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Reactions of the mixed-metal alkyne-bridged complexes $[(\eta^5\text{-}C_5H_5)(OC)_2M\{\mu\text{-}C_2(CO_2Me)_2\}Co(CO)_3]$ (M = Mo or W) with $Ph_2PC{\equiv}C^tBu$[1]

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Abstract

Reaction of the mixed-metal alkyne-bridged complexes $[(\eta^5\text{-}C_5H_5)(OC)_2M\{\mu\text{-}C_2(CO_2Me)_2\}Co(CO)_3]$ (M = Mo or W) with $Ph_2PC{\equiv}C^tBu$ in refluxing toluene gives the complexes $[(\eta^5\text{-}C_5H_5)(OC)_2M\{\mu\text{-}{}^tBuCCC(CO_2Me){=}C(CO_2Me)PPh_2\}Co(CO)_2]$, $[(\eta^5\text{-}C_5H_5)(OC)_2M\{\mu\text{-}C_2(CO_2Me)_2\}Co(CO)_2(Ph_2PC{\equiv}C^tBu)]$ (M=Mo or W) and $[(\eta^5\text{-}C_5H_5)(OC)W\{\mu\text{-}C(CO_2Me){=}C(CO_2Me)C{\equiv}C^tBu\}(\mu\text{-}PPh_2)Co(CO)_2]$. The structures of the two complexes, $[(\eta^5\text{-}C_5H_5)(OC)_2Mo\{\mu\text{-}{}^tBuCCC(CO_2Me){=}C(CO_2Me)PPh_2\}Co(CO)_2]$ and $[(\eta^5\text{-}C_5H_5)(OC)W\{\mu\text{-}C(CO_2Me){=}C(CO_2Me)C{\equiv}C^tBu\}(\mu\text{-}PPh_2)Co(CO)_2]$, have been determined by X-ray analysis. Possible reaction pathways for the formation of the new complexes are proposed and discussed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Mixed metal complexes; Alkyne bridged complexes; Phosphido complexes; Molybdenum; Cobalt; Tungsten

1. Introduction

The ligands P_2Ph_4, and $Ph_2P(SR)$ (R = alkyl or aryl) react at elevated temperatures with alkyne-bridged dicobalt and cobalt-molybdenum/tungsten complexes via P–P or P–S bond cleavage, respectively to give the range of products shown in Fig. 1 [1–4]. One of the two ligand fragments derived from the P–P or P–S bond cleavage usually bridges the metal-metal bond in the dinuclear products while the other often becomes part of a metallacyclic bridging ligand which also incorporates the alkyne. The particular combination and relative amounts of the products obtained in a given reaction depend on the nature of the dimetallic system, the substituents on the bridging alkyne and, in the case of $Ph_2P(SR)$, on the nature of the R substituent on sulfur. A particularly diverse range of products is obtained in the reaction of $Ph_2P(SR)$ with the heterodinuclear complexes $[(\eta^5\text{-}C_5H_5)(OC)_2M\{\mu\text{-}C_2(CO_2Me)_2\}Co(CO)_3]$ (M = Mo or W). This is because not only is there a choice as to whether the Ph_2P or SR fragments are integrated into the metallacyclic ring but there is also a choice as to whether the ring contains the Co or Mo/W atoms. The factors which lead to the formation of one type of product rather than another in any given reaction are not well understood.

Phosphinoalkynes readily undergo P–C bond cleavage on reaction with a variety of metal complexes to give new species incorporating Ph_2P and $C{\equiv}CR$ fragments [5–7]. In principle the reactions of $Ph_2PC{\equiv}CR$ (R = alkyl or aryl) with dinuclear alkyne-bridged complexes could give dinuclear products analogous to those obtained with P_2Ph_4 and $Ph_2P(SR)$. In practice a previous investigation of the reaction of $Ph_2PC{\equiv}CPh$ with $[Co_2(CO)_6\{\mu\text{-}C_2(Me)_2\}]$ showed that a tetranuclear butterfly cluster is formed rather than dinuclear products incorporating separate Ph_2P and $C{\equiv}CPh$ fragments [8].

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[1] Dedicated to Brian Johnson on the occasion of his 60th birthday—a fine chemist and valued friend and colleague.

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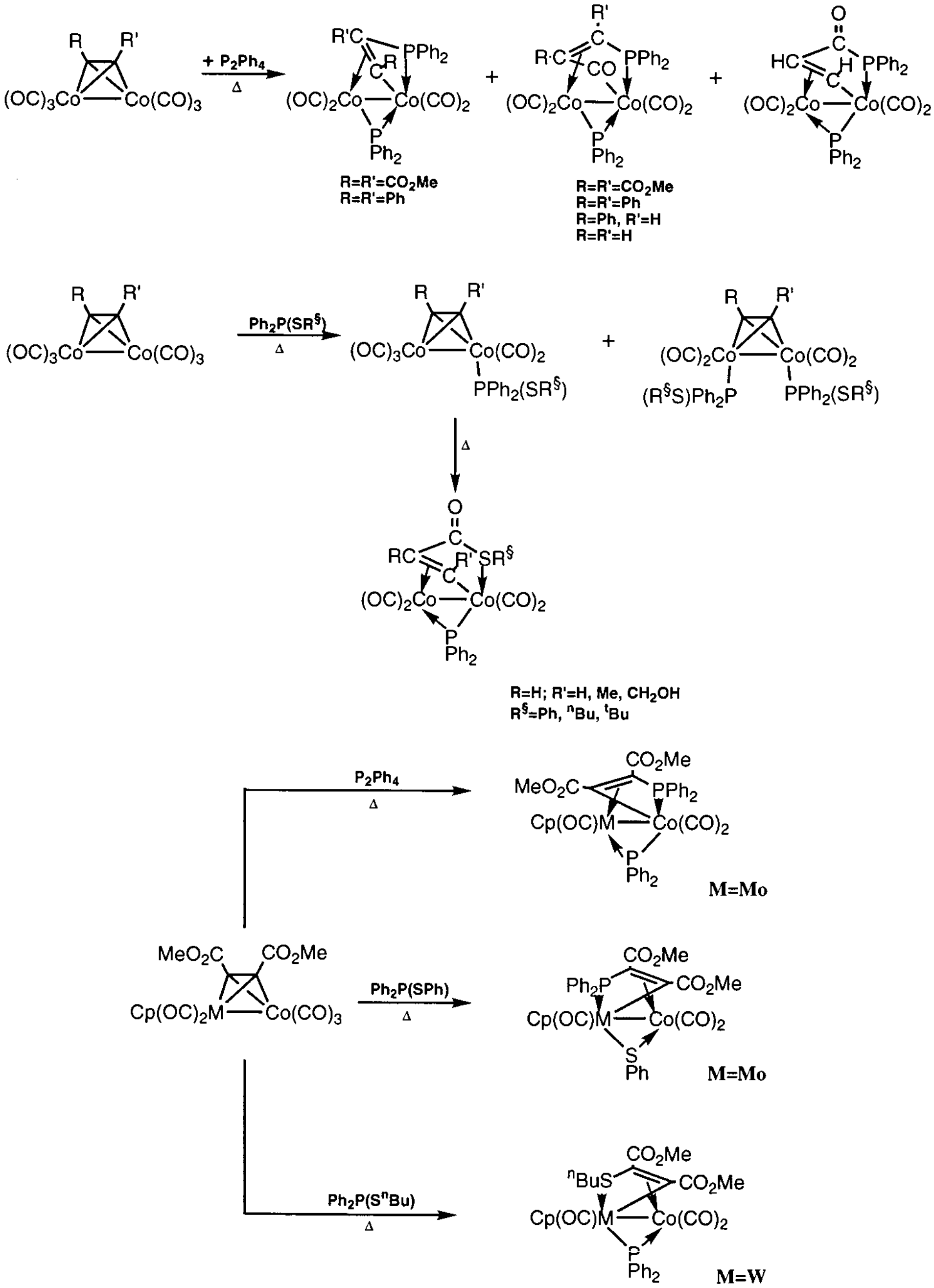


