Reactions of P_2Ph_4 with Alkyne-bridged Dicobalt Carbonyl Complexes; Crystal Structures of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}\text{-}(\mu\text{-}P_2Ph_4)(CO)_4]$, $[Co_2\{\mu\text{-}PPh_2CHCPhC(O)\}(\mu\text{-}PPh_2)(CO)_4]$ and $[Co_2\{\mu\text{-}PPh_2C(O)CHCH\}(\mu\text{-}PPh_2)(CO)_3(PPh_3)]$†

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The reactions of P_2Ph_4 with a variety of substituted alkyne complexes $[Co_2(\mu\text{-}RC{\equiv}CR')(CO)_6]$ in toluene give the complexes $[Co_2(\mu\text{-}RC{\equiv}CR')(CO)_5(P_2Ph_4)]$ **1** (R = R' = CO_2Me **1a** or Ph **1b**; R = Ph, R' = H **1c** and $[Co_2(\mu\text{-}RC{\equiv}CR')(\mu\text{-}P_2Ph_4)(CO)_4]$ **2** (R = R' = Ph **2b**; R = Ph, R' = H **2c**. All three derivatives of type **1** are cleanly converted into **2** on thermolysis. An X-ray diffraction study of **2a** reveals a square-planar Co_2P_2 core with the symmetrical alkyne perpendicular to the Co–Co bond. Further thermolysis of complexes **2** produces $[Co_2(\mu\text{-}PPh_2CRCR')(\mu\text{-}PPh_2)(CO)_4]$ **3** (R = R' = CO_2Me **3a** or Ph **3b** and $[Co_2\{\mu\text{-}PPh_2CRCR'\text{-}C(O)\}(\mu\text{-}PPh_2)(CO)_4]$ **4c** (R = H, R' = Ph). The structure of **4c** has been determined by X-ray analysis. The $PPh_2CHCPhC(O)$ ligand forms a five-membered metallacyclic ring incorporating one Co atom and is π-bonded to the other Co atom. Complexes **3a** and **3b** are partially converted into **4a** (R = R' = CO_2Me) and **4b** (R = R' = Ph) on treatment with CO. This reaction is reversed by heating **4a** and **4b** in solution or, more slowly, on standing at room temperature. The parent acetylene complex $[Co_2(\mu\text{-}HC{\equiv}CH)(CO)_6]$ reacts with P_2Ph_4 differently from the substituted derivatives to give as the principal product $[Co_2\{\mu\text{-}PPh_2\text{-}C(O)CHCH\}(\mu\text{-}PPh_2)(CO)_4]$ **5d**. The structure of the PPh_3 derivative of this complex, $[Co_2\{\mu\text{-}PPh_2\text{-}C(O)CHCH\}(\mu\text{-}PPh_2)(CO)_3(PPh_3)]$ **6d**, has been determined by X-ray diffraction.

The reaction of biphosphines (P_2R_4) (R = alkyl or aryl) with metal carbonyls was one of the earliest methods of obtaining complexes containing bridging phosphido groups ($\mu\text{-}PR_2$) and has proved to be one of the most successful.[1] In general, thermolytic reaction leads to cleavage of the phosphorus–phosphorus bond, giving bis(phosphido)-bridged complexes.[1–3] In some cases, however, under mild conditions, complexes containing intact P_2R_4 ligands have been isolated.[1,4,5]

The reaction of $\mu\text{-}PR_2$ complexes with alkynes can give rise to products containing new bridging ligands consisting of the phosphido group, the alkyne ligand and often one carbonyl group as well (if this is present in the original complex).[6,7] A possible alternative route to such products is the reaction of P_2R_4 with complexes containing bridging alkyne ligands[8] and in this paper we report the reactions of the biphosphine, P_2Ph_4, with alkynehexacarbonyldicobalt complexes of general formula $[Co_2(\mu\text{-}RC{\equiv}CR')(CO)_6]$ (R = R' = CO_2Me, Ph, or H; R = Ph, R' = H). The chemistry of the alkyne ligand itself in complexes of this type has been thoroughly studied[9] as has the substitution of terminal carbonyl groups, particularly by mono- and multi-dentate tertiary phosphine ligands.[10]

We now show that reaction of $[Co_2(\mu\text{-}RC{\equiv}CR')(CO)_6]$ (R = R' = CO_2Me, Ph or H; R = Ph, R' = H) with P_2Ph_4 can lead not only to carbonyl substitution but also to novel ligand transformations involving phosphorus–carbon and, in some cases, carbon–carbon bond formation (Scheme 1).

Results and Discussion

(1*a*) *Reaction of* $[Co_2(\mu\text{-}RC{\equiv}CR')(CO)_6]$ (R = R' = CO_2Me *or* Ph; R = Ph, R' = H) *with* P_2Ph_4.—Reaction of $[Co_2(\mu\text{-}RC{\equiv}CR')(CO)_6]$ (R = R' = CO_2Me or Ph; R = Ph, R' = H) with P_2Ph_4 at 318 K in toluene gives, in addition to unreacted starting material, the complexes $[Co_2(\mu\text{-}RC{\equiv}CR')(CO)_5\text{-}(P_2Ph_4)]$ (R = R' = CO_2Me **1a** or Ph **1b**; R = Ph, R' = H **1c** and $[Co_2(\mu\text{-}RC{\equiv}CR')(\mu\text{-}P_2Ph_4)(CO)_4]$ (R = R' = Ph **2b**; R = Ph, R' = H **2c**). Complex **2a** (R = R' = CO_2Me) is not obtained directly in the above reaction but is cleanly formed on thermolysis of $[Co_2(\mu\text{-}RC{\equiv}CR')(CO)_5(P_2Ph_4)]$ **1a** (R = R' = CO_2Me) (see below). All the complexes **1** and **2** have been characterised spectroscopically (see Table 1 and Experimental section) and the molecular structure of **2a** has been determined by X-ray diffraction.

The $^{31}P\text{-}\{^1H\}$ NMR spectra of complexes **1** are consistent with the presence of a terminal P_2Ph_4 ligand. In each case two doublet resonances are observed, with large coupling constants [*J*(PP) *ca.* 315 Hz], indicative of one-bond phosphorus–phosphorus coupling. The lower-field resonance, which is appreciably broader than the higher-field resonance, is assigned to the phosphorus directly bonded to cobalt and the broadening of the signal is attributed to coupling to quadrupolar ^{59}Co.

The ^{13}C NMR spectra at 293 K of the symmetrical alkyne complexes **1a** and **1b** show two carbonyl resonances in an intensity ratio of 2:3. This suggests that the three carbonyl ligands residing on the unsubstituted cobalt atom are fluxional at 293 K. The ligands on the P-substituted cobalt could also be

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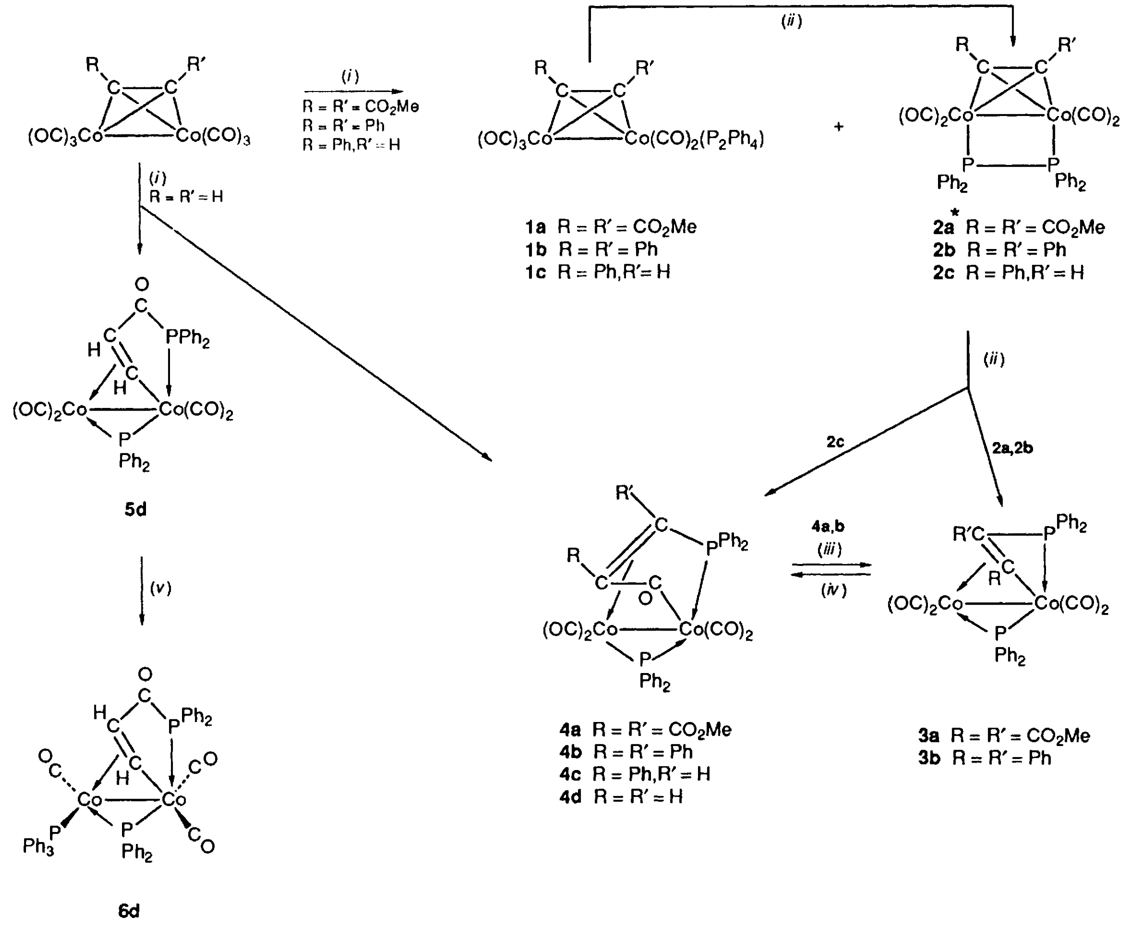
[†] μ-1(η^2):2(η^2)-Dimethyl acetylenedicarboxylate-μ-tetraphenyl-diphosphane-1κ*P*:2κ*P'*-bis(dicarbonylcobalt) (*Co–Co*), μ-diphenyl-phosphido-μ-2(2,3-η)-3-diphenylphosphino-1κ*P*-2-phenylprop-2-enoyl-1κC^1-bis(dicarbonylcobalt) (*Co–Co*), and tricarbonyl-1κ^2*C*,-2κ*C*-μ-diphenylphosphido-μ-2(1,2-η)-3-diphenylphosphino-1κ*P*-3-oxoprop-1-enyl-1κC^1-triphenylphosphine-2κ*P*-dicobalt (*Co–Co*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii xxii.



Scheme 1 Products from the reaction of $[Co_2(\mu\text{-}RC{\equiv}CR')(CO)_6]$ with P_2Ph_4 (*i*) P_2Ph_4, heat; (*ii*) heat; (*iii*) N_2, heat or standing in solution; (*iv*) CO, heat; (*v*) PPh_3, heat. * In this case further heating of the initially isolated **1a** is necessary

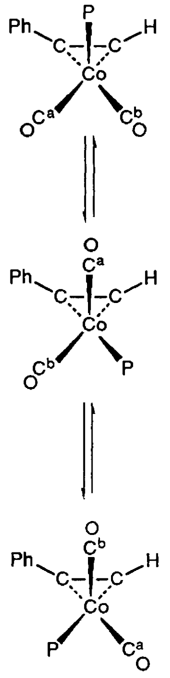


Fig. 1 Proposed fluxional process for the P_2Ph_4-substituted Co atom in complex **1c**; P = P_2Ph_4

fluxional or, alternatively, they could be non-fluxional but with the biphosphine ligand substituted in a pseudo-axial position. A ^{13}C NMR study on the compounds $[Co_2(\mu\text{-}RC{\equiv}CR')(CO)_5L]$ (R = R′ = H, L = $AsPh_3$ or $PPhEt_2$; R = R′ = Ph, L = PPh_3; R = H, R′ = Bu^t, L = $PPhEt_2$) also showed two carbonyl resonances with integrated intensities of 2:3.[11] In this case localised site exchange of the carbonyls around each cobalt atom was proposed. In contrast, the spectrum at 293 K of the unsymmetrical phenylacetylene complex **1c** (R = Ph, R′ = H) shows three CO peaks with integrated intensities 1:1:3. This implies that the two carbonyls residing on the substituted cobalt atom are inequivalent. This result is inconsistent with localised site exchange of these two carbonyl ligands. The ligands on the substituted cobalt atom are thus either non-fluxional at 293 K or, alternatively, a fluxional process can be invoked, involving a series of twists of the three ligands (Fig. 1). Such a process does not render the two carbonyl ligands equivalent. We are not able to distinguish between these two possibilities.

