

The Influence of the Ring Substituent, R, on the Substitution of Carbonyl Groups by Phosphine Ligands in $[\text{Co}_2\{\mu\text{-PPh}_2\text{CHCRC}(\text{O})\}(\mu\text{-PPh}_2)(\text{CO})_4]$ (R = H, Ph or SiMe₃)[†]

Andrew J. M. Caffyn, Avelino Martín, Martin J. Mays,* Paul R. Raithby and Gregory A. Solan
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK

The room-temperature reaction of the complexes $[\text{Co}_2\{\mu\text{-PPh}_2\text{CHCRC}(\text{O})\}(\mu\text{-PPh}_2)(\text{CO})_4]$ (R = H **1a**, Ph **1b** or SiMe₃ **1c**) with 1 equivalent of PPhMe₂ gave a combination of phosphine substituted products which depends on the nature of R. When R = H **1a**, two isomeric monosubstituted complexes of formula $[\text{Co}_2\{\mu\text{-PPh}_2\text{CHCHC}(\text{O})\}(\mu\text{-PPh}_2)(\text{CO})_3(\text{PPhMe}_2)]$ **2a** and **3a** are afforded in a ratio of approximately 1:1 in which the phosphine co-ordinates either at the cobalt atom π -co-ordinated by the carbon-carbon double bond (**2a**) or at the cobalt to which the PPh₂ and CO groups of the metallacyclic ligand are σ bonded (**3a**). When R = Ph **1b**, the corresponding monosubstituted derivatives, $[\text{Co}_2\{\mu\text{-PPh}_2\text{CHCPhC}(\text{O})\}(\mu\text{-PPh}_2)(\text{CO})_3(\text{PPhMe}_2)]$ **2b** and **3b** are formed together with traces of the disubstituted complex $[\text{Co}_2\{\mu\text{-PPh}_2\text{CHCPhC}(\text{O})\}(\mu\text{-PPh}_2)(\text{CO})_2(\text{PPhMe}_2)_2]$ **4b**. In the case of R = SiMe₃ **1c**, only the monosubstituted isomer $[\text{Co}_2\{\mu\text{-PPh}_2\text{CHC}(\text{SiMe}_3)\text{C}(\text{O})\}(\mu\text{-PPh}_2)(\text{CO})_3(\text{PPhMe}_2)]$ **3c** is obtained. Conversion of the monosubstituted complexes **2a**, **2b** and **3a**, **3b** to the disubstituted complexes $[\text{Co}_2\{\mu\text{-PPh}_2\text{CHCRC}(\text{O})\}(\mu\text{-PPh}_2)(\text{CO})_2(\text{PPhMe}_2)_2]$ (R = H **4a** or Ph **4b**) takes place on thermal reaction of respectively **2a**, **3a** and **2b**, **3b** with a further equivalent of PPhMe₂. An X-ray crystal structural determination has been performed on complex **4a** and reveals a pseudo-axial/*cis* arrangement of the phosphine groups which are located one on each cobalt atom. The complex $[\text{Co}_2\{\mu\text{-PPh}_2\text{CHCPhC}(\text{O})\}(\mu\text{-PPh}_2)(\text{CO})_4]$ **1b** reacted with the secondary phosphine PPh₂H initially in the same way as with PPhMe₂ to give isomeric species of formula $[\text{Co}_2\{\mu\text{-PPh}_2\text{CHCPhC}(\text{O})\}(\mu\text{-PPh}_2)(\text{CO})_3(\text{PPh}_2\text{H})]$ **2d** and **3d**. Thermolysis of complex **2d** resulted in 42% conversion to the isomeric **3d** along with traces of **1b** and $[\text{Co}_2\{\mu\text{-PPh}_2\text{CHCPhC}(\text{O})\}(\mu\text{-PPh}_2)(\text{CO})_2(\text{PPh}_2\text{H})_2]$ **4d**.

We have previously investigated the reactivity of the complexes $[\text{Co}_2\{\mu\text{-PPh}_2\text{CHCRC}(\text{O})\}(\mu\text{-PPh}_2)(\text{CO})_4]$ (R = H, SiMe₃ or aryl) **1** (Scheme 1), towards a range of unsaturated small molecules including alkynes, allene and carbon disulfide.^{1,2} These reactions lead to products resulting from expansion of the five-membered metallacyclic bridging ligand, $\text{Co-PPh}_2\text{-CH=CR-C}(\text{O})$, and from insertion reactions involving the $\mu\text{-PPh}_2$ ligand. Some possible mechanistic pathways for these rather complex reactions were proposed.^{1,2}

In an attempt to gain an insight into the mode of reaction of **1** with unsaturated small molecules and in particular about the initial site of co-ordination, we have now also studied the reactivity of this type of complex towards organophosphines. The non-equivalence of the two cobalt atoms in **1**, resulting from the asymmetry of the bridging metallacyclic ring, provides four inequivalent CO sites for possible substitution by phosphines or other ligands (Fig. 1). In order to explore the possible influence of the R group of the metallacyclic ring on the preferred site of co-ordination of the phosphine we have studied the reactions of a range of complexes of type **1**, $[\text{Co}_2\{\mu\text{-PPh}_2\text{CHCRC}(\text{O})\}(\mu\text{-PPh}_2)(\text{CO})_4]$ (R = H **1a**, Ph **1b** or SiMe₃ **1c**), with PPhMe₂ (Scheme 2).

Results and Discussion

(a) *Reaction of* $[\text{Co}_2\{\mu\text{-PPh}_2\text{CHCRC}(\text{O})\}(\mu\text{-PPh}_2)(\text{CO})_4]$ (R = H **1a**, Ph **1b** or SiMe₃ **1c**) with PPhMe₂.—The reaction of $[\text{Co}_2\{\mu\text{-PPh}_2\text{CHCHC}(\text{O})\}(\mu\text{-PPh}_2)(\text{CO})_4]$ **1a** with PPhMe₂ in toluene at room temperature gives two isomeric complexes of formula $[\text{Co}_2\{\mu\text{-PPh}_2\text{CHCHC}(\text{O})\}(\mu\text{-PPh}_2)(\text{CO})_3(\text{PPhMe}_2)]$ **2a** and **3a** in a combined high yield (46 and 49%).

The corresponding reaction of $[\text{Co}_2\{\mu\text{-PPh}_2\text{CHCPhC}(\text{O})\}(\mu\text{-PPh}_2)(\text{CO})_4]$ **1b** with PPhMe₂ in toluene at room temperature also gives two isomeric complexes of formula $[\text{Co}_2\{\mu\text{-PPh}_2\text{CHCPhC}(\text{O})\}(\mu\text{-PPh}_2)(\text{CO})_3(\text{PPhMe}_2)]$ **2b** and **3b** but in lower combined yield (25 and 33%) along with the disubstituted complex $[\text{Co}_2\{\mu\text{-PPh}_2\text{CHCPhC}(\text{O})\}(\mu\text{-PPh}_2)(\text{CO})_2(\text{PPhMe}_2)_2]$ **4b** (9% yield).

Finally the reaction of $[\text{Co}_2\{\mu\text{-PPh}_2\text{CHC}(\text{SiMe}_3)\text{C}(\text{O})\}(\mu\text{-PPh}_2)(\text{CO})_4]$ **1c** with PPhMe₂ in toluene at room temperature gives $[\text{Co}_2\{\mu\text{-PPh}_2\text{CHC}(\text{SiMe}_3)\text{C}(\text{O})\}(\mu\text{-PPh}_2)(\text{CO})_3(\text{PPhMe}_2)]$ **3c** in near-quantitative yield (95%). No trace of a complex of type **2** was detected in this reaction.

All the complexes **2a**, **2b**, **3a-3c** and **4b** have been characterised spectroscopically (see Table 1 and Experimental section). Thus, the fast atom bombardment (FAB) mass spectra of complexes **2a** and **3a** are consistent with the formulation $[\text{Co}_2\{\mu\text{-PPh}_2\text{CHCHC}(\text{O})\}(\mu\text{-PPh}_2)(\text{CO})_3(\text{PPhMe}_2)]$, showing four CO losses from a molecular ion peak at *m/z* 764.

