Synthesis of Tetracobalt Clusters from Dicobalt Alkyne Complexes†

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The room-temperature reactions of $[Co_2(\mu\text{-PhCCH})(CO)_6]$ or $[Co_2(\mu\text{-MeCCMe})(CO)_6]$ with $Ph_2PC{\equiv}CPh$ (L) afford $[Co_2(\mu\text{-PhCCH})(CO)_5(\eta^1\text{-L})]$ or $[Co_2(\mu\text{-MeCCMe})(CO)_5(\eta^1\text{-L})]$ and $[Co_2(\mu\text{-MeCCMe})(CO)_4(\eta^1\text{-L})_2]$, respectively, in which L is bound *via* the phosphine functionality. The structure of $[Co_2(\mu\text{-MeCCMe})(CO)_4(\eta^1\text{-L})_2]$ has been established by X-ray crystallography and comprises two $Co(CO)_2(\eta^1\text{-L})$ units bridged by a $MeC{\equiv}CMe$ ligand. Reactions of $[Co_2(\mu\text{-R}^1CCR^2)(CO)_5(\eta^1\text{-L})]$ with $[Co_2(CO)_8]$ afford $[Co_2(\mu\text{-R}^1CCR^2)(CO)_5(\mu\text{-}\eta^1\text{:}\eta^2\text{-L})Co_2(CO)_6]$ (R^1 = Ph, R^2 = H; $R^1 = R^2$ = Me), in which L is bound to the $Co_2(CO)_6$ unit *via* the alkyne functionality. Pyrolysis of $[Co_2(\mu\text{-MeCCMe})(CO)_5(\mu\text{-}\eta^1\text{:}\eta^2\text{-L})Co_2(CO)_6]$ results in phosphorus–carbon bond cleavage and cobalt–cobalt and carbon–carbon bond formation to afford a butterfly cluster $[Co_4\{\mu_4\text{-}\eta^3\text{-PhCCC(Me)=C(Me)C(O)}\}(\mu\text{-PPh}_2)(\mu\text{-CO})_2(CO)_6]$, whose structure has been established by X-ray diffraction.

The reactions of phosphinoacetylene ligands with transition-metal carbonyl clusters have led to a rich chemistry.[1] Cleavage of the P–C bond is a common process and leads to $\mu\text{-PR}_2$ ligands which enhance cluster stability and to $-C{\equiv}CR$ fragments that have been shown to insert into M–H bonds[2,3] and couple to acetylide fragments or acetylene ligands.[4] Recent studies involving tetrairidium clusters have been particularly fruitful[5] and in this paper we describe the synthesis of tetracobalt clusters with phosphinoacetylene derived ligands. Initial attempts to access such systems *via* reaction of $[Co_4(CO)_{12}]$ or $[Co_4(\mu\text{-PhC}{\equiv}\text{CPh})(CO)_{10}]$ with $Ph_2PC{\equiv}CPh$ resulted in cluster fragmentation, not unexpectedly, due to the relative weakness of cobalt–cobalt bonds compared to iridium–iridium bonds.[6] In this paper we report an alternative method of cluster synthesis involving dicobalt building blocks.

Phosphinoalkynes can react with $[Co_2(CO)_8]$ to afford three different types of product depending on the choice of phosphinoalkyne and reaction conditions.[7] The phosphinoalkynes can bond to a dicobalt fragment by either the phosphorus or the triple bond or both, simultaneously. In this paper we describe the new tetranuclear cobalt cluster $[Co_4\{\mu_4\text{-}\eta^3\text{-PhCCC(Me)=C(Me)C(O)}\}(\mu\text{-PPh}_2)(\mu\text{-CO})_2(CO)_6]$ prepared by the condensation of $[Co_2(\mu\text{-MeCCMe})(CO)_5(\eta^1\text{-Ph}_2PC{\equiv}CPh)]$ with $[Co_2(CO)_8]$, in which the $Ph_2PC{\equiv}CPh$ ligand acts as an anchor directing the formation of the cobalt–cobalt bonds. A similar strategy for cluster build-up has recently been reported by Bruce and co-workers[8] using 1,4-bis(diphenylphosphino)buta-1,3-diyne and cobalt–cobalt bond formation has been observed in reductive dehalogenation of chloro(alkynyl)phosphines by $[Co_2(CO)_8]$.[9]

Results and Discussion

Treatment of $[Co_2(\mu\text{-MeCCMe})(CO)_6]$ with $Ph_2PC{\equiv}CPh$ (L) at room temperature in CH_2Cl_2 affords $[Co_2(\mu\text{-MeCCMe})(CO)_5(\eta^1\text{-L})]$ **1** and $[Co_2(\mu\text{-MeC}{\equiv}\text{CMe})(CO)_4(\eta^1\text{-L})_2]$ **2**. The IR and NMR spectra of **1** (see Tables 1 and 2) confirmed that simple carbonyl substitution had occurred, without further rearrangement. A weak absorption at 2172 cm^{-1}, observed in the IR spectra of both compounds, was assigned to the $C{\equiv}C$ stretch of the *P*-bound η^1-L ligands. The $^{31}P\text{-}\{^1H\}$ NMR spectra of **1** and **2** contain peaks at δ 24.8 and 29.2, respectively, in the range for co-ordinated phosphine ligands. The FAB mass spectrum of **1** contains peaks assigned to $[M - n\text{CO}]^+$ (n = 4 or 5), while **2** was further characterised by X-ray crystallography. Selected structural parameters are listed in Table 3 and the molecular structure is shown in Fig. 1.

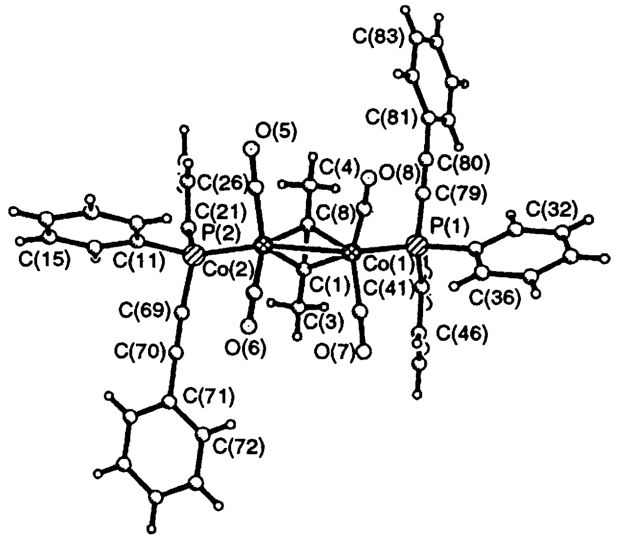

Fig. 1 The molecular structure of $[Co_2(\mu\text{-MeCCMe})(CO)_4(\eta^1\text{-Ph}_2PC{\equiv}CPh)_2]$ **2** showing the atom labelling system

As expected, the molecule contains two $Co(CO)_2(\eta^1\text{-L})$ units bridged by a $MeC{\equiv}CMe$ ligand. The phosphinoalkynes occupy axial positions on the cobalt centres and are antiparallel giving the complex approximate C_2 symmetry. The core '$Co_2(\mu\text{-MeCCMe})L_2$' geometry is similar to that observed for other complexes of the type $[Co_2(\mu\text{-alkyne})(CO)_4(PR_3)_2]$ (alkyne =