Fig. 1. Products from the reactions of Ph_4P_2 or $Ph_2P(SR)$ with alkyne-bridged dicobalt or cobalt-molybdenum/tungsten complexes.

In this paper we report that the reactions of the phosphinoacetylene $Ph_2PC{\equiv}C^tBu$ with the heterodinuclear alkyne-bridged complexes $[(\eta^5\text{-}C_5H_5)(OC)_2M\{\mu\text{-}C_2(CO_2Me)_2\}Co(CO)_3]$ (**1**, M = Mo; **2**, M = W) do lead to dinuclear products incorporating Ph_2P and $C{\equiv}C^tBu$ fragments. We have obtained new complexes in which either the acetylido ligand alone or both the acetylido and the phosphido fragments couple to the bridging alkyne and propose possible reaction pathways for their formation.

2. Results and discussion

2.1. Reaction of $[(\eta^5\text{-}C_5H_5)(OC)_2Mo\{\mu\text{-}C_2(CO_2Me)_2\}Co(CO)_3]$ 1 with $Ph_2PC{\equiv}C^tBu$

The reaction of $[(\eta^5\text{-}C_5H_5)(OC)_2Mo\{\mu\text{-}C_2(CO_2Me)_2\}Co(CO)_3]$ with $Ph_2PC{\equiv}C^tBu$ at 383 K in toluene affords the complexes $[(\eta^5\text{-}C_5H_5)(OC)_2Mo\{\mu\text{-}^tBuCCC(CO_2Me){=}C(CO_2Me)PPh_2\}Co(CO)_2]$ **3** and $[(\eta^5\text{-}C_5H_5)(OC)_2Mo\{\mu\text{-}C_2(CO_2Me)_2\}Co(CO)_2(PPh_2C{\equiv}C^t\text{-}Bu)]$ **4** (Fig. 2). Complexes **3** and **4** have been character-

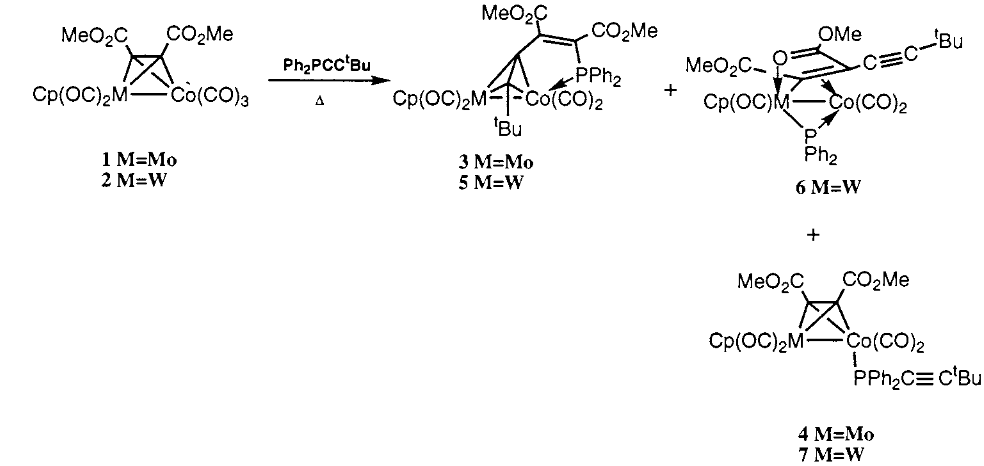


Fig. 2. New products from the reactions of $Ph_2PC{\equiv}C^tBu$ with alkyne-bridged cobalt-molybdenum/tungsten complexes.

ised spectroscopically (Table 1 and Section 4) and, in addition, the molecular structure of **3** has been determined by a single-crystal X-ray diffraction study. The structure is illustrated in Fig. 3 while Table 2 lists selected bond distances and angles.

Crystals of complex **3** suitable for the X-ray diffraction study were obtained by slow evaporation of a CH_2Cl_2-hexane solution at 273 K. The structure reveals a $(\eta^5\text{-}C_5H_5)(OC)_2Mo{-}Co(CO)_2$ moiety bridged by a $^tBuCCC(CO_2Me){=}C(CO_2Me)PPh_2$ ligand, which is located with the C(12)–C(11) bond vector perpendicular to the Mo–Co bond; the C(12) and C(11) atoms are both bonded to the Mo(1) and Co(1) atoms. The $^tBuCCC(CO_2Me){=}C(CO_2Me)PPh_2$ ligand is additionally co-ordinated to Co(1) via P(1), to complete a five membered metallacyclic Co–P–C = C–C ring. The Mo(1)–Co(1) distance [2.681(2) Å] in **3** is similar to that for the corresponding bond in the majority of other structurally characterised Co–Mo complexes containing bridging organic ligands [3,9]. The five-membered metallacyclic ring, Co(1)–P–C=C–C(11), adopts a puckered arrangement with the bond distances C(11)–C(8) [1.47 (2) Å], C(8)–C(7) [1.36 (2) Å], C(7)–P(1) [1.845 (12) Å] and P(1)–Co(1) [2.216 (3) Å] falling within the normal ranges for corresponding bonds in related complexes [1,10–12].

