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The reaction of diphenylphosphine, PPh_2H, with an alkyne-bridged dicobalt carbonyl complex; the synthesis crystal structure and reactivity of the complex $[Co_2\{\mu\text{-}C(CO_2Me){=}CHCO_2Me\}(\mu\text{-}PPh_2)(CO)_4]$

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Abstract

The reaction between $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_6]$ and diphenylphosphine gives the mono- and di-substituted complexes $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_{6-n}(PPh_2H)_n]$ [$n = 1$ (**1**), 2 (**2**)]. Thermolysis of (**1**) leads to phosphorus–hydrogen bond cleavage and formation of the phosphido-, vinyl-bridged complex $[Co_2\{\mu\text{-}C(CO_2Me){=}CHCO_2Me\}(\mu\text{-}PPh_2)(CO)_4]$ (**3**) together with the trinuclear cobalt complex $[Co_3\{\mu\text{-}C_2(CO_2Me)_2\}(\mu\text{-}PPh_2)(CO)_7]$ (**4**). An X-ray diffraction study of **3** reveals that one of the methylcarboxylate substituents of the vinyl ligand is coordinated via oxygen to cobalt, forming an almost planar M–C–C–C–O five-membered metallacyclic ring. The reactions of (**3**) with a tertiary phosphine and with phenylacetylene are described.

Introduction

The chemistry of the alkyne ligand in alkyne-hexacarbonyl dicobalt complexes of general formula $[Co_2(\mu\text{-}RC{\equiv}CR')(CO)_6]$ (R, R' = alkyl, aryl or H) has been thoroughly studied because of the widespread applications of these complexes in organic synthesis [1]. The substitution of carbonyl ligands in the complexes by monodentate and multidentate tertiary phosphines has also been extensively investigated [2,3] but there have been no reports of substitution reactions involving secondary phosphines. Such reactions are of interest because P–H bond cleavage in dinuclear complexes containing secondary phosphines can lead to hydrogen transfer and to consequent modification of a coordinated organic ligand [4], although in $[Co_2(\mu\text{-}RC{\equiv}CR')(CO)_6]$ complexes the reactivity of the C≡C triple bond is in most cases markedly reduced by coordination.

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In this paper we report the reaction of diphenylphosphine with the alkyne-bridged dicobalt complex, $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_6]$ which leads to simple mono- and di-substituted derivatives. Thermolysis of the monosubstituted derivative, $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_5(PPh_2H)]$ (**1**), does lead to products resulting from P–H bond cleavage. The X-ray structural analysis and some reactions of one of these products, $[Co_2\{\mu\text{-}C(CO_2Me){=}CHCO_2Me\}(\mu\text{-}PPh_2)(CO)_4]$ (**3**) are described.

Results and discussion

Reaction of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_6]$ with one equivalent of PPh_2H in toluene at 323 K gave the complexes $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_5(PPh_2H)]$ (**1**) and $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_4(PPh_2H)_2]$ (**2**) in 70% and 10% yields respectively. Complexes **1** and **2** have been characterised spectroscopically (Tables 1–3).

The spectroscopic properties of **1** are similar to those of other phosphine monosubstituted alkyne dicobalt complexes [3,5–8]. The ^{13}C NMR spectrum of **1** exhibits two carbonyl resonances with integrated intensities of 2:3 which has been interpreted for related derivatives [7] in terms of localised site exchange of the carbonyls around each cobalt atom in solution, although this mechanism is not always operative and alternative explanations of the data are possible [8]. X-ray diffraction studies on similar complexes [5] suggest that in the solid state the phosphine ligand in **1** occupies a pseudoaxial site as shown in Fig. 1.

The spectroscopic properties of **2** are again similar to those of other disubstituted derivatives [3] and suggest that **2** is diaxially substituted as shown in Fig. 1. The crystal structure of a related complex, $[Co_2(\mu\text{-}HC{\equiv}CH)(CO)_4(PMe_3)_2]$, is of this type [9] although the ^{13}C NMR spectrum of **2** in solution, which exhibits only one carbonyl resonance, is also compatible with a fluxional system involving either

Table 1

Mass spectroscopic and microanalytical data for the di- and tricobalt complexes

Compound	Mass spectra		Analysis (%) [a]		
	M	Fragmentation	C	H	P
1 $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_5(PPh_2H)]$	586	M-*n*CO(*n* = 0–5)	47.1 (47.1)	2.9 (2.9)	5.6 (5.3)
2 $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_4(PPh_2H)_2]$	744	M-*n*CO(*n* = 0–4)	54.8 (54.8)	3.7 (3.8)	8.3 (8.3)
3 $[Co_2\{\mu\text{-}C(CO_2Me){=}CHCO_2Me\}$, $(\mu\text{-}PPh_2)(CO)_4]$	558	M-*n*CO(*n* = 0–4)	47.6 (47.3)	3.0 (3.1)	5.4 (5.6)
4 $[Co_3\{\mu\text{-}C_2(CO_2Me)_2\}(\mu\text{-}PPh_2)(CO)_7]$	700	M-*n*CO(*n* = 0–7)	42.7 (42.9)	2.2 (2.3)	4.5 (4.4)
5 $[Co_2\{\mu\text{-}C(CO_2Me){=}CHCO_2Me\}(\mu\text{-}PPh_2)$, $(CO)_3\{P(C_6H_4Me\text{-}4)_3\}]$	834 [b]	M-*n*CO(*n* = 0–3)	60.3 (60.4)	5.1 (4.8)	
6 $[Co_2\{\mu\text{-}PPh_2CPhCHCPhCHC(CO_2Me)$, $CHCO_2Me\}(CO)_4]$	762 [b]	M-*n*CO(*n* = 0,2–4)	60.2 (59.9)	4.0 (3.8)	3.6 (4.1)

[a] Calculated values in parentheses. [b] Fast atom bombardment spectrum.

