Synthesis of $[Co_2(\mu\text{-}PPh_2C_3H_4)(\mu\text{-}PPh_2)(CO)_4]$; its Reactions with $P(OMe)_3$ and with Alkynes *

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The bis(phosphido)-bridged complex $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ **1** undergoes an insertion reaction of allene into one of the phosphido bridges, to give the new ligand-bridged dinuclear cobalt complex $[Co_2(\mu\text{-}PPh_2C_3H_4)(\mu\text{-}PPh_2)(CO)_4]$ **2** in high yield. Complex **2** reacts with $P(OMe)_3$ to give the monosubstituted derivative $[Co_2(\mu\text{-}PPh_2C_3H_4)(\mu\text{-}PPh_2)(CO)_3\{P(OMe)_3\}]$ **3** in which substitution has occurred at the allyl-co-ordinated cobalt atom. Complex **2** also reacts with alkynes, RC≡CH (R=CH_2OH, Me or H), which insert into the remaining phosphido bridge along with a molecule of CO to give $[Co_2(\mu\text{-}PPh_2C_3H_4)\{\mu\text{-}PPh_2C(O)CHCR\}(CO)_3]$ (R = CH_2OH **4a**, Me **4b** or H **4c**). In the case of MeC≡CH which gives **4b**, a second isomer, $[Co_2(\mu\text{-}PPh_2C_3H_4)\{\mu\text{-}PPh_2C(O)CMeCH\}(CO)_3]$ **5**, which differs in the mode of insertion of the alkyne, is also obtained. The isomeric complexes $[Co_2\{\mu\text{-}PPh_2C(O)CHCR\}(\mu\text{-}PPh_2)(CO)_4]$ (R = CH_2OH **6a** or Me **6b**) and $[Co_2\{\mu\text{-}PPh_2C(O)CRCH\}(\mu\text{-}PPh_2)(CO)_4]$ (R = CH_2OH **7a** or Me **7b**), which may be regarded respectively as analogues of **4** and **5** but with a phosphido bridge and an additional terminal CO group in place of the $\mu\text{-}PPh_2C_3H_4$ ligand, have been prepared from $[Co_2(\mu\text{-}RCCH)(CO)_6]$ (R = CH_2OH or Me) and P_2Ph_4. The complexes $[Co_2\{\mu\text{-}PPh_2CHCRC(O)\}(\mu\text{-}PPh_2)(CO)_4]$ (R = CH_2OH **8a** or Me **8b**), which are also isomers of complexes **6a**, **7a** and **6b**, **7b** respectively, have also been obtained in these latter reactions. The complexes **8** contain a bridging ligand which differs from that present in **6** and **7** in that the ordering of the PPh_2, alkene and CO components of the bridging ligand is not the same. The crystal structures of the complexes **3** and **4c** have been determined by X-ray diffraction studies.

The insertion of alkynes into the metal–phosphorus bonds of phosphido-bridged dinuclear complexes is more common than originally thought and usually gives new dinuclear complexes with a bridging ligand derived from one phosphido group, one molecule of alkyne and sometimes also a CO or –C≡CR group if these are present in the original complex.[1-8]

Starting from the bis(phosphido)-bridged complex $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ **1**, we recently reported the stepwise synthesis of the complexes $[Co_2\{\mu\text{-}PPh_2CR^1{=}CR^2C(O)CR^3{=}CR^4\text{-}PPh_2\}(CO)_4]$ (R = H, alkyl, aryl, CO_2Me or silyl).[9] These complexes each contain a bridging nine-membered dimetallacyclic ring formed from the coupling of both phosphido groups in **1** with two alkyne molecules and one CO molecule. In the light of this ability of $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ **1** to undergo alkyne insertions to give novel ligand-bridged species we decided to explore its reactivity with allene.

In this paper we present a study of the reaction of **1** with allene and of the reactivity of the product, $[Co_2(\mu\text{-}PPh_2C_3H_4)(\mu\text{-}PPh_2)(CO)_4]$ **2**, towards $P(OMe)_3$ and alkynes (Scheme 1). The reactions of **2** with alkynes, RC≡CH, gives the alkyne-inserted products $[Co_2(\mu\text{-}PPh_2C_3H_4)\{\mu\text{-}PPh_2C(O)CHCR\}(CO)_3]$ (R = CH_2OH **4a**, Me **4b** or H **4c**) and $[Co_2(\mu\text{-}PPh_2C_3H_4)\{\mu\text{-}PPh_2C(O)CRCH\}(CO)_3]$ (R = Me **5**). For comparative purposes the five-membered metallacyclic ring-containing complexes $[Co_2\{\mu\text{-}PPh_2C(O)CHCR\}(\mu\text{-}PPh_2)(CO)_4]$ (R = CH_2OH **6a** or Me **6b**) and $[Co_2\{\mu\text{-}PPh_2C(O)CRCH\}(\mu\text{-}PPh_2)(CO)_4]$ (R = CH_2OH **7a** or Me **7b**) have also been prepared. These differ from **4** and **5** in that the five-electron donating $\mu\text{-}PPh_2C_3H_4$ ligand is replaced in **6** and **7** by a three-electron donating μ-phosphido ligand and a terminal CO group.

Results and Discussion

(*a*) *Reaction of* $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ **1** *with Allene.*—The reaction of a toluene solution of $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ with allene at room temperature gives the complex $[Co_2(\mu\text{-}PPh_2C_3H_4)(\mu\text{-}PPh_2)(CO)_4]$ **2** in 81% yield. Complex **2** has been characterised spectroscopically (see Table 1 and Experimental section) and its proposed structure is shown in Scheme 1.

The $^{31}P\text{-}\{^1H\}$ NMR spectrum of complex **2** shows a signal at δ 62.4 consistent with the presence of a bridging phosphido group and a signal at δ −86.5 which may be assigned to an allene-inserted phosphido group. In each case the resonance is a doublet with a coupling constant of 102 Hz, indicative of a two-bond phosphorus–phosphorus coupling. The ^1H NMR displays, in addition to phenyl resonances, two very broad signals centred at δ 2.12 and 1.76, which may be assigned respectively to the *syn* and *anti* protons of an allyl group.

Four separate signals are seen in the $^{13}C\text{-}\{^1H\}$ NMR spectrum of **2** at 293 K in the carbonyl region revealing the absence at this temperature of any fluxional process at either metal centre. The carbon atom of the allyl fragment joined directly to the phosphorus gives a doublet resonance at δ 67.4 [$^1J(PC)$ 38 Hz] and the terminal carbons of the allyl group exhibit separate resonances, one a doublet at δ 59.8 [$^2J(PC)$ 14 Hz] and the other a singlet at δ 44.2. The inequivalence of the terminal allyl carbon atoms suggests that the $\mu\text{-}PPh_2C_3H_4$ and $\mu\text{-}PPh_2$ ligands are not *trans* to one another and indeed the solid-state structure of the monosubstituted phosphite deriv-

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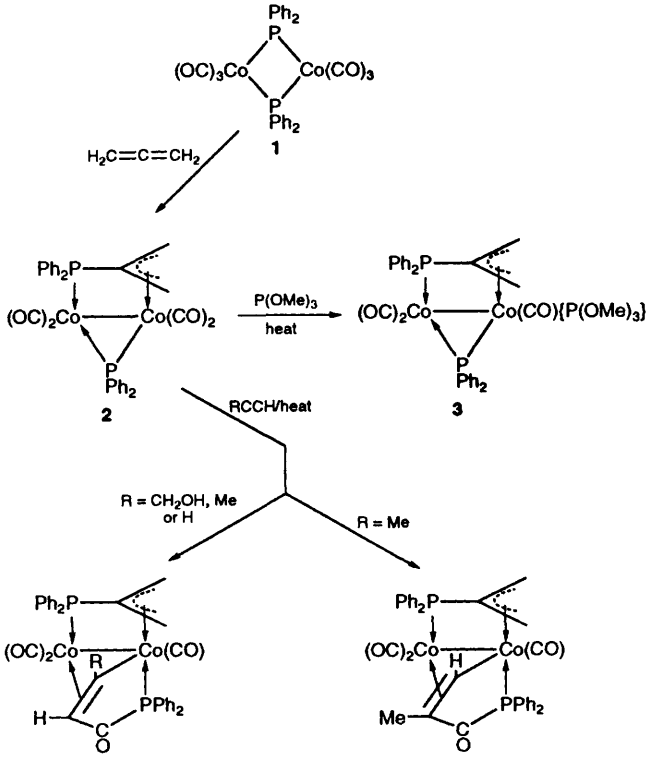
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