(*b*) *Thermolysis of* $[Co_2(\mu\text{-}RC{\equiv}CR')(CO)_5(P_2Ph_4)]$ **1** *and X-Ray Analysis of* $[Co_2(\mu\text{-}RC{\equiv}CR')(\mu\text{-}P_2Ph_4)(CO)_4]$ **2a** (R = R′ = CO_2Me).—Thermolysis of the terminal biphosphine complexes **1a**–**1c** at 323–333 K in toluene produces the corresponding biphosphine bridged complexes **2a**–**2c** in 60–80% yields. The few metal–metal bonded biphosphine-bridged complexes reported previously include $[Fe_2(\mu\text{-}CHR)(\mu\text{-}P_2Ph_4)(NO)_4]$ (R = H or Me)[12] and $[Fe_2(\mu\text{-}P_2Me_4)(\mu\text{-}PMe_2)_2(CO)_4]$.[13]

The molecular structure of complex **2a** (R = R′ = CO_2Me) has been determined by a single-crystal X-ray diffraction study. The structure is illustrated in Fig. 2 Table 2 lists selected bond distances and angles and atomic coordinates are given in Table 5.

The two $Co(CO)_2$ groups in **2a** are bridged both by a dmad (dmad = dimethyl acetylenedicarboxylate) and a tetraphenylbiphosphine ligand (Fig. 2). As with $[Co_2\{\mu\text{-}RC{\equiv}CR'\}(CO)_6]$[14] (R = R′ = CO_2Me) a 'sawhorse' geometry is observed. The

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

Compound	$\nu(CO)^a$/cm^{-1}	^{1}H NMR^b (δ)
1a $[Co\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_5(P_2Ph_4)]$	2081s, 2035s, 2022s, 1994m, 1702m	7.5–7.1 (m, 20 H, Ph) 3.34 (s, 6 H, Me)
1b $[Co_2(\mu\text{-}PhC{\equiv}CPh)(CO)_5(P_2Ph_4)]$	2058s, 2011s, 1999m^c	7.5–6.9 (m, 30 H, Ph)
1c $[Co_2(\mu\text{-}PhC{\equiv}CH)(CO)_5(P_2Ph_4)]$	2064s, 2016s, 2006s, 1973m	7.5–7.0 (m, 25 H, Ph) 5.22 [d, 1 H, ^3J(PH) 4.2, CH]
2a $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(\mu\text{-}P_2Ph_4)(CO)_4]$	2045m, 2020s, 1993m, 1701w^c	7.5–7.1 (m, 20 H, Ph) 3.80 (s, 6 H, Me)
2b $[Co_2(\mu\text{-}PhC{\equiv}CPh)(\mu\text{-}P_2Ph_4)(CO)_4]$	2022m, 1994s, 1966m^c	7.6–7.0 (m, 30 H, Ph)
2c $[Co_2(\mu\text{-}PhC{\equiv}CH)(\mu\text{-}P_2Ph_4)(CO)_4]$	2028m, 2003s, 1976m, 1962w	7.8–7.1 (m, 25 H, Ph) 5.69 [t, 1 H, ^3J(PH) 3.2, CH]
3a $[Co_2\{\mu\text{-}PPh_2C(CO_2Me)C(CO_2Me)\}(\mu\text{-}PPh_2)(CO)_4]$	2028s, 2003s, 1993m, 1706m	8.2–7.1 (m, 20 H, Ph) 3.55 (s, 3 H, Me) 3.09 (s, 3 H, Me)
3b $[Co_2(\mu\text{-}PPh_2CPhCPh)(\mu\text{-}PPh_2)(CO)_4]$	2027w, 2001s, 1983m, 1961w^c	8.2–7.1 (m, 30 H, Ph)
4a $[Co_2\{\mu\text{-}PPh_2C(CO_2Me)C(CO_2Me)C(O)\}(\mu\text{-}PPh_2)(CO)_4]$	2060m, 2037s, 2020m, 1998w, 1704w, 1637w, 1606w^c	8.1–7.3 (m, 20 H, Ph) 3.67 (s, 3 H, Me), 3.50 (s, 3 H, Me)
4b $[Co_2\{\mu\text{-}PPh_2CPhCPhC(O)\}(\mu\text{-}PPh_2)(CO)_4]$	2049m, 2015s, 1973m, 1638w	8.3–7.1 (m, 30 H, Ph)
4c $[Co_2\{\mu\text{-}PPh_2CHCPhC(O)\}(\mu\text{-}PPh_2)(CO)_4]$	2048m, 2019s, 2010 (sh), 1978m, 1661w	8.2–6.8 (m, 25 H, Ph) 5.23 [dd, 1 H, ^2J(PH) 2.5, ^3J(P′H) 2.5, PPh$_2$C*H*]^d
4d $[Co_2\{\mu\text{-}PPh_2CHCHC(O)\}(\mu\text{-}PPh_2)(CO)_4]$	2048m, 2016s, 2007 (sh), 1976m, 1664w	8.3–7.2 (m, 20 H, Ph) 4.68 [ddd, ^3J(HH) 4.7, ^2J(PH) 2.7, ^3J(P′H) 2.7, 1 H, PPh$_2$C*H*] 4.07 [dd, ^3J(PH) 40.7, 1 H, PPH$_2$CHC*H*]
5d $[Co_2\{\mu\text{-}PPh_2C(O)CHCH\}(\mu\text{-}PPh_2)(CO)_4]$	2044m, 2016s, 2003m, 1978m, 1638w	7.9–7.3 (m, 20 H, Ph) 6.10 [ddd, 1 H, ^3J(PH) 19.7, ^3J(HH) 4.5, ^3J(P′H) 2.1, C(O)CHC*H*] 4.77 [ddd, 1 H, ^3J(PH) 40.7, ^3J(P′H) 4.6, C(O)CH]
6d $[Co_2\{\mu\text{-}PPh_2C(O)CHCH\}(\mu\text{-}PPh_2)(CO)_3(PPh_3)]$	2028s, 1987s, 1947m, 1579m^c	7.9–6.9 (m, 35 H, Ph) 5.29 [dd, 1 H, ^3J(PH) 20.7, ^3J(HH) 4.2, C(O)CHC*H*] 3.94 [dddd, 1 H, ^3J(PH) 40.2, ^3J(P′H) 10.8, ^3J(P″H) 4.6, C(O)CH]^e

[a] Infrared spectrum recorded in hexane solution unless otherwise indicated. [b] Chemical shifts (δ) in ppm, coupling constants in Hz, recorded in CD_2Cl_2 unless otherwise indicated. [c] Recorded in CH_2Cl_2 solution. [d] Recorded in $CDCl_3$ solution. [e] Recorded in $(CD_3)_2SO$ solution.

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

Co(1)–Co(2)	2.452(1)	Co(1)–P(1)	2.224(1)
Co(2)–P(2)	2.232(1)	P(1)–P(2)	2.254(2)
C(5)–C(6)	1.370(6)	Co(1)–C(5)	1.961(5)
C(7)–O(5)	1.202(6)	Co(1)–C(6)	1.937(5)
C(7)–O(6)	1.334(7)	Co(2)–C(5)	1.951(5)
O(6)–C(8)	1.450(7)	Co(2)–C(6)	1.947(5)
C(6)–C(9)	1.458(7)	O(8)–C(10)	1.469(7)
C(9)–O(7)	1.176(6)	C(9)–O(8)	1.251(6)
Co–C(carbonyl)	1.775(6)–1.809(6)		
C–O(carbonyl)	1.122(6)–1.136(6)		
P–C(phenyl)	1.810(4)–1.823(4)		
Co(2)–Co(1)–P(1)	87.3(1)	C(11)–P(1)–C(17)	105.8(2)
Co(1)–Co(2)–P(2)	87.3(1)	C(23)–P(2)–C(29)	103.9(2)
Co(1)–P(1)–P(2)	92.6(1)	C(6)–C(5)–C(7)	130.7(5)
Co(2)–P(2)–P(1)	92.2(1)	C(5)–C(6)–C(9)	136.0(4)

bridging alkyne ligand in **2a** lies almost perpendicular (within *ca.* 1°) to the cobalt–cobalt bond. If the methyl carboxylate and phenyl groups are ignored, the framework of the molecule possesses a plane of symmetry containing C(5) and C(6) and cutting through the midpoints of the Co–Co and P–P bonds.

An interesting feature of this structure is that Co–P–P–Co ring forms an almost perfect square (this contrasts with the puckered Fe–P–P–Fe ring observed for $[Fe_2(\mu\text{-}CH_2)(\mu\text{-}P_2Ph_4)(NO)_4]$.[12] The four atoms are coplanar and the two Co–P bond lengths are almost identical within experimental error [Co(1)–P(1) 2.224(1) and Co(2)–P(2) 2.232(1) Å]. The P–P bond distance is similar to both of the Co–P bond distances at 2.254(2) Å and it is only the length of the Co–Co bond [2.452(1) Å] that marginally causes distortion from perfect square geometry. This distortion is reflected in the two bond angles at cobalt, P(1)–Co(1)–Co(2) and P(2)–Co(2)–Co(1) which, at 87.3(1)° each, are less than those at phosphorus, P(2)–P(1)–Co(1) 92.6(1)° and P(1)–P(2)–Co(2) 92.2(1)°. The P–P bond of the bridging diphosphine is considerably longer than that observed in $[Fe_2(\mu\text{-}CH_2)(\mu\text{-}P_2Ph_4)(NO)_4]$ [P–P 2.179(1) Å],[12] and lies just outside the previously suggested range for phosphines containing P–P bonds, 2.17–2.24 Å.[15] The midpoints of the C(5)–C(6), Co–Co and P–P bonds form an angle of *ca.* 130°. A similar situation was reported for $[Co_2(\mu\text{-}PhC{\equiv}CPh)(\mu\text{-}dppm)(CO)_4]$ (dppm = $Ph_2PCH_2PPh_2$), where the dppm ligand lies equatorial relative to the alkyne.[16] The pseudo-equatorial carbonyls, CO(2) and CO(3) (Fig. 2) which are *trans* to one of the alkyne carbon atoms, C(5), have slightly longer Co–C distances [1.809(6) and 1.804(6) Å respectively] than those of the pseudo-axial carbonyls, CO(1) and CO(4)

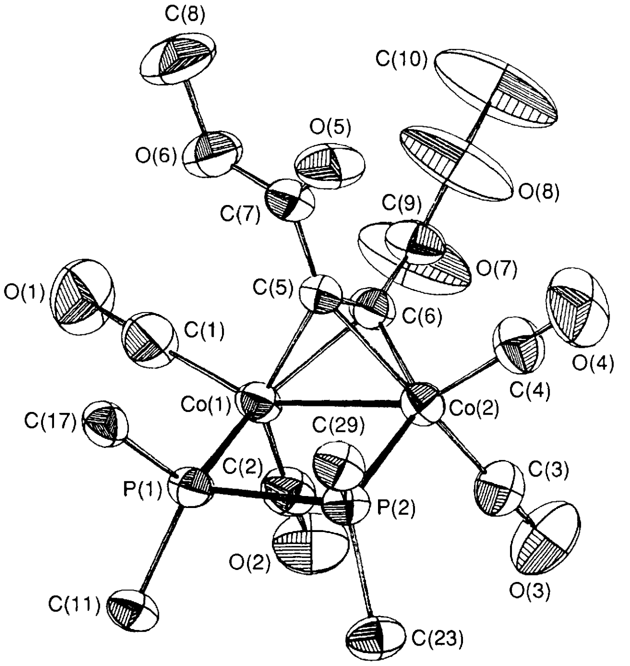


Fig. 2 Molecular structure of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(\mu\text{-}P_2Ph_4)(CO)_4]$ **2a** including the atom numbering scheme

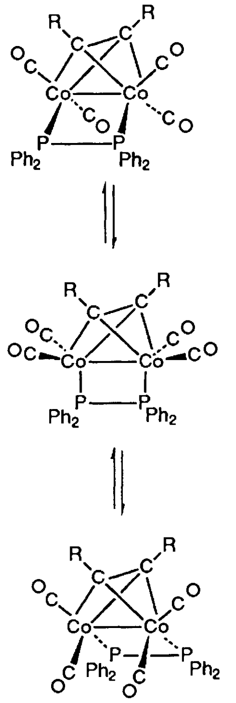


Fig. 3 Proposed fluxional process for the complexes **2**

[1.775(6) and 1.783(6) Å]. It appears from Fig. 2 that one of the methyl carboxylate groups [C(10)–O(8)–C(9)–O(7)] has an appreciable torsional freedom around the C(6)–C(9) bond as shown by the extension and preferential orientation of the anisotropic displacement parameters.