Table 2

Infrared, ^{1}H NMR and ^{31}P NMR data for the complexes

Compound	ν(CO) (cm^{-1}) [a]	^{1}H NMR (δ) [b]	^{31}P NMR (δ) [c]
1	2084s, 2040s, 2028s, 1996s, 1715m	7.7–7.4 (m, 10H, Ph), 6.36 (d, ^1J(PH) 376, 1H, PPh$_2$*H*), 3.64 (s, 6H, Me)	−121.0(s)
2	2050s, 2008(sh), 1998s, 1706w	7.6–7.3 (m, 20H, Ph), 6.13 (d, ^1J(PH) 366, 2H, PPh$_2$*H*), 3.33 (s, 6H, Me)	−119.6(s)
3 [d]	2063m, 2018s, 1972m, 1686w, 1560w	7.6–7.2 (m, 10H, Ph), 3.89 (d, ^3J(PH) 5.5, 1H, C*H*), 3.67 (s, 3H, Me), 3.02 (s, 3H, Me)	31.7(s)
4	2080m, 2050s, 2041s, 2024m, 1990w, 1965w, 1721m	7.9–7.2 (m, 10H, Ph), 3.49 (s, 6H, Me)	82.0(s, br)
5 [d]	2001m, 1978s, 1949s, 1668w, 1601vw, 1553w	7.5–6.7 (m, 22H, Ph), 3.92 (dd, ^3J(PH) 4.5, ^3J(P′H) 4.5, 1H, C*H*), 3.40 (s, 3H, Me), 2.99 (s, 3H, Me), 2.34 (s, 9H, Me)	16.5 (s, μ-*P*Ph$_2$) −105.8 [s, *P*(C$_6$H$_4$Me-4)$_3$]
6	2062m, 2042s, 2024s, 1709w	7.5–6.9 (m, 20H, Ph), 6.68 (d, *J*(PH) 0.6, 1H, PPh$_2$CPhCHCPhC*H*), 6.11 (d, ^3J(PH)32, 1H, PPh$_2$CPhC*H*), 3.77 (s, 3H, Me), 3.40 (s, 3H, Me), 2.70 (d, *J*(PH) 1.0, 1H, C*H*CO$_2$Me)	−81.6(s)

[a] Recorded in n-hexane solution. [b] ^{1}H chemical shifts (δ) in ppm relative to SiMe$_4$ (0.0 ppm); coupling constants in Hz measured in CD$_2$Cl$_2$ at 293 K. [c] ^{31}P chemical shifts (δ) in ppm relative to external P(OMe)$_3$ (0.0 ppm) (upfield shifts negative); {^{1}H}-gated decoupled, measured in CDCl$_3$ at 293 K. [d] IR spectrum recorded in CH$_2$Cl$_2$ solution.

Table 3
^{13}C NMR data [a] for the complexes

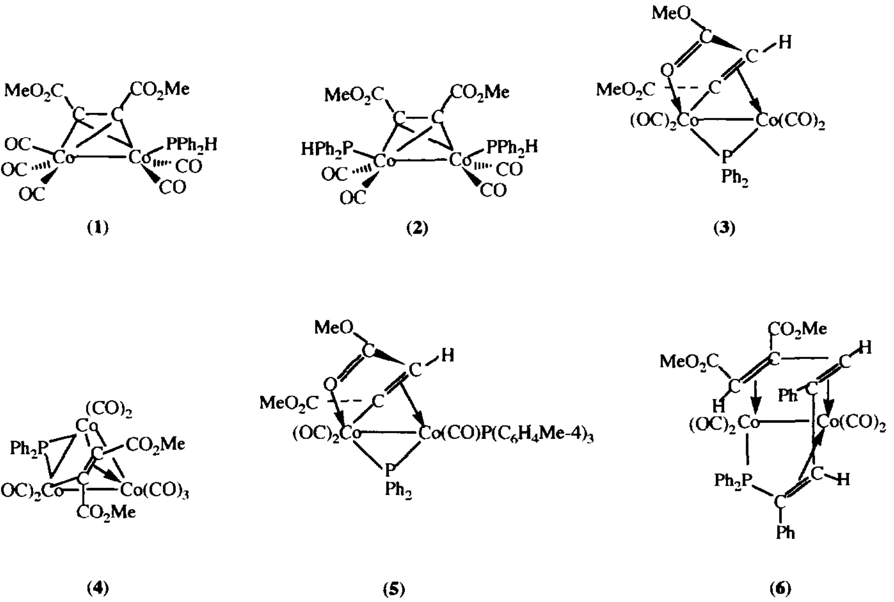
Compound	^{13}CO resonances	Other ^{13}C resonances
1	202.5 (s, 2CO), 198.7 (s, 3CO)	170.8 (s, CO$_2$Me), 132–128 (m, Ph) 74.2 (s, CCO$_2$Me), 52.5 (s, Me)
2	204.0 (s, 4CO)	171.7 (s, CO$_2$Me), 132–128 (m, Ph) 71.2 (s, CCO$_2$Me), 51.7 (s, Me)
3	208.9 (s, CO), 202.3 (s, CO) 199.7 (s, CO), 198.3 (s, CO)	188.8 (s, CO$_2$Me), 175.1 (s, CO$_2$Me) 142.1 (d, ^2J(PC) 20.7, C(CO$_2$Me)=CHCO$_2$Me) 135–127 (m, Ph), 53.8 (s, Me), 51.3 (s, Me), 48.7 (s, CHCO$_2$Me)
4	205, 202 (s, br, 7CO)	170.1 (s, CO$_2$Me), 152.8 (s, CCO$_2$Me) 142–127 (m, Ph), 52.0 (s, Me)