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

Compound	ν(CO)[a]/cm^{-1}	^{1}H NMR[b] (δ)
2 $[Co_2(\mu\text{-}PPh_2C_3H_4)(\mu\text{-}PPh_2)(CO)_4]$	2033s, 1994s, 1961s, 1911s	7.8–7.2 (m, 20 H, Ph), 2.12 (br, 2 H, H_{syn}), 1.76 (br, 2 H, H_{anti})
3 $[Co_2(\mu\text{-}PPh_2C_3H_4)(\mu\text{-}PPh_2)(CO)_3\{P(OMe)_3\}]$	1985m, 1959vs, 1916s	7.8–7.1 (m, 20 H, Ph), 3.36 [d, ^3J(PH) 10.0, 9 H, $P(OMe)_3$], 2.1–1.4 (m, 4 H, C_3H_4)
4a $[Co_2(\mu\text{-}PPh_2C_3H_4)\{\mu\text{-}PPh_2C(O)CHC(CH_2OH)\}(CO)_3]$	2008(sh), 1996s, 1962m, 1600w	7.7–6.9 (m, 20 H, Ph), 5.01 [dd, $^2J(H_bH_a)$ 13.0, ^4J(PH) 6.0, 1 H, $C(CH_aH_bOH)$], 4.96 [dd, ^3J(PH) 34.0, ^3J(P′H) 2.0, 1 H, $PPh_2C(O)CHC(CH_2OH)$], 4.84 [dd, ^4J(PH) 6.0, 1 H, $C(CH_aH_bOH)$], 2.4–1.8 (m, 4 H, C_3H_4)
4b $[Co_2(\mu\text{-}PPh_2C_3H_4)\{\mu\text{-}PPh_2C(O)CHCMe\}(CO)_3]$	2012m, 1999vs, 1967s, 1612w	7.9–6.9 (m, 20 H, Ph), 4.78 [d, ^3J(PH) 32.0, 1 H, $PPh_2C(O)CHCMe$], 2.89 (s, 3 H, Me), 2.3–1.7 (m, 4 H, C_3H_4)
4c $[Co_2(\mu\text{-}PPh_2C_3H_4)\{\mu\text{-}PPh_2C(O)CHCH\}(CO)_3]$	2013m, 2002vs, 1969s, 1622w	8.78 [dd, ^3J(HH) 5.7, ^3J(PH) 1.1, 1 H, $PPh_2C(O)CHCH$], 7.8–6.9 (m, 20 H, Ph), 4.95 [ddd, ^3J(PH) 32.5, ^3J(P′H) 2.4, 1 H, $PPh_2C(O)CHCH$], 2.4–1.6 (m, 4 H, C_3H_4)
5 $[Co_2(\mu\text{-}PPh_2C_3H_4)\{\mu\text{-}PPh_2C(O)CMeCH\}(CO)_3]$	2011(sh), 2001s, 1966m, 1611w	8.67 [s, 1 H, $PPh_2C(O)CMeCH$], 7.8–6.9 (m, 20 H, Ph), 2.3–1.6 (m, 4 H, C_3H_4), 1.96 [d, ^4J(PH) 2.5, 3 H, Me][c]
6a $[Co_2\{\mu\text{-}PPh_2C(O)CHC(CH_2OH)\}(\mu\text{-}PPh_2)(CO)_4]$	2042w, 2015s, 2002(sh), 1975m, 1616w	7.9–7.0 (m, 20 H, Ph), 4.52 [dd, ^3J(PH) 41.6, ^3J(P′H) 4.4, 1 H, $PPh_2C(O)CHC(CH_2OH)$], 3.85 [d, $J(H_aH_b)$ 12.8, 1 H, $C(CH_aH_bOH)$], 3.74 [d, 1 H, $C(CH_aH_bOH)$]
6b $[Co_2\{\mu\text{-}PPh_2C(O)CHCMe\}(\mu\text{-}PPh_2)(CO)_4]$	2042w, 2012s, 2000(sh), 1972s, 1607w[d]	7.9–7.1 (m, 20 H, Ph), 4.36 [dd, ^3J(PH) 41.8, ^3J(P′H) 3.8, 1 H, $PPh_2C(O)CHCMe$], 1.80 (s, 3 H, Me)
7a $[Co_2\{\mu\text{-}PPh_2C(O)C(CH_2OH)CH\}(\mu\text{-}PPh_2)(CO)_4]$	2045m, 2015s, 2006(sh), 1975s, 1587w[d]	8.0–7.1 (m, 20 H, Ph), 6.0 [dd, ^3J(PH) 19.8, ^3J(P′H) 1.3, 1 H, $PPh_2C(O)(CH_2OH)CH$], 4.10 [s, br, 1 H, $C(CH_aH_bOH)$], 3.98 [s, br, 1 H, $C(CH_aH_bOH)$]
7b $[Co_2\{\mu\text{-}PPh_2C(O)CMeCH\}(\mu\text{-}PPh_2)(CO)_4]$	2044m, 2012s, 2002(sh), 1970m, 1613w[d]	7.9–7.1 (m, 20 H, Ph), 6.0 [dd, ^3J(PH) 20.8, ^3J(P′H) 2.1, 1 H, $PPh_2C(O)CMeCH$], 1.83 [d, ^4J(PH) 3.7, 3 H, Me][c]

[a] Infrared spectra recorded in *n*-hexane solution unless otherwise indicated. [b] ^{1}H chemical shifts (δ) relative to $SiMe_4$ (δ 0.0), coupling constants in Hz, measured in $CDCl_3$. [c] Recorded in CD_2Cl_2 solution. [d] Recorded in CH_2Cl_2 solution.



Scheme 1 Products derived from the reaction of $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ **1** with allene

ative of **2**, $[Co_2(\mu\text{-}PPh_2C_3H_4)(\mu\text{-}PPh_2)(CO)_3\{P(OMe)_3\}]$ **3** (see below), is consistent with this.

To our knowledge, the only other example of the insertion of allene into a metal–phosphorus bond of a bridging phosphido group to give a stable complex containing a μ-$PPh_2C_3H_4$ ligand is provided by the preparation of the species $[Mn_2(\mu\text{-}PPh_2C_3H_4)(\mu\text{-}PPh_2)(CO)_7]$ in low yield from the photolytic reaction of $[Mn_2(\mu\text{-}PPh_2)_2(CO)_8]$ with allene.[10] This complex differs from **2** most notably in that there is no bond between the metal centres.

(*b*) *Reaction of* $[Co_2(\mu\text{-}PPh_2C_3H_4)(\mu\text{-}PPh_2)(CO)_4]$ **2** *with* $P(OMe)_3$.—The reaction of $[Co_2(\mu\text{-}PPh_2C_3H_4)(\mu\text{-}PPh_2)(CO)_4]$ **2** with $P(OMe)_3$ at 363 K gives a simple monosubstituted trimethyl phosphite derivative $[Co_2(\mu\text{-}PPh_2C_3H_4)(\mu\text{-}PPh_2)(CO)_3\{P(OMe)_3\}]$ **3** in 65% yield. Complex **3** has been characterised spectroscopically (see Table 1 and Experimental section) and by X-ray crystal-structure analysis.

The molecular structure of **3** is shown in Fig. 1 together with a view in which both the terminal ligands and phenyl groups have been omitted. Selected bond distances and angles are given in Table 2 and atomic coordinates in Table 3. The two cobalt atoms, joined by a single metal–metal bond [2.650(2) Å], are bridged by a PPh_2 ligand and a $PPh_2C_3H_4$ ligand which is σ-bonded to Co(1) *via* the phosphorus atom [Co(1)–P(1) 2.167(3) Å] and η^3-bonded to Co(2) *via* the C_3H_4 allyl group. The Co(1) atom is further bound by two terminal carbonyls and the Co(2) atom by one terminal carbonyl and by the P(3) atom of the $P(OMe)_3$ ligand [Co(2)–P(3) 2.152(4) Å] residing in a pseudo-axial site [Co(1)–Co(2)–P(3) 153.5(1)°]. The phosphido bridge is slightly asymmetric, with the Co(2)–P(2) bond [2.195(3) Å] being longer than Co(1)–P(2) [2.146(3) Å]. The three carbon–metal bond lengths of the allyl group co-ordinated to Co(2) are similar [Co(2)–C(4) 2.026(9), Co(2)–C(5) 2.069(12) and Co(2)–C(6) 2.137(10) Å] and the C(5)–C(4)–C(6) angle of 115.1(10)° is in the range expected for an allyl group η^3-bonded to a metal atom[11] although slightly less than the corresponding angle of 120.9(4)° found in the $PPh_2C_3H_4$ ligand in $[Mn_2(\mu\text{-}PPh_2C_3H_4)(\mu\text{-}PPh_2)(CO)_7]$.[10] In addition, the P–C bond of the $PPh_2C_3H_4$ ligand in **3** [P(1)–C(4) 1.805(11) Å] is shorter than that in $[Mn_2(\mu\text{-}PPh_2C_3H_4)(\mu\text{-}PPh_2)(CO)_7]$ [1.862(4) Å], perhaps because the ligand bridges metal–metal bonded centres in the former complex [Co(1)–Co(2) 2.650(2) Å] and non-bonded

