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Reaction of the dinuclear cobalt complex $[Co_2\{\mu\text{-}PPh_2CHCHC(O)CHCHPPh_2\}(CO)_4]$ with two-electron donor ligands; the stabilisation of cobalt–alkene bonds by incorporation of alkenes into a bridging diphosphine ligand

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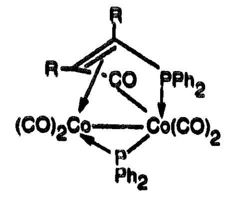
Abstract

The thermal reaction of $[Co_2\{\mu\text{-}PPh_2CHCHC(O)CHCHPPh_2\}(CO)_4]$ (**2**) with two-electron donor ligands, L, leads to the mono- and bis-substituted complexes $[Co_2\{\mu\text{-}PPh_2CHCHC(O)CHCHPPh_2\}(CO)_3(L)]$ (L = $PPhMe_2$ (**3a**), PPh_2H (**3b**), $P(OMe)_3$ (**3c**), CN'Bu (**3d**)) and $[Co_2\{\mu\text{-}PPh_2CHCHC(O)CHCHPPh_2\}(CO)_2(L)_2]$ (L = $PPhMe_2$ (**4a**), PPh_2H (**4b**), $P(OMe)_3$ (**4c**), CN'Bu (**4d**)), in which CO groups rather than bound alkenes have been displaced from the metal centres. Single crystal X-ray diffraction has been used to determine the structure of $[Co_2\{\mu\text{-}PPh_2CHCHC(O)CHCHPPh_2\}(CO)_2(PPhMe_2)_2]\cdot 0.25[C_6H_{14}]$ (**4a**) (which crystallises in the monoclinic space group $P2_1/c$ with $a = 15.932(2)$, $b = 12.608(4)$, $c = 23.847(3)$ Å, $\beta = 98.87(3)°$, $Z = 4$).

Keywords: Crystal structures; Cobalt complexes; Diphosphine complexes; Alkene complexes; Dinuclear complexes

1. Introduction

The cobalt catalysed hydrogenation and hydroformylation of alkenes is postulated to involve in each case the formation of intermediate complexes in which the alkene is η^2-coordinated to a low-valent cobalt centre [1]. In the Co(I) complex, $[(\eta^5\text{-}C_5H_5)Co(C_2H_4)_2]$, the η^2-coordinated alkene groups are regarded as being weakly bound, a view which is supported by their ready displacement from the cobalt centre by a variety of two-electron donor ligands [2]. We have been interested in the chemistry of low-valent bimetallic cobalt complexes in which an alkene functionality η^2-coordinated to one of the metal centres is also attached to the second metal centre via incorporation into a metallacyclic ring containing this second metal centre [3–8]. Such incorporation into a metallacyclic ring results in the η^2-coordination of the alkene becoming much more difficult to displace. Thus in $[Co_2(\mu\text{-}PPh_2)\{\mu\text{-}PPh_2CRCRC(O)\}(CO)_4]$ (**1**) (R = H, alkyl or aryl) (Fig. 1), in which an alkene group is incorporated into a five-membered metallacycle, P–C=C–C–Co, the η^2-coordination to the other metal centre is, in the main, unaffected by reaction of **1** with a wide variety of multi-electron donor ligands [3–8]. Substitution of terminal carbonyl groups, or insertion of the incoming ligand either into the Co–C(O) bond of the metallacycle or into the Co–P bond of the bridging phosphido group, is the preferred outcome of these reactions.



R = H, alkyl or aryl

Fig. 1. Molecular structure of the complex $[Co_2(\mu\text{-}PPh_2)\{\mu\text{-}PPh_2\text{-}CRCRC(O)\}(CO)_4]$ (**1**).

In a recent paper we reported the synthesis of a number of diphosphine substituted dinuclear cobalt carbonyl complexes $[Co_2\{\mu\text{-}PPh_2CRCRC(O)CRCRPPh_2\}(CO)_4]$ (**2**) (R = H, alkyl or aryl), in which the bridging diphosphine ligand has two alkene functionalities, one of which is η^2-coordinated to each cobalt centre (Scheme 1) [8]. These complexes contain

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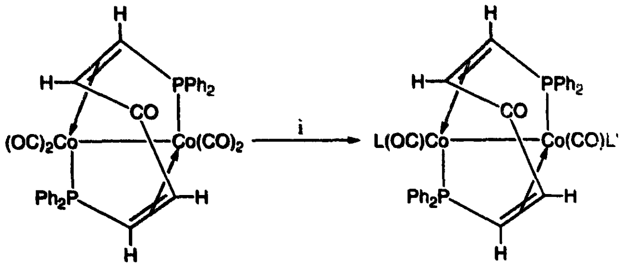

2

L = CO; L' = PPhMe$_2$ **3a**
L = L' = PPhMe$_2$ **4a**
L = CO; L' = PPh$_2$H **3b**
L = L' = PPh$_2$H **4b**
L = CO; L' = P(OMe)$_3$ **3c**
L = L' = P(OMe)$_3$ **4c**
L = CO; L' = CNBu^t **3d**
L = L' = CNBu^t **4d**

Scheme 1. Products from the reaction of [Co$_2${μ-PPh$_2$CHCH-C(O)CHCHPPh$_2$}(CO)$_4$] (**2**) with L (L = PPhMe$_2$, PPh$_2$H, P(OMe)$_3$ or ^{t}BuNC) ((i) L, refluxing toluene).

a nine-membered dimetallacyclic ring and it was of interest to determine whether the η^2-coordinated alkene groups in the nine-membered ring would be more easily displaced from the metal centres than the alkene group in the five-membered metallacycle present in **1**. Accordingly this note presents the results of a study of the reactions of [Co$_2${μ-PPh$_2$CHCHC(O)CHCHPPh$_2$}(CO)$_4$] (**2**) with a variety of two-electron donor ligands.