The spectroscopic properties of complex **3** are in accordance with the solid-state structure being maintained in solution. In the IR spectrum of **3** three terminal ν(CO) bands are observed in the region 2050–1900 cm^{-1} with a weak intensity band at 1708 cm^{-1} being assigned to ν(CO) of the methylcarboxylate groups. The ^{1}H-NMR spectrum comprises multiplet peaks due to the phenyl groups and a singlet for the cyclopentadienyl group. The spectrum also shows singlets at δ 3.85 and 3.45 which may be assigned to the non-equivalent methyl groups and a singlet resonance at δ 1.03, integrating to nine protons, due to the tertiary butyl group. The ^{31}P-{^{1}H} NMR spectrum displays a broad singlet resonance, as expected if Ph_2P is bound directly to the cobalt atom through phosphorus. In the ^{13}C-{^{1}H} NMR spectrum, recorded at 293 K, four distinct signals are observed in the terminal carbonyl region indicating a lack of fluxionality of the carbonyl groups at this temperature.

The IR and NMR spectra of **4** confirmed that simple substitution of a carbonyl group on the cobalt atom in **1** by the phosphinoalkyne had occurred, without further rearrangement. A weak absorption at 2168 cm^{-1} in the IR spectrum was assigned to the C≡C stretch of the alkyne. In the ^{31}P-{^{1}H} NMR spectrum there is a peak at δ 26.3, in the normal range for co-ordinated phosphines.

A plausible route to **3** and the tungsten analogue **5** (see below) is shown in Scheme 1. It is proposed that displacement of a carbonyl group in **1** or **2** by the phosphinoacetylene to give the monosubstituted complex **4** or **7** is followed by phosphorus-carbon bond cleavage at the cobalt centre to give intermediate **I**. Migration of the acetylide ligand to the bridging alkyne ligand would then give **II**, containing a co-ordinated vinyl group. Similar P–C bond cleavage in alkyl and aryl phosphines followed by the migration of the alkyl or aryl group to a bridging alkyne ligand has been observed previously in the reaction of organophosphines with alkyne-bridged dimolybdenum complexes [13]. It is proposed that phosphorus-carbon bond formation at the molybdenum centre in **II** and displacement of the co-ordinated alkene by the alkyne group gives **III** and that the final product **3** then results from adoption of a bridging position by the alkyne functionality to relieve the unsaturation at the

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

Compound	$\nu(CO)/cm^{-1}$	^1H-NMR (δ)	^{31}P-NMR (δ)
3	2003m, 1965vs 1941s, 1708w	7.7-7.1 (m, 10H, Ph) 5.38 (s, 5H, Cp) 3.85 (s, 3H, Me) 3.45 (s, 3H, Me) 1.03 (s, 9H, ^{t}Bu)	67.8 (s, μ-$PPh_2C(CO_2Me)C(CO_2Me)CCC^tBu$)
4	2072w, 2028m, 1996vs, 1967s	7.7-7.1 (m, 10H, Ph) 5.29 (s, 5H, Cp) 3.47 (s, 6H, Me) 1.34 (s, 9H, ^{t}Bu)	26.3 (s, $PPh_2C{\equiv}C^tBu$)
5	2001m, 1961vs, 1935s, 1706w	7.7-7.1 (m, 10H, Ph) 5.43 (s, 5H, Cp) 3.84 (s, 3H, Me) 3.42 (s, 3H, Me) 1.02 (s, 9H, ^{t}Bu)	59.1 (s, μ-$PPh_2C(CO_2Me)C(CO_2Me)CCC^tBu$)
6	2010m, 1967vs 1920sh, 1683w 1548w	7.3-7.1 (m, 10H, Ph) 5.43 (s, 5H, Cp) 3.59 (s, 3H, Me) 3.12 (s, 3H, Me) 1.14 (s, 9H, ^{t}Bu)	117.8 (s, μ-PPh_2)
7	2069w, 2026m, 1992vs, 1962s	7.7-7.3 (m, 10H, Ph) 5.3 (s, 5H, Cp) 3.48 (s, 6H, Me) 1.25 (s, 9H, ^{t}Bu)	16.1 (s, $PPh_2C{\equiv}C^tBu$)

molybdenum centre. Alternatively the complexes **3** and **5** could be formed by P–C bond formation at the cobalt centre in **I** to give **IV** following which acetylide-acetylene coupling could then give the final product. Acetylide-acetylene coupling and carbon-carbon bond formation at the α-carbon atom of an acetylide, analogous to that proposed in Scheme 1, have been observed previously in the reaction of the σ-π acetylide ligand in $[Fe_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}CR)(\mu\text{-}PPh_2)]$ (R = alkyl or aryl) with alkynes [14] and also in the thermolysis of the complex $[Co_2(\mu\text{-}C_2Me_2)(CO)_5(\mu\text{-}\eta^1{:}\eta^2\text{-}Ph_2PC{\equiv}CPh)Co_2(CO)_6]$ [8].

2.2. Reaction of $[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}C_2(CO_2Me)_2\}Co(CO)_3]$ 2 with $Ph_2PC{\equiv}C^tBu$

Reaction of $[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}C_2(CO_2Me)_2\}Co(CO)_3]$ with $Ph_2PC{\equiv}C^tBu$ at 383 K affords the complexes $[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}^tBuCCC(CO_2Me){=}C(CO_2Me)PPh_2\}Co(CO)_2]$ **5**, $[(\eta^5\text{-}C_5H_5)(OC)W\{\mu\text{-}C(CO_2Me){=}C(CO_2Me)C{\equiv}C^tBu\}(\mu\text{-}PPh_2)Co(CO)_2]$ **6** and $[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}C_2(CO_2Me)_2\}Co(CO)_2(Ph_2PC{\equiv}C^tBu)]$ **7**. Complexes **5**, **6** and **7** have been characterised spectroscopically (Table 1 and Section 4). The molecular structure of **6** has been determined by a single-crystal X-ray diffraction study.

