Phosphorus–oxygen bond formation on organo-capped tricobalt centres *via* phosphorus–hydrogen or phosphorus–phosphorus bond scission

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Chromatographic work-up of the initial products of the reaction of the secondary phosphine PPh_2H with $[Co_3(\mu_3\text{-}CR)(CO)_9]$ (R = Me **1a** or CO_2Me **1b**) at 308 K in heptane gave the mono- and bis-substituted complexes $[Co_3(\mu_3\text{-}CR)(CO)_8(PPh_2H)]$ (R = Me **2a** or CO_2Me **2b**) and $[Co_3(\mu_3\text{-}CR)(CO)_7(PPh_2H)_2]$ (R = Me **3a** or CO_2Me **3b**) and, in addition, when R = Me, the complex $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}Ph_2POPPh_2)(CO)_6(PPh_2H)]$ **4a**, in which phosphorus–oxygen bond formation has occurred. Thermolysis of complex **2a** at 343 K in heptane gave **1a** and $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_7]$ **5a**, while thermolysis of **3a** under the same conditions afforded **4a**, a trace of **5a** and $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6(PPh_2H)]$ **6a**. Similar reactions with the $\mu_3\text{-}CCO_2Me$ capped species **2b** and **3b** resulted in unstable non-isolable species. Treatment of complexes **3a**, **3b** with CO at 343 K causes the replacement of first one and then the other PPh_2H ligand by CO to give **2a**, **2b** and then **1a**, **1b** respectively, while reformation of a phosphorus–hydrogen bond to give initially **2a** or **3a** can be achieved on carbonylation of either complex **5a** or **6a**. Substitution of a PPh_2H group in **4a** can be achieved by purging with CO to give $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}Ph_2POPPh_2)(CO)_7]$ **7a**. Complex **7a** can also be prepared directly by the reaction of **1a** with the diphosphane P_2Ph_4 as can the analogue $[Co_3(\mu_3\text{-}CCO_2Me)(\mu\text{-}Ph_2POPPh_2)(CO)_7]$ **7b** on reaction of **1b**. The intermediates $[Co_3(\mu_3\text{-}CR)(CO)_8(P_2Ph_4)]$ (R = Me **8a** or CO_2Me **8b**) and $[Co_3(\mu_3\text{-}CR)(\mu\text{-}P_2Ph_4)(CO)_7]$ (R = Me **9a** or CO_2Me **9b**) isolated in the reactions can be converted under the same reaction conditions into **7a** and **7b** respectively. Complex $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}Ph_2POPPh_2)(CO)_6(PPhMe_2)]$ **4a′**, the tertiary phosphine analogue of **4a**, has been prepared from the reaction of **7a** with $PPhMe_2$. The structures of complexes **4a′** and **5a** have been determined by single crystal X-ray diffraction studies.

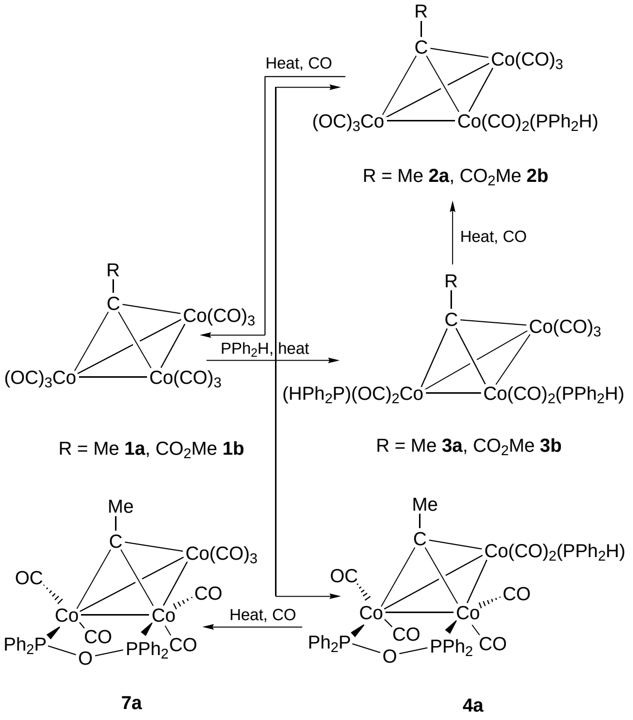
The reaction of secondary phosphines (PR_2H) with bi- and tri-nuclear transition-metal carbonyl complexes has often been employed as a method of introducing bridging phosphido and hydrido ligands into the metal framework.[1] In the same way, diphosphanes (P_2R_4) have been used successfully to synthesize bis(phosphido)-bridged transition-metal complexes.[2] Incorporation of an organic fragment into the framework of the polynuclear assembly and treatment with PR_2H or P_2Ph_4 can lead to products in which a hydride or phosphide has effectively migrated to the organic fragment.[3,4]

In this regard the reactions of PPh_2H or P_2Ph_4 with the alkyne-bridged dicobalt family of complexes $[Co_2(\mu\text{-}CRCR)(CO)_6]$ (R = aryl, alkyl or CO_2Me) have been examined and found to give a number of unusual products, the formation of which involves the making and/or breaking of carbon–hydrogen, phosphorus–carbon and/or carbon–carbon bonds. The precise nature of the products depends on the substituents on the organic fragment.[5,6] It was envisaged that a similar approach could be extended to the isolobal trinuclear complexes, $[Co_3(\mu_3\text{-}CR)(CO)_9]$ **1** (R = Me or CO_2Me),[7] and might afford products in which migration to the capping organic alkylidyne CR group had taken place. In the event, however, the new products obtained from the generation of phosphide and/or hydride fragments within the cluster co-ordination sphere result only from transformations occurring at the Co–Co edges, which include most notably the unexpected formation of phosphorus–oxygen bonds.

Herein we describe the results of these transformations and report the single-crystal structures of $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}Ph_2POPPh_2)(CO)_6(PPhMe_2)]$ and $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_7]$.

Results and Discussion

(*a*) Reaction of $[Co_3(\mu_3\text{-}CR)(CO)_9]$ (R = Me 1a or CO_2Me 1b) with PPh_2H



Scheme 1 Products from the reactions of $[Co_3(\mu\text{-}CR)(CO)_9]$ (R = Me **1a** or CO_2Me **1b**) with PPh_2H

The complexes $[Co_3(\mu_3\text{-}CR)(CO)_9]$ (R = Me **1a** or CO_2Me **1b**) were heated to 313 K for 20 h in heptane in the presence of PPh_2H to give, after work-up on silica, $[Co_3(\mu_3\text{-}CR)(CO)_8(PPh_2H)]$ (R = Me **2a** 22% or CO_2Me **2b** 56%), $[Co_3(\mu_3\text{-}CR)(CO)_7(PPh_2H)_2]$ (R = Me **3a** 30% or CO_2Me **3b** 9.5%) and in the case of R = Me also $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}Ph_2POPPh_2)(CO)_6(PPh_2H)]$ **4a** (14%) (Scheme 1). All the complexes **2a**, **2b**, **3a**, **3b** and **4a** have been characterised by mass spectrometry