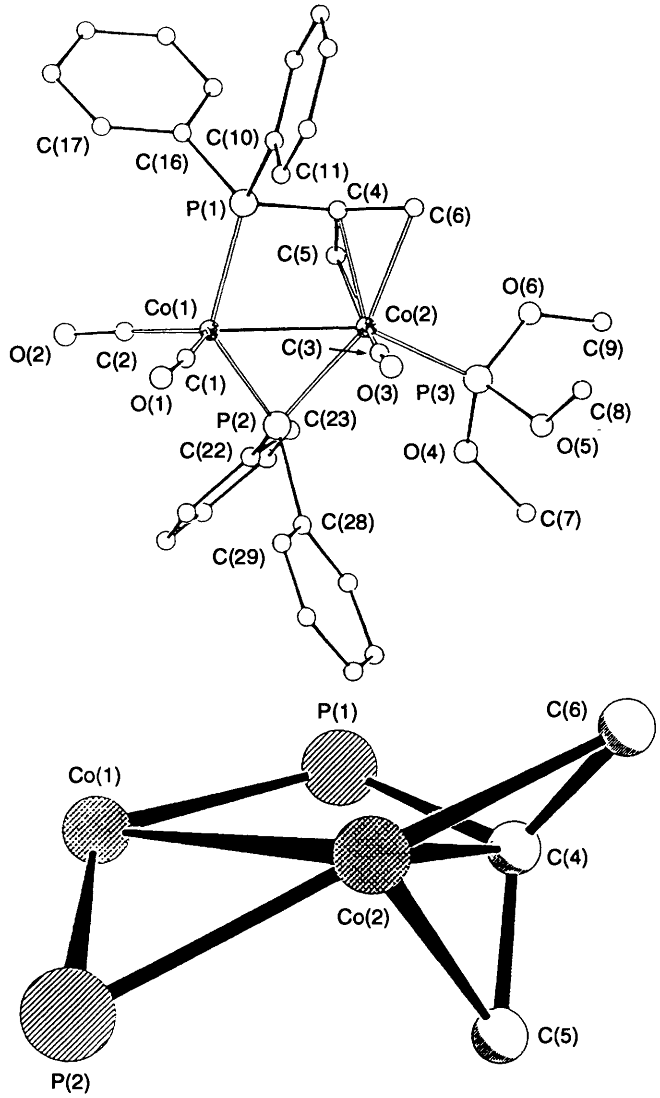


Fig. 1 Molecular structure of $[Co_2(\mu\text{-}PPh_2C_3H_4)(\mu\text{-}PPh_2)(CO)_3\{P(OMe)_3\}]$ **3** including the atom numbering scheme and a view of the structure in which the terminal ligands and phenyl groups have been omitted

Table 2 Selected bond distances (Å) and angles (°) for **3**

Co(1)–Co(2)	2.650(2)	P(1)–C(4)	1.805(11)
Co(1)–P(1)	2.167(3)	P(1)–C(10)	1.825(10)
Co(1)–P(2)	2.146(3)	P(1)–C(16)	1.829(11)
Co(2)–P(2)	2.195(3)	C(4)–C(5)	1.424(15)
Co(2)–P(3)	2.152(4)	C(4)–C(6)	1.402(17)
Co(1)–C(1)	1.742(12)	P(3)–O(4)	1.540(10)
Co(1)–C(2)	1.738(13)	P(3)–O(5)	1.576(12)
Co(2)–C(3)	1.760(13)	P(3)–O(6)	1.584(11)
Co(2)–C(4)	2.026(9)	C(1)–O(1)	1.163(16)
Co(2)–C(5)	2.069(12)	C(2)–O(2)	1.150(16)
Co(2)–C(6)	2.137(10)	C(3)–O(3)	1.140(15)
Co(2)–Co(1)–P(1)	73.4(1)	P(1)–C(4)–C(5)	116.6(8)
Co(2)–Co(1)–P(2)	53.2(1)	P(1)–C(4)–C(6)	121.8(8)
Co(1)–Co(2)–P(2)	51.5(1)	C(5)–C(4)–C(6)	115.1(10)
Co(1)–Co(2)–P(3)	153.5(1)	Co(1)–C(1)–O(1)	172.1(11)
Co(1)–P(1)–C(4)	101.5(3)	Co(1)–C(2)–O(2)	174.5(11)
Co(1)–P(2)–Co(2)	75.2(1)	Co(2)–C(3)–O(3)	176.5(10)

Table 3 Fractional atomic coordinates ($\times 10^4$) with estimated standard deviations (e.s.d.s) in parentheses for the non-hydrogen atoms of **3**

Atom	*X/a*	*Y/b*	*Z/c*
Co(1)	1679(1)	2556(1)	2188(1)
Co(2)	2374(1)	2022(1)	449(1)
P(1)	2888(2)	2616(2)	2904(2)
P(2)	1242(1)	2545(2)	256(2)
P(3)	2447(2)	1771(2)	−1423(3)
O(1)	886(5)	1506(6)	3545(8)
O(2)	1191(5)	4079(6)	2713(8)
O(3)	1931(5)	534(5)	1255(9)
O(4)	1881(7)	2193(7)	−2415(8)
O(5)	2244(7)	942(7)	−1954(9)
O(6)	3261(6)	1957(8)	−1721(9)
C(1)	1227(6)	1883(7)	2970(10)
C(2)	1410(6)	3488(7)	2473(10)
C(3)	2083(6)	1128(7)	940(10)
C(4)	3278(5)	2529(6)	1521(9)
C(5)	2983(6)	3038(7)	547(11)
C(6)	3551(6)	1827(7)	1159(12)
C(7)	1644(11)	1995(12)	−3692(11)
C(8)	2610(12)	256(9)	−1475(17)
C(9)	3533(11)	1904(15)	−2816(14)
C(10)	3421(6)	1877(6)	3863(9)
C(11)	3067(8)	1207(6)	4118(10)
C(12)	3472(8)	614(8)	4800(11)
C(13)	4247(9)	708(9)	5202(12)
C(14)	4599(8)	1369(9)	4966(11)
C(15)	4192(7)	1957(8)	4285(10)
C(16)	3308(7)	3501(6)	3617(11)
C(17)	3014(9)	3818(8)	4561(11)
C(18)	3314(11)	4495(10)	5133(16)
C(19)	3903(11)	4847(11)	4693(19)
C(20)	4192(10)	4535(9)	3761(17)
C(21)	3893(7)	3870(7)	3215(14)
C(22)	1009(6)	3432(6)	−596(8)
C(23)	1475(7)	3777(7)	−1286(10)
C(24)	1248(9)	4465(7)	−1928(11)
C(25)	564(9)	4795(8)	−1871(13)
C(26)	96(10)	4450(9)	−1241(14)
C(27)	310(7)	3775(7)	−568(12)
C(28)	466(5)	1918(6)	−469(10)
C(29)	130(6)	1395(6)	214(12)
C(30)	−423(7)	889(7)	−357(14)
C(31)	−636(8)	897(8)	−1604(16)
C(32)	−319(9)	1403(10)	−2278(14)
C(33)	221(7)	1922(8)	−1711(11)

centres in the latter [Mn ··· Mn 4.125(1) Å]. The plane defined by Co(1)–Co(2)–P(1) forms an angle of 154.9(1)° with the plane passing through Co(1)–Co(2)–P(2). The central allyl carbon C(4) and C(5) are to one side of the plane defined by Co(1)–Co(2)–P(1) (maximum deviations from plane 0.513 and 1.695 Å respectively), whereas C(6) is on the other side of this plane (maximum deviation from plane 0.414 Å).

Monosubstitution by $P(OMe)_3$ takes place preferentially at Co(2). Substitution at Co(1) was not observed, perhaps because of the steric inhibition resulting from the proximity of four phosphido-phenyl groups to this metal atom, although electronic factors may also play an important role.

The ^1H, ^{31}P and ^{13}C NMR spectra of complex **3** (see Table 1 and Experimental section) indicate that the solid-state structure determined by X-ray analysis is maintained in solution. In the $^{13}C\text{-}\{^1H\}$ NMR spectrum of **3** at 293 K all three carbonyls give rise to distinct resonances showing that, as with complex **2**, there is no carbonyl fluxionality at this temperature. The carbon atom of the allyl fragment joined directly to phosphorus gives a doublet of doublets at δ 63.3 [^1J(PC) 39, ^2J(P′C) 10 Hz]. The larger coupling of 39 Hz is assigned, by comparison with the corresponding signal in **2**, to a one-bond coupling to phosphorus and the smaller value of 10 Hz to a two-bond coupling to the phosphorus atom of the $P(OMe)_3$ ligand. The two terminal carbons of the allyl group, as in **2**, give rise to separate resonances, with the lower field signal showing a doublet splitting [^2J(PC) 16 Hz].

