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Alkyne–phosphinoalkyne coupling reactions on mixed-metal tungsten–cobalt centres; P–C(alkyne) bond cleavage *versus* P–C(alkyne) bond preservation

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Reactions of the alkyne-bridged tungsten–cobalt complexes $[(\eta^5\text{-}C_5H_5)(OC)_2W(\mu\text{-}R^1CCR^2)Co(CO)_3]$ ($R^1 = R^2 = CO_2Me$ **1a**; $R^1 = H$, $R^2 = Bu^t$ **1b**) with $Ph_2PC{\equiv}CPh$ in refluxing toluene result in two different reaction pathways. On reaction with **1a** three products are isolated namely, $[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}C_2(CO_2Me)_2\}Co(CO)_3(PPh_2C{\equiv}CPh)]$ **2**, the result of substitution of a cobalt carbonyl ligand by a phosphorus-bound molecule of $Ph_2PC{\equiv}CPh$, $[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}PhCCC(CO_2Me){=}C(CO_2Me)PPh_2\}Co(CO)_2]$ **3** and $[(\eta^5\text{-}C_5H_5)(OC)W\{\mu\text{-}C(CO_2Me){=}C(C{\equiv}CPh)C(OMe)O\}(\mu\text{-}PPh_2)Co(CO)_2]$ **4**, in which phosphorus–carbon(alkyne) bond cleavage of the phosphinoalkyne has ocurred along with phosphorus–carbon bond formation (**3**) and/or carbon–carbon bond formation (**3** and **4**). In contrast, reaction of **1b** with $Ph_2PC{\equiv}CPh$ affords two products, $[(\eta^5\text{-}C_5H_5)(OC)W\{\mu\text{-}CBu^tCHCPhC(PPh_2)\}Co(CO)_2]$ **5** and $[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}CBu^tCHC(PPh_2)CPh\}Co(CO)_2]$ **6**, in which the bridging alkyne has coupled with an intact molecule of the phosphinoalkyne $Ph_2PC_\alpha{\equiv}C_\beta Ph$ at either its β- or α-carbon atoms, respectively. However, on reaction of **1b** with the *tert*-butyl-substituted phosphinoalkyne, $Ph_2PC{\equiv}CBu^t$, regiospecific coupling and oxidation of the phosphino moiety occur to give $[(\eta^5\text{-}C_5H_5)(OC)W\{\mu\text{-}CBu^t{=}CHCBu^t{=}C(PPh_2O)\}Co(CO)_2]$ **8**, as the sole product. The reactivity of **6** towards diiron nonacarbonyl has been explored and found to afford the trimetallic complex $[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}CBu^tCHC(PPh_2Fe(CO)_4)CPh\}Co(CO)_2]$ **7** in good yield. Single crystal X-ray diffraction studies have been performed on **4**, **6**, **7** and **8** and possible reaction pathways for the formation of the new complexes are proposed and discussed.

1 Introduction

The facility for phosphinoalkynes ($R'_2PC{\equiv}CR$) to act as sources of acetylide (–C≡CR) and phosphide (PR'_2) fragments on transition metal centres has been well documented.[1–3] In some cases one or both of these fragments can further react with small organic molecules or coordinated organic ligands to give a range of new complexes, in which the phosphide and/or the acetylide has coupled with the organic species.[2–4] Conversely, the related coupling chemistry of an intact phosphinoalkyne is uncommon.[5]

As part of our continuing studies into the chemistry of mixed-metal alkyne-bridged Group 6–group 9 complexes[4–9] we have recently observed contrasting reaction pathways for the molybdenum–cobalt family on their treatment with phosphinoalkynes (Fig. 1). These pathways are either (a) phosphorus–carbon(alkyne) bond cleavage and coupling of the resultant phosphide and acetylide with the bridging alkyne[4] or (b) conservation of the phosphorus–carbon(alkyne) bond and regiospecific coupling of the intact phosphinoalkyne with the bridging alkyne.[5] In these earlier studies it would appear that the pathway followed is largely determined by the nature of both the substituent R on the phosphinoalkyne and the substituents, R^1 and R^2, on the bridging alkyne. In an extension of this work, we examine here the effect of changing the Group 6 metal centre from molybdenum to tungsten. Preliminary results revealed a preference for a pathway of type (a) to prevail when $[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}C_2(CO_2Me)_2\}Co(CO)_3]$ **1a** and $Ph_2PC{\equiv}CBu^t$ are employed.[4] In this paper we report a more thorough study of the reaction chemistