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

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The reactions of  $P_2Ph_4$  with a variety of substituted alkyne complexes  $[Co_2(\mu-RC\equiv CR')(CO)_6]$  in toluene give the complexes  $[Co_2(\mu-RC\equiv CR')(CO)_5(P_2Ph_4)]$  1 ( $R = R' = CO_2Me$  1a or Ph 1b; R = Ph, R' = H 1c and  $[Co_2(\mu-RC\equiv CR')(\mu-P_2Ph_4)(CO)_4]$  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  $[Co_2(\mu-PPh_2CRCR')(\mu-PPh_2)(CO)_4]$  3 ( $R = R' = CO_2Me$  3a or Ph 3b and  $[Co_2\{\mu-PPh_2CRCR'-C(O)\}(\mu-PPh_2)(CO)_4]$  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  $\pi$ -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  $[Co_2(\mu-HC\equiv CH)(CO)_6]$ reacts with  $P_2Ph_4$  differently from the substituted derivatives to give as the principal product  $[Co_2\{\mu-PPh_2-C(O)CHCH\}(\mu-PPh_2)(CO)_4]$  5d. The structure of the PPh\_3 derivative of this complex,  $[Co_2\{\mu-PPh_2-C(O)CHCH\}(\mu-PPh_2)(CO)_4]$  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 ( $\mu$ -PR<sub>2</sub>) and has proved to be one of the most successful.<sup>1</sup> In general, thermolytic reaction leads to cleavage of the phosphorusphosphorus bond, giving bis(phosphido)-bridged complexes.<sup>1-3</sup> In some cases, however, under mild conditions, complexes containing intact P<sub>2</sub>R<sub>4</sub> ligands have been isolated.<sup>1,4,5</sup>

The reaction of  $\mu$ -PR<sub>2</sub> 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).<sup>6,7</sup> A possible alternative route to such products is the reaction of P<sub>2</sub>R<sub>4</sub> with complexes containing bridging alkyne ligands<sup>8</sup> and in this paper we report the reactions of the biphosphine, P<sub>2</sub>Ph<sub>4</sub>, with alkynehexacarbonyldicobalt complexes of general formula [Co<sub>2</sub>( $\mu$ -RC=CR')(CO)<sub>6</sub>] (R = R' = CO<sub>2</sub>Me, Ph, or H; R = Ph, R' = H). The chemistry of the alkyne ligand itself in complexes of this type has been thoroughly studied<sup>9</sup> as has the substitution of terminal carbonyl groups, particularly by monoand multi-dentate tertiary phosphine ligands.<sup>10</sup>

We now show that reaction of  $[Co_2(\mu-RC\equiv CR')(CO)_6]$  $(R = R' = CO_2Me$ , Ph or H; R = Ph, R' = H) with  $P_2Ph_4$  can lead not only to carbonyl substitution but also to novel

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ligand transformations involving phosphorus-carbon and, in some cases, carbon-carbon bond formation (Scheme 1).

#### **Results and Discussion**

(1a) Reaction of  $[Co_2(\mu - RC \equiv CR')(CO)_6]$  (R = R' = CO<sub>2</sub>Me or Ph; R = Ph, R' = H) with P<sub>2</sub>Ph<sub>4</sub>.—Reaction of  $[Co_2(\mu - RC \equiv CR')(CO)_6]$  (R = R' = CO<sub>2</sub>Me or Ph; R = Ph, R' = H) with P<sub>2</sub>Ph<sub>4</sub> at 318 K in toluene gives, in addition to unreacted starting material, the complexes  $[Co_2(\mu - RC \equiv CR')(CO)_5 - (P_2Ph_4)]$  (R = R' = CO<sub>2</sub>Me 1a or Ph 1b; R = Ph, R' = H 1c and  $[Co_2(\mu - RC \equiv CR')(\mu - P_2Ph_4)(CO)_4]$  (R = R' = Ph 2b; R = Ph, R' = H 2c). Complex 2a (R = R' = CO<sub>2</sub>Me) is not obtained directly in the above reaction but is cleanly formed on thermolysis of  $[Co_2(\mu - RC \equiv CR')(CO)_5(P_2Ph_4)]$  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 <sup>31</sup>P-{<sup>1</sup>H} NMR spectra of complexes 1 are consistent with the presence of a terminal P<sub>2</sub>Ph<sub>4</sub> ligand. In each case two doublet resonances are observed, with large coupling constants [J(PP) ca. 315 Hz], indicative of one-bond phosphorusphosphorus 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 <sup>59</sup>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

<sup>&</sup>lt;sup>+</sup> μ-1(η<sup>2</sup>): 2(η<sup>2</sup>)-Dimethyl acetylenedicarboxylate-μ-tetraphenyldiphosphane-1κ*P*: 2κ*P'*-bis(dicarbonylcobalt) (*Co*-*Co*), μ-diphenylphosphido-μ-2(2,3-η)-3-diphenylphosphino-1κ*P*-2-phenylprop-2enoyl-1κ*C*<sup>1</sup>-bis(dicarbonylcobalt) (*Co*-*Co*), and tricarbonyl-1κ<sup>2</sup>*C*,-2κ*C*-μ-diphenylphosphido-μ-2(1,2-η)-3-diphenylphosphino-1κ*P*-3oxoprop-1-enyl-1κ*C*<sup>1</sup>-triphenylphosphine-2κ*P*-dicobalt (*Co*-*Co*).



**Scheme 1** Products from the reaction of  $[Co_2(\mu-RC \equiv CR')(CO)_6]$  with  $P_2Ph_4$  (*i*)  $P_2Ph_4$ , heat; (*ii*) heat; (*iii*)  $N_2$ , heat or standing in solution; (*iv*) CO, heat; (*v*) PPh<sub>3</sub>, heat. \* In this case further heating of the initially isolated **1a** is necessary

 $(R = R' = H, L = AsPh_3$  or PPhEt<sub>2</sub>;  $R = R' = Ph, L = PPh_3$ ;  $R = H, R' = Bu^1$ ,  $L = PPhEt_2$ ) also showed two carbonyl resonances with integrated intensities of 2:3.<sup>11</sup> 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  $[Co_2(\mu-RC\equiv CR')(CO)_5(P_2Ph_4)]$  1 and X-Ray Analysis of  $[Co_2(\mu-RC\equiv CR')(\mu-P_2Ph_4)(CO)_4]$  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  $[Fe_2(\mu-CHR)(\mu-P_2Ph_4)-(NO)_4]$   $(R = H \text{ or } Me)^{12}$  and  $[Fe_2(\mu-P_2Me_4)(\mu-PMe_2)_2-(CO)_4]^{13}$ 

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



fluxional or, alternatively, they could be non-fluxional but with the biphosphine ligand substituted in a pseudo-axial position. A <sup>13</sup>C NMR study on the compounds  $[Co_2(\mu-RC\equiv CR')(CO)_5L]$ 