[a] Recorded in CDCl$_3$ solution at 293 K, ^{1}H composite pulse decoupled.

localised site exchange or a trigonal twisting of the phosphine and two carbonyl ligands on each cobalt [8].

Thermolysis of **1** at 333 K in toluene for 40 h gave the phosphido-, vinyl-bridged complex [Co$_2${μ-C(CO$_2$Me)=CHCO$_2$Me}(μ-PPh$_2$)(CO)$_4$] (**3**) as the major product. The trimeric complex [Co$_3${μ-C$_2$(CO$_2$Me)$_2$}(μ-PPh$_2$)(CO)$_7$] (**4**) was also isolated from the reaction (Scheme 1) as a minor product. Both complexes **3** and **4** have been characterised spectroscopically (Tables 1–3). In addition complex **3** has been the subject of a single crystal X-ray structural analysis.

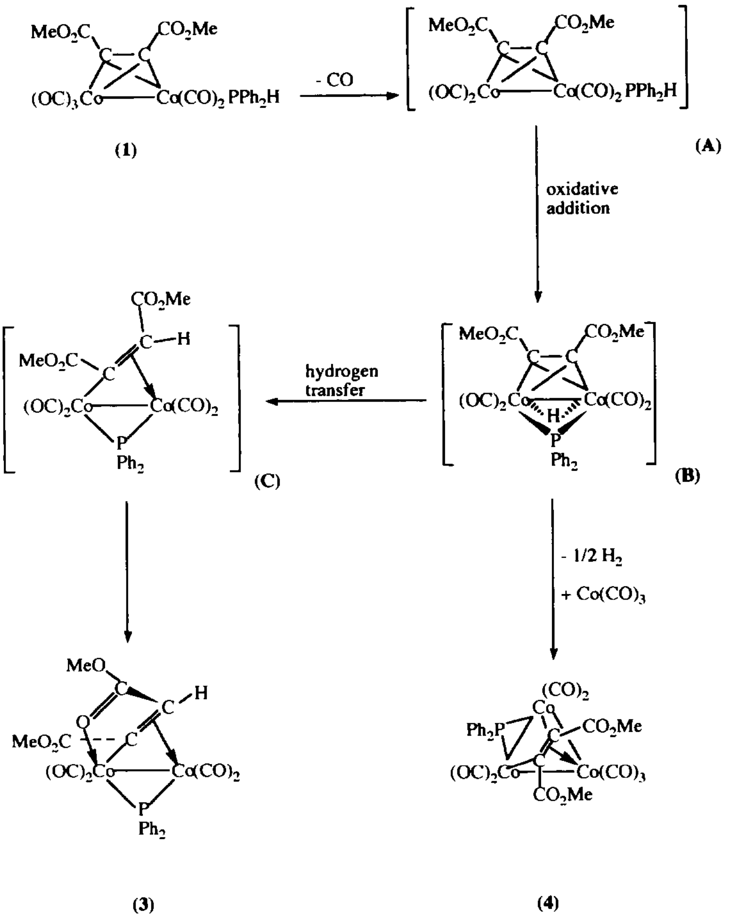
The molecular structure of **3** is shown in Fig. 2; Tables 4 and 5 list the bond lengths and angles respectively. The vinyl group in **3** is σ-bonded to Co(1) through



(1) (2) (3)

(4) (5) (6)

Fig. 1. Proposed structures of the new complexes.



Scheme 1. A possible mechanism for the formation of 3 and 4 on thermolysis of 1.

