

The reactions of tricobalt alkylidyne complexes  $[\text{Co}_3(\mu_3\text{-CR})(\text{CO})_9]$  ( $\text{R} = \text{Me}, \text{CO}_2\text{Me}$ ) with the vinyl phosphine ligands  $\text{PPh}_2\text{CH}=\text{CH}_2$  and *cis*- $\text{Ph}_2\text{PCH}=\text{CHPh}_2$ ; crystal structure of  $[\text{Co}_3(\mu_3\text{-CCO}_2\text{Me})(\mu\text{-Ph}_2\text{PCH}=\text{CHPh}_2)(\text{CO})_7]$

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Abstract

The alkylidyne-capped complexes  $[\text{Co}_3(\mu_3\text{-CR})(\text{CO})_9]$  ( $\text{R} = \text{Me}$  **1a**,  $\text{CO}_2\text{Me}$  **1b**) react with  $\text{PPh}_2\text{CH}=\text{CH}_2$  in heptane at 308 K to give the phosphine-substituted complexes  $[\text{Co}_3(\mu_3\text{-CR})(\text{CO})_8(\text{PPh}_2\text{CH}=\text{CH}_2)]$  ( $\text{R} = \text{Me}$  **2a**,  $\text{CO}_2\text{Me}$  **2b**),  $[\text{Co}_3(\mu_3\text{-CR})(\text{CO})_7(\text{PPh}_2\text{CH}=\text{CH}_2)_2]$  ( $\text{R} = \text{Me}$  **3a**,  $\text{CO}_2\text{Me}$  **3b**) and, in the case of  $\text{R} = \text{CO}_2\text{Me}$ , the *tris*-substituted complex  $[\text{Co}_3(\mu_3\text{-CCO}_2\text{Me})(\text{CO})_6(\text{PPh}_2\text{CH}=\text{CH}_2)_3]$  **4**. Heating of complexes **2a** and **2b** at 343 K results in loss of a CO group and coordination of the vinyl moiety of the  $\text{PPh}_2\text{CH}=\text{CH}_2$  ligand to afford  $[\text{Co}_3(\mu_3\text{-CR})(\mu\text{-PPh}_2\text{CH}=\text{CH}_2)(\text{CO})_7]$  ( $\text{R} = \text{Me}$  **5a**,  $\text{CO}_2\text{Me}$  **5b**). In contrast, reaction of  $[\text{Co}_3(\mu_3\text{-CR})(\text{CO})_9]$  ( $\text{R} = \text{Me}$  **1a**,  $\text{CO}_2\text{Me}$  **1b**) with *cis*- $\text{Ph}_2\text{PCH}=\text{CHPh}_2$  (dppee) gives  $[\text{Co}_3(\mu_3\text{-CR})(\mu\text{-Ph}_2\text{PCH}=\text{CHPh}_2)(\text{CO})_7]$  ( $\text{R} = \text{Me}$  **6a**,  $\text{CO}_2\text{Me}$  **6b**) in which the dppee ligand bridges two adjacent cobalt atoms *via* both phosphino moieties. Nuclear magnetic resonance studies on **5a** and **5b** indicate that two isomeric structures in a ratio of 7:3 are present in solution at 293 K. Conversion of  $[\text{Co}_3(\mu_3\text{-CR})(\mu\text{-PPh}_2\text{CH}=\text{CH}_2)(\text{CO})_7]$  **5a** and **5b** back to  $[\text{Co}_3(\mu_3\text{-CR})(\text{CO})_8(\text{PPh}_2\text{CH}=\text{CH}_2)]$  **2a** and **2b** can be achieved by purging with CO at 293 K while further purging at 343 K results in conversion to  $[\text{Co}_3(\mu_3\text{-CR})(\text{CO})_9]$  **1a** and **1b**. The structure of  $[\text{Co}_3(\mu_3\text{-CCO}_2\text{Me})(\mu\text{-Ph}_2\text{PCH}=\text{CHPh}_2)(\text{CO})_7]$  **6b** was determined by single-crystal X-ray diffraction. All the complexes have been characterized spectroscopically and by elemental analysis.

Keywords: Tricobalt; Alkylidyne; Vinylphosphine; Crystal structure; Carbonyl; Vinyl

1. Introduction

The use of the vinyl phosphines  $[\text{PR}^1(\text{CR}^2=\text{CR}^3\text{R}^4)]$  ( $\text{R} = \text{H}, \text{alkyl}, \text{aryl}$ ) as ligands in organometallic transition metal complexes continues to be the focus of a series of reports [1]. In such complexes the ligand has the potential to act as a four-electron donor via the vinyl and phosphino groups. Introduction of a further two-electron donor group, e.g.  $\text{R}^4 = \text{PPh}_2$ , on the  $\beta$ -carbon of the vinyl phosphine results in a ligand capable of coordination to one or more metal centres via up to three separate donor sites [2].

In recent years the cobalt clusters  $[\text{Co}_3(\mu_3\text{-CR})(\text{CO})_9]$  and in particular the diphosphine-bridged complexes

$[\text{Co}_3(\mu_3\text{-CR})(\mu\text{-L-L})(\text{CO})_7]$  ( $\text{L-L} = \text{diphosphine}$ ) have received much attention since the diphosphine ligand can stabilize and activate the cluster as a hydroformylation catalyst [3,4]. Our interest in this type of tricobalt system,  $\text{Co}_3\text{C}$ , stems from an investigation of the isolobal dimetallic system  $\text{Co}_2\text{C}_2$  [5,6] in complexes of the type  $[\text{Co}_2(\mu\text{-C}_2\text{R}_2)(\text{CO})_6]$  towards multifunctional phosphine ligands [7–10].

In this work we describe the reactions of two tricobalt alkylidyne complexes  $[\text{Co}_3(\mu_3\text{-CR})(\text{CO})_9]$  ( $\text{R} = \text{Me}$  **1a**,  $\text{CO}_2\text{Me}$  **1b**) with the vinyl phosphines  $\text{PPh}_2\text{CH}=\text{CH}_2$  and *cis*- $\text{Ph}_2\text{PCH}=\text{CHPh}_2$  (dppee). In our dicobalt work we have found that the nature of the R groups on the bridging fragment,  $\mu\text{-RCCR}$ , can influence the outcome of reactions [7,8,10]. As a consequence, in this investigation, we have chosen an electron donating ( $\text{R} = \text{Me}$  **1a**) and an electron withdrawing ( $\text{R} = \text{CO}_2\text{Me}$  **1b**) R group in the cobalt clusters **1**.

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## 2. Results and discussion

### 2.1. Reactions of $[\text{Co}_3(\mu_3\text{-CR})(\text{CO})_9]$ ( $\text{R} = \text{Me}$ **1a**, $\text{CO}_2\text{Me}$ **1b**) with $\text{PPh}_2\text{CH}=\text{CH}_2$

The complexes  $[\text{Co}_3(\mu_3\text{-CR})(\text{CO})_9]$  ( $\text{R} = \text{Me}$  **1a**,  $\text{CO}_2\text{Me}$  **1b**) were heated together with the ligand in heptane at 308 K for 20 h to afford a range of vinyl phosphine substituted complexes, the degree of substitution being influenced by the nature of the R groups. When  $[\text{Co}_3(\mu_3\text{-CMe})(\text{CO})_9]$  **1a** was reacted with  $\text{PPh}_2\text{CH}=\text{CH}_2$  in an approximately 1:1 molar ratio, the products, in order of elution, were  $[\text{Co}_3(\mu_3\text{-CMe})(\text{CO})_8(\text{PPh}_2\text{CH}=\text{CH}_2)]$  **2a** (37% yield) and  $[\text{Co}_3(\mu_3\text{-CR})(\text{CO})_7(\text{PPh}_2\text{CH}=\text{CH}_2)_2]$  **3a** (33% yield). On the contrary, reaction of  $[\text{Co}_3(\mu_3\text{-CCO}_2\text{Me})(\text{CO})_9]$  **1b** with  $\text{PPh}_2\text{CH}=\text{CH}_2$  in similar proportions gave  $[\text{Co}_3(\mu_3\text{-CCO}_2\text{Me})(\text{CO})_8(\text{PPh}_2\text{CH}=\text{CH}_2)]$  **2b** (5% yield),  $[\text{Co}_3(\mu_3\text{-CCO}_2\text{Me})(\text{CO})_7(\text{PPh}_2\text{CH}=\text{CH}_2)_2]$  **3b** (55% yield) and  $[\text{Co}_3(\mu_3\text{-CCO}_2\text{Me})(\text{CO})_6(\text{PPh}_2\text{CH}=\text{CH}_2)_3]$  **4** (27% yield) (Scheme 1).