2. Results and discussion

2.1. Reaction of [Co$_2${μ-PPh$_2$CHCHC(O)CHCHPPh$_2$}(CO)$_4$] (2) with PPhMe$_2$, PPh$_2$H, P(OMe)$_3$ or CN^{t}Bu

The reactions of [Co$_2${μ-PPh$_2$CHCHC(O)CHCHPPh$_2$}(CO)$_4$] (**2**) with an excess of each of the above ligands in refluxing toluene solution gives a mixture of the mono-substituted and bis-substituted complexes [Co$_2${μ-PPh$_2$CHCHC(O)CHCHPPh$_2$}(CO)$_3$(L)] (**3**) and [Co$_2${μ-PPh$_2$CHCHC(O)CHCHPPh$_2$}(CO)$_2$(L)$_2$] (**4**) in combined yields ranging from 35 to 50%. The mixtures are readily separated by column or thin layer chromatography (TLC) and the individual complexes have been characterised by infrared, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, by mass spectrometry and by microanalysis (see Table 1 and Section 4). In addition the structure of the bis-substituted complex [Co$_2${μ-PPh$_2$CHCHC(O)CHCHPPh$_2$}(CO)$_2$(PPhMe$_2$)$_2$] (**4a**) has been determined by X-ray diffraction analysis. The

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

Complex	ν(CO) [a] (cm^{-1})	^{1}H NMR (δ) [b]
3a	2014s, 1975s, 1940br, 1621w	8.1–6.9 (m, 25H, Ph), 4.09 (d, ^3J(HH) = 7.9, 1H, (CO)$_2$CoPPh$_2$C*H*CH), 3.61 (ddd, ^2J(PH) = 28.8, ^3J(HH) = 7.9, ^4J(P'H) = 1.4, 1H, (CO)$_2$CoPPh$_2$CHC*H*), 3.12 (ddd, ^2J(PH) = 9.7, ^3J(HH) = 8.3, ^4J(P'H) = 1.3, 1H, (PPhMe$_2$)(CO)CoPPh$_2$C*H*CH), 2.99 (dddd, ^2J(PH) = 10.7, ^3J(HH) = 8.2, ^4J(P'H) = 1.3, 1H, (PPhMe$_2$)(CO)CoPPh$_2$CHC*H*), 1.27 (d, ^2J(PH) = 8.9, 6H, PPh*Me*$_2$)
4a	1951s, 1910w, 1586w, br	7.7–6.9 (m, 30H, Ph), 2.98 (dddd, ^2J(PH) = 29.7, ^3J(HH) = 6.9, ^3J(P'H) = 6.2, ^3J(P''H) = 3.6, 2H, PPh$_2$CHC*H*), 2.73 (ddd, ^3J(HH) = 6.9, ^3J(PH) = 6.7, ^3J(P'H) = 6.6, 2H, PPh$_2$C*H*CH), 1.25 (d, ^2J(PH) = 7.6, 12H, PPh*Me*$_2$)
3b	2012s, 1971s, 1940w, 1604m	7.9–7.2 (m, 30H, Ph), 4.65 (dd, ^1J(PH) = 346.5, ^3J(P'H) = 8.3, 1H, PPh$_2$*H*), 4.15 (d, ^2J(HH) = 7.6, 1H, (CO)$_2$CoPPh$_2$C*H*CH), 3.58 (dd, ^2J(PH) = 28.4, ^3J(HH) = 7.6, 1H, (CO)$_2$CoPPh$_2$CHC*H*), 3.16 (dd, ^2J(PH) = 8.5, ^3J(HH) = 7.5, 1H, (PPh$_2$H)(CO)CoPPh$_2$C*H*CH), 2.96 (ddd, ^2J(PH) = 29.7, ^3J(P'H) = 11.3, 1H, (PPh$_2$H)(CO)CoPPh$_2$CHC*H*)
4b	1959s, 1919w, 1593w,br	7.7–6.8 (m, 40H, Ph), 4.74 (dd, ^1J(PH) = 340.4, ^3J(PH) = 7.9, 2H, PPh$_2$*H*), 3.08 (dd, ^3J(PH) = 10.3, ^3J(HH) = 7.6, 2H, PPh$_2$C*H*CH), 2.88 (ddd, ^2J(PH) = 29.6, ^3J(PH) = 6.2, ^3J(HH) = 7.6, 2H, PPh$_2$CHC*H*)
3c	2012vs, 1973s, 1948sh, 1604w	8.1–7.2 (m, 20H, Ph), 4.13 (dd, ^3J(HH) = 8.9, ^3J(PH) = 6.3, ^3J(P'H) = 2.7, 1H, (CO)$_2$CoPPh$_2$C*H*CH), 3.82 (ddd, ^2J(PH) = 13.4, ^3J(HH) = 6.8, ^3J(P'H) = 1.3, 1H, (CO)$_2$CoPPh$_2$CHC*H*), 3.69–3.49 (m, 2H, [P(OMe)$_3$](CO)CoPPh$_2$C*H*CH), 3.1 (d, ^3J(PH) = 10.8, 9H, P(O*Me*)$_3$)
4c	1968s, 1925w, 1593w	8.1–7.1 (m, 20H, Ph), 3.67 (dd, ^3J(PH) = 14.1, ^3J(HH) = 7.0, 2H, PPh$_2$C*H*CH), 3.58 (m, 2H, PPh$_2$CHC*H*), 3.06 (dd, ^2J(PH) = 10.8, ^3J(HH) = 5.5, ^3J(P'H) = 5.40, 18H, P(O*Me*)$_3$)
3d	2012vs, 1973s, 1946sh, 1604w, 2143m (ν(CN))	8.1–7.2 (m, 20H, Ph), 4.16 (d, ^3J(HH) = 8.1, 1H, (CO)$_2$CoPPh$_2$C*H*CH), 4.09 (d, ^3J(HH) = 8.1, 1H, (CO)$_2$CoPPh$_2$CHC*H*), 3.5 (m, 2H, (CO)(^{t}BuNC)CoPPh$_2$C*H*C*H*), 1.0 (s, 9H, ^{t}*Bu*NC)
4d	1971s, 1930br, 1594w,br,2128vs (ν(CN))	8.1–7.1 (m, 20H, Ph), 3.94 (d, ^3J(HH) = 8.0, 2H, PPh$_2$C*H*CH), 3.29 (dd, ^3J(PH) = 31.9, ^3J(HH) = 7.9, 2H, PPh$_2$CHC*H*), 0.98 (s, 18H, ^{t}*Bu*NC)

