Ph₂ bridging ligand in **2** at a coordinatively unsaturated Fe(CO)₄ unit furnishes **3**. It is worthy of note that in a separate reaction we have confirmed that complex **2** yields **3** on treatment with [Fe₂(CO)₉] in benzene at room temperature.

The reaction of **1** with excess P(OMe)₃ at room temperature in benzene for 3 days gives [Co₄(μ₃-AsPh)(μ₄-η²:η²:η¹-As₄Ph₄)(μ-CO)₂(CO)₅{P(OMe)₃}₃] (**4**) in moderate yield (Scheme 1). Complex **4** has been characterised by ¹H-, ¹³C-, ³¹P-NMR and IR spectroscopy, mass spectrometry (Table 1) and, in addition, has been the subject of a single-crystal X-ray diffraction study.

The molecular structure of **4** is illustrated in Fig. 4 while selected bond distances are listed in Table 4. The structure consists of two discrete singly bonded Co₂ units each bridged by a single carbonyl group and linked by an As₄Ph₄ chain and by an AsPh group. The coordination spheres of Co(2), Co(3) and Co(4) are completed by one P(OMe)₃ group and one carbonyl group while for Co(1) by two carbonyl groups. At Co(4) the P(OMe)₃ group occupies an pseudo-axial position [Co(3)–Co(4)–P(1) 148.3(2)°] while at Co(2) and Co(3) the P(OMe)₃ groups occupy equatorial sites [Co(1)–Co(2)–P(2) 110.3(3)°, Co(4)–Co(3)–P(3) 101.6(3)°]. In general, poorer π-acceptor ligands than carbonyl such as trialkylphosphites occupy axial sites on a dicobalt skeleton [19] and the equatorial substitution observed in **4** at Co(2) and Co(3) can be attributed to steric effects. The average Co–P bond distance of 2.25 Å is comparable with reported Co–P distances present in other phosphite-substituted complexes [20–23]. Comparison of the structural parameters for **1** and **4** reveals that substitution of phosphite ligands has a small but perceptible effect on the structure of the core. Thus the Co(3)–Co(4) distance has decreased from 2.522(4) to 2.500(5) Å and the Co(1)–Co(2) distance has increased from 2.516(3) to 2.523(5) Å. The average cobalt to bridging carbonyl and terminal carbonyl distances of 1.90 and 1.72 Å, respectively, compare to the average distance of 1.94 and 1.80 Å in **1**, reflecting the increase in π back-donation from metal to the carbonyl carbon in **4** to relieve the extra electron density gained from the phosphite ligands. Other significant skeletal changes that accompany substitution of trimethylphosphite are the enlargement of the bond angles Co(4)–As(5)–Co(1), Co(1)–As(1)–Co(3), Co(3)–As(4)–As(3) and Co(3)–As(4)–As(2) by ca. 6° compared to **1**. It appears that, on substitution, the molecule has adopted a structure which minimises intra-molecular interactions between the phenyl rings, the methoxy groups and the carbonyl ligands.