The ³¹P-¹H NMR spectrum of **3a** shows three phosphorus resonances. The furthest downfield, at $\delta -1.3$ [relative to P(OMe)₃ (δ 0.0)], is assigned to the $\mu\text{-PPh}_2$ ligand. A resonance at $\delta -93.4$ is assigned to the PPh₂CHCHC(O) phosphorus atom, since the corresponding resonance for $[\text{Co}_2\{\mu\text{-PPh}_2\text{-CHCHC}(\text{O})\}(\mu\text{-PPh}_2)(\text{CO})_4]$ occurs at $\delta -92.3$.³ The signal due to the PPhMe₂ ligand is observed at $\delta -125.6$. In the ¹H NMR spectrum of **3a** the PPh₂CHCHC(O) proton appears as a doublet of doublets of doublets centred at δ 4.56. The couplings are assigned as $J(\text{PH})_{\text{trans}}$ 36.0, $J(\text{HH})$ 4.7, $J(\text{P}'\text{H})$ 1.1 ($\text{P}' = \mu\text{-PPh}_2$) and $J(\text{P}''\text{H})$ 0.4 Hz ($\text{P}'' = \text{PPhMe}_2$). The insignificant size of the $J(\text{P}''\text{H})$ coupling is most compatible with a four-bond coupling and suggests that the PPhMe₂ ligand is situated on the cobalt σ bonded to the CO group of the metallacyclic ring as in structures **A** and **C** in Fig. 1. For structures **B** and **D** a larger three-bond coupling to the PPhMe₂

[†] Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii-xxviii.

ligand would have been expected (see discussion of spectrum of **2a** below). The signal for the $\text{PPh}_2\text{CHCHC}(\text{O})$ proton is not well resolved, but takes the form of a triplet of triplets with $[J(\text{PH}) = J(\text{HH}) = 4.7$ and $J(\text{P}'\text{H}) = J(\text{P}''\text{H}) = 2.3$ Hz] centred at δ 4.44.

In the $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum of **3a** the $\text{PPh}_2\text{CHCHC}(\text{O})$ singlet resonance is shifted 11.7 ppm downfield to δ 229.7 with respect to the corresponding resonance for $[\text{Co}_2\{\mu\text{-PPh}_2\text{-CHCHC}(\text{O})\}(\mu\text{-PPh}_2)(\text{CO})_4]$. A shift of this magnitude is again consistent with the co-ordination of the PPhMe_2 ligand to the cobalt σ bonded to the ketonic CO group of the metallacyclic ring. The absence of a $J(\text{PC})$ coupling suggests that the phosphine lies pseudo-*cis* to the $\text{Co}\text{-C}(\text{O})\text{CH}$ bond (structure A in Fig. 1).

Three singlet resonances are observed in the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of **2a**. The furthest downfield signal at δ -13.1 is assigned to the $\mu\text{-PPh}_2$ ligand, while signals at δ -92.6 and -112.6 are assigned to the $\mu\text{-PPh}_2\text{CHCHC}(\text{O})$ and PPhMe_2 ligands respectively. A doublet of doublets of doublets at δ 3.39 in the ^1H NMR spectrum is observed for the $\text{PPh}_2\text{CHCHC}(\text{O})$ proton. The couplings are assigned as $^3J(\text{PH})_{\text{trans}}$ 34.0, $J(\text{P}''\text{H})$ 13.5 ($\text{P}'' = \text{PPhMe}_2$) and $^3J(\text{HH})$ 4.4 Hz. A comparison of the ^1H NMR spectra of **1a** and **3a** with that of **2a** indicates that the coupling of 13.5 Hz in **2a** is too large for it to be due to coupling to the μ -phosphido phosphorus atom. It must therefore be due to coupling to the μ -phosphido phosphorus atom. It must therefore be due to coupling to the PPhMe_2 ligand and its magnitude implies that in **2a** the PPhMe_2 ligand is bonded to the cobalt atom π co-ordinated by the carbon-carbon double bond as in structures B

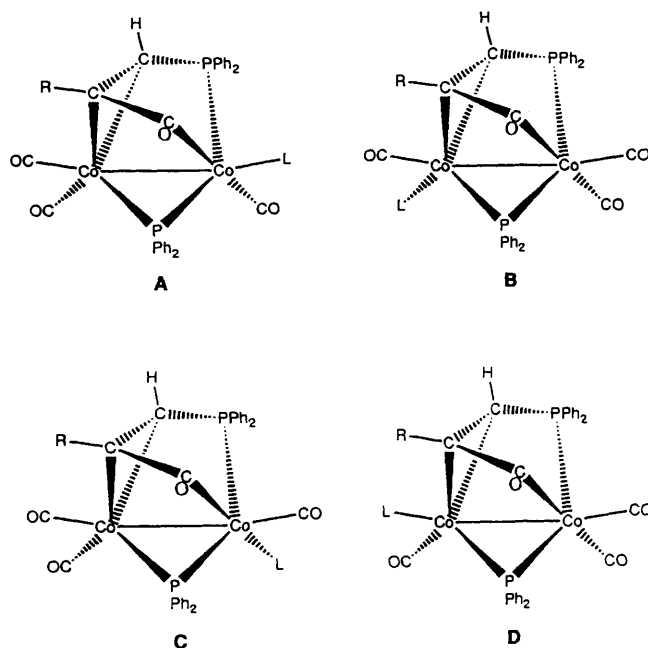
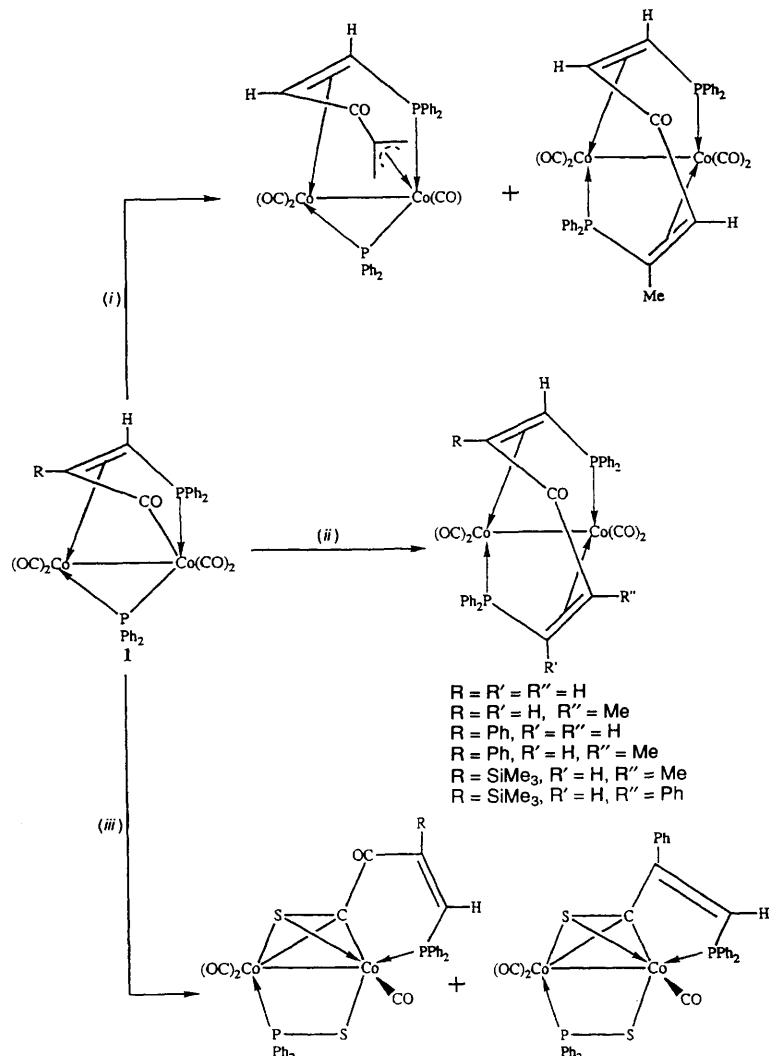
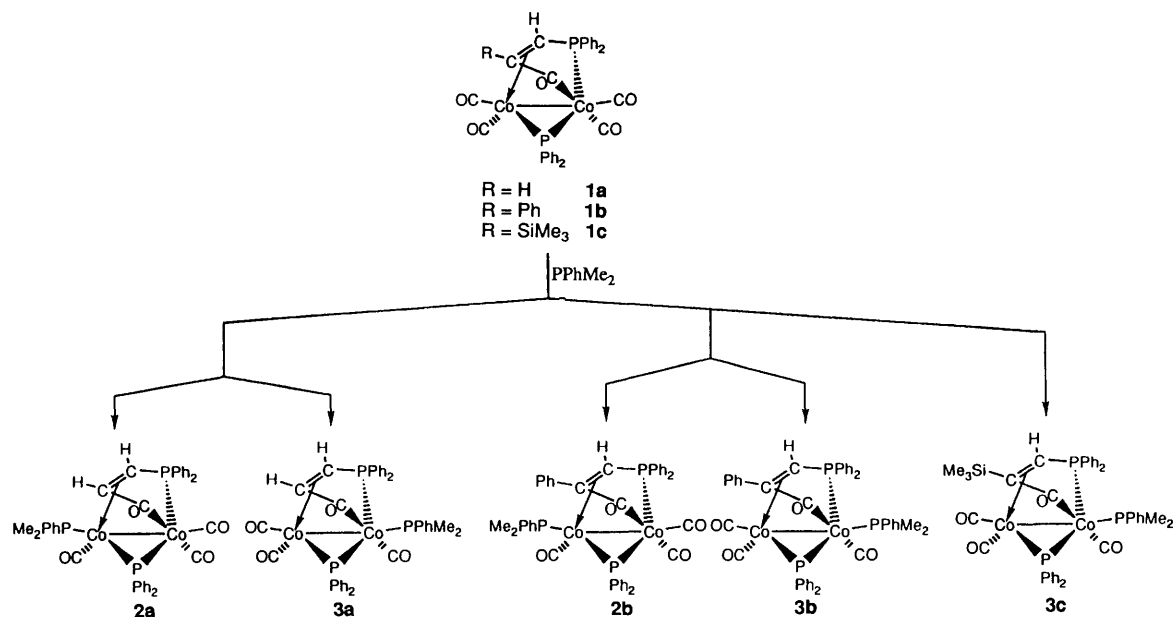