[a] Recorded in CH$_2$Cl$_2$ solution.

[b] ^{1}H chemical shifts (δ) in ppm related to SiMe$_4$ (0.0 ppm), coupling constants in Hz in CDCl$_3$ at 293 K.

structure is depicted in Fig. 2 and selected bond parameters are listed in Table 2.

The eight-electron donor ligand, $PPh_2CH{=}CHC(O)$-$CH{=}CHPPh_2$, in **4a** bridges the two Co atoms through the P-termini, forming a nine-membered dimetallacyclic ring. The conjugated alkene system is $\eta^2{:}\eta^{2\prime}$-coordinated to the two metal centres. All the bond lengths and bond angles involving the bridging ligand are closely comparable to those for the bridging ligand in **2** [8]. Notably, the Co–Co distance (2.643(2) Å), as in **2** (2.655(1) Å), is at the longer end of the range for single Co–Co bonds in related complexes [9], a feature which may be attributed to the geometrical requirements imposed by the fly-over ligand. The two $PPhMe_2$ ligands in **4a** occupy the two pseudo-axial sites *trans* to the

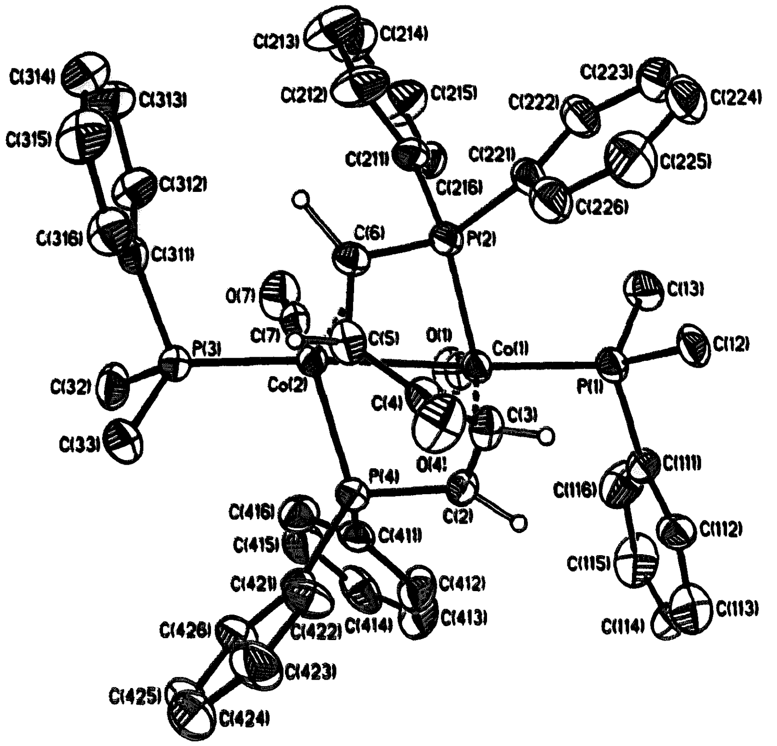

Fig. 2. Molecular structure of $[Co_2\{\mu\text{-}PPh_2CHCHC(O)CHCHPPh_2\}(CO)_2(PPhMe_2)_2]$ (**4a**), including the atom numbering scheme, with displacement ellipsoids drawn at 30% probability.