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

Co(1)–Co(2)	2.491(1)	Co(3)–Co(4)	2.582(1)
Co(1)–C(3)	1.907(5)	Co(2)–C(3)	1.951(5)
As(1)–As(2)	2.427(1)	As(1)–Co(1)	2.320(1)
As(1)–Co(2)	2.999(1)	As(2)–Co(3)	2.338(1)
As(3)–Co(2)	2.404(1)	As(3)–Co(3)	2.338(1)
As(3)–Co(4)	2.399(1)	As(4)–Co(1)	2.374(1)
As(4)–Co(3)	2.321(1)	As(4)–Co(4)	2.392(1)
Mean Co–C (terminal carbonyl)	1.77		
Co(1)–C(3)–Co(2)	80.4(2)	C(3)–Co(1)–Co(2)	50.60(2)
C(3)–Co(2)–Co(1)	49.0(1)	As(3)–Co(4)–Co(3)	55.82(3)
As(4)–Co(4)–Co(3)	55.47(3)	As(4)–Co(4)–As(3)	74.80(3)
As(2)–Co(3)–Co(4)	144.09(3)	As(3)–Co(3)–Co(4)	58.12(3)
As(4)–Co(3)–As(2)	95.58(3)	As(4)–Co(3)–As(3)	77.31(3)
As(3)–Co(2)–Co(1)	94.81(3)	As(1)–Co(2)–Co(1)	55.77(3)
Co(3)–As(4)–Co(1)	120.51(3)	Co(3)–As(4)–Co(4)	66.43(3)
Co(1)–As(4)–Co(4)	121.82(3)	As(1)–Co(1)–As(4)	88.38(3)
As(4)–Co(1)–Co(2)	95.18(3)	As(1)–Co(2)–As(3)	85.65(3)
As(1)–Co(1)–Co(2)	56.96(3)	Co(2)–As(1)–Co(1)	65.27(3)
Co(1)–As(1)–As(2)	125.42(3)	Co(1)–As(1)–As(2)	114.72(3)
Co(3)–As(2)–As(1)	95.41(3)	Co(3)–As(3)–Co(4)	66.06(3)
Co(3)–As(3)–Co(2)	121.08(3)	Co(4)–As(3)–Co(2)	119.45(3)