All the complexes **2a**, **2b**, **3a**, **3b** and **4** have been characterized by mass spectrometry and by IR,  $^1\text{H}$ ,  $^{31}\text{P}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectroscopy (Table 1 and Section 4). The mass spectra of complexes **2a**, **2b**, **3a**, **3b** and **4** all exhibit molecular ion peaks and/or peaks corresponding to fragmentation of the molecular ions. The IR spectra in the  $\nu_{\text{CO}}$  region

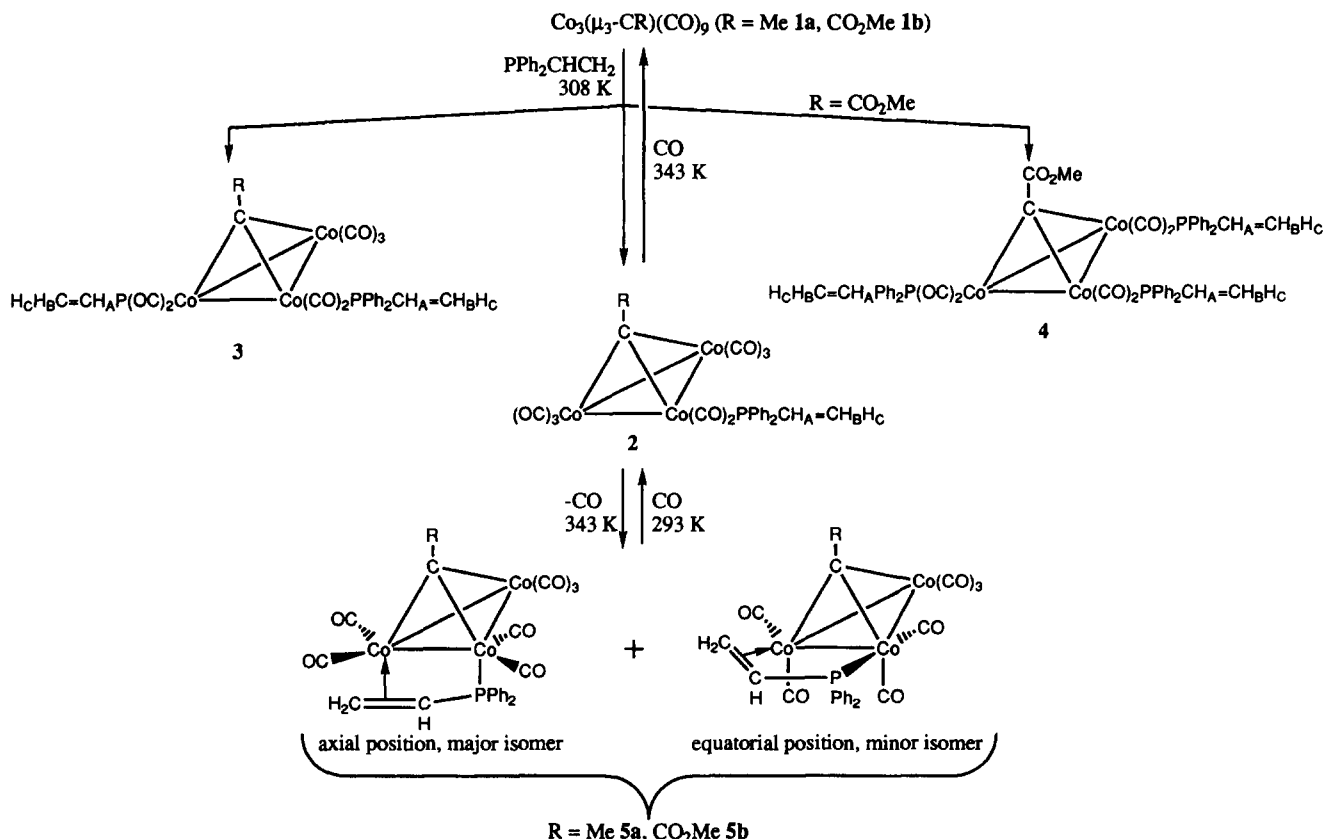
for complexes **2a**, **2b**, **3a**, **3b** and **4** exhibit absorption bands with a similar pattern to those reported for other *mono*-, *bis*- and *tris*-substituted phosphine derivatives of  $[\text{Co}_3(\mu_3\text{-CR})(\text{CO})_9]$  **1** [11–14].

The  $^1\text{H}$  NMR spectra at 293 K for the *mono*-substituted **2a** and **2b**, *bis*-substituted **3a** and **3b** and the *tris*-substituted complex **4** display, in addition to phenyl resonances and resonances for the capping groups, three sets of doublets of doublets of doublets (ddd) for the three vinyl protons  $\text{H}_\text{A}$ ,  $\text{H}_\text{B}$  and  $\text{H}_\text{C}$  (Scheme 1) in the expected 1:1:1 relative intensity ratios. The furthest downfield ddd resonance is attributed to  $\text{H}_\text{A}$ , the more upfield signal to  $\text{H}_\text{B}$  and the most upfield signal to  $\text{H}_\text{C}$ . The  $^{31}\text{P}$  NMR spectra of **2a**, **2b**, **3a**, **3b** and **4** consist of broad singlet resonances in the range  $\delta = -103.1$  to  $-117.3$  ppm (relative to  $\text{P}(\text{OMe})_3$  at 0.0 ppm); these chemical shifts are consistent with phosphine ligands bonded terminally to tricobalt centres [11–15].

On the basis of the above data the structures shown in Scheme 1 are proposed for complexes **2a**, **2b**, **3a**, **3b** and **4**. Note that  $\text{H}_\text{C}$  is *trans* to  $\text{H}_\text{A}$ .

### 2.2. Thermolysis of $[\text{Co}_3(\mu_3\text{-CR})(\text{CO})_8(\text{PPh}_2\text{CH}=\text{CH}_2)]$ ( $\text{R} = \text{Me}$ **2a**, $\text{CO}_2\text{Me}$ **2b**)

When the complexes  $[\text{Co}_3(\mu_3\text{-CR})(\text{CO})_8(\text{PPh}_2\text{CH}=\text{CH}_2)]$  ( $\text{R} = \text{Me}$  **2a**,  $\text{CO}_2\text{Me}$  **2b**) are heated in heptane



Scheme 1. Products from the reactions of  $[\text{Co}_3(\mu_3\text{-CR})(\text{CO})_9]$  ( $\text{R} = \text{Me}$  **1a**,  $\text{CO}_2\text{Me}$  **1b**) with  $\text{PPh}_2\text{CH}=\text{CH}_2$ .

at 343 K there is no evidence for P–C bond cleavage within the diphosphine ligand as observed in related complexes [2]. Instead the main products are  $[\text{Co}_3(\mu_3\text{-CR})(\mu\text{-PPh}_2\text{CH}=\text{CH}_2)(\text{CO})_7]$  ( $\text{R} = \text{Me}$  **5a**,  $\text{CO}_2\text{Me}$  **5b**) in yields of 78%–84%. Similar heating of **3a**, **3b** and **4** did not have any effect but in refluxing

toluene (384 K) cluster decomposition occurred. Complexes **5a** and **5b** have been characterized by mass spectrometry, IR,  $^1\text{H}$ ,  $^{31}\text{P}$  and  $^{13}\text{C}$  NMR spectroscopy (Table 1 and Section 4).