The spectroscopic properties of **5** show that it has a structure analogous to that of **3**. Thus in the IR spectrum three $\nu(CO)$ bands observed in the region 2050–1950 cm^{-1} are assigned to terminal carbonyls and a band at 1708 cm^{-1} is ascribed to the methylcarboxylate group. The ^1H-NMR spectrum comprises multiplet peaks due to the phenyl protons, a singlet for the cyclopentadienyl group and two singlets for the methyl protons of the non-equivalent methylcarboxylate groups. The $^{31}P\text{-}\{^1H\}$ NMR spectrum shows a singlet at δ 59.1, which is typical of a μ-PPh_2 ligand which has become part of a five-membered metallacycle [10]. The broadness of the resonance is due to the quadrapolar ^{59}Co and is indicative of a phosphorus atom directly bound to cobalt.

The molecular structure of **6** is shown in Fig. 4 while Table 3 lists selected bond distances and angles. Crystals of **6** suitable for X-ray diffraction were obtained by slow evaporation of a CH_2Cl_2-hexane solution at 273 K. The molecule consists of a $(\eta^5\text{-}C_5H_5)(OC)WCo(CO)_2$ unit, the metal-metal bond of which is bridged by a diphenyl phosphido group and by a $\overline{W{-}C{=}C{-}C{=}O}$ five-membered tungstacyclic ring π-co-ordinated through the carbon-carbon double bond to Co(1). The vinyl group in the ring is σ-bonded to W(1) through C(7) [2.15 (2) Å] and is π-bonded to Co(1) asymmetrically [C(7)–Co(1) 1.99 (2) Å, C(6)–Co(1) 2.12 (2) Å]. The C(7)–C(6) bond distance is similar to that in related complexes [4]. The methyl carboxylate groups are in *trans* positions and O(5) is co-ordinated to W [W–O distance 2.201 (10) Å]. A similar type of oxygen co-ordination is observed in a number of bimetallic complexes including $[(OC)_3Fe\{\mu\text{-}C(CO_2Me){=}CH(CO_2Me)\}Co(CO)_3]$ [10], $[(OC)_2Co\{\mu\text{-}C(CO_2Me){=}CH(CO_2Me)\}(\mu\text{-}PPh_2){-}Co(CO)_2]$ [15], $[(\eta^5\text{-}C_5H_5)(OC)Mo\{\mu\text{-}C(CO_2Me){=}CH(CO_2Me)\}(\mu\text{-}PPh_2)Co(CO)_2]$, [3] $[(\eta^5\text{-}C_5H_5)_2(OC)_2Mo_2\{\mu\text{-}C(CO_2Me){=}CH(CO_2Me)\}(\mu\text{-}SR)]$ (R = Et, ^{i}Pr) [16] and $[(\eta^5\text{-}C_5H_5){-}(OC)W\{\mu\text{-}C\text{-}(CO_2Me){=}CH(CO_2Me)\}(\mu\text{-}SPh)Co\text{-}(CO)\{PPh_2(SPh)\}]$ [4]. In **6** the C–C bond formed by the linking of the acetylide to the β-carbon of the vinyl group of the metallacyclic ring has a length of 1.41 (2) Å indicating some conjugation between the acetylide group and the ring. The C_α–C_β bond distance in the vinyl group is 1.44 (2) Å, identical within experimental error to the corresponding bond length in $[(\eta^5\text{-}C_5H_5)(OC)W\{\mu\text{-}C(CO_2Me){=}CH(CO_2Me)\}(\mu\text{-}SPh)Co(CO)\{PPh_2(SPh)\}]$ [4]. The uncoordinated alkyne C≡C bond distance is 1.24 (2) Å, in the normal range for free alkynes [17]. There is a deviation from linearity of the uncoordinated alkyne, [C(6)–C(10)–C(11)

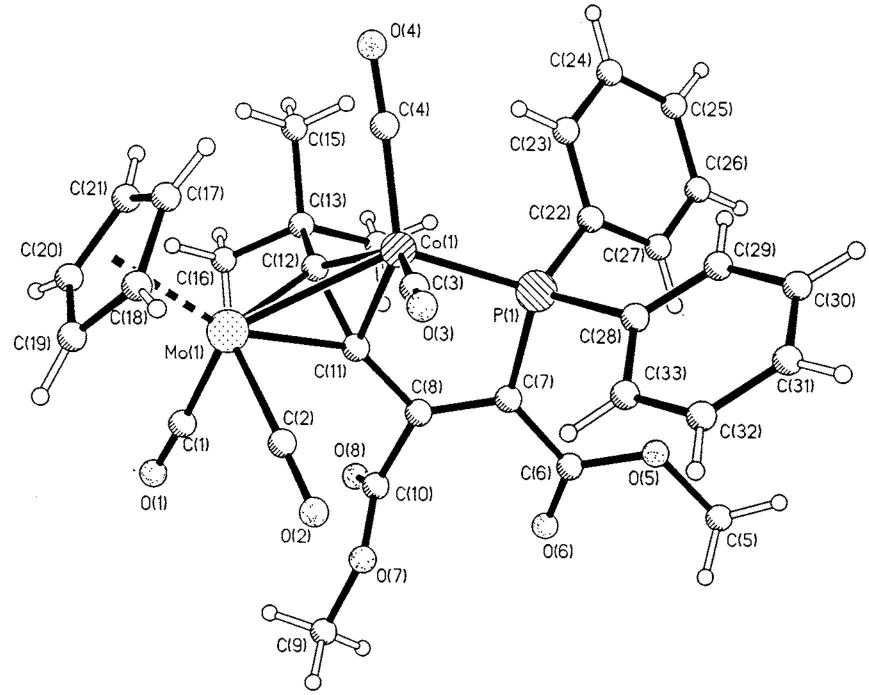


Fig. 3. Molecular structure of [(η^5-C_5H_5)(OC)$_2$Mo{μ-^{t}BuCCC(CO_2Me)=C(CO_2Me)PPh_2}Co(CO)$_2$] 3 showing the atom numbering scheme.