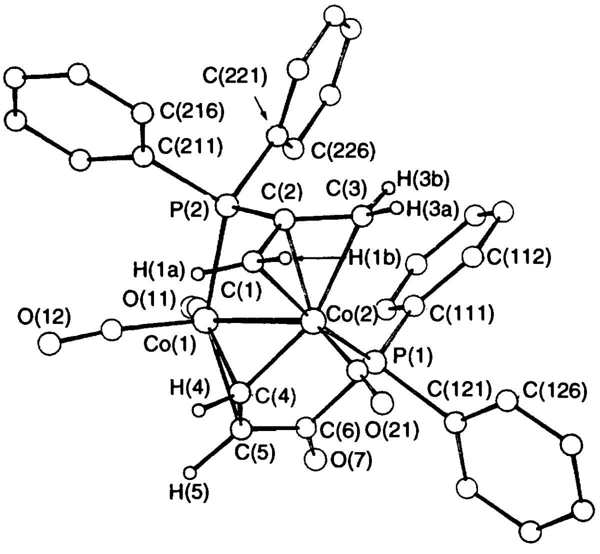


Fig. 2 Molecular structure of [Co$_2$(μ-PPh$_2$C$_3$H$_4$){μ-PPh$_2$C(O)CHCH}(CO)$_3$] **4c** including the atom numbering scheme

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

Co(1)–Co(2)	2.586(2)	Co(1)–P(2)	2.210(4)
Co(1)–C(4)	1.939(12)	Co(1)–C(5)	2.083(16)
Co(2)–P(1)	2.174(5)	Co(2)–P(2)	2.777(4)
Co(2)–C(1)	2.111(16)	Co(2)–C(2)	1.942(15)
Co(2)–C(3)	2.131(13)	Co(2)–C(4)	1.887(10)
P(1)–C(6)	1.894(12)	P(2)–C(2)	1.796(13)
C(1)–C(2)	1.395(19)	C(2)–C(3)	1.400(18)
C(4)–C(5)	1.391(22)	C(5)–C(6)	1.470(22)
C(6)–O-7)	1.242(20)		
P(2)–Co(1)–Co(2)	70.2(1)	C(5)–Co(1)–Co(2)	75.3(4)
C(5)–Co(1)–C(4)	40.3(6)	P(1)–Co(2)–Co(1)	81.3(1)
P(2)–Co(2)–Co(1)	48.5(1)	P(2)–Co(2)–P(1)	104.1(1)
C(1)–Co(2)–Co(1)	94.3(3)	C(2)–Co(2)–Co(1)	86.9(4)
C(2)–Co(2)–P(1)	129.1(4)	C(2)–Co(2)–P(2)	40.0(4)
C(2)–Co(2)–C(1)	40.0(5)	C(3)–Co(2)–Co(1)	115.1(4)
C(3)–Co(2)–C(1)	68.7(6)	C(3)–Co(2)–C(2)	39.9(5)
C(4)–Co(2)–Co(1)	48.3(4)	C(4)–Co(2)–C(1)	97.7(5)
C(4)–Co(2)–C(2)	120.0(5)	C(4)–Co(2)–C(3)	159.3(6)
C(6)–P(1)–Co(2)	101.9(5)	Co(2)–P(2)–Co(1)	61.2(1)
C(2)–C(1)–Co(2)	63.5(9)	C(1)–C(2)–Co(2)	76.5(9)
C(1)–C(2)–P(2)	115.9(8)	C(3)–C(2)–Co(2)	77.3(9)
C(3)–C(2)–P(2)	122.0(1)	C(3)–C(2)–C(1)	118.0(1)
C(2)–C(3)–Co(2)	62.8(7)	Co(2)–C(4)–Co(1)	85.1(5)
C(5)–C(4)–Co(1)	75.5(8)	C(5)–C(4)–Co(2)	122.1(9)
C(4)–C(5)–Co(1)	64.3(8)	C(6)–C(5)–Co(1)	99.0(9)
C(6)–C(5)–C(4)	120.0(1)	C(5)–C(6)–P(1)	107.0(1)
O(7)–C(6)–P(1)	124.0(1)	O(7)–C(6)–C(5)	129.0(1)

(*c*) *Reaction of* [Co$_2$(μ-PPh$_2$C$_3$H$_4$)(μ-PPh$_2$)(CO)$_4$] **2** *with* RC≡CH (R = CH$_2$OH, Me *or* H).—Reaction of [Co$_2$(μ-PPh$_2$C$_3$H$_4$)(μ-PPh$_2$)(CO)$_4$] **2** with RC≡CH (R = CH$_2$OH, Me or H) at 363 K in toluene gives, in addition to unreacted starting material and unidentified decomposition products, the complexes [Co$_2$(μ-PPh$_2$C$_3$H$_4$){μ-PPh$_2$C(O)CHCR}(CO)$_3$] (R = CH$_2$OH **4a**, Me **4b** or H **4c**) and [Co$_2$(μ-PPh$_2$C$_3$H$_4$){μ-PPh$_2$C(O)CRCH}(CO)$_3$] (R = Me **5**) in yields ranging from 2–21%). All the complexes **4a**–**4c** and **5** have been characterised spectroscopically (see Table 1 and Experimental section) and the structure of **4c** has been determined by an X-ray crystal-structure analysis.

The molecular structure of [Co$_2$(μ-PPh$_2$C$_3$H$_4$){μ-PPh$_2$C(O)CHCH}(CO)$_3$] **4c** is illustrated in Fig. 2 together with the atom numbering scheme; Table 4 lists selected bond distances and angles and atomic coordinates are given in Table 5.

The single metal–metal bond in **4c** is bridged by two ligands. The first consists of an allyl group substituted on the central carbon atom by a PPh$_2$ group; this ligand bonds through the phosphorus atom to Co(1) and through all three carbon atoms of the allyl group to Co(2). The second ligand consists of a PPh$_2$C(O)CHCH moiety which with Co(2) forms a five-membered metallacyclic ring, the unsaturated C–C bond of which is η^2-co-ordinated to the second cobalt atom, Co(1). In addition to these bridging ligands, Co(1) has two terminally co-ordinated carbonyl groups, and Co(2) has one.

The metal–metal bond distance in **4c** [Co(1)–Co(2) 2.586(2) Å] is consistent with the presence of a single Co–Co bond as required by the EAN (effective atomic number) rule. The metal–metal bond length lies between those found for single Co–Co bonds in two related compounds, *viz*. [Co$_2${μ-C(CO$_2$Me)=CH(CO$_2$Me)}(μ-PPh$_2$)(CO)$_4$] [Co(1)–Co(2) 2.458(1) Å][12] and [Co$_2$(μ-PPh$_2$C$_3$H$_4$)(μ-PPh$_2$)(CO)$_3${P(OMe)$_3$}] **3** [Co(1)–Co(2) 2.650(2) Å].

The phosphorus atom of the μ-PPh$_2$C$_3$H$_4$ ligand in **4c** donates two electrons to Co(1) [Co(1)–P(2) 2.210(4) Å], and the three-electron donating allyl fragment bonds almost symmetrically to the second cobalt atom [Co(2)–C(1) 2.111(16), Co(2)–C(2) 1.942(15) and Co(2)–C(3) 2.131(13) Å]. These cobalt–carbon distances may be compared with those of the identical bridging ligand in the related complex **3** [Co(1)–P(1) 2.167(3), Co(2)–C(4) 2.026(9), Co(2)–C(5) 2.069(12), Co(2)–C(6) 2.137(10) Å]. The other bridging ligand in **4c**, μ-PPh$_2$C(O)CHCH, is similar to that present in the complex [Co$_2${μ-PPh$_2$C(O)CHCH}(μ-PPh$_2$)(CO)$_3$(PPh$_3$)] which has been previously studied by X-ray analysis.[13] The bond lengths within the ligand in **4c** [P(1)–C(6) 1.894(12), C(6)–C(5) 1.470(22), C(5)–C(4) 1.391(22) Å] are similar to the corresponding distances in the latter complex [P–C 1.857(7), C–C 1.461 (11), C=C 1.408(6) Å] as is the P(1)–Co(1) distance [2.174(5) *vs*. 2.209(2) Å]. The Co–C bond lengths to the π-bonded carbon atoms are also similar to those in [Co$_2${μ-PPh$_2$C(O)CHCH}(μ-PPh$_2$)(CO)$_3$(PPh$_3$)] [Co(1)–C(4) 1.939(12), Co(1)–C(5) 2.083(16) *vs*. Co–C 1.929(7), Co–C 2.085(7) Å] whereas the Co–C bond length to the σ-bonded carbon atom in **4c** is considerably shorter [Co(2)–C(4) 1.887(10) *vs*. Co–C 1.984(6) Å]. The three carbonyl ligands in **4c** are essentially linear [Co–C(carbonyl) distances 1.732(12)–1.755(16) Å, Co–C–O(carbonyl) angles 173(2)–174(1)°].

The spectroscopic properties of complex **4c** suggest that the solid-state structure is maintained in solution. In the IR spectrum a weak band at 1622 cm^{-1} is assigned to ν(C=O) of the five-membered metallacyclic ring. In the ^{31}P-{^{1}H} NMR spectrum two closely spaced broad upfield singlet resonances centred at δ −92.6 and −95.0 are seen, these being consistent with the presence of a PPh$_2$C$_3$H$_4$ group and a phosphorus atoms which is part of a five-membered metallacyclic ring,[2,13] although which signal is due to which phosphorus atom is uncertain. In the ^{13}C-{^{1}H} NMR spectrum, recorded at 293 K, three distinct broad resonances are observed for the terminal CO ligands. The cobalt atom ligated by two CO groups is therefore non-fluxional at this temperature. A sharper doublet carbonyl resonance at higher field is assigned to the phosphorus-bound CO of the metallacyclic ring [^1J(PC) 40 Hz]. The PPh$_2$C(O)CH*C*H carbon appears as a singlet at δ 152.5, whilst the PPh$_2$C(O)*C*HCH carbon resonance at δ 83.4 is a doublet of doublets [^2J(PC) 75, ^2J(P′C) 5 Hz]. The allyl carbons give rise to three separate resonances with a similar pattern of chemical shifts to that for the allyl complex [Co$_2$(μ-PPh$_2$C$_3$H$_4$)(μ-PPh$_2$)(CO)$_4$] **2**. Unlike **2**, however, the resonances due to the terminal allyl carbons in **4c** show coupling to the phosphorus atom of the five-membered metallacycle {δ 53.6 [^2J(PC) 20, ^2J(P′C) 14] and 46.0 [^2J(PC) 10 Hz] [P = PPh$_2$C$_3$H$_4$, P′ = PPh$_2$C(O)CHCH]}.