The  $^1\text{H}$  NMR spectra of **5a** and **5b** show clearly that the vinyl group of the phosphine ligand is coordinated

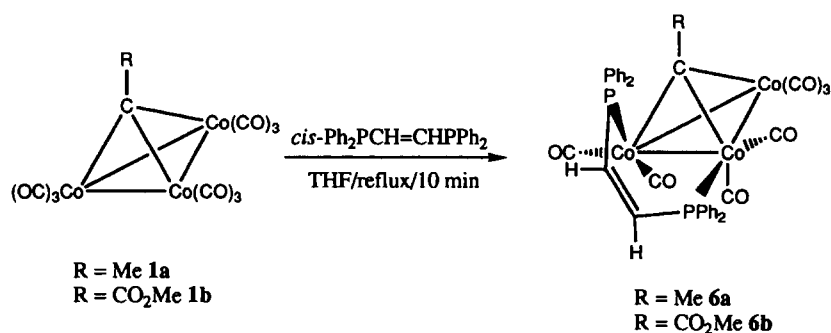
Table 1  
IR  $^1\text{H}$  nuclear magnetic resonance and  $^{31}\text{P}$  nuclear magnetic resonance data for the complexes

Compound	$\nu$ (CO) ( $\text{cm}^{-1}$ ) <sup>a</sup>	$^1\text{H}$ NMR: $\delta$ (ppm) <sup>b</sup>	$^{31}\text{P}$ NMR: $\delta$ (ppm) <sup>c</sup>
<b>2a</b>	2076s, 2031vs, 2020vs, 2011vs, 1986m, 1968m, 1878w, 1856w	7.7–7.2 (m, 10H, Ph), 6.67 (ddd, $^2J(\text{H}_\text{A}\text{P}) = 24.3$ , $^3J(\text{H}_\text{A}\text{H}_\text{C}) = 17.8$ Hz, $^3J(\text{H}_\text{A}\text{H}_\text{B}) = 12.0$ Hz, 1H, $\text{PCH}_\text{A}=\text{CH}_2$ ), 6.00 (ddd, $^3J(\text{H}_\text{B}\text{P}) = 37.0$ Hz, $^2J(\text{H}_\text{B}\text{H}_\text{C}) = 1.2$ Hz, 1H, $\text{PCH}=\text{CH}_\text{B}\text{H}$ ), 5.30 (ddd, $^3J(\text{HCP}) = 19.1$ Hz, 1H, $\text{PCH}=\text{CH}_\text{H}_\text{C}$ ), 3.25 (d, $^4J(\text{HP}) = 0.4$ Hz, 3H, Me)	– 117.3 (s, $\text{PPh}_2\text{CH}=\text{CH}_2$ )
<b>2b</b>	2086m, 2047s, 2033s, 2025s, 1981w, 1682w	7.7–7.3 (m, 10H, Ph), 6.62 (ddd, $^2J(\text{H}_\text{A}\text{P}) = 24.8$ Hz, $^3J(\text{H}_\text{A}\text{H}_\text{C}) = 17.7$ Hz, $^3J(\text{H}_\text{A}\text{H}_\text{B}) = 12.0$ Hz, 1H, $\text{PCH}_\text{A}=\text{CH}_2$ ), 6.01 (ddd, $^3J(\text{H}_\text{B}\text{P}) = 37.6$ Hz, $^2J(\text{H}_\text{B}\text{H}_\text{C}) = 1.2$ Hz, 1H, $\text{PCH}=\text{CH}_\text{B}\text{H}$ ), 5.34 (ddd, $^3J(\text{H}_\text{C}\text{P}) = 19.2$ Hz, 1H, $\text{PCH}=\text{CH}_\text{H}_\text{C}$ ), 3.76 (s, 3H, Me)	– 101.6 (s, $\text{PPh}_2\text{CH}=\text{CH}_2$ )
<b>3a</b>	2049s, 1994vs, 1981s, 1958m, 1944w, 1850w	7.8–7.2 (m, 20H, Ph), 6.67 (ddd, $^2J(\text{H}_\text{A}\text{P}) = 24.5$ Hz, $^3J(\text{H}_\text{A}\text{H}_\text{C}) = 18.0$ Hz, $^3J(\text{H}_\text{A}\text{H}_\text{B}) = 12.0$ Hz, 2H, $\text{PCH}_\text{A}=\text{CH}_2$ ), 5.94 (ddd, $^3J(\text{H}_\text{B}\text{P}) = 35.7$ Hz, $^2J(\text{H}_\text{B}\text{H}_\text{C}) = 1.2$ Hz, 2H, $\text{PCH}=\text{CH}_\text{B}\text{H}$ ), 5.24 (ddd, $^3J(\text{H}_\text{C}\text{P}) = 19.2$ Hz, 2H, $\text{PCH}=\text{CH}_\text{H}_\text{C}$ ), 2.70 (t, $^4J(\text{HP}) = 3.2$ Hz, 3H, Me)	– 104.0 (s, $\text{PPh}_2\text{CH}=\text{CH}_2$ )
<b>3b</b>	2060s, 2025s, 2012vs, 2001s, 1972m, 1671w	7.7–7.3 (m, 20H, Ph), 6.64 (ddd, $^2J(\text{H}_\text{A}\text{P}) = 25.0$ Hz, $^3J(\text{H}_\text{A}\text{H}_\text{C}) = 17.8$ Hz, $^3J(\text{H}_\text{A}\text{H}_\text{B}) = 12.0$ Hz, 2H, $\text{PCH}_\text{A}=\text{CH}_2$ ), 5.93 (ddd, $^3J(\text{H}_\text{B}\text{P}) = 36.4$ Hz, $^2J(\text{H}_\text{B}\text{H}_\text{C}) = 1.3$ Hz, 2H, $\text{PCH}=\text{CH}_\text{B}\text{H}$ ), 5.25 (ddd, $^3J(\text{HCP}) = 18.0$ Hz, 2H, $\text{PCH}=\text{CH}_\text{H}_\text{C}$ ), 3.59 (s, 3H, Me)	– 104.0 (s, $\text{PPh}_2\text{CH}=\text{CH}_2$ )
<b>4b</b>	2045m, 2022m, 2012s, 1988vs, 1967s, 1827w, 1817w	7.7–7.3 (m, 30H, Ph), 6.71 (ddd, $^2J(\text{H}_\text{A}\text{P}) = 24$ Hz, $^3J(\text{H}_\text{A}\text{H}_\text{C}) = 18$ Hz, $^3J(\text{H}_\text{A}\text{H}_\text{B}) = 12$ Hz, 3H, $\text{PCH}_\text{A}=\text{CH}_2$ ), 5.89 (ddd, $^3J(\text{H}_\text{B}\text{P}) = 36$ Hz, $^2J(\text{H}_\text{B}\text{H}_\text{C}) = 0.8$ Hz, 3H, $\text{PCH}=\text{CH}_\text{B}\text{H}$ ), 5.21 (td, $^3J(\text{H}_\text{C}\text{P}) = 18$ Hz, 3H, $\text{PCH}=\text{CH}_\text{H}_\text{C}$ ), 3.18 (s, 3H, Me)	– 103.1 (s, $\text{PPh}_2\text{CH}=\text{CH}_2$ )
<b>5a</b>	2069s, 2016vs, 2003s, 1981m, 1970m	8.0–7.3 (m, 10H, Ph), 4.3–2.0 (m, 3H, $\text{PCH}=\text{CH}_2$ ), 3.50 (s, 3H, Me–minor isomer), 2.89 (d, $^4J(\text{HP}) = 0.9$ Hz, 3H, Me–major isomer)	– 110.1 (s, $\mu\text{-PPh}_2\text{CH}=\text{CH}_2$ )
<b>5b</b>	2078s, 2034vs, 2014s, 2003m, 1991m, 1679m	7.9–7.3 (m, 10H, Ph), 4.3–2.8 (m, 3H, $\text{PCH}=\text{CH}_2$ ), 3.53 (s, 3H, Me–major isomer), 3.46 (s, 3H, Me–minor isomer)	– 107.8 (s, $\mu\text{-PPh}_2\text{CH}=\text{CH}_2$ )
<b>6a</b>	2059s, 2020s, 2010vs, 2008vs, 1992s, 1976m, 1970m, 1954w, 1870w, 1828w	7.8–7.0 (m, 20H, Ph), 2.87 (t, $^4J(\text{HP}) = 2.7$ Hz, 3H, Me), olefinic protons masked by phenyl signals	– 86.9 (s, $\mu\text{-PPh}_2\text{CH}=\text{CHPh}_2$ )
<b>6b</b>	2070vs, 2027vs, 2018vs, 2005m, 1992w, 1982m, 1965w, 1671w	7.6–7.0 (m, 20H, Ph), 3.59 (s, 3H, Me), olefinic protons masked by phenyl signals	– 100.1 (s, $\mu\text{-PPh}_2\text{CH}=\text{CHPh}_2$ )

<sup>a</sup> Recorded in *n*-hexane solution.

<sup>b</sup> Chemical shifts  $\delta$  relative to  $\text{SiMe}_4$  (0.0 ppm), coupling constants in  $\text{CDCl}_3$  at 293 K.

<sup>c</sup>  $^{31}\text{P}$  chemical shifts relative to external  $\text{P}(\text{OMe})_3$  (0.0 ppm) (upfield shifts negative),  $^1\text{H}$  gated decoupled, measured in  $\text{CDCl}_3$  at 293 K.