C(34) [1.960(4) Å] and asymmetrically π-bonded to Co(2) through C(34) [1.937(4) Å] and C(33) [2.074(4) Å] (Fig. 2). The C(33)–C(34) bond length [1.428(5) Å] is close to the value [1.425(22) Å] reported for [$FeCo\{\mu\text{-}C(CO_2Me)$=$CH\text{-}CO_2Me\}(CO)_6$] [10]. The methylcarboxylate groups adopt a *trans* configuration with O(31) coordinated to Co(1) [2.068(3) Å] and forming an almost planar M–C–C–C–O five-membered metallacycle as observed for [$FeCo\{\mu\text{-}C(CO_2Me)$=$CHCO_2Me\}(CO)_6$] except that oxygen coordination occurs at Fe and not Co in the latter case. Although complex **3** obeys the effective atomic number (EAN) rule overall, Co(2) is electron-deficient, while Co(1) is electron-rich. This electron imbalance is reflected in asymmetric bridging of the Co–Co bond by the phosphido ligand. The P–Co(2) bond distance is *ca.* 0.07 Å shorter than the P–Co(1) distance, so that the stronger donation is to the electron-deficient metal atom. The observed Co–Co bond length [2.458(1) Å] is similar to those found in the majority of other alkyne-hexacarbonyldicobalt derivatives studied [11]. The carbonyl ligands in **3** lie *cis* relative to the phosphido bridge, and are distorted slightly from a perfectly co-planar eclipsed conformation. The Co–C (carbonyl) bond distances lie

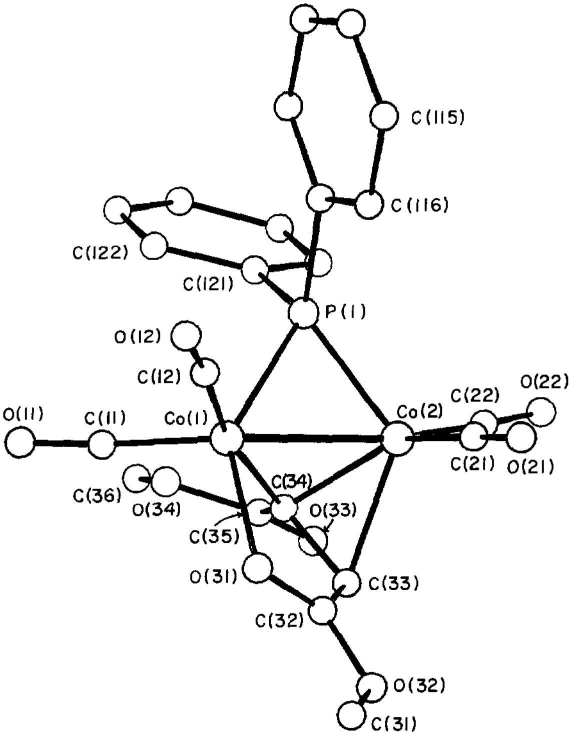


Fig. 2. Molecular structure of [$Co_2\{\mu\text{-}C(CO_2Me)=CHCO_2Me\}(\mu\text{-}PPh_2)(CO)_4$] (3) including the atom numbering scheme.

Table 4

Bond lengths (Å) for 3 with estimated standard deviations in parentheses

Co(1)-Co(2)	2.458(1)	Co(1)-P(1)	2.201(1)
Co(1)-C(11)	1.782(4)	Co(1)-C(12)	1.813(4)
Co(1)-C(34)	1.960(4)	Co(1)-O(31)	2.068(3)
Co(2)-P(1)	2.130(1)	Co(2)-C(21)	1.804(4)
Co(2)-C(22)	1.774(5)	Co(2)-C(33)	2.074(4)
Co(2)-C(34)	1.937(4)	P(1)-C(111)	1.818(4)
P(1)-C(121)	1.832(4)	C(11)-O(11)	1.130(6)
C(12)-O(12)	1.135(6)	C(21)-O(21)	1.135(6)
C(22)-O(22)	1.135(6)	C(31)-O(32)	1.145(6)
C(32)-C(33)	1.448(6)	C(32)-O(31)	1.244(5)
C(32)-O(32)	1.324(5)	C(33)-C(34)	1.428(5)
C(33)-H(33)	1.029(4)	C(34)-C(35)	1.488(6)
C(35)-O(33)	1.196(6)	C(35)-O(34)	1.334(5)
C(36)-O(34)	1.452(5)	C(111)-C(112)	1.396(6)
C(111)-C(116)	1.403(6)	C(112)-C(113)	1.402(6)
C(113)-C(114)	1.367(7)	C(114)-C(115)	1.377(7)
C(115)-C(116)	1.388(6)	C(121)-C(122)	1.380(6)
C(121)-C(126)	1.385(7)	C(122)-C(123)	1.387(7)
C(123)-C(124)	1.378(9)	C(124)-C(125)	1.364(8)
C(125)-C(126)	1.392(7)		