The structure of complex **4c** can be compared to that postulated for the related species [Co$_2$(μ-PPh$_2$C$_3$H$_4$){μ-PPh$_2$CHCHC(O)}(CO)$_3$] which was proposed as a possible inter-

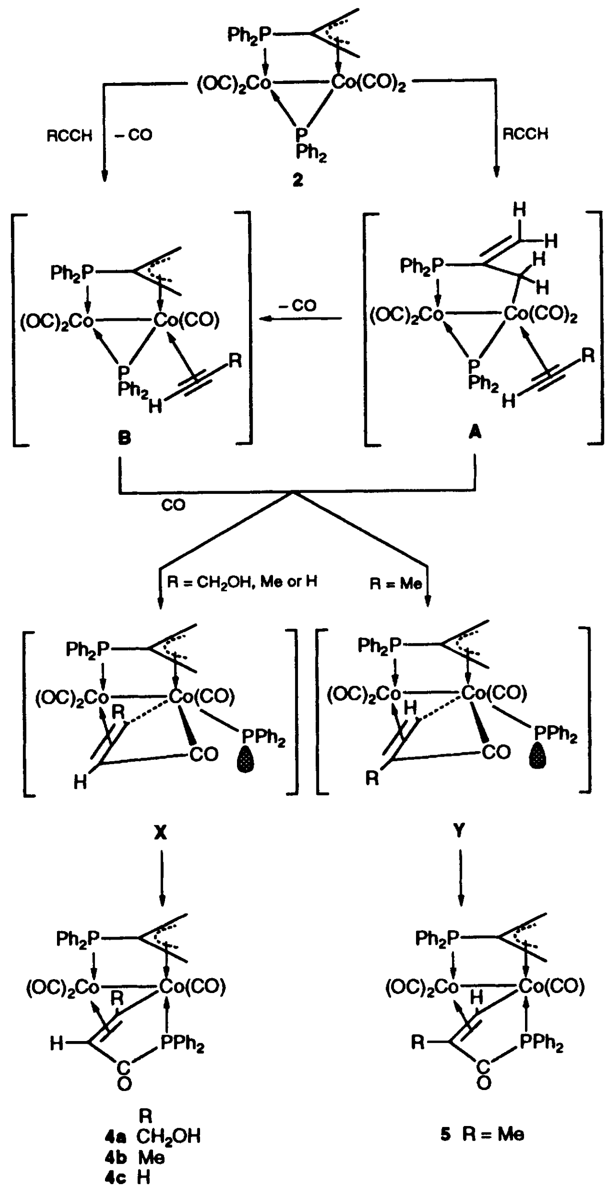
Table 5 Fractional atomic coordinates with e.s.d.s in parentheses for the non-hydrogen atoms of **4c**

Atom	*x*	*y*	*z*
Co(1)	−0.2740(1)	0.0207(2)	0.1002(2)
Co(2)	−0.1239(1)	0.1024(2)	0.2602(2)
P(1)	−0.1295(2)	0.2413(3)	0.1449(4)
P(2)	−0.2839(2)	0.0958(3)	0.3478(4)
C(11)	−0.3561(9)	0.0931(14)	0.0270(16)
O(11)	−0.4089(7)	0.1358(11)	−0.0351(13)
C(12)	−0.3166(10)	−0.1447(16)	0.0456(18)
O(12)	−0.3455(7)	−0.2556(12)	−0.0065(14)
C(21)	−0.0176(9)	0.0810(13)	0.2686(16)
O(21)	0.0531(7)	0.0564(10)	0.2763(13)
C(1)	−0.1374(8)	−0.0122(12)	0.3942(15)
C(2)	−0.1757(8)	0.1070(13)	0.4366(14)
C(3)	−0.1222(9)	0.2265(14)	0.4948(16)
C(4)	−0.1614(7)	−0.0342(11)	0.0656(14)
C(5)	−0.1922(9)	−0.0068(14)	−0.0618(17)
C(6)	−0.1825(8)	0.1303(13)	−0.0560(15)
O(7)	−0.2044(6)	0.1718(9)	−0.1590(11)
C(111)	−0.1835(5)	0.3949(9)	0.1987(9)
C(112)	−0.1513(5)	0.4990(9)	0.3379(9)
C(113)	−0.1911(5)	0.6167(9)	0.3859(9)
C(114)	−0.2631(5)	0.6303(9)	0.2947(9)
C(115)	−0.2953(5)	0.5263(9)	0.1555(9)
C(116)	−0.2555(5)	0.4086(9)	0.1075(9)
C(121)	−0.0275(5)	0.3027(9)	0.1141(9)
C(122)	−0.0172(5)	0.3071(9)	−0.0276(9)
C(123)	0.0602(5)	0.3590(9)	−0.0474(9)
C(124)	0.1275(5)	0.4065(9)	0.0746(9)
C(125)	0.1172(5)	0.4021(9)	0.2163(9)
C(126)	0.0398(5)	0.3502(9)	0.2360(9)
C(211)	−0.3478(6)	−0.0166(9)	0.4020(8)
C(212)	−0.4258(6)	−0.0763(9)	0.3112(8)
C(213)	−0.4779(6)	−0.1593(9)	0.3531(8)
C(214)	−0.4520(6)	−0.1827(9)	0.4857(8)
C(215)	−0.3740(6)	−0.1230(9)	0.5766(8)
C(216)	−0.3219(6)	−0.0399(9)	0.5347(8)
C(221)	−0.3205(5)	0.2586(8)	0.4519(10)
C(222)	−0.3131(5)	0.3066(8)	0.6116(10)
C(223)	−0.3427(5)	0.4287(8)	0.6922(10)
C(224)	−0.3796(5)	0.5028(8)	0.6130(10)
C(225)	−0.3869(5)	0.4548(8)	0.4533(10)
C(226)	−0.3573(5)	0.3327(8)	0.3727(10)

mediate in the formation of the nine-membered dimetallacyclic ring-containing complex [Co_2{μ-PPh_2CHCHC(O)CHCMe-PPh_2}$(CO)_4$] from the reaction of [Co_2{μ- PPh_2CHCHC(O)}-(μ-PPh_2)$(CO)_4$] with allene.[9] The structure of **4c** differs from this proposed intermediate, however, in that the position of the CO in the five-membered metallacyclic ring is not the same. In the proposed mechanism for the reaction of the five-membered ring complex [Co_2{μ-PPh_2CHCHC(O)}(μ-PPh_2)$(CO)_4$] with allene, the intermediate [Co_2(μ-$PPh_2C_3H_4$){μ-PPh_2CHCH-C(O)}$(CO)_3$] leads to the nine-membered ring complex *via* a 1,3-H shift within the $PPh_2C_3H_4$ ligand. This 1,3-H shift is followed by linking of the two bridging ligands *via* carbon–carbon bond formation.[9] A similar linking of the two bridging ligands in **4c** is presumably inhibited by the alternative positioning of the CO within the five-membered metallacyclic ring.

The proposed structures of the complexes **4a**, **4b** and **5** (Scheme 1) are assigned on the basis of their spectroscopic properties which are closely related to those of **4c** (see Table 1 and Experimental section).

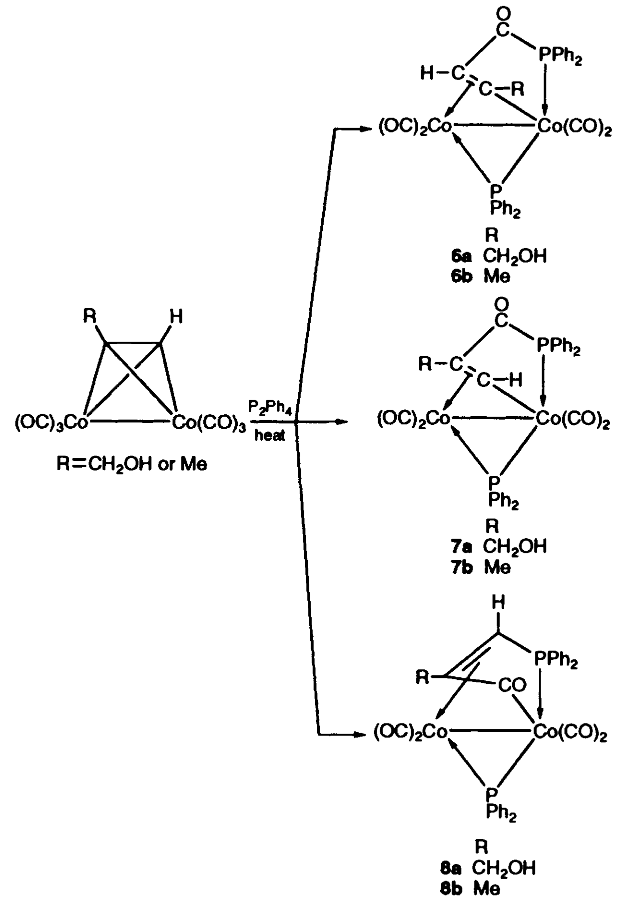
In the reaction of [Co_2(μ-$PPh_2C_3H_4$)(μ-PPh_2)$(CO)_4$] **2** with MeC≡CH an approximately 6:1 mixture of the isomeric complexes **4b** and **5** is isolated, corresponding to the two alternative modes of insertion of the alkyne. In the reaction of **2** with $HOCH_2$≡CH, however, only one isomer is isolated, [Co_2-(μ-$PPh_2C_3H_4$){μ-PPh_2C(O)CHC(CH_2OH)}$(CO)_3$] **4a**. The reason for the absence in this reaction of an isomer of **4a** of



Scheme 2 Some possible pathways for the formation of complexes **4a**–**4c** and **5** from **2**

type **5**, containing the ligand μ-PPh_2C(O)C(CH_2OH)CH, is almost certainly not thermodynamic in origin since the closely related complex **7a** (see below) contains a ligand of this type. It should be noted that **4a** itself is only obtained in low yield.