Scheme 2. Reactions of complexes **1a** and **1b** with *cis*-Ph<sub>2</sub>PCH=CHPh<sub>2</sub> (dppee).

rather than free in each case. The vinyl signals, which in the uncoordinated species (**2a**, **2b**, **3a**, **3b** and **4**) appear in the region  $\delta = 5$  to 7 ppm, are now shifted upfield to the range  $\delta = 2$ –4 ppm. Furthermore, two inseparable isomers exist for each complex giving rise in total to six overlapping sets of ddd. There are also phenyl resonances and, for **5a**, a doublet at  $\delta = 2.89$  ppm ( $^4J(\text{HP}) = 0.9$  Hz) due to the methyl protons of the major isomer and a singlet at  $\delta = 3.50$  ppm due to the methyl protons of the minor isomer. For **5b** the methyl protons of the major and minor isomers give rise to singlets at  $\delta = 3.53$  ppm and  $\delta = 3.46$  ppm respectively.

The <sup>31</sup>P (<sup>1</sup>H) NMR spectra of complexes **5a** and **5b** both consist of broad singlet resonances at  $\delta = -110.1$  ppm (**5a**) and  $\delta = -107.8$  ppm (**5b**). The peaks probably consist in each case of overlapping signals arising from the presence of the two isomers.

The <sup>13</sup>C(<sup>1</sup>H) NMR spectra at 293 K of **5a** and **5b** reveal the presence of two isomers (in a ratio of 7 : 3 in each case) most distinctly. For **5a**, the carbonyl ligands of both isomers give rise to only one broad signal while for **5b** two carbonyl resonances are seen. Every other resonance for **5a** and **5b** is observed to consist of two signals owing to the major and minor isomers. As is the case with the proton NMR spectrum, coordination of the vinyl group shifts the vinyl carbon peaks upfield.

On the basis of the above data proposed structures for the two isomers of complexes **5a** and **5b** are shown in Scheme 1. These differ in that in one the coordinated vinyl ligand occupies two equatorial positions whereas in the other it occupies two axial positions. The <sup>1</sup>H NMR spectrum of the major isomer of **5a** exhibits a doublet resonance ( $^4J(\text{HP}) = 0.9$  Hz) for the methyl group on the capping carbon atom, whereas the corre-

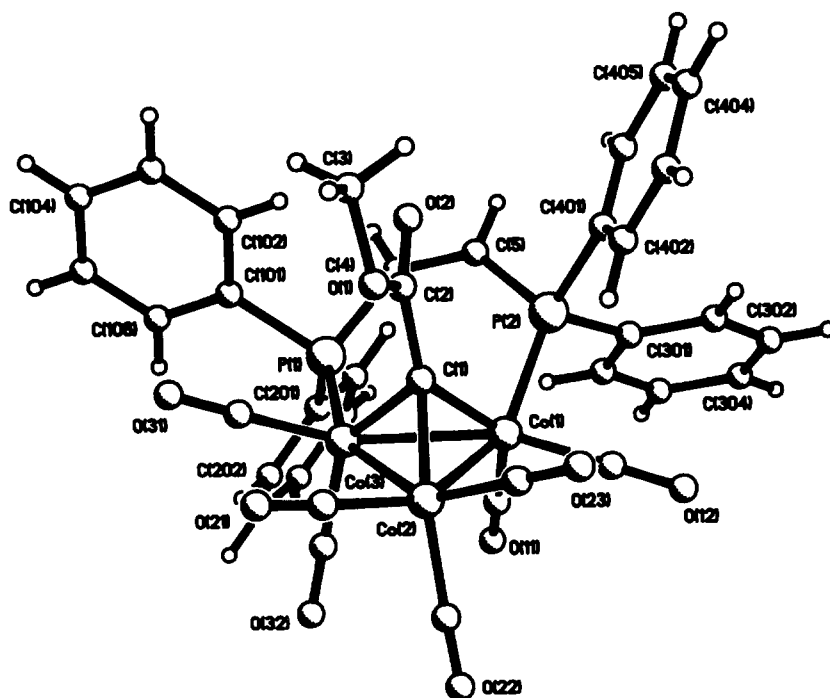
Fig. 1. Molecular structure of  $[\text{Co}_3(\mu_3\text{-CCO}_2\text{Me})(\mu\text{-Ph}_2\text{PCH=CHPh}_2)(\text{CO})_7]$  **6b** including the atom numbering scheme.

Table 2

Bond lengths (ångströms) for the complex  $[\text{Co}_3(\mu_3\text{-CCO}_2\text{Me})(\mu\text{-Ph}_2\text{PCH=CHPh}_2)(\text{CO})_7]$  **6b** with estimated standard deviations in parentheses

Co(1)–Co(2)	2.481(1)	Co(1)–Co(3)	2.464(1)
Co(1)–C(1)	1.892(6)	Co(1)–C(11)	1.796(6)
Co(1)–C(12)	1.759(7)	Co(1)–P(2)	2.166(2)
Co(2)–Co(3)	2.492(1)	Co(2)–C(1)	1.918(6)
Co(2)–C(21)	1.797(8)	Co(2)–C(22)	1.809(7)
Co(2)–C(23)	1.793(6)	Co(3)–C(1)	1.903(5)
Co(3)–C(31)	1.775(7)	Co(3)–C(32)	1.796(6)
Co(3)–P(1)	2.222(2)	C(1)–C(2)	1.464(8)
C(2)–O(1)	1.340(7)	C(2)–O(2)	1.205(8)
O(1)–C(3)	1.453(10)	C(11)–O(11)	1.141(8)
C(12)–O(12)	1.152(9)	C(21)–O(21)	1.144(10)
C(22)–O(22)	1.128(10)	C(23)–O(23)	1.132(7)
C(31)–O(31)	1.144(9)	C(32)–O(32)	1.128(8)
P(1)–C(4)	1.824(6)	P(1)–C(101)	1.822(5)
P(1)–C(201)	1.844(4)	C(4)–C(5)	1.329(8)
C(5)–P(2)	1.810(6)	P(2)–C(301)	1.841(4)
P(2)–C(401)	1.837(3)		

Table 3

Bond angles (degrees) for complex  $[\text{Co}_3(\mu_3\text{-CCO}_2\text{Me})(\mu\text{-Ph}_2\text{PCH=CHPh}_2)(\text{CO})_7]$  **6b** with estimated standard deviations in parentheses