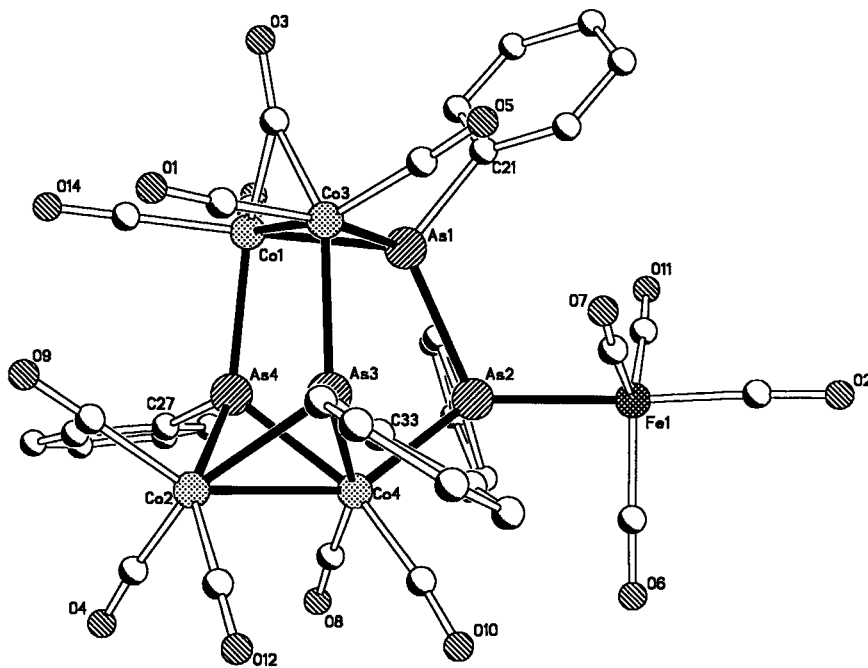


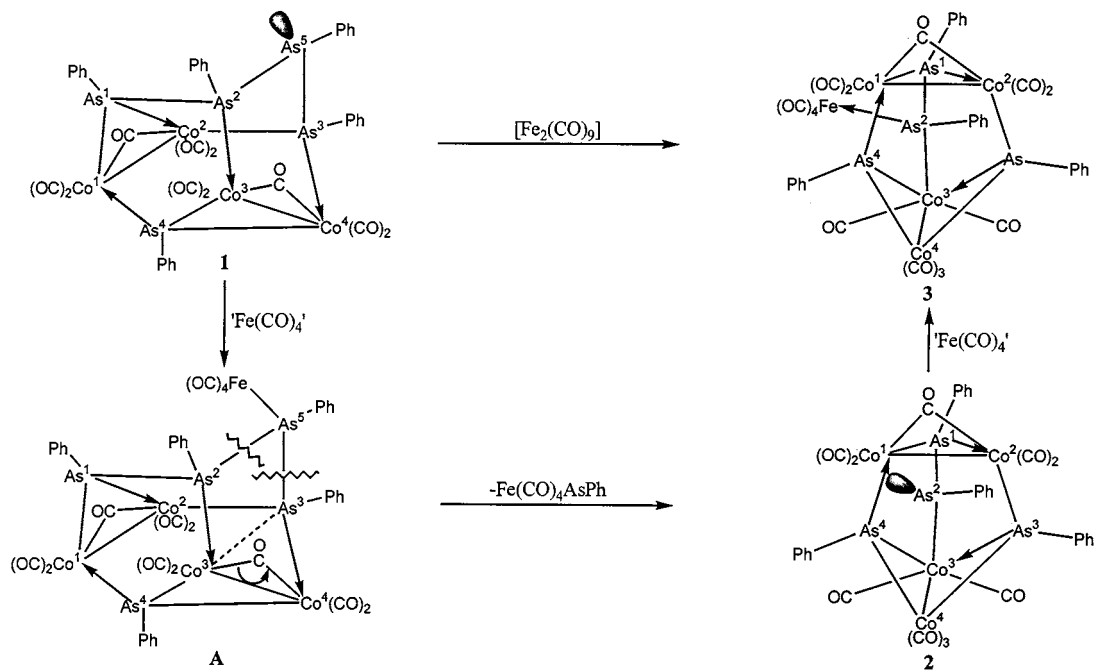
Fig. 3. Molecular structure of $[\text{Co}_4(\mu_3\text{-AsPh})_2(\mu_3\text{-}\eta^2\text{:}\eta^1\text{-As}_2\text{Ph}_2)\text{Fe}(\text{CO})_4](\mu\text{-CO})(\text{CO})_9$ (**3**) including the atom numbering scheme. All hydrogen atoms have been omitted for clarity.

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

Co(1)–Co(3)	2.478(4)	Co(2)–Co(4)	2.569(4)
Co(1)–C(3)	1.93(2)	Co(3)–C(3)	1.97(2)
As(1)–As(2)	2.458(3)	As(1)–Co(1)	2.310(3)
As(1)–Co(3)	2.308(3)	As(2)–Co(4)	2.341(3)
As(3)–Co(2)	2.404(3)	As(3)–Co(4)	2.361(3)
As(3)–Co(3)	2.422(3)	As(4)–Co(2)	2.379(4)
As(4)–Co(4)	2.359(3)	As(4)–Co(1)	2.393(3)
Fe(1)–As(2)	2.366(3)	Mean Fe(1)–C(terminal carbonyl)	1.76
Mean Co–C (terminal carbonyl)	1.79		
Co(1)–C(3)–Co(2)	78.9(6)	C(3)–Co(1)–Co(3)	51.3(6)
As(4)–Co(4)–Co(2)	57.5(1)	As(3)–Co(4)–Co(2)	58.2(1)
As(2)–Co(4)–Co(2)	144.6(1)	As(4)–Co(4)–As(3)	77.2(1)
As(4)–Co(4)–As(2)	97.0(1)	As(3)–Co(3)–Co(1)	96.6(1)
As(3)–Co(2)–Co(4)	56.6(1)	As(4)–Co(4)–As(3)	77.2(1)
Co(4)–As(4)–Co(1)	119.9(1)	As(1)–Co(3)–Co(1)	57.6(1)
Co(1)–As(4)–Co(2)	123.5(1)	Co(4)–As(4)–Co(2)	65.7(1)
As(4)–Co(1)–Co(3)	94.5(1)	As(1)–Co(1)–As(4)	89.7(1)
As(1)–Co(1)–Co(3)	57.5(1)	As(1)–Co(3)–As(3)	88.9(1)
Co(1)–As(1)–As(2)	118.4(1)	Co(3)–As(1)–Co(1)	64.9(1)
Co(4)–As(2)–As(1)	97.6(1)	Co(4)–As(3)–Co(2)	65.3(1)
Co(4)–As(3)–Co(3)	118.9(1)	Co(2)–As(3)–Co(3)	119.5(1)
Fe(1)–As(2)–Co(4)	127.2(1)	Fe(1)–As(2)–As(1)	109.9(1)