Table 1 Infrared, ^1H and ^{31}P NMR data for the new complexes

Compound	$\tilde{\nu}(CO)^a/cm^{-1}$	^1H NMR $(\delta)^b$	^{31}P NMR $(\delta)^c$
2a	2080m, 2034vs, 2024vs, 2013s, 1987w	7.3–7.7 (m, 10 H, Ph), 6.25 [d, ^1J(PH) 352, 1 H, $PPh_2\mathit{H}$], 3.43 (s, 3 H, Me)	−114.4 (s, PPh_2H)
2b	2065s, 2025vs, 2018vs, 2008s, 2000s, 1981w, 1671w	7.6–7.2 (m, 10 H, Ph), 6.25 [d, ^1J(PH) 362, 1 H, $PPh_2\mathit{H}$], 3.53 (s, 2 H, Me)	−117.7 (s, PPh_2H)
3a	2062 (sh), 2052s, 2009vs, 1854w, 1835w, 1730m	7.7–7.2 (m, 20 H, Ph), 6.10 [d, ^1J(HP) 350.0, 2 H, $PPh_2\mathit{H}$], 3.08 [t, ^4J(PH) 32.6, 3 H, Me]	−114.2 (s, PPh_2H)
3b	2062m, 2026s, 2105s, 2000s, 1976 (sh), 1715w	7.6–7.2 (m, 20 H, Ph), 6.15 [d, ^1J(PH) 358.0, 2 H, $PPh_2\mathit{H}$], 3.33 (s, 3 H, Me)	−115.7 (s, PPh_2H)
4a	2033s, 1993vs, 1979s, 1968 (sh), 1949w	7.8–7.2 (m, 30 H, Ph), 6.27 [dt, ^1J(PH) 346.1, ^4J(PH) 2.8, 1 H, $PPh_2\mathit{H}$], 3.25 [d, ^4J(PH) 2.7, 3 H, Me]^d	7.5 (s, br, 2P, μ-Ph_2PO), −110.8 (s, br, 1P, PPh_2H)
4a′	2028s, 1983vs, 1972 (sh), 1960 (sh), 1943w	7.8–7.2 (m, 25 H, Ph), 3.27 [d, ^4J(PH) 2.3, 3 H, CMe]	7.7 (s, br, 2P, μ-Ph_2PO), −121.0 (s, br, 1P, $PPhMe_2$)
5a	2102w, 2051vs, 2038s, 2017w	7.9–6.2 (m, 10 H, Ph), 2.29 (s, 3 H, Me), −16.09 [d, ^2J(PH) 23.1, 1 H, μ-H]	108.5 (s, μ-PPh_2)
6a	2044w, 2019s, 1993vs, 1983m, 1874w	7.8–7.0 (m, 2 H, Ph), 6.42 [dd, ^1J(PH) 348, ^3J(P′H) 3.2, 1 H, $PPh_2\mathit{H}$], 2.46 [t, ^4J(PH) 7.8, 3 H, Me], −15.64 [t, ^2J(PH) 28.0, 1 H, μ-H]	84.1 (s, br, μ-PPh_2), −94.6 (s, br, PPh_2H)
7a	2064s, 2012vs, 1997m, 1976w, 1964w	7.8–7.2 (m, 20 H, Ph), 3.40 [t, ^4J(PH) 0.9, 3 H, Me]^d	10.8 (s, μ-PPh_2O)
7b	2087m, 2072s, 2048s, 2022vs, 2007s, 1987m, 1674m	7.7–7.2 (m, 20 H, Ph), 3.12 (s, 3 H, Me)^d	11.0 (s, μ-PPh_2O)
8a	2077m, 2033vs, 2021vs, 2012s, 1988m, 1972m, 1876w, 1859w	7.7–7.4 (m, 20 H, Ph), 3.50 [d, ^4J(PH) 1.8, 3 H, Me]^d	−102.4 [d, br, ^1J(PP) 300, $Co\mathit{P}Ph_2PPh_2$], −138.3 (d, $CoPPh_2\mathit{P}Ph_2$)
8b	2089m, 2049s, 2032s, 2027s, 1981w, 1683w	7.6–7.2 (m, 20 H, Ph), 3.73 (s, 3 H, Me)^d	−98.1 [d, br, ^1J(PP) 305, $Co\mathit{P}Ph_2PPh_2$], −136.1 (d, $CoPPh_2\mathit{P}Ph_2$)
9a	2061s, 2008vs, 1995s, 1978m, 1962m	7.7–7.3 (m, 20 H, Ph), 3.49 [t, ^4J(PH) 0.8, 3 H, Me]^d	−161.2 (s, μ-PPh_2PPh_2)
9b	2087w, 2071m, 2047w, 2026s, 2009m, 1995w, 1984w, 1721w	7.5–7.0 (m, 20 H, Ph), 3.64 (s, 3 H, Me)^d	−152.6 (s, μ-PPh_2PPh_2)

[a] Recorded in *n*-hexane solution. [b] Chemical shifts in ppm relative to $SiMe_4$ (δ 0.0), coupling constants *J* in Hz in $CDCl_3$ at 293 K. [c] Chemical shifts in ppm relative to external $P(OMe)_3$ (δ 0.0) (upfield shifts negative). Add 140.2 to tabulated values in order to reference relative to external 85% H_3PO_4. Spectra were $\{^1H\}$-gated decoupled and measured in $CDCl_3$ at 293 K. [d] Recorded in CD_2Cl_2 solution.

and by IR, ^1H, ^{31}P and ^{13}C NMR spectroscopy (see Table 1 and Experimental section).

The IR spectra of complexes **2** and **3** in the ν_{CO} region are characteristic of mono- and bis-substituted alkylidyne-capped complexes[8] and the fast atom bombardment (FAB) mass spectra are consistent with the proposed molecular formulae. In the ^1H NMR spectra doublet resonances for the phosphine proton are seen in the range δ 6.10–6.25 with characteristically large coupling constants [^1J(PH) between 350 and 362 Hz].

On the basis of spectroscopic data the structure of $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}Ph_2POPPh_2)(CO)_6(PPh_2H)]$ **4a** is less certain. In the ^{31}P-$\{^1H\}$ NMR spectrum two signals in a 2:1 ratio are observed. The less intense signal at δ −110.8 [^{31}P chemical shifts relative to external $P(OMe)_3$ (δ 0.0)] is attributed to the terminal PPh_2H phosphorus atom while the more intense upfield signal at δ 7.5 could, based on previous reports, be attributed to PPh_2 groups bridging bonded cobalt–cobalt vectors[5a,6,9] and the NMR data are consistent with a complex of composition $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}PPh_2)_2(CO)_5(PPh_2H)]$. The FAB mass spectrum of **4a**, however, shows a molecular ion peak 44 mass units greater than required for this proposed formula, corresponding to the presence of an additional carbonyl group and an oxygen atom. Attempts at growing a single crystal of **4a** proved unsuccessful but the tertiary phosphine analogue $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}Ph_2POPPh_2)(CO)_6(PPhMe_2)]$ **4a′** was successfully prepared by the reaction of $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}Ph_2POPPh_2)(CO)_7]$ **7a** (see later) with $PPhMe_2$, and a suitable single crystal for an X-ray diffraction study grown. The molecular structure of **4a′** is shown in Fig. 1; Table 2 lists selected bond lengths and angles.

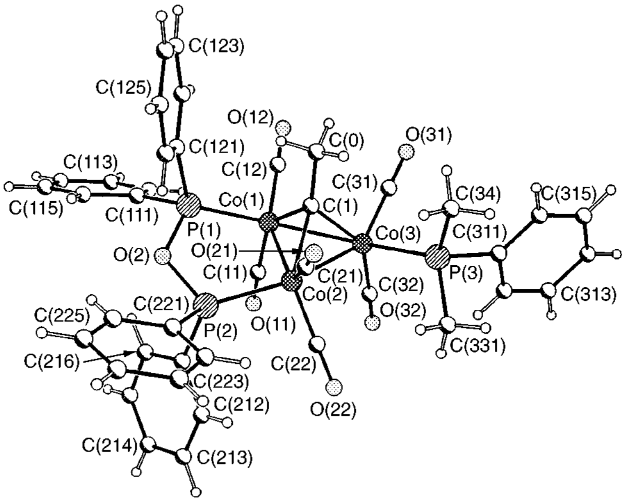


Fig. 1 Molecular structure of $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}Ph_2POPPh_2)(CO)_6(PPhMe_2)]$ **4a′** including the atom numbering scheme

The structure of compound **4a′** consists of a Co_3 triangle capped by a μ_3-ethylidyne ligand, edge-bridged by a Ph_2POPPh_2 ligand and bound terminally by six carbonyl groups and one $PPhMe_2$ molecule. The Ph_2POPPh_2 ligand co-ordinates equatorially,[10] to the Co(1)–Co(2) edge so as to form a five-membered Co–Co–P–O–P metallacyclic ring which adopts a twist conformation. The P–O–P angle of 116.9(3)° lies at the bottom end of the range for μ-POP ligands, presumably a consequence of the shorter bridged metal–metal distance [Co(1)–Co(2) 2.4801(1) Å] in **4a′** as compared to those of previously reported species.[11,12] Each metal centre is in addition co-ordinated by two terminally bound carbonyl groups while the unbridged cobalt centre, Co(3), is also co-ordinated by the monodentate phosphine ligand, $PPhMe_2$, which occupies an equatorial site.

Tetraphenyldiphosphoxane, $Ph_2P\text{–}O\text{–}PPh_2$, has previously been isolated in chelating and bridging modes in mono- and binuclear transition-metal complexes[11] but the free compound exists as the tautomer $Ph_2PP(O)Ph_2$. Previous examples of complexes containing Ph_2POPPh_2 have been synthesized, notably

Table 2 Selected bond lengths (Å) and angles (°) for complex [$Co_3(\mu_3$-CMe)(μ-$Ph_2POPPh_2)(CO)_6(PPhMe_2)$] **4a′**

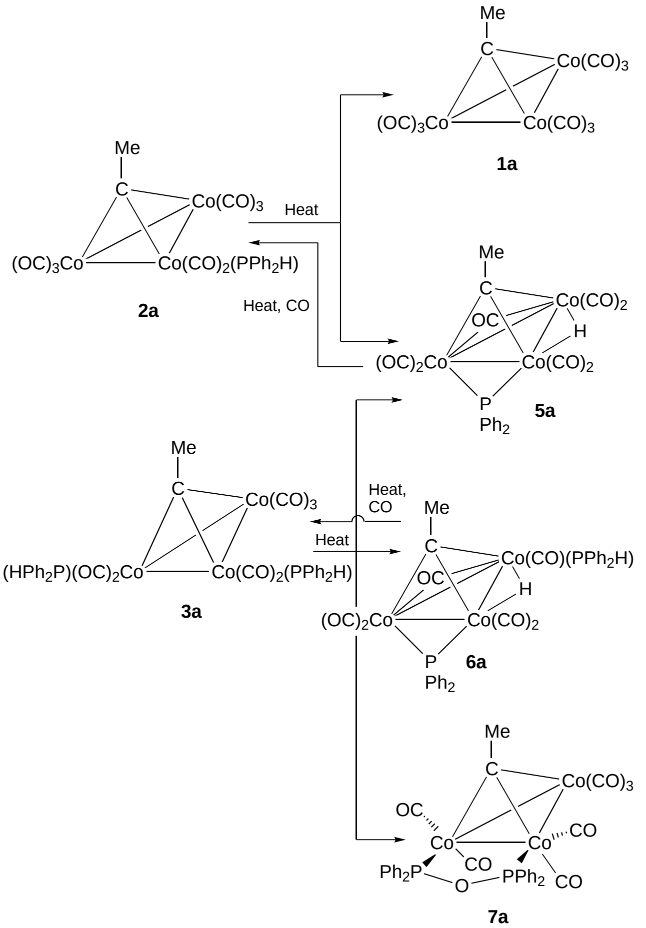
Co(1)–C(1)	1.896(7)	Co(1)–P(1)	2.159(2)
Co(1)–Co(3)	2.4773(13)	Co(1)–Co(2)	2.4801(13)
Co(2)–C(1)	1.926(7)	Co(2)–P(2)	2.151(2)
Co(2)–Co(3)	2.4805(14)	Co(3)–C(1)	1.910(7)
Co(3)–P(3)	2.210(2)	P(1)–O(2)	1.645(5)
P(2)–O(2)	1.639(5)	P(3)–C(34)	1.798(9)
C(0)–C(1)	1.506(10)		
C–O (carbonyl) 1.133(10)–1.176(11)			
C(12)–Co(1)–C(11)	105.5(4)	C(12)–Co(1)–C(1)	100.6(4)
C(11)–Co(1)–C(1)	141.5(3)	C(12)–Co(1)–P(1)	98.2(3)
C(11)–Co(1)–P(1)	103.2(2)	C(1)–Co(1)–P(1)	100.6(2)
C(12)–Co(1)–Co(3)	99.5(3)	C(11)–Co(1)–Co(3)	97.8(2)
C(1)–Co(1)–Co(3)	49.6(2)	P(1)–Co(1)–Co(3)	147.74(7)
C(12)–Co(1)–Co(2)	150.4(3)	C(11)–Co(1)–Co(2)	98.9(3)
C(1)–Co(1)–Co(2)	50.1(2)	P(1)–Co(1)–Co(2)	92.37(6)
Co(3)–Co(1)–Co(2)	60.05(4)	C(21)–Co(2)–C(22)	113.4(5)
C(21)–Co(2)–C(1)	87.8(4)	C(22)–Co(2)–C(1)	132.9(4)
C(21)–Co(2)–P(2)	100.3(3)	C(22)–Co(2)–P(2)	97.1(3)
C(1)–Co(2)–P(2)	120.8(2)	C(21)–Co(2)–Co(1)	132.3(4)
C(22)–Co(2)–Co(1)	111.6(3)	C(1)–Co(2)–Co(1)	49.0(2)
P(2)–Co(2)–Co(1)	89.06(6)	C(21)–Co(2)–Co(3)	110.6(3)
C(22)–Co(2)–Co(3)	83.5(3)	C(1)–Co(2)–Co(3)	49.4(2)
P(2)–Co(2)–Co(3)	146.09(7)	Co(1)–Co(2)–Co(3)	59.92(4)
C(31)–Co(3)–C(1)	96.9(4)	C(32)–Co(3)–C(1)	143.9(3)
C(31)–Co(3)–P(3)	92.6(3)	C(32)–Co(3)–P(3)	100.9(3)
C(1)–Co(3)–P(3)	107.3(2)	C(31)–Co(3)–Co(1)	97.5(3)
C(32)–Co(3)–Co(1)	98.5(3)	C(1)–Co(3)–Co(1)	49.1(2)
P(3)–Co(3)–Co(1)	155.26(8)	C(31)–Co(3)–Co(2)	146.7(3)
C(32)–Co(3)–Co(2)	103.7(3)	C(1)–Co(3)–Co(2)	50.0(2)
P(3)–Co(3)–Co(2)	100.29(7)	Co(1)–Co(3)–Co(2)	60.03(4)
O(2)–P(2)–Co(2)	114.3(2)	P(2)–O(2)–P(1)	116.9(3)
C(0)–C(1)–Co(1)	130.3(6)	C(0)–C(1)–Co(3)	129.9(6)
Co(1)–C(1)–Co(3)	81.2(3)	C(0)–C(1)–Co(2)	134.2(6)
Co(1)–C(1)–Co(2)	80.9(3)	Co(3)–C(1)–Co(2)	80.6(3)
		O(2)–P(1)–Co(1)	111.9(2)

under forcing conditions, from phosphorus-co-ordinated Group 6 carbonyl complexes, $M(CO)_5L$ [L = $PPh_2P(O)Ph_2$, PPh_2Cl or PPh_2H; M = Cr, Mo or W].

The carbonylation reactions of compounds **2**, **3** and **4a** have also been investigated. Bubbling carbon monoxide gas through a solution of **3a**, **3b** at 343 K causes the replacement of first one and then the other PPh_2H ligand by CO to reform **2a**, **2b** and then [$Co_3(\mu_3$-CR)$(CO)_9$] (R = Me **1a** or CO_2Me **1b**). In the carbonylation reaction of **4a**, however, only the terminal PPh_2H ligand can be displaced to give **7a** (Scheme 1).

(*b*) Thermolysis of [$Co_3(\mu_3$-CR)$(CO)_8(PPh_2H)$] (R = Me 2a or CO_2Me 2b) and [$Co_3(\mu_3$-CMe)$(CO)_7(PPh_2H)_2$] (R = Me 3a or CO_2Me 3b)

Complexes **2a**, **2b** and **3a**, **3b** were heated at 343 K in heptane and worked-up on silica thin-layer chromatography (TLC) plates. In the reaction of **2a** the complexes, [$Co_3(\mu_3$-CMe)$(CO)_9$] **1a** (yield 32%) and [$Co_3(\mu_3$-CMe)(μ-H)(μ-$PPh_2)(CO)_7$] **5a** (yield 29%) were isolated. For **3a**, [$Co_3(\mu_3$-CMe)(μ-H)(μ-$PPh_2)(CO)_7$] **5a** (yield 2%), [$Co_3(\mu_3$-CMe)(μ-H)(μ-$PPh_2)(CO)_6(PPh_2H)$] **6a** (yield 13%), [$Co_3(\mu$-$PPh_2)_3(CO)_6$]^{9c} (yield 22%) and [$Co_3(\mu_3$-CMe)(μ-$Ph_2POPPh_2)(CO)_7$] **7a** (yield 2%) were obtained (Scheme 2). The corresponding reactions of the CCO_2Me capped complexes **2b** and **3b**, however, resulted in unstable complexes which could not be characterised. All the new complexes **5a**, **6a** and **7a** have been characterised by mass spectrometry, IR, ^1H, ^{31}P and ^{13}C NMR spectroscopy (see Table 1 and Experimental section). The structure of complex **5a** has in addition been determined by an X-ray diffraction study.



Scheme 2 Principal products from the thermolysis reactions of compounds **2a** and **3a**

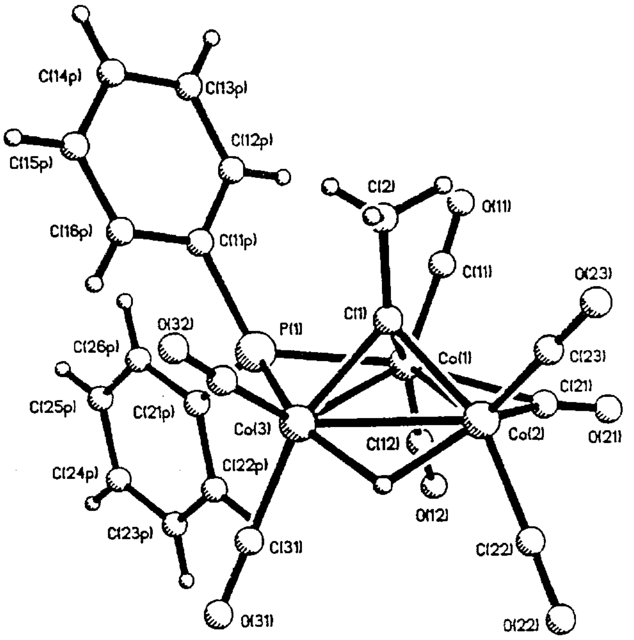


Fig. 2 Molecular structure of [$Co_3(\mu_3$-CMe)(μ-H)(μ-$PPh_2)(CO)_7$] **5a** including the atom numbering scheme

Suitable crystals of [$Co_3(\mu_3$-CMe)(μ-H)(μ-$PPh_2)(CO)_7$] **5a** were grown by prolonged cooling at 253 K of a concentrated solution in pentane. The structure of complex **5a** is shown in Fig. 2; Table 3 lists selected bond lengths and angles. As in complex **4a′** a triangle of cobalt atoms in **5a** is capped by a face-bridging ethylidyne group. The three Co–μ_3-C bond lengths are within 0.016(3) Å of each other, the average distance being 1.915 Å. The three Co–Co bonds are all bridged by different equatorially co-ordinated ligands: carbonyl, hydrido and phosphido. The shortest edge [Co(1)–Co(3) 2.487(1) Å] is bridged by the phosphido group in a slightly asymmetric fashion [Co(1)–P(1) 2.293(1), Co(3)–P(1) 2.167(1) Å] which contrasts with the more symmetric PPh_2 ligand in [$Co_2W(\mu_3$-CMe)(μ-H)(μ-PPh_2)-

Table 3 Selected bond lengths (Å) and angles (°) for complex $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_7]$ **5a**

Co(1)–Co(2)	2.496(1)	Co(1)–Co(3)	2.487(1)
Co(1)–P(1)	2.193(1)	Co(1)–C(1)	1.926(3)
Co(2)–Co(3)	2.528(1)	Co(2)–H(3)	1.661(28)
Co(2)–C(1)	1.910(3)	Co(3)–H(23)	1.678(31)
Co(3)–P(1)	2.167(1)	Co(3)–C(1)	1.910(3)
C(1)–C(2)	1.498(4)		
C–O (carbonyl)	1.120(4)–1.152(4)		
Co(2)–Co(1)–Co(3)	61.0(1)	Co(2)–Co(1)–P(1)	114.9(1)
Co(3)–Co(1)–P(1)	54.7(1)	Co(2)–Co(1)–C(1)	49.1(1)
Co(3)–Co(1)–C(1)	49.3(1)	P(1)–Co(1)–C(1)	80.6(1)
Co(1)–Co(2)–Co(3)	59.4(1)	Co(1)–Co(2)–H(23)	96.6(11)
Co(3)–Co(2)–H(23)	41.0(11)	Co(1)–Co(2)–C(1)	49.7(1)
Co(3)–Co(2)–C(1)	48.6(1)	H(23)–Co(2)–C(1)	84.9(10)
Co(1)–Co(3)–Co(2)	59.7(1)	Co(1)–Co(3)–H(23)	96.5(10)
Co(2)–Co(3)–H(23)	40.6(10)	Co(1)–Co(3)–P(1)	55.7(1)
Co(2)–Co(3)–P(1)	114.6(1)	H(23)–Co(3)–P(1)	151.4(10)
Co(1)–Co(3)–C(1)	49.8(1)	Co(2)–Co(3)–C(1)	48.6(1)
H(23)–Co(3)–C(1)	84.5(10)	P(1)–Co(3)–C(1)	81.6(1)
Co(2)–H(23)–Co(3)	98.4(16)	Co(1)–P(1)–Co(3)	69.6(1)
Co(1)–C(1)–Co(2)	81.2(1)	Co(1)–C(1)–Co(3)	80.9(1)
Co(2)–C(1)–Co(3)	82.9(1)	Co(1)–C(1)–C(2)	130.4(2)
Co(2)–C(1)–C(2)	130.3(2)	Co(3)–C(1)–C(2)	132.2(2)

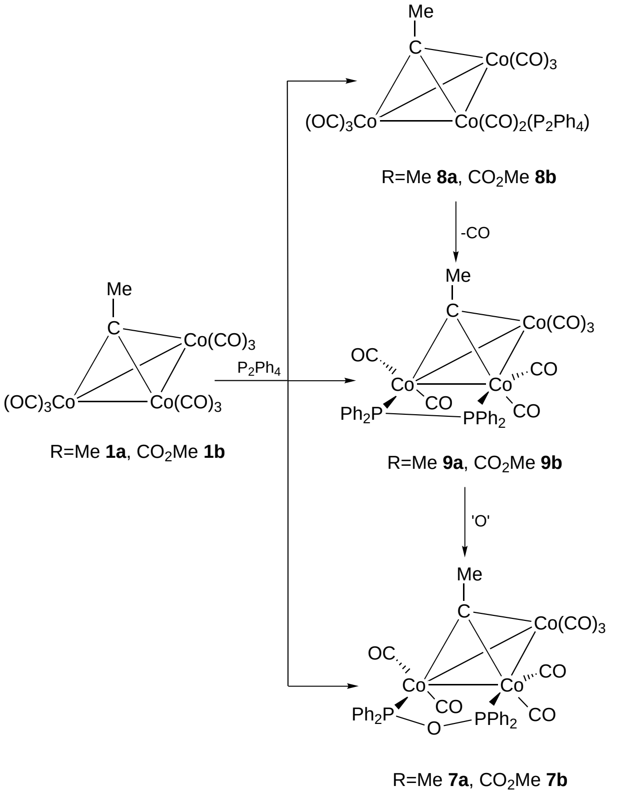
$(CO)_6(\eta^5\text{-}C_5H_5)]$ [Co–P 2.176(2) and 2.172(2) Å].[1e] The longest Co–Co edge [Co(2)–Co(3) 2.528(1) Å] is bridged by a hydrido ligand [Co(2)–H(23) 1.66(3) and Co(3)–H(23) 1.68(3) Å] while the third edge of the metal triangle [Co(1)–Co(2) 2.496(1) Å] is bridged by a carbonyl ligand which is significantly closer to Co(2) [1.815(3) Å] than to Co(1) [2.149(3) Å].

While the Co–Co distances in compound **5a** vary, all three Co–Co edges are longer than those in $[Co_3(\mu_3\text{-}CMe)(CO)_9]$,[13] $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}dppm)(CO)_7]$ (dppm = $Ph_2PCH_2PPh_2$),[14] $[Co_2W(\mu_3\text{-}CMe)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6(\eta^5\text{-}C_5H_5)]$[1e] and **4a′**. This is presumably due to the steric constraints imposed by three bridging ligands. The co-ordination spheres round the metal are completed by six terminal carbonyl groups in equivalent positions to those in **4a′**.