Table 2
Selected bond distances (Å) and angles (°) for $[Co_2\{\mu\text{-}PPh_2CHCHC(O)CHCHPPh_2\}(CO)_2(PPhMe_2)_2]$ (**4a**)

Co(1)–Co(2)	2.643(2)	Co(1)–P(1)	2.211(3)
Co(1)–C(1)	1.718(14)	Co(1)–P(2)	2.171(3)
Co(1)–C(2)	2.017(11)	Co(1)–C(3)	2.032(11)
P(2)–C(6)	1.783(11)	C(5)–C(6)	1.44(2)
C(4)–C(5)	1.45(2)	C(4)–O(4)	1.226(13)
C(3)–C(4)	1.48(2)	C(2)–C(3)	1.434(14)
P(4)–C(2)	1.776(11)	Co(2)–P(4)	2.180(3)
Co(2)–P(3)	2.203(3)	Co(2)–C(7)	1.716(14)
Co(2)–C(6)	2.047(10)	Co(2)–C(5)	2.044(11)
C(1)–O(1)	1.159(12)	C(7)–O(7)	1.169(13)
P–C(phenyl)	1.822(12)–1.829(12)	P–C(methyl)	1.804(11)–1.823(11)
Co(1)–Co(2)–P(4)	70.48(9)	Co(1)–Co(2)–C(7)	91.5(4)
Co(1)–C(1)–O(1)	176.8(10)	C(1)–Co(1)–P(1)	90.4(4)
P(1)–Co(1)–P(2)	105.13(13)	C(1)–Co(1)–Co(2)	94.2(4)
P(1)–Co(1)–Co(2)	174.68(12)	C(1)–Co(1)–P(2)	111.4(4)
P(2)–Co(1)–Co(2)	70.67(10)	C(6)–P(2)–Co(1)	101.7(4)
C(5)–C(6)–P(2)	118.5(8)	C(4)–C(5)–C(6)	125.8(10)
O(4)–C(4)–C(5)	120.9(12)	C(5)–C(4)–C(3)	119.7(11)
O(4)–C(4)–C(3)	119.4(12)	C(2)–C(3)–C(4)	123.8(10)
C(3)–C(2)–P(4)	118.0(8)	C(2)–P(4)–Co(2)	100.1(4)
C(7)–Co(2)–P(4)	108.8(4)	P(4)–Co(2)–P(3)	105.94(13)
C(7)–Co(2)–P(3)	91.0(4)	O(7)–C(7)–Co(2)	176.2(10)

metal–metal bond, one on each Co atom, which in **2** are occupied by CO groups. The P(1)–Co(1)–Co(2) bond angle of 174.68(12)° in **4a** may be compared with the average C–Co–Co bond angle of 177.6° for the pseudo-axial CO groups in **2**. As with a number of other bridged dicobalt carbonyl complexes, a preference is shown for substitution of pseudo-axial carbonyl groups over the equatorial ones by mono-dentate phosphine ligands even though steric considerations would favour occupation of the equatorial sites [3–5,7,10].

The spectroscopic properties of **4a** show that the structure in the solid state is maintained in solution (see Table 1 and Section 4). Thus in the $^{31}P\{^1H\}$ NMR spectrum two singlet resonances are observed. On the basis of the corresponding ^{31}P chemical shift in **2** the higher field resonance in **4a** at δ 14.6 is assigned to the phosphorus atoms within the metallacyclic ring and the more downfield signal at δ 20.8 (^{31}P chemical shifts relative to 85% external H_3PO_4 (0.0 ppm)) to the *P*PhMe$_2$ phosphorus atoms. The PPh$_2$CH=C*H*-C(O)C*H*=CHPPh$_2$ alkene protons each couple to the neighbouring alkene proton, unequally to each of the phosphorus termini of the bridging ligand, and to the PPhMe$_2$ phosphorus atom on the same Co atom to which the particular alkene functionality is coordinated. Accordingly in the ^1H NMR spectrum (Table 1) these protons give rise to a signal which is observed as a doublet of doublets of doublets of doublets (dddd), the four coupling constants being assigned by comparison of their magnitude with those of the three coupling constants observed for **2**. The spectroscopic properties of the remaining mono-substituted (**3a–3d**) and bis-substituted (**4b–4d**) complexes are analogous to those of **4a** and these complexes are assigned similar structures on this basis (Scheme 1).

Since the conjugated alkene system in **4a** is not displaced from the metal centres by reaction with two-electron donor ligands, the possibility of bringing about such displacement by hydrogenation of the alkene double bonds was explored. Complex **4a** did not, however, react at room temperature with hydrogen gas either in toluene solution or in the presence of a Pt/C catalyst in ethanol solution. At elevated temperatures complete decomposition occurred under both sets of conditions.