Fig. 1 Possible sites for substitution of a carbonyl ligand by a phosphine L ligand in the complex $[\text{Co}_2\{\mu\text{-PPh}_2\text{CHCRC}(\text{O})\}(\mu\text{-PPh}_2)(\text{CO})_4]$ **1**



Scheme 1 Ring-expansion reactions of $[\text{Co}_2\{\mu\text{-PPh}_2\text{CHCRC}(\text{O})\}(\mu\text{-PPh}_2)(\text{CO})_4]$ **1**.^{1,2} (i) H_2CCCH_2 ($\text{R} = \text{H}$); (ii) $\text{R}'\text{C}\equiv\text{CR}''$ ($\text{R} = \text{H}, \text{Ph}$ or SiMe_3); (iii) CS_2 ($\text{R} = \text{Ph}$ or SiMe_3)



Scheme 2 Monosubstituted products from the reaction of $[\text{Co}_2\{\mu\text{-PPh}_2\text{CHCRC(O)}\}(\mu\text{-PPh}_2)(\text{CO})_4]$ ($\text{R} = \text{H}$ **1a**, Ph **1b** or SiMe_3 **1c**) with PPhMe_2

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

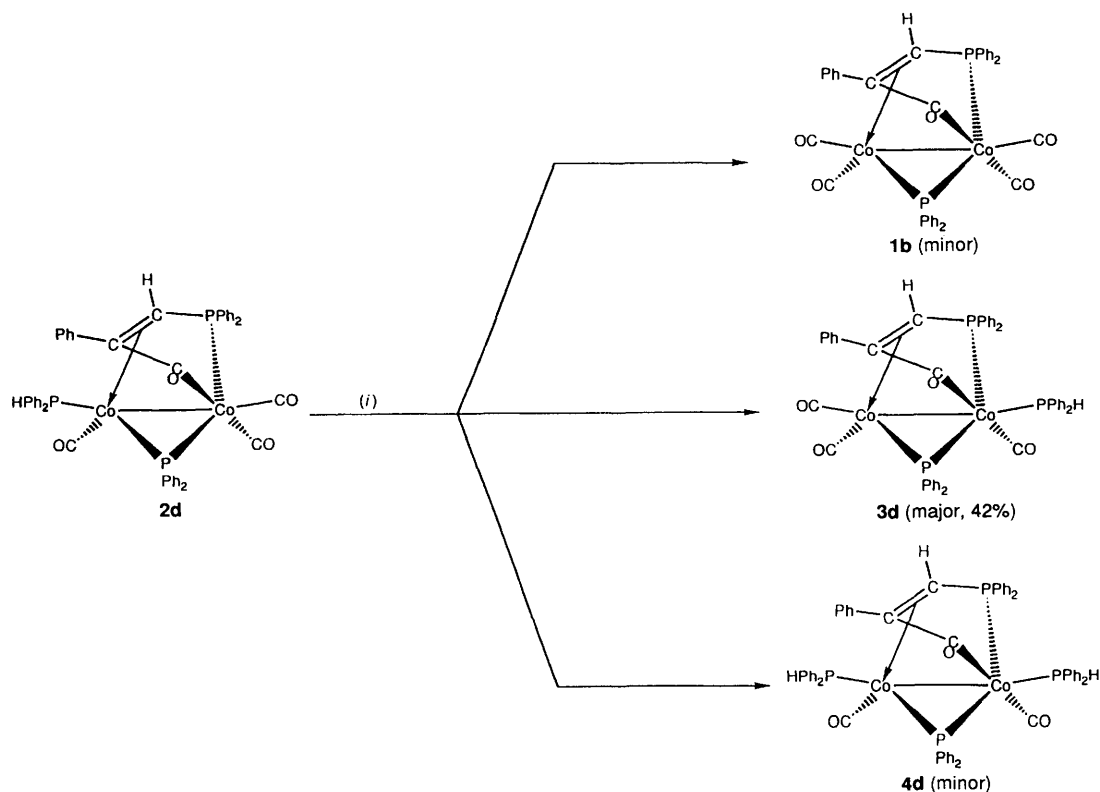
Compound	$\nu(\text{CO})^a/\text{cm}^{-1}$	^1H NMR b (δ)	^{31}P NMR c (δ)
2a	2032s, 1955s, 1946m, 1623w	8.0–7.1 (m, 25 H, Ph), 3.39 [ddd, $^3J(\text{PH})$ 34.0, $^3J(\text{P}^{\text{H}})$ 13.5, $^3J(\text{HH})$ 4.4, 1 H, $\text{PPh}_2\text{CHCHC}(\text{O})$], 3.30 [m, 1 H, $\text{PPh}_2\text{CHCHC}(\text{O})$], 1.63 [d, $^2J(\text{PH})$ 8.7, 3 H, Me], 1.36 [d, $^2J(\text{PH})$ 9.0, 3 H, Me]	–13.1 (s, $\mu\text{-PPh}_2$), –92.6 [s, $\mu\text{-PPh}_2\text{CHCHC}(\text{O})$], –112.6 (s, PPhMe_2)
2b	2036s, 2000s, 1944m, 1643w	8.2–6.4 (m, 30 H, Ph), 4.37 [m, 1 H, $\text{PPh}_2\text{CHCPhC}(\text{O})$], 1.33 [d, $^2J(\text{PH})$ 8.8, 3 H, Me], 0.95 [d, $^2J(\text{PH})$ 8.7, 3 H, Me]	–25.6 (s, $\mu\text{-PPh}_2$), –98.6 [s, $\mu\text{-PPh}_2\text{CHCPhC}(\text{O})$], –106.6 (s, PPhMe_2)
2d	2032s, 1993s, 1947m, 1624w ^d	8.2–6.4 (m, 35 H, Ph), 5.30 [dd, $^1J(\text{PH})$ 354.0, $^3J(\text{P}^{\text{H}})$ 4.7, 1 H, PPh_2H], 4.23 [m, 1 H, $\text{PPh}_2\text{CHCPhC}(\text{O})$]	–16.3 (s, $\mu\text{-PPh}_2$), –91.9 (s, PPh_2H), –97.6 [s, $\mu\text{-PPh}_2\text{CHCPhC}(\text{O})$]
3a	2016s, 1978m, 1967m, 1615w	8.1–7.1 (m, 25 H, Ph), 4.56 [dddd, $^3J(\text{PH})$ 36.0, $^3J(\text{HH})$ 4.7, $^3J(\text{P}^{\text{H}})$ 1.1, $^4J(\text{P}^{\text{H}})$ 0.4, 1 H, $\text{PPh}_2\text{CHCHC}(\text{O})$], 4.44 [dddd, $J(\text{PH})$ 4.7, $J(\text{P}^{\text{H}})$ 2.3, $J(\text{P}^{\text{H}})$ 2.3, 1 H, $\text{PPh}_2\text{CHCHC}(\text{O})$], 1.27 [d, $^2J(\text{PH})$ 9.7, 3 H, Me], 1.07 [d, $^2J(\text{PH})$ 9.1, 3 H, Me]	–1.3 (s, $\mu\text{-PPh}_2$), –93.4 [s, $\mu\text{-PPh}_2\text{CHCHC}(\text{O})$], –125.6 (s, PPhMe_2)
3b	2014s, 1981s, 1963w, 1625w	8.2–7.0 (m, 30 H, Ph), 4.18 [dd, $J(\text{PH})$ 5.7, $J(\text{P}^{\text{H}})$ 2.4, 1 H, $\text{PPh}_2\text{CHCPhC}(\text{O})$], 1.34 [d, $^2J(\text{PH})$ 8.6, 3 H, Me], 1.12 [d, $^2J(\text{PH})$ 9.6, 3 H, Me]	–14.9 (s, $\mu\text{-PPh}_2$), –98.9 [s, $\text{PPh}_2\text{CHCPhC}(\text{O})$], –127.3 (s, PPhMe_2)
3c	2006s, 1975s, 1957w, 1607w	8.1–7.1 (m, 25 H, Ph), 4.34 [ddd, $^2J(\text{PH})$ 4.6, $^3J(\text{P}^{\text{H}})$ 3.1, $J(\text{P}^{\text{H}})$ 1.8, 1 H, $\text{PPh}_2\text{CHC}(\text{SiMe}_3)\text{C}(\text{O})$], 1.32 [d, $^2J(\text{PH})$ 8.5, 3 H, Me], 1.18 [d, $^2J(\text{PH})$ 9.4, 3 H, Me]	–13.9 (s, $\mu\text{-PPh}_2$), –87.8 [s, $\mu\text{-PPh}_2\text{CHC}(\text{SiMe}_3)\text{C}(\text{O})$], –126.8 (s, PPhMe_2)
3d	2010s, 1981s, 1957m, 1615w ^d	7.1–6.8 (m, 35 H, Ph), 6.05 [dd, $^1J(\text{PH})$ 363, $^3J(\text{P}^{\text{H}})$ 3.7, 1 H, PPh_2H], 5.07 [br s, $\text{PPh}_2\text{CHCPhC}(\text{O})$]	–11.4 (s, $\mu\text{-PPh}_2$), –90.6 (s, PPh_2H), –98.1 [s, $\mu\text{-PPh}_2\text{CHCPhC}(\text{O})$]
4a	1979s, 1933s, 1605w	7.9–7.0 (m, 30 H, Ph), 3.82 [ddd, $^3J(\text{PH})$ 34.0, $^3J(\text{P}^{\text{H}})$ 12.4, $^3J(\text{HH})$ 4.4, 1 H, $\text{PPh}_2\text{CHCHC}(\text{O})$], 3.22 [m, 1 H, $\text{PPh}_2\text{CHCHC}(\text{O})$], 1.50 [d, $^2J(\text{PH})$ 8.0, 3 H, Me], 1.36 [d, $^2J(\text{PH})$ 8.2, 3 H, Me], 1.25 [d, $^2J(\text{PH})$ 8.9, 3 H, Me], 1.07 [d, $^2J(\text{PH})$ 8.3, 3 H, Me]	–34.5 (s, $\mu\text{-PPh}_2$), –95.5 [s, $\mu\text{-PPh}_2\text{CHCHC}(\text{O})$], –107.7 (s, PPhMe_2), –117.0 (s, PPhMe_2)
4b	1977s, 1930m, 1618w	8.0–6.8 (m, 35 H, Ph), 4.03 [m, 1 H, $\text{PPh}_2\text{CHCPhC}(\text{O})$], 1.24 [d, $^2J(\text{PH})$ 8.1, Me], 1.13 [d, $^2J(\text{PH})$ 8.8, Me], 0.87 [d, $^2J(\text{PH})$ 8.0, Me], 0.77 [d, $^2J(\text{PH})$ 8.2, Me]	–51.4 (s, $\mu\text{-PPh}_2$), –99.7 [s, $\mu\text{-PPh}_2\text{CHCPhC}(\text{O})$], –106.9 (s, PPhMe_2), –130.0 (s, PPhMe_2)
4d	1974s, 1929m, 1607w ^d	7.9–6.4 (m, 45 H, Ph), 5.98 [d, $^1J(\text{PH})$ 349.0, 1 H, PPh_2H], 5.10 [d, $^1J(\text{PH})$ 348.0, 1 H, PPh_2H], 3.92 [m, 1 H, $\text{PPh}_2\text{CHCPhC}(\text{O})$]	–39.6 (s, $\mu\text{-PPh}_2$), –91.7 (br s, $2\text{PPh}_2\text{H}$), –99.1 [$\mu\text{-PPh}_2\text{CHCPhC}(\text{O})$]