169(2)°], perhaps due to crystal packing, whilst the C(10)–C(11)–C(12) angle is 177 (2)°. The metal-metal bond is asymmetrically bridged by the phosphido lig and [W(1)–P(1) 2.394 (5) Å, Co(1)–P(1) 2.197 (5) Å] in keeping with the larger atomic radius of tungsten. The observed W–Co bond length [2.658 (2) Å] is similar to those found in other structurally characterised W–Co complexes [4].

The IR spectrum of complex **6**, recorded in dichloromethane (Table 1), shows two absorptions due to ν(CO) bands of the ester groups at 1683 and 1548 cm^{-1}. The absorption band at lower frequency is indicative of oxygen co-ordination and suggests that the solid state structure of **6** is maintained in solution. The ^{1}H-NMR spectrum in $CDCl_3$ at 293 K shows, in addition to phenyl resonances, a signal assigned to the η^5-C_5H_5 groups which is split into a doublet with ^3J(PH) 1.3 Hz. Two separate singlets were observed for the non-equivalent methyl groups. The ^{31}P-{^{1}H} NMR spectrum displays a singlet at δ 117.8 with ^{183}W satellites observed with ^1J(PW) 127 Hz. In the ^{13}C-{^{1}H} NMR at 293 K, all three carbonyl ligands give rise to distinct resonances showing there is no carbonyl fluxionality at this temperature. The IR and NMR spectra of **7** confirmed that simple substitution had occurred.

The proposed pathway leading to the formation of **6** (Scheme 1) is the same as that for **3** and **5** up to the formation of intermediate **II**. Co-ordination of an oxygen of one of the ester groups to tungsten with displacement of a carbonyl group, rather than the reductive elimination and P–C bond formation which leads to **3** and **5** would then yield **6** directly. It is not clear why a molybdenum complex analogous to **6** is not formed, since CO groups are normally easier to displace from a molybdenum centre than from a tungsten centre. It may be that the reductive elimination reaction which leads to **3** and **5** is more favourable for molybdenum than for tungsten in line with the generally observed enhanced stability of third row metals in higher oxidation states as compared to second row metals.

3. Conclusion

Reaction of the phosphinoacetylene $Ph_2PC{\equiv}C^tBu$ with [(η^5-C_5H_5)(OC)$_2$M{μ-C_2(CO_2Me)$_2$}Co(CO)$_3$] (**1**, M = Mo; **2**, M = W) proceeds via P–C bond cleavage to give Ph_2P and $C{\equiv}C^tBu$ fragments. The derived products result from attachment of the $C{\equiv}C^tBu$ fragment alone or the attachment of both the Ph_2P and $C{\equiv}C^tBu$ fragments to the bridging alkyne ligand in **1** and **2**. The products are not analogous to the products of the reactions of P_2Ph_4 or Ph_2P(SR) with the same heterodinuclear alkyne-bridged starting complexes.

4. Experimental

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled under nitrogen from appropriate drying agents. Infrared spectra were recorded in dichloromethane solution in 0.5 mm NaCl cells, using a Perkin-Elmer 1710 Fourier-transform spectrometer. Fast atom bombardment (FAB) mass spectra were recorded on a Kratos MS 890 instrument using 3-nitrobenzyl alcohol as a matrix. Proton (reference to $SiMe_4$) and ^{31}P-NMR spectra were recorded on either a Bruker WM250 or Am-400 spectrometer, ^{31}P-NMR chemical shifts are referenced to 85% H_3PO_4. 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 given in order of decreasing R_f values. Elemental analyses were performed at the University Chemical Laboratory, Cambridge. Unless otherwise stated all reagents were obtained from commercial suppliers and used without further purification. The complexes $[(\eta^5\text{-}C_5H_5)(OC)_2Mo\{\mu\text{-}C_2(CO_2Me)_2\}Co(CO)_3]$, and $[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}C_2(CO_2Me)_2\}Co(CO)_3]$ [18] and the ligand $Ph_2PC{\equiv}C^tBu$ [19] were prepared by literature methods.

Table 2
Selected bond lengths (Å) and angles (°) for $[(\eta^5\text{-}C_5H_5)(OC)_2Mo\{\mu\text{-}^tBuCCC(CO_2Me){=}C(CO_2Me)PPh_2\}Co(CO)_2]$ (**3**)