Table 5

Bond angles (deg) for **3** with estimated standard deviations in parentheses

P(1)–Co(1)–Co(2)	54.1(1)	C(11)–Co(1)–Co(2)	143.1(2)
C(11)–Co(1)–P(1)	111.0(2)	C(12)–Co(1)–Co(2)	117.0(1)
C(12)–Co(1)–P(1)	94.9(2)	C(12)–Co(1)–C(11)	96.3(2)
C(34)–Co(1)–Co(2)	50.5(1)	C(34)–Co(1)–P(1)	81.2(1)
C(34)–Co(1)–C(11)	97.1(2)	C(34)–Co(1)–C(12)	166.5(2)
O(31)–Co(1)–Co(2)	88.6(1)	O(31)–Co(1)–P(1)	140.5(1)
O(31)–Co(1)–C(11)	107.0(2)	O(31)–Co(1)–C(12)	91.2(2)
O(31)–Co(1)–C(34)	83.9(1)	P(1)–Co(2)–Co(1)	56.8(1)
C(21)–Co(2)–Co(1)	104.3(1)	C(21)–Co(2)–P(1)	111.8(1)
C(22)–Co(2)–Co(1)	151.2(2)	C(22)–Co(2)–P(1)	105.5(2)
C(22)–Co(2)–C(21)	103.7(2)	C(33)–Co(2)–Co(1)	73.7(1)
C(33)–Co(2)–P(1)	123.2(1)	C(33)–Co(2)–C(21)	105.4(2)
C(33)–Co(2)–C(22)	105.5(2)	C(34)–Co(2)–Co(1)	51.3(1)
C(34)–Co(2)–P(1)	83.6(1)	C(34)–Co(2)–C(21)	138.8(2)
C(34)–Co(2)–C(22)	108.6(2)	C(34)–Co(2)–C(33)	41.5(1)
Co(2)–P(1)–Co(1)	69.1(1)	C(111)–P(1)–Co(1)	119.1(1)
C(111)–P(1)–Co(2)	125.3(1)	C(121)–P(1)–Co(1)	116.8(1)
C(121)–P(1)–Co(2)	121.3(1)	C(121)–P(1)–C(111)	103.1(2)
O(11)–C(11)–Co(1)	175.9(5)	O(12)–C(12)–Co(1)	176.5(4)
O(21)–C(21)–Co(2)	178.1(4)	O(22)–C(22)–Co(2)	178.4(4)
O(31)–C(32)–C(33)	122.1(3)	O(32)–C(32)–C(33)	115.8(3)
O(32)–C(32)–O(31)	122.1(4)	C(32)–C(33)–Co(2)	104.3(3)
C(34)–C(33)–Co(2)	64.1(2)	C(34)–C(33)–C(32)	113.5(3)
Co(2)–C(34)–Co(1)	78.2(1)	C(33)–C(34)–Co(1)	106.6(3)
C(33)–C(34)–Co(2)	74.4(2)	C(35)–C(34)–Co(1)	133.8(3)
C(35)–C(34)–Co(2)	123.3(3)	C(35)–C(34)–C(33)	118.1(3)
O(33)–C(35)–C(34)	124.6(4)	O(34)–C(35)–C(34)	111.7(4)
O(34)–C(35)–O(33)	123.6(4)	C(32)–O(31)–Co(1)	106.4(3)
C(32)–O(32)–C(31)	117.1(3)	C(36)–O(34)–C(35)	116.0(3)
C(112)–C(111)–P(1)	122.9(3)	C(116)–C(111)–P(1)	118.5(3)
C(116)–C(111)–C(112)	118.6(4)	C(113)–C(112)–C(111)	120.4(4)
C(114)–C(113)–C(112)	120.0(4)	C(115)–C(114)–C(113)	120.3(4)
C(116)–C(115)–C(114)	120.8(4)	C(115)–C(116)–C(111)	119.9(4)
C(122)–C(121)–P(1)	121.0(3)	C(126)–C(121)–P(1)	119.9(3)
C(126)–C(121)–C(122)	119.1(4)	C(123)–C(122)–C(121)	120.8(5)
C(124)–C(123)–C(122)	120.0(5)	C(125)–C(124)–C(123)	119.3(5)
C(126)–C(125)–C(124)	121.5(5)	C(125)–C(126)–C(121)	119.3(4)

in the range 1.774(5) Å to 1.813(4) Å and as with $[Fe_2(\mu\text{-}CPh{=}CPhH)(\mu\text{-}PPh_2)(CO)_6]$ [12] all carbonyl ligands are essentially linear. This contrasts with the geometry of $[Mn_2(\mu\text{-}CH{=}CH_2)(\mu\text{-}PPh_2)(CO)_7]$, where an electron imbalance between the two metals is partially counteracted by the presence of an incipient semibridging carbonyl group [13].

In the IR spectrum of **3**, recorded in dichloromethane solution, two absorptions corresponding to $\nu(C{=}O)$ bands of the ester groups are seen at 1686 and 1560 cm^{-1}. The absorption band at lower frequency is indicative of coordination of one ester group to one metal through a carbonyl oxygen [10] and suggests that the solid state structure of **3** is maintained in solution. This is corroborated by the ^1H, ^{31}P and ^{13}C NMR spectra of the complex (Tables 2 and 3). In the ^{13}C NMR spectrum of **3** at 293 K all four carbonyl ligands give rise to distinct resonances showing that there is no carbonyl fluxionality at this temperature. The α-carbon of the vinyl group appears as a doublet centred at δ 142.1 with $^2J(PC)$ 20 Hz. Off resonance decoupling distinguished the two methyl resonances (δ 53.8 and δ 51.3) from that of the C=*C*HR, β-carbon of the vinyl group (δ 48.7).

The proposed structure of the trinuclear complex $[Co_3\{\mu\text{-}C_2(CO_2Me)_2\}(\mu\text{-}PPh_2)(CO)_7]$ (**4**) (Fig. 1) is based on spectroscopic evidence. Thus the $^{31}P\{^1H\}$ NMR spectrum of the complex shows a broad singlet at δ 82.0, consistent with a μ-PPh_2 ligand. The ^1H NMR spectrum comprises multiplet peaks due to the phenyl protons and one singlet for the methyl protons of the methylcarboxylate groups, integrating to six protons. The IR spectrum, in addition to six terminal carbonyl stretching bands, shows only one low frequency carboxylate stretching band at 1721 cm^{-1}. These observations combined with the fact that the methyl carbons (δ 52.0), the carboxylate carbons (δ 170.1) and the acetylenic carbons (δ 152.8) all appear as singlets in the ^{13}C NMR spectrum of **4**, indicate that the methylcarboxylate groups of the alkyne are equivalent. Although the above data are entirely consistent with the structure for **4** depicted in Fig. 1, it is also possible that the complex adopts a less symmetrical structure but is fluxional at 293 K.