^a Recorded in hexane solution. ^b ^1H chemical shifts (δ) in ppm relative to SiMe_4 (δ 0.0), coupling constants in Hz in CDCl_3 at 293 K. ^c ^{31}P chemical shifts (δ) in ppm relative to external $\text{P}(\text{OMe})_3$ (δ 0.0) (upfield shifts negative), $\{^1\text{H}\}$ -gated decoupled, measured in CDCl_3 at 293 K. ^d Recorded in CH_2Cl_2 solution.

and **D** (Fig. 1). The $\text{PPh}_2\text{CHCHC}(\text{O})$ proton is observed as a poorly resolved multiplet with no coupling greater than 5 Hz. In the $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum of **2a** the resonance due to the carbonyl carbon atom of the $\mu\text{-PPh}_2\text{CHCHC}(\text{O})$ ligand appears as a singlet at a comparable chemical shift (δ 217.1)

to that of the corresponding carbon atom in $[\text{Co}_2(\mu\text{-PPh}_2\text{CHCHC}(\text{O}))(\mu\text{-PPh}_2)(\text{CO})_4]$ **1a** (δ 218.0).³

It is not possible to distinguish between structures **B** (pseudo-equatorial) and **D** (pseudo-axial substitution) for **2a** on the basis of the NMR spectroscopic data. The molecular structure



Scheme 3 Products from the thermolysis of $[\text{Co}_2\{\mu\text{-PPH}_2\text{CHCPhC(O)}\}(\mu\text{-PPH}_2)(\text{CO})_3(\text{PPh}_2\text{H})]$ **2d**; (i) heat

of the disubstituted PPhMe_2 complex **4a** determined by single-crystal X-ray analysis shows, however, that the phosphine ligands occupy pseudo-axial sites on each cobalt atom (see below, Fig. 2). If it can be assumed that the monosubstituted derivatives are also substituted in pseudo-axial positions then **D** is the correct structure for **2a**. Some indication that this is not an unreasonable assumption is provided by the fact that structure **A** is similarly predicted as the correct structure for **3a**, a prediction which may be verified from the NMR data for this complex. Furthermore, pseudo-axial sites for phosphine substitution are also found for all monophosphine substituted dicobalt alkyne-bridged complexes, $[\text{Co}_2(\mu\text{-RCCR}')(\text{CO})_5(\text{PR}_3)]$,⁴ the structures of which have been determined by single-crystal diffraction studies and for the phosphine ligands in the disubstituted species $[\text{Co}_2(\mu\text{-HCCH})(\text{CO})_4(\text{PMe}_3)_2]$.⁵

The structures of the monosubstituted complexes **2b** and **3b/3c** (Scheme 2) are assigned as being analogous to **2a** and **3a** respectively on the basis of their spectroscopic properties (see Table 1 and Experimental section) and a comparison of these properties with those of **2a** and **3a**.

(b) *Synthesis and Thermolysis of* $[\text{Co}_2\{\mu\text{-PPH}_2\text{CHCPhC(O)}\}(\mu\text{-PPH}_2)(\text{CO})_3(\text{PPh}_2\text{H})]$ **2d**.—When the complex $[\text{Co}_2\{\mu\text{-PPH}_2\text{CHCPhC(O)}\}(\mu\text{-PPH}_2)(\text{CO})_4]$ **1b** was treated in toluene at room temperature with the secondary phosphine PPh_2H two isomeric complexes $[\text{Co}_2\{\mu\text{-PPH}_2\text{CHCPhC(O)}\}(\mu\text{-PPH}_2)(\text{CO})_3(\text{PPh}_2\text{H})]$ **2d** and **3d** were again isolated, in this case in an approximately 3:7 ratio, and characterised spectroscopically (see Table 1 and Experimental section).

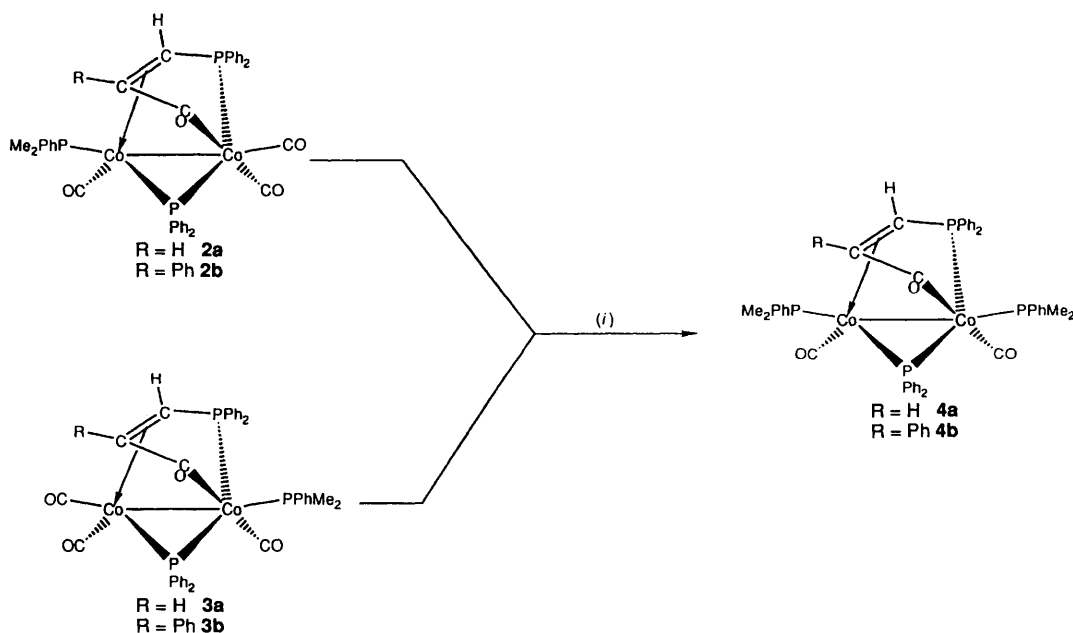
The thermolysis of bimetallic complexes containing both organic bridging ligands and terminally bonded secondary phosphines sometimes leads to phosphorus–hydrogen bond cleavage followed by migration of the hydrogen atom of the organic bridge, and the formation of a phosphido bridge.^{6–9} Thus, the thermolysis of $[\text{Co}_2\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}(\text{CO})_5(\text{PPh}_2\text{H})]$ leads to the μ -phosphido, μ -vinyl complex $[\text{Co}_2\{\mu\text{-C}(\text{CO}_2\text{Me})=\text{CH}(\text{CO}_2\text{Me})\}(\mu\text{-PPH}_2)(\text{CO})_4]$.⁶ In contrast, the thermolysis of $[\text{Co}_2\{\mu\text{-PPH}_2\text{CHCPhC(O)}\}(\mu\text{-PPH}_2)(\text{CO})_3$ -