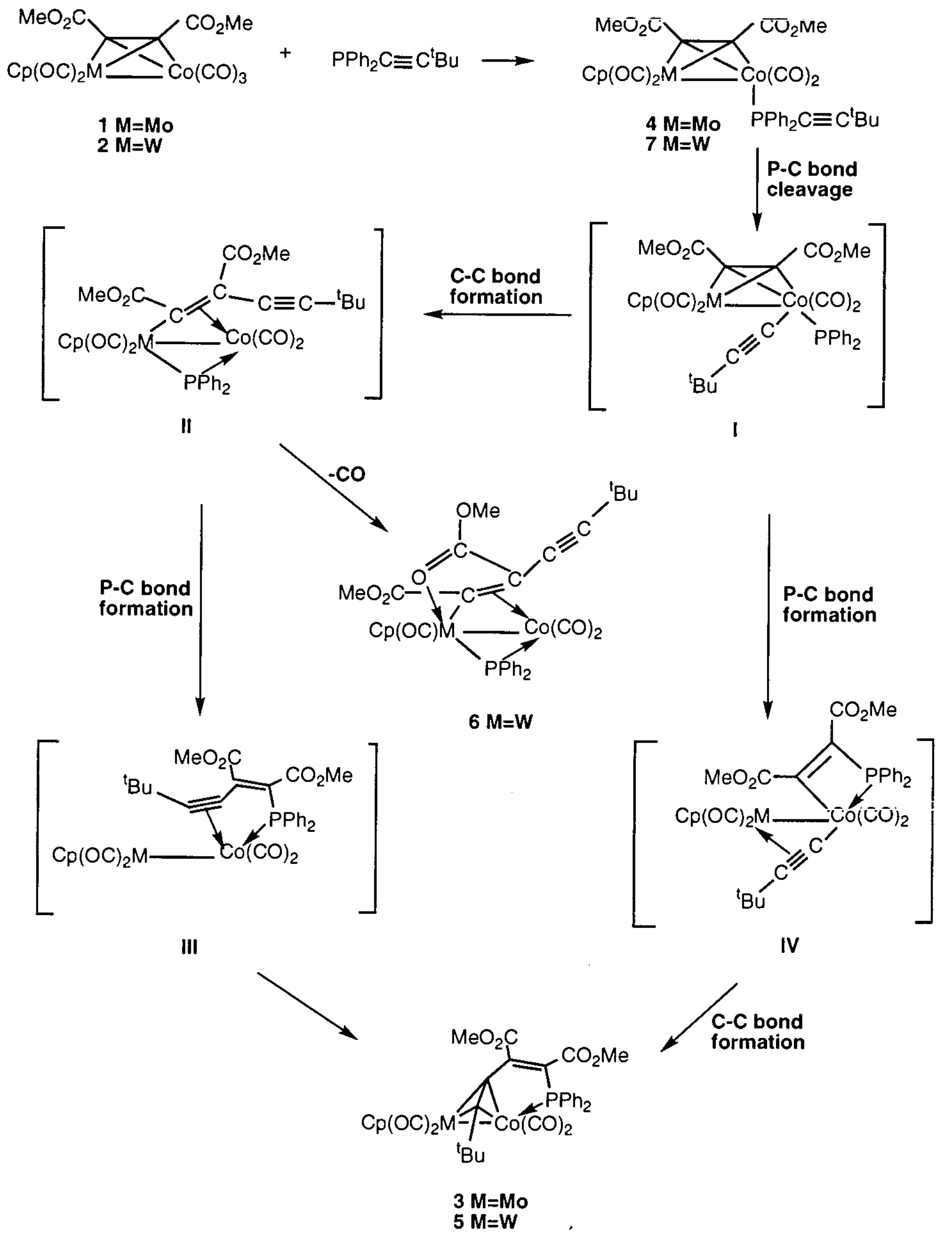
Bond lengths (Å)			
Mo(1)–C(12)	2.167(12)	Co(1)–C(11)	1.950(12)
Co(1)–P(1)	2.216(3)	C(7)–C(8)	1.36(2)
C(8)–C(11)	1.47(2)	C(11)–C(12)	1.37(2)
Mo(1)–C(11)	2.174(11)	Mo(1)–Co(1)	2.681(2)
Co(1)–C(12)	2.016(12)	P(1)–C(7)	1.845(12)
C(6)–C(7)	1.50(2)	O(8)–C(10)	1.19(2)
C(12)–C(13)	1.55(2)		
Bond angles (°)			
C(12)–Mo(1)–Co(1)	47.7(3)	C(11)–Co(1)–C(12)	40.3(5)
C(12)–Co(1)–P(1)	104.4(4)	C(12)–Co(1)–Mo(1)	52.7(3)
C(12)–Mo(1)–C(11)	36.8(4)	C(11)–Mo(1)–Co(1)	45.9(3)
C(11)–Co(1)–P(1)	83.3(3)	C(11)–Co(1)–Mo(1)	53.2(3)
P(1)–Co(1)–Mo(1)	134.26(10)	C(8)–C(7)–P(1)	112.6(9)
C(7)–C(8)–C(11)	117.3(13)	C(12)–C(11)–C(8)	138.0(11)
C(8)–C(11)–Mo(1)	144.5(8)	C(11)–C(12)–C(13)	133.5(11)
C(13)–C(12)–Co(1)	137.9(8)	C(13)–C(12)–Mo(1)	137.0(9)
C(12)–C(11)–Co(1)	72.4(7)	C(7)–P(1)–Co(1)	102.2(4)
C(12)–C(11)–Mo(1)	71.3(7)	Co(1)–C(11)–Mo(1)	80.9(4)
C(11)–C(12)–Co(1)	67.3(7)	C(11)–C(12)–Mo(1)	71.9(7)
Co(1)–C(12)–Mo(1)	79.7(4)		

4.1. Synthesis of *$[(\eta^5\text{-}C_5H_5)(OC)_2Mo\{\mu\text{-}^tBuCCC(CO_2Me){=}C(CO_2Me)PPh_2\}Co(CO)_2\}]$* **3** *and* *$[(\eta^5\text{-}C_5H_5)(OC)_2Mo\text{-}\{\mu\text{-}C_2(CO_2Me)_2\}Co(CO)_2(Ph_2PC{\equiv}C^tBu)]$* **4**

$[(\eta^5\text{-}C_5H_5)(OC)_2Mo\{\mu\text{-}C_2(CO_2Me)_2\}Co(CO)_3]$ **1** (1.0 g, 1.99 mmol) was dissolved in toluene (60 cm^3) and $Ph_2PC{\equiv}C^tBu$ (0.52 g, 1.95 mmol) added. After the solution had been heated to 383 K for 5 h the solvent was removed under reduced pressure. The residue was redissolved in the minimum volume of dichloromethane and loaded onto the top of a chromatography column. Elution with hexane-ethyl acetate (4:1) gave $[(\eta^5\text{-}C_5H_5)(OC)_2Mo\{\mu\text{-}^tBuCCC(CO_2Me){=}C(CO_2Me)PPh_2\}Co(CO)_2]$ **3** (0.50 g, 36%) and $[(\eta^5\text{-}C_5H_5)(OC)_2Mo\{\mu\text{-}C_2(CO_2Me)_2\}Co(CO)_2(Ph_2PC{\equiv}C^tBu)]$ **4** (0.30 g, 20%). Complex **3**: FAB mass spectrum m/z 740 (M^+) and $M^+ - n$CO ($n = 0$–3). NMR ($CDCl_3$): ^{13}C (^{1}H composite pulse decoupled), δ 225.0 (s, Mo*C*O), 224.0 (s, Mo*C*O), 212.9 (s, Co*C*O), 209.4 (s, Co*C*O), 173.4 (s, *C*O$_2$Me), 171.2 (s, *C*O$_2$Me), 169.2 (d, ^2J(PC) 31.0, PPh$_2$*C*(CO$_2$Me)=C(CO$_2$Me)), 162.7 (s, PPh$_2$C(CO$_2$Me)=*C*(CO$_2$Me)), 132.2 (s, ^{t}BuC*C*C(CO$_2$Me)=C(CO$_2$Me)PPh$_2$) 137.2–128.8 (m, *Ph*), 88.9 (s, *Cp*), 60.4 (s, ^{t}Bu*C*CC(CO$_2$Me)=C(CO$_2$Me)PPh$_2$), 52.5 (s, CO$_2$*Me*), 51.7 (s, CO$_2$*Me*), 32.9 (s, C*Me*$_3$), 29.5 (s, *C*Me$_3$). Complex **4**: FAB Mass spectrum m/z 740 (M^+) and $M^+ - n$CO ($n = 0$–4). NMR ($CDCl_3$): ^{13}C (^{1}H composite pulse decoupled), δ 224.4 (s, Mo*C*O), 220.2 (s, Mo*C*O), 204.9 (s, Co*C*O), 173.3 (s, *C*O$_2$Me), 135.8–128.1 (m, *Ph*), 120.7 (d, ^2J(PC) 11, C_β), 90.7 (s, *Cp*), 72.2 (*C*CO$_2$Me), 72.9 (d, J(PC) 83.8 C_α), 52.0 (s, CO$_2$*Me*), 30.4 (s, C*Me*$_3$), 28.9 (s, *C*Me$_3$).