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Analytical[a] and physical data

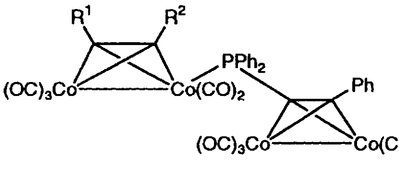
Complex	Appearance	Yield (%)	$\tilde{\nu}_{max}$(CO)/cm^{-1}	Analysis (%) C	Analysis (%) H
1	Red oil	60	1968w, 2000s, 2060m[b]	58.2 (58.2)	3.5 (3.5)
2	Brown solid	20	1995s, 2013s[c]	66.3 (67.3)	4.2 (4.2)
3	Brown solid	74	1952w, 2000s, 2040m, 2060s, 2094w[b]	47.1 (47.5)	2.3 (2.4)
4	Brown solid	64	1686m, 1848s, 1988s, 2036s, 2074w[d]	47.3 (47.9)	2.4 (2.6)
5	Red oil	36	1965m, 2010s, 2020s, 2060s[b]	—	—
6	Brown solid	69	1968w, 2012s, 2038w, 2064s, 2096m[b]	50.3 (50.2)	2.3 (2.3)
7	Green solid	18	1846w, 2014s, 2064m[c]	47.4 (47.6)	2.8 (2.8)

[a] Calculated values in parentheses. [b] In light petroleum. [c] In CH_2Cl_2. [d] Nujol mull.

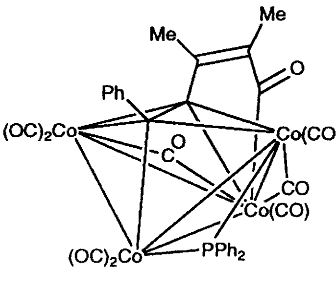
Table 2 Hydrogen-1, carbon-13 and phosphorus-31 NMR data[a]

Compound	δ_H	δ_C[b]	δ_P[b,c]
1	2.34 (s, 6 H, CH_3), 7.0–7.8 (m, 15 H, Ph)	18.9 (CH_3), 82.9 [d, C_α, J(PC) 78], 91.1 (CCH$_3$), 110.7 [d, C_β, J(PC) 12], 120–135 (Ph), 205.1, 205.3 (CO)	24.8[d]
2	2.12 (s, 6 H, CH_3), 7.0–7.8 (m, 30 H, Ph)	17.9 (CH_3), 83.5 [d, C_α, J(PC) 72], 87.2 (CCH$_3$), 109.6 [d, C_β, J(PC) 4], 120–140 (Ph), 206.5 (CO)	29.2[d]
3	1.74 (s, 6 H, CH_3), 6.9–7.8 (m, 15 H, Ph)	18.6 (CH_3), 90.0 (CCH$_3$), 92.4 (C_α), 108.0 (C_β), 128–135(Ph), 198.9, 202.5, 207.1 (CO)	62.7[d]
4	1.50 (s, 3 H, CH_3), 1.6 (s, 3 H, CH_3), 7.2–7.5 (m, 15H, Ph)	13.6 (CH_3), 16.8 (CH_3), 128–142 (Ph), 149.5, 175.7	217.5[d]
5	5.74 [d, 1 H, CH, J(PH) 3.3], 6.9–7.9 (m, 20 H, Ph)	72.8 (CH), 82.8 [d, C_α, J(PC) 84], 87.4 (CPh), 111.1 [d, C_β, J(PC) 13], 120–140 (Ph), 204.6, 205.4, 205.6 (CO)	23.1[d]
6	5.52 (br s, 1 H, CH), 6.9–7.9 (m, 20 H, Ph)	71.0 (CH), 87.4 (CPh), 89.0 (C_α), 106.5 [d, C_β, J(PC) 10], 125–140 (Ph), 200.0, 201.7, 206.4 (CO)	55.5[d]
7	[e] 5.65 [d, 1 H, CH), J(PH) 43.1], 6.9–7.7 (m, 20 H, Ph)	[d]112.4 [d, CH, J(PC) 127], 123–159 (Ph), 212.3 (br, CO)	49.8

[a] Measured at room temperature, chemical shifts (δ) in ppm, coupling constants in Hz. Measured in CD_2Cl_2 solution unless otherwise stated. [b] Hydrogen-1 decoupled. [c] Chemical shifts are positive to high frequency of 85% H_3PO_4 (external). [d] Measured in $CDCl_3$ solution. [e] Measured in CD_3COCD_3.



R1 R2
3 Me Me
6 Ph H



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HC≡CH, $PR_3 = PMe_3$;[10] alkyne = CHOC≡CCHO, $PR_3 = PPh_3$;[11] alkyne = C_8F_6, $PR_3 = PPh_3$, PPh_2Me or PMe_3[12]). Only one carbonyl resonance is observed in the $^{13}C-\{^1H\}$ NMR spectrum of **2**, suggesting that rotation about the phosphorus–cobalt bonds is rapid at room temperature. Heating **1** in CH_2Cl_2 under reflux resulted in the formation of **2** and $[Co_2(\mu\text{-}MeCCMe)(CO)_6]$ without any evidence of phosphorus–carbon bond cleavage.

Further co-ordination of the *P*-bound phosphinoalkyne was investigated by treating compound **1** with $[Co_2(CO)_8]$ with the aim of producing a tetranuclear cobalt cluster. The reaction of **1** with 1.5 equivalents of $[Co_2(CO)_8]$ is conveniently followed by monitoring the disappearance of the C≡C stretching absorption and afforded $[Co_2(\mu\text{-}MeCCMe)(CO)_5(\mu\text{-}\eta^1:\eta^2\text{-}Ph_2PCCPh)Co_2(CO)_6]$ **3** in good yield. The FAB mass spectrum of **3** contains an isotope envelope centred at *m/z* 884, corresponding to $[M]^+$ and envelopes due to carbonyl losses corresponding to $[M - n\text{CO}]^+$ (n = 3–11). The ^1H NMR spectrum contains a singlet at δ 1.74 assigned to the CH_3 groups, shifted from δ 2.34 in **1**, and a multiplet for the Ph protons. Three resonances assigned to acetylenic carbons are observed in the $^{13}C-\{^1H\}$ NMR spectrum. The resonance at δ 90.0 is assigned to the but-2-yne ligand, by comparison with δ 91.1 in **1** and its double height. The other two peaks at δ 92.4 and 108.0 are weak and broad with no ^{31}P coupling observed, in contrast to **1**, where phosphorus coupling was observed to C_α and C_β. Previous reports have also observed this effect when phosphinoacetylenes are bound through both the phosphorus and the triple bond.[13] Three broad carbonyl resonances are observed as expected for $Co(CO)_3$, $Co(CO)_2L$ and $Co_2(CO)_6$ groupings.

Heating **3** in CH_2Cl_2 under reflux for 30 h results in complete consumption of **3** and formation of **4** in 64% yield. A single resonance in the $^{31}P-\{^1H\}$ NMR spectrum at δ 217.5 suggested that phosphorus–carbon bond cleavage had occurred with formation of a phosphido ligand bridging across a cobalt–cobalt bond,[14] while a peak at *m/z* 800 and eight successive carbonyl loss peaks indicated that **4** was still a tetracobalt species. This was confirmed by a single-crystal X-ray diffraction study. Selected structural parameters are listed in Table 4 and the molecular structure is shown in Fig. 2.