The ^{13}C NMR spectra of the symmetrical alkyne complexes **2a** and **2b** (R = R′ = CO_2Me or Ph) show just one singlet in the carbonyl region. This observation is in accord with the spectra of the dppm-bridged complex $[Co_2\{\mu\text{-}C_2(CF_3)_2\}(\mu\text{-}dppm)(CO)_4]$ which also shows only one carbonyl resonance.[10c]

In the complexes **2** the biphosphine ligand must be constrained to pseudo-equatorial positions on the same side of the molecule. An attempt by either or both phosphorus atoms to occupy a pseudo-axial position would confer too much strain on the relatively inflexible P_2Ph_4 ligand. For the same reason an arrangement with each phosphorus residing in pseudo-equatorial positions on opposite sides of the molecule is untenable. Accordingly the singlet carbonyl ^{13}C NMR signal must signify that the molecule is fluxional, since in a non-fluxional situation two equal-intensity resonances would be expected, one corresponding to the pseudo-axial and the other to the pseudo-equatorial carbonyls. Two possible fluxional processes can be envisaged for **2a** and **2b**, both of which account for the observed spectra. The first involves localised carbonyl exchange on each cobalt, with the biphosphine remaining static. The second is a variation on the process mentioned previously in connection with complex **1**, namely a series of twists of the biphosphine and carbonyl ligands. For the complexes **2** however, a complete 360° rotation of these ligands is impossible, due to unfavourable steric interactions between the bridging alkyne and bridging biphosphine ligands. The second mechanism, if operative, must therefore only involve alternate clockwise and anticlockwise rotations of approximately 120° (Fig. 3). In other words the phosphorus atoms of the biphosphine ligand can only rotate from one pseudo-equatorial site to the other, without being able to occupy a pseudo-axial position. Such a rotation enables each carbonyl ligand to alternate between a pseudo-axial position and one of the pseudo-equatorial positions (Fig. 3).

A distinction between the two possible mechanisms can be made in the case of the unsymmetrical alkyne complex **2c** (R = Ph, R′ = H) which exhibits two singlet carbonyl ^{13}C NMR signals of equal intensity. This observation provides conclusive evidence that the localised carbonyl site-exchange mechanism is inoperative at 293 K, since, if it were, only one singlet carbonyl resonance would be expected. The spectrum is, of course, compatible with **2c** being non-fluxional but this seems unlikely in view of the fluxionality of **2a** and **2b**. Accordingly, the limited twist mechanism (Fig. 3), which accounts for the observed spectra of all three complexes, is almost certainly operative in each case.

(*c*) *Thermolysis of* $[Co_2(\mu\text{-}RC{\equiv}CR')(\mu\text{-}P_2Ph_4)(CO)_4]$ **2** *and X-Ray Analysis of* $[Co_2\{\mu\text{-}PPh_2CHCPhC(O)\}(\mu\text{-}PPh_2)(CO)_4]$ **4c**.—The thermolysis of complexes **2** was explored to see whether P–P bond cleavage could be induced. As previously discussed the scission of the P–P bond of biphosphines, upon vigorous thermolysis with metal carbonyls, is well documented.[1–3,17] In particular the alkylidene, biphosphine-bridged complexes $[Fe_2(\mu\text{-}CHR)(\mu\text{-}P_2Ph_4)(NO)_4]$ (R = H or Me) were found to undergo P–P cleavage under thermolysis, isomerising to produce the compounds $[Fe_2(\mu\text{-}PPh_2CHR)(\mu\text{-}PPh_2)(NO)_4]$.[12]

Thermolysis of **2a** (R = R′ = CO_2Me) at 363 K and **2b** (R = R′ = Ph) at 328 K in toluene gave the compounds $[Co_2(\mu\text{-}PPh_2CR'CR)(\mu\text{-}PPh_2)(CO)_4]$ (R = R′ = CO_2Me **3a** or Ph **3b**) in 70–80% yields. Thermolysis of **2c** at 333 K gave the complex $[Co_2\{\mu\text{-}PPh_2CR'CRC(O)\}(\mu\text{-}PPh_2)(CO)_4]$ **4c** (R = Ph, R′ = H) in 80% yield (Scheme 1). Complexes **3** and **4c** have been characterised by IR, ^1H, ^{13}C and ^{31}P NMR spectroscopy, mass spectrometry and microanalysis. The molecular structure of complex **4c** has also been determined by an X-ray diffraction study. In addition to **3b**, traces of a red complex were noted in the thermolysis of **2b**. This red complex was obtained in higher yield from the carbonylation of **3b** (see below) and characterised spectroscopically as $[Co_2\{\mu\text{-}PPh_2CR'CRC(O)\}(\mu\text{-}PPh_2)(CO)_4]$ **4b** (R = R′ = Ph). The mass spectrum of **3a** (R = R′ = CO_2Me) shows a molecular ion peak at m/z 742 with four successive carbonyl losses. This is in accord with **2a** and **3a** both possessing four carbonyl ligands and having the same molecular weight. The ^1H NMR spectrum of **3a** indicates that the methyl groups are inequivalent, while the $^{31}P\text{-}\{^1H\}$ NMR spectrum shows two doublet resonances with J(PP) 100 Hz. The lower-field signal at δ 29.2 [relative to $P(OMe)_3$ (δ 0.0)] is consistent with a phosphido bridge. The higher-field signal at δ −173.1 is typical of a μ-phosphido group combined with an

Table 3 Selected bond distances (Å) and angles (°) for complex **4c** in the two independent molecules **1** and **2**

Co(1)–Co(2)	2.519(3)	2.508(3)
Co(1)–P(1)	2.216(5)	2.209(4)
Co(1)–P(2)	2.176(5)	2.184(5)
Co(2)–P(2)	2.154(5)	2.176(4)
Co(2)–C(5)	2.07(2)	2.05(2)
Co(2)–C(6)	2.09(1)	2.06(1)
Co(1)–C(7)	1.98(1)	1.99(2)
C(5)–C(6)	1.42(2)	1.45(2)
C(6)–C(7)	1.50(2)	1.52(2)
C(6)–C(8)	1.50(2)	1.47(2)
C(7)–O(5)	1.22(1)	1.20(2)
P(1)–C(5)	1.79(2)	1.78(2)
Co–C(carbonyl)	1.71(2)–1.83(2)	
C–O(carbonyl)	1.11(2)–1.18(2)	
P–C(phenyl)	1.79(1)–1.84(1)	
Co(1)–P(1)–C(5)	95.5(6)	94.8(5)
Co(1)–P(2)–Co(2)	71.1(2)	70.2(1)
P(1)–C(5)–C(6)	110(1)	111(1)
C(5)–C(6)–C(7)	115(1)	112(1)
C(6)–C(7)–Co(1)	110(1)	110(1)

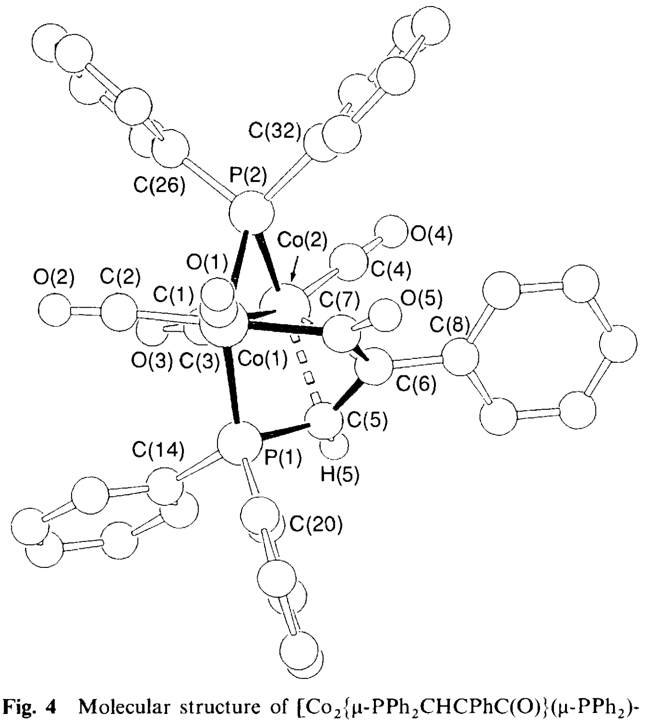


Fig. 4 Molecular structure of $[Co_2\{\mu\text{-}PPh_2CHCPhC(O)\}(\mu\text{-}PPh_2)(CO)_4]$ **4c** including the atom numbering scheme

alkyne such that it is part of a four-membered P–C–C–M metallacyclic ring.[6,7,18,19] The ^{13}C NMR spectrum of **3a** confirms that the CO_2Me groups are inequivalent. A resonance at δ 44.3 with *J*(PC) 41 and *J*(P′C) 8 Hz is assigned to the $P\mathit{C}(CO_2Me)C(CO_2Me)$ carbon while another resonance at δ 108.4 with *J*(PC) = *J*(P′C) = 30 Hz is assigned to the $PC(CO_2Me)\mathit{C}(CO_2Me)$ carbon. In the carbonyl region of the spectrum four separate signals are observed corresponding to four inequivalent carbonyl ligands, implying that **3a** is non-fluxional at room temperature. Complex **3b** is assigned an analogous structure to **3a** on the basis of spectroscopic data (see Table 1 and Experimental section).

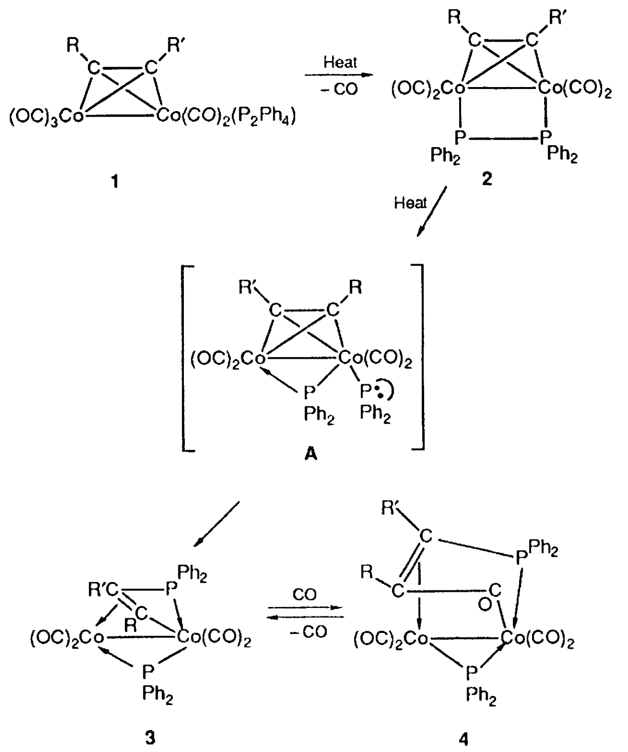
The structure of complex **4c** is shown in Fig. 4. Table 3 lists selected bond lengths and bond angles and atomic coordinates are given in Table 6. Because of the presence of two independent molecules in the unit cell the average values of the most relevant structural parameters will be used throughout the following discussion; bond lengths and angles are listed separately for the two molecules 1 and 2 in Table 3. The only appreciable difference between the two molecular units arises from the orientation of the phenyl groups.

In complex **4c** the two Co atoms are bridged by a diphenylphosphido ligand, while one Co atom [Co(1) in Fig. 4] is incorporated in a five-membered Co–P–C=C–C metallacyclic ring, whose unsaturated C–C bond is η^2-co-ordinated to the second Co atom [Co(2)]. The two Co and the two P atoms are strictly coplanar [maximum deviation from mean plane 0.009 Å for Co(1)], while the P–C=C–C system is folded so as to make the Co–Co and the C=C axes almost perpendicular. The electron distribution over the two Co atoms appears to be uneven, with Co(1) formally receiving three electrons from the Co–P and Co–C(O) σ interaction and Co(2) receiving two electrons from the π interaction with the C=C system. This is accompanied by a slight asymmetry of the Co–P(phosphido)–Co bridge with the Co–P distance being shorter for the η^2-co-ordinated Co atom than for the P-bound one [2.165(5) *vs.* 2.180(6) Å]. The Co–Co distance [2.513(3) Å] is longer than in **2a** [2.452(1) Å], falling in the upper range of values observed for single Co–Co bond distances in similar compounds.[16,19]

The Co–C(O) σ interaction is only slightly shorter than the Co–C(alkene) π interaction [1.99(2) *versus* 2.07(2) Å]. These latter bond distances are notably longer than the corresponding bonds in $[(C_5H_5Co)_2\{\mu\text{-}\eta^4\text{-}PMe_2C(CO_2Me)=C(CO_2Me)PMe_2\}]$[1.971(5) Å], while the C=C bond lengths are comparable [1.43(2) in **4c** *versus* 1.452(7) Å]. As in **2a**, the pseudo-axial carbonyls [C(1) and C(4)] show shorter Co–C distances [1.75(3) Å] than the pseudo-equatorial ones [1.81(1) Å]. The four metal-bonded atoms, P(1)–C(5)–C(6)–C(7), of the $\mu\text{-}PPh_2CHCPhC(O)$ ligand are coplanar and this plane forms an approximately 50° angle with the plane passing through the P(1)–Co(1)–C(7) atoms. There is no appreciable difference between the P–C(alkene) and the P–C(phenyl) distances. The values of the P–C=C and C=C–C angles [111(1) and 112(1)°], as well as those of the Co–C(O)–C and Co–P–C ones [110(1) and 94.8(5)°], are clearly indicative of a tense steric situation within the Co–P–C=C–C ring.