Co(2)–Co(1)–Co(3)	60.5(1)	Co(2)–Co(1)–C(1)	49.8(2)
Co(3)–Co(1)–Co(1)–C(1)	49.7(1)	Co(2)–Co(1)–C(11)	111.5(2)
Co(3)–Co(1)–C(11)	85.0(2)	C(1)–Co(1)–C(11)	134.8(3)
Co(2)–Co(1)–C(12)	92.6(2)	Co(3)–Co(1)–C(12)	152.1(2)
C(1)–Co(1)–C(12)	119.7(3)	C(11)–Co(1)–C(12)	99.4(3)
Co(2)–Co(1)–P(2)	143.0(1)	Co(3)–Co(1)–P(2)	111.2(1)
C(1)–Co(1)–P(2)	95.9(2)	C(11)–Co(1)–P(2)	102.9(2)
C(12)–Co(1)–P(2)	94.7(2)	Co(1)–Co(2)–Co(3)	59.4(1)
Co(1)–Co(2)–C(1)	48.9(2)	Co(3)–Co(2)–C(1)	49.0(1)
Co(1)–Co(2)–C(21)	150.5(2)	Co(3)–Co(2)–C(21)	95.3(2)
C(1)–Co(2)–C(21)	103.8(3)	Co(1)–Co(2)–C(22)	94.9(2)
Co(3)–Co(2)–C(22)	101.4(2)	C(1)–Co(2)–C(22)	139.9(3)
C(21)–Co(2)–C(22)	105.7(3)	Co(1)–Co(2)–C(23)	97.3(2)
Co(3)–Co(2)–C(23)	147.5(2)	C(1)–Co(2)–C(23)	98.9(3)
C(21)–Co(2)–C(23)	98.5(3)	C(22)–Co(2)–C(23)	103.0(3)
Co(1)–Co(3)–Co(2)	60.1(1)	Co(1)–Co(3)–C(1)	49.3(2)
Co(2)–Co(3)–C(1)	49.5(2)	Co(1)–Co(3)–C(31)	147.1(2)
Co(2)–Co(3)–C(31)	98.3(2)	C(1)–Co(3)–C(31)	97.9(3)
Co(1)–Co(3)–C(32)	103.1(2)	Co(2)–Co(3)–C(32)	94.2(2)
C(1)–Co(3)–C(32)	140.6(3)	C(31)–Co(3)–C(32)	102.9(3)
Co(1)–Co(3)–P(1)	97.6(1)	Co(2)–Co(3)–P(1)	154.6(1)
C(1)–Co(3)–P(1)	107.5(2)	C(31)–Co(3)–P(1)	95.6(2)
C(32)–Co(3)–P(1)	103.4(2)	Co(1)–C(1)–Co(2)	81.2(2)
Co(1)–C(1)–Co(3)	80.9(2)	Co(2)–C(1)–Co(3)	81.4(2)
Co(1)–C(1)–C(2)	137.1(4)	Co(2)–C(1)–C(2)	132.6(4)
Co(3)–C(1)–C(2)	123.3(4)	C(1)–C(2)–O(1)	112.7(5)
C(1)–C(2)–O(2)	126.1(5)	O(1)–C(2)–O(2)	121.2(5)
C(2)–O(1)–C(3)	114.4(6)	Co(1)–C(11)–O(11)	177.6(7)
Co(1)–C(12)–O(12)	179.2(6)	Co(2)–C(21)–O(21)	177.0(6)
Co(2)–C(22)–O(22)	177.7(7)	Co(2)–C(23)–O(23)	178.3(6)
Co(3)–C(31)–O(31)	179.0(6)	Co(3)–C(32)–O(32)	174.5(6)
Co(3)–P(1)–C(4)	122.5(2)	Co(3)–P(1)–C(101)	111.1(1)
C(4)–P(1)–C(101)	97.7(2)	Co(3)–P(1)–C(201)	117.5(2)
C(4)–P(1)–C(201)	101.4(2)	C(101)–P(1)–C(201)	103.4(2)
P(1)–C(4)–C(5)	132.3(5)	C(4)–C(5)–P(2)	128.4(5)
Co(1)–P(2)–C(5)	119.2(2)	Co(1)–P(2)–C(301)	111.3(1)
C(5)–P(2)–C(301)	100.1(2)	Co(1)–P(2)–C(401)	118.6(1)
C(5)–P(2)–C(401)	102.8(2)	C(301)–P(2)–C(401)	102.0(2)
P(1)–C(101)–C(102)	117.3(1)	P(1)–C(101)–C(106)	122.6(1)
P(1)–C(201)–C(202)	118.2(1)	P(1)–C(201)–C(206)	121.8(1)
P(2)–C(301)–C(302)	121.2(1)	P(2)–C(301)–C(306)	118.7(1)
P(2)–C(401)–C(402)	119.9(1)	P(2)–C(401)–C(406)	120.1(1)

sponding resonance for the minor isomer is a singlet. This suggests that the major isomer is that in which the vinyl phosphine ligand occupies equatorial positions, since similar sized coupling constants of *ca.* 1 Hz have been observed for the methyl resonances of related  $[\text{Co}_3(\mu_3\text{-CMe})(\mu\text{-diphosphine})(\text{CO})_7]$  species in which the diphosphine occupies equatorial sites [17].

The vinyl coordination in **5a** and **5b** can be released by purging with CO at 293 K to give **2a** and **2b** respectively. Prolonged heating at 343 K in an atmosphere of CO results in displacement of the  $\text{PPh}_2\text{CH=CH}_2$  ligand entirely to give  $[\text{Co}_3(\mu_3\text{-CR})(\text{CO})_9]$  (R = Me **1a**,  $\text{CO}_2\text{Me} **1b**).$

### 2.3. Reaction of $[\text{Co}_3(\mu_3\text{-CR})(\text{CO})_9]$ (R = Me **1a**, $\text{CO}_2\text{Me} **1b**) with *cis*- $\text{Ph}_2\text{PCH=CHPh}_2$$

In order to compare its reactivity with that of the vinyl phosphine  $\text{PPh}_2\text{CH=CH}_2$ , the ligand *cis*-

$\text{Ph}_2\text{PCH}=\text{CH}_2\text{PPh}_2$  (dppee) was studied. This ligand differs from the vinyl phosphine in that a *cis*- $\beta$ -hydrogen has been replaced by a phosphino group.

The complexes  $[\text{Co}_3(\mu_3\text{-CR})(\text{CO})_9]$  (R = Me **1a**,  $\text{CO}_2\text{Me}$  **1b**) were refluxed for 15 min in THF with one equivalent of dppee to afford  $[\text{Co}_3(\mu_3\text{-CR})(\mu\text{-Ph}_2\text{PCH}=\text{CHPh}_2)(\text{CO})_7]$  (R = Me **6a**,  $\text{CO}_2\text{Me}$  **6b**) in yields of 85%–93% (Scheme 2). Complexes **6a** and **6b** have been characterized by mass spectrometry, microanalysis, IR,  $^1\text{H}$ ,  $^{31}\text{P}$  and  $^{13}\text{C}$  NMR spectroscopy (Table 1 and Section 4). In addition, complex **6b** has been the subject of a single-crystal X-ray structure determination.

Suitable crystals of **6b** for single-crystal X-ray diffraction analysis were grown by cooling a concentrated pentane solution at 273 K. The molecular structure of  $[\text{Co}_3(\mu_3\text{-CCO}_2\text{Me})(\mu\text{-dppee})(\text{CO})_7]$  **6b** is depicted in Fig. 1; Tables 2 and 3 list bond lengths and angles respectively and fractional atomic coordinates are given in Table 4. Complex **6b** exists as discrete molecules in the unit cell with no unusually short inter- or intramolecular contacts.

The structure of complex **6b** resembles that of the recently reported  $[\text{Co}_3(\mu_3\text{-CPh})(\mu\text{-dppee})(\text{CO})_7]$  in which the capping group is CPh while in **6b** it is  $\text{CCO}_2\text{Me}$  [18]. The structural features of the two complexes are essentially the same with a face-bridging CR group, an edge-bridging *cis*-dppee ligand and terminally bonded carbonyl groups, but there are some noticeable differences. The  $\text{Co}-\mu_3\text{-C}$  bond lengths are similar to within 0.026 Å in **6b** while in  $[\text{Co}_3(\mu_3\text{-CPh})(\mu\text{-dppee})(\text{CO})_7]$  a variation of 0.06 Å is observed. The mean value for the non-bridged  $\text{Co}-\text{Co}$  distances in **6b** of 2.487 Å is closely similar to the corresponding value of 2.485 Å in  $[\text{Co}_3(\text{CPh})(\text{dppee})(\text{CO})_7]$  but longer than the mean value of the  $\text{Co}-\text{Co}$  distances of 2.467 Å in the parent complex  $[\text{Co}_3(\mu_3\text{-CMe})(\text{CO})_9]$  **1a** [17]. On the contrary, the shorter bridged  $\text{Co}-\text{Co}$  distance of 2.464(1) Å in **6b** is similar to the mean value for the  $\text{Co}-\text{Co}$  distances for **1a** while slightly shorter than that for the bridged distance in  $[\text{Co}_3(\mu_3\text{-CPh})(\mu\text{-dppee})(\text{CO})_7]$  (2.473(2) Å).

Unlike the structure of  $[\text{Co}_3(\mu_3\text{-CPh})(\mu\text{-dppee})(\text{CO})_7]$  in which the dppee ligand bridges equatorial sites, some twisting of the dppee ligand in **6b** is observed on its coordination to the  $\text{Co}(1)-\text{Co}(3)$  edge. The phosphorus atom (P(1)) of the ligand and C(31)O(31) bond equatorially to  $\text{Co}(3)$  while the remaining carbonyl group on  $\text{Co}(3)$  occupies an axial position. At  $\text{Co}(1)$ , however, all three ligands are twisted round so that P(2) bonds to  $\text{Co}(1)$  in a nearly axial position from above the  $\text{Co}_3$  plane (towards the capping group instead of away from it). The two carbonyl groups adopt pseudoequatorial positions but point slightly beneath the  $\text{Co}_3$  plane instead of slightly above it as is the case at the other two  $\text{Co}$  atoms. This is most clearly exemplified by the angle  $\text{Co}(1)-\text{Co}(3)-\text{P}(1)$  of 97.6(1)° whereas  $\text{Co}(3)-$

$\text{Co}(1)-\text{P}(2)$  is 111.2(1)°. Also  $\text{C}(1)-\text{Co}(3)-\text{P}(1)$  is 107.5(2)° whilst  $\text{C}(1)-\text{Co}(1)-\text{P}(2)$  is 95.9(2)°.