3. Conclusions

The alkene functionalities in the dinuclear cobalt complex [Co$_2$\{μ-PPh$_2$CHCHC(O)CHCHPPh$_2$\}(CO)$_4$] (**2**) are just as difficult to displace from the Co centres as are the alkene ligands in **1** [7] and much more difficult to displace than the alkene ligands in known low valent mono-nuclear cobalt complexes such as [(η^5-C_5H_5)Co(C_2H_4)$_2$] [2]. The fact that the substituting ligands displace carbonyl groups in **1** and **2** rather than the alkene functionalities can be ascribed to a chelate effect arising from the inclusion of the alkene functionalities in metallacyclic rings. It will consequently be entropically more favorable for carbonyl rather than alkene groups to be substituted in both **1** and **2** and it is this, rather than an increase in the strength of the metal–alkene bonds, which is presumably responsible for the observed pattern of substitution.

4. Experimental

4.1. General

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 coated with a 0.25 mm layer of silica or on 1 mm silica plates prepared at the Department of Chemistry, University of Cambridge. Products are given in order of decreasing R_F values. The instrumentation used to obtain spectroscopic data has been described previously [11]. Elemental analysis was performed at the Department of Chemistry, University of Cambridge. Unless otherwise stated all reagents were obtained from commercial suppliers and used without further purification. The complex [Co$_2$\{μ-PPh$_2$CHCHC(O)CHCH-PPh$_2$\}(CO)$_4$] (**2**) was prepared by the standard literature method [8].

4.2. Syntheses

4.2.1. Reaction of [Co$_2$\{μ-PPh$_2$CHCHC(O)CHCHPPh$_2$\}(CO)$_4$] (2) with PPhMe$_2$

To a solution of **2** (0.122 g, 0.179 mmol) in toluene (50 ml) was added PPhMe$_2$ (0.10 ml, 0.703 mmol) and the resulting solution heated at 373 K for 2 h. The solvent was then removed on a rotary evaporator, the residue taken up in the minimum amount of CH_2Cl_2 and adsorbed onto silica. The silica was pumped dry and added to the top of a silica chromatography column. Elution with CH_2Cl_2 gave starting material, red–brown [Co$_2$\{μ-PPh$_2$CHCHC(O)CHCH-PPh$_2$\}(CO)$_3$(PPhMe$_2$)] (**3a**) (0.014 g, 9.8%) and dark green [Co$_2$\{μ-PPh$_2$CHCHC(O)CHCHPPh$_2$\}(CO)$_2$(PPh-Me$_2$)$_2$] (**4a**) (0.064 g, 40%).

4.2.1.1. Complex 3a

Anal. Found: C, 60.78; H, 4.46. Calc. for $C_{40}H_{35}O_4Co_2P_3$: C, 60.91; H, 4.43%. FAB-MS: m/z 792 (M^+) and $M^+ - n$CO (n = 1–3). ^{31}P NMR ($CDCl_3$) (^1H composite pulse decoupled): δ 26.6 (s, *P*PhMe$_2$), 15.8 (s, (PPhMe$_2$)(CO)Co(μ-*P*Ph$_2$)), 9.3 (s, (CO)$_2$Co(μ-*P*Ph$_2$)).

4.2.1.2. Complex 4a

Anal. Found: C, 62.27; H, 5.15. Calc. for $C_{47}H_{46}O_3Co_2P_4$: C, 62.43; H, 5.11%. FAB-MS: m/z 901 (M^+) and $M^+ - n$CO (n = 1). ^{13}C NMR ($CDCl_3$) (^1H composite pulse decoupled): δ 209.5 (s, CO), 209.1 (t, J(PC) = 22 Hz, –CH-C(O)CH–), 207.4 (s, CO), 138.9–127.8 (m, Ph), 61.5 (s, PPh$_2$CHCH), 37.2 (dd, J(PC) = 37 Hz, J(P′C) = 14 Hz, PPh$_2$$C$HCH), 17.4 (t, J(PC) = 2 Hz, PPhMe, Me) and 11.6 (t, J(PC) = 1.6 Hz, PPhMe, Me). ^{31}P NMR (^{1}H composite pulse decoupled): δ 20.8 (s, PPhMe), 14.6 (s, μ-PPh$_2$).

4.2.2. *Reaction of [Co$_2${μ-PPh$_2$CHCHC(O)CHCH-PPh$_2$}(CO)$_4$] (2) with PPh$_2$H*

To a solution of **2** (0.090 g, 0.123 mmol) in toluene (50 ml) was added PPh$_2$H (0.05 ml, 0.287 mmol) and the resulting solution heated at 373 K for 3 h. After removal of the solvent on a rotary evaporator, the residue was redissolved in the minimum of CH_2Cl_2 and separation carried out by preparative TLC using CH_2Cl_2 as the eluent. Three bands were eluted. The first was the starting material, the second brown [Co$_2${μ-PPh$_2$CHCHC(O)CHCHPPh$_2$}(CO)$_3$(PPh$_2$H)] (**3b**) (0.021 g, 20%) and the third red–green [Co$_2${μ-PPh$_2$CHCHC(O)CHCHPPh$_2$}(CO)$_2$(PPh$_2$H)$_2$] (**4b**) (0.030 g, 24%).