The new compound, $[Co_4\{\mu_4\text{-}\eta^3\text{-}PhCCC(Me)=C(Me)C(O)\}(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_6]$, is a butterfly cluster[15] and was formed by loss of two carbonyl ligands, insertion of a carbonyl group into a cobalt–alkyne bond, cleavage of the P–C bond, with formation of a μ-PPh_2 ligand and a –C≡CPh

Table 3 Selected internuclear distances (Å) and angles (°) for $[Co_2(\mu\text{-}MeCCMe)(CO)_4(Ph_2PC{\equiv}CPh)_2]$ **2**

Co(1)–C(8)	1.764(12)	Co(1)–C(1)	1.958(9)
Co(1)–P(1)	2.187(3)	Co(2)–C(6)	1.769(13)
Co(2)–C(1)	1.976(10)	Co(2)–P(2)	2.178(3)
P(1)–C(31)	1.825(6)	P(2)–C(69)	1.750(10)
P(2)–C(11)	1.832(7)	C(1)–C(3)	1.510(12)
C(5)–O(5)	1.131(10)	C(7)–O(7)	1.139(11)
C(69)–C(70)	1.175(12)	C(79)–C(80)	1.177(12)
Co(1)–C(7)	1.787(12)	Co(1)–C(2)	1.967(9)
Co(1)–Co(2)	2.459(2)	Co(2)–C(5)	1.789(12)
Co(2)–C(2)	1.978(9)	P(1)–C(79)	1.763(12)
P(1)–C(41)	1.828(6)	P(2)–C(21)	1.817(7)
C(1)–C(2)	1.302(11)	C(2)–C(4)	1.495(12)
C(6)–O(6)	1.144(11)	C(8)–O(8)	1.161(12)
C(70)–C(71)	1.441(13)	C(80)–C(81)	1.429(13)

C(8)–Co(1)–C(7)	110.1(5)	C(2)–Co(2)–Co(1)	51.2(3)
C(8)–Co(1)–C(2)	107.3(4)	C(2)–C(1)–Co(1)	71.0(6)
C(8)–Co(1)–P(1)	99.0(4)	C(3)–C(1)–Co(2)	133.7(7)
C(2)–Co(1)–P(1)	99.0(3)	C(1)–C(2)–Co(1)	70.3(6)
C(1)–Co(1)–Co(2)	51.6(3)	C(4)–C(2)–Co(2)	134.5(7)
C(6)–Co(2)–C(5)	111.4(5)	O(6)–C(6)–Co(2)	178.1(12)
C(6)–Co(2)–C(2)	140.8(5)	C(70)–C(69)–P(2)	172.3(10)
C(6)–Co(2)–P(2)	94.6(4)	C(79)–C(80)–C(81)	179.1(12)
C(2)–Co(2)–P(2)	106.1(3)	C(7)–Co(1)–C(1)	96.1(4)
C(1)–Co(2)–Co(1)	51.0(3)	C(1)–Co(1)–C(2)	38.7(3)
C(2)–C(1)–C(3)	141.1(10)	C(1)–Co(1)–P(1)	104.9(3)
C(2)–C(1)–Co(2)	70.8(6)	C(7)–Co(1)–Co(2)	100.1(3)
C(1)–C(2)–C(4)	141.3(9)	P(1)–Co(1)–Co(2)	150.48(10)
C(1)–C(2)–Co(2)	70.7(6)	C(5)–Co(2)–C(1)	134.7(4)
O(5)–C(5)–Co(2)	177.4(10)	C(1)–Co(2)–C(2)	38.5(3)
O(8)–C(8)–Co(1)	175.8(10)	C(1)–Co(2)–P(2)	97.8(3)
C(80)–C(79)–P(1)	178.3(11)	C(5)–Co(2)–Co(1)	101.8(3)
C(8)–Co(1)–C(1)	140.7(4)	P(2)–Co(2)–Co(1)	148.81(10)
C(7)–Co(1)–C(2)	134.3(4)	C(3)–C(1)–Co(1)	135.1(7)
C(7)–Co(1)–P(1)	100.1(3)	Co(1)–C(1)–Co(2)	77.4(3)
C(8)–Co(1)–Co(2)	94.0(4)	C(4)–C(2)–Co(1)	134.8(7)
C(2)–Co(1)–Co(2)	51.6(3)	Co(1)–C(2)–Co(2)	77.1(4)
C(6)–Co(2)–C(1)	107.0(5)	O(7)–C(7)–Co(1)	175.9(10)
C(5)–Co(2)–C(2)	96.6(4)	C(69)–C(70)–C(71)	178.3(12)
C(5)–Co(2)–P(2)	102.1(3)		
C(6)–Co(2)–Co(1)	95.1(4)		

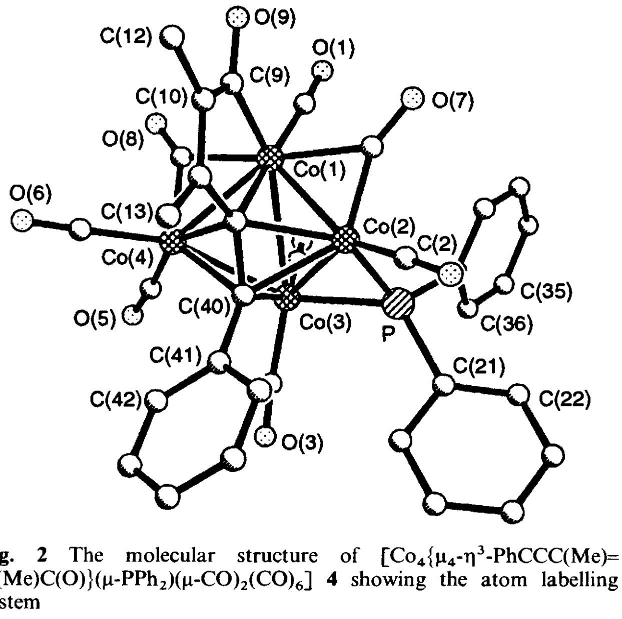

Fig. 2 The molecular structure of $[Co_4\{\mu_4\text{-}\eta^3\text{-}PhCCC(Me){=}C(Me)C(O)\}(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_6]$ **4** showing the atom labelling system