The dppee ligand itself only rarely bridges two metal atoms [18–22]. It is more usual for it to chelate a single metal atom [19,21,22a,23]. The bond lengths within the

Table 4  
Atomic coordinates and equivalent isotropic displacement coefficients

	$x(\times 10^4)$	$y(\times 10^4)$	$z(\times 10^4)$	$U(\text{eq})$ ( $\times 10^3 \text{ \AA}^2$ )
Co(1)	2616(1)	7528(1)	8166(1)	33(1)
Co(2)	3762(1)	8207(1)	6643(1)	37(1)
Co(3)	1435(1)	8450(1)	6747(1)	35(1)
C(1)	2701(5)	7173(4)	6753(4)	34(2)
C(2)	2678(5)	6223(4)	6152(4)	37(2)
O(1)	3499(5)	6114(4)	5316(3)	69(2)
C(3)	3471(9)	5203(7)	4675(6)	90(4)
O(2)	2013(4)	5584(3)	6350(3)	57(2)
C(11)	1736(6)	8610(5)	8949(5)	52(2)
O(11)	1148(5)	9275(4)	9456(4)	82(2)
C(12)	3971(6)	7200(5)	8848(5)	48(2)
O(12)	4855(5)	6997(5)	9300(4)	80(2)
C(21)	3931(6)	8488(6)	5278(6)	59(3)
O(21)	4070(6)	8624(6)	4405(5)	100(3)
C(22)	3952(6)	9410(5)	7269(6)	55(3)
O(22)	4056(6)	10146(4)	7689(5)	100(3)
C(23)	5243(6)	7310(5)	6760(5)	45(2)
O(23)	6164(5)	6727(4)	6850(4)	69(2)
C(31)	1235(6)	8515(6)	5402(6)	55(3)
O(31)	1093(6)	8550(6)	4538(4)	99(3)
C(32)	1166(6)	9843(5)	7090(6)	53(3)
O(32)	1085(5)	10721(4)	7262(6)	98(3)
P(1)	-386(1)	7990(1)	7221(1)	34(1)
C(4)	-491(5)	6725(4)	7894(5)	41(2)
C(5)	310(5)	6045(4)	8439(4)	37(2)
P(2)	1860(1)	6158(1)	8751(1)	33(1)
C(102)	-789(4)	6826(3)	5571(3)	59(2)
C(103)	-1336	6646	4676	78(2)
C(104)	-2296	7431	4309	83(2)
C(105)	-2710	8396	4837	79(2)
C(106)	-2163	8575	5732	55(2)
C(101)	-1202	7790	6098	44(1)
C(202)	-1743(4)	10044(3)	7718(3)	52(2)
C(203)	-2654	10799	8265	64(2)
C(204)	-3386	10466	9094	68(2)
C(205)	-3208	9380	9377	76(2)
C(206)	-2297	8625	8830	58(2)
C(201)	-1564	8958	8000	38(1)
C(302)	2467(3)	5465(3)	10772(3)	48(2)
C(303)	2320	5525	11848	63(2)
C(304)	1343	6278	12325	65(2)
C(305)	512	6970	11727	64(2)
C(306)	659	6909	10651	51(2)
C(301)	1637	6157	10173	38(1)
C(402)	3993(3)	4668(2)	8005(3)	53(2)
C(403)	4687	3638	7788	59(2)
C(404)	4178	2739	8063	52(2)
C(405)	2974	2869	8556	51(2)
C(406)	2280	3900	8774	48(2)
C(401)	2790	4799	8499	34(1)

Equivalent isotropic  $U$  defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor

bridging ligand in **6b** are comparable with other examples; thus the C(4)–C(5) double-bond length (1.329(8) Å) is in very good agreement with the value of 1.31(1) observed for  $[\text{Co}_3(\mu_3\text{-CPh})(\mu\text{-dppee})(\text{CO})_7]$  [18].

In the  $^1\text{H}$  NMR spectra of **6a** and **6b**, in addition to phenyl resonances, signals for the methyl groups are observed at  $\delta = 2.87$  ppm (t,  $^4J(\text{HP}) = 2.7$  Hz) (**6a**) and  $\delta = 3.59$  ppm (s) (**6b**). The olefinic resonances of the bridging dppee ligands are not seen but may be masked by the broad phenyl region. In the  $^{13}\text{C}$  ( $^1\text{H}$ ) NMR of **6a** and **6b** at 293 K, triplet resonances are seen for the olefinic carbons of the dppee ligand at  $\delta = 146.6$  ppm ( $^1J(\text{CP}) = ^2J(\text{CP}) = 26$  Hz) and at  $\delta = 145.6$  ppm ( $^1J(\text{CP}) = ^2J(\text{CP}) = 22$  Hz) respectively. Because of the close similarity of the spectroscopic data for **6a** and **6b** it may be assumed that **6a** possesses a similar structure to that of **6b**.

### 3. Conclusions

The outcome of the reactions of the tricobalt alkylidyne complexes  $[\text{Co}_3(\mu_3\text{-CR})(\text{CO})_9]$  ( $\text{R} = \text{Me}$  **1a**,  $\text{CO}_2\text{Me}$  **1b**) with the vinylphosphine ligands  $\text{PPh}_2\text{CH}=\text{CHL}$  ( $\text{L} = \text{H}$ ,  $\text{PPh}_2$ ) is influenced both by the nature of the R group on the cluster and by the substituent L on the vinyl phosphine. Thus tris substitution of a  $\text{Ph}_2\text{PCH}=\text{CH}_2$  ligand can be induced only in the case of **1b**. The ligand  $\text{Ph}_2\text{PCH}=\text{CH}_2$  can bridge two cobalt atoms of the cobalt alkylidyne unit by making use of the vinyl moiety; in principle the *cis*- $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$  could also bridge two cobalt atoms in this way but in practice coordination through the second phosphorus atom is more favourable.

### 4. Experimental details

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

The instrumentation used to obtain spectroscopic data has been described previously [24]. 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  $[\text{Co}_3(\mu_3\text{-CR})(\text{CO})_9]$  ( $\text{R} = \text{Me}$  **1a**,  $\text{CO}_2\text{Me}$  **1b**) [25,26] were prepared by published methods.

#### 4.1. Reaction of $[\text{Co}_3(\mu_3\text{-CR})(\text{CO})_9]$ ( $\text{R} = \text{Me}$ **1a**, $\text{CO}_2\text{Me}$ **1b**) with $\text{PPh}_2\text{CH}=\text{CH}_2$

(a) The complex  $[\text{Co}_3(\mu_3\text{-CMe})(\text{CO})_9]$  **1a** (0.200 g, 0.44 mmol) was dissolved in heptane (50 ml) and  $\text{PPh}_2\text{CH}=\text{CH}_2$  (0.10 ml, 0.50 mmol) was added. The mixture was stirred at 308 K for 20 h and the solvent then removed under reduced pressure. The residue was dissolved in the minimum quantity of  $\text{CH}_2\text{Cl}_2$  and applied to the base of TLC plates. Elution with hexane–acetone (17 : 3) gave purple  $[\text{Co}_3(\mu_3\text{-CMe})(\text{CO})_8(\text{PPh}_2\text{CH}=\text{CH}_2)]$  **2a** (0.105 g, 37%),  $[\text{Co}_3(\mu_3\text{-CMe})(\text{CO})_7(\text{PPh}_2\text{CH}=\text{CH}_2)_2]$  **3a** (0.120 g, 33%) and a trace of an uncharacterized brown complex. Complex **2a**: fast atom bombardment (FAB) mass spectrum,  $m/z = 640$  ( $M^+$ ) and  $M^+ - n\text{CO}$  ( $n = 2-8$ ). NMR ( $\text{CDCl}_3$ ):  $^{13}\text{C}$  ( $^1\text{H}$  composite pulse decoupled),  $\delta = 199.7$  (s, 8CO), 129.3–123.9 (m, Ph), 124.9 (s,  $\text{PC}=\text{CH}_2$ ) and 39.2 (s, Me) ppm. Complex **3a**: FAB mass spectrum,  $m/z = 824$  ( $M^+$ ) and  $M^+ - n\text{CO}$  ( $n = 2-7$ ). NMR ( $\text{CDCl}_3$ ):  $^{13}\text{C}$  ( $^1\text{H}$  composite pulse decoupled),  $\delta = 211.8$  (s, 7CO), 134.3–128.4 (m, Ph), 131.6 (d,  $^1J(\text{CP}) = 59$  Hz,  $\text{PC}=\text{CH}_2$ ), 128.8 (s,  $\text{PCH}=\text{CH}_2$ ) and 42.2 (s, Me).