A plausible mechanistic scheme for the production of **3** and **4** from the thermolysis of **1** is outlined in Scheme 1. Loss of CO from the unsubstituted cobalt atom in **1**, followed by oxidative addition of the diphenylphosphine ligand coordinated to the other cobalt would produce, as an intermediate, a phosphido-, hydrido-bridged complex (intermediate **B** in Scheme 1). Hydride migration on to one of the alkyne carbon atoms would give a coordinatively unsaturated μ-vinyl complex (intermediate **C** in Scheme 1) and subsequent coordination of the carbonyl oxygen from the μ-vinyl to comply with the EAN rule would yield **3**. The isolation of **4** as a minor product can be rationalised in terms of hydrogen loss at the phosphido-, hydrido-bridged intermediate stage, with subsequent scavenging of a $Co(CO)_3$ fragment. The proposed existence of a phosphido-, hydrido-bridged intermediate is supported by the fact that Hanson and Fanwick [14] have isolated the related complex $[Co_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_4]$.

Phosphines can react with μ_2-vinyl-bridged complexes either at one of the metal centres by simple substitution of other ligands [10,15] or at the α- or β-carbon atoms of the vinyl ligand [16–18]. Attack by phosphines at one of the metal centres can also induce ligand rearrangement or reaction of the μ_2-vinyl ligand with other coordinated groups [16,19–22]. In order to determine which of these alternative pathways would be followed for **3** the reaction of the complex with $P(C_6H_4Me\text{-}4)_3$ was studied. At 293 K in toluene solution the reaction afforded a brown complex formulated on the basis of spectroscopic data (Tables 1–3) as $[Co_2\{\mu\text{-}C(CO_2Me)\text{=}CHCO_2Me\}(\mu\text{-}PPh_2)(CO)_3\{P(C_6H_4Me\text{-}4)_3\}]$ (**5**). The reaction was reversed on bubbling CO through a toluene solution of **5** at 293 K but only relatively low yields of **3** were recovered, since **3** itself reacts with CO at 293 K to produce several unstable orange and yellow coloured products which defied satisfactory characterisation.

In the IR spectrum of **5** a $\nu(CO)$ band at 1553 cm^{-1} is ascribed to a coordinated methylcarboxylate group, providing evidence that the phosphine does not displace the carboxylate oxygen from its coordination to the metal. In the ^1H NMR spectrum of the complex the vinyl proton appears as a doublet of doublets centred at δ 3.92 and coupled with equal magnitude (4.5 Hz) to both phosphorus atoms.

This implies that the $P(C_6H_4Me\text{-}4)_3$ ligand in **5** has become bonded to Co(2) in **3** (Fig. 2) rather than Co(1). Had the phosphine attacked Co(1), the phosphorus atom of this ligand and the vinyl proton would have been separated by four bonds rather than three and it is unlikely that a P–H coupling as large as 4.5 Hz would have been observed. The proposed structure of **5**, shown in Fig. 1, is not unexpected in the light of the outcome of the reaction of $[FeCo\{\mu\text{-}C(CO_2Me){=}CHCO_2Me\}(CO)_6]$ with $PPhMe_2$ which led to phosphine substitution on cobalt with retention of the iron-coordinated carboxyl oxygen [10]. In this case it was suggested that the increase in electron density on iron due to coordination of the carboxyl oxygen is responsible for directing the phosphine substituent to the other metal atom.

Reaction of μ_2-vinyl complexes with alkynes can lead to carbon–carbon bond formation and to the synthesis of complexes containing new bridging ligands incorporating the μ_2-vinyl and alkyne groups [22–24]. Thus for example, reaction of $[FeW\{\mu\text{-}CH{=}CHR\}(CO)_6(\eta^5\text{-}C_5H_5)]$ ($R = C_6H_4Me\text{-}4$) with $R'C{\equiv}CR'$ ($R' =$ Me, Et) gave $[FeW\{\mu\text{-}CR'CR'CHCRH\}(\mu\text{-}CO)(CO)_4(\eta^5\text{-}C_5H_5)]$ and $[FeW\{\mu\text{-}CEtCEtCHCRH\}(CO)_6(\eta^5\text{-}C_5H_5)]$ in which one molecule of alkyne has inserted into the iron–(μ_2-vinyl) σ-bond [25].

Reaction of a solution of **3** in toluene with an excess of phenylacetylene at 313 K gave an orange compound in 17% yield, formulated as $[Co_2\{\mu\text{-}PPh_2CPhCHCPhCHC(CO_2Me)CHCO_2Me\}(CO)_4]$ **6**, together with several other uncharacterised products in low yield. Crystals of **6** suitable for an X-ray study could not be obtained and the complex is tentatively assigned the structure shown in Fig. 1 on the basis of spectroscopic evidence. Thus the FAB mass spectrum of **6** shows the required molecular ion peak at m/z 762 together with peaks due to loss of n CO's ($n = 2, 3, 4$). The observation of an upfield phosphorus resonance at δ -81.6 in the $^{31}P\{^1H\}$ NMR spectrum of **6** indicates that a coordinated phosphine rather than a μ-phosphido ligand is present.