4.2. Synthesis of *$[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}^tBuCCC(CO_2Me){=}C(CO_2Me)PPh_2\}Co(CO)_2]$* **5**, *$[(\eta^5\text{-}C_5H_5)(OC)W\text{-}\{\mu\text{-}C(CO_2Me){=}CC{\equiv}C^tBu(CO_2Me)\}(\mu\text{-}PPh_2)Co(CO)_2]$* **6** *and* *$[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}C_2(CO_2Me)_2\}\text{-}Co(CO)_2(Ph_2PC{\equiv}C^tBu)]$* **7**

$[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}C_2(CO_2Me)_2\}Co(CO)_3]$ **2** (0.87 g, 1.47 mmol) was dissolved in toluene (60 cm^{-3}) and $Ph_2PC{\equiv}C^tBu$ (0.39 g, 1.47 mmol) added. After the solution had been heated to 383 K for 8 h the solvent was removed under reduced pressure. The residue was redissolved in the minimum volume of dichloromethane and loaded onto the top of a chromatography column. Elution with hexane-ethyl acetate (4:1) gave $[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}^tBuCCC(CO_2Me){=}C(CO_2Me)PPh_2\}Co(CO)_2]$ **5** (0.23 g 19%) $[(\eta^5\text{-}C_5H_5)(OC)W\{\mu\text{-}C(CO_2Me){=}C(CO_2Me)C{\equiv}C^tBu\}(\mu\text{-}PPh_2)Co(CO)_2]$ **6** (0.15 g, 13%) and $[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}C_2(CO_2Me)_2\}Co(CO)_2(Ph_2PC{\equiv}C^tBu)]$ **7** (0.30 g, 25%). Complex **5**: (Found: C, 47.57; H, 3.63; $C_{33}H_{30}CoWO_8P$ requires C, 47.8; H, 3.85); FAB



Scheme 1. Proposed reaction pathways for the formation of complexes **3**–**7**.

mass spectrum m/z 828 (M^+) and $M^+ - n$CO ($n = 0$–4). NMR ($CDCl_3$): ^{13}C (^{1}H composite pulse decoupled), δ 133.3–128.0 (m, *Ph*), 87.0 (s, *Cp*), 52.4 (s, CO_2*Me*), 51.6 (s, CO_2*Me*), 33.0 (s, C*Me*$_3$). Complex **6**: (Found: C, 48.18; H, 3.6; $C_{32}H_{30}CoO_7PW$ requires C, 48.0; H, 3.7); FAB mass spectrum m/z 800 (M^+) and $M^+ - n$CO ($n = 0$–3). NMR ($CDCl_3$): ^{13}C (^{1}H composite pulse decoupled), δ 235.0 (s, W*CO*), 211.0 (s, Co*CO*), 207.4 (s, Co*CO*), 187.3 (s, *C*O_2Me), 179.1 (s, *C*O_2Me), 143.8 (d, ^2J(PC), 36.6, *C*(CO_2Me)=C(COOMe)C≡C^{t}Bu), 142.5–127.7 (m, *Ph*), 93.9 (s, –*C*≡C^{t}Bu), 89.8 (s, *Cp*), 78.5 (s, C(CO_2Me)=*C*C≡C^{t}Bu(CO_2Me)), 46.3 (s, –C≡*C*^{t}Bu), 54.8 (s, CO_2*Me*), 50.9 (s, CO_2*Me*), 31.1 (s, C*Me*$_3$), 27.8 (s, *C*Me$_3$). Complex **7**; FAB mass spectrum m/z 828 (M^+) and $M^+ - n$CO ($n = 0$–4). NMR ($CDCl_3$): ^{13}C (^{1}H composite pulse decoupled), 211.3 (s, Co*CO*), 174.1 (s, *C*O_2Me), 136.2–128.0 (m, *Ph*), 88.5 (s, *Cp*), 51.7 (s, CO_2*Me*), 30.4 (s, C*Me*$_3$), 28.9 (s, *C*Me$_3$).

4.3. Crystal structure analyses of complexes **3** and **6**

Data for **3** and **6** were collected (Table 4) by the $\omega/2\theta$ scan method on a Rigaku AFC5R four-

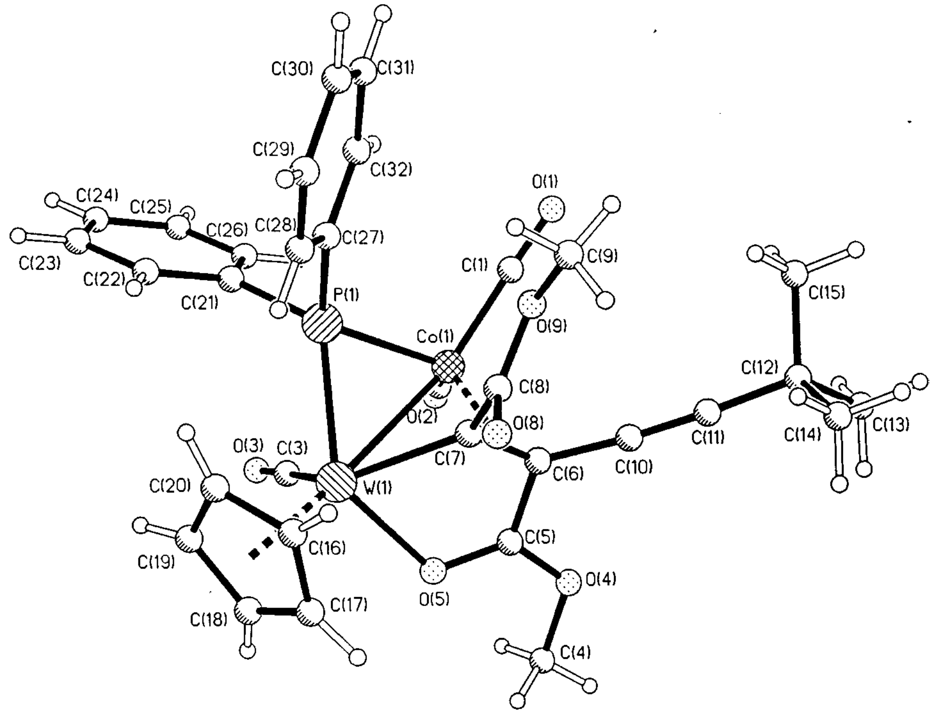


Fig. 4. Molecular structure of [(η^5-C_5H_5)(OC)W{μ-C(CO_2Me)=C(CO_2Me)C≡C^{t}Bu}(μ-PPh_2)Co$(CO)_2$] **6** showing the atom numbering scheme.