The spectroscopic properties of **4** are in agreement with the solid state structure being maintained in solution. Four ν_{CO} bands are visible in the IR spectrum including an absorption at 1771 cm^{-1} corresponding to the presence of bridging CO groups in the molecule. The significant lowering of frequencies of both terminal and bridging carbonyl groups, compared to **1**, can be attributed to the filling of π antibonding orbitals of the

CO ligands due to a high level of back donation from the metals. The $^1\text{H-NMR}$ spectrum shows, in addition to phenyl resonances, three separate doublets at δ 3.40, 3.29 and 3.26 with two-bond phosphorus-hydrogen coupling constants of 10.7, 10.6 and 11.5 Hz and corresponding to the one axial and two equatorial trimethylphosphite groups. In the $^{31}\text{P}\{-^1\text{H}\}$ -NMR spectrum three broad resonances are seen at δ 159.5, 151.2



Scheme 2. Possible reaction pathway to account for the formation of 3 from 1.

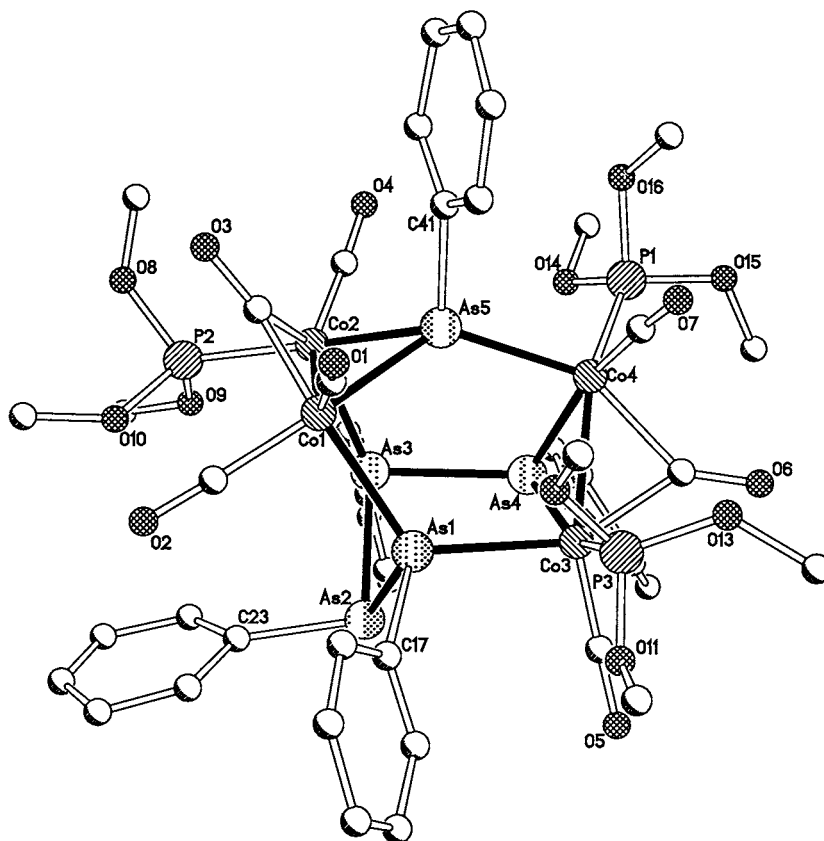
Fig. 4. Molecular structure of $[\text{Co}_4(\mu_3\text{-AsPh})(\mu_4\text{-}\eta^2\text{:}\eta^2\text{:}\eta^1\text{-As}_4\text{Ph}_4)(\mu\text{-CO})_2(\text{CO})_5\{\text{P}(\text{OMe})_3\}_3]$ (4) including the atom numbering scheme. All hydrogen atoms have been omitted for clarity.