The spectroscopic properties of complex **4c** are in accordance with the solid-state structure being maintained in solution, with a weak IR band at 1661 cm^{-1} being assigned to ν(C=O) of the five-membered metallacyclic ring. In the $^{31}P\text{-}\{^1H\}$ NMR spectrum a broad resonance at δ 15.5 is diagnostic of a phosphido-bridging ligand, whilst a similarly broad resonance at δ −98.2 is consistent with the second phosphorus atom being part of a five-membered metallacyclic ring rather than a four-membered ring, for which a higher-field signal would have been expected.[6,7,18–20] In the ^{13}C NMR spectrum only three broad signals are observed which can be assigned to terminal CO ligands, and it must be assumed that the resonances due to two of these groups coincide. A slightly sharper singlet carbonyl resonance at lower field is assigned to the CO of the metallacyclic ring. The $PPh_2CH\mathit{C}PhC(O)$ carbon appears as a doublet, ^2J(PC) 33 Hz at δ 86.4, whilst the $PPh_2\mathit{C}HCPhC(O)$ carbon resonance is a doublet of doublets, ^1J(PC) 42, ^2J(P′C) 6 Hz, at δ 41.8. The correct assignment of these two carbon resonances was confirmed by an attached-proton test experiment.

The proposed mechanism for the formation of complexes **3** and **4** is illustrated in Scheme 2. The first step in the thermolysis of **2** is likely to involve cleavage of the relatively weak P–P bond of the biphosphine to give an intermediate **A** containing a terminal phosphido group. Similar intermediates leading to the generation of four-membered metallacyclic rings have been postulated previously in related systems.[18] With the symmetrical alkynes, R = R′ = CO_2Me or Ph, phosphorus–carbon bond formation between the terminal phosphido group and the alkyne in **A** could then give **3**. With the unsymmetrical alkyne, R = Ph,



Scheme 2 Proposed mechanism for the formation of complexes **3** and **4** on thermolysis of $[Co_2(\mu\text{-}RC{\equiv}CR')(\mu\text{-}P_2Ph_4)(CO)_4]$

R′ = H, phosphide–alkyne coupling must occur regioselectively at the CH carbon, since the ^{1}H NMR spectrum of **4c** provides no evidence for the formation of a second isomer incorporating a $\mu\text{-}PPh_2CPhCHC(O)$ ligand. This may be because, for the unsymmetrical alkyne, attack of the terminal PPh_2 group in intermediate **A** is sterically more favourable at the carbon atom bearing the H rather than the phenyl substituent.

Complex **4c** could conceivably be formed *via* the insertion of CO into the cobalt–carbon bond of the four-membered metallacyclic ring in an intermediate complex of type **3**. No trace of a complex of this type was identified in the thermolysis of **2c** which leads to **4c**, but complexes **3a** and **3b** were partially converted into **4a** and **4b** respectively on treatment with CO in toluene at 323–343 K. After 6 h *ca.* 10% of **4a** and 18% of **4b** had been formed; heating for longer periods did not increase these yields. The reaction was completely reversed when **4a** and **4b** were refluxed in CH_2Cl_2 or allowed to stand at room temperature (r.t.) for prolonged periods, the formation of **3b** from **4b** being noticeably more rapid than that of **3a** from **4a** under these latter conditions.

Although the above results suggest that complex **4c** may be formed *via* the rapid carbonylation of an unstable intermediate, **3c**, this remains unproven and the reaction of $[Co_2(\mu\text{-}HC{\equiv}CH)(CO)_6]$ with P_2Ph_4 (see below) suggests a possible alternative route.

(*d*) *Reaction of* $[Co_2(\mu\text{-}HC{\equiv}CH)(CO)_6]$ *with* P_2Ph_4.—Reaction of $[Co_2(\mu\text{-}HC{\equiv}CH)(CO)_6]$ with P_2Ph_4 at 313 K in toluene for 24 h gave, in addition to unreacted starting material, the complexes $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$,[21] $[Co_3(\mu\text{-}PPh_2)_3(CO)_6]$,[21] $[Co_2\{\mu\text{-}PPh_2CHCHC(O)\}(\mu\text{-}PPh_2)(CO)_4]$ **4d** (2% yield) and $[Co_2\{\mu\text{-}PPh_2C(O)CHCH\}(\mu\text{-}PPh_2)(CO)_4]$ **5d** 26% yield).

Complex **4d** was characterised by IR, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, mass spectrometry and microanalysis. On the basis of these data **4d** is assigned an analogous structure to **4c**. In the ^{1}H NMR spectrum the $PPh_2CHCH(O)$ proton occurs as a doublet of doublets centred at δ 4.07 [$^3J(PH)_{trans}$ 40.1 Hz and $^3J(HH)$ 4.7 Hz] whereas the $PPh_2CHCHC(O)$ proton resonance is observed as a doublet of doublets of doublets centred at δ 4.68 [$J(PH) = J(P'H) = 2.7$ Hz].

The main product of the reaction of $[Co_2(\mu\text{-}HC{\equiv}CH)(CO)_6]$ with P_2Ph_4, compound **5d**, has been characterised by IR, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, mass spectrometry and microanalysis. In addition the PPh_3-substituted derivative of **5d**, complex **6d**, has been the subject of a single-crystal X-ray crystallographic determination.*

The mass spectrum of complex **5d** shows a molecular ion peak at *m/z* 654 with peaks corresponding to the successive loss of five carbonyl ligands. The IR spectrum of **5d** in hexane shows four terminal ν_{CO} absorption bands. An absorption at lower wavenumber (1638 cm^{-1}) is attributed to the presence of an inserted carbonyl in the form of a $\mu\text{-}PPh_2C(O)CHCH$ ligand. This compares with a band at 1625 cm^{-1} due to the inserted carbonyl ligand in $[RuCo\{\mu\text{-}PPh_2C(O)CHCH\}(\mu\text{-}CO)(CO)_5]$.[6b] In the ^{31}P-{^{1}H} NMR spectrum of **5d** two doublets are observed. The low-field signal at δ 29.8 [$^2J(PP)$ 86 Hz] is assigned to a $\mu\text{-}PPh_2$ ligand. The high-field signal at δ −75.9 is consistent with a PPh_2 fragment inserted such that it forms part of a five-membered metallacyclic ring. The ^{1}H NMR spectrum shows, in addition to phenyl resonances integrating as twenty protons, two doublets of doublets of doublets integrating as one proton each. A low-field signal at δ 6.10 with $^3J(PH)$ 19.7, $^3J(HH)$ 4.5 and $^3J(P'H)$ 2.1 Hz is assigned to the $PPh_2C(O)CHCH$ proton. The other resonance at δ 4.77 with $^3J(P'H)$ 4.6 Hz and a large $^3J(PH)_{trans}$ 40.7 Hz, is assigned to the $PPh_2C(O)CHCH$ proton. The assignment of the H–H coupling was confirmed by a homonuclear decoupling experiment. Dixneuf and co-workers[6b] also observed a pattern of low-field shift, small $^3J(PH)$ for $PPh_2C(O)CRCH$ protons and high-field shift, large $^3J(PH)$ for $PPh_2C(O)CHCR$ protons in ^{1}H NMR spectra of the complexes $[RuCo\{\mu\text{-}PPh_2C(O)CRCR'\}(\mu\text{-}CO)(CO)_5]$ (R = H, R′ = Ph, Bu^t or H; R = SiMe$_3$, R′ = H). The presence of the inserted carbonyl ligand was confirmed by ^{13}C NMR spectroscopy, with a resonance being observed at δ 189.9 [$^2J(PC)$ 36 Hz].

Clearly the reaction of the parent acetylene-bridged dicobalt complex $[Co_2(\mu\text{-}HC{\equiv}CH)(CO)_6]$ with P_2Ph_4 follows a different pathway to that of its dmad, diphenyl- and phenylacetylene homologues. The major product of the reaction, complex **5d**, is obtained under milder conditions than those required to generate **3** and **4** in the analogous reactions using substituted alkynes. This suggests that a species of type **2**, $[Co_2(\mu\text{-}HC{\equiv}CH)(\mu\text{-}P_2Ph_4)(CO)_4]$ **2d**, is unlikely to be an intermediate in the formation of **5d**. The proposed mechanism for the formation of **5d** is illustrated in Scheme 3. The first step in the reaction is presumably the substitution of a CO group by P_2Ph_4, to give an imtermediate analogous to **1**. A possible second step would involve CO insertion into the alkyne ligand allowing co-ordination of the second phosphorus atom to give an intermediate **A** (Scheme 3) with $\mu\text{-}CHCHC(O)$ and $\mu\text{-}P_2Ph_4$ ligands. Three bonding modes have been reported for $\mu\text{-}CRCRC(O)$ ligands at a dinuclear centre, namely $\mu\text{-}\eta^2{:}\eta^2$ [22–24] and $\mu\text{-}\sigma{:}\eta^3$ [25–28] modes in which the ligand is a four-electron donor, and a $\mu\text{-}\sigma{:}\sigma$ mode[29] in which it is a two-electron donor. Although any of these modes are possible for the ligand in **A** the $\mu\text{-}\eta^2{:}\eta^2$ mode is preferred in Scheme 3 since each cobalt atom then satisfies the effective atomic number (e.a.n.) rule without the requirement of dative Co→Co or multiple metal–metal bonds.

Plausible further steps in the mechanism (Scheme 3) are P–P bond cleavage to give **B** containing a $\mu\text{-}PPh_2$ and a terminal PPh_2 group. Insertion of this terminal phosphido group into the $CHCHC(O)$–M bond would then give **5d**. As indicated earlier this mechanism suggests a possible alternative route to the complexes **4** from that shown in Scheme 2, since insertion of the

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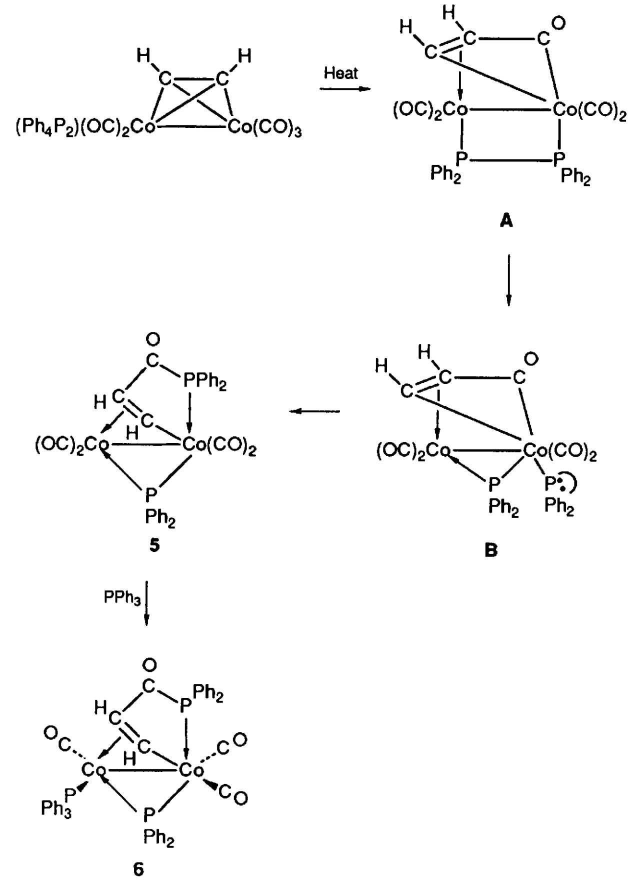
* Although crystals of **5d** itself were grown and X-ray diffraction data collected, the data could not be solved.