4.2.2.1. *Complex 3b*

Anal. Found: C, 63.02; H, 4.21. Calc. for $C_{44}H_{35}O_4Co_2P_3$: C, 63.00; H, 4.12%. FAB-MS: m/z 839.5 (M^+) and $M^+ - n$CO (n = 1–3). ^{31}P NMR (CDCl$_3$) (^{1}H composite pulse decoupled): δ 47.7 (s, PPh$_2$H), 14.5 (s, (PPh$_2$H)-(CO)Co(μ-PPh$_2$CH)), 10.8 (s, (CO)$_2$Co(μ-PPh$_2$CH).

4.2.2.2. *Complex 4b*

Anal. Found: C, 66.12; H, 4.51. Calc. for $C_{55}H_{46}O_3Co_2P_4$: C, 66.13; H, 4.61%. FAB-MS: m/z 998.3 (M^+) and $M^+ - n$CO (n = 1–2). ^{13}C NMR (CDCl$_3$) (^{1}H composite pulse decoupled): δ 208.6 (s, CO), 208.4 (s, CO), 207.7 (t, J(PC) = 24 Hz, –CHC(O)CH–), 207.0 (s, CO), 141.8–127.8 (m, Ph), 63.1 (s, PPh$_2$CHCH), 37.2 (d, J(PC) = 37 Hz, PPh$_2$$C$ HCH). ^{31}P NMR (^{1}H composite pulse decoupled): δ 42.1 (s, PPh$_2$H), 14.2 (s, μ-P Ph$_2$CH).

4.2.3. *Reaction of [Co$_2${μ-PPh$_2$CHCHC(O)CHCHPPh$_2$}-(CO)$_4$] (2) with P(OMe)$_3$*

To a solution of **2** (0.090 g, 0.123 mmol) in toluene (50 ml) was added P(OMe)$_3$ (0.5 ml, 4.24 mmol) and the resulting solution heated at 353 K for 3 h. After removal of the solvent on a rotary evaporator, the residue was redissolved in the minimum of CH_2Cl_2 and separation carried out by preparative TLC using CH_2Cl_2/ethyl acetate (4:1) as the eluent. Three bands were eluted. The first was starting material and the second, red–brown [Co$_2${μ-PPh$_2$CHCH-C(O)CHCHPPh$_2$}(CO)$_3${P(OMe)$_3$}] (**3c**) (0.031 g, 27%) and the third red–brown [Co$_2${μ-PPh$_2$CH-CHC(O)CHCHPPh$_2$}(CO)$_2${P(OMe)$_3$}$_2$] (**4c**) (0.030 g, 8%).

4.2.3.1. *Complex 3c*

Anal. Found: C, 54.14; H, 4.28. Calc. for $C_{35}H_{33}O_7Co_2P_3$: C, 54.14; H, 4.25%. FAB-MS: m/z 778 (M^+) and $M^+ - n$CO (n = 1–4). ^{13}C NMR (CDCl$_3$) (^{1}H composite pulse decoupled): δ 205.2 (s, CO), 205.0 (t, J(PC) = 24 Hz, –CHC(O)CH–), 204.7 (s, CO), 137.6–125.3 (m, Ph), 64.1 (s, (CO)$_2$Co(μ-PPh$_2$CHCH)), 61.3 (s, (CO)$_2$Co(μ-PPh$_2$$C$HCH), 51.5 (d, J(PC) 5.6, P(OMe)$_3$), 36.4 (t, J(PC) = 5.6 Hz, (P(OMe)$_3$)(CO)Co(μ-PPh$_2$$C$HCH)), 29.7 (s, (P(OMe)$_3$)(CO)Co(μ-PPh$_2CHC$H)). ^{31}P NMR (^{1}H composite pulse decoupled): δ 156.8 (s, P(OMe)$_3$), 14.1 (s, (P(OMe)$_3$)(CO)Co(μ-PPh$_2$CH)), 10.2 (s, (CO)$_2$-Co(μ-PPh$_2$CH).

4.2.3.2. *Complex 4c*

Anal. Found: C, 50.94; H, 4.85. Calc. for $C_{37}H_{42}O_9Co_2P_4$: C, 50.92; H, 4.82%. FAB-MS: m/z 873 (M^+) and $M^+ - n$CO (n = 1–2). ^{13}C NMR (CDCl$_3$) (^{1}H composite pulse decoupled): δ 207.0 (t, J(PC) = 22 Hz, –CH-C(O)CH–), 206.7 (s, CO), 138.7–127.6 (m, Ph), 61.5 (s, PPh$_2$CHCH), 51.5 (s, P(OMe)$_3$), 34.9 (m, PPh$_2$$C$HCH). ^{31}P NMR (^{1}H composite pulse decoupled): δ 126.6 (s, P(OMe)$_3$), 13.4 (s, μ-PPh$_2$CH).