(b) The complex  $[\text{Co}_3(\mu_3\text{-CCO}_2\text{Me})(\text{CO})_9]$  **1b** (0.300 g, 0.60 mmol) and  $\text{PPh}_2\text{CH}=\text{CH}_2$  (0.14 ml, 0.70 mmol) were treated as in (a) to yield green  $[\text{Co}_3(\mu_3\text{-CCO}_2\text{Me})(\text{CO})_8(\text{PPh}_2\text{CH}=\text{CH}_2)]$  **2b** (0.020 g, 5%), green  $[\text{Co}_3(\mu_3\text{-CCO}_2\text{Me})(\text{CO})_7(\text{PPh}_2\text{CH}=\text{CH}_2)_2]$  **3b** (0.286 g, 55%) and green  $[\text{Co}_3(\mu_3\text{-CCO}_2\text{Me})(\text{CO})_6(\text{PPh}_2\text{CH}=\text{CH}_2)_3]$  **4** (0.173 g, 27%). Complex **2b**: FAB mass spectrum,  $m/z = 684$  ( $M^+$ ) and  $M^+ - n\text{CO}$  ( $n = 1-8$ ). NMR ( $\text{CDCl}_3$ ):  $^{13}\text{C}$  ( $^1\text{H}$  composite pulse decoupled),  $\delta = 201.7$  (s, 8CO), 182.9 (s,  $\text{CO}_2\text{Me}$ ), 133.9–128.6 (m, Ph), 132.8 (d,  $^1J(\text{CP}) = 40$  Hz,  $\text{PCH}=\text{CH}_2$ ), 129.9 (s,  $\text{PCH}=\text{CH}_2$ ) and 52.2 (s, Me) ppm. Complex **3b**: FAB mass spectrum,  $m/z = 868$  ( $M^+$ ) and  $M^+ - n\text{CO}$  ( $n = 1-3, 5$ ). NMR ( $\text{CDCl}_3$ ):  $^{13}\text{C}$  ( $^1\text{H}$  composite pulse decoupled),  $\delta = 283.0$  (s,  $\mu\text{-CCO}_2\text{Me}$ ), 205.6 (s, 7CO), 182.4 (s,  $\text{CO}_2\text{Me}$ ), 134.2–128.3 (m, Ph), 133.3 (m,  $\text{PCH}=\text{CH}_2$ ), 128.8 (s,  $\text{PCH}=\text{CH}_2$ ) and 51.4 (s, Me) ppm. Complex **4**: FAB mass spectrum,  $m/z = 1052$  ( $M^+$ ) and  $M^+ - n\text{CO}$  ( $n = 1-6$ ). NMR ( $\text{CDCl}_3$ ):  $^{13}\text{C}$  ( $^1\text{H}$  composite pulse decoupled),  $\delta = 272.0$  (s,  $\mu\text{-CCO}_2\text{Me}$ ), 213.2 (s, 6CO), 182.5 (s,  $\text{CO}_2\text{Me}$ ), 134.3–128.1 (m, Ph), 132.9 (m,  $\text{PCH}=\text{CH}_2$ ), 127.9 (s,  $\text{PCH}=\text{CH}_2$ ) and 50.8 (s, Me) ppm.

#### 4.2. Reaction of $[\text{Co}_3(\mu_3\text{-CR})(\text{CO})_9]$ ( $\text{R} = \text{Me}$ **1a**, $\text{CO}_2\text{Me}$ **1b**) with dppee

(a) The complex  $[\text{Co}_3(\mu_3\text{-CMe})(\text{CO})_9]$  **1a** (0.340 g, 0.75 mmol) was dissolved in THF (50 ml) and *cis*- $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$  (0.326 mg, 0.83 mmol) was added.

The mixture was refluxed for 10 min and the solvent then removed under reduced pressure. The residue was then dissolved in the minimum amount of  $\text{CH}_2\text{Cl}_2$  and applied to the base of TLC plates. Elution with hexane–acetone (3:2) gave red  $[\text{Co}_3(\mu_3\text{-CMe})(\mu\text{-Ph}_2\text{PCH=CHPPH}_2)(\text{CO})_7]$  **6a** (0.550 g, 93%). Complex **6a** (found: C, 52.74%; H, 3.11%; P, 7.79%.  $\text{C}_{35}\text{H}_{25}\text{Co}_3\text{O}_7\text{P}_2$  requires C, 52.78%; H, 3.16%; P, 7.78%): FAB mass spectrum,  $m/z = 796$  ( $M^+$ ) and  $M^+ - n\text{CO}$  ( $n = 1-7$ ). NMR ( $\text{CDCl}_3$ ):  $^{13}\text{C}$  ( $^1\text{H}$  composite pulse decoupled),  $\delta = 208.9$  (s, 7CO), 146.6 (t,  $^1J(\text{CP}) = ^2J(\text{CP})$  26 Hz,  $\text{Ph}_2\text{PCH}$ ), 135.5–128.6 (m, Ph) and 43.4 (s, Me) ppm.

(b) The complex  $[\text{Co}_3(\mu_3\text{-CCO}_2\text{Me})(\text{CO})_9]$  **1b** (0.102 g, 0.20 mmol) and *cis*- $\text{Ph}_2\text{PCH=CHPPH}_2$  (0.087 g, 0.22 mmol) were treated as in (a) to yield dark red  $[\text{Co}_3(\mu_3\text{-CCO}_2\text{Me})(\mu\text{-Ph}_2\text{PCH=CHPPH}_2)(\text{CO})_7]$  **6b** (0.146 g, 85%). Complex **6b** (found: C, 51.62%; H, 3.05%; P, 6.83%.  $\text{C}_{36}\text{H}_{25}\text{Co}_3\text{O}_9\text{P}_2$  requires C, 51.44%, H, 3.00%, P, 7.38%): FAB mass spectrum,  $m/z = 840$  ( $M^+$ ) and  $M^+ - n\text{CO}$  ( $n = 1-7$ ). NMR ( $\text{CDCl}_3$ ):  $^{13}\text{C}$  ( $^1\text{H}$  composite pulse decoupled),  $\delta = 204.3$  (s, 7CO), 182.0 (s,  $\text{CO}_2\text{Me}$ ), 145.3 (t,  $^1J(\text{CP}) = ^2J(\text{CP})$  25 Hz,  $\text{Ph}_2\text{PCH}$ ), 136.7–128.5 (m, Ph) and 51.4 (s, Me) ppm.

#### 4.3. Thermolysis of $[\text{Co}_3(\mu_3\text{-CR})(\text{CO})_8(\text{PPh}_2\text{CH=CH}_2)]$ ( $R = \text{Me}$ **2a**, $\text{CO}_2\text{Me}$ **2b**), $[\text{Co}_3(\mu_3\text{-CR})(\text{CO})_7(\text{PPh}_2\text{CH=CH}_2)_2]$ ( $R = \text{Me}$ **3a**, $\text{CO}_2\text{Me}$ **3b**) and $[\text{Co}_3(\mu_3\text{-CCO}_2\text{Me})(\text{CO})_6(\text{PPh}_2\text{CH=CH}_2)_3]$ **4**

(a) A solution of the complex  $[\text{Co}_3(\mu_3\text{-CMe})(\text{CO})_8(\text{PPh}_2\text{CH=CH}_2)]$  **2a** (0.250 g, 0.39 mmol) in heptane (70 ml) was heated at 343 K for 2 h and the solvent then removed under reduced pressure.

The residue was dissolved in  $\text{CH}_2\text{Cl}_2$  was applied to the base of TLC plates. Elution with hexane–acetone (17:3) gave black  $[\text{Co}_3(\mu_3\text{-CMe})(\mu\text{-PPh}_2\text{CH=CH}_2)(\text{CO})_7]$  **5a** (0.187 g, 78%). Complex **5a**: FAB mass spectrum,  $m/z = 612$  ( $M^+$ ) and  $M^+ - n\text{CO}$  ( $n = 1-7$ ). NMR ( $\text{CDCl}_3$ ):  $^{13}\text{C}$  ( $^1\text{H}$  composite pulse decoupled),  $\delta = 204.4$  (s, 7CO), 136.0–128.4 (m, Ph) ppm, minor isomer: 56.2 (d,  $^2J(\text{CP}) = 6$  Hz,  $\text{PCH=CH}_2$ ), 44.5 (s, Me) and 35.6 (d,  $^1J(\text{CP}) = 45$  Hz,  $\text{PCH=CH}_2$ ) ppm, major isomer: 55.4 (d,  $^2J(\text{CP}) = 7$  Hz,  $\text{PCH=CH}_2$ ), 42.0 (s, Me) and 37.2 (d,  $^1J(\text{CP}) = 43$  Hz,  $\text{PCH=CH}_2$ ) ppm.