 Table 1
 Infrared and <sup>1</sup>H NMR data for the new complexes

| Compound  | v(CO) <sup><i>a</i></sup> /cm <sup>-1</sup>                           | <sup>1</sup> H NMR <sup><i>b</i></sup> ( $\delta$ )  |
|---|---|--|
| $1a [Co{\mu-C_2(CO_2Me)_2}(CO)_5(P_2Ph_4)]$   | 2081s, 2035s,<br>2022s, 1994m,<br>1702m                               | 7.5–7.1 (m, 20 H, Ph)<br>3.34 (s, 6 H, Me)   |
| $1b \left[Co_2(\mu-PhC\equiv CPh)(CO)_5(P_2Ph_4)\right]$  | 2058s, 2011s,<br>1999m <sup>c</sup>                                   | 7.5–6.9 (m, 30 H, Ph)  |
| $lc [Co_2(\mu-PhC=CH)(CO)_5(P_2Ph_4)]$  | 2064s, 2016s,<br>2006s, 1973m   | 7.5–7.0 (m, 25 H, Ph)<br>5 22 [d 1 H <sup>3</sup> /(PH) 4.2 CH]  |
| <b>2a</b> $[Co_2{\mu-C_2(CO_2Me)_2}(\mu-P_2Ph_4)(CO)_4]$  | 2000s, 1975in<br>2045m, 2020s,<br>1993m, 1701w <sup>c</sup>           | 7.5-7.1 (m, 20 H, Ph)<br>3.80 (c 6 H Me)   |
| $2b \left[ Co_2(\mu - PhC \equiv CPh)(\mu - P_2Ph_4)(CO)_4 \right]$   | 2022m, 1994s,<br>1966m <sup>c</sup>                                   | 7.6-7.0 (m, 30 H, Ph)  |
| $2c \left[Co_2(\mu-PhC=CH)(\mu-P_2Ph_4)(CO)_4\right]$   | 2028m, 2003s,<br>1976m, 1962w   | 7.8–7.1 (m, 25 H, Ph)<br>5 69 [t, 1 H, <sup>3</sup> /(PH) 3 2, CH]   |
| $3a [Co_2{\mu-PPh_2C(CO_2Me)C(CO_2Me)}(\mu-PPh_2)(CO)_4]$   | 2028s, 2003s,<br>1993m, 1706m   | 8.2–7.1 (m, 20 H, Ph)<br>3.55 (s, 3 H, Me)<br>3.09 (s. 3 H, Me)  |
| <b>3b</b> $[Co_2(\mu-PPh_2CPhCPh)(\mu-PPh_2)(CO)_4]$  | 2027w, 2001s,<br>1983m, 1961w <sup>c</sup>                            | 8.2–7.1 (m, 30 H, Ph)  |
| $4a [Co_2{\mu-PPh_2C(CO_2Me)C(CO_2Me)C(O)}(\mu-PPh_2)(CO)_4]$   | 2060m, 2037s,<br>2020m, 1998w,<br>1704w, 1637w,<br>1606w <sup>c</sup> | 8.1–7.3 (m, 20 H, Ph)<br>3.67 (s, 3 H, Me), 3.50 (s, 3 H, Me)  |
| $\textbf{4b} \ [Co_2\{\mu\text{-PPh}_2\text{CPhCPhC}(O)\}(\mu\text{-PPh}_2)(\text{CO})_4]$                          | 2049m, 2015s,<br>1973m 1638w  | 8.3-7.1 (m, 30 H, Ph)  |
| $4c [Co_{2}{\mu-PPh_{2}CHCPhC(O)}(\mu-PPh_{2})(CO)_{4}]$  | 2048m, 2019s,<br>2010 (sh), 1978m,<br>1661w                           | 8.2–6.8 (m, 25 H, Ph)<br>5.23 [dd, 1 H, ${}^{2}J$ (PH) 2.5,<br>${}^{3}J$ (P'H) 2.5, PPh <sub>2</sub> CH1 <sup>4</sup>  |
| <b>4d</b> [Co <sub>2</sub> {μ-PPh <sub>2</sub> CHCHC(O)}(μ-PPh <sub>2</sub> )(CO) <sub>4</sub> ]                    | 2048m, 2016s,<br>2007 (sh), 1976m,<br>1664w                           | 8.3–7.2 (m, 20 H, Ph)<br>4.68 [ddd, <sup>3</sup> <i>J</i> (HH) 4.7, <sup>2</sup> <i>J</i> (PH) 2.7,<br><sup>3</sup> <i>J</i> (P'H) 2.7, 1 H, PPh <sub>2</sub> CH]<br>4.07 [dd, <sup>3</sup> <i>J</i> (PH) 40.7, 1 H, PPH <sub>2</sub> CHCH]                      |
| <b>5d</b> [Co <sub>2</sub> {μ-PPh <sub>2</sub> C(O)CHCH}(μ-PPh <sub>2</sub> )(CO) <sub>4</sub> ]                    | 2044m, 2016s,<br>2003m, 1978m,<br>1638w                               | 7.9–7.3 (m, 20 H, Ph)<br>6.10 [ddd, 1 H, <sup>3</sup> <i>J</i> (PH) 19.7,<br><sup>3</sup> <i>J</i> (HH) 4.5, <sup>3</sup> <i>J</i> (P'H) 2.1, C(O)CHC <i>H</i> ]<br>4.77 [ddd, 1 H, <sup>3</sup> <i>J</i> (PH) 40.7,<br><sup>3</sup> <i>J</i> (P'H) 4.6, C(O)CH] |
| <b>6d</b> [Co <sub>2</sub> {μ-PPh <sub>2</sub> C(O)CHCH}(μ-PPh <sub>2</sub> )(CO) <sub>3</sub> (PPh <sub>3</sub> )] | 2028s, 1987s,<br>1947m, 1579m°  | 7.9–6.9 (m, 35 H, Ph)<br>5.29 [dd, 1 H, <sup>3</sup> J(PH) 20.7,<br><sup>3</sup> J(HH) 4.2, C(O)CHC <i>H</i> ]<br>3.94 [dddd, 1 H, <sup>3</sup> J(PH) 40.2,<br><sup>3</sup> J(P'H) 10.8, <sup>3</sup> J(P''H) 4.6, C(O)CH] <sup>e</sup>                          |

<sup>*a*</sup> Infrared spectrum recorded in hexane solution unless otherwise indicated. <sup>*b*</sup> Chemical shifts ( $\delta$ ) in ppm, coupling constants in Hz, recorded in CD<sub>2</sub>Cl<sub>2</sub> unless otherwise indicated. <sup>*c*</sup> Recorded in CH<sub>2</sub>Cl<sub>2</sub> solution. <sup>*d*</sup> Recorded in CDCl<sub>3</sub> solution. <sup>*e*</sup> Recorded in (CD<sub>3</sub>)<sub>2</sub>SO 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(carbonvl) | 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)   | 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  $\dot{F}e-P-P-\dot{F}e$  ring observed for  $[Fe_2(\mu-CH_2)(\mu-P_2Ph_4)-$ (NO)<sub>4</sub>].<sup>12</sup> 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  $87.3(1)^{\circ}$  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  $[Fe_2(\mu-CH_2)(\mu-P_2Ph_4)(NO)_4] [P-P 2.179(1) Å]^{12}$ and lies just outside the previously suggested range for phosphines containing P-P bonds, 2.17-2.24 Å.<sup>15</sup> 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  $[Co_2(\mu PhC \equiv CPh)(\mu - dppm)(CO)_{4}$  (dppm =  $Ph_2PCH_2PPh_2$ ), where the dppm ligand lies equatorial relative to the alkyne.<sup>16</sup> 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) A respectively] than those of the pseudo-axial carbonyls, CO(1) and CO(4)



Fig. 2 Molecular structure of  $[Co_2{\mu-C_2(CO_2Me)_2}(\mu-P_2Ph_4)-(CO)_4]$  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 <sup>13</sup>C NMR spectra of the symmetrical alkyne complexes **2a** and **2b** ( $\mathbf{R} = \mathbf{R'} = \mathbf{CO}_2\mathbf{Me}$  or Ph) show just one singlet in the carbonyl region. This observation is in accord with the spectra of the dppm-bridged complex  $[\mathbf{CO}_2\{\mu-\mathbf{C}_2(\mathbf{CF}_3)_2\}(\mu-dppm)(\mathbf{CO})_4]$  which also shows only one carbonyl resonance.<sup>10c</sup>

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

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arrangement with each phosphorus residing in pseudoequatorial positions on opposite sides of the molecule is untenable. Accordingly the singlet carbonyl <sup>13</sup>C NMR signal must signify that the molecule is fluxional, since in a nonfluxional 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 <sup>13</sup>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  $[Co_2(\mu-RC\equiv CR')(\mu-P_2Ph_4)(CO)_4]$  2 and X-Ray Analysis of  $[Co_2\{\mu-PPh_2CHCPhC(O)\}(\mu-PPh_2)(CO)_4]$ 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.<sup>1–3,17</sup> In particular the alkylidene, biphosphine-bridged complexes  $[Fe_2(\mu-CHR)(\mu-P_2Ph_4)(NO)_4]$  (R = H or Me) were found to undergo P–P cleavage under thermolysis, isomerising to produce the compounds  $[Fe_2(\mu-PPh_2CHR)(\mu-Pph_2)(NO)_4]$ .<sup>12</sup>