$(\text{PPh}_2\text{H})]$ **2d** in toluene at 333 K did not lead to phosphorus–hydrogen bond cleavage but gave instead the isomeric $[\text{Co}_2\{\mu\text{-PPH}_2\text{CHCPhC(O)}\}(\mu\text{-PPH}_2)(\text{CO})_3(\text{PPh}_2\text{H})]$ **3d**, as the major product (42% yield) along with small quantities of $[\text{Co}_2\{\mu\text{-PPH}_2\text{CHCPhC(O)}\}(\mu\text{-PPH}_2)(\text{CO})_4]$ **1b** and $[\text{Co}_2\{\mu\text{-PPH}_2\text{CHCPhC(O)}\}(\mu\text{-PPH}_2)(\text{CO})_2(\text{PPh}_2\text{H})_2]$ **4d** (Scheme 3). Complex **4d** has been characterised spectroscopically (see Table 1 and Experimental section) and by a comparison of its properties with complex **4a** (see later).

(c) *Reaction of* $[\text{Co}_2\{\mu\text{-PPH}_2\text{CHCPhC(O)}\}(\mu\text{-PPH}_2)(\text{CO})_3(\text{PPhMe}_2)]$ (R = H **2a**, **3a** or Ph **2b**, **3b**) with PPhMe_2 .—Reaction of $[\text{Co}_2\{\mu\text{-PPH}_2\text{CHCPhC(O)}\}(\mu\text{-PPH}_2)(\text{CO})_3(\text{PPhMe}_2)]$ (R = H **2a**, **3a** or Ph **2b**, **3b**) with PPhMe_2 at temperatures between 313 and 333 K in toluene gives in each case, in addition to unreacted starting material, the disubstituted complexes $[\text{Co}_2\{\mu\text{-PPH}_2\text{CHCPhC(O)}\}(\mu\text{-PPH}_2)(\text{CO})_2(\text{PPhMe}_2)_2]$ (R = H **4a** or Ph **4b**) (77–85% yield) (Scheme 4). Both complexes **4a** and **4b** have been characterised spectroscopically (see Table 1 and Experimental section) and the molecular structure of **4a** has in addition been determined by a single-crystal X-ray diffraction study.

The structure of complex **4a** is shown in Fig. 2 along with a space-filling diagram; Table 2 lists selected bond lengths and angles.

In **4a** the two Co atoms are joined by a single metal–metal bond and are bridged by a diphenylphosphido group. The $\mu\text{-PPH}_2\text{CHCHC(O)}$ ligand also bridges the two cobalt atoms *via* η^2 - co -ordination of the unsaturated C–C bond to Co(1) and *via* σ interactions of P(1) and C(202) to Co(2). Each cobalt atom is in addition *co*-ordinated by one pseudo-equatorial carbonyl group and one pseudo-axial PPhMe_2 group. The PPhMe_2 groups adopt a pseudo-*cis* configuration with respect to each other with a torsion angle of 41.6°, this arrangement being similar to that of the P(OMe)_3 groups in the phenylthio-bridged complex $[\text{Co}_2\{\mu\text{-PPH}_2\text{CHCHC(O)}\}(\mu\text{-SPh})(\text{CO})_2\{\text{P(OMe)}_3\}_2]$.¹⁰ The structural parameters of the five-membered metallacyclic Co(2)–C(202)–C(2)=C(1)–P(1) ring in



Scheme 4 Products from the reactions of complexes **2a**, **2b** and **3a**, **3b** with PPhMe_2 ; (i) PPhMe_2 , heat

Table 2 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) for complex **4a**

Co(1)–Co(2)	2.531(2)	C(1)–C(2)	1.429(9)
Co(2)–P(1)	2.196(3)	C(2)–C(202)	1.468(10)
Co(2)–P(2)	2.242(2)	C(202)–O(202)	1.207(7)
Co(1)–P(2)	2.176(5)	P(1)–C(1)	1.794(6)
Co(1)–C(1)	2.021(7)	Co(1)–P(3)	2.165(2)
Co(1)–C(2)	2.054(6)	Co(2)–P(4)	2.230(2)
Co(2)–C(202)	1.987(5)		
Co(2)–P(1)–C(1)	96.1(3)	P(3)–Co(1)–Co(2)	155.0(1)
Co(2)–P(2)–Co(1)	69.7(1)	P(4)–Co(2)–Co(1)	164.0(1)
P(1)–C(1)–C(2)	108.9(5)	P(2)–Co(1)–C(101)	109.8(3)
C(1)–C(2)–C(202)	116.9(5)	P(2)–Co(2)–C(201)	89.1(2)
C(2)–C(202)–Co(2)	109.1(4)		

this latter complex are virtually identical to those in **4a**. Thus in **4a** the angle between the least-squares plane formed by the four metal-bonded atoms, P(1)–C(1)–C(2)–C(202) (maximum deviation 0.023 Å), and the plane passing through P(1)–Co(2)–C(202) is 48.1° whereas in $[\text{Co}_2\{\mu\text{-PPh}_2\text{CHCHC}(\text{O})\}(\mu\text{-SPh})(\text{CO})_2\{\text{P}(\text{OMe})_3\}_2]$ the corresponding angle is 49.1°.

The Co(1)–P(2) bond [2.176(5) Å] in **4a** is 0.066 Å shorter than the Co(2)–P(2) bond [2.242(2) Å]. In the complex $[\text{Co}_2\{\mu\text{-PPh}_2\text{CHCPhC}(\text{O})\}(\mu\text{-PPh}_2)(\text{CO})_4]$,³ in which two independent molecules were found in the unit cell, the corresponding average distances only differ by 0.015 Å. The Co–Co distance [2.531(2) Å] is longer than that for $[\text{Co}_2\{\mu\text{-PPh}_2\text{-CHCPhC}(\text{O})\}(\mu\text{-PPh}_2)(\text{CO})_4]$ [2.524(3) Å]³ and $[\text{Co}_2\{\mu\text{-PPh}_2\text{CHCHC}(\text{O})\}(\mu\text{-SPh})(\text{CO})_2\{\text{P}(\text{OMe})_3\}_2]$ [2.466(2) Å]¹⁰ and is in the mid-range for single Co–Co bond distances in complexes of this type.^{1,3,6,10–13}

The spectroscopic properties of complex **4a** are in accordance with the solid-state structure being maintained in solution, with a weak IR band at 1605 cm^{-1} being assigned to $\nu(\text{C}=\text{O})$ of the five-membered metallacyclic ring. In the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum four singlet resonances are observed, the lowest field signal at $\delta -34.5$ being assigned to the $\mu\text{-PPh}_2$ bridge, the resonance at $\delta -95.5$ to the $\mu\text{-PPh}_2\text{CHCHC}(\text{O})$ ligand and the two higher field resonances, at $\delta -107.7$ and -117.0 , to the terminal PPhMe_2 on Co(1) and Co(2) by comparison with the data for **2a** and **3a**, respectively. In the $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum one broad signal is observed in the CO region (δ

211.5) and it must be assumed that the resonances due to the two non-identical CO ligands coincide. A singlet resonance at slightly lower field ($\delta 231.3$) is assigned to the CO of the metallacyclic ring. The $\text{PPh}_2\text{CHCHC}(\text{O})$ and $\text{PPh}_2\text{CHCHC}(\text{O})$ carbon resonances appear as doublets respectively at $\delta 73.7$ [$^2J(\text{PC}) 28 \text{ Hz}$] and $\delta 33.0$ [$^1J(\text{PC}) 38 \text{ Hz}$].

The structures of the disubstituted complexes **4b** and **4d** (this latter complex being formed as a minor product in the thermolysis of **2d**) are assigned on the basis of their spectroscopic properties (see Table 1 and Experimental section) and a comparison of these properties with those of **4a**.