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

Co(1)–Co(2)	2.523(5)	Co(3)–Co(4)	2.500(5)
Co(1)–C(3)	1.88(3)	Co(2)–C(3)	1.87(3)
Co(4)–C(6)	1.96(2)	Co(3)–C(6)	1.91(2)
Co(1)–As(5)	2.358(4)	Co(2)–As(5)	2.366(4)
Co(2)–As(3)	2.392(4)	Co(3)–As(4)	2.298(5)
Co(3)–As(1)	2.470(4)	Co(3)–As(4)	2.367(4)
Co(4)–As(4)	2.284(1)	Co(4)–As(5)	2.385(4)
As(1)–As(2)	2.458(3)	Co(4)–C(6)	1.96(2)
As(3)–As(4)	2.457(3)	As(2)–As(3)	2.447(4)
Co(4)–P(1)	2.130(9)	Co(2)–P(2)	2.159(7)
Mean Co–C (terminal carbonyl)	1.72	Co(3)–P(3)	2.155(8)
C(6)–Co(3)–Co(4)	50.5(7)	C(6)–Co(4)–Co(3)	49.0(7)
C(3)–Co(1)–Co(2)	47.4(8)	C(3)–Co(2)–Co(1)	47.8(9)
As(1)–Co(1)–Co(2)	104.5(1)	As(1)–Co(1)–As(5)	88.4(1)
As(5)–Co(1)–Co(2)	57.9(1)	As(5)–Co(2)–Co(1)	57.6(1)
As(5)–Co(2)–As(3)	92.6(1)	As(3)–Co(2)–Co(1)	93.2(2)
As(4)–Co(3)–Co(4)	56.7(1)	As(4)–Co(4)–Co(3)	57.2(1)
As(4)–Co(3)–As(1)	88.1(1)	As(5)–Co(4)–Co(3)	99.0(2)
As(4)–Co(4)–As(5)	89.2(1)	As(1)–Co(3)–Co(4)	100.7(2)
Co(1)–As(1)–Co(3)	122.3(2)	Co(1)–As(1)–As(2)	109.8(1)
Co(3)–As(1)–As(2)	95.7(1)	Co(2)–As(3)–As(2)	123.1(2)
As(1)–As(2)–As(3)	84.6(1)	Co(3)–As(4)–As(3)	118.5(1)
Co(2)–As(3)–As(2)	123.1(1)	Co(4)–As(5)–Co(2)	127.1(1)
Co(3)–Co(4)–P(1)	148.3(2)	Co(2)–As(3)–As(4)	101.9(7)
Co(4)–Co(3)–P(3)	101.6(3)	As(2)–As(3)–As(4)	86.4(1)
		Co(1)–Co(2)–P(2)	110.3(3)

and 150.1 which can be attributed to the three inequivalent trimethylphosphite ligands. The $^{13}\text{C}\{-^1\text{H}\}$ -NMR spectrum displays four broad downfield resonances at δ 211.0, 206.0, 205.0 and 204.0 corresponding to the terminal carbonyl groups. The three $\text{P}(\text{OMe})_3$ groups are seen as distinct doublets at δ 53.0, 52.0 and 51.0 [$^2J(\text{PC})$ 8 Hz].

In conclusion, the fragility of the tetraarsine unit in **1** has been probed by examining its reactivity towards thermolysis, a two electron donor ligand and towards a metal carbonyl complex. While fragmentation of the tetraarsine chain in **1** occurs on thermolysis in benzene or in the presence of $[\text{Fe}_2(\text{CO})_9]$ at room temperature, the As_4Ph_4 unit is preserved on carbonyl substitution by $\text{P}(\text{OMe})_3$. Although the fragmentation of **1** does not allow an alternative route to the Co_{16} cluster of Rheingold [11], it does suggest possible fragments that may be involved in its formation during the reaction of $[\text{Co}_2(\text{CO})_8]$ with *cyclo*-(As_6Ph_6).