Thermolysis of **2a** ( $\mathbf{R} = \mathbf{R}' = \mathbf{CO}_2\mathbf{M}\mathbf{e}$ ) at 363 K and **2b**  $(\mathbf{R} = \mathbf{R}' = \mathbf{Ph})$  at 328 K in toluene gave the compounds  $[Co_2(\mu - PPh_2CR'CR)(\mu - PPh_2)(CO)_4] (R = R' = CO_2Me \ 3a$ or Ph 3b) in 70-80% yields. Thermolysis of 2c at 333 K gave the complex  $[Co_2{\mu-PPh_2CR'CRC(O)}(\mu-PPh_2)(CO)_4]$  4c (R =Ph,  $\mathbf{R}' = \mathbf{H}$ ) in 80% yield (Scheme 1). Complexes 3 and 4c have been characterised by IR, <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>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  $[Co_2\{\mu-PPh_2CR'CRC(O)\}(\mu-PPh_2)-(CO)_4]$  **4b** (R = R' = Ph). The mass spectrum of **3a** (R = R' = Ph).  $CO_2Me$ ) 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 <sup>1</sup>H NMR spectrum of **3a** indicates that the methyl groups are inequivalent, while the <sup>31</sup>P-{<sup>1</sup>H} NMR spectrum shows two doublet resonances with J(PP) 100 Hz. The lowerfield signal at  $\delta$  29.2 [relative to  $P(OMe)_3~(\delta~0.0)]$  is consistent with a phosphido bridge. The higher-field signal at  $\delta$ -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) - 1.8 | 3(2)     |
| C-O(carbonyl)    | 1.11(2)-1.1   | 8(2)     |
| PC(phenyl)       | 1.79(1)-1.8   | 4(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  $[Co_2\{\mu-PPh_2CHCPhC(O)\}(\mu-PPh_2)-(CO)_4]$  4c including the atom numbering scheme

alkyne such that it is part of a four-membered P-C-C-Mmetallacyclic ring.<sup>6.7,18,19</sup> The <sup>13</sup>C NMR spectrum of **3a** confirms that the CO<sub>2</sub>Me groups are inequivalent. A resonance at  $\delta$  44.3 with J(PC) 41 and J(P'C) 8 Hz is assigned to the  $PC(CO_2Me)C(CO_2Me)$  carbon while another resonance at  $\delta$ 108.4 with J(PC) = J(P'C) = 30 Hz is assigned to the  $PC(CO_2Me)C(CO_2Me)$  carbon. In the carbonyl region of the spectrum four separate signals are observed corresponding to four inequivalent carbonyl ligands, implying that **3a** is nonfluxional 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 n<sup>2</sup>-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)  $\sigma$  interaction and Co(2) receiving two electrons from the  $\pi$  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  $\eta^2$ -coordinated 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.<sup>16,19</sup>

The Co-C(O)  $\sigma$  interaction is only slightly shorter than the Co–C(alkene)  $\pi$  interaction [1.99(2) versus 2.07(2) Å]. These latter bond distances are notably longer than the corresponding bonds in  $[(C_5H_5Co)_2\{\mu-\eta^4-PMe_2C(CO_2Me)=C(CO_2Me)-$ PMe<sub>2</sub>}][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 µ-PPh<sub>2</sub>CHCPhC(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  $94.8(5)^{\circ}$ , 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<sup>-1</sup> being assigned to v(C=O) of the five-membered metallacyclic ring. In the  ${}^{31}P-{}^{1}H$  NMR spectrum a broad resonance at  $\delta$  15.5 is diagnostic of a phosphido-bridging ligand, whilst a similarly broad resonance at  $\delta - 98.2$  is consistent with the second phosphorus atom being part of a five-membered metallacyclic ring rather than a fourmembered ring, for which a higher-field signal would have been expected.<sup>6,7,18-20</sup> In the <sup>13</sup>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<sub>2</sub>CHCPhC(O) carbon appears as a doublet,  ${}^{2}J(PC)$  33 Hz at  $\delta$  86.4, whilst the PPh<sub>2</sub>CHCPhC(O) carbon resonance is a doublet of doublets,  ${}^{1}J(PC)$  42,  ${}^{2}J(P'C)$  6 Hz, at  $\delta$  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.<sup>18</sup> 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  $[Co_2(\mu-RC\equiv CR')(\mu-P_2Ph_4)(CO)_4]$ 

R' = H, phosphide-alkyne coupling must occur regioselectively at the CH carbon, since the <sup>1</sup>H NMR spectrum of **4c** provides no evidence for the formation of a second isomer incorporating a  $\mu$ -PPh<sub>2</sub>CPhCHC(O) ligand. This may be because, for the unsymmetrical alkyne, attack of the terminal PPh<sub>2</sub> 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  $[Co_2(\mu-HC \equiv CH)(CO)_6]$  with P<sub>2</sub>Ph<sub>4</sub> (see below) suggests a possible alternative route.

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

Complex 4d was characterised by IR, <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectroscopy, mass spectrometry and microanalysis. On the basis of these data 4d is assigned an analogous structure to 4c. In the <sup>1</sup>H NMR spectrum the PPh<sub>2</sub>CHCH(O) proton occurs as a doublet of doublets centred at  $\delta$  4.07 [<sup>3</sup>J(PH)<sub>trans</sub> 40.1 Hz and <sup>3</sup>J(HH) 4.7 Hz] whereas the PPh<sub>2</sub>CHCHC(O) proton

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resonance is observed as a doublet of doublets of doublets centred at  $\delta 4.68 [J(PH) = J(P'H) = 2.7 \text{ Hz}].$ 

The main product of the reaction of  $[Co_2(\mu-HC\equiv CH)(CO)_6]$ with P<sub>2</sub>Ph<sub>4</sub>, compound **5d**, has been characterised by IR, <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectroscopy, mass spectrometry and microanalysis. In addition the PPh<sub>3</sub>-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 v<sub>co</sub> absorption bands. An absorption at lower wavenumber (1638  $cm^{-1}$ ) is attributed to the presence of an inserted carbonyl in the form of a  $\mu$ -PPh<sub>2</sub>C(O)CHCH ligand. This compares with a band at 1625 cm<sup>-1</sup> due to the inserted carbonyl ligand in  $[RuCo{\mu-PPh_2C(O)CHCH}(\mu-CO)-$ (CO)<sub>5</sub>].<sup>6</sup> In the <sup>31</sup>P-{<sup>1</sup>H} NMR spectrum of **5d** two doublets are observed. The low-field signal at  $\delta$  29.8 [<sup>2</sup>J(PP) 86 Hz] is assigned to a  $\mu$ -PPh<sub>2</sub> ligand. The high-field signal at  $\delta - 75.9$  is consistent with a PPh2 fragment inserted such that it forms part of a five-membered metallacyclic ring. The <sup>1</sup>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  $\delta$  6.10 with  ${}^{-3}J(PH)$  19.7,  ${}^{3}J(HH)$  4.5 and  ${}^{3}J(P'H)$  2.1 Hz is assigned to the  $PPh_2C(O)CHCH$  proton. The other resonance at  $\delta$  4.77 with  ${}^{3}J(P'H)$  4.6 Hz and a large  ${}^{3}J(PH)_{trans}$  40.7 Hz, is assigned to the PPh<sub>2</sub>C(O)CHCH proton. The assignment of the H-H coupling was confirmed by a homonuclear decoupling experiment. Dixneuf and co-workers <sup>6b</sup> also observed a pattern of lowfield shift, small  ${}^{3}J(PH)$  for PPh<sub>2</sub>C(O)CRCH protons and highfield shift, large  ${}^{3}J(PH)$  for PPh<sub>2</sub>C(O)CHCR protons in NMR spectra of the complexes [RuCo{ $\mu$ -PPh<sub>2</sub>C(O)CRCR'}- $(\mu$ -CO)(CO)<sub>5</sub>] (R = H, R' = Ph, Bu<sup>t</sup> or H; R = SiMe<sub>3</sub>,  $\mathbf{R}' = \mathbf{H}$ ). The presence of the inserted carbonyl ligand was confirmed by <sup>13</sup>C NMR spectroscopy, with a resonance being observed at  $\delta$  189.9 [<sup>2</sup>J(PC) 36 Hz].

Clearly the reaction of the parent acetylene-bridged dicobalt complex  $[Co_2(\mu-HC\equiv CH)(CO)_6]$  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,  $[Co_2(\mu-HC=CH)(\mu-P_2Ph_4)(CO)_4]$  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 intermediate 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  $\mu$ -CHCHC(O) and  $\mu$ -P<sub>2</sub>Ph<sub>4</sub> ligands. Three bonding modes have been reported for  $\mu$ -CRCRC(O) ligands at a dinuclear centre, namely  $\mu$ - $\eta^2$ : $\eta^2$ : $2^2$ <sup>24</sup> and  $\mu$ - $\sigma$ : $\eta^{3}$ <sup>25-28</sup> modes in which the ligand is a four-electron donor, and a  $\mu$ - $\sigma$ :  $\sigma$  mode<sup>29</sup> in which it is a two-electron donor. Although any of these modes are possible for the ligand in A the  $\mu$ - $\eta^2$ : $\eta^2$  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  $\mu$ -PPh<sub>2</sub> and a terminal PPh<sub>2</sub> 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

<sup>\*</sup> 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  $[Co_2(\mu-HC\equiv CH)-(CO)_6]$  with P<sub>2</sub>Ph<sub>4</sub>



Fig. 5 Molecular structure of  $[Co_2{\mu-PPh_2C(O)CHCH}(\mu-PPh_2)-(CO)_3(PPh_3)]$  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(diphenyl-phosphido) complex  $[Co_2(\mu-PPh_2)_2(CO)_6]^{21}$  is likely to be formed *via* loss of acetylene from  $[Co_2(\mu-HC\equiv CH)(CO)_6]$ , accompanied by oxidative addition of  $P_2Ph_4$ . The trinuclear

complex  $[Co_3(\mu-PPh_2)_3(CO)_6]$  is presumably formed through decomposition of light-sensitive  $[Co_2(\mu-PPh_2)_2(CO)_6]^{21}$  It should be noted that a pure sample of  $[Co_2(\mu-PPh_2)_2(CO)_6]$ reacts with HC=CH at ambient temperature to give 4d in nearquantitative yield <sup>30</sup> and hence the traces of 4d formed in the reaction of  $[Co_2(\mu-HC=CH)(CO)_6]$  with P<sub>2</sub>Ph<sub>4</sub> may alternatively arise in this way.