(b) Complex  $[\text{Co}_3(\mu_3\text{-CCO}_2\text{Me})(\text{CO})_8(\text{PPh}_2\text{CH=CH}_2)]$  **2b** (0.250 g, 0.37 mmol) was treated as in (a) to yield green  $[\text{Co}_3(\mu_3\text{-CCO}_2\text{Me})(\mu\text{-PPh}_2\text{CH=CH}_2)(\text{CO})_7]$  **5b** (0.202 g, 84%). Complex **5b**: FAB mass spectrum,  $m/z = 656$  ( $M^+$ ) and  $M^+ - n\text{CO}$  ( $n = 1-7$ ). NMR ( $\text{CDCl}_3$ ):  $^{13}\text{C}$  ( $^1\text{H}$  composite pulse decoupled), major isomer:  $\delta = 204.6$  (s, 7CO), 136.9–128.2 (m, Ph), 180.6 (s,  $\text{CO}_2\text{Me}$ ), 57.1 (d,  $^2J(\text{CP}) = 6$  Hz,  $\text{PCH=CH}_2$ ), 51.7 (s, Me) and 41.8 (d,  $^1J(\text{CP}) = 42$  Hz,  $\text{PCH=CH}_2$ ) ppm, minor isomer:  $\delta = 201.1$  (s, 7CO),

136.9–128.2 (m, Ph), 181.5 (s,  $\text{CO}_2\text{Me}$ ), 58.2 (d,  $^2J(\text{CP}) = 6$  Hz,  $\text{PCH=CH}_2$ ), 51.9 (s, Me) and 42.3 (d,  $^1J(\text{CP}) = 51$  Hz,  $\text{PCH=CH}_2$ ) ppm.

(c) Complex  $[\text{Co}_3(\mu_3\text{-CMe})(\text{CO})_7(\text{PPh}_2\text{CH=CH}_2)_2]$  **3a** (0.120 g, 0.15 mmol) was treated as in (a) then redissolved in toluene (50 ml) and heated to 383 K but no change was observed.

(d) Complex  $[\text{Co}_3(\mu_3\text{-CCO}_2\text{Me})(\text{CO})_7(\text{PPh}_2\text{CH=CH}_2)_2]$  **3b** (0.075 g, 0.09 mmol) was treated as in (c) but no change was observed.

(e) Complex  $[\text{Co}_3(\mu_3\text{-CCO}_2\text{Me})(\text{CO})_6(\text{PPh}_2\text{CH=CH}_2)_3]$  **4** (0.045 g, 0.04 mmol) was treated as in (c) but no change was observed.

#### 4.4. Reaction of $[\text{Co}_3(\mu_3\text{-CR})(\text{CO})_8(\text{PPh}_2\text{CH=CH}_2)]$ ( $R = \text{Me}$ **2a**, $\text{CO}_2\text{Me}$ **2b**) with CO

(a) A solution of the complex  $[\text{Co}_3(\mu_3\text{-CMe})(\text{CO})_8(\text{PPh}_2\text{CH=CH}_2)]$  **2a** (0.125 g, 0.19 mmol) in heptane (50 ml) was heated to 343 K at 2 h, while CO was bubbled through. Separation by TLC using hexane–acetone (17:3) as eluent gave unchanged **2a** and  $[\text{Co}_3(\mu_3\text{-CMe})(\text{CO})_9]$  **1a** (0.075 g, 87%).

(b) Complex  $[\text{Co}_3(\mu_3\text{-CCO}_2\text{Me})(\text{CO})_8(\text{PPh}_2\text{CH=CH}_2)]$  **2b** (0.095 g, 0.14 mmol) was treated as in (a) to yield a trace of **2b** and  $[\text{Co}_3(\mu_3\text{-CCO}_2\text{Me})(\text{CO})_9]$  (0.052 g, 74%).

#### 4.5. Reaction of $[\text{Co}_3(\mu_3\text{-CR})(\mu\text{-PPh}_2\text{CH=CH}_2)(\text{CO})_7]$ ( $R = \text{Me}$ **5a**, $\text{CO}_2\text{Me}$ **5b**) with CO

(a) A solution of complex  $[\text{Co}_3(\mu_3\text{-CMe})(\mu\text{-PPh}_2\text{CH=CH}_2)(\text{CO})_7]$  **5a** (0.115 g, 0.19 mmol) in heptane (50 ml) was stirred at 293 K for 7 h while CO was bubbled through. Separation by TLC using hexane–acetone (17:3) gave  $[\text{Co}_3(\mu_3\text{-CMe})(\text{CO})_8(\text{PPh}_2\text{CH=CH}_2)]$  **2a** (0.109 g, 90%) and a trace of  $[\text{Co}_3(\mu_3\text{-CMe})(\text{CO})_9]$  **1a**.

(b) Complex  $[\text{Co}_3(\mu_3\text{-CCO}_2\text{Me})(\mu\text{-PPh}_2\text{CH=CH}_2)(\text{CO})_7]$  **5b** (0.130 g, 0.20 mmol) was treated as in (a) to yield  $[\text{Co}_3(\mu_3\text{-CCO}_2\text{Me})(\text{CO})_8(\text{PPh}_2\text{CH=CH}_2)]$  **2b** (0.098 g, 72%) and  $[\text{Co}_3(\mu_3\text{-CCO}_2\text{Me})(\text{CO})_9]$  **1b** (0.012 g, 12%).

#### 4.6. X-ray crystal structure determination of **6b**

Suitable crystals of  $[\text{Co}_3(\mu_3\text{-CCO}_2\text{Me})(\mu\text{-Ph}_2\text{PCH=CHPPH}_2)(\text{CO})_7]$  **6b** were grown by keeping a concentrated pentane solution at 273 K. A single crystal was mounted on a goniometer head using epoxy resin and transferred to a Siemens R3m/V diffractometer.

#### Crystal data

$\text{C}_{36}\text{H}_{25}\text{Co}_3\text{O}_9\text{P}_2$ ,  $M = 840.3$ , triclinic, space group  $P\bar{1}$ ,  $a = 10.936(4)$  Å,  $b = 12.699(3)$  Å,  $c = 12.979(5)$  Å,  $\alpha = 88.20(3)^\circ$ ,  $\beta = 85.22(3)^\circ$ ,  $\gamma = 78.12(2)^\circ$ ,  $U =$



1757.5(10) Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.588 \text{ g cm}^{-3}$ ,  $F(000) = 848$ ,  $\mu(\text{Mo K}\alpha) = 15.39 \text{ cm}^{-1}$ ,  $T = 290 \text{ K}$ .

A dark red prism with approximate dimensions 0.20 mm × 0.31 mm × 0.41 mm was used. Accurate cell dimensions were obtained from 25 reflections in the range  $20^\circ \leq 2\theta \leq 25^\circ$ . Intensity data were recorded using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ), and an  $\omega$ - $2\theta$  scan mode to a maximum  $2\theta$  value of  $45^\circ$ . Three standard reflections were monitored every 97 reflections throughout the data collection and showed no significant variation in intensity.

A total of 4723 intensities were measured within the range  $-11 \leq h \leq 11$ ,  $-13 \leq k \leq 0$ ,  $-13 \leq l \leq 13$  and averaged to give 4344 unique reflections ( $R_{\text{int}} = 0.02$ ) of which 3584 were judged as significant using the criterion  $F_{\text{obs}} > 4s(F_{\text{obs}})$ . Corrections for Lorentz and polarization effects were applied. A semiempirical absorption correction based on 323  $\psi$  scan data was applied; minimum and maximum transmission, 0.2553–0.3079. The structure was solved by a combination of direct methods and Fourier difference techniques. The structure was refined by full-matrix least squares with all non-hydrogen atoms assigned anisotropic displacement parameters [27]. Hydrogen atoms were placed in idealized positions and allowed to ride on the relevant carbon atom with a C–H distance of 0.96 Å; each type of H atom was refined with a common isotropic displacement parameter. In the final cycles of refinement a weighting scheme of the form  $w^{-1} = s^2(F) + 0.0014F^2$  which gave satisfactory agreement analysis was introduced. The refinement converged to  $R = 0.048$  and  $R_w = 0.053$ ; goodness of fit, 1.47. Final atomic coordinates and equivalent isotropic displacement parameters for the non-hydrogen atoms are listed in Table 4.

Additional crystallographic data including hydrogen-atom coordinates, displacement parameters and full lists of bond parameters have been deposited with the Cambridge Crystallographic Data Centre.

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