Some possible pathways for the formation of complexes **4a**–**4c** and **5** are illustrated in Scheme 2. Initial co-ordination of the alkyne to the allyl-co-ordinated cobalt atom with either conversion of the allyl from an η^3 to a σ ligand or CO loss to give respectively intermediates **A** and **B**, could be the first step. Intermediate **B** is, of course, analogous to **3** with an alkyne in place of the $P(OMe)_3$ group. The complex [Co_2{μ-C(OMe)C(Bu)C(O)}$(CO)_6$] provides an example of a stable dicobalt complex containing a similar type of four-membered metallacycle to that postulated in the intermediates **X** and **Y**.[14] The combination of a carbonyl group and the alkyne leading to the formation of **X** and **Y** must be the controlling factor in determining the isomer distribution of the products **4** and **5**. Related intermediates of the type **X**/**Y** involving a four-membered Co–CH=CH–C(O) metallacyclic ring have been previously proposed in the reaction of [Co_2(μ-HCCH)$(CO)_6$] with the biphosphine P_2Ph_4, which gives as the principal product the complex [Co_2{μ-PPh_2C(O)CHCH}(μ-PPh_2)-



Scheme 3 Products from the reaction of $[Co_2(\mu\text{-}RCCH)(CO)_6]$ (R = CH_2OH or Me) with P_2Ph_4

$(CO)_4]$.[13] We have accordingly investigated the reactions of $[Co_2(\mu\text{-}RCCH)(CO)_6]$ (R = CH_2OH or Me) with P_2Ph_4 to see whether the related intermediates, proposed for this type of reaction, might lead to an isomer distribution for the products similar to that obtained in the reactions of **2** with RCCH (R = CH_2OH or Me).

(*d*) *Reaction of* $[Co_2(\mu\text{-}RCCH)(CO)_6]$ (R = CH_2OH *or* Me) *with* P_2Ph_4.—Reaction of $[Co_2(\mu\text{-}RCCH)(CO)_6]$ (R = CH_2OH or Me) with P_2Ph_4 in toluene at 318 K gives $[Co_2\{\mu\text{-}PPh_2CHCRC(O)\}(\mu\text{-}PPh_2)(CO)_4]$ (R = CH_2OH **8a** or Me **8b**) in 51–54% yield, $[Co_2\{\mu\text{-}PPh_2C(O)CRCH\}(\mu\text{-}PPh_2)(CO)_4]$ (R = CH_2OH **7a** or Me **7b**) (8–13%) and $[Co_2\{\mu\text{-}PPh_2C(O)CHCR\}(\mu\text{-}PPh_2)(CO)_4]$ (R = CH_2OH **6a** or Me **6b**) (7–12%). Complexes **8a** and **8b** have been previously synthesised from the reaction of $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ with $HOCH_2C{\equiv}CH$ and $MeC{\equiv}CH$ respectively.[9] The complexes **6a**, **6b** and **7a**, **7b** have been characterised spectroscopically (see Table 1 and Experimental section) and their structures (Scheme 3) are assigned on the basis of a comparison of these properties with those of the previously reported complex $[Co_2\{\mu\text{-}PPh_2C(O)CHCH\}(\mu\text{-}PPh_2)(CO)_4]$.[13] In no case is the formation of metallacycles containing a Co–PPh_2–C(O)–CR=CR′ (R = H, R′ = Me or CH_2OH; R = Me or CH_2OH, R′ = H) ring regiospecific. In fact, the yield ratio **6a**:**7a** and **6b**:**7b** of these isomeric species is approximately 1 : 1 in each case, contrasting quite significantly with the relative yields of the related isomeric complexes **4** and **5** which indicate that the R substituent on the metallacyclic bridging ligand prefers to be localised on the carbon atom σ-bonded to the cobalt as in **4**. The explanation for this difference is uncertain but it would seem probable that electronic factors play an important role. Interestingly, strict regiospecificity was observed in the reaction of $[(OC)_4Ru(\mu\text{-}PPh_2)Co(CO)_3]$ with $RC{\equiv}CR'$ to give the related ruthenacyclic ring 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).[2]

Experimental

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use. Preparative thin-layer chromatography (TLC) was carried out on commercial Merck plates with a 0.25 mm layer of silica, or on 1 mm silica plates prepared at the University Chemical Laboratory, Cambridge. Column chromatography was performed on Kieselgel 60 (70–230 or 230–400 mesh). Products are given in order of decreasing R_f values.

The instrumentation used to obtain spectroscopic data has been described previously.[15] Phosphorus-31 NMR chemical shifts are given relative to $P(OMe)_3$ with upfield shifts negative. Unless otherwise stated all reagents were obtained from commercial suppliers and used without further purification. The compounds $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ **1**,[9,16] $[Co_2(\mu\text{-}RCCH)(CO)_6]$ (R = CH_2OH or Me)[17,18] and P_2Ph_4[19] were prepared by literature methods.

(*i*) *Reaction of* $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ **1** *with Allene*.—Complex **1** (0.80 g, 1.22 mmol) was dissolved in toluene (50 cm^3) and allene was slowly purged through the solution for 0.75 h. After stirring the solution for 15 h at room temperature, the solvent was removed on a rotary evaporator. The residue was taken up in the minimum amount of CH_2Cl_2, adsorbed onto silica, pumped dry and added to the top of a chromatography column. Elution with hexane–CH_2Cl_2 (1 : 1) gave one red-brown crystalline complex $[Co_2(\mu\text{-}PPh_2C_3H_4)(\mu\text{-}PPh_2)(CO)_4]$ **2** (0.63 g, 81%) (Found: C, 58.2; H, 3.8; P, 9.6. $C_{31}H_{24}Co_2O_4P_2$ requires C, 58.2; H, 3.8; P, 9.7%); fast atom bombardment (FAB) mass spectrum, *m*/*z* 640 (M^+) and $M^+ - n$CO (*n* = 1–4); NMR ($CDCl_3$): ^{13}C (^1H composite pulse decoupled), δ 208.7 (s, 1 CO), 207.2 (s, 1 CO), 203.7 (s, 1 CO), 203.0 (s, 1 CO), 142–128 (m, Ph), 67.4 [d, ^1J(PC) 38, $PPh_2\mathit{C}(CH_2)(CH_2)$], 59.8 [d, ^2J(PC) 14, $PPh_2C(\mathit{C}H_2)(CH_2)$] and 44.2 [s, $PPh_2C(CH_2)(\mathit{C}H_2)$]; ^{31}P (^{1}H gated decoupled), δ 62.4 [d, ^2J(PP) 102 Hz, μ-PPh_2] and −86.5 (d, μ-$PPh_2C_3H_4$).

(*ii*) *Reaction of* $[Co_2(\mu\text{-}PPh_2C_3H_4)(\mu\text{-}PPh_2)(CO)_4]$ **2** *with* $P(OMe)_3$.—Complex **2** (0.20 g, 0.313 mmol) was dissolved in toluene (30 cm^3) and $P(OMe)_3$ (0.038 cm^3, 0.313 mmol) added dropwise. After heating the solution at 363 K for 1.5 h the solvent was removed *in vacuo*. The residue was dissolved in the minimum quantity of CH_2Cl_2 and applied to the base of TLC plates. Elution with hexane–CH_2Cl_2 (1 : 4) gave green crystalline $[Co_2(\mu\text{-}PPh_2C_3H_4)(\mu\text{-}PPh_2)(CO)_3\{P(OMe)_3\}]$ **3** (0.15 g, 65%) and traces of other uncharacterised compounds. Complex **3**: FAB mass spectrum, *m*/*z* 736 (M^+) and $M^+ - n$CO (*n* = 1–3). NMR ($CDCl_3$): ^{13}C (^1H composite pulse decoupled), δ 211.8 (s, 1 CO), 208.0 (s, 1 CO), 206.5 (s, 1 CO), 144–127 (m, Ph), 63.3 [dd, ^1J(PC) 39, ^2J(P′C) 10, $PPh_2\mathit{C}(CH_2)(CH_2)$], 56.1 [d, ^2J(PC) 16, $PPh_2C(\mathit{C}H_2)(CH_2)$], 51.9 [d, ^2J(PC) 6 Hz, $P(OMe)_3$] and 45.4 [s, $PPh_2C(CH_2)(\mathit{C}H_2)$]; ^{31}P (^{1}H gated decoupled), δ 48.7 (s, μ-PPh_2), 19.7 [s, br, $P(OMe)_3$] and −89.5 (s, $PPh_2C_3H_4$).