(e) Synthesis and X-Ray Analysis of [Co<sub>2</sub>{µ-PPh<sub>2</sub>C(O)-CHCH}(µ-PPh<sub>2</sub>)(CO)<sub>3</sub>(PPh<sub>3</sub>)] 6d.—Dixneuf and co-workers<sup>6</sup> have observed that, upon thermolysis, the ruthenium-cobalt complex [RuCo{ $\mu$ -PPh<sub>2</sub>C(O)CRCR'}( $\mu$ -CO)(CO)<sub>5</sub>] (R = Ph, R' = Ph or C=CPh; R = H, R' = Ph or  $Bu^{t}$ ) undergoes facile decarbonylation to generate  $[RuCo(\mu-PPh_2CRCR')(\mu-CO) (CO)_5$  with extrusion of the ketonic carbonyl groups. In contrast, thermolysis of a xylene solution of 5d at 393 K for 3 d gives а low yield of  $[Co_2{\mu-PPh_2C(O)CHCH}(\mu PPh_2(CO)_3(PPh_3)$ ] 6d as the only isolable product. Complex 6d is obtained in higher yield from the reaction of 5d with a slight excess of PPh3 in toluene at 373 K and has been characterised by IR, <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy, mass spectrometry and microanalysis. In order to determine unambiguously the position of substitution of the PPh<sub>3</sub> 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  $\mu$ -PPh<sub>2</sub> and  $\mu$ -PPh<sub>2</sub>C(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  $\pi$  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<sub>3</sub> [Co(1)] and two terminal CO groups [Co(2)]. The  $\mu$ -PPh<sub>2</sub>C(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  $[RuCo{\mu-PPh_2C(O)C(SiMe_3)CH}(\mu-CO)(CO)_5]^6 1.865(3) \text{ Å} in [RuCo{\mu-PPh_2C(O)CPhCPh}(\mu-CO)(CO)_5]^6 and 1.918(6)$ Å in  $[Fe_2{\mu-PPh_2C(O)C(Bu^t)CC(CO_2Et)C(CO_2Et)}(CO)_5]^{31}$ 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.<sup>32</sup> The PPh<sub>3</sub> 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 phosphorusphosphorus 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 comp | lex <b>6d</b> |
|----------|-----------------|-------------|----------------------------|---------------|
| Co(1)-Co | o(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)-C | D(232)          | 1.236(9)    | C(231)-C(233)              | 1.461(11)     |
| C(233)-C | C(234)          | 1.408(9)    | C(233)-H(233)              | 1.039(6)      |
| C(234)-H | I(234)          | 1.039(7)    |                            |               |
|          | Co-C(           | carbonyl)   | 1.752(8)-1.770(8)          |               |
|          | C–O(ca          | arbonyl)    | 1.135(10)-1.161(10)        |               |
|          | P-C(pl          | henyl)      | 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)-C | Co(1)–Co(2)     | 79.4(2)     | C(234)-Co(1)-Co(2)         | 51.5(2)       |
| C(234)-C | Co(1)-C(233)    | 40.8(3)     | P(2)-Co(2)-Co(1)           | 83.7(1)       |
| C(234)-C | Co(2)-Co(1)     | 49.5(2)     | C(231)-P(2)-Co(2)          | 102.6(3)      |
| O(232)-O | C(231) - P(2)   | 124.8(6)    | C(233)-C(231)-P(2)         | 107.9(5)      |
| C(233)-C | C(231) - O(232) | 127.2(6)    | C(231)–C(233)–Co(1)        | 97.0(4)       |
| C(234)-C | 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 | 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  $P_2Ph_4$  with these alkyne-bridged dicobalt complexes than in the corresponding reactions of  $P_2Ph_4$  with the closely related alkyne-bridged dimolybdenum complexes  $[Mo_2(\eta^5-C_5H_5)_2(\mu-RC=CR')(CO)_4]$ .<sup>8</sup>

#### 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.<sup>33</sup> 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  $[Co_2(\mu-RC\equiv CR')(CO)_6]$  ( $R = R' = CO_2Me$ , Ph or H; R = Ph, R' = H),<sup>10a,34,35</sup> and  $P_2Ph_4^{36}$  were prepared by literature methods.

(i)Reaction of  $[Co_2(\mu-RC\equiv CR')(CO)_6]$  (R = R' = CO<sub>2</sub>Me or Ph; R = Ph, R' = H) with P<sub>2</sub>Ph<sub>4</sub>.--(a) The complex  $[Co_2{\mu-C_2(CO_2Me)_2}(CO)_6]$  (0.63 g, 1.5 mmol) was added to a solution of P<sub>2</sub>Ph<sub>4</sub> (0.60 g, 1.6 mmol) in toluene (100 cm<sup>3</sup>). 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<sub>2</sub>Cl<sub>2</sub> and separated by preparative TLC using hexane-CH<sub>2</sub>Cl<sub>2</sub> (1:1) as eluent. A red band eluted which, on evaporation to dryness, gave red crystalline  $[Co_2{\mu-C_2(CO_2Me)_2}(CO)_5(P_2Ph_4)]$  1a (0.34 g, 30%) (Found: C, 54.4; H, 3.3; P, 8.0.  $C_{35}H_{26}Co_2O_9P_2$  requires C, 54.6; H, 3.4; P, 8.1%); fast atom bombardment (FAB) mass spectrum, m/z 770 ( $M^+$ ) and  $M^+ - nCO$  (n = 1-5). NMR (CDCl<sub>3</sub>): <sup>13</sup>C, (<sup>1</sup>H composite pulse decoupled),  $\delta$  202.7 (s, 2CO), 198.7 (s, 3CO), 169.3 (s,

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 $CO_2Me$ ), 135–127 (m, Ph), 71.9 (s,  $CCO_2Me$ ) and 52.0 (s, Me); <sup>31</sup>P (<sup>1</sup>H-gated decoupled),  $\delta$  –99.0 [d, br, <sup>1</sup>J(PP) 313 Hz,  $CoPPh_2PPh_2$ ] and –143.1 (d,  $CoPPh_2PPh_2$ ).

(b) The complex  $[Co_2(\mu-PhC\equiv CPh)(CO)_6]$  (3.35 g, 7.2 mmol) was added to a solution of  $P_2Ph_4$  (2.67 g, 7.2 mmol) in toluene (150 cm<sup>3</sup>). 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<sub>2</sub>Cl<sub>2</sub> 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<sub>2</sub>Cl<sub>2</sub> (2:1) gave unreacted  $[Co_2(\mu-PhC=CPh)(CO)_6]$  (0.89 g), followed by a trace of an uncharacterised red band, dark green 1b (1.56 g, 36% conversion) and dark green  $[Co_2(\mu-PhC\equiv CPh)(\mu-P_2Ph_4)(CO)_4]$  2b (1.44 g, 35% conversion). Complex 1b (Found: C, 63.9; H, 3.7; P, 7.8. C43H30C02O5P2 requires C, 64.0; H, 3.7; P, 7.7%); FAB mass spectrum, m/z 806 ( $M^+$ ) and  $M^+ - nCO$  (n = 1-5). NMR (CDCl<sub>3</sub>): <sup>13</sup>C (<sup>1</sup>H composite pulse decoupled),  $\delta$  204.7 (s, 2CO), 200.9 (s, 3CO), 140–126 (m, Ph) and 86.9 (s, CPh); <sup>31</sup>P (<sup>1</sup>H-gated decoupled),  $\delta - 100.0$  [d, br, <sup>1</sup>J(PP) 315 Hz,  $CoPPh_2PPh_2$  and -142.8 (d,  $CoPPh_2PPh_2$ ). Complex 2b (Found: C, 64.8; H, 3.8; P, 8.0. C<sub>42</sub>H<sub>30</sub>Co<sub>2</sub>O<sub>4</sub>P<sub>2</sub> requires C, 64.8; H, 3.9; P, 8.0%); mass spectrum, m/z 778 ( $M^+$ ) and  $M^+ - nCO$ (n = 1-4). NMR (CDCl<sub>3</sub>): <sup>13</sup>C (<sup>1</sup>H composite pulse decoupled), δ 205.1 (s, 4CO), 142-125 (m, Ph) and 88.1 (s, CPh); <sup>31</sup>P (<sup>1</sup>Hgated decoupled),  $\delta - 137.3$  (s,  $\mu$ -P<sub>2</sub>Ph<sub>4</sub>).