circle diffractometer. Three standard reflections monitored at intervals of 200 reflections showed no significant variation in intensity. Cell parameters were obtained by least-squares refinement on diffractometer angles from 25 centred reflections ($15 < \theta < 20°$). Semi-empirical absorption corrections based on ψ-scan data were applied [20, 21].

Table 3
Selected bond lengths (Å) and angles (°) for [(η^5-C_5H_5)(OC)W{μ-C(CO_2Me)=C(CO_2Me)C≡C^{t}Bu}(μ-PPh_2)Co$(CO)_2$] (**6**)

Bond lengths (Å)			
W(1)–O(5)	2.201(10)	W(1)–P(1)	2.394(5)
Co(1)–C(7)	1.99(2)	Co(1)–P(1)	2.197(5)
O(5)–C(5)	1.25(2)	C(6)–C(10)	1.41(2)
C(8)–O(9)	1.30(2)	C(10)–C(11)	1.24(2)
W(1)–C(7)	2.15(2)	W(1)–Co(1)	2.658(2)
Co(1)–C(6)	2.12(2)	C(6)–C(7)	1.44(2)
C(11)–C(12)	1.44(2)		
Bond angles (°)			
C(7)–W(1)–O(5)	74.6(5)	O(5)–W(1)–Co(1)	79.5(3)
P(1)–W(1)–Co(1)	51.23(12)	C(7)–Co(1)–C(6)	40.9(6)
C(6)–Co(1)–P(1)	125.0(4)	C(6)–Co(1)–W(1)	77.8(4)
C(7)–Co(1)–W(1)	52.7(4)	C(5)–O(5)–W(1)	114.5(9)
O(5)–C(5)–C(6)	121.5(14)	C(10)–C(6)–C(7)	123.2(14)
C(7)–C(6)–C(5)	109.6(14)	C(7)–C(6)–Co(1)	64.6(8)
C(11)–C(10)–C(6)	169(2)	Co(1)–P(1)–W(1)	70.61(14)
C(10)–C(6)–C(5)	121.9(14)	C(10)–C(6)–Co(1)	119.4(11)
C(5)–C(6)–Co(1)	74.5(9)	C(6)–C(7)–W(1)	113.8(11)
Co(1)–C(7)–W(1)	79.9(5)	C(10)–C(11)–C(12)	177(2)

The structures were solved by direct methods (SIR 92 [22]) and subsequent Fourier difference syntheses and refined anisotropically on metal, P, O and some C atoms by full-matrix least-squares on F^2 (SHELXL 93 [23]). Hydrogen atoms were placed in idealised positions and refined using a riding model or as rigid methyl groups. For complex **6**, phenyl rings were refined as rigid groups and restraints were applied to interatomic distances in the cyclopentadienyl ring. In the final cycles of refinement a weighting scheme was introduced which produced a flat analysis of variance.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 101307. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (Fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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Table 4
Crystal data for complexes (**3**) and (**6**)

	3	**6**
Molecular formula	$C_{33}H_{30}CoMoO_8P$	$C_{32}H_{30}CoO_7PW$
M	740.41	800.31
Crystal system	Monoclinic	Monoclinic
a/Å	9.344 (5)	9.166 (3)
b/Å	9.509 (5)	19.143 (6)
c/Å	17.919 (4)	18.266 (3)
β/°	92.71 (3)	93.94 (2)
U/Å^3	1590.4 (12)	3198 (2)
Space group	$P2_1$	$P2_1/c$
Z	2	4
$D_{calc.}$/mg m^{-3}	1.546	1.663
Crystal size/mm	$0.25\times0.24\times0.15$	$0.20\times0.10\times0.10$
Crystal habit	Red block	Red prism
$F(000)$	752	1576
μ/mm^{-1}	1.016	4.208
Maximum, minimum relative transmission	0.999, 0.909	0.994, 0.818
Data collection range/°	$4.36<2\theta<50.0°$	$5.30<2\theta<48.0°$
Index ranges	$0\leq h\leq 11$ $0\leq k\leq 11$ $-21\leq l\leq 21$	$0\leq h\leq 10$ $0\leq k\leq 21$ $-20\leq l\leq 20$
Reflections measured	3175	3157
Independent reflections	2981 (R_{int} = 0.067)	5021 (R_{int} = 0.096)
Parameters, restraints	299, 1	257, 16
wR^2(all data)[a]	0.2707	0.3031
x, y[a]	0.0494, 3.4713	0.0267, 20.510
$R^1[I>2\sigma(I)]$[a]	0.0526	0.0675
Observed reflections	2064	2474
Goodness-of-fit on F^2 (all data)[a]	1.048	1.032
Maximum shift/σ	0.007	0.001
Peak, hole in final difference map/e Å^{-3}	0.594, −0.762	1..118, −1.454
Absolute structure parameter [24]	−0.01(5)	–

Data in common: graphite-monochromated Mo–K$_\alpha$ radiation, λ = 0.71073 Å, T = 293 (2) K.
[a] $R_1=\Sigma\|F_o|-|F_c\|/\Sigma|F_o|$, $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{0.5}$, $w=1/[\sigma^2(F_o)^2+(xP)^2+yP]$, $P=(F_o^2+2F_o^2)/3$ where x and y are constants adjusted by the program; Goodness-of-fit $=[\Sigma[w(F_o^2-F_o^2)^2]/(n-p)]^{0.5}$ where n is the number of reflections and p the number of parameters.

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