fragment, which coupled with the MeC≡CMe ligand and a CO molecule to produce an μ_4-η^3 ligand, PhCCC(Me)=C(Me)C(O). The cluster contains three new cobalt–cobalt bonds and, considering the μ_4-η^3 ligand as a five-electron donor,[15] the cluster has 60 valence electrons, in common with tetranuclear butterfly structures bound to μ_4-η^2-RCCR ligands.[16–18] The hinge bond length, Co(1)–Co(3) [2.798(2) Å], is significantly longer than those found in related clusters of the type $[Co_4(\mu_4\text{-}\eta^2\text{-}RCCR)(\mu\text{-}CO)_2(CO)_6L_2]$ (R = H or Et, L = CO; R = H, L = PPh_3), which fall in the range 2.552–2.562 Å and the dihedral angle between the wings of the butterfly (121°) is slightly larger than the range (116–118°) for this structural type.[16–18] There are six carbonyl ligands in terminal positions, two bonded to each of Co(3) and Co(4) and one bonded to each of Co(1) and Co(2), while the remaining two carbonyl ligands bridge the Co(1)–Co(4) and Co(1)–Co(2) bonds. Interestingly the butterfly clusters of the type $[Co_4(\mu_4\text{-}\eta^2\text{-}RCCR)(\mu\text{-}CO)_2(CO)_6L_2]$ also have carbonyls bridging between hinge and wing-tip atoms, but on opposite sides of the molecule so all four cobalt atoms are involved in bonding to a bridging carbonyl.[16–18] In compound **4** one hinge atom [Co(1)] has two bridging carbonyls spanning bonds to wing-tip atoms. The phosphido ligand bridges between wing-tip and hinge positions [Co(2) and Co(3)] in a similar manner to the phosphido ligand in $[RuCo_3(\mu_4\text{-}\eta^2\text{-}HCCBu^t)(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_7]$.[19] The Co(2)–P bond [2.109(4) Å] is significantly shorter than Co(3)–P [2.173(4) Å] and may reflect the more electropositive nature of the wing-tip atoms and the local electron book-keeping at Co(2) and Co(3).[18] The C(39)–C(40) bond length [1.41(2) Å] is typical of alkyne-substituted butterfly clusters and the bond length C(10)–C(11) [1.36(2) Å] is typical for carbon–carbon double bonds.

The ^1H NMR spectrum of **4** is straightforward and consists of two singlets, assigned to the two inequivalent methyl groups, and a multiplet due the phenyl groups. At room temperature, the $^{13}C\text{-}\{^1H\}$ NMR spectrum also contains two resonances assigned to the methyl groups and resonances in the region δ 128–142 assigned to the phenyl groups. However no carbonyl resonances and only two resonances assignable to the C_5 chain were observed at δ 149.5 and 175.7, indicating that the molecule is highly fluxional. Upon cooling the sample to −80 °C further resonances were observed. A very weak broad resonance at δ 231 was observed and could be assigned to a bridging carbonyl while a relatively sharp resonance at δ 223.8 was observed and could reasonably be assigned to the acetyl carbon.[20] An absorption of medium intensity is observed at 1686 cm^{-1} in the IR spectrum of **4** when recorded as a Nujol mull and at 1683 cm^{-1} when recorded in solution which is assigned to the acetyl functionality. Further broad peaks were observed in the low-temperature $^{13}C\text{-}\{^1H\}$ NMR spectrum at δ 206, 201, 196, 190 and 159 and are assigned to terminal carbonyl ligands. For comparison the $^{13}C\text{-}\{^1H\}$ NMR spectrum of $[Co_4(\mu_4\text{-}\eta^2\text{-}HCCH)(\mu\text{-}CO)_2(CO)_6(PPh_3)_2]$, recorded at −30 °C, contains carbonyl resonances at δ 192.9, 176.3 and 169.6. The peaks at δ 175.7 and 149.5 in the room-temperature spectrum are tentatively assigned to the alkyne carbons and it is possible that the alkene carbon resonances are obscured by the aromatic resonances. The $^{31}P\text{-}\{^1H\}$ NMR spectrum remains unchanged down to −80 °C and contains just the single phosphido resonance at δ 217.5. The ^{13}C NMR spectrum suggests that the carbonyl fluxionality includes the acetyl carbonyl with possible reversible carbonyl insertion. Extrusion of a carbonyl would give a 62 electron vinyl intermediate and would involve reversible cleavage of one of the cobalt–cobalt bonds that is not bridged by the phosphido ligand, as suggested by the variable-temperature ^{31}P NMR spectra.[14] Carbonyl extrusion is also suggested by the FAB mass spectrum which shows eight successive carbonyl losses from *m*/*z* 800, however the molecular weight of **4** is 828 suggesting that the molecular ion is not observed and the molecule loses nine carbonyl groups.

Treatment of $[Co_2(\mu\text{-}PhCCH)(CO)_6]$ with L at room temperature affords $[Co_2(\mu\text{-}PhCCH)(CO)_5(\eta^1\text{-}L)]$ **5** with no evidence for the formation of a disubstituted product analogous to **2**. Treatment of **5** with $[Co_2(CO)_8]$ affords **6** in an analogous manner to the formation of **3**. However, thermolysis of **6** does

Table 4 Selected internuclear distances (Å) and angles (°) for $[Co_4\{\mu_4\text{-}\eta^3\text{-PhCCC(Me)=C(Me)C(O)}\}(\mu\text{-PPh}_2)(\mu\text{-CO})_2(CO)_6]$ **4**

Co(1)–C(1)	1.788(14)	Co(1)–C(9)	1.87(2)	Co(1)–C(8)	1.99(2)	Co(1)–C(39)	2.010(11)
Co(1)–C(7)	2.096(14)	Co(1)–Co(2)	2.401(2)	Co(1)–Co(4)	2.439(2)	Co(1)–Co(3)	2.798(2)
Co(2)–C(2)	1.754(14)	Co(2)–C(7)	1.813(14)	Co(2)–C(39)	2.023(11)	Co(2)–P	2.109(4)
Co(2)–C(40)	2.118(10)	Co(2)–Co(3)	2.439(2)	Co(3)–C(4)	1.784(14)	Co(3)–C(3)	1.80(2)
Co(3)–C(40)	1.983(10)	Co(3)–P	2.173(4)	Co(4)–C(5)	1.75(2)	Co(4)–C(6)	1.821(13)
Co(4)–C(8)	1.87(2)	Co(4)–C(39)	2.059(11)	Co(4)–C(40)	2.116(10)	Co(4)–Co(3)	2.470(2)
P–C(31)	1.815(12)	P–C(21)	1.817(13)	C(1)–O(1)	1.13(2)	C(2)–O(2)	1.12(2)
C(3)–O(3)	1.12(2)	C(4)–O(4)	1.13(2)	C(5)–O(5)	1.16(2)	C(6)–O(6)	1.106(14)
C(7)–O(7)	1.15(2)	C(8)–O(8)	1.15(2)	C(9)–O(9)	1.28(2)	C(9)–C(10)	1.45(2)
C(10)–C(11)	1.36(2)	C(10)–C(12)	1.48(2)	C(11)–C(39)	1.47(2)	C(11)–C(13)	1.51(2)
C(39)–C(40)	1.41(2)	C(40)–C(41)	1.51(2)				