(c) The complex  $[Co_2(\mu-PhC=CH)(CO)_6]$  (3.15 g, 8.12 mmol) and  $P_2Ph_4$  (3.00 g, 8.12 mmol) were used in an analogous procedure to (b) above. Column chromatography using hexane-CH<sub>2</sub>Cl<sub>2</sub> (2:1) as eluent gave unreacted  $[Co_2(\mu-PhC=CH)(CO)_6]$  (1.33 g) followed by red-brown  $[Co_2(\mu-PhC=CH)(CO)_5$ - $(P_2Ph_4)]$  1c (1.59 g, 46% conversion) and purple  $[Co_2(\mu-PhC=CH)(\mu-P_2Ph_4)(CO)_4]$  2c (1.02 g, 31% conversion). Complex 1c (Found: C, 60.9; H, 3.4; P, 8.7.  $C_{37}H_{26}Co_2O_5P_2$  requires C, 60.8; H, 3.6; P, 8.5%); FAB mass spectrum, m/z 730 ( $M^+$ ) and  $M^+ - nCO$  (n = 1-5). NMR (CDCl<sub>3</sub>):  $^{13}C$  (<sup>1</sup>H composite pulse decoupled),  $\delta$  205.7 (s, 1CO), 204.5 (s, 1CO), 201.8 (s, 3CO), 138–126 (m, Ph), 86.9 (s, CPh) and 72.0 (s, CH);  $^{31}P$  (<sup>1</sup>H-gated decoupled),  $\delta$  –96.2 [d, br, <sup>1</sup>J(PP) 315 Hz, CoPPh<sub>2</sub>PPh<sub>2</sub>] and –144.4 (d, CoPPh<sub>2</sub>PPh<sub>2</sub>). Complex 2c: mass spectrum, m/z 702 ( $M^+$ ) and  $M^+ - nCO$  (n = 1-4). NMR (CDCl<sub>3</sub>):  $^{13}C$  (<sup>1</sup>H composite pulse decoupled),  $\delta$  205.8 [d, J(PC) 11, 2CO], 204.3 [d, J(PC) 16 Hz, 2CO], 141–126 (m, Ph), 89.5 (s, CPh) and 66.1 (s, CH);  $^{31}P$  (<sup>1</sup>H-gated decoupled),  $\delta$  –129.6 (s,  $\mu$ -P\_2Ph\_4).

(i) Thermolysis of  $[Co_2(\mu-RC\equiv CR')(CO)_5(P_2Ph_4)]$  (R = R' = CO<sub>2</sub>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<sup>3</sup>). The solution was heated at 333 K for 15 h. After removal of the solvent *in vacuo*, TLC separation with hexane–CH<sub>2</sub>Cl<sub>2</sub> (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<sub>34</sub>H<sub>26</sub>Co<sub>2</sub>O<sub>8</sub>P<sub>2</sub> requires C, 55.0; H, 3.5; P, 8.4%); mass spectrum, *m/z* 742 (*M*<sup>+</sup>) and *M*<sup>+</sup> – *n*CO (*n* = 1–4). NMR (CDCl<sub>3</sub>): <sup>13</sup>C (<sup>1</sup>H composite pulse decoupled),  $\delta$  202.5 (s, 4CO), 172.8 (s, CO<sub>2</sub>Me), 135–126 (m, Ph), 72.4 (s, CCO<sub>2</sub>Me) and 52.5 (s, Me); <sup>31</sup>P (<sup>1</sup>H-gated decoupled),  $\delta$  – 137.7 (s,  $\mu$ -P<sub>2</sub>Ph<sub>4</sub>).

(b) Complex **1b** (0.038 g, 0.047 mmol) was dissolved in toluene (25 cm<sup>3</sup>). The solution was heated at 323 K for 6 h. After removal of the solvent, TLC separation with hexane– $CH_2Cl_2$  (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– $CH_2Cl_2$  (3:1) as eluent giving purple 2c (0.30 g, 77%).

(*iii*) Thermolysis of  $[Co_2(\mu-RC\equiv CR')(\mu-P_2Ph_4)(CO)_4]$ (R = R' = CO<sub>2</sub>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<sup>3</sup>) was heated at 363 K for 5 h. After removal of the solvent *in vacuo*, TLC of the residue with hexane–CH<sub>2</sub>Cl<sub>2</sub> (1:4) as eluent

Table 5 Fractional atomic coordinates for complex 2a

| Atom  | X            | у           | Ξ           | Atom  | X          | у             | Ξ          |
|-------|--------------|-------------|-------------|-------|------------|---------------|------------|
| Co(1) | 0.149 88(7)  | 0.152 61(3) | 0.324 08(4) | C(12) | 0.0262 (3) | $0.296\ 2(1)$ | 0.1254(2)  |
| Co(2) | 0.393 25(7)  | 0.117 98(3) | 0.296 56(4) | C(13) | 0.0119(3)  | 0.3553(1)     | 0.1214(2)  |
| P(1)  | 0.144 90(13) | 0.194 62(5) | 0.196 37(8) | C(14) | 0.0929(3)  | 0.3895(1)     | 0.179 9(2) |
| P(2)  | 0.377 79(13) | 0.171 16(5) | 0.177 89(8) | C(15) | 0.1882(3)  | 0.3647(1)     | 0.2424(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) | 0.1647(2)     | 0.1062(2)  |
| O(3)  | 0.569 3(5)   | 0.183 6(2)  | 0.424 5(3)  | C(18) | -0.0756(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) | -0.1583(4) | 0.101 8(2)    | 0.0563(2)  |
| O(5)  | 0.203 9(4)   | -0.0048(2)  | 0.197 0(3)  | C(20) | -0.1285(4) | 0.1130(2)     | -0.0284(2) |
| O(6)  | 0.006 1(4)   | 0.0201(1)   | 0.262 9(3)  | C(21) | -0.0159(4) | 0.150 0(2)    | -0.0458(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)    | 0.0215(2)  |
| O(8)  | 0.280 0(8)   | 0.001 6(2)  | 0.439 2(3)  | C(23) | 0.480 0(4) | 0.2370(2)     | 0.172 1(2) |
| C(1)  | -0.0357(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) | 0.3303(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) | 0.3352(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) | 0.1381(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)  | -0.0671(8)   | -0.029 6(3) | 0.225 8(7)  | C(31) | 0.356 9(4) | 0.055 5(1)    | -0.0173(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)    | -0.0836(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)    | -0.0713(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  $[Co_2\{\mu-PPh_2C(CO_2Me)C(CO_2Me)\}(\mu-PPh_2)(CO)_4]$  **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  $M^+ - nCO$  (n = 1-4). NMR (CDCl<sub>3</sub>): <sup>13</sup>C (<sup>1</sup>H composite pulse decoupled),  $\delta$  205.4 (s, 1CO), 204.8 (s, 1CO), 202.7 (s, 1CO), 201.4 (s, 1CO), 173.4 (s, CO\_2Me), 169.6 (s, CO\_2Me), 142–128 (m, Ph), 108.4 [dd, J(PC), J(P'C) 30, PC(CO\_2Me)C(CO\_2Me)], 51.42 (s, Me), 51.38 (s, Me) and 44.3 [dd, J(PC) 41, J(P'C) 8, PC(CO\_2Me)]; <sup>31</sup>P (<sup>1</sup>H-gated decoupled),  $\delta$  29.2 [d, <sup>2</sup>J(PP) 100 Hz,  $\mu$ -PPh<sub>2</sub>] and -173.1 [d, $\mu$ -PPh<sub>2</sub>C(CO<sub>2</sub>Me)C(CO<sub>2</sub>Me)].