Scheme 3 Proposed mechanism for the reaction of $[Co_2(\mu\text{-}HC{\equiv}CH)(CO)_6]$ with P_2Ph_4

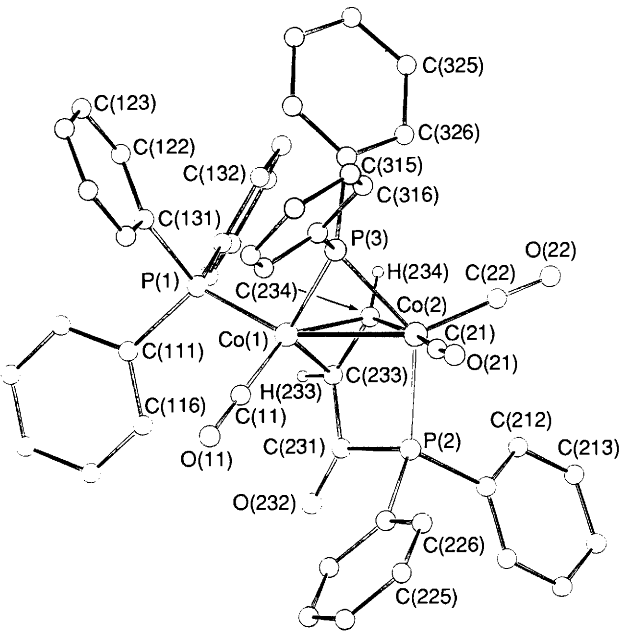


Fig. 5 Molecular structure of $[Co_2\{\mu\text{-}PPh_2C(O)CHCH\}(\mu\text{-}PPh_2)(CO)_3(PPh_3)\}]$ **6d** including the atom numbering scheme

terminal phosphido group in intermediate **B** (Scheme 3) into the M–CHCHC(O)M bond would also give a type **4** complex. Such a complex **4d** is obtained in low yield in the reaction of the parent acetylene complex with P_2Ph_4. Of the other products observed in this reaction, the previously reported bis(diphenylphosphido) complex $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$[21] is likely to be formed *via* loss of acetylene from $[Co_2(\mu\text{-}HC{\equiv}CH)(CO)_6]$, accompanied by oxidative addition of P_2Ph_4. The trinuclear complex $[Co_3(\mu\text{-}PPh_2)_3(CO)_6]$ is presumably formed through decomposition of light-sensitive $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$.[21] It should be noted that a pure sample of $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ reacts with HC≡CH at ambient temperature to give **4d** in near-quantitative yield[30] and hence the traces of **4d** formed in the reaction of $[Co_2(\mu\text{-}HC{\equiv}CH)(CO)_6]$ with P_2Ph_4 may alternatively arise in this way.

(*e*) *Synthesis and X-Ray Analysis of* $[Co_2\{\mu\text{-}PPh_2C(O)CHCH\}(\mu\text{-}PPh_2)(CO)_3(PPh_3)]$ **6d**.—Dixneuf and co-workers[6] have observed that, upon thermolysis, the ruthenium–cobalt complex $[RuCo\{\mu\text{-}PPh_2C(O)CRCR'\}(\mu\text{-}CO)(CO)_5]$ (R = Ph, R′ = Ph or C≡CPh; R = H, R′ = Ph or Bu^t) undergoes facile decarbonylation to generate $[RuCo(\mu\text{-}PPh_2CRCR')(\mu\text{-}CO)(CO)_5]$ with extrusion of the ketonic carbonyl groups. In contrast, thermolysis of a xylene solution of **5d** at 393 K for 3 d gives a low yield of $[Co_2\{\mu\text{-}PPh_2C(O)CHCH\}(\mu\text{-}PPh_2)(CO)_3(PPh_3)]$ **6d** as the only isolable product. Complex **6d** is obtained in higher yield from the reaction of **5d** with a slight excess of PPh_3 in toluene at 373 K and has been characterised by IR, ^1H and ^{31}P NMR spectroscopy, mass spectrometry and microanalysis. In order to determine unambiguously the position of substitution of the PPh_3 ligand and to confirm the proposed structure for **5d** a single-crystal X-ray diffraction study of **6d** was undertaken.

The molecular structure of **6d** is shown in Fig. 5. Selected bond lengths and angles are listed in Table 4 and atomic coordinates are given in Table 7. The two cobalt atoms are bridged by μ-PPh_2 and μ-$PPh_2C(O)CHCH$ ligands. The latter ligand is co-ordinated *via* phosphorus and C(234) and Co(2) to give an almost planar five-membered metallacyclic ring and it is additionally π bonded to Co(1) *via* C(233) and C(234), the alkyne-derived carbon atoms. The cobalt atoms are further ligated by one terminal CO and one PPh_3 [Co(1)] and two terminal CO groups [Co(2)]. The μ-$PPh_2C(O)CHCH$ ligand is attached such that the atoms P(2) and C(234) lie pseudo-*trans* and pseudo-*cis* respectively relative to the phosphido bridge (Fig. 5). In the ketophosphine unit the P(2)–C(231) distance of 1.857(7) Å is comparable to P–C(O) distances of 1.887(3) Å in $[RuCo\{\mu\text{-}PPh_2C(O)C(SiMe_3)CH\}(\mu\text{-}CO)(CO)_5]$,[6] 1.865(3) Å in $[RuCo\{\mu\text{-}PPh_2C(O)CPhCPh\}(\mu\text{-}CO)(CO)_5]$[6] and 1.918(6) Å in $[Fe_2\{\mu\text{-}PPh_2C(O)C(Bu^t)CC(CO_2Et)C(CO_2Et)\}(CO)_5]$.[31] The latter two complexes undergo facile P–C(O) bond cleavage reactions upon thermolysis, whereas in the present work attempts to cleave the P–C(O) bonds in **5d** and **6d** have proved unsuccessful.

The e.a.n. rule requires the bridging phosphido group in complex **6d** to donate two electrons to Co(1) and one electron to Co(2) and this is consistent with the asymmetry of the two Co–P bond lengths [Co(1)–P(3) 2.146(2) and Co(2)–P(3) 2.222(2) Å]. The observed Co–Co bond length [2.489(1) Å] is comparable to that in related alkynehexacarbonyldicobalt derivatives.[32] The PPh_3 ligand in **6d** is oriented *cis* relative to the alkyne-derived carbon atom C(233) and is displaced slightly from a position directly *trans* to the metal–metal bond [P(1)–Co(1)–Co(2) 150.4(1)°]. The three carbonyl ligands are all essentially linear.

Conclusion

The reactions of P_2Ph_4 with alkynehexacarbonyldicobalt complexes involve co-ordination of one phosphorus atom of the ligand to one of the cobalt atoms as the first step. This can be followed by co-ordination of the second phosphorus atom to the other metal centre to give stable complexes with an intact phosphorus–phosphorus bond. Cleavage of this phosphorus–phosphorus bond takes place readily, however, to give dicobalt complexes containing a bridging phosphido group and either a four-membered metallacyclic ring incorporating the other phosphido group and the alkyne or a five-membered metallacyclic ring which additionally incorporates CO. The relative stabilities of the complexes containing the four- and five-

Table 4 Selected bond distances (Å) and angles (°) for complex **6d**

Co(1)–Co(2)	2.489(1)	Co(1)–P(1)	2.193(2)
Co(1)–P(3)	2.146(2)	Co(1)–C(233)	2.085(7)
Co(1)–C(234)	1.929(7)	Co(2)–P(2)	2.209(2)
Co(2)–P(3)	2.222(2)	Co(2)–C(234)	1.984(6)
C(231)–O(232)	1.236(9)	C(231)–C(233)	1.461(11)
C(233)–C(234)	1.408(9)	C(233)–H(233)	1.039(6)
C(234)–H(234)	1.039(7)		
Co–C(carbonyl)	1.752(8)–1.770(8)		
C–O(carbonyl)	1.135(10)–1.161(10)		
P–C(phenyl)	1.815(8) 1.857(7)		
P(1)–Co(1)–Co(2)	150.4(1)	P(3)–Co(1)–Co(2)	56.7(1)
C(233)–Co(1)–Co(2)	79.4(2)	C(234)–Co(1)–Co(2)	51.5(2)
C(234)–Co(1)–C(233)	40.8(3)	P(2)–Co(2)–Co(1)	83.7(1)
C(234)–Co(2)–Co(1)	49.5(2)	C(231)–P(2)–Co(2)	102.6(3)
O(232)–C(231)–P(2)	124.8(6)	C(233)–C(231)–P(2)	107.9(5)
C(233)–C(231)–O(232)	127.2(6)	C(231)–C(233)–Co(1)	97.0(4)
C(234)–C(233)–Co(1)	63.6(4)	C(234)–C(233)–C(231)	121.0(6)
Co(2)–C(234)–Co(1)	79.0(2)	C(233)–C(234)–Co(1)	75.5(4)
C(233)–C(234)–Co(2)	119.1(5)		

membered metallacyclic rings depend critically on the nature of the alkyne substituents. In the case of the unsymmetrical alkyne, PhC≡CH, the reaction leading to the five-membered metallacyclic ring complex is highly regiospecific. The fact that the parent acetylene complex reacts differently from the substituted derivatives to give, as the principal product, a five-membered metallacyclic ring complex in which the CO is incorporated in a different place in the ring suggests that more than one mechanism is operative in the formation of this class of compound.

Finally it should be noted that phosphorus–carbon bond formation takes place much more readily in the reactions of P$_2$Ph$_4$ with these alkyne-bridged dicobalt complexes than in the corresponding reactions of P$_2$Ph$_4$ with the closely related alkyne-bridged dimolybdenum complexes [Mo$_2$(η^5-C$_5$H$_5$)$_2$(μ-RC≡CR′)(CO)$_4$].[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; products are presented in order of decreasing R_f values.

The instrumentation used to obtain spectroscopic data has been described previously.[33] Phosphorus-31 NMR chemical shifts are given relative to P(OMe)$_3$ with upfield shifts negative. All NMR spectra were recorded at 293 K. The compounds [Co$_2$(μ-RC≡CR′)(CO)$_6$] (R = R′ = CO$_2$Me, Ph or H; R = Ph, R′ = H),[10a,34,35] and P$_2$Ph$_4$[36] were prepared by literature methods.

(*i*) *Reaction of* [Co$_2$(μ-RC≡CR′)(CO)$_6$] (R = R′ = CO$_2$Me *or* Ph; R = Ph, R′ = H) *with* P$_2$Ph$_4$.—(*a*) The complex [Co$_2${μ-C$_2$(CO$_2$Me)$_2$}(CO)$_6$] (0.63 g, 1.5 mmol) was added to a solution of P$_2$Ph$_4$ (0.60 g, 1.6 mmol) in toluene (100 cm^3). The solution was heated at 318 K for 16 h. After removal of the solvent on a rotary evaporator, the residue was redissolved in the minimum of CH$_2$Cl$_2$ and separated by preparative TLC using hexane–CH$_2$Cl$_2$ (1:1) as eluent. A red band eluted which, on evaporation to dryness, gave red crystalline [Co$_2${μ-C$_2$(CO$_2$Me)$_2$}(CO)$_5$(P$_2$Ph$_4$)] **1a** (0.34 g, 30%) (Found: C, 54.4; H, 3.3; P, 8.0. C$_{35}$H$_{26}$Co$_2$O$_9$P$_2$ requires C, 54.6; H, 3.4; P, 8.1%); fast atom bombardment (FAB) mass spectrum, *m/z* 770 (M^+) and $M^+ - n$CO (n = 1–5). NMR (CDCl$_3$): ^{13}C, (^{1}H composite pulse decoupled), δ 202.7 (s, 2CO), 198.7 (s, 3CO), 169.3 (s, *C*O$_2$Me), 135–127 (m, Ph), 71.9 (s, *C*CO$_2$Me) and 52.0 (s, Me); ^{31}P (^{1}H-gated decoupled), δ −99.0 [d, br, ^1J(PP) 313 Hz, Co*P*Ph$_2$PPh$_2$] and −143.1 (d, CoPPh$_2$*P*Ph$_2$).

(*b*) The complex [Co$_2$(μ-PhC≡CPh)(CO)$_6$] (3.35 g, 7.2 mmol) was added to a solution of P$_2$Ph$_4$ (2.67 g, 7.2 mmol) in toluene (150 cm^3). The solution was heated at 318 K for 6 h. The solvent was then removed on a rotary evaporator and the dark green residue dissolved in the minimum quantity of CH$_2$Cl$_2$ and adsorbed onto silica. The silica was pumped dry and added to the top of a chromatography column [Kieselgel 60 (70–230 mesh)]. Elution with hexane–CH$_2$Cl$_2$ (2:1) gave unreacted [Co$_2$(μ-PhC≡CPh)(CO)$_6$] (0.89 g), followed by a trace of an uncharacterised red band, dark green **1b** (1.56 g, 36% conversion) and dark green [Co$_2$(μ-PhC≡CPh)(μ-P$_2$Ph$_4$)(CO)$_4$] **2b** (1.44 g, 35% conversion). Complex **1b** (Found: C, 63.9; H, 3.7; P, 7.8. C$_{43}$H$_{30}$Co$_2$O$_5$P$_2$ requires C, 64.0; H, 3.7; P, 7.7%); FAB mass spectrum, *m/z* 806 (M^+) and $M^+ - n$CO (n = 1–5). NMR (CDCl$_3$): ^{13}C (^{1}H composite pulse decoupled), δ 204.7 (s, 2CO), 200.9 (s, 3CO), 140–126 (m, Ph) and 86.9 (s, *C*Ph); ^{31}P (^{1}H-gated decoupled), δ −100.0 [d, br, ^1J(PP) 315 Hz, Co*P*Ph$_2$PPh$_2$] and −142.8 (d, CoPPh$_2$*P*Ph$_2$). Complex **2b** (Found: C, 64.8; H, 3.8; P, 8.0. C$_{42}$H$_{30}$Co$_2$O$_4$P$_2$ requires C, 64.8; H, 3.9; P, 8.0%); mass spectrum, *m/z* 778 (M^+) and $M^+ - n$CO (n = 1–4). NMR (CDCl$_3$): ^{13}C (^{1}H composite pulse decoupled), δ 205.1 (s, 4CO), 142–125 (m, Ph) and 88.1 (s, *C*Ph); ^{31}P (^{1}H-gated decoupled), δ −137.3 (s, μ-P$_2$Ph$_4$).