C(1)–Co(1)–C(9)	96.5(7)	C(1)–Co(1)–C(8)	87.5(6)	C(9)–Co(1)–C(8)	87.8(6)
C(1)–Co(1)–C(39)	175.3(6)	C(9)–Co(1)–C(39)	82.2(5)	C(8)–Co(1)–C(39)	97.0(5)
C(1)–Co(1)–C(7)	86.5(6)	C(9)–Co(1)–C(7)	89.3(6)	C(8)–Co(1)–C(7)	173.0(6)
C(39)–Co(1)–C(7)	88.9(5)	C(1)–Co(1)–Co(2)	123.1(5)	C(9)–Co(1)–Co(2)	110.8(4)
C(8)–Co(1)–Co(2)	140.0(4)	C(39)–Co(1)–Co(2)	53.7(3)	C(7)–Co(1)–Co(2)	47.0(4)
C(1)–Co(1)–Co(4)	130.6(5)	C(9)–Co(1)–Co(4)	102.4(4)	C(8)–Co(1)–Co(4)	48.8(4)
C(39)–Co(1)–Co(4)	54.1(3)	C(7)–Co(1)–Co(4)	138.2(4)	Co(2)–Co(1)–Co(4)	91.82(8)
C(1)–Co(1)–Co(3)	113.9(6)	C(9)–Co(1)–Co(3)	149.5(4)	C(8)–Co(1)–Co(3)	90.5(5)
C(39)–Co(1)–Co(3)	67.7(3)	C(7)–Co(1)–Co(3)	95.2(4)	Co(2)–Co(1)–Co(3)	55.33(6)
Co(4)–Co(1)–Co(3)	55.76(6)	C(2)–Co(2)–C(7)	97.7(6)	C(2)–Co(2)–C(39)	118.3(6)
C(7)–Co(2)–C(39)	97.0(5)	C(2)–Co(2)–P	97.5(4)	C(7)–Co(2)–P	109.7(4)
C(39)–Co(2)–P	131.8(4)	C(2)–Co(2)–C(40)	115.1(5)	C(7)–Co(2)–C(40)	134.0(5)
C(39)–Co(2)–C(40)	39.8(4)	P–Co(2)–C(40)	97.4(3)	C(2)–Co(2)–Co(1)	147.7(4)
C(7)–Co(2)–Co(1)	57.6(5)	C(39)–Co(2)–Co(1)	53.2(3)	P–Co(2)–Co(1)	109.86(13)
C(40)–Co(2)–Co(1)	78.7(3)	C(2)–Co(2)–Co(3)	141.2(4)	C(7)–Co(2)–Co(3)	117.2(5)
C(39)–Co(2)–Co(3)	75.7(3)	P–Co(2)–Co(3)	56.53(10)	C(40)–Co(2)–Co(3)	51.0(3)
Co(1)–Co(2)–Co(3)	70.63(7)	C(4)–Co(3)–C(3)	99.5(8)	C(4)–Co(3)–C(40)	149.4(6)
C(3)–Co(3)–C(40)	102.9(7)	C(4)–Co(3)–P	96.6(5)	C(3)–Co(3)–P	100.3(5)
C(40)–Co(3)–P	99.6(3)	C(4)–Co(3)–Co(2)	117.4(5)	C(3)–Co(3)–Co(2)	135.5(5)
C(40)–Co(3)–Co(2)	56.1(3)	P–Co(3)–Co(2)	54.04(10)	C(4)–Co(3)–Co(4)	97.3(5)
C(3)–Co(3)–Co(4)	109.9(5)	C(40)–Co(3)–Co(4)	55.4(3)	P–Co(3)–Co(4)	144.00(12)
Co(2)–Co(3)–Co(4)	90.16(8)	C(4)–Co(3)–Co(1)	81.3(5)	C(3)–Co(3)–Co(1)	164.3(5)
C(40)–Co(3)–Co(1)	71.6(3)	C(5)–Co(4)–C(6)	97.2(6)	C(5)–Co(4)–C(8)	98.5(7)
C(6)–Co(4)–C(8)	97.8(6)	C(5)–Co(4)–C(39)	152.7(6)	C(6)–Co(4)–C(39)	100.9(5)
C(8)–Co(4)–C(39)	99.1(6)	C(5)–Co(4)–C(40)	114.1(6)	C(6)–Co(4)–C(40)	112.5(5)
C(8)–Co(4)–C(40)	130.9(5)	C(39)–Co(4)–C(40)	39.5(4)	C(5)–Co(4)–Co(1)	128.7(5)
C(6)–Co(4)–Co(1)	125.2(4)	C(8)–Co(4)–Co(1)	52.9(5)	C(39)–Co(4)–Co(1)	52.3(3)
C(40)–Co(4)–Co(1)	77.9(3)	C(5)–Co(4)–Co(3)	81.1(4)	C(6)–Co(4)–Co(3)	157.9(4)
C(8)–Co(4)–Co(3)	104.2(5)	C(39)–Co(4)–Co(3)	74.4(3)	C(40)–Co(4)–Co(3)	50.5(3)
Co(1)–Co(4)–Co(3)	69.51(7)	P–Co(3)–Co(1)	95.18(11)	Co(2)–Co(3)–Co(1)	54.05(6)
Co(4)–Co(3)–Co(1)	54.72(6)	C(31)–P–C(21)	102.9(6)	C(31)–P–Co(2)	124.5(5)
C(21)–P–Co(2)	118.0(4)	C(31)–P–Co(3)	117.9(4)	C(21)–P–Co(3)	123.0(4)
Co(2)–P–Co(3)	69.43(11)	O(1)–C(1)–Co(1)	177(2)	O(2)–C(2)–Co(2)	174.8(13)
O(3)–C(3)–Co(3)	177(2)	O(4)–C(4)–Co(3)	176.4(14)	O(5)–C(5)–Co(4)	174.9(13)
O(6)–C(6)–Co(4)	178.0(13)	O(7)–C(7)–Co(2)	151.2(13)	O(7)–C(7)–Co(1)	133.4(12)
Co(2)–C(7)–Co(1)	75.4(5)	O(8)–C(8)–Co(4)	143.5(13)	O(8)–C(8)–Co(1)	138.1(12)
Co(4)–C(8)–Co(1)	78.3(6)	O(9)–C(9)–C(10)	119(2)	O(9)–C(9)–Co(1)	122.3(10)
C(10)–C(9)–Co(1)	118.3(10)	C(11)–C(10)–C(9)	111.7(13)	C(11)–C(10)–C(12)	126.3(14)
C(9)–C(10)–C(12)	121.7(14)	C(10)–C(11)–C(39)	116.4(11)	C(10)–C(11)–C(13)	123.5(12)
C(39)–C(11)–C(13)	119.6(11)	C(40)–C(39)–C(11)	136.0(10)	C(40)–C(39)–Co(1)	113.1(8)
C(11)–C(39)–Co(1)	110.6(8)	C(40)–C(39)–Co(2)	73.7(6)	C(11)–C(39)–Co(2)	125.2(8)
Co(1)–C(39)–Co(2)	73.1(4)	C(40)–C(39)–Co(4)	72.4(6)	C(11)–C(39)–Co(4)	116.4(8)
Co(1)–C(39)–Co(4)	73.6(4)	Co(2)–C(39)–Co(4)	116.8(6)	C(39)–C(40)–C(41)	127.5(10)
C(39)–C(40)–Co(3)	107.5(7)	C(41)–C(40)–Co(3)	125.0(8)	C(39)–C(40)–Co(4)	68.1(6)
C(41)–C(40)–Co(4)	122.6(8)	Co(3)–C(40)–Co(4)	74.0(3)	C(39)–C(40)–Co(2)	66.5(6)
C(41)–C(40)–Co(2)	126.7(8)	Co(3)–C(40)–Co(2)	72.9(3)	Co(4)–C(40)–Co(2)	110.4(4)

not proceed in an analogous manner to **3**. A green solid (**7**) was obtained in low yield and could not be fully characterised because insufficient material was obtained to observe the alkyne derived carbons in the ^{13}C NMR spectrum. The FAB mass spectrum exhibits an isotope envelope centred at *m/z* 848, indicating loss of three carbonyl ligands has occurred upon thermolysis, and therefore the formation of new cobalt–cobalt bonds must have taken place. The $^{31}P\text{-}\{^1H\}$ NMR spectrum contains a single resonance at δ 49.8, rather close to that obtained for the precursor **6** at δ 55.5. This result suggests that P–C bond cleavage might not have occurred or that it did occur but the μ-PPh$_2$ fragment spans an edge of the polyhedron without a cobalt–cobalt interaction.[4]

Experimental

The general experimental procedures have been described previously.[21] The compounds $[Co_2(\mu\text{-PhCCH})(CO)_6]$ and $[Co_2(\mu\text{-MeCCMe})(CO)_6]$ were prepared by literature methods.[6] Analytical and other data for the new compounds are given in Tables 1 and 2.