(b) A solution of complex **2b** (0.050 g, 0.064 mmol) in xylene (30 cm<sup>3</sup>) was heated at 328 K for 15 h. After removal of the solvent *in vacuo*, TLC of the residue with hexane–CH<sub>2</sub>Cl<sub>2</sub>(1:1) as eluent gave green crystalline **3b** (0.035 g, 70%) and a trace of red  $[Co_2{\mu-PPh_2CPhCPhC(O)}(\mu-PPh_2)(CO)_4]$  **4b**. Complex **3b** (Found: C, 65.0; H, 3.7; P, 7.9. C<sub>4.2</sub>H<sub>30</sub>Co<sub>2</sub>O<sub>4</sub>P<sub>2</sub> requires C, 64.8; H, 3.9; P, 8.0%); FAB mass spectrum, *m*/*z* 778 (*M*<sup>+</sup>) and *M*<sup>+</sup> – *n*CO (*n* = 1–4). NMR (CDCl<sub>3</sub>): <sup>13</sup>C (<sup>1</sup>H composite pulse decoupled),  $\delta$  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, PCPh]; <sup>31</sup>P (<sup>1</sup>H-gated decoupled),  $\delta$  45.8 [d, <sup>2</sup>*J*(PP) 110 Hz,  $\mu$ -PPh<sub>2</sub>] and –176.0 (d,  $\mu$ -PPh<sub>2</sub>CPhCPh). Complex **4b**: mass spectrum, *m*/*z* 778 (*M*<sup>+</sup> – CO) and *M*<sup>+</sup> – *n*CO (*n* = 2–5). <sup>31</sup>P NMR (CDCl<sub>3</sub>, <sup>1</sup>H gated decoupled):  $\delta$  16.7 (s,  $\mu$ -PPh<sub>2</sub>) and –84.2 [s,  $\mu$ -PPh\_CPhCPhC(O)].

(c) A solution of complex **2c** (0.035 g, 0.05 mmol) in toluene (30 cm<sup>3</sup>) was heated at 333 K for 15 h. After removal of the solvent *in vacuo*, TLC of the residue with hexane–CH<sub>2</sub>Cl<sub>2</sub> (1:1) as eluent gave red crystalline  $[Co_2{\mu-PPh_2CHCPhC(O)}(\mu-PPh_2)(CO)_4]$  **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  $M^+$  – nCO (n = 2-5). NMR <sup>13</sup>C(CD<sub>2</sub>Cl<sub>2</sub>, <sup>1</sup>H composite pulse decoupled),  $\delta$  215.4 [s, PPh<sub>2</sub>CHCPhC(O)], 207 (s, 1CO), 205 (s, 2CO), 201 (s, 1CO), 143–127 (m, Ph), 86.4 [d, J(PC) 33, PPh<sub>2</sub>CHCPh] and 41.8 [dd, J(PC) 42, J(P'C) 6 Hz, PPh<sub>2</sub>CHCPh]; <sup>31</sup>P(CDCl<sub>3</sub>, <sup>1</sup>H-gated decoupled),  $\delta$  15.5 (s,  $\mu$ -PPh<sub>2</sub>) and -98.2 [s,  $\mu$ -PPh<sub>2</sub>CH-CPhC(O)].

(*iv*) Carbonylation of  $[Co_2(\mu-PPh_2RC=CR')(\mu-PPh_2)(CO)_4]$ (R = R' = CO<sub>2</sub>Me **3a** or Ph **3b**.—(a) A solution of complex **3a** (0.100 g, 0.135 mmol) in toluene (50 cm<sup>3</sup>) 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<sub>2</sub>Cl<sub>2</sub> (100%) as eluent gave unreacted  $[Co_2\{\mu-PPh_2C(CO_2Me)C(CO_2Me)\{(\mu-PPh_2)(CO)_4]$  **3a** (0.076 g, 76%) and orange  $[Co_2\{\mu-PPh_2C(CO_2Me)C(CO_2Me)C(O)\}(\mu-PPh_2)(CO)_4]$  **4a** (0.011 g, 11%). Complex **4a** (Found: C, 53.7; H, 3.1. C<sub>35</sub>H<sub>26</sub>Co<sub>2</sub>O<sub>9</sub>P<sub>2</sub> requires C, 54.5; H, 3.4%): mass spectrum, *m*/*z* 770 (*M*<sup>+</sup>) and *M*<sup>+</sup> – *n*CO (*n* = 1–5). <sup>31</sup>P NMR (CDCl<sub>3</sub>, <sup>1</sup>H-gated decoupled):  $\delta$  20.1 (s,  $\mu$ -PPh<sub>2</sub>) and -86.7 [s,  $\mu$ -PPh<sub>2</sub>C(CO<sub>2</sub>Me)C(CO<sub>2</sub>-Me)C(CO).

(b) A solution of complex **3b** (0.041 g, 0.053 mmol) in toluene (30 cm<sup>3</sup>) 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<sub>2</sub>Cl<sub>2</sub> (1:1) as eluent gave unreacted  $[Co_2(\mu-PPh_2-CPhCPh)(\mu-PPh_2)(CO)_4]$  **3b** (0.029 g, 72%) and red  $[Co_2\{\mu-PPh_2-CPhCPhC(O)\}(\mu-PPh_2)(CO)_4]$  **4b** (0.008 g, 19%).

(v) Decarbonylation of  $[Co_2\{\mu-PPh_2CRCR'C(O)\}(\mu-PPh_2)-(CO)_4]$  (R = R' = CO<sub>2</sub>Me 4a or Ph 4b.—(a) A solution of complex 4a (0.050 g, 0.065 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 cm<sup>3</sup>) was purged with N<sub>2</sub> and heated to reflux for 5 h. The solvent was removed *in vacuo* and TLC of the residue with CH<sub>2</sub>Cl<sub>2</sub> (100%) as eluent gave red  $[Co_2\{\mu-PPh_2C(CO_2Me)C(CO_2Me)\}(\mu-PPh_2)(CO)_4]$  3a (0.039 g, 80%) as the only product.

(b) A solution of complex **4b** (0.008 g, 0.010 mmol) in  $CH_2Cl_2$ (20 cm<sup>3</sup>) was purged with N<sub>2</sub> and heated to reflux for 4.5 h. The solvent was removed *in vacuo* and TLC of the residue with hexane-CH<sub>2</sub>Cl<sub>2</sub> (1:1) as eluent gave green  $[Co_2{\mu-PPh_2-CPh}(\mu-PPh_2)(CO)_4]$  **3b** (0.007 g, 85%).

(vi) Reaction of  $[Co_2(\mu+HC\equiv CH)(CO)_6]$  with  $P_2Ph_4$ .—The complex  $[Co_2(\mu+HC\equiv CH)(CO)_6]$  (0.28 g, 0.90 mmol) in toluene (150 cm<sup>3</sup>) was added to a flask charged with  $P_2Ph_4$  (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  $CH_2Cl_2$  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  $[Co_2(\mu-PPh_2)_2(CO)_6]^{21}$  (0.058 g),  $[Co_3(\mu-PPh_2)_3(CO)_6]^{21}$  (0.073 g), red crystalline  $[Co_2\{\mu-PPh_2CHCHC(O)\}(\mu-PPh_2)(CO)_4]$  **4d** (0.012 g, 2%), purple crystalline  $[Co_2\{\mu-PPh_2CHCHC_1)_4]$  **4d** (0.153 g, 26%) and small quantities of an uncharacterised brown complex.