(*c*) The complex [Co$_2$(μ-PhC≡CH)(CO)$_6$] (3.15 g, 8.12 mmol) and P$_2$Ph$_4$ (3.00 g, 8.12 mmol) were used in an analogous procedure to (*b*) above. Column chromatography using hexane–CH$_2$Cl$_2$ (2:1) as eluent gave unreacted [Co$_2$(μ-PhC≡CH)(CO)$_6$] (1.33 g) followed by red-brown [Co$_2$(μ-PhC≡CH)(CO)$_5$(P$_2$Ph$_4$)] **1c** (1.59 g, 46% conversion) and purple [Co$_2$(μ-PhC≡CH)(μ-P$_2$Ph$_4$)(CO)$_4$] **2c** (1.02 g, 31% conversion). Complex **1c** (Found: C, 60.9; H, 3.4; P, 8.7. C$_{37}$H$_{26}$Co$_2$O$_5$P$_2$ requires C, 60.8; H, 3.6; P, 8.5%); FAB mass spectrum, *m/z* 730 (M^+) and $M^+ - n$CO (n = 1–5). NMR (CDCl$_3$): ^{13}C (^{1}H composite pulse decoupled), δ 205.7 (s, 1CO), 204.5 (s, 1CO), 201.8 (s, 3CO), 138–126 (m, Ph), 86.9 (s, *C*Ph) and 72.0 (s, CH); ^{31}P (^{1}H-gated decoupled), δ −96.2 [d, br, ^1J(PP) 315 Hz, Co*P*Ph$_2$PPh$_2$] and −144.4 (d, CoPPh$_2$*P*Ph$_2$). Complex **2c**: mass spectrum, *m/z* 702 (M^+) and $M^+ - n$CO (n = 1–4). NMR (CDCl$_3$): ^{13}C (^{1}H composite pulse decoupled), δ 205.8 [d, *J*(PC) 11, 2CO], 204.3 [d, *J*(PC) 16 Hz, 2CO], 141–126 (m, Ph), 89.5 (s, *C*Ph) and 66.1 (s, CH); ^{31}P (^{1}H-gated decoupled), δ −129.6 (s, μ-P$_2$Ph$_4$).

(*i*) *Thermolysis of* [Co$_2$(μ-RC≡CR′)(CO)$_5$(P$_2$Ph$_4$)] (R = R′ = CO$_2$Me **1a** *or* Ph **1b**; R = Ph, R′ = H **1c**).—(*a*) Complex **1a** (0.25 g, 0.32 mmol) was dissolved in toluene (50 cm^3). The solution was heated at 333 K for 15 h. After removal of the solvent *in vacuo*, TLC separation with hexane–CH$_2$Cl$_2$ (1:4) as eluent gave a trace of **1a** followed by red **2a** (0.145 g, 60%). Complex **2a** (Found: C, 54.9; H, 3.4; P, 8.3. C$_{34}$H$_{26}$Co$_2$O$_8$P$_2$ requires C, 55.0; H, 3.5; P, 8.4%); mass spectrum, *m/z* 742 (M^+) and $M^+ - n$CO (n = 1–4). NMR (CDCl$_3$): ^{13}C (^{1}H composite pulse decoupled), δ 202.5 (s, 4CO), 172.8 (s, *C*O$_2$Me), 135–126 (m, Ph), 72.4 (s, *C*CO$_2$Me) and 52.5 (s, Me); ^{31}P (^{1}H-gated decoupled), δ −137.7 (s, μ-P$_2$Ph$_4$).

(*b*) Complex **1b** (0.038 g, 0.047 mmol) was dissolved in toluene (25 cm^3). The solution was heated at 323 K for 6 h. After removal of the solvent, TLC separation with hexane–CH$_2$Cl$_2$ (3:1) as eluent gave green **2b** (0.028 g, 76%).

(*c*) Complex **1c** (0.40 g, 0.55 mmol) was used in an analogous procedure to (*b*) above, TLC separation with hexane–CH$_2$Cl$_2$ (3:1) as eluent giving purple **2c** (0.30 g, 77%).

(*iii*) *Thermolysis of* [Co$_2$(μ-RC≡CR′)(μ-P$_2$Ph$_4$)(CO)$_4$] (R = R′ = CO$_2$Me **2a** *or* Ph **2b**; R = Ph, R′ = H **2c**.—(*a*) A solution of complex **2a** (0.014 g, 0.019 mmol) in toluene (30 cm^3) was heated at 363 K for 5 h. After removal of the solvent *in vacuo*, TLC of the residue with hexane–CH$_2$Cl$_2$ (1:4) as eluent

Table 5 Fractional atomic coordinates for complex **2a**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co(1)	0.149 88(7)	0.152 61(3)	0.324 08(4)	C(12)	0.0262 (3)	0.296 2(1)	0.125 4(2)
Co(2)	0.393 25(7)	0.117 98(3)	0.296 56(4)	C(13)	0.011 9(3)	0.355 3(1)	0.121 4(2)
P(1)	0.144 90(13)	0.194 62(5)	0.196 37(8)	C(14)	0.092 9(3)	0.389 5(1)	0.179 9(2)
P(2)	0.377 79(13)	0.171 16(5)	0.177 89(8)	C(15)	0.188 2(3)	0.364 7(1)	0.242 4(2)
O(1)	−0.153 5(5)	0.133 9(2)	0.356 8(3)	C(16)	0.202 5(3)	0.305 6(1)	0.246 3(2)
O(2)	0.228 8(5)	0.236 6(2)	0.457 9(3)	C(17)	0.037 0(4)	0.164 7(2)	0.106 2(2)
O(3)	0.569 3(5)	0.183 6(2)	0.424 5(3)	C(18)	−0.075 6(4)	0.127 6(2)	0.123 6(2)
O(4)	0.591 0(5)	0.029 6(2)	0.245 6(3)	C(19)	−0.158 3(4)	0.101 8(2)	0.056 3(2)
O(5)	0.203 9(4)	−0.004 8(2)	0.197 0(3)	C(20)	−0.128 5(4)	0.113 0(2)	−0.028 4(2)
O(6)	0.006 1(4)	0.020 1(1)	0.262 9(3)	C(21)	−0.015 9(4)	0.150 0(2)	−0.045 8(2)
O(7)	0.228 0(8)	0.070 9(2)	0.517 2(3)	C(22)	0.066 8(4)	0.175 9(2)	0.021 5(2)
O(8)	0.280 0(8)	0.001 6(2)	0.439 2(3)	C(23)	0.480 0(4)	0.237 0(2)	0.172 1(2)
C(1)	−0.035 7(6)	0.142 4(2)	0.343 7(4)	C(24)	0.435 3(4)	0.281 2(2)	0.116 8(2)
C(2)	0.196 8(6)	0.205 9(2)	0.404 9(3)	C(25)	0.519 7(4)	0.330 3(2)	0.113 0(2)
C(3)	0.504 9(5)	0.159 0(2)	0.373 3(3)	C(26)	0.648 8(4)	0.335 2(2)	0.164 5(2)
C(4)	0.515 3(6)	0.063 8(2)	0.266 5(3)	C(27)	0.693 6(4)	0.291 0(2)	0.219 8(2)
C(5)	0.208 6(5)	0.077 2(2)	0.285 5(3)	C(28)	0.609 2(4)	0.241 9(2)	0.223 6(2)
C(6)	0.251 7(5)	0.086 0(2)	0.370 1(3)	C(29)	0.395 1(4)	0.138 1(1)	0.073 5(2)
C(7)	0.142 9(6)	0.027 5(2)	0.242 3(4)	C(30)	0.344 1(4)	0.082 6(1)	0.061 3(2)
C(8)	−0.067 1(8)	−0.029 6(3)	0.225 8(7)	C(31)	0.356 9(4)	0.055 5(1)	−0.017 3(2)
C(9)	0.251 6(6)	0.053 1(2)	0.449 2(3)	C(32)	0.420 7(4)	0.083 8(1)	−0.083 6(2)
C(10)	0.272 9(16)	−0.036 5(4)	0.513 3(6)	C(33)	0.471 7(4)	0.139 3(1)	−0.071 3(2)
C(11)	0.121 5(3)	0.271 4(1)	0.187 8(2)	C(34)	0.458 9(4)	0.166 5(1)	0.007 2(2)

gave red crystalline [Co$_2${μ-PPh$_2$C(CO$_2$Me)C(CO$_2$Me)}(μ-PPh$_2$)(CO)$_4$] **3a** (0.011 g, 79%) (Found: C, 55.1; H, 3.6; P, 8.1. $C_{34}H_{26}Co_2O_8P_2$ requires C, 55.0; H, 3.5; P, 8.4%); mass spectrum, *m/z* 742 (M^+) and $M^+ - n$CO (n = 1–4). NMR (CDCl$_3$): ^{13}C (^{1}H composite pulse decoupled), δ 205.4 (s, 1CO), 204.8 (s, 1CO), 202.7 (s, 1CO), 201.4 (s, 1CO), 173.4 (s, *C*O$_2$Me), 169.6 (s, *C*O$_2$Me), 142–128 (m, Ph), 108.4 [dd, *J*(PC), *J*(P′C) 30, PC(CO$_2$Me)*C*(CO$_2$Me)], 51.42 (s, Me), 51.38 (s, Me) and 44.3 [dd, *J*(PC) 41, *J*(P′C) 8, P*C*(CO$_2$Me)]; ^{31}P (^{1}H-gated decoupled), δ 29.2 [d, ^2J(PP) 100 Hz, μ-PPh$_2$] and −173.1 [d,μ-PPh$_2$C(CO$_2$Me)C(CO$_2$Me)].

(*b*) A solution of complex **2b** (0.050 g, 0.064 mmol) in xylene (30 cm^3) was heated at 328 K for 15 h. After removal of the solvent *in vacuo*, TLC of the residue with hexane–CH$_2$Cl$_2$ (1:1) as eluent gave green crystalline **3b** (0.035 g, 70%) and a trace of red [Co$_2${μ-PPh$_2$CPhCPhC(O)}(μ-PPh$_2$)(CO)$_4$] **4b**. Complex **3b** (Found: C, 65.0; H, 3.7; P, 7.9. $C_{42}H_{30}Co_2O_4P_2$ requires C, 64.8; H, 3.9; P, 8.0%); FAB mass spectrum, *m/z* 778 (M^+) and $M^+ - n$CO (n = 1–4). NMR (CDCl$_3$): ^{13}C (^{1}H composite pulse decoupled), δ 208.3 (s, 1CO), 206.4 (s, 1CO), 205.5 (s, 1CO), 204.7 (s, 1CO), 146–125 (m, Ph) and 58.4 [d, *J*(PC) 41, P*C*Ph]; ^{31}P (^{1}H-gated decoupled), δ 45.8 [d, ^2J(PP) 110 Hz, μ-PPh$_2$] and −176.0 (d, μ-PPh$_2$CPhCPh). Complex **4b**: mass spectrum, *m/z* 778 (M^+ − CO) and $M^+ - n$CO (n = 2–5). ^{31}P NMR (CDCl$_3$, ^{1}H gated decoupled): δ 16.7 (s, μ-PPh$_2$) and −84.2 [s, μ-PPh$_2$CPhCPhC(O)].