Synthesis of $[Co_2(\mu\text{-MeCCMe})(CO)_5(\eta^1\text{-Ph}_2PC{\equiv}CPh)]$ **1** *and* $[Co_2(\mu\text{-MeCCMe})(CO)_4(\eta^1\text{-Ph}_2PC{\equiv}CPh)_2]$ **2**.—To a solution of $[Co_2(\mu\text{-MeCCMe})(CO)_6]$ (0.62 g, 1.82 mmol) in CH_2Cl_2 (30 cm^3) was added $Ph_2PC{\equiv}CPh$ (0.52 g, 1.82 mmol). The resulting mixture was stirred for 26 h, after which time the solvent was removed *in vacuo* and the residue chromatographed on a silica gel column (11 × 3.5 cm). Eluting with light petroleum (b.p. 40–60 °C) produced a trace of unreacted $[Co_2(\mu\text{-}MeC{\equiv}CMe)(CO)_6]$ and then elution with light petroleum–CH_2Cl_2 (9 : 1) produced a red band of **1** followed by a red band of **2** eluted with a 7 : 3 solvent mixture. Removal of the solvent *in vacuo* afforded **1** (0.65 g, 1.09 mmol) and **2** (0.31 g, 0.36 mmol).

Synthesis of $[Co_2(\mu\text{-}MeCCMe)(CO)_5(\mu\text{-}\eta^1{:}\eta^2\text{-}Ph_2PCCPh)Co_2(CO)_6]$ **3**.—To a solution of **1** (0.60 g, 1.00 mmol) in CH_2Cl_2 (30 cm^3) was added $[Co_2(CO)_8]$ (0.51 g, 1.49 mmol). The resulting mixture was stirred for 8 h, after which time the solvent was removed *in vacuo* and the residue chromatographed on a silica gel column (11 × 3.5 cm). Eluting with light petroleum–CH_2Cl_2 (9 : 1) produced a trace of unreacted **1** and then elution with light petroleum–CH_2Cl_2 (4 : 1) produced a brown band of **3**. Removal of the solvent *in vacuo* afforded **3** (0.65 g, 0.74 mmol).

Pyrolysis of **3**.—A solution of **3** (0.70 g, 0.79 mmol) in CH_2Cl_2 (30 cm^3) was refluxed for 30 h after which time the solvent was removed *in vacuo*. The residue was chromatographed on a Florisil column (11 × 3.5 cm). Elution with light petroleum afforded a trace of $[Co_2(\mu\text{-}MeCCMe)(CO)_6]$ and then elution with a light petroleum–CH_2Cl_2 (1 : 1) produced a brown band of **4**. Removal of the solvent *in vacuo* afforded **4** (0.42 g, 0.51 mmol).

Synthesis of $[Co_2(\mu\text{-}PhCCH)(CO)_5(\eta^1\text{-}Ph_2PC{\equiv}CPh)]$ **5**.—To a solution of $[Co_2(\mu\text{-}PhCCH)(CO)_6]$ (0.94 g, 2.42 mmol) in CH_2Cl_2 (30 cm^3) was added $Ph_2PC{\equiv}CPh$ (0.69 g, 2.42 mmol). The resulting mixture was stirred for 26 h, after which time the solvent was removed *in vacuo* and the residue chromatographed on a silica gel column (11 × 3.5 cm). Eluting with light petroleum produced a trace of unreacted $[Co_2(\mu\text{-}PhCCH)(CO)_6]$ and then elution with light petroleum–CH_2Cl_2 (9 : 1) produced a red band of **5**. Removal of the solvent *in vacuo* afforded **5** (0.57 g, 0.88 mmol).

Synthesis of $[Co_2(\mu\text{-}PhCCH)(CO)_5(\mu\text{-}\eta^1{:}\eta^2\text{-}Ph_2PCCPh)Co_2(CO)_6]$ **6**.—To a solution of **5** (0.57 g, 0.88 mmol) in CH_2Cl_2 (30 cm^3) was added $[Co_2(CO)_8]$ (0.35 g, 1.02 mmol). The resulting mixture was stirred for 16 h, after which time the solvent was removed *in vacuo* and the residue chromatographed on a silica gel column (11 × 3.5 cm). Eluting with light petroleum produced a trace of unreacted **5** and then elution with light petroleum–CH_2Cl_2 (4 : 1) produced a brown band of **6**. Removal of the solvent *in vacuo* afforded **6** (0.57 g, 0.61 mmol).

Pyrolysis of **6**.—A solution of **6** (0.30 g, 0.32 mmol) in CH_2Cl_2 (30 cm^3) was refluxed for 30 h after which time the solvent was removed *in vacuo*. The residue was chromatographed on a silica gel column (11 × 3.5 cm). Elution with light petroleum–CH_2Cl_2 (4 : 1) produced a trace of unreacted **6** and further elution with light petroleum–CH_2Cl_2 (3 : 2) produced a green band of **7**. Removal of the solvent *in vacuo* afforded **7** (0.05 g).

Crystal Structure Determinations.—Crystals of **2** were obtained from CH_2Cl_2–light petroleum as deep red prisms with crystal dimensions *ca.* 0.40 × 0.60 × 0.30 mm. Data were collected using a Siemens R3m/V diffractometer (293 K, Mo-Kα X-radiation, graphite monochromator, $\bar{\lambda} = 0.710\ 73$ Å). Of the 6024 data collected (Wyckoff ω-scans, $2\theta \leqslant 45°$), 5666 unique data were used for the structure solution and refinement. The data were corrected for Lorentz, polarisation and X-ray absorption effects, the latter by a method based upon azimuthal scan data.[22]

Crystal data for **2**. $C_{48}H_{36}Co_2O_4P_2$, $M = 856.6$, monoclinic, space group $P2_1/n$, $a = 10.651(5)$, $b = 19.398(9)$, $c = 21.385(9)$ Å, $\beta = 97.74(3)°$, $U = 4378(3)$ Å^3, $Z = 4$, $D_c = 1.30$ g cm^{-3}, $F(000) = 1760$, μ(Mo-Kα) = 8.72 cm^{-1}.