(d) *The Influence of the Ring Substituent R on Carbonyl Substitution by Phosphines in $[\text{Co}_2\{\mu\text{-PPh}_2\text{CHCRC}(\text{O})\}(\mu\text{-PPh}_2)(\text{CO})_4]$ 1.*—It is clear from the above results that the nature of the R substituent in **1** is important in determining the site at which initial substitution of a carbonyl group by a phosphine ligand takes place. Thus, whereas complex **1a** (R = H) reacts with PPhMe_2 to give approximately equal proportions of **2a** and **3a** complex **1c** (R = SiMe_3) gives only **3c** (Scheme 2). The space-filling model for **4a** (Fig. 2) suggests that a large substituent on C(2) is likely to inhibit sterically the formation of a complex of type D (Fig. 1), by attack of a phosphine ligand at Co(1). This is in accord with the observed results for substitution by PPhMe_2 of **1c** which gives only **3c** and with the slight preference for the formation of **3b** over **2b** in the substitution of **1b** (R group of intermediate size). This last observation, however, must be treated with particular caution since **3b** and **2b** are not the only products of the reaction of **1b** with PPhMe_2 , and it may be that the other products of this reaction are derived from the readier decomposition of **3b** or **2b** under the conditions of the experiment. That complexes of type 2 and 3 may differ in their stability is shown by the almost complete isomerisation of **2d** to **3d** at 333 K (although this is not observed for **2a** or **2b** at the same temperature).

Although the bulky R group in **1c** prevents substitution of a carbonyl group by a phosphine ligand on the cobalt atom π coordinated by the carbon–carbon double bond, it does not inhibit the reactions of **1c** with alkynes, $\text{R}'\text{C}\equiv\text{CR}''$, and with CS_2 (Scheme 1).¹ It seems reasonable to assume therefore that the reactions of **1c** with alkynes or CS_2 proceed *via* initial coordination of the alkyne or CS_2 to the cobalt atom bound to the ketonic CO and PPh_2 groups of the five-membered metalla-

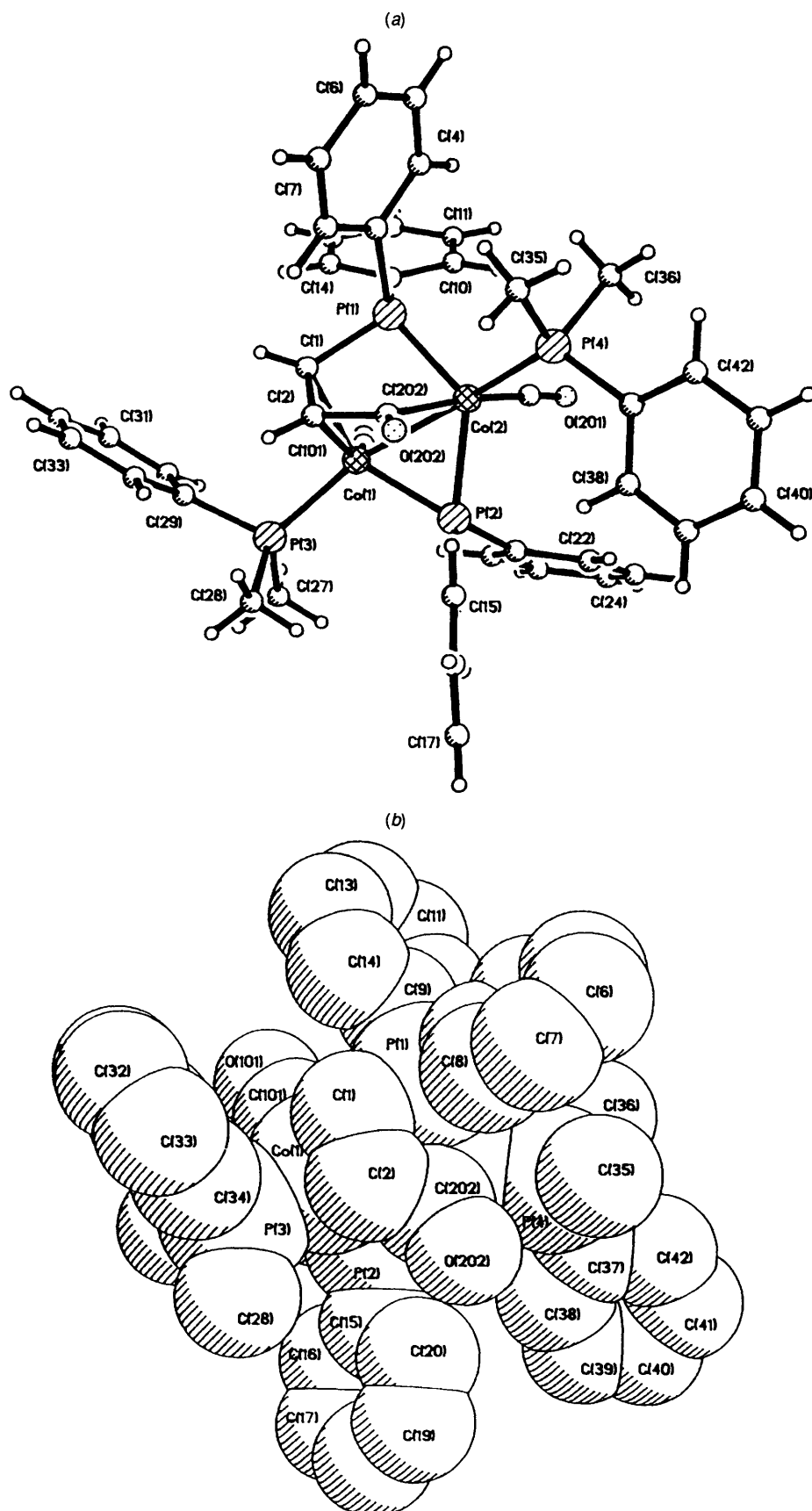


Fig. 2 Molecular structure of $[\text{Co}_2\{\mu\text{-PPh}_2\text{CHCHC(O)}\}(\mu\text{-PPh}_2)(\text{CO})_2(\text{PPhMe}_2)_2]$ **4a** including the atom numbering scheme and space-filling diagram

cyclic ring. This is in any event the most plausible site for the reaction with alkynes, since the co-ordinated alkyne remains

bound to this cobalt atom when it becomes part of the nine-membered metallacyclic ring in the final product. The reactions

of other complexes of type **1** (with less bulky R groups) with alkynes and with CS₂, which are comparable in rate to those of **1c**, may proceed in the same way. Clearly, however, since two isomeric monosubstituted products are obtained in the reactions of **1a** and **1b** with phosphines, these reactions do not enable the initial site of substitution in the reactions of alkynes and CS₂ with **1a** and **1b** to be inferred with any certainty.

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 given in order of decreasing R_f values.

The instrumentation used to obtain spectroscopic data has been described previously.¹⁴ All NMR spectra were recorded at 293 K. Unless otherwise stated all reagents were obtained from commercial suppliers and used without further purification. The compounds [Co₂{μ-PPh₂CHC(R)C(O)}(μ-PPh₂)(CO)₄] (R = H **1a**, Ph **1b** or SiMe₃ **1c**) were prepared by the reaction of [Co₂(μ-PPh₂)₂(CO)₆] with RC≡CH (R = H, Ph or SiMe₃).¹

(i) *Reaction of [Co₂{μ-PPh₂CHC(R)C(O)}(μ-PPh₂)(CO)₄] (R = H **1a**, Ph **1b** or SiMe₃ **1c**) with PPhMe₂.*—(a) Complex [Co₂{μ-PPh₂CHC(R)C(O)}(μ-PPh₂)(CO)₄] **1a** (0.100 g, 0.160 mmol) was dissolved in toluene (50 cm³) and PPhMe₂ (0.023 cm³, 0.172 mmol) was added. After stirring the solution for 1 h at room temperature the solvent was removed *in vacuo*. The residue was redissolved in the minimum quantity of CH₂Cl₂ and applied to the base of TLC plates. Elution with hexane-CH₂Cl₂ (1:1) gave two brown crystalline complexes of formula [Co₂{μ-PPh₂CHC(R)C(O)}(μ-PPh₂)(CO)₃(PPhMe₂)₂] **3a** (0.060 g, 49%) and **2a** (0.056 g, 46%). Complex **3a** (Found: C, 60.0; H, 4.5. C₃₈H₃₃Co₂O₄P₃ requires C, 59.7; H, 4.3%); FAB mass spectrum, *m/z* 764 (*M*⁺) and *M*⁺ - *n*CO (*n* = 0-4). NMR(CDCl₃): ¹³C (1H composite pulse decoupled), δ 229.7 [s, PPh₂CHC(R)C(O)], 207 (br s, 3CO), 142-127 (m, Ph), 73.9 [d, *J*(PC) 32, PPh₂CHC(R)C(O)], 38.1 [d, *J*(PC) 37, PPh₂-CHC(R)C(O)], 15.3 [d, *J*(PC) 27, PMe] and 14.9 [d, *J*(PC) 26, PMe]. Complex **2a** (Found: C, 60.0; H, 4.5. C₃₈H₃₃Co₂O₄P₃ requires C, 59.7; H, 4.3%); FAB mass spectrum, *m/z* 764 (*M*⁺) and *M*⁺ - *n*CO (*n* = 0-4). NMR(CDCl₃): ¹³C (1H composite pulse decoupled), δ 217.1 [s, PPh₂CHC(R)C(O)], 210.8 (s, 1CO), 202.9 (s, 1CO), 202.4 (s, 1CO), 145-127 (m, Ph), 67.9 [d, *J*(PC) 31, PPh₂CHC(R)C(O)], 35.2 [d, *J*(PC) 37, PPh₂CHC(R)C(O)], 19.2 [d, *J*(PC) 28, PMe] and 15.3 [d, *J*(PC) 28, PMe].