The spectroscopic data for complex **5a** confirm that the solid-state structure is maintained in solution. On the basis of a comparison of these data with those for **6a** a related structure is proposed for complex **6a** in which a terminal carbonyl group in **5a** has been substituted by a PPh_2H ligand. The ^1H NMR spectrum of **5a** consists of phenyl resonances, a signal due to the ethylidyne protons at δ 2.29 and a doublet at δ −16.09 assigned to the hydrido ligand split by the phosphido phosphorus atom [^2J(PH) 23 Hz]. In the ^1H NMR spectrum of **6a**, in addition to signals for the phenyl and capping ethylidyne resonances, a doublet of doublets centred at δ 6.42 is assigned to the proton on the terminal secondary phosphine. This signal is coupled to the adjacent phosphorus atom [^1J(PH) 348 Hz] and to the phosphido-phosphorus atom [^3J(PH) 3.2 Hz] while the bridging hydride appears at δ −15.64 as a doublet of doublets [^2J(PH) 28 and ^2J(P′H) 28 Hz].

In the $^{31}P\text{-}\{^1H\}$ NMR spectra of compounds **5a** and **6a**, downfield resonances are observed in each case (δ 108.5 **5a**, 84.1 **6a**), both being consistent with chemical shifts for phosphido-phosphorus atoms bridging a single cobalt–cobalt bond.[5a,6,9] For **6a** a further signal is seen at δ −94.6 and this is assigned to the terminal phosphine group.

The assignment of complex **7a** was made by a comparison of the spectroscopic data with those for the monophosphine-substituted derivatives **4a** and the structurally characterised **4a′**. The FAB mass spectrum displays a molecular ion peak and fragmentation peaks corresponding to the loss of seven carbonyl ligands. In the $^{31}P\text{-}\{^1H\}$ NMR spectrum the signal for the bridging $Ph_2P\text{–}O\text{–}PPh_2$ phosphorus atoms is seen as a singlet at δ 10.8 which compares with the corresponding chemical shifts of δ 7.5 and 7.7 for **4a** and **4a′** respectively.



Scheme 3 Products from the thermally or sodium–benzophenone induced reactions of $[Co_3(\mu_3\text{-}CR)(CO)_9]$ (R = Me **1a** or CO_2Me **1b**) with P_2Ph_4

Interestingly, the reactions of compound **2a** to give **5a** or of **3a** to give **6a** are reversible. When carbon monoxide gas is bubbled through the solutions of **5a** or **6a** at 343 K phosphorus–hydrogen bond formation occurs with uptake of an additional CO ligand (Scheme 2). Further uptake of CO on continued carbonylation causes displacement of the terminal PPh_2H ligands in **3a** or **2a** to give ultimately **1a** (as in Scheme 1).

No $\mu_3\text{-}CCO_2Me$ capped analogues of compounds **5a** and **6a** could be isolated. Complexes **2b** and **3b** certainly react on thermolysis, which would be expected since oxidative addition of a phosphorus–hydrogen bond to cobalt ought to be more favourable with an electron-accepting capping group, but the complexes produced are too unstable to characterise. These may well be analogues of **5a** and **6a** which indeed themselves decompose fairly readily. A possible explanation of the decreased stability of the $\mu_3\text{-}CCO_2Me$ analogues is that as the cap attracts more electron density the hydrido ligand becomes increasingly capable of leaving the cluster as a proton, initiating decomposition.

It is noteworthy that $[Co_3(\mu\text{-}PPh_2)_3(CO)_6]$[9c] is a by-product of most of the reactions and a μ_3-CR capped complex cannot be generated from it. The reactions leading to this complex are irreversible.

(*c*) Reaction of $[Co_3(\mu_3\text{-}CR)(CO)_9]$ (R = Me 1a or CO_2Me 1b) with P_2Ph_4

The complexes $[Co_3(\mu_3\text{-}CR)(CO)_9]$ (R = Me **1a** or CO_2Me **1b**) have been treated with P_2Ph_4 under two equally successful sets of conditions. First, thermolysis at 310 K for 24 h in heptane and secondly in the presence of a few drops of sodium–benzophenone[15] at room temperature for 2 h in tetrahydrofuran (thf). The yields of the products $[Co_3(\mu_3\text{-}CR)(CO)_8(P_2Ph_4)]$ (R = Me **8a** 35% or CO_2Me **8b** 2%), $[Co_3(\mu_3\text{-}CR)(\mu\text{-}Ph_2POPPh_2)(CO)_7]$ (R = Me **7a** 7% or CO_2Me **7b** 4%) and $[Co_3(\mu_3\text{-}CR)(\mu\text{-}P_2Ph_4)(CO)_7]$ (R = Me **9a** 4% or CO_2Me **9b** 48%) were approximately the same under either set of conditions (Scheme 3). All the new complexes **7b**, **8a**, **8b** and **9a**, **9b** have been characterised spectroscopically (see Table 1 and Experimental section).

The μ-CCO$_2$Me analogue of **7a**, complex **7b**, shows a molecular ion consistent with the proposed structure and the single peak at δ 11.0 in the ^{31}P-{^{1}H} NMR spectrum is comparable with the chemical shifts of other μ-POP ligands[11,12] along with that observed for **7a**.

The IR spectra of complexes **8**, as for **2**, are consistent with products in which a carbonyl group has been substituted by one phosphorus centre of the diphosphane.[8] This is further supported by the ^{31}P-{^{1}H} NMR spectra in which broad doublet resonances [^1J(PP) ≈300 Hz] for the phosphorus atoms co-ordinated to the quadrupolar cobalt atom and well resolved doublets for the non-co-ordinated phosphorus atoms are observed.

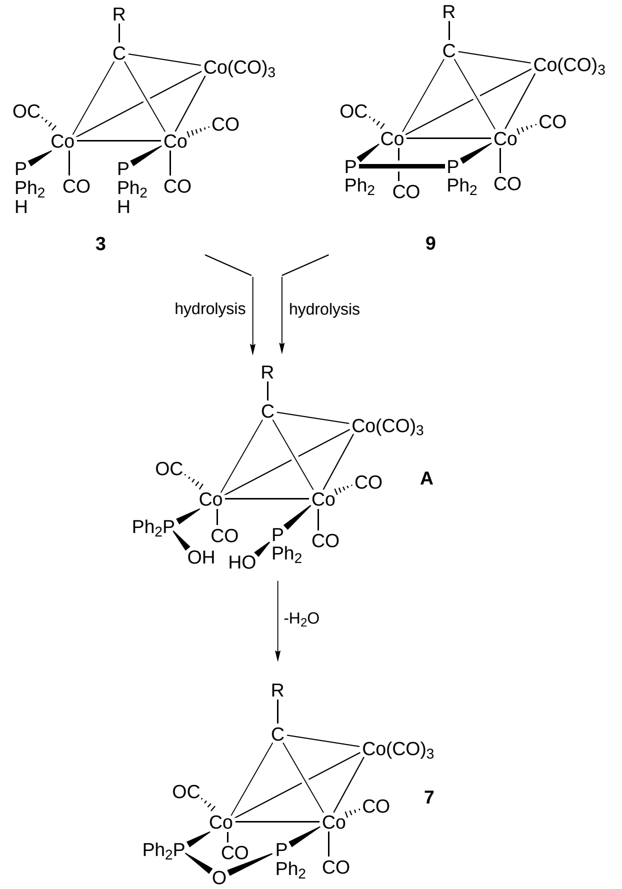
The FAB mass spectra of compound **9** show molecular ion peaks 28 mass units less than those observed for **8** while IR spectra reveal a close similarity in the ν(CO) regions when compared with the Ph$_2$POPPh$_2$-bridged complexes **7**. In the ^{31}P-{^{1}H} NMR spectra of **9** one broad signal is seen well upfield (δ −161.2 **9a**, −152.6 **9b**). Similar chemical shifts for four-membered M$_2$P$_2$ metallacyclic complexes have been observed in dicobalt[5a] and diiron chemistry.[16]

It seems reasonable to assume that, in the reactions leading to complexes **7**–**9**, **8a**, **8b** are formed first, and that **9a**, **9b** and **7a**, **7b** follow in sequence (Scheme 3). This was tested by isolating complexes **8a**, **8b** and heating them to 313 K in heptane. Complexes **9a**, **9b** and **7a**, **7b** were produced. Isolating [Co$_3$(μ_3-CR)(μ-P$_2$Ph$_4$)(CO)$_7$] (R = Me **9a** or CO$_2$Me **9b**) and heating them under the same reaction conditions produced some **7a**, **7b**. Similar monosubstitution followed by bridging of the diphosphane has been observed in reactions with [Co$_2$(μ-RCCR′)(CO)$_6$].[5a] However, cleavage of the co-ordinated P–P bond in [Co$_2$(μ-RCCR′)(μ-Ph$_2$PPPh$_2$)(CO)$_4$] results in products in which one of the phosphido fragments couples with the bridging alkyne group and the other bridges the metal centres. In contrast, cleavage of a P–P bond in **9a**, **9b** results in the coupling of two phosphide groups with an oxygen to generate edge-bridged diphosphoxane (Ph$_2$POPPh$_2$) complexes **7**.