Crystals of **2** diffracted poorly and the diffracted intensities had relatively broad peak profiles. The structure was solved by conventional heavy-atom methods and successive difference Fourier syntheses were used to locate all non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. The phenyl rings systems have large anisotropic thermal parameters and the best refinement was achieved by treating them as idealised rigid groups. Hydrogen atoms were included in calculated positions [C–H 0.96 (Me) and 0.93 Å (Ph)] with isotropic thermal parameters *ca.* 1.5 (Me) or 1.2 (phenyl) that of the equivalent isotropic thermal parameters of their parent carbon atoms. Final full-matrix least-squares refinement led to $wR_2 = 0.217$ {based on all F_o^2 data, where $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$ and $w^{-1} = [\sigma^2(F_o^2) + (0.0865P)^2 + 7.97P]$ where $P = [\max(F_o^2, 0) + 2F_c^2]/3$}. For comparison it should be noted that a conventional refinement on F would have given $R_1 = 0.077$ for 2961 data with $F_o \geqslant 4\sigma(F_o)$. The final electron density difference synthesis showed no peaks > 0.35 or < -0.28 e Å^{-3}. Atomic coordinates are listed in Table 5.

Crystals of **4** were obtained by solvent diffusion of light petroleum into a CH_2Cl_2 solution of the complex as black octahedra and that used for data collection had crystal dimensions *ca.* 0.34 × 0.35 × 0.50 mm. Although superficially well formed the crystals all showed one strongly stepped re-entrant face and all of those examined had very broad peak profiles. Data were collected using a Siemens R3m/V diffractometer (293 K, Mo-Kα X-radiation, graphite monochromator, $\bar{\lambda} = 0.710\ 73$ Å). Of the 6491 data collected (Wyckoff ω-scans, $2\theta \leqslant 50°$), 5876 unique data were used for the structure solution and refinement. The data were corrected for Lorentz, polarisation and X-ray absorption effects, the latter by a method based upon azimuthal scan data.[22]

Crystal data for **4**. $C_{33}H_{21}Co_4O_9P$, $M = 828.19$, orthorhombic, space group $Pbca$, $a = 17.220(6)$, $b = 14.906(4)$, $c = 26.055(5)$ Å, $U = 6688(3)$ Å^3, $Z = 8$, $D_c = 1.65$ g cm^{-3}, $F(000) = 3312$, μ(Mo-Kα) = 20.50 cm^{-1}.

Crystals of **4** diffracted poorly and the intensities had broad peak profiles. The structure was solved by conventional heavy-atom methods and successive difference Fourier syntheses were used to locate all non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions [C–H 0.96 (Me) and 0.93 Å (Ph)] with isotropic thermal parameters *ca.* 1.5 (Me) or 1.2 (phenyl) that of the equivalent isotropic thermal parameters of their parent carbon atoms. Final full-matrix least-squares refinement led to $wR_2 = 0.299$ {based on all F_o^2 data, where $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$ and $w^{-1} = [\sigma^2(F_o^2) + (0.1324P)^2 + 68.53P]$ where $P = [\max(F_o^2,0) + 2F_c^2]/3$}. For comparison it should be noted that a conventional refinement on F would have given $R_1 = 0.096$ for 3691 data with $F_o \geqslant 4\sigma(F_o)$. The final electron density difference synthesis showed large residual peaks of *ca.* 3 e Å^{-3} in the vicinity of the Co atoms. Since the crystals did not show major absorption effects the latter residual peaks are not due to a poor absorption correction. The overall level of refinement achieved is more likely to reflect the presence of sub-crystals associated with the very poorly developed re-entrant faces of the crystals. Atomic coordinates are listed in Table 6.

Initial calculations were performed on a DEC micro-VAX II computer with the SHELXTL PLUS system of programs.[22] The final least-squares refinements (on F^2) were carried out on a Silicon Graphics Indigo R4000 computer using SHELXL 93.[23] Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

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Table 5 Atomic coordinates (× 10^4) for [Co_2(μ-MeCCMe)$(CO)_4$($η^1$-$Ph_2PC≡CPh$)$_2$] **2**, with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co(1)	1927(1)	1711(1)	3579(1)	C(31)	4206(6)	459(4)	3632(4)
Co(2)	371(1)	2654(1)	3427(1)	C(32)	4796(9)	−57(5)	3328(4)
P(1)	2578(2)	692(1)	3327(1)	C(33)	6020(9)	−263(5)	3562(5)
P(2)	−1603(2)	2980(1)	3274(1)	C(34)	6653(6)	48(5)	4099(5)
C(1)	75(8)	1649(5)	3450(5)	C(35)	6063(9)	564(5)	4404(4)
C(2)	465(8)	1809(5)	2917(5)	C(36)	4839(9)	770(4)	4170(4)
C(3)	−893(10)	1205(5)	3714(6)	C(41)	1643(6)	−24(3)	3573(4)
C(4)	221(10)	1649(5)	2227(4)	C(42)	1033(8)	−488(5)	3138(3)
C(5)	1082(9)	3220(5)	2916(5)	C(43)	254(9)	−996(5)	3335(5)
O(5)	1533(8)	3559(4)	2577(4)	C(44)	85(8)	−1041(4)	3967(5)
C(6)	638(11)	2940(6)	4219(6)	C(45)	695(8)	−578(5)	4402(3)
O(6)	807(9)	3107(5)	4737(4)	C(46)	1474(7)	−69(4)	4205(3)
C(7)	2106(9)	1632(5)	4419(6)	C(69)	−2454(9)	2746(5)	3886(5)
O(7)	2147(8)	1568(4)	4951(4)	C(70)	−2901(10)	2607(6)	4343(5)
C(8)	3168(11)	2213(6)	3349(5)	C(71)	−3417(10)	2443(5)	4915(4)
O(8)	3933(8)	2576(5)	3192(5)	C(72)	−2681(10)	2115(6)	5414(6)
C(11)	−1958(9)	3904(3)	3253(4)	C(73)	−3199(15)	1952(6)	5958(5)
C(12)	−967(6)	4376(5)	3334(5)	C(74)	−4453(15)	2118(6)	6003(5)
C(13)	−1223(11)	5079(5)	3325(5)	C(75)	−5189(9)	2445(7)	5504(6)
C(14)	−2470(13)	5310(4)	3235(5)	C(76)	−4671(10)	2608(6)	4960(5)
C(15)	−3460(9)	4838(6)	3154(5)	C(79)	2559(10)	538(6)	2513(5)
C(16)	−3204(7)	4135(5)	3163(5)	C(80)	2539(11)	454(6)	1967(6)
C(21)	−2582(7)	2635(4)	2583(3)	C(81)	2495(10)	355(7)	1302(4)
C(22)	−3550(8)	2167(4)	2633(3)	C(82)	2741(13)	892(5)	906(7)
C(23)	−4249(7)	1898(4)	2092(5)	C(83)	2715(15)	776(9)	263(6)
C(24)	−3979(9)	2098(5)	1500(4)	C(84)	2442(17)	122(10)	16(4)
C(25)	−3011(10)	2567(5)	1450(3)	C(85)	2195(16)	−416(7)	412(7)
C(26)	−2313(7)	2836(4)	1991(5)	C(86)	2221(13)	−299(6)	1055(6)