(b) Complex [Co₂{μ-PPh₂CHCPhC(O)}(μ-PPh₂)(CO)₄] **1b** (0.100 g, 0.137 mmol) was dissolved in toluene (50 cm³) and PPhMe₂ (0.019 cm³, 0.137 mmol) was added. After stirring the solution for 3 h at room temperature the solvent was removed *in vacuo*. Purification as in (a) using CH₂Cl₂-hexane (7:3) as eluent gave two brown crystalline complexes with formula [Co₂{μ-PPh₂CHCPhC(O)}(μ-PPh₂)(CO)₃(PPhMe₂)₂] **3b** (0.038 g, 33%) and **2b** (0.029 g, 25%) along with green crystalline [Co₂{μ-PPh₂CHCPhC(O)}(μ-PPh₂)(CO)₂(PPhMe₂)₂] **4b** (0.012 g, 9%). Complex **3b**: FAB mass spectrum, *m/z* 840 (*M*⁺) and *M*⁺ - *n*CO (*n* = 0-4). NMR(CDCl₃): ¹³C (1H composite pulse decoupled), δ 226.4 [s, PPh₂CHCPhC(O)], 208.4 (s, 1CO), 205.7 (br s, 2CO), 143-126 (m, Ph), 90.7 [d, *J*(PC) 30, PPh₂CHCPhC(O)], 40.4 [d, *J*(PC) 42, PPh₂CHCPhC(O)], 17.9 [d, *J*(PC) 27, PMe] and 12.7 [d, *J*(PC) 26, PMe]. Complex **2b**: FAB mass spectrum, *m/z* 840 (*M*⁺) and *M*⁺ - *n*CO (*n* = 0-4). Complex **4b** (Found: C, 64.8; H, 5.2. C₅₁H₄₈Co₂O₃P₄ requires C, 64.4; H, 5.1%); FAB mass spectrum, *m/z* 950 (*M*⁺) and *M*⁺ - *n*CO (*n* = 0-3).

(c) Complex [Co₂{μ-PPh₂CHC(SiMe₃)C(O)}(μ-PPh₂)(CO)₄] **1c** (0.100 g, 0.138 mmol) was dissolved in toluene (25

cm³) and PPhMe₂ (0.019 cm³, 0.138 mmol) was added. After stirring the solution for 7 h at room temperature the solvent was removed *in vacuo*. Purification as in (a) gave the brown crystalline complex [Co₂{μ-PPh₂CHC(SiMe₃)C(O)}(μ-PPh₂)(CO)₃(PPhMe₂)₂] **3c** (0.109 g, 95%) as the only product. Complex **3c** (Found: C, 59.1; H, 5.2. C₄₁H₄₁Co₂O₄P₃Si requires C, 58.9; H, 5.0%); FAB mass spectrum, *m/z* 836 (*M*⁺) and *M*⁺ - *n*CO (*n* = 0-4). NMR(CDCl₃): ¹³C (1H composite pulse decoupled), δ 231.4 [d, *J*(PC) 15, PPh₂CHC(SiMe₃)C(O)], 209.5 (s, 1CO), 208.3 (s, 1CO), 205.7 (s, 1CO), 144-127 (m, Ph), 83.4 [d, *J*(PC) 16, PPh₂CHC(SiMe₃)C(O)], 45.7 [d, *J*(PC) 27, PPh₂CHC(SiMe₃)C(O)], 17.8 [d, *J*(PC) 27, PMe], 13.2 [d, *J*(PC) 26, PMe] and -1.7 (s, SiMe₃).

(ii) *Reaction of [Co₂{μ-PPh₂CHCPhC(O)}(μ-PPh₂)(CO)₄] **1b** with PPh₂H.*—Complex [Co₂{μ-PPh₂CHCPhC(O)}(μ-PPh₂)(CO)₄] **1b** (0.200 g, 0.274 mmol) was dissolved in toluene (5 cm³) and PPh₂H (0.038 cm³, 0.274 mmol) was added. After stirring the solution for 20 h at room temperature the solvent was removed *in vacuo* and the dark brown residue redissolved in the minimum quantity of CH₂Cl₂. TLC separation with hexane-CH₂Cl₂ (1:1) as eluent gave two brown crystalline complexes with formula [Co₂{μ-PPh₂CHCPhC(O)}(μ-PPh₂)(CO)₃(PPh₂H)] **3d** (0.100 g, 41%) and **2d** (0.044 g, 18%). Complex **3d** (Found: C, 65.2; H, 4.3. C₄₈H₃₇Co₂O₄P₃ requires C, 64.9; H, 4.2%); FAB mass spectrum, *m/z* 888 (*M*⁺) and *M*⁺ - *n*CO (*n* = 0-4). NMR(CDCl₃): ¹³C (1H composite pulse decoupled), δ 225.0 [s, PPh₂CHCPhC(O)], 208.7 (s, 1CO), 205.0 (s, 2CO), 143-127 (m, Ph), 89.9 [d, *J*(PC) 16, PPh₂CHCPhC(O)] and 41.9 [d, *J*(PC) 27, PPh₂CHCPhC(O)]. Complex **2d** (Found: C, 65.2; H, 4.3. C₄₈H₃₇Co₂O₄P₃ requires C, 64.9; H, 4.2%); FAB mass spectrum, *m/z* 888 (*M*⁺) and *M*⁺ - *n*CO (*n* = 0-4). NMR(CDCl₃): ¹³C (1H composite pulse decoupled), δ 215.7 [s, PPh₂CHCPhC(O)], 210.9 (s, 1CO), 202.8 (s, 1CO), 201.9 (s, 1CO), 149-126 (m, Ph), 83.8 [d, *J*(PC) 34, PPh₂CHCPhC(O)] and 35.9 [d, *J*(PC) 41, PPh₂CHCPhC(O)].

(iii) *Reaction of [Co₂{μ-PPh₂CHC(R)C(O)}(μ-PPh₂)(CO)₃(PPhMe₂)₂] (R = H **3a**, **2a** or Ph **3b**, **2b**) with PPhMe₂.*—(a) Complex [Co₂{μ-PPh₂CHC(R)C(O)}(μ-PPh₂)(CO)₃(PPhMe₂)₂] **3a** (0.080 g, 0.122 mmol) was dissolved in toluene (25 cm³) and PPhMe₂ (0.017 cm³, 0.122 mmol) was added. After stirring the solution for 1.5 h at 333 K the solvent was removed *in vacuo*. The residue was redissolved in the minimum of CH₂Cl₂ and separated by preparative TLC using hexane-CH₂Cl₂ (1:4) as eluent. A green band eluted which on evaporation to dryness gave green crystalline [Co₂{μ-PPh₂CHC(R)C(O)}(μ-PPh₂)(CO)₂(PPhMe₂)₂] **4a** (0.078 g, 85%). Complex **4a** (Found: C, 62.1; H, 5.2. C₄₅H₄₄Co₂O₃P₄ requires C, 61.8; H, 5.1%); FAB mass spectrum, *m/z* 874 (*M*⁺) and *M*⁺ - *n*CO (*n* = 0-3). NMR(CDCl₃): ¹³C (1H composite pulse decoupled), δ 231.3 [s, PPh₂CHC(R)C(O)], 211.5 (br s, 2CO), 145-129 (m, Ph), 73.7 [d, *J*(PC) 28, PPh₂CHC(R)C(O)], 33.0 [d, *J*(PC) 38, PPh₂CHC(R)C(O)], 18.5 [d, *J*(PC) 26, PMe], 15.9 [d, *J*(PC) 25, 2PMe] and 14.9 [d, *J*(PC) 24, PMe].

(b) Complex [Co₂{μ-PPh₂CHCPhC(O)}(μ-PPh₂)(CO)₃(PPhMe₂)₂] **3b** (0.100 g, 0.120 mmol) was dissolved in toluene (50 cm³) and PPhMe₂ (0.017 cm³, 0.120 mmol) was added. After stirring the solution for 1.5 h at 313 K the solvent was removed *in vacuo*. TLC separation using hexane-CH₂Cl₂ (1:1) as eluent gave green crystalline [Co₂{μ-PPh₂CHCPhC(O)}(μ-PPh₂)(CO)₂(PPhMe₂)₂] **4b** (0.090 g, 80%).