The pathway by which an oxygen atom is inserted between the two phosphido groups in compound **7** is uncertain, but the synthesis of **7** from the reactions of [Co$_3$(μ_3-CR)(CO)$_9$] **1** with either 2 equivalents of PPh$_2$H or 1 equivalent of P$_2$Ph$_4$ suggests a common intermediate. Scheme 4 shows a possible route to **7** *via* such a common intermediate, **A**, formed from either **3** or **9** by hydrolysis, and it is noteworthy that a disubstituted arsine complex related to **3**, [Co$_3$(μ_3-CMe)(Me$_2$AsNMe$_2$)$_2$(CO)$_7$], is readily hydrolysed by traces of water to give [Co$_3$(μ_3-CMe)(μ-Me$_2$AsOAsMe$_2$)(CO)$_7$].[17] On the other hand phosphine complexes are less susceptible to hydrolysis than their arsenic analogues and the alternative possibility that **7** is formed by air oxidation of **3** or **9** rather than by hydrolysis cannot be excluded. It is noteworthy that signals corresponding to the Ph$_2$POPPh$_2$ ligand in **7** are absent in the ^{31}P-{^{1}H} NMR spectrum of the reaction mixtures initially obtained from reaction of **1a**, **1b** with P$_2$Ph$_4$ or PPh$_2$H, so that the hydrolysis or oxidation must take place during the chromatographic work-up and is possibly catalysed by the silica.

Conclusion

The reactions of [Co$_3$(μ_3-CR)(CO)$_9$] **1** with PPh$_2$H or P$_2$Ph$_4$ are comparable to those of [Co$_2$(μ-RCCR′)(CO)$_6$] with these ligands only to a limited extent.[5a] The substitution of one and two carbonyl ligands by PPh$_2$H or P$_2$Ph$_4$ followed by P–H or P–P bond cleavage is parallel. There, however, the similarity ends. While migration of a hydrido or phosphido fragment to the organic portion of the complex is achieved on reaction with alkyne-bridged bimetallics, the new products obtained in the corresponding reactions with organo-capped tricobalt complexes result only from transformations occurring on the cobalt–cobalt edges of the cluster. Most notably, in the presence of 2 equivalents of PPh$_2$H or 1 equivalent of P$_2$Ph$_4$, the coupling of two phosphido groups with an oxygen atom gives the Ph$_2$POPPh$_2$-bridged complexes **7**.



Scheme 4 Possible route to the formation of the Ph$_2$POPPh$_2$-bridged complexes **7** *via* hydrolysis of **3** or **8**

Experimental

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use. 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 University Chemical Laboratory, Cambridge. Column chromatography was performed on Kieselgel 60 (70–230 mesh or 230–400 mesh). Products are given in order of decreasing R_f values.

The instrumentation used to obtain spectroscopic data has been described previously.[18] Unless otherwise stated all reagents were obtained from commercial suppliers and used without further purification. The compounds [Co$_3$(μ_3-CR)(CO)$_9$] (R = Me **1a** or CO$_2$Me **1b**)[19,20] and P$_2$Ph$_4$[21] were prepared by literature methods.

(*i*) Reaction of [Co$_3$(μ_3-CR)(CO)$_9$] (R = Me 1a or CO$_2$Me 1b) with PPh$_2$H

(*a*) Complex [Co$_3$(μ_3-CMe)(CO)$_9$] **1a** (0.150 g, 0.33 mmol) and PPh$_2$H (0.2 cm^3, 1.20 mmol) were dissolved in heptane (40 cm^3) and stirred at 313 K for 20 h. The solvent was removed at reduced pressure and the residue dissolved in the minimum quantity of CH$_2$Cl$_2$ and applied to the base of TLC plates. Elution with hexane–acetone (19:1) gave a trace amount of [Co$_3$(μ_3-CMe)(CO)$_9$] **1a**, purple [Co$_3$(μ_3-CMe)(CO)$_8$(PPh$_2$H)] **2a** (0.042 g, 22%), purple [Co$_3$(μ_3-CMe)(CO)$_7$(PPh$_2$H)$_2$] **3a** (0.076 g, 30%), $[Co_3(\mu\text{-}PPh_2)_3(CO)_6]$[9c] and purple $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}Ph_2POPPh_2)(CO)_6(PPh_2H)]$ **4a** (0.040 g, 14%). Compounds **2a**, **3a** and **4a** are all oily in nature.

An alternative method of obtaining these same products was to dissolve $[Co_3(\mu_3\text{-}CMe)(CO)_9]$ **1a** (0.090 g, 0.20 mmol) and PPh_2H (0.09 cm^3, 0.50 mmol) in thf (25 cm^3) and add a few drops of diphenyl ketyl and stir for 2 h. Separation as above gave complexes **2a**, **3a** and **4a** in similar yields with equivalent amounts of PPh_2H. Complex **2a**: FAB mass spectrum, *m/z* 614 (M^+) and ($M^+ - n$CO) ($n = 1$–8); ^{13}C NMR ($CDCl_3$, ^1H composite pulse decoupled) δ 289.7 (s, μ_3-*C*Me), 203.3 (s, 8CO), 133–129 (m, Ph) and 43.7 (s, Me). Complex **3a**: FAB mass spectrum, *m/z* 772 (M^+) and ($M^+ - n$CO) ($n = 1$–7); ^{13}C NMR ($CDCl_3$, ^1H composite pulse decoupled) δ 274.5 (s, μ_3-*C*Me), 208.5 (s, 7CO), 133–128 (m, Ph) and 42.3 (s, Me). Complex **4a**: FAB mass spectrum, *m/z* 944 (M^+) and ($M^+ - n$CO) ($n = 1$–6); ^{13}C NMR ($CDCl_3$, ^1H composite pulse decoupled) δ 285.3 (s, μ_3-*C*Me), 216.9 (s, 4CO), 207.5 (s, 2CO), 134–128 (m, Ph) and 40.9 (s, Me).

(*b*) Complex $[Co_3(\mu_3\text{-}CCO_2Me)(CO)_9]$ **1b** (0.330 g, 0.66 mmol) and PPh_2H (0.12 cm^3, 0.70 mmol) were treated in a manner analogous to that in (*a*) above to yield $[Co_3(\mu\text{-}PPh_2)_3(CO)_6]$, green $[Co_3(\mu_3\text{-}CCO_2Me)(CO)_8(PPh_2H)]$ **2b** (0.243 g, 56%) and green $[Co_3(\mu_3\text{-}CCO_2Me)(CO)_7(PPh_2H)_2]$ **3b** (0.051 g, 9.5%). Compounds **2b** and **3b** are both oily in nature. Complex **2b**: FAB mass spectrum, *m/z* 652 (M^+) and ($M^+ - n$CO) ($n = 1$–8); ^{13}C NMR ($CDCl_3$, ^1H composite pulse decoupled) δ 290.0 (s, μ_3-*C*CO_2Me), 204.5 (s, 8CO), 133–129 (m, Ph) and 51.6 (s, Me). Complex **3b**: FAB mass spectrum, *m/z* 816 (M^+) and ($M^+ - n$CO) ($n = 1$–7); ^{13}C NMR ($CDCl_3$, ^1H composite pulse decoupled) δ 277.1 (s, μ_3-*C*CO_2Me), 208.2 (s, 7CO), 183.5 (s, *C*O_2Me), 134–128 (m, Ph) and 51.3 (s, Me).

(*ii*) Reaction of complexes 2a, 2b, 3a, 3b and 4a with CO

(*a*) Complex $[Co_3(\mu_3\text{-}CMe)(CO)_8(PPh_2H)]$ **2a** (0.065 g, 0.11 mmol) was dissolved in heptane (25 cm^3) and heated to 343 K for 6 h while CO was bubbled through the solution. The solvent was removed under reduced pressure and the residue dissolved in the minimum quantity of CH_2Cl_2 and applied to the base of TLC plates. Elution with hexane–acetone (19 : 1) gave $[Co_3(\mu_3\text{-}CMe)(CO)_9]$ **1a** (0.014 g, 82%) and some starting material.