(*iii*) *Reaction of* $[Co_2(\mu\text{-}PPh_2C_3H_4)(\mu\text{-}PPh_2)(CO)_4]$ **2** *with* $RC{\equiv}CH$ (R=CH_2OH, Me *or* H).—(*a*) Complex **2** (0.40 g, 1.81 mmol) was dissolved in toluene (40 cm^3) and a five-fold excess of prop-2-yn-1-ol added. After heating the solution to 363 K for 1 h the solvent was removed on the rotary evaporator. The residue was taken up in the minimum amount of CH_2Cl_2, adsorbed onto silica, pumped dry and added to the top of a chromatography column. Elution with hexane–ethyl acetate (4 : 1) gave unreacted **2** (0.100 g, 25%) and the green crystalline complex $[Co_2(\mu\text{-}PPh_2C_3H_4)\{\mu\text{-}PPh_2C(O)CHC(CH_2OH)\}$-

(CO)$_3$] **4a** (0.061 g, 14%) along with some unidentified decomposition products. Complex **4a** (Found: C, 58.4; H, 4.0. C$_{34}$H$_{28}$Co$_2$O$_5$P$_2$ requires C, 58.6; H, 4.0%): FAB mass spectrum, *m*/*z* 696 (M^+) and $M^+ - n$CO (*n* = 1–4). NMR (CDCl$_3$): ^{13}C (^{1}H composite pulse decoupled), δ 208.7 (s, 1 CO), 203.7 (s, 1 CO), 202.6 (s, 1 CO), 189.4 [d, ^1J(PC) 42, PPh$_2$*C*(O)CHC(CH$_2$OH)], 179.9 [s, PPh$_2$C(O)CH*C*(CH$_2$OH)], 139–128 (m, Ph), 80.4 [d, ^2J(PC) 73, PPh$_2$C(O)*C*HC(CH$_2$OH)], 74.3 [s, PPh$_2$C(O)CHC(*C*H$_2$OH)], 64.3 [d, ^1J(PC) 38, PPh$_2$*C*(CH$_2$)(CH$_2$)], 52.2 [dd, ^2J(PC) 10, ^2J(P′C) 10, PPh$_2$C(*C*H$_2$)(CH$_2$)] and 46.7 [d, ^2J(PC) 10 Hz, PPh$_2$C(CH$_2$)(*C*H$_2$)]; ^{31}P (^{1}H gated decoupled), δ −91.6 and −92.9 [s, μ-PPh$_2$C(O)CHC(CH$_2$OH) and μ-PPh$_2$C$_3$H$_4$].

(*b*) Complex **2** (0.30 g, 0.47 mmol) was dissolved in toluene (40 cm^3) and the solution purged with methylacetylene. After heating the solution at 363 K for 1 h the solvent was removed on the rotary evaporator. Column chromatographic separation eluting with hexane–ethyl acetate (4:1) gave unreacted **2** (0.085 g, 21%) and a mixture of the green crystalline complexes [Co$_2$(μ-PPh$_2$C$_3$H$_4$){μ-PPh$_2$C(O)CHCMe}(CO)$_3$] **4b** and [Co$_2$(μ-PPh$_2$C$_3$H$_4$){μ-PPh$_2$C(O)CMeCH}(CO)$_3$] **5** along with unidentified decomposition products. Complexes **4b** and **5** were dissolved in the minimum of CH$_2$Cl$_2$ and applied to the base of TLC plates and repeatedly eluted with CH$_2$Cl$_2$ to give [Co$_2$(μ-PPh$_2$C$_3$H$_4$){μ-PPh$_2$C(O)CMeCH}(CO)$_3$] **5** (0.006 g, 2%) and [Co$_2$(μ-PPh$_2$C$_3$H$_4$){μ-PPh$_2$C(O)CHCMe}(CO)$_3$] **4b** (0.038 g, 12%). Complex **5**: FAB mass spectrum, *m*/*z* 680 (M^+) and $M^+ - n$CO (*n* = 1–4). ^{31}P NMR (CDCl$_3$, ^{1}H gated decoupled), δ −91.6 [s, μ-PPh$_2$C$_3$H$_4$ and μ-PPh$_2$C(O)CMeCH]. Complex **4b** (Found: C, 59.7; H, 4.3. C$_{34}$H$_{28}$Co$_2$O$_4$P$_2$ requires C, 60.0; H, 4.2%): FAB mass spectrum, *m*/*z* 680 (M^+) and $M^+ - n$CO (*n* = 1–4). NMR (CDCl$_3$): ^{13}C (^{1}H composite pulse decoupled), δ 209.3 (s, 1 CO), 204.1 (s, 1 CO), 202.5 (s, 1 CO), 187.9 [d, ^1J(PC) 37, PPh$_2$*C*(O)CHCMe], 180.3 [s, PPh$_2$C(O)CH*C*Me], 137–128 (m, Ph), 85.0 [d, ^2J(PC) 76, PPh$_2$C(O)*C*HCMe], 64.5 [d, ^1J(PC) 37, PPh$_2$*C*(CH$_2$)(CH$_2$)], 53.9 [dd, ^2J(PC) 10, ^2J(P′C) 10, PPh$_2$C(*C*H$_2$)(CH$_2$)], 45.4 [d, ^2J(PC) 10 Hz, PPh$_2$C(CH$_2$)(*C*H$_2$)] and 36.4 (s, Me); ^{31}P (^{1}H gated decoupled), δ −91.5 [s, μ-PPh$_2$C$_3$H$_4$ and μ-PPh$_2$C(O)CHCMe].

(*c*) Complex **2** (0.40 g, 1.81 mmol) was dissolved in toluene (40 cm^3) and the solution purged with acetylene. After heating the solution to 363 K for 1 h the solvent was removed on the rotary evaporator. Column chromatographic separation eluting with hexane–ethyl acetate (4:1) gave unreacted **2** (0.088 g, 22%) and the green crystalline complex [Co$_2$(μ-PPh$_2$C$_3$H$_4$){μ-PPh$_2$C(O)CHCH}(CO)$_3$] **4c** (0.087 g, 21%). Complex **4c**: FAB mass spectrum, *m*/*z* 666 (M^+) and $M^+ - n$CO(*n* = 1–4). NMR (CDCl$_3$): ^{13}C (^{1}H composite pulse decoupled), δ 208.7 (s, 1 CO), 202.8 (s, 1 CO), 202.0 (s, 1 CO), 190.3 [d, ^1J(PC) 40, PPh$_2$*C*(O)CHCH], 152.5 [s, PPh$_2$C(O)CH*C*H], 140–128 (m, Ph), 83.4 [dd, ^2J(PC) 75, ^2J(P′C) 5, PPh$_2$C(O)*C*HCH], 64.8 [d, ^1J(PC) 37, PPh$_2$*C*(CH$_2$)(CH$_2$)], 53.6 [dd, ^2J(PC) 20, ^2J(P′C) 14, PPh$_2$C(*C*H$_2$)(CH$_2$)] and 46.0 [d, ^2J(PC) 10 Hz, PPh$_2$C(CH$_2$)(*C*H$_2$)]. ^{31}P (^{1}H gated decoupled), δ −92.6 and −95.0 [s, μ-PPh$_2$C(O)CHCH and μ-PPh$_2$C$_3$H$_4$].