(*c*) A solution of complex **2c** (0.035 g, 0.05 mmol) in toluene (30 cm^3) was heated at 333 K for 15 h. After removal of the solvent *in vacuo*, TLC of the residue with hexane–CH$_2$Cl$_2$ (1:1) as eluent gave red crystalline [Co$_2${μ-PPh$_2$CHCPhC(O)}(μ-PPh$_2$)(CO)$_4$] **4c** (0.30 g, 80%) (Found: C, 61.3; H, 3.7; P, 8.1. $C_{37}H_{26}Co_2O_5P_2$ requires C, 60.8; H, 3.6; P, 8.5%); mass spectrum, *m/z* 702 (M^+ − CO) and $M^+ - n$CO (n = 2–5). NMR ^{13}C(CD$_2$Cl$_2$, ^{1}H composite pulse decoupled), δ 215.4 [s, PPh$_2$CHCPh*C*(O)], 207 (s, 1CO), 205 (s, 2CO), 201 (s, 1CO), 143–127 (m, Ph), 86.4 [d, *J*(PC) 33, PPh$_2$CH*C*Ph] and 41.8 [dd, *J*(PC) 42, *J*(P′C) 6 Hz, PPh$_2$*C*HCPh]; ^{31}P(CDCl$_3$, ^{1}H-gated decoupled), δ 15.5 (s, μ-PPh$_2$) and −98.2 [s, μ-PPh$_2$CHCPhC(O)].

(*iv*) *Carbonylation of* [Co$_2$(μ-PPh$_2$RC=CR′)(μ-PPh$_2$)(CO)$_4$] (R = R′ = CO$_2$Me **3a** *or* Ph **3b**.—(*a*) A solution of complex **3a** (0.100 g, 0.135 mmol) in toluene (50 cm^3) was purged with CO and heated to 343 K for 5 h. The solvent was removed *in vacuo* and TLC of the residue with CH$_2$Cl$_2$ (100%) as eluent gave unreacted [Co$_2${μ-PPh$_2$C(CO$_2$Me)C(CO$_2$Me){(μ-PPh$_2$)(CO)$_4$] **3a** (0.076 g, 76%) and orange [Co$_2${μ-PPh$_2$C-(CO$_2$Me)C(CO$_2$Me)C(O)}(μ-PPh$_2$)(CO)$_4$] **4a** (0.011 g, 11%). Complex **4a** (Found: C, 53.7; H, 3.1. $C_{35}H_{26}Co_2O_9P_2$ requires C, 54.5; H, 3.4%): mass spectrum, *m/z* 770 (M^+) and $M^+ - n$CO (n = 1–5). ^{31}P NMR (CDCl$_3$, ^{1}H-gated decoupled): δ 20.1 (s, μ-PPh$_2$) and −86.7 [s, μ-PPh$_2$C(CO$_2$Me)C(CO$_2$Me)C(O)].

(*b*) A solution of complex **3b** (0.041 g, 0.053 mmol) in toluene (30 cm^3) was purged with CO and heated to 323 K for 5 h. The solvent was removed *in vacuo* and TLC of the residue with hexane–CH$_2$Cl$_2$ (1:1) as eluent gave unreacted [Co$_2$(μ-PPh$_2$-CPhCPh)(μ-PPh$_2$)(CO)$_4$] **3b** (0.029 g, 72%) and red [Co$_2${μ-PPh$_2$CPhCPhC(O)}(μ-PPh$_2$)(CO)$_4$] **4b** (0.008 g, 19%).

(*v*) *Decarbonylation of* [Co$_2${μ-PPh$_2$CRCR′C(O)}(μ-PPh$_2$)-(CO)$_4$] (R = R′ = CO$_2$Me **4a** *or* Ph **4b**.—(*a*) A solution of complex **4a** (0.050 g, 0.065 mmol) in CH$_2$Cl$_2$ (30 cm^3) was purged with N$_2$ and heated to reflux for 5 h. The solvent was removed *in vacuo* and TLC of the residue with CH$_2$Cl$_2$ (100%) as eluent gave red [Co$_2${μ-PPh$_2$C(CO$_2$Me)C(CO$_2$Me)}(μ-PPh$_2$)(CO)$_4$] **3a** (0.039 g, 80%) as the only product.

(*b*) A solution of complex **4b** (0.008 g, 0.010 mmol) in CH$_2$Cl$_2$ (20 cm^3) was purged with N$_2$ and heated to reflux for 4.5 h. The solvent was removed *in vacuo* and TLC of the residue with hexane–CH$_2$Cl$_2$ (1:1) as eluent gave green [Co$_2${μ-PPh$_2$-CPhCPh}(μ-PPh$_2$)(CO)$_4$] **3b** (0.007 g, 85%).

(*vi*) *Reaction of* [Co$_2$(μ-HC≡CH)(CO)$_6$] *with* P$_2$Ph$_4$.—The complex [Co$_2$(μ-HC≡CH)(CO)$_6$] (0.28 g, 0.90 mmol) in toluene (150 cm^3) was added to a flask charged with P$_2$Ph$_4$ (0.33 g, 0.90 mmol). The solution was heated at 313 K for 24 h. After removal of the solvent *in vacuo* the residue was dissolved in the minimum quantity of CH$_2$Cl$_2$ and adsorbed on to silica. The silica was pumped dry and added to the top of a chromatography column. Elution with hexane–ethyl acetate (4:1) gave [Co$_2$(μ-PPh$_2$)$_2$-(CO)$_6$][21] (0.058 g), [Co$_3$(μ-PPh$_2$)$_3$(CO)$_6$][21] (0.073 g), red crystalline [Co$_2${μ-PPh$_2$CHCHC(O)}(μ-PPh$_2$)(CO)$_4$] **4d** (0.012 g, 2%), purple crystalline [Co$_2${μ-PPh$_2$C(O)CHCH}(μ-PPh$_2$)(CO)$_4$] **5d** (0.153 g, 26%) and small quantities of an uncharacterised brown complex.

Table 6 Fractional atomic coordinates for complex **4c**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co(1)	0.269 09(16)	0.017 94(10)	0.168 64(8)	Co(1′)	0.130 22(16)	0.416 96(10)	0.080 15(7)
Co(2)	0.175 86(16)	−0.089 56(10)	0.169 50(8)	Co(2′)	0.223 38(15)	0.321 52(10)	0.120 80(8)
P(1)	0.161 5(3)	0.019 7(2)	0.225 9(2)	P(1′)	0.277 4(3)	0.454 2(2)	0.129 3(1)
P(2)	0.288 5(3)	−0.058 9(2)	0.120 8(2)	P(2′)	0.071 6(3)	0.319 7(2)	0.067 3(2)
O(1)	0.467 6(12)	0.102 6(7)	0.169 8(6)	O(1′)	−0.055 5(11)	0.506 9(7)	0.051 6(5)
O(2)	0.105 6(12)	0.089 1(7)	0.101 2(5)	O(2′)	0.257 0(11)	0.417 5(7)	−0.000 7(5)
O(3)	−0.065 6(9)	−0.071 3(7)	0.123 4(5)	O(3′)	0.419 6(11)	0.300 3(8)	0.069 1(6)
O(4)	0.186 8(14)	−0.223 3(8)	0.158 7(5)	O(4′)	0.229 4(12)	0.199 5(7)	0.165 9(5)
O(5)	0.470 0(8)	−0.036 6(6)	0.225 4(4)	O(5′)	−0.029 1(8)	0.411 8(6)	0.147 9(4)
C(1)	0.388 5(17)	0.072 0(9)	0.170 5(6)	C(1′)	0.017 1(14)	0.471 6(9)	0.062 2(6)
C(2)	0.167 6(13)	0.060 6(9)	0.125 5(6)	C(2′)	0.207 2(14)	0.418 4(9)	0.030 3(7)
C(3)	0.025 2(15)	−0.076 2(9)	0.143 5(6)	C(3′)	0.345 7(16)	0.310 1(9)	0.089 0(6)
C(4)	0.179 4(14)	−0.171 2(9)	0.162 8(7)	C(4′)	0.227 3(12)	0.249 6(10)	0.148 0(6)
C(5)	0.172 9(12)	−0.063 1(8)	0.237 8(6)	C(5′)	0.279 7(12)	0.389 6(7)	0.168 6(6)
C(6)	0.286 3(12)	−0.085 3(7)	0.232 7(5)	C(6′)	0.161 5(10)	0.369 8(7)	0.173 8(5)
C(7)	0.363 5(12)	−0.037 4(8)	0.214 0(6)	C(7′)	0.069 2(12)	0.403 2(8)	0.139 9(5)
C(8)	0.338 9(10)	−0.144 1(6)	0.255 7(4)	C(8′)	0.129 7(8)	0.337 2(5)	0.214 6(3)
C(9)	0.436 9(10)	−0.172 6(6)	0.241 3(4)	C(9′)	0.026 3(8)	0.302 1(5)	0.210 6(3)
C(10)	0.485 7(10)	−0.226 3(6)	0.263 9(4)	C(10′)	0.000 8(8)	0.265 5(5)	0.247 6(3)
C(11)	0.436 5(10)	−0.251 6(6)	0.300 9(4)	C(11′)	0.078 8(8)	0.263 9(5)	0.288 7(3)
C(12)	0.338 6(10)	−0.223 1(6)	0.315 3(4)	C(12′)	0.182 2(8)	0.299 0(5)	0.292 8(3)
C(13)	0.289 8(10)	−0.169 4(6)	0.292 7(4)	C(13′)	0.207 7(8)	0.335 7(5)	0.255 7(3)
C(14)	0.008 1(9)	0.039 5(5)	0.214 8(4)	C(14′)	0.418 7(8)	0.461 2(5)	0.110 8(4)
C(15)	−0.022 1(9)	0.098 8(5)	0.196 2(4)	C(15′)	0.428 4(8)	0.504 8(5)	0.075 8(4)
C(16)	−0.139 8(9)	0.115 8(5)	0.185 6(4)	C(16′)	0.537 2(8)	0.516 3(5)	0.061 6(4)
C(17)	−0.227 3(9)	0.073 4(5)	0.193 7(4)	C(17′)	0.636 3(8)	0.484 1(5)	0.082 5(4)
C(18)	−0.197 2(9)	0.014 1(5)	0.212 4(4)	C(18′)	0.626 7(8)	0.440 4(5)	0.117 5(4)
C(19)	−0.079 5(9)	−0.002 9(5)	0.222 9(4)	C(19′)	0.517 8(8)	0.429 0(5)	0.131 7(4)
C(20)	0.208 6(9)	0.064 1(5)	0.279 3(4)	C(20′)	0.267 5(7)	0.529 4(5)	0.160 4(4)
C(21)	0.149 0(9)	0.056 1(5)	0.317 3(4)	C(21′)	0.366 9(7)	0.555 1(5)	0.186 5(4)
C(22)	0.181 1(9)	0.091 5(5)	0.357 4(4)	C(22′)	0.358 8(7)	0.612 0(5)	0.210 0(4)
C(23)	0.272 8(9)	0.134 8(5)	0.359 5(4)	C(23′)	0.251 3(7)	0.643 1(5)	0.207 4(4)
C(24)	0.332 5(9)	0.142 8(5)	0.321 4(4)	C(24′)	0.151 9(7)	0.617 3(5)	0.181 3(4)
C(25)	0.300 4(9)	0.107 5(5)	0.281 3(4)	C(25′)	0.160 0(7)	0.560 5(5)	0.157 8(4)
C(26)	0.231 3(12)	−0.047 9(7)	0.060 4(6)	C(26′)	0.082 6(10)	0.284 6(5)	0.011 3(4)
C(27)	0.291 4(12)	−0.008 2(7)	0.033 7(6)	C(27′)	0.139 3(10)	0.226 6(5)	0.009 3(4)
C(28)	0.251 9(12)	−0.000 7(7)	−0.013 4(6)	C(28′)	0.139 2(10)	0.196 3(5)	−0.033 1(4)
C(29)	0.152 3(12)	−0.033 0(7)	−0.033 7(6)	C(29′)	0.082 3(10)	0.223 8(5)	−0.073 5(4)
C(30)	0.092 2(12)	−0.072 7(7)	−0.007 0(6)	C(30′)	0.025 5(10)	0.281 7(5)	−0.071 5(4)
C(31)	0.131 7(12)	−0.080 1(7)	0.040 1(6)	C(31′)	0.025 7(10)	0.312 1(5)	−0.029 1(4)
C(32)	0.425 3(13)	−0.097 5(5)	0.115 5(5)	C(32′)	−0.076 6(9)	0.292 5(5)	0.073 1(4)
C(33)	0.533 9(13)	−0.067 8(5)	0.125 7(5)	C(33′)	−0.093 7(9)	0.228 1(5)	0.079 6(4)
C(34)	0.636 1(13)	−0.099 9(5)	0.119 1(5)	C(34′)	−0.207 1(9)	0.203 5(5)	0.074 7(4)
C(35)	0.629 6(13)	−0.161 6(5)	0.102 2(5)	C(35′)	−0.303 4(9)	0.243 3(5)	0.063 4(4)
C(36)	0.521 0(13)	−0.191 3(5)	0.092 0(5)	C(36′)	−0.286 3(9)	0.307 7(5)	0.056 9(4)
C(37)	0.418 8(13)	−0.159 3(5)	0.098 6(5)	C(37′)	−0.172 9(9)	0.332 3(5)	0.061 8(4)