4.2.4. *Reaction of [Co$_2${μ-PPh$_2$CHCHC(O)CHCHPPh$_2$}-(CO)$_4$] (2) with ^{t}BuNC*

To a solution of **2** (0.100 g, 1.470 mmol) in toluene (50 ml) was added ^{t}BuNC (0.20 ml, 1.768 mmol) and the resulting solution heated at 313 K for 0.5 h. The solvent was then removed on a rotary evaporator, the residue taken up in the minimum amount of CH_2Cl_2 and adsorbed onto silica. The silica was pumped dry and added to the top of a silica chromatography column. Elution with CH_2Cl_2 gave starting material, red–brown [Co$_2${μ-PPh$_2$CHCHC(O)CHCHPPh$_2$}-(CO)$_3$(CN^{t}Bu)] (**3d**) (0.222 g, 21%) and red–green [Co$_2${μ-PPh$_2$CHCHC(O)CHCHPPh$_2$}(CO)$_2$(CN^{t}Bu)$_2$] (**4d**) (0.293 g, 25%).

4.2.4.1. *Complex 3d*

Anal. Found: C, 60.42; H, 4.52; N, 1.90. Calc. for $C_{37}H_{33}O_4NCo_2P_2$: C, 60.33; H, 4.48; N, 1.90%. FAB-MS: m/z 736(M^+) and $M^+ - n$CO (n = 1–4). ^{13}C NMR (CDCl$_3$) (^{1}H composite pulse decoupled): δ 208.8 (s, CO), 205.3 (t, J(PC) = 24 Hz, –CHC(O)CH–), 205.0 (s, CO), 149.5 (s, CNBu^t), 137.0–128.2 (m, Ph), 61.4 (m, (CO)$_2$Co(μ-PPh$_2$CHCH)), 36.5 (m, (CO)(^{t}BuNC)-Co(μ-PPh$_2$CHCH)), 30.3 (s, (CO)(^{t}BuNC)Co(μ-PPh$_2$-CHCH)), 33.0 (m, (CO)$_2$Co(μ-PPh$_2$$C$HCH)), 29.7 (s, CN$C(Me)_3$), 1.0 (s, CNC($Me$)$_3$). ^{31}P NMR (^{1}H composite pulse decoupled): δ 15.1 (s, (^{t}BuNC)(CO)Co(μ-PPh$_2$)), 10.4 (s, (CO)$_2$Co(μ-PPh$_2$CH)).

4.2.4.2. *Complex 4d*

Anal. Found: C, 62.29; H, 5.35; N, 3.50. Calc. for $C_{41}H_{42}O_3N_2Co_2P_2$: C, 62.28; H, 5.32; N, 3.54%. FAB-MS: m/z 792 (M^+) and $M^+ - n$CO (n = 1–2). ^{13}C NMR

($CDCl_3$) (^1H composite pulse decoupled): δ 208.0 (s, CO), 207.3 (t, J(PC) = 24 Hz, –CH*C*(O)CH–), 151.0 (s, *C*NBu^t), 138.6–127.8 (m, *Ph*), 64.3 (d, J(PC) = 6 Hz, PPh_2CH*C*H), 34.6 (dd, J(PC) = 36 Hz, J(P′C) = 14 Hz, PPh_2*C*HCH), 29.7 (s, CN*C*(Me)$_3$), 1.0 (s, CNC(*Me*)$_3$). ^{31}P NMR (^1H composite pulse decoupled): δ 14.9 (s, (μ-*P*Ph_2CH)).

4.3. X-ray crystal structure determination of [Co_2{μ-$PPh_2CHCHC(O)CHCHPPh_2$}$(CO)_2(PPhMe_2)_2$] (4a)

A dark green single crystal suitable for diffraction analysis was grown by slow diffusion from CH_2Cl_2/hexane solution. Data were collected by the ω/θ-scan method on a Stoe-Siemens four-circle diffractometer with graphite-monochromated Mo Kα radiation, λ = 0.71073 Å. Three standard reflections monitored at intervals 60 min showed no significant variation in intensity. Crystal data collection and refinement results are summarised in Table 3. Cell parameters were obtained by least-squares refinement on diffractometer angles from 25 centred reflections (20 < 2θ < 25°). A semi-empirical absorption correction based on ψ-scan data was applied.

The structures were solved by direct methods [12] and subsequent Fourier difference syntheses and refined anisotropically on all non-H atoms, except those of solvent, by full-matrix least-squares on F^2 [13]. Hydrogen atoms were placed in idealised positions and refined using a riding model or as rigid methyl groups. The structure contains one molecule of hexane solvent per unit cell, which lies on an inversion centre and is also disordered about two orientations with equal occupancies of 0.25. Appropriate restraints were applied to its positional and thermal parameters. In the final cycles of refinement a weighting scheme was introduced which produced a flat analysis of variance. Coordinates of non-H atoms are given in Table 4 and selected bond parameters are summarised in Table 2.