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 [24]. Infrared spectra were recorded in hexane solution in 0.5 mm NaCl cells, using a Perkin–Elmer 1710 Fourier-transform spectrometer. Fast atom bombardment (FAB) mass spectra were recorded on 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 on either a Bruker WM250 or AM400 spectrometer, ^{31}P -NMR chemical shifts are referenced to 85% H_3PO_4 . Preparative thin-layer chromatography (TLC) was carried out on commercial Merck plates with a 0.25 mm layer of silica, or on 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 synthesis of $[\text{Co}_4(\mu_3\text{-AsPh})(\mu_4\text{-}\eta^2\text{:}\eta^2\text{:}\eta^1\text{-As}_4\text{Ph}_4)(\mu\text{-CO})_2(\text{CO})_8]$ (**1**) [12] has been reported previously.

3.1. Thermolysis of $[\text{Co}_4(\mu_3\text{-AsPh})(\mu_4\text{-}\eta^2\text{:}\eta^2\text{:}\eta^1\text{-As}_4\text{Ph}_4)(\mu\text{-CO})_2(\text{CO})_8]$ (**1**)

A solution of $[\text{Co}_4(\mu_3\text{-AsPh})(\mu_4\text{-}\eta^2\text{:}\eta^2\text{:}\eta^1\text{-As}_4\text{Ph}_4)(\mu\text{-CO})_2(\text{CO})_8]$ (**1**) (0.077 g, 0.06 mmol) in benzene (25 cm^3) was thermolysed at 60°C for 48 h. The solvent was then removed under reduced pressure and the residue dissolved in the minimum volume of CH_2Cl_2 and applied to the base of TLC plates. Elution with hexane– CH_2Cl_2 (4:1) gave, in addition to a trace quantity of unreacted starting material, the red complex $[\text{Co}_4(\mu_3\text{-AsPh})_2(\mu_3\text{-}\eta^2\text{:}\eta^1\text{-As}_2\text{Ph}_2)(\mu\text{-CO})(\text{CO})_9]$ (**2**) (0.015 g, 22%).

3.2. Reaction of $[\text{Co}_4(\mu_3\text{-AsPh})(\mu_4\text{-}\eta^2\text{:}\eta^2\text{:}\eta^1\text{-As}_4\text{Ph}_4)(\mu\text{-CO})_2(\text{CO})_8]$ (**1**) with $[\text{Fe}_2(\text{CO})_9]$

To a solution of $[\text{Co}_4(\mu_3\text{-AsPh})(\mu_4\text{-}\eta^2\text{:}\eta^2\text{:}\eta^1\text{-As}_4\text{Ph}_4)(\mu\text{-CO})_2(\text{CO})_8]$ (**1**) (0.046 g, 0.036 mmol) in benzene (25 cm^3) was added $[\text{Fe}_2(\text{CO})_9]$ (0.050 g, 0.137 mmol) and the resulting solution stirred at ambient temperature for 48 h. After removed of solvent under reduced pressure the residue was dissolved in the minimum volume of CH_2Cl_2 and applied to the base of preparative TLC plates. Elution with hexane– CH_2Cl_2 (4:1) gave, in addition to traces of uncharacterised unstable products, the dark brown crystalline compound $[\text{Co}_4(\mu_3\text{-AsPh})_2\{(\mu_3\text{-}\eta^2\text{:}\eta^1\text{-As}_2\text{Ph}_2)\text{Fe}(\text{CO})_4\}(\text{CO})_{10}]$ (**3**) (0.025 g, 53%).

Table 5
Crystallographic and data processing parameters for complexes **2**, **3** and **4**^a