(c) Complex [Co₂{μ-PPh₂CHC(R)C(O)}(μ-PPh₂)(CO)₃(PPhMe₂)₂] **2a** (0.060 g, 0.079 mmol) was dissolved in toluene (40 cm³) and PPhMe₂ (0.011 cm³, 0.079 mmol) was added. After stirring the solution for 1 h at 333 K the solvent was removed *in vacuo*. Purification as in (a) gave green crystalline [Co₂{μ-PPh₂CHC(R)C(O)}(μ-PPh₂)(CO)₂(PPhMe₂)₂] **4a** (0.056 g, 82%).

(d) Complex [Co₂{μ-PPh₂CHCPhC(O)}(μ-PPh₂)(CO)₃(PPhMe₂)₂] **2b** (0.050 g, 0.060 mmol) was dissolved in toluene

Table 3 Fractional atomic coordinates ($\times 10^5$) with e.s.d.s in parentheses for the non-hydrogen atoms of the complex **4a**

Atom	x	y	z	Atom	x	y	z
Co(1)	26 542(8)	70 592(6)	40 623(6)	C(16)	63 118(67)	67 474(52)	44 835(51)
Co(2)	26 687(7)	73 062(6)	23 097(5)	C(17)	76 634(71)	71 600(65)	49 761(54)
P(1)	9 286(15)	76 286(11)	25 465(11)	C(18)	83 665(74)	81 513(68)	49 777(56)
P(2)	37 711(15)	67 534(11)	33 754(11)	C(19)	77 171(75)	87 195(62)	45 199(64)
P(3)	36 658(16)	72 569(11)	57 122(11)	C(20)	63 838(66)	83 291(56)	40 157(58)
P(4)	26 841(16)	79 749(12)	10 316(12)	C(21)	35 881(58)	53 857(44)	28 634(44)
C(101)	13 771(68)	58 878(49)	38 288(48)	C(22)	39 059(65)	51 209(51)	20 678(50)
O(101)	5 649(56)	51 434(42)	37 436(49)	C(23)	35 329(71)	40 837(54)	15 717(53)
C(201)	15 661(61)	59 906(50)	14 705(47)	C(24)	28 341(74)	32 940(53)	18 595(57)
O(201)	10 372(49)	51 507(36)	9 746(37)	C(25)	25 292(83)	35 432(54)	26 520(62)
C(202)	35 299(58)	86 561(44)	34 003(43)	C(26)	29 065(73)	45 882(47)	31 549(52)
O(202)	44 424(41)	93 732(30)	34 652(32)	C(27)	37 216(77)	60 862(51)	61 251(55)
C(1)	17 727(59)	80 709(41)	39 367(43)	C(28)	53 655(63)	81 273(51)	63 762(53)
C(2)	31 136(58)	86 294(41)	42 352(42)	C(29)	29 121(58)	77 599(45)	64 152(41)
C(3)	4 992(58)	86 934(45)	21 072(44)	C(30)	18 514(70)	70 933(58)	64 956(54)
C(4)	-4 627(63)	85 180(51)	11 163(52)	C(31)	12 063(77)	74 559(69)	69 329(62)
C(5)	-6 845(68)	93 444(58)	7 595(54)	C(32)	61 098(89)	85 149(83)	73 291(63)
C(6)	521(76)	103 559(57)	13 810(58)	C(33)	26 660(90)	92 013(65)	72 756(60)
C(7)	9 829(75)	105 360(53)	23 581(56)	C(34)	33 184(72)	88 202(52)	68 132(52)
C(8)	12 225(68)	97 177(49)	27 211(53)	C(35)	28 893(76)	93 366(48)	11 332(53)
C(9)	-6 586(57)	66 287(45)	21 739(46)	C(36)	12 576(66)	73 270(58)	-2 124(50)
C(10)	-12 818(66)	58 674(55)	12 327(55)	C(37)	39 649(59)	79 412(46)	6 613(46)
C(11)	-24 930(69)	50 959(61)	9 397(66)	C(38)	49 320(74)	76 724(58)	12 667(58)
C(12)	-30 792(76)	50 928(64)	15 843(72)	C(39)	58 944(82)	76 460(71)	10 139(71)
C(13)	-24 968(80)	58 655(69)	24 880(66)	C(40)	59 003(86)	78 877(67)	1 317(73)
C(14)	-12 930(66)	66 169(57)	27 821(55)	C(41)	49 974(96)	81 944(85)	-4 782(71)
C(15)	56 549(59)	73 2345(48)	39 881(44)	C(42)	40 213(84)	82 201(79)	-1 978(66)

(25 cm³) and PPhMe₂ (0.010 cm³, 0.070 mmol) was added. After stirring the solution for 1 h at 333 K the solvent was removed *in vacuo*. TLC separation using CH₂Cl₂-hexane (1:1) as eluent gave green crystalline [Co₂{μ-PPh₂CHCPhC(O)}(μ-PPh₂)(CO)₂(PPhMe₂)₂] **4b** (0.044 g, 77%).

(iv) *Thermolysis of* [Co₂{μ-PPh₂CHCPhC(O)}(μ-PPh₂)(CO)₃(PPh₂H)] **2d**. Complex [Co₂{μ-PPh₂CHCPhC(O)}(μ-PPh₂)(CO)₃(PPh₂H)] **2d** (0.100 g, 0.113 mmol) was dissolved in toluene (30 cm³) and the solution heated at 333 K for 14 h. After removal of solvent on the rotary evaporator the dark brown residue was dissolved in the minimum quantity of CH₂Cl₂ and applied to the base of TLC plates. Elution with hexane-CH₂Cl₂ (1:1) gave [Co₂{μ-PPh₂CHCPhC(O)}(μ-PPh₂)(CO)₄] **1b** (0.005 g, 6%), [Co₂{μ-PPh₂CHCPhC(O)}(μ-PPh₂)(CO)₃(PPh₂H)] **3d** (0.042 g, 42%) and [Co₂{μ-PPh₂CHCPhC(O)}(μ-PPh₂)(CO)₂(PPh₂H)₂] **4d** (0.007 g, 6%). Complex **4d**: FAB mass spectrum, *m/z* 1046 (*M*⁺) and *M*⁺ - *n*CO (*n* = 0-3). NMR(CDCl₃): ¹³C (1 H composite pulse decoupled), δ 225.0 [s, PPh₂CHCPhC(O)], 212.1 (s, 2CO), 143-125 (m, Ph), 88.6 [d, *J*(PC) 30, PPh₂CHCPhC(O)] and 36.3 [d, *J*(PC) 38, PPh₂CHCPhC(O)].

Crystal Structure Determination of [Co₂{μ-PPh₂CHCPhC(O)}(μ-PPh₂)(CO)₂(PPhMe₂)₂] **4a**.—Crystals of complex **4a** were grown by diffusion of hexane into dichloromethane solution and a suitable black crystal with dimensions of 0.25 × 0.30 × 0.35 mm was selected.

Crystal data. C₄₅H₄₄Co₂O₃P₄, *M* = 874.5, triclinic, space group *P* $\bar{1}$ (no. 2), *a* = 12.174(6), *b* = 14.041(6), *c* = 14.444(8) Å, α = 96.74(4), β = 112.16(14), γ = 108.54(4)°, *U* = 2087(2) Å³ (by least-squares refinement of angles from 25 reflections), Mo-Kα radiation, λ = 0.710 73 Å, *D*_c = 1.39 g cm⁻³, *Z* = 2, *F*(000) = 904, μ(Mo-Kα) = 9.87 cm⁻¹, *T* = 290 K.

Data collection and processing. Siemens R3m/V diffractometer, graphite-monochromated Mo-Kα radiation, ω-2θ scan mode, 5997 reflections measured (5.0 ≤ 2θ ≤ 45.0°), 5478 (*R*_{int} = 0.008), 4285 with *F*_o > 4σ(*F*_o) used in refinement. A semi-empirical absorption correction based on ψ scan data was applied, transmission factors in range 0.04813-0.5888.

Three standard reflections showed no significant variations in intensity during data collection.

Structure analysis and refinement. The structure was solved by a combination of direct methods (Co and P atoms) and Fourier difference techniques with all non-hydrogen atoms assigned anisotropic thermal parameters. The H atoms were placed in idealised positions and allowed to ride on the relevant carbon atom (C-H 0.96 Å). The weighting scheme *w*⁻¹ = σ²(*F*) + 0.002*F*² was introduced for the final cycles of refinement. The converged residuals were *R* = 0.049 and *R*' = 0.072. A final Fourier difference map showed no significant electron density except in positions close to the Co atom (*ca.* 1.0 e Å⁻³). Final atomic coordinates are listed in Table 3. All calculations were carried out on a MicroVax II computer using the SHELXTL PLUS¹⁵ program package.

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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