(*b*) Complex $[Co_3(\mu_3\text{-}CCO_2Me)(CO)_8(PPh_2H)]$ **2b** (0.040 g, 0.06 mmol) was treated as in (*a*) above to yield $[Co_3(\mu_3\text{-}CCO_2Me)(CO)_9]$ **1b** (0.022 g, 80%) and some starting material.

(*c*) Complex $[Co_3(\mu_3\text{-}CMe)(CO)_7(PPh_2H)_2]$ **3a** (0.060 g, 0.08 mmol) was treated as in (*a*) above to yield $[Co_3(\mu_3\text{-}CMe)(CO)_9]$ **1a** (0.024 g, 65%) and $[Co_3(\mu_3\text{-}CMe)(CO)_8(PPh_2H)]$ **2a** (0.015 g, 30%).

(*d*) Complex $[Co_3(\mu_3\text{-}CCO_2Me)(CO)_7(PPh_2H)_2]$ **3b** (0.035 g, 0.04 mmol) was treated as in (*a*) above to yield $[Co_3(\mu_3\text{-}CCO_2Me)(CO)_9]$ **1b** (0.010 g, 50%), $[Co_3(\mu_3\text{-}CCO_2Me)(CO)_8(PPh_2H)]$ **2b** (0.010 g, 37%) and some starting material.

(*e*) Complex $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}Ph_2POPPh_2)(CO)_6(PPh_2H)]$ **4a** (0.040 g, 0.04 mmol) was treated as in (*a*) above to yield starting material, $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}Ph_2POPPh_2)(CO)_7]$ **7a** (0.070 g, 23%) and decomposition products. Complex **7a** (Found: C, 50.5; H, 3.0; P, 7.7. $C_{33}H_{23}Co_3O_8P_2$ requires C, 50.4; H, 2.9; P, 7.9%): FAB mass spectrum, *m/z* 786 (M^+) and ($M^+ - n$CO) ($n = 1$–7); ^{13}C NMR ($CDCl_3$, ^1H composite pulse decoupled) δ 288.9 (s, μ_3-*C*Me), 204.7 (s, 6CO), 140–127 (m, Ph) and 45.6 (s, C*Me*).

(*iii*) Thermolysis of complexes 2a, 2b, 3a and 3b

(*a*) Complex $[Co_3(\mu_3\text{-}CMe)(CO)_8(PPh_2H)]$ **2a** (0.070 g, 0.11 mmol) was dissolved in heptane (25 cm^3) and heated at 343 K for 2 h. The solvent was removed under reduced pressure and the residue applied to the top of a chromatography column. Elution with hexane yielded $[Co_3(\mu_3\text{-}CMe)(CO)_9]$ **1a** (0.016 g, 32%), green $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_7]$ **5a** (0.019 g, 29%) and some starting material. Complex **5a** (Found: C, 42.7; H, 2.4; P, 5.4. $C_{21}H_{14}Co_3O_7P$ requires C, 43.0; H, 2.4; P, 5.3%): FAB mass spectrum, *m/z* 586 (M^+) and ($M^+ - n$CO) ($n = 1$–7).

(*b*) Complex $[Co_3(\mu_3\text{-}CMe)(CO)_7(PPh_2H)_2]$ **3a** (0.060 g, 0.08 mmol) was treated as in (*a*) above to yield green **5a** (0.010 g, 2%), green $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6(PPh_2H)]$ **6a** (0.080 g, 13%), $[Co_3(\mu\text{-}PPh_2)_3(CO)_6]$[9c] and purple $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}Ph_2POPPh_2)(CO)_7]$ **7a** (0.010 g, 2%). Complex **6a** (Found: C, 51.7; H, 3.2; P, 8.4. $C_{32}H_{25}Co_3O_6P_2$ requires C, 51.6; H, 3.4; P, 8.3%): FAB mass spectrum, *m/z* 744 (M^+) and ($M^+ - n$CO) ($n = 1$–6).

(*c*) Complex $[Co_3(\mu_3\text{-}CCO_2Me)(CO)_8(PPh_2H)]$ **2b** (0.080 g, 0.12 mmol) was treated as in (*a*) above. A reaction occurred but the products were too unstable to isolate before they decomposed.

(*d*) Complex $[Co_3(\mu_3\text{-}CCO_2Me)(CO)_7(PPh_2H)_2]$ **3b** (0.050 g, 0.06 mmol) was treated as in (*a*) above. A reaction occurred but the products were too unstable to isolate before they decomposed.

(*iv*) Reaction of complexes 5a, 6a and 7a with CO

(*a*) Complex $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_7]$ **5a** (0.045 g, 0.08 mmol) was dissolved in heptane (25 cm^3) and heated to 343 K for 6 h while CO was bubbled through the solution. The solvent was removed under reduced pressure and the residue was applied to the base of TLC plates. Elution with hexane–acetone (19 : 1) gave $[Co_3(\mu_3\text{-}CMe)(CO)_8(PPh_2H)]$ **2a** (0.035 g, 72%) and $[Co_3(\mu_3\text{-}CMe)(CO)_9]$ **1a** (0.007 g, 18%).

(*b*) Complex $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6(PPh_2H)]$ **6a** (0.020 g, 0.03 mmol) was treated as in (*a*) above to yield trace amounts of $[Co_3(\mu_3\text{-}CMe)(CO)_7(PPh_2H)_2]$ **3a** and **1a**.

(*c*) Complex $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}Ph_2POPPh_2)(CO)_7]$ **7a** (0.055 g, 0.07 mmol) was treated as in (*a*) above but no reversal of the reaction leading to this complex occurred. Only starting material and decomposition products were obtained.

(*v*) Reaction of complex 7a with PPh_2H or $PPhMe_2$

(*a*) Complex $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}Ph_2POPPh_2)(CO)_7]$ **7a** (0.065 g, 0.09 mmol) and an excess of PPh_2H were dissolved in heptane (25 cm^3) and stirred at 323 K for 20 h. The solvent was removed under reduced pressure and the residue dissolved in the minimum quantity of CH_2Cl_2 and applied to the base of TLC plates. Elution with hexane–acetone (19 : 1) yielded starting material, a trace of $[Co_3(\mu\text{-}PPh_2)_3(CO)_6]$[9c] and $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}Ph_2POPPh_2)(CO)_6(PPh_2H)]$ **4a** (0.016 g, 20%).

(*b*) Complex **7a** (0.065 g, 0.09 mmol) and an excess of $PPhMe_2$ were dissolved in heptane (25 cm^3) and treated as in (*a*) yielding starting material and $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}Ph_2POPPh_2)(CO)_6(PPhMe_2)]$ **4a′** (0.018 g, 23%) (Found: C, 53.4; H, 3.7; P, 10.5. $C_{40}H_{34}Co_3O_7P_3$ requires C, 53.6; H, 3.8; P, 10.4%). FAB mass spectrum, *m/z* 896 (M^+) and ($M^+ - n$CO) ($n = 1$–6). ^{13}C NMR ($CDCl_3$, ^1H composite pulse decoupled): δ 283.0 (s, μ_3-*C*Me), 215.1 (s, 4CO), 208.0 (s, 2CO), 140–127 (m, Ph) and 41.1 (s, C*Me*).

(*vi*) Reaction of complexes 1a and 1b with P_2Ph_4

(*a*) Complex $[Co_3(\mu_3\text{-}CMe)(CO)_9]$ (0.500 g, 1.10 mmol) was added to a freshly prepared solution of P_2Ph_4 in thf (75 cm^3). A few drops of diphenyl ketyl were added *via* cannula and the solution was stirred at room temperature for 2 h. The solvent was removed under reduced pressure and the residue dissolved in the minimum quantity of CH_2Cl_2 and applied to the base of TLC plates. Elution with hexane–acetone (22 : 3) yielded some starting material, purple $[Co_3(\mu_3\text{-}CMe)(CO)_8(P_2Ph_4)]$ **8a** (0.292 g, 35%), purple $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}Ph_2POPPh_2)(CO)_7]$ **7a** (0.058 g, 7%) and purple-brown $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}Ph_2PPPh_2)(CO)_7]$ **9a** (0.034 g, 4%). Complex **8a**: FAB mass spectrum, *m/z* 798 (M^+) and ($M^+ - n$CO) ($n = 1$–8); ^{13}C NMR ($CDCl_3$, ^1H composite pulse decoupled) δ 292.1 (s, μ_3-*C*Me), 203.7 (s, 8CO), 135–128 (m, Ph) and 43.8 (s, Me). Complex **9a**: FAB mass spectrum, *m/z* 770 (M^+) and ($M^+ - n$CO) ($n = 1$–7); ^{13}C NMR (CDCl$_3$, ^{1}H composite pulse decoupled) δ 277.0 (s, μ$_3$-*C*Me), 206.7 (s, 7CO), 136–126 (m, Ph) and 44.6 (s, Me).