 Table 6
 Fractional atomic coordinates for complex 4c

| Atom               | X                          | у             | z              | Atom                   | X              | у              | 5           |
|--------------------|----------------------------|---------------|----------------|------------------------|----------------|----------------|-------------|
| 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)     | <b>P</b> (1')          | 0.277 4(3)     | 0.454 2(2)     | 0.129 3(1)  |
| P(2)               | 0.288 5(3)                 | -0.0589(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')                  | -0.0555(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)     | -0.0007(5)  |
| O(3)               | -0.065 6(9)                | -0.0713(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)                | -0.2233(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)                 | -0.0366(6)    | 0.225 4(4)     | O(5')                  | -0.0291(8)     | 0.411 8(6)     | 0.147 9(4)  |
| CÌÌ                | 0.3885(17)                 | 0.0720(9)     | 0.170 5(6)     | C(1')                  | 0.0171(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')                  | 0.2072(14)     | 0.4184(9)      | 0.0303(7)   |
| $\vec{C}(\vec{3})$ | 0.025 2(15)                | -0.0762(9)    | 0.143 5(6)     | C(3')                  | 0.345 7(16)    | 0.3101(9)      | 0.089 0(6)  |
| C(4)               | 0.179 4(14)                | -0.1712(9)    | 0.162 8(7)     | C(4')                  | 0.2273(12)     | 0.249 6(10)    | 0.148 0(6)  |
| C(5)               | 0.172 9(12)                | -0.0631(8)    | 0.237 8(6)     | C(5')                  | 0.2797(12)     | 0.389 6(7)     | 0.168 6(6)  |
| Č(6)               | 0.286 3(12)                | -0.0853(7)    | 0.232 7(5)     | C(6')                  | 0.161 5(10)    | 0.369 8(7)     | 0.173 8(5)  |
| $\vec{C}(\vec{7})$ | 0.3635(12)                 | -0.0374(8)    | 0.214 0(6)     | $\hat{\mathbf{C}}(7')$ | 0.0692(12)     | 0.403 2(8)     | 0.139 9(5)  |
| C(8)               | 0.3389(10)                 | -0.1441(6)    | 0.255 7(4)     | Č(8')                  | 0.129 7(8)     | 0.3372(5)      | 0.214 6(3)  |
| $\mathbf{C}(9)$    | 0.4369(10)                 | -0.1726(6)    | $0.241 \ 3(4)$ | C(9')                  | 0.026 3(8)     | 0.3021(5)      | 0.210 6(3)  |
| C(10)              | 0.4857(10)                 | -0.2263(6)    | 0.2639(4)      | C(10)                  | 0.000 8(8)     | $0.265\ 5(5)$  | 0.247 6(3)  |
| $\mathbf{C}(1)$    | 0.4365(10)                 | -0.2516(6)    | 0.3009(4)      | C(11')                 | 0.078 8(8)     | 0.2639(5)      | 0.288 7(3)  |
| C(12)              | 0.338.6(10)                | -0.2231(6)    | 0.315.3(4)     | C(12')                 | 0.182.2(8)     | 0.299.0(5)     | 0.292.8(3)  |
| C(12)              | 0.330 8(10)<br>0.289 8(10) | -0.1694(6)    | 0.2927(4)      | C(12')                 | 0.207.7(8)     | 0.3357(5)      | 0.2527(3)   |
| C(14)              | 0.008 1(9)                 | 0.039 5(5)    | 0.214.8(4)     | C(14')                 | 0.4187(8)      | 0.461.2(5)     | 0 1 10 8(4) |
| C(15)              | -0.0221(9)                 | 0.098.8(5)    | 0.1962(4)      | C(15')                 | 0.4284(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)                | 0.0734(5)     | 0.1937(4)      | C(17')                 | 0.636.3(8)     | 0.4841(5)      | 0.082 5(4)  |
| C(18)              | -0.197.2(9)                | 0.014 1(5)    | 0.2124(4)      | C(18')                 | 0.626 7(8)     | 0.4404(5)      | 0.1175(4)   |
| C(19)              | -0.079.5(9)                | -0.002.9(5)   | 0.2229(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)    | 0.2793(4)      | C(20')                 | 0.267.5(7)     | 0.5294(5)      | 0.1604(4)   |
| C(21)              | 0.1490(9)                  | 0.0561(5)     | 0.317.3(4)     | C(21')                 | 0.366 9(7)     | 0.555 1(5)     | 0.186 5(4)  |
| C(22)              | 0.181(9)                   | 0.091 5(5)    | 0.3574(4)      | C(22')                 | 0.3588(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)     | 0.6431(5)      | 0.2074(4)   |
| C(24)              | 0.3325(9)                  | 0.142.8(5)    | 0.3214(4)      | C(24')                 | 0.151.9(7)     | 0.6173(5)      | 0.181 3(4)  |
| C(25)              | 0.302 2(9)                 | 0.1075(5)     | 0.281 3(4)     | C(25')                 | 0.160.0(7)     | 0.560 5(5)     | 0.157.8(4)  |
| C(26)              | 0.230 (12)                 | -0.047.9(7)   | 0.0604(6)      | C(26')                 | 0.082.6(10)    | 0.284.6(5)     | 0.011 3(4)  |
| C(27)              | 0.291.4(12)                | -0.0082(7)    | 0.033 7(6)     | C(27')                 | 0.139(10)      | 0.226.6(5)     | 0.009.3(4)  |
| C(28)              | 0.251.9(12)                | -0.000.7(7)   | -0.0134(6)     | C(28')                 | $0.139\ 2(10)$ | 0.196.3(5)     | -0.0331(4)  |
| C(29)              | $0.152 \ 3(12)$            | -0.0330(7)    | -0.0337(6)     | C(29')                 | 0.082(10)      | 0.223.8(5)     | -0.0735(4)  |
| C(30)              | $0.092\ 2(12)$             | -0.0727(7)    | -0.007.0(6)    | C(30')                 | 0.0255(10)     | $0.223 \ 0(5)$ | -0.0715(4)  |
| C(31)              | 0.0922(12)<br>0.1317(12)   | -0.0801(7)    | 0.040 1(6)     | C(31')                 | 0.025.7(10)    | 0.3121(5)      | -0.029.1(4) |
| C(32)              | 0.4253(13)                 | -0.0975(5)    | 0.0155(5)      | C(32')                 | -0.0766(9)     | 0.2925(5)      | 0.0731(4)   |
| C(33)              | 0.5339(13)                 | -0.067.8(5)   | 0.1257(5)      | C(33')                 | -0.0937(9)     | 0.228 1(5)     | 0.079.6(4)  |
| C(34)              | 0.6361(13)                 | -0.099.9(5)   | 0.119.1(5)     | C(34')                 | -0.2071(9)     | 0.2035(5)      | 0.0747(4)   |
| C(35)              | 0.629.6(13)                | -0.161.6(5)   | $0.102\ 2(5)$  | C(35')                 | -0.3034(9)     | 0.243 3(5)     | 0.0634(4)   |
| C(36)              | 0.5210(13)                 | -0.1913(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)                | -0.1593(5)    | 0.098 6(5)     | C(37')                 | -0.1729(9)     | 0.332 3(5)     | 0.061 8(4)  |
| -()                |                            |               | 0.070 0(0)     | -(                     |                |                |             |

Complex 4d (Found: C, 57.0; H, 3.5; P, 9.7.  $C_{31}H_{22}C_{2}O_{5}P_{2}$ requires C, 56.9; H, 3.4; P, 9.5%): FAB mass spectrum, *m/z* 654 (*M*<sup>+</sup>) and *M*<sup>+</sup> – *n*CO (*n* = 1–5). NMR: <sup>13</sup>C(CD<sub>2</sub>Cl<sub>2</sub>, <sup>1</sup>H composite pulse decoupled),  $\delta$  218 [s, PPh<sub>2</sub>CHCHC(O)], 207 (s, 1CO), 206 (s, 1CO), 201 (s, 2CO), 142–128 (m, Ph), 68.4 [d, *J*(PC) 34, PPh<sub>2</sub>CHCH] and 40.6 [dd, *J*(PC) 39, *J*(P'C) 6 Hz, PPh<sub>2</sub>CHCH]; <sup>31</sup>P(CDCl<sub>3</sub>, <sup>1</sup>H-gated decoupled),  $\delta$  22.2 (s,  $\mu$ -PPh<sub>2</sub>) and -92.3 [s,  $\mu$ -PPh<sub>2</sub>CHCHC(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*<sup>+</sup>) and *M*<sup>+</sup> – *n*(CO) (*n* = 1–5). NMR (CDCl<sub>3</sub>): <sup>13</sup>C (<sup>1</sup>H composite pulse decoupled),  $\delta$  205.8 (s, 1CO), 203.8 (s, 2CO), 201.8 (s, 1CO), 189.9 [d, *J*(PC) 36, PPh<sub>2</sub>C(O)CHCH], 141–128 (m, Ph), 123.0 [dd, *J*(PC) 32, *J*(P'C) 14, PPh<sub>2</sub>C(O)CHCH] and 75.8 [d, *J*(PC) 90 Hz, PPh<sub>2</sub>C(O)CHCH]; <sup>31</sup>P (<sup>1</sup>H-gated decoupled),  $\delta$  29.8 [d, <sup>2</sup>*J*(PP) 86,  $\mu$ -PPh<sub>2</sub>] and –75.9 [d,  $\mu$ -PPh<sub>2</sub>C(O)CHCH].