The ^1H NMR spectrum shows singlets at δ 3.77 and 3.40 which may be assigned to the non-equivalent methyl groups and resonances in the range δ 7.5–6.9 integrating to twenty protons due to the phenyl protons. Two signals at δ 6.11 and δ 6.68 of unit intensity are assigned to the protons of the inserted phenylacetylene units. The former exhibits a coupling constant of 32 Hz which is consistent with a three bond *trans* ($PCPh{=}CH$–) coupling rather than a two bond geminal ($PCH{=}CPh$) coupling [8,26]. The latter exhibits only weak coupling to phosphorus. A further doublet signal of unit intensity at δ 2.70 may reasonably be assigned to the phosphorus-coupled proton of the coordinated vinyl ligand. Overall the $PPh_2CPhCHCPhCHC(CO_2Me){=}CHCO_2Me$ ligand donates eight electrons to the dicobalt unit which is consistent with the requirements of the EAN rule.

Experimental

All reactions were carried out under dinitrogen by standard Schlenk techniques. Solvents were distilled under dinitrogen 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 University Chemical Laboratory, Cambridge; products are presented in order of decreasing R_f values.

The instrumentation used to obtain spectroscopic data has been described previously [27]. 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 complex $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_6]$ was prepared by the published method [2].

Reaction of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_6]$ *with* PPh_2H. $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_6]$ (4.60 g, 10.7 mmol) was dissolved in toluene (150 cm^3) and PPh_2H (1.86 cm^3, 10 mmol) was added. The solution was heated at 323 K for 1 h. The solvent was removed on a rotary evaporator and the red residue was dissolved in the minimum quantity of CH_2Cl_2 and adsorbed onto silica. The silica was pumped dry and placed on the top of a chromatography column (Kieselgel 60, 70–230 mesh). Elution with hexane-ethyl acetate (6 : 1) gave a trace of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_6]$, followed by red crystalline $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_5(PPh_2H)]$ (**1**) (4.38 g, 70%). Further elution of the column with hexane-ethyl acetate (3 : 1) afforded red crystalline $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_4(PPh_2H)_2]$ (**2**) (0.80 g, 10%). Repetition of the above reaction with two equivalents of PPh_2H, greatly increased the yield of **2** relative to **1**.

Thermolysis of 1. A solution of complex **1** (2.55 g, 4.34 mmol) in toluene (100 cm^3) was heated at 333 K for 40 h. The solvent was removed on a rotary evaporator and the residue dissolved in the minimum quantity of CH_2Cl_2 and adsorbed onto silica. The silica was pumped dry and placed on the top of a chromatography column. Elution with hexane-CH_2Cl_2 (1 : 4) gave purple crystalline $[Co_2\{\mu\text{-}C(CO_2Me)\text{=}CHCO_2Me\}(\mu\text{-}PPh_2)(CO)_4]$ (**3**) (0.98 g, 40%) followed by purple crystalline $[Co_3\{\mu\text{-}C_2(CO_2Me)_2\}(\mu\text{-}PPh_2)(CO)_7]$ (**4**) (0.36 g, 12%).

Reaction of 3 with $P(C_6H_4Me\text{-}4)_3$. A solution of complex **3** (0.043 g, 0.077 mmol) and $P(C_6H_4Me\text{-}4)_3$ (0.024 g, 0.079 mmol) in toluene (25 cm^3) was stirred for 4 h at 293 K. After removal of the solvent on a rotary evaporator the residue was dissolved in the minimum quantity of CH_2Cl_2 and the solution applied to the base of TLC plates. Elution with hexane-CH_2Cl_2 (2 : 1) gave **3** (0.011 g) and black crystalline $[Co_2\{\mu\text{-}C(CO_2Me)\text{=}CHCO_2Me\}(\mu\text{-}PPh_2)(CO)_3\{P(C_6H_4Me\text{-}4)_3\}]$ (**5**) (0.035 g, 54%).

Reaction of 3 with $PhC{\equiv}CH$. A large excess of $PhC{\equiv}CH$ (*ca.* 0.2 cm^3) was added to a solution of complex **3** (0.156 g, 0.280 mmol) in toluene (25 cm^3) and the mixture was stirred at 313 K for 36 h. After removal of solvent on a rotary evaporator TLC separation, with CH_2Cl_2 as eluant, gave orange crystalline $[Co_2\{\mu\text{-}PPh_2CPhCHCPhCHC(CO_2Me)CHCO_2Me\}(CO)_4]$ (**6**) (0.037 g, 17%) and several other compounds in very low yield.

Reaction of 5 with CO. A solution of **5** (0.010 g, 0.012 mmol) in toluene (10 cm^3) was purged with CO for 40 min. TLC separation, with hexane-CH_2Cl_2 (2 : 1) as eluant, gave **3** (0.005 g, 33%). Trace amounts of several orange and yellow products were also observed, but these either decomposed upon the TLC plate or gave insufficient material for characterisation.