(*iv*) *Reaction of* [Co$_2$(μ-RCCH)(CO)$_6$] (R = CH$_2$OH *or* Me) *with* P$_2$Ph$_4$.—(*a*) Complex [Co$_2${μ-(HOCH$_2$)CCH}(CO)$_6$] (0.57 g, 1.67 mmol) was dissolved in a toluene solution (75 cm^3) containing P$_2$Ph$_4$ (0.62 g, 1.67 mmol) and heated to 318 K for 15 h. After removal of the solvent on the rotary evaporator, the residue was redissolved in the minimum of CH$_2$Cl$_2$ and added to the top of a chromatography column. Elution with CH$_2$Cl$_2$ gave red crystalline [Co$_2${μ-PPh$_2$CHC(CH$_2$OH)C(O)}(μ-PPh$_2$)(CO)$_4$] **8a** (0.58 g, 51%), purple crystalline [Co$_2${μ-PPh$_2$C(O)C(CH$_2$OH)CH}(μ-PPh$_2$)(CO)$_4$] **7a** (0.150 g, 13%) and green-brown [Co$_2${μ-PPh$_2$C(O)CHC(CH$_2$OH)}(μ-PPh$_2$)(CO)$_4$] **6a** (0.148 g, 12%). Complex **7a** (Found: C, 56.8; H, 3.9. C$_{32}$H$_{24}$Co$_2$O$_6$P$_2$ requires C, 56.2; H, 3.5%): FAB mass spectrum, *m*/*z* 684 (M^+) and $M^+ - n$CO (*n* = 1–5). NMR (CDCl$_3$): ^{13}C (^{1}H composite pulse decoupled), δ 206.1 (s, 1 CO), 204.0 (s, 1 CO), 203.1 (s, 1 CO), 200.6 (s, 1 CO), 188.2 [s, br, PPh$_2$*C*(O)C(CH$_2$OH)CH], 141–128 (m, Ph), 123.5 [dd, ^2J(PC) 30, ^3J(P′C) 12, PPh$_2$C(O)C(CH$_2$OH)*C*H], 93.9 [d, ^2J(PC) 82, PPh$_2$C(O)*C*(CH$_2$OH)CH] and 65.3 [d, ^3J(PC) 8 Hz, PPh$_2$C(O)C(*C*H$_2$OH)CH]; ^{31}P (^{1}H gated decoupled), δ 30.6 (s, μ-PPh$_2$) and −76.7 [s, PPh$_2$C(O)C(CH$_2$OH)CH]. Complex **6a**: FAB mass spectrum, *m*/*z* 684 (M^+) and $M^+ - n$CO (*n* = 1–5). NMR (CDCl$_3$): ^{13}C (^{1}H composite pulse decoupled), δ 205.2 (s, 1 CO), 204.4 (s, 1 CO), 204.0 (s, 1 CO), 201.4 (s, 1 CO), 193.0 [d, ^1J(PC) 32, PPh$_2$*C*(O)CHC(CH$_2$OH)], 149.6 [d, ^2J(PC) 31, PPh$_2$C(O)CH*C*(CH$_2$OH)], 143–127 (m, Ph), 69.9 [s, PPh$_2$C(O)CHC(*C*H$_2$OH)] and 69.8 [d, ^2J(PC) 90 Hz, PPh$_2$C(O)*C*HC(CH$_2$OH)]; ^{31}P (^{1}H gated decoupled), δ 43.3 [d, ^2J(PP) 137, μ-PPh$_2$] and −76.7 [d, PPh$_2$C(O)CHC(CH$_2$OH)].

(*b*) The complex [Co$_2$(μ-MeCCH)(CO)$_6$] (0.43 g, 1.32 mmol) was added to a solution of P$_2$Ph$_4$ (0.49 g, 1.32 mmol) in toluene (75 cm^3). The solution was heated at 318 K for 21 h. The solvent was then removed on the rotary evaporator and the residue dissolved in the minimum amount of CH$_2$Cl$_2$ and applied to the base of preparative TLC plates. Elution with CH$_2$Cl$_2$ gave red crystalline [Co$_2${μ-PPh$_2$CHCMeC(O)}(μ-PPh$_2$)(CO)$_4$] **8b** (0.48 g, 54%), purple crystalline [Co$_2${μ-PPh$_2$C(O)CMeCH}(μ-PPh$_2$)(CO)$_4$] **7b** (0.070 g, 8%) and green-brown [Co$_2${μ-PPh$_2$C(O)CHCMe}(μ-PPh$_2$)(CO)$_4$] **6b** (0.062 g, 7%). Complex **7b** (Found: C, 57.3; H, 3.6; P, 9.3. C$_{32}$H$_{24}$Co$_2$O$_5$P$_2$ requires C, 57.5; H, 3.6; P, 9.3%): FAB mass spectrum, *m*/*z* 668 (M^+) and $M^+ - n$CO (*n* = 1–5). NMR (CDCl$_3$): ^{13}C (^{1}H composite pulse decoupled), δ 207.0 (s, 1 CO), 206.7 (s, 1 CO), 204.3 (s, 1 CO), 203.7 (s, 1 CO), 185.3 [d, ^1J(PC) 41, PPh$_2$*C*(O)CMeCH], 141–128 (m, Ph), 125.3 [dd, ^2J(PC) 30, ^3J(P′C) 15, PPh$_2$C(O)C(Me)*C*H], 90.7 [d, ^2J(PC) 87, PPh$_2$C(O)*C*MeCH] and 21.6 [d, ^3J(PC) 9 Hz, PPh$_2$C(O)C*Me*CH]; ^{31}P (^{1}H gated decoupled), δ 29.0 [d, ^2J(PP) 101 Hz, μ-PPh$_2$] and −78.8 [d, PPh$_2$C(O)CMeCH]. Complex **6b** (Found: C, 57.2; H, 3.7. C$_{32}$H$_{24}$Co$_2$O$_5$P$_2$ requires C, 57.5; H, 3.6%): FAB mass spectrum, *m*/*z* 668 (M^+) and $M^+ - n$CO (*n* = 1–5). NMR (CDCl$_3$): ^{13}C (^{1}H composite pulse decoupled), δ 205.0 (s, 1 CO), 204.3 (s, 2 CO), 202.1 (s, 1 CO), 191.2 [d, ^1J(PC) 32, PPh$_2$*C*(O)CHCMe], 147.8 [dd, ^2J(PC) 27, ^3J(PC) 15, PPh$_2$C(O)CH*C*Me], 143–128 (m, Ph), 74.1 [d, ^2J(PC) 87, PPh$_2$C(O)*C*HCMe] and 31.5 [d, ^3J(PC) 4 Hz, PPh$_2$C(O)CHC*Me*]; ^{13}P (^{1}H gated decoupled), δ 43.8 [d, ^2J(PP) 100 Hz, μ-PPh$_2$] and −76.5 [d, PPh$_2$C(O)CHCMe].

(*v*) *Crystal-structure Determinations*.—*Crystal data for* **3**. C$_{33}$H$_{33}$Co$_2$O$_6$P$_3$, *M* = 736.41, monoclinic, space group $P2_1/c$, *a* = 17.889(8), *b* = 17.411(7), *c* = 11.111(5) Å, β = 100.53(1)°, *U* = 3402(3) Å^3, *Z* = 4, D_c = 1.438 g cm^{-3}, *F*(000) = 1512, μ(Mo-Kα) = 11.52 cm^{-1}. A crystal of size 0.20 × 0.22 × 0.28 mm, grown by diffusion of hexane into a dichloromethane solution, was used in the data collection.

Crystal data for **4c**. C$_{33}$H$_{26}$Co$_2$O$_4$P$_2$, *M* = 666.05, triclinic, space group $P\bar{1}$ (no.2), *a* = 15.888(3), *b* = 10.868(2), *c* = 9.506(2) Å, α = 112.12(3), β = 97.13(2), γ = 92.47(1)°, *U* = 1501.56 Å^3, *Z* = 2, D_c = 1.47 g cm^{-3}, *F*(000) = 680, μ(Mo-Kα) = 11.77 cm^{-1}. A black crystal of size 0.32 × 0.16 × 0.10 mm, grown by diffusion of hexane into dichloromethane solution, was used in the data collection.

Data collection. Data for complex **3** were collected at room temperature on a Philips PW 1100 single-crystal diffractometer using the graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) and the θ–2θ scan mode in the θ range 3–23°. For **4c**, data were collected in the θ range 3–23°, with a scan width of 0.80° using the technique described previously.[20] Equivalent reflections were merged to give 2219 data for **3** with $I/\sigma(I) > 2.0$ and 1809 data for **4c** with $I/\sigma(I) > 3.0$. No correction for absorption was applied for **3**, whereas for **4c** absorption corrections were applied after initial refinement with isotropic thermal parameters for all atoms.[21]

Structure solution and refinement **3**.[22,23] The structure was solved by direct and Fourier methods and refined by full-matrix least squares first with isotropic and then with anisotropic thermal parameters in the last cycles for all the non-hydrogen atoms. Four hydrogen atoms (of the allyl group) of **3** were clearly localised in the final ΔF map and refined isotropically, the remaining were placed at their geometrically calculated positions and refined 'riding' on the corresponding carbon atoms. In the last cycles of refinement the weighting scheme $w = [\sigma^2(F_o) + gF_o^2]^{-1}$ was employed with $g = 0.0035$ at convergence. Final R and R' values were 0.0349 and 0.0437. Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 24. Final atomic coordinates for the non-hydrogen atoms are given in Table 3.

Structure solution and refinement **4c**.[22] The coordinates of the two cobalt atoms were deduced from a Patterson synthesis, and the remaining non-hydrogen atoms were located from subsequent Fourier-difference syntheses. The hydrogen atoms attached to the allyl fragment [C(1)–C(3)] and to the C=C section of the metallacyclic ring, C(4) and C(5), were located in a Fourier-difference synthesis calculated using data with $\sin\theta < 0.35$. These were included in the structure-factor calculations with fixed thermal parameters of 0.08 Å^2 but their parameters were not refined. The remaining hydrogen atoms of the four phenyl groups were included in geometrically idealised positions and were constrained to 'ride' on the relevant carbon atoms with fixed thermal parameters of 0.08 Å^2. The two cobalt atoms and both phosphorus atoms were assigned anisotropic thermal parameters in the final cycles of full-matrix refinement which converged at $R = 0.0660$ and $R' = 0.0635$ with weights of $w = 1/\sigma^2 F_o$ assigned to the individual reflections. Fractional atomic coordinates for the non-hydrogen atoms are given in Table 5.

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

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