(*b*) Complex [Co$_3$(μ$_3$-CCO$_2$Me)(CO)$_9$] **1b** (0.475 g, 0.95 mmol) and P$_2$Ph$_4$ (0.528 g, 1.42 mmol) were used in an analogous procedure to (*a*) above to give some starting material, green [Co$_3$(μ$_3$-CCO$_2$Me)(CO)$_8$(P$_2$Ph$_4$)] **8b** (0.016 g, 2%), purple [Co$_3$(μ$_3$-CCO$_2$Me)(μ-Ph$_2$POPPh$_2$)(CO)$_7$] **7b** (0.030 g, 4%) and green [Co$_3$(μ$_3$-CCO$_2$Me)(μ-Ph$_2$PPPh$_2$)(CO)$_7$] **9b** (0.371 g, 48%). Complex **8b** (Found: C, 49.8; H, 2.6; P, 7.5. $C_{35}H_{23}Co_3O_{10}P_2$ requires C, 49.9; H, 2.7; P, 7.4%); FAB mass spectrum, *m/z* 842 (M^+) and ($M^+ - n$CO) ($n = 1$–8). Complex **5b** (Found: C, 49.1; H, 2.6; P, 7.6. $C_{34}H_{23}Co_3O_{10}P_2$ requires C, 49.2; H, 2.8; P, 7.5%); FAB mass spectrum, *m/z* 830 (M^+) and ($M^+ - n$CO) (n = 1–7). Complex **9b** (Found: C, 50.0; H, 2.8; P, 7.7. $C_{34}H_{23}Co_3O_9P_2$ requires C, 50.1; H, 2.8; P, 7.6%); FAB mass spectrum, *m/z* 814 (M^+) and ($M^+ - n$CO) (n = 1–7); ^{13}C NMR (CDCl$_3$, ^{1}H composite pulse decoupled) δ 276.0 (s, μ$_3$-*C*CO$_2$Me), 209.5 (s, 7CO), 185.4 (s, *C*O$_2$Me), 135–128 (m, Ph) and 51.5 (s, Me).

(*vii*) Conversions of complex 8a into 9a and 7a

Complex [Co$_3$(μ$_3$-CMe)(CO)$_8$(P$_2$Ph$_4$)] **8a** (0.275 g, 0.34 mmol) was dissolved in heptane (60 cm^3) and a few drops of diphenyl ketyl were added *via* cannula to the solution stirred at room temperature for 2 h. Monitoring of the reaction mixture by spot TLC over the 2 h saw first the appearance of [Co$_3$(μ$_3$-CMe)(μ-Ph$_2$PPPh$_2$)(CO)$_7$] **9a** and then [Co$_3$(μ$_3$-CMe)(μ$_2$-Ph$_2$POPPh$_2$)(CO)$_7$] **7a**. At the end of 2 h the solvent was removed under reduced pressure and the residue dissolved in the minimum quantity of CH$_2$Cl$_2$ and applied to the base of TLC plates. Elution with hexane–acetone (22:3) gave [Co$_3$(μ$_3$-CMe)(CO)$_9$] **1a** (0.030 g, 19%), **8a** (0.025 g, 9%), **7a** (0.020 g, 8%) and **9a** (0.032 g, 12%).

(*viii*) Crystallography

Complex 4a′. *Crystal_data.* $C_{40}H_{34}Co_3O_7P_3$, $M = 896.37$, triclinic, space group $P1$ (no.2), $a = 11.748(2)$, $b = 19.048(3)$, $c = 10.724(2)$ Å, $\alpha = 102.593(6)$, $\beta = 113.710(8)$, $\gamma = 76.932(9)°$, $U = 2118.4(6)$ Å^3 (by least-squares refinement of all 9148 reflections in the data set), μ(Mo-Kα) = 1.319 mm^{-1}, $T = 293(2)$ K, graphite-monochromated Mo-Kα radiation, λ = 0.710 73 Å, $Z = 2$, $D_c = 1.405$ Mg m^{-3}, $F(000) = 912$. A dark red block of size 0.1 × 0.1 × 0.05 mm, grown by slow diffusion of hexane into a dichloromethane solution, was used in data collection.

Data collection and refinement. On a Rigaku R-Axis IIc image plate two data sets were collected, one of 60 × 3° oscillation frames, 10 min exposure, then crystal rotated through 90° about an axis 45° to the vertical and 40 × 3° oscillation frames, 10 min exposure, $2.2 < 2\theta < 51.8°$, $-14 \leqslant h \leqslant 14$, $-23 \leqslant k \leqslant 23$, $-13 \leqslant l \leqslant 12$; 9148 reflections measured, 6081 unique ($R_{int} = 0.0582$) used in all calculations. An empirical absorption correction was achieved by means of interframe scaling. Solution by direct methods (SIR 92)[22] and subsequent Fourier syntheses, full-matrix refinement on F^2 (SHELXL 96)[23] with non-H atoms anisotropic, hydrogen atoms included using riding model. Final $wR(F^2)$ 0.2082, $R(F) = 0.0783$ on all data, $wR(F^2) = 0.2050$, $R(F)$ 0.0744 for 5770 observed reflections [$I > 2\sigma(I)$], weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0855P)^2 + 7.9318P]$ where $P = (F_o^2 + 2F_c^2)/3$, 478 parameters, goodness of fit = 1.232, maximum Δ/σ = 0.010, maximum Δρ = 0.897, minimum Δρ = −0.589 e Å^{-3}.

Complex 5a. *Crystal_data.* $C_{21}H_{14}Co_3O_7P$, $M = 586.1$, triclinic, space group $P1$ (no.2), $a = 9.848(3)$, $b = 10.303(3)$, $c = 11.409(3)$ Å, $\alpha = 85.10(2)$, $\beta = 89.62(2)$, $\gamma = 82.28(2)$, $U = 1142.9(6)$ Å^3 (by least-squares refinement of 25 centred reflections $20 < \theta < 25°$), μ(Mo-Kα) = 2.256 mm^{-1}, $T = 291(2)$ K, graphite-monochromated Mo-Kα radiation, λ = 0.710 73 Å, $Z = 2$, $D_c = 1.703$ Mg m^{-3}, $F(000) = 584$. A dark red block of size 0.10 × 0.22 × 0.28 mm, grown by prolonged cooling to 253 K of a concentrated pentane solution, was used in data collection.

Data collection and refinement. Data were collected on a Nicolet R3m/V four-circle diffractometer in the ranges $5.0 < 2\theta < 50.0°$ $-11 \leqslant h \leqslant 11$, $-12 \leqslant k \leqslant 0$, $-13 \leqslant l \leqslant 13$; 4356 reflections measured, semi-empirical absorption correction based on ψ scans applied (transmission factors 0.522–0.559), 3979 unique data ($R_{int} = 0.0137$). Solution by direct methods and subsequent Fourier syntheses, full-matrix refinement on F (SHELXTL PLUS),[24] for 3420 observed reflections [$I > 2\sigma(I)$], with non-H atoms anisotropic, methyl and phenyl hydrogen atoms included using riding model, position of bridging hydrido atom refined freely. Final $wR(F)$ 0.0384, $R(F)$ 0.0354 for all data, $wR(F)$ 0.0364, conventional $R(F)$ 0.0282 for 3420 observed data, weighting scheme $w = 1/[\sigma^2(F) + 0.0005F^2]$, 295 parameters, goodness of fit = 1.16, maximum Δ/σ = 0.002, maximum Δρ = 0.24, minimum Δρ = −0.39 e Å^{-3}

CCDC reference number 186/643.

Acknowledgements

We thank the EPSRC (G. A. A. and G. A. S.) for financial support.

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Received 18*th April* 1997; *Paper* 7/02669B