Reaction of 3 with CO. A solution of **3** (0.010 g, 0.018 mmol) in toluene (10 cm^3) was purged with CO for 3h. TLC indicated the presence of several orange and yellow products in low yields, none of which were characterised, together with unchanged **3**.

Crystal data for 3. $C_{22}H_{17}O_8P_1Co_2$, $M = 557.99$, triclinic, space group $P\bar{1}$ (no. 2) $a = 12.069(4)$, $b = 10.500(3)$, $c = 9.438(3)$ Å, $\alpha = 98.85(3)$, $\beta = 99.51(3)$, $\gamma =$

87.44(2)°, U 1165.32 Å^3, $D_c = 1.59$ g cm^{-3}, $F(000) = 564$. Suitable crystals of **3** were grown by slow evaporation of a hexane-dichloromethane solution. A black crystal of size 0.29 × 0.30 × 0.24 mm, $\mu(\text{Mo-}K_\alpha) = 14.57$ cm^{-1}, was used in the data collection.

Data collection. Data were collected in the θ-range 3–25°, with a scan width of 0.80°, using the technique described previously [28]. Equivalent reflections were merged to give 2950 data with $I/\sigma(I) > 3.0$.

Structure solution and refinement. Standard methods were used [29,30]. The coordinates of the metal atoms and the phosphorus atom were deduced from a Patterson synthesis, and the remaining non-hydrogen atoms were located from the subsequent difference-Fourier synthesis. The hydrogen atoms were located in the next difference-Fourier synthesis, which was calculated with sin $\theta < 0.35$. These were included in the structure factor calculations with thermal factors of 0.08 Å^2 but their parameters were not refined. The non-hydrogen atoms were assigned

Table 6

Fractional atomic coordinates and equivalent isotropic thermal parameters (Å^2) for **3**

Atom	x	y	z	U_{iso} or U_{eq}
Co(1)	0.30250(4)	0.22431(5)	0.13113(6)	0.0395(3)
Co(2)	0.36709(4)	0.22157(5)	0.39168(6)	0.0413(3)
P(1)	0.23947(8)	0.09922(10)	0.26586(11)	0.0403(6)
C(11)	0.1910(4)	0.2787(4)	0.0045(5)	0.057(3)
O(11)	0.1175(3)	0.3063(4)	−0.0767(4)	0.097(3)
C(12)	0.3502(3)	0.0926(4)	0.0062(5)	0.052(3)
O(12)	0.3776(3)	0.0133(4)	−0.0777(4)	0.079(2)
C(21)	0.5042(4)	0.1446(4)	0.3996(5)	0.053(3)
O(21)	0.5918(3)	0.0994(4)	0.4065(4)	0.084(3)
C(22)	0.3409(4)	0.2373(4)	0.5732(5)	0.058(3)
O(22)	0.3237(3)	0.2443(4)	0.6888(4)	0.093(3)
C(31)	0.6451(4)	0.4333(5)	0.1951(6)	0.077(3)
C(32)	0.4666(3)	0.3926(4)	0.2510(5)	0.045(2)
C(33)	0.3896(3)	0.4078(4)	0.3551(4)	0.045(2)
C(34)	0.2817(3)	0.3546(4)	0.2976(4)	0.041(2)
C(35)	0.1816(3)	0.4217(4)	0.3497(5)	0.050(3)
C(36)	−0.0115(4)	0.4716(5)	0.2864(6)	0.071(3)
O(31)	0.4420(2)	0.3303(3)	0.1272(3)	0.048(2)
O(32)	0.5632(2)	0.4527(3)	0.2940(3)	0.060(2)
O(33)	0.1805(3)	0.4769(4)	0.4702(4)	0.078(2)
O(34)	0.0922(2)	0.4142(3)	0.2447(3)	0.054(2)
C(111)	0.2527(3)	−0.0747(4)	0.2191(4)	0.043(2)
C(112)	0.1612(3)	−0.1564(4)	0.1948(5)	0.053(3)
C(113)	0.1766(4)	−0.2900(4)	0.1601(5)	0.065(3)
C(114)	0.2817(4)	−0.3410(4)	0.1499(5)	0.066(3)
C(115)	0.3729(4)	−0.2618(5)	0.1744(6)	0.066(3)
C(116)	0.3598(4)	−0.1292(4)	0.2085(5)	0.055(3)
C(121)	0.0922(3)	0.1232(4)	0.2906(4)	0.043(2)
C(122)	0.0074(3)	0.1209(4)	0.1728(5)	0.056(3)
C(123)	−0.1043(4)	0.1334(5)	0.1918(6)	0.075(3)
C(124)	−0.1315(4)	0.1527(5)	0.3298(7)	0.081(4)
C(125)	−0.0475(5)	0.1575(5)	0.4465(6)	0.082(4)
C(126)	0.0649(4)	0.1435(5)	0.4294(5)	0.061(3)

anisotropic thermal parameters in the final cycles of full matrix refinement which converged at R 0.0368 and R' 0.0382 with weights of $w = 1/\sigma^2 F_o$ assigned to the individual reflections. The final atomic coordinates and equivalent isotopic thermal parameters for **3** are given in Table 6. Tables of hydrogen atom coordinates and a list of structure factors are available from the authors.

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