Complex **4d** (Found: C, 57.0; H, 3.5; P, 9.7. $C_{31}H_{22}Co_2O_5P_2$ requires C, 56.9; H, 3.4; P, 9.5%): FAB mass spectrum, *m/z* 654 (M^+) and $M^+ - n$CO (n = 1–5). NMR: ^{13}C(CD_2Cl_2, ^{1}H composite pulse decoupled), δ 218 [s, PPh_2CHCHC(O)], 207 (s, 1CO), 206 (s, 1CO), 201 (s, 2CO), 142–128 (m, Ph), 68.4 [d, *J*(PC) 34, PPh_2CHCH] and 40.6 [dd, *J*(PC) 39, *J*(P′C) 6 Hz, PPh_2CHCH]; ^{31}P($CDCl_3$, ^{1}H-gated decoupled), δ 22.2 (s, μ-PPh_2) and −92.3 [s, μ-PPh_2CHCHC(O)]. Complex **5d** (Found: C, 56.7; H, 3.4; P, 9.5. $C_{31}H_{22}Co_2O_5P_2$ requires C, 56.9; H, 3.4; P, 9.5%): mass spectrum, *m/z* 654 (M^+) and M^+ − *n*(CO) (n = 1–5). NMR ($CDCl_3$): ^{13}C (^{1}H composite pulse decoupled), δ 205.8 (s, 1CO), 203.8 (s, 2CO), 201.8 (s, 1CO), 189.9 [d, *J*(PC) 36, PPh_2C(O)CHCH], 141–128 (m, Ph), 123.0 [dd, *J*(PC) 32, *J*(P′C) 14, PPh_2C(O)CHCH] and 75.8 [d, *J*(PC) 90 Hz, PPh_2C(O)CHCH]; ^{31}P (^{1}H-gated decoupled), δ 29.8 [d, ^2J(PP) 86, μ-PPh_2] and −75.9 [d, μ-PPh_2C(O)CHCH].

(*vii*) *Thermolysis of* [Co_2{μ-PPh_2C(O)CHCH}(μ-PPh_2)-$(CO)_4$] **5d**.—Complex **5d** (0.17 g, 0.25 mmol) was dissolved in xylene (60 cm^3) and heated at 393 K for 3 d. After removal of the solvent *in vacuo*, TLC of the residue with hexane–CH_2Cl_2 (1 : 1) as eluent gave **5d** (0.064 g) and dark green [Co_2{μ- PPh_2C(O)CHCH}(μ-PPh_2)$(CO)_3(PPh_3)$] **6d** (0.049 g, 21%) (Found: C, 64.7; H, 4.3. $C_{48}H_{37}Co_2O_4P_3$ requires C, 64.9; H, 4.2%); mass spectrum, *m/z* 888 (M^+) and $M^+ - n$CO (n = 1–4). ^{31}P NMR ($CDCl_3$, ^{1}H-gated decoupled): δ −7.9 [d, ^2J((PP) 97 Hz, μ-PPh_2], −74.9 [d, μ-PPh_2C(O)CHCH] and −83.4 (s, PPh_3).

(*viii*) *Reaction of Complex* **5d** *with* PPh_3.—Complex **5d** (0.025 g, 0.038 mmol) and PPh_3 (0.011 g, 0.042 mmol) were dissolved in toluene (15 cm^3) and heated at 373 K for 15 h. After removal of the solvent *in vacuo*, TLC of the residue, with hexane–CH_2Cl_2 (1 : 5) as eluent, gave complex **6d** (0.014 g, 41%).

(*ix*) *Crystal Structure Determinations.—Crystal data for complex* **2a**. $C_{34}H_{26}Co_2O_8P_2$, M = 742.3, monoclinic, space group $P2_1/n$, a = 9.217(4), b = 23.494(2), c = 15.624(2) Å, β = 93.92(2)°, U = 3375.4 Å^3, μ(Mo-Kα) = 10.6 cm^{-1}, D_c = 1.46 g cm^{-3}, Z = 4, F(000) = 1512. A crystal of size 0.15 × 0.25 × 0.30 mm, grown by diffusion of hexane into a dichloromethane solution, was used in data collection.

Crystal data for complex **4c**. $C_{37}H_{26}Co_2O_5P_2$, M = 730.4, monoclinic, space group $P2_1/c$, a = 11.518(6), b = 21.180(5), c = 29.190(5) Å, β = 98.02(3)°, U = 7051.3 Å^3, μ(Mo-Kα) =

Table 7 Fractional atomic coordinates for complex **6d**

Atom	*x*	*y*	*z*
Co(1)	0.260 17(6)	0.150 11(7)	0.190 48(8)
Co(2)	0.278 25(6)	0.331 25(7)	0.319 43(9)
P(1)	0.224 18(12)	−0.027 39(14)	0.167 80(16)
P(2)	0.204 0(1)	0.372 4(1)	0.169 1(2)
P(3)	0.354 5(1)	0.201 6(1)	0.340 8(2)
C(11)	0.312 3(5)	0.163 1(6)	0.054 7(7)
O(11)	0.347 4(4)	0.171 3(5)	−0.035 0(5)
C(21)	0.377 7(6)	0.425 4(7)	0.310 7(8)
O(21)	0.442 5(4)	0.488 9(5)	0.311 9(7)
C(22)	0.240 8(5)	0.392 7(7)	0.456 4(7)
O(22)	0.212 2(4)	0.431 0(5)	0.541 4(5)
C(221)	0.260 5(5)	0.421 2(6)	0.042 1(7)
C(222)	0.234 2(9)	0.382 1(10)	−0.068 6(9)
C(223)	0.285 7(13)	0.419 2(11)	−0.165 3(10)
C(224)	0.354 6(9)	0.497 0(13)	−0.149 4(11)
C(231)	0.130 5(5)	0.240 9(6)	0.107 8(7)
O(232)	0.089 5(3)	0.220 5(4)	0.009 2(5)
C(233)	0.127 1(4)	0.170 1(5)	0.198 5(6)
C(234)	0.179 7(4)	0.203 1(5)	0.306 2(6)
C(311)	0.475 6(4)	0.231 8(5)	0.331 1(7)
C(312)	0.517 2(5)	0.209 1(7)	0.224 7(7)
C(313)	0.610 0(6)	0.234 4(8)	0.219 3(9)
C(314)	0.660 4(6)	0.285 6(8)	0.318 5(10)
C(315)	0.621 7(6)	0.309 7(7)	0.425 0(9)
C(316)	0.529 3(5)	0.283 8(7)	0.432 5(7)
C(321)	0.343 4(4)	0.138 8(6)	0.476 3(6)
C(322)	0.385 9(5)	0.051 4(6)	0.483 3(7)
C(323)	0.372 0(5)	−0.005 9(7)	0.578 8(8)
C(324)	0.318 5(6)	0.024 9(7)	0.668 9(7)
C(325)	0.278 4(5)	0.112 0(7)	0.665 7(7)
C(326)	0.291 6(5)	0.170 5(6)	0.570 1(7)
C(111)	0.182 1(4)	−0.093 9(5)	0.016 3(6)
C(112)	0.177 7(5)	−0.204 5(6)	−0.018 1(7)
C(113)	0.142 0(5)	−0.256 1(6)	−0.130 3(7)
C(114)	0.110 8(5)	−0.197 3(6)	−0.209 0(7)
C(115)	0.114 0(5)	−0.087 7(6)	−0.176 0(6)
C(116)	0.149 1(4)	−0.036 2(6)	−0.062 9(6)
C(121)	0.314 4(5)	−0.100 1(6)	0.192 1(6)
C(122)	0.304 0(6)	−0.186 8(7)	0.253 9(7)
C(123)	0.381 9(7)	−0.237 1(8)	0.265 0(9)
C(124)	0.458 4(7)	−0.199 7(8)	0.213 9(9)
C(125)	0.468 4(7)	−0.116 9(8)	0.151 5(8)
C(126)	0.395 0(5)	−0.066 0(6)	0.140 4(7)
C(131)	0.133 7(4)	−0.077 5(5)	0.261 6(6)
C(132)	0.149 5(5)	−0.068 2(6)	0.384 1(7)
C(133)	0.079 0(5)	−0.101 7(6)	0.456 3(8)
C(134)	−0.005 4(6)	−0.139 4(6)	0.408 9(8)
C(135)	−0.021 2(5)	−0.148 3(6)	0.288 0(7)
C(136)	0.047 7(5)	−0.117 5(5)	0.212 6(7)
C(211)	0.121 0(5)	0.457 7(6)	0.205 8(7)
C(212)	0.064 5(6)	0.439 6(7)	0.297 9(8)
C(213)	−0.004 7(7)	0.496 7(8)	0.327 2(9)
C(214)	−0.017 7(7)	0.571 6(9)	0.258 2(10)
C(215)	0.029 0(7)	0.586 5(9)	0.160 4(11)
C(216)	0.102 0(8)	0.531 2(9)	0.133 2(10)
C(225)	0.364 2(12)	0.573 1(14)	−0.024 2(18)
C(226)	0.310 5(11)	0.529 7(14)	0.069 8(15)
C(227)	0.402 0(17)	0.473 9(21)	−0.062 9(25)
C(228)	0.357 0(16)	0.441 1(18)	0.042 1(21)

11.1 cm^{-1}, D_c = 1.38 g, cm^{-3}, Z = 8, F(000) = 2976. A crystal of size 0.30 × 0.20 × 0.20 mm, grown by diffusion of hexane into a dichloromethane solution, was used in data collection.

Crystal data for complex **6d**. $C_{48}H_{37}Co_2O_4P_3$, M = 899.21, triclinic, space group $P\bar{1}$ (no. 2), a = 15.193(3), b = 12.708(3), c = 11.292(2) Å, α = 99.06(2), β = 90.72(1), γ = 100.64(2)°, U = 2114.01 Å^3, μ(Mo-Kα) = 8.80 cm^{-1}, D_c = 1.40 g cm^{-3}, Z = 2, F(000) = 912. A black crystal of size 0.32 × 0.21 × 0.24 mm, grown by slow evaporation of a hexane–dichloromethane (1 : 1) solution, was used in data collection.

Data collection. Data were collected on a Enraf-Nonius CAD4 diffractometer in the range θ 2.5–25° for complexes **2a** and **4c**, with a scan width of 0.65° for **2a** and 1.00° for **4c**. For **6d**, data were collected on a Philips PW 1100 instrument in the range θ 3–25° with a scan width of 0.90°, using the technique described previously.[37] Equivalent reflections were merged to give 3130 data for **2a**, 3499 for **4c** and 3946 for **6d** with $I/\sigma(I)$ >2.0 for **2a** and **4c** and >3.0 for **6d**. Absorption corrections were applied by azimuthal scanning of reflections at >80° for **2a**, whereas for **4c** and **6d** corrections were applied after initial refinement with isotropic thermal parameters for all atoms.[38]

Structure solution and refinement.[39] The coordinates of all the metal atoms in the three structures were deduced from a Patterson synthesis, and the remaining non-hydrogen atoms were located from subsequent Fourier-difference syntheses. For complex **6d** high thermal parameters and regions of extended electron density for the carbon atoms indicated disorder of one of the phenyl rings on P(2), which appears to correspond to two orientations of the ring randomly distributed throughout the crystal. It proved possible to resolve two carbon atoms into two components of occupancy 0.60 [C(225) and C(226)] and 0.4 [C(227) and C(228)]. The electron density for the remaining atoms did not show any localised maxima for the two components but the high thermal parameters obtained on refinement are consistent with the disordered model. The hydrogen atoms attached to C(233) and C(234) in **6d** were located in a Fourier-difference synthesis calculated using data with sin θ < 0.35. These were included in the structure-factor calculations with thermal factors of 0.08 Å^2 but their parameters were not refined. For all three structures the remaining hydrogen atoms were included in geometrically idealised positions and were constrained to 'ride' on the relevant carbon atoms. All non-hydrogen atoms were assigned anisotropic thermal parameters in **2a**. Similarly, for **4c** all non-hydrogen atoms (except the carbon atoms of the phenyl rings) were assigned anisotropic thermal parameters. In **6d** the cobalt, phosphorus, all carbon atoms in the rings C(311), C(321), all non-ring carbon and oxygen atoms, and the atoms C(121), C(122), C(123) and C(124) in the disordered ring were assigned anisotropic thermal parameters in the final cycles of full-matrix refinement. For all three structures weights of $w = 1/\sigma^2 F_o$ were assigned to the individual reflections. Refinement converged at R 0.0350, R' 0.0370 for **2a**, 0.0650, 0.0710 for **4c**, and 0.0556, 0.0547 for **6d**.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

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