Table 3
Crystal data for [Co_2{μ-$PPh_2CHCHC(O)CHCHPPh_2$}$(CO)_2(PPhMe_2)_2$]·0.25(C_6H_{14}) (4a)

Molecular formula	$C_{47}H_{46}Co_2O_3P_4 \cdot 0.25(C_6H_{14})$
M	922.12
Crystal system	monoclinic
a (Å)	15.932(2)
b (Å)	12.608(4)
c (Å)	23.847(3)
β (°)	98.87(3)
U (Å^3)	4733(2)
Space group	*P*2/*c*
Z	4
D_c (Mg m^{-3})	1.294
Crystal size (mm)	0.29 × 0.23 × 0.22
Temperature (K)	293
F(000)	1914
μ (mm^{-1})	0.874
Relative transmission	0.728–0.765
Data collection range (°)	$5.12 < 2\theta < 45.1$, $\pm h, +k, +l$
Independent reflections measured	5387
Parameters, restraints	534, 16
$wR2$ [a] (all data)	0.1963
Weighting scheme [b]	$P = (F_o^2 + 2F_c^2)/3$
$R1$ [c] ($I > 2\sigma(I)$)	0.0737
Observed reflections ($I > 2\sigma(I)$)	2931
GOF on F^2 [d]	1.086
Maximum shift (σ)	−0.002
Peak, hole final difference map (e Å^{-3})	0.567, −0.341

[a] $[\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w F_o^4]^{1/2}$.

[b] $w = 1/[\sigma^2(F_o)^2 + (0.0679P)^2 + 13.01P]$.

[c] $\Sigma||F_o| - |F_c|| / \Sigma|F_o|$.

[d] $[\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}$ where n is the number of reflections and p the number of parameters (all data).

Table 4
Atomic coordinates (× 10^4) for [Co_2{μ-$PPh_2CHCHC(O)CHCHPPh_2$}-$(CO)_2(PPhMe_2)_2$]·0.25(C_6H_{14}) (4a)

Atom	*x*	*y*	*z*
Co(1)	7419(1)	5829(1)	1871(1)
Co(2)	7337(1)	6346(1)	790(1)
P(1)	7360(2)	5436(2)	2768(1)
P(2)	6620(2)	7220(2)	1692(1)
P(3)	7269(2)	6663(2)	−124(1)
P(4)	7811(2)	4728(2)	921(1)
C(111)	8004(9)	4265(10)	2974(4)
C(112)	7646(9)	3273(11)	2942(5)
C(113)	8122(12)	2386(14)	3033(6)
C(114)	8970(14)	2453(13)	3140(6)
C(115)	9379(9)	3395(16)	3165(6)
C(116)	8873(10)	4314(12)	3073(6)
C(12)	6355(7)	5128(10)	3002(5)
C(13)	7783(8)	6436(10)	3288(5)
C(211)	7050(9)	8566(9)	1747(5)
C(212)	6644(10)	9380(11)	1433(7)
C(213)	6968(12)	10383(12)	1450(7)
C(214)	7728(14)	10582(12)	1779(8)
C(215)	8149(11)	9807(13)	2100(7)
C(216)	7817(9)	8789(10)	2076(5)
C(221)	5720(8)	7374(10)	2075(5)
C(222)	5785(9)	8009(11)	2556(5)
C(223)	5147(12)	7974(13)	2897(6)
C(224)	4454(12)	7341(15)	2774(7)
C(225)	4360(9)	6737(13)	2284(8)
C(226)	4989(9)	6735(11)	1935(6)
C(311)	6648(9)	7860(9)	−322(5)
C(312)	6991(9)	8832(10)	−141(5)
C(313)	6530(13)	9763(11)	−232(6)
C(314)	5728(13)	9720(13)	−500(7)
C(315)	5362(10)	8789(16)	−679(6)
C(316)	5820(10)	7825(11)	−582(5)
C(32)	8268(8)	6911(10)	−368(5)
C(33)	6800(8)	5698(10)	−649(5)
C(411)	8946(9)	4502(10)	1139(5)
C(412)	9244(11)	3713(12)	1519(6)
C(413)	10093(13)	3566(13)	1690(6)
C(414)	10688(10)	4204(15)	1473(7)
C(415)	10391(11)	4952(12)	1086(7)
C(416)	9544(10)	5115(11)	923(6)
C(421)	7543(9)	3745(9)	358(5)
C(422)	6738(10)	3373(10)	220(6)
C(423)	6468(12)	2727(12)	−255(7)
C(424)	7057(14)	2479(13)	−603(7)

(continued)

Table 4 (*continued*)

Atom	x	y	z
C(425)	7871(13)	2805(13)	−468(7)
C(426)	8121(10)	3462(10)	−7(6)
C(1)	8470(9)	6171(9)	2045(5)
C(2)	7340(8)	4368(9)	1522(5)
C(3)	6507(8)	4765(9)	1558(5)
C(4)	5891(9)	5096(10)	1060(5)
C(5)	6070(7)	6016(10)	732(5)
C(6)	6249(7)	7067(9)	952(5)
C(7)	8173(9)	7209(10)	946(5)
O(1)	9171(6)	6425(7)	2186(4)
O(4)	5242(6)	4573(7)	923(4)
O(7)	8744(6)	7801(8)	1020(4)
C(01)	8967(36)	10769(59)	772(25)
C(02)	9757(27)	11061(28)	509(17)
C(03)	9646(27)	10420(35)	−47(13)
C(04)	9396(41)	11259(56)	947(22)
C(05)	9210(22)	10672(43)	376(19)
C(06)	10098(16)	10308(53)	281(17)

5. Supplementary material

Full tables of atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for this material should quote the full literature citation and the reference number.

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