Table 6 Atomic coordinates (× 10^4) for [Co_4{$μ_4$-$η^3$-PhCCC(Me)=C(Me)C(O)}(μ-PPh_2)(μ-CO)$_2$(CO)$_6$] **4** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co(1)	330(1)	458(1)	6716(1)	C(10)	−59(8)	−1298(9)	6358(6)
Co(2)	−168(1)	1088(1)	5934(1)	C(12)	57(10)	−2266(9)	6258(8)
Co(4)	−949(1)	502(1)	7118(1)	C(11)	−711(7)	−820(8)	6258(5)
Co(3)	−683(1)	1923(1)	6664(1)	C(13)	−1406(9)	−1199(10)	5975(6)
P	−159(2)	2500(2)	5980(1)	C(21)	−709(7)	3125(8)	5504(5)
C(1)	1267(8)	727(11)	6969(6)	C(22)	−373(8)	3651(10)	5131(5)
O(1)	1852(7)	872(11)	7143(5)	C(23)	−797(10)	4010(11)	4745(6)
C(2)	−258(8)	1000(9)	5265(5)	C(24)	−1584(10)	3841(11)	4715(6)
O(2)	−319(8)	1013(8)	4838(4)	C(25)	−1942(9)	3331(11)	5082(6)
C(3)	−1472(10)	2697(11)	6763(6)	C(26)	−1526(8)	2964(9)	5470(6)
O(3)	−1948(8)	3201(10)	6807(6)	C(31)	709(7)	3176(9)	6060(5)
C(4)	−1(9)	2369(10)	7111(6)	C(32)	1433(8)	2822(11)	5977(8)
O(4)	398(7)	2668(9)	7408(5)	C(33)	2089(10)	3349(15)	6094(10)
C(5)	−1301(8)	1251(10)	7578(5)	C(34)	2026(11)	4196(14)	6260(7)
O(5)	−1532(7)	1697(8)	7910(4)	C(35)	1308(12)	4551(12)	6324(6)
C(6)	−1498(7)	−475(10)	7328(5)	C(36)	652(8)	4042(10)	6231(6)
O(6)	−1821(7)	−1084(7)	7445(4)	C(39)	−682(6)	142(8)	6376(4)
C(7)	816(8)	664(9)	5988(6)	C(40)	−1205(5)	870(8)	6352(4)
O(7)	1411(6)	501(8)	5813(4)	C(41)	−2021(7)	868(8)	6141(5)
C(8)	−4(8)	214(11)	7433(6)	C(42)	−2648(7)	874(11)	6468(6)
O(8)	277(6)	31(11)	7818(4)	C(43)	−3396(8)	846(14)	6277(7)
C(9)	504(8)	−773(11)	6643(5)	C(44)	−3536(10)	831(13)	5769(8)
O(9)	1148(7)	−1142(8)	6768(6)	C(45)	−2934(10)	818(12)	5440(7)
				C(46)	−2176(8)	835(11)	5619(6)

References

1 A. J. Carty, *Pure Appl. Chem.*, 1982, **54**, 113; A. A. Cherkas, L. H. Randall, S. A. MacLaughlin, G. N. Mott, N. J. Taylor and A. J. Carty, *Organometallics*, 1988, **7**, 969; D. Nucciarone, S. A. MacLaughlin, N. J. Taylor, H. N. Paik and A. J. Carty, *Inorg. Chem.*, 1977, **16**, 1593.

2 F. V. Gastel, S. A. MacLaughlin, M. Lynch, A. J. Carty, E. Sappa, A. Tiripicchio and M. Tiripicchio Camellini, *J. Organomet. Chem.*, 1987, **326**, C65; J. Suades, F. Dahran and M. Mathieu, *Organometallics*, 1989, **8**, 842; M. H. A. Benvenutti, M. D. Vargas, D. Braga, F. Grepioni, E. Parisini and B. E. Mann, *Organometallics*, 1993, **12**, 2955.

3 M. H. A. Benvenutti, M. D. Vargas, D. Braga, F. Grepioni, B. E. Mann and S. Naylor, *Organometallics*, 1993, **12**, 2947.

4 B. J. Bobbie, N. J. Taylor and A. J. Carty, *J. Chem. Soc., Chem. Commun.*, 1991, 1511; E. Sappa, A. Pasquinelli, A. Tiripicchio and M. Tiripicchio Camellini, *J. Chem. Soc., Dalton Trans.*, 1989, 601.

5 M. D. Vargas, R. M. S. Pereira, D. Braga and F. Grepioni, *J. Chem. Soc., Chem. Commun.*, 1993, 1008.

6 R. S. Dickson and P. Fraser, *Adv. Organomet. Chem.*, 1974, **12**, 323.

7 H. A. Patel, A. J. Carty and N. K. Hota, *J. Organomet. Chem.*, 1973, **50**, 247.

8 C. J. Adams, M. I. Bruce, E. Horn, B. W. Skelton, E. R. T. Tiekink and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1993, 3313.

9 H. Lang, M. Leise and L. Zsolnai, *J. Organomet. Chem.*, 1991, **410**, 379.

10 J. J. Bonnet and R. Mathieu, *Inorg. Chem.*, 1978, **17**, 1973.

11 A. Meyer, A. Gorgues, Y. Le Floc'h, Y. Pineau, J. Guillevic and J. Y. Le Marouille, *Tetrahedron Lett.*, 1981, **22**, 5181.

12 R. P. Hughes, S. J. Doig, R. C. Hemond, W. L. Smith, R. E. Davis, S. M. Gadol and K. D. Holland, *Organometallics*, 1990, **9**, 2745.

13 A. K. Powell and M. J. Went, *J. Chem. Soc., Dalton Trans.*, 1992, 439.

14 A. J. Carty, S. A. MacLaughlin and D. Nucciarone, in *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis; Organic Compounds and Metal Complexes*, eds. J. G. Veilkampte and L. D. Quinn, VCH, New York, 1987, ch. 16.

15 E. Sappa, A. Tiripicchio, A. J. Carty and G. E. Toogood, *Prog. Inorg. Chem.*, 1987, **35**, 437.

16 L. F. Dahl and D. L. Smith, *J. Am. Chem. Soc.*, 1962, **84**, 2450.

17 G. Gervasio, R. Rossetti and P. L. Staghellini, *Organometallics*, 1985, **4**, 1612.

18 D. Osella, M. Ravera, C. Nervi, C. E. Housecroft, P. R. Raithby, P. Zanello and F. Laschi, *Organometallics*, 1991, **10**, 3253.

19 D. F. Jones, P. H. Dixneuf, A. Benoit and J. Y. Le Morouille, *J. Chem. Soc., Chem. Commun.*, 1982, 1217.

20 A. J. M. Caffyn, A. Martin, M. J. Mays, P. R. Raithby and G. A. Solan, *J. Chem. Soc., Dalton Trans.*, 1994, 609.

21 S. C. Bennett, A. Gelling and M. J. Went, *J. Organomet. Chem.*, 1992, **439**, 189.

22 SHELXTL PLUS program system (S 320), Nicolet Instrument Corporation, 1987; SHELXTL PLUS^{TM} program system, Siemens Analytical X-Ray Instruments, Madison WI, 1989.

23 G. M. Sheldrick, SHELXL 93, Program for refining crystal structures, University of Göttingen, 1993.

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