Complex	2	3	4
Formula	C ₃₄ H ₂₀ As ₄ Co ₄ O ₁₀	C ₃₈ H ₂₀ As ₄ Co ₄ FeO ₁₄ .CH ₂ Cl ₂	C ₄₆ H ₅₂ As ₅ Co ₄ O ₁₆ P ₃
<i>M</i>	1123.90	1376.70	1564.11
Crystal size (mm)	0.30 × 0.25 × 0.20	0.25 × 0.20 × 0.10	0.30 × 0.18 × 0.10
Temperature (K)	293(2)	293(2)	180(2)
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>Pca</i> 2 ₁
Lattice parameters			
Unit cell dimensions			
<i>a</i> (Å)	12.030(4)	11.592(10)	20.480(3)
<i>b</i> (Å)	17.065(4)	20.710(7)	18.813(4)
<i>c</i> (Å)	10.018(3)	20.276(7)	14.830(5)
α (°)	99.44(2)	90	90
β (°)	97.49(2)	98.48(5)	90
γ (°)	78.44(2)	90	90
<i>U</i> (Å ³)	1977.5(10)	4815(5)	5714(2)
<i>Z</i>	2	4	4
<i>D</i> _{calc} (Mg m ⁻³)	1.888	1.897	1.818
<i>F</i> (000)	1088	2664	3096
Reflections collected	7566	6651	7006
μ (Mo–K α) (mm ⁻¹)	5.012	4.543	4.162
Independent reflections (<i>R</i> _{int})	5274 (0.1044)	6287 (0.1183)	5796 (0.0730)
Parameters	469	579	426
Final <i>R</i> indices			
<i>I</i> > 2 σ (<i>I</i>)	<i>R</i> ₁ = 0.0273, <i>wR</i> ₂ = 0.0599	<i>R</i> ₁ = 0.0534, <i>wR</i> ₂ = 0.1280	<i>R</i> ₁ = 0.0696, <i>wR</i> ₂ = 0.1394
All data	<i>R</i> ₁ = 0.0470, <i>wR</i> ₂ = 0.0656	<i>R</i> ₁ = 0.2210, <i>wR</i> ₂ = 0.2271	<i>R</i> ₁ = 0.1630, <i>wR</i> ₂ = 0.1761
Goodness-of-fit on <i>F</i> ² (all data)	1.077	0.916	1.036

^a Data in common: graphite-monochromated Mo–K α radiation, $\lambda = 0.71073$ Å; $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$, $w^{-1} = [\sigma^2(F_o^2) + (aP)^2]$, $P = [\max(F_o^2, 0) + 2(F_c^2)]/3$, 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.

3.3. Reaction of [Co₄(μ₃-AsPh)(μ₄-η²:η²:η¹-As₄Ph₄)-(μ-CO)₂(CO)₈] (**1**) with P(OMe)₃

To a solution of [Co₄(μ₃-AsPh)(μ₄-η²:η²:η¹-As₄Ph₄)-(μ-CO)₂(CO)₈] (**1**) (0.100 g, 0.078 mmol) in benzene (25 cm³) was added P(OMe)₃ (0.17 cm³, 0.700 mmol) and the resulting solution stirred at ambient temperature for 48 h. After removed of solvent under reduced pressure the residue was dissolved in the minimum volume of CH₂Cl₂ and separated by preparative TLC. Elution with hexane–CH₂Cl₂ (1:1) gave, in addition to a trace quantity of the disubstituted complex, the dark brown crystalline compound [Co₄(μ₃-AsPh)(μ₄-η²:η²:η¹-As₄Ph₄)-(μ-CO)₂(CO)₅{P(OMe)₃}₃] (**4**) (0.030 g, 25%).

3.4. Crystallography

Diffraction data were collected by the ω -2 θ scan method on a Rigaku AFC5R diffractometer. In each case cell parameters were obtained by least-squares refinement on diffractometer angles from 25 centred reflections (15 < θ < 20°) and semiempirical absorption corrections based on φ -scan data were applied [25,26].

The structures were solved by direct methods (SHELXS-86 [27]) and subsequent Fourier-difference syntheses. For **2** and **3**, all ordered non-hydrogen atoms were assigned anisotropic T factors and refined by full-matrix least-squares on *F*² (SHELXL-93 [28]). For **4**, the crystal was poorly diffracting and the parameter/data ratio is poor. In this case anisotropic T factors were refined by the Co, As and P atoms only; all other atoms were assigned isotropic temperature factors. 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 5.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 153783 for compound **2**, CCDC no. 153784 for compound **3** and CCDC no. 153785 for compound **4**. 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 <http://www.ccdc.cam.ac.uk>).

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