(vii) Thermolysis of  $[Co_2{\mu-PPh_2C(O)CHCH}(\mu-PPh_2)-(CO)_4]$  **5d**.—Complex **5d** (0.17 g, 0.25 mmol) was dissolved in xylene (60 cm<sup>3</sup>) and heated at 393 K for 3 d. After removal of the solvent *in vacuo*, TLC of the residue with hexane–CH<sub>2</sub>Cl<sub>2</sub>(1:1) as eluent gave **5d** (0.064 g) and dark green  $[Co_2{\mu-PPh_2C}-$ 

(O)CHCH}( $\mu$ -PPh<sub>2</sub>)(CO)<sub>3</sub>(PPh<sub>3</sub>)] **6d** (0.049 g, 21%) (Found: C, 64.7; H, 4.3. C<sub>48</sub>H<sub>37</sub>Co<sub>2</sub>O<sub>4</sub>P<sub>3</sub> requires C, 64.9; H, 4.2%); mass spectrum, *m/z* 888 (*M*<sup>+</sup>) and *M*<sup>+</sup> – *n*CO (*n* = 1–4). <sup>31</sup>P NMR (CDCl<sub>3</sub>, <sup>1</sup>H-gated decoupled):  $\delta$  –7.9 [d, <sup>2</sup>*J*((PP) 97 Hz,  $\mu$ -PPh<sub>2</sub>], –74.9 [d,  $\mu$ -PPh<sub>2</sub>C(O)CHCH] and –83.4 (s, PPh<sub>3</sub>).

(viii) Reaction of Complex 5d with PPh<sub>3</sub>.—Complex 5d (0.025 g, 0.038 mmol) and PPh<sub>3</sub> (0.011 g, 0.042 mmol) were dissolved in toluene (15 cm<sup>3</sup>) and heated at 373 K for 15 h. After removal of the solvent *in vacuo*, TLC of the residue, with hexane-CH<sub>2</sub>Cl<sub>2</sub> (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,  $\beta = 93.92(2)^\circ$ , U = 3375.4 Å<sup>3</sup>,  $\mu$ (Mo-K $\alpha$ ) = 10.6 cm<sup>-1</sup>,  $D_c =$ 1.46 g cm<sup>-3</sup>, 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,  $\beta = 98.02(3)^\circ$ , U = 7051.3 Å<sup>3</sup>,  $\mu$ (Mo-K $\alpha$ ) =

Table 7 Fractional atomic coordinates for complex 6d

| Atom   | x            | У            | 2            | Atom   | X           | у           | 2           |
|--------|--------------|--------------|--------------|--------|-------------|-------------|-------------|
| Co(1)  | 0.260 17(6)  | 0.150 11(7)  | 0.190 48(8)  | C(326) | 0.291 6(5)  | 0.170 5(6)  | 0.570 1(7)  |
| Co(2)  | 0.278 25(6)  | 0.331 25(7)  | 0.319 43(9)  | C(111) | 0.182 1(4)  | -0.0939(5)  | 0.016 3(6)  |
| P(1)   | 0.224 18(12) | -0.02739(14) | 0.167 80(16) | C(112) | 0.177 7(5)  | -0.2045(6)  | -0.018 1(7) |
| P(2)   | 0.204 0(1)   | 0.372 4(1)   | 0.169 1(2)   | C(113) | 0.142 0(5)  | -0.2561(6)  | -0.1303(7)  |
| P(3)   | 0.354 5(1)   | 0.201 6(1)   | 0.340 8(2)   | C(114) | 0.110 8(5)  | -0.1973(6)  | -0.2090(7)  |
| C(11)  | 0.312 3(5)   | 0.163 1(6)   | 0.054 7(7)   | C(115) | 0.114 0(5)  | -0.0877(6)  | -0.1760(6)  |
| O(11)  | 0.347 4(4)   | 0.171 3(5)   | -0.0350(5)   | C(116) | 0.149 1(4)  | -0.0362(6)  | -0.0629(6)  |
| C(21)  | 0.377 7(6)   | 0.425 4(7)   | 0.310 7(8)   | C(121) | 0.314 4(5)  | -0.1001(6)  | 0.192 1(6)  |
| O(21)  | 0.442 5(4)   | 0.488 9(5)   | 0.311 9(7)   | C(122) | 0.304 0(6)  | -0.1868(7)  | 0.253 9(7)  |
| C(22)  | 0.240 8(5)   | 0.392 7(7)   | 0.456 4(7)   | C(123) | 0.381 9(7)  | -0.2371(8)  | 0.265 0(9)  |
| O(22)  | 0.212 2(4)   | 0.431 0(5)   | 0.541 4(5)   | C(124) | 0.458 4(7)  | -0.199 7(8) | 0.213 9(9)  |
| C(221) | 0.260 5(5)   | 0.421 2(6)   | 0.042 1(7)   | C(125) | 0.468 4(7)  | -0.1169(8)  | 0.151 5(8)  |
| C(222) | 0.234 2(9)   | 0.382 1(10)  | -0.068 6(9)  | C(126) | 0.395 0(5)  | -0.0660(6)  | 0.140 4(7)  |
| C(223) | 0.285 7(13)  | 0.419 2(11)  | -0.165 3(10) | C(131) | 0.133 7(4)  | -0.0775(5)  | 0.261 6(6)  |
| C(224) | 0.354 6(9)   | 0.497 0(13)  | -0.149 4(11) | C(132) | 0.149 5(5)  | -0.0682(6)  | 0.384 1(7)  |
| C(231) | 0.130 5(5)   | 0.240 9(6)   | 0.107 8(7)   | C(133) | 0.079 0(5)  | -0.1017(6)  | 0.456 3(8)  |
| O(232) | 0.089 5(3)   | 0.220 5(4)   | 0.009 2(5)   | C(134) | -0.0054(6)  | -0.1394(6)  | 0.408 9(8)  |
| C(233) | 0.127 1(4)   | 0.170 1(5)   | 0.198 5(6)   | C(135) | -0.0212(5)  | -0.1483(6)  | 0.288 0(7)  |
| C(234) | 0.179 7(4)   | 0.203 1(5)   | 0.306 2(6)   | C(136) | 0.047 7(5)  | -0.1175(5)  | 0.212 6(7)  |
| C(311) | 0.475 6(4)   | 0.231 8(5)   | 0.331 1(7)   | C(211) | 0.121 0(5)  | 0.457 7(6)  | 0.205 8(7)  |
| C(312) | 0.517 2(5)   | 0.209 1(7)   | 0.224 7(7)   | C(212) | 0.064 5(6)  | 0.439 6(7)  | 0.297 9(8)  |
| C(313) | 0.610 0(6)   | 0.234 4(8)   | 0.219 3(9)   | C(213) | -0.0047(7)  | 0.496 7(8)  | 0.327 2(9)  |
| C(314) | 0.660 4(6)   | 0.285 6(8)   | 0.318 5(10)  | C(214) | -0.017 7(7) | 0.571 6(9)  | 0.258 2(10) |
| C(315) | 0.621 7(6)   | 0.309 7(7)   | 0.425 0(9)   | C(215) | 0.029 0(7)  | 0.586 5(9)  | 0.160 4(11) |
| C(316) | 0.529 3(5)   | 0.283 8(7)   | 0.432 5(7)   | C(216) | 0.102 0(8)  | 0.531 2(9)  | 0.133 2(10) |
| C(321) | 0.343 4(4)   | 0.138 8(6)   | 0.476 3(6)   | C(225) | 0.364 2(12) | 0.573 1(14) | -0.0242(18) |
| C(322) | 0.385 9(5)   | 0.051 4(6)   | 0.483 3(7)   | C(226) | 0.310 5(11) | 0.529 7(14) | 0.069 8(15) |
| C(323) | 0.372 0(5)   | -0.005 9(7)  | 0.578 8(8)   | C(227) | 0.402 0(17) | 0.473 9(21) | -0.0629(25) |
| C(324) | 0.318 5(6)   | 0.024 9(7)   | 0.668 9(7)   | C(228) | 0.357 0(16) | 0.441 1(18) | 0.042 1(21) |
| C(325) | 0.278 4(5)   | 0.112 0(7)   | 0.665 7(7)   |        |             |             |             |
|        |              |              |              |        |             |             |             |

11.1 cm<sup>-1</sup>,  $D_c = 1.38$  g, cm<sup>-3</sup>, Z = 8, F(000) = 2976. A crystal of size  $0.30 \times 0.20 \times 0.20$  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  $P\overline{1}$  (no. 2), a = 15.193(3), b = 12.708(3), c = 11.292(2) Å,  $\alpha = 99.06(2)$ ,  $\beta = 90.72(1)$ ,  $\gamma = 100.64(2)^\circ$ , U = 2114.01 Å<sup>3</sup>,  $\mu$ (Mo-K $\alpha$ ) = 8.80 cm<sup>-1</sup>,  $D_c = 1.40$  g cm<sup>-3</sup>, 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  $\theta$  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  $\theta$  3–25° with a scan width of 0.90°, using the technique described previously.<sup>37</sup> 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.<sup>38</sup>

Structure solution and refinement.<sup>39</sup> 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  $\theta$  < 0.35. These were included in the structure-factor calculations with thermal factors of 0.08 Å<sup>2</sup> 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 nonhydrogen 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  $w = 1/\sigma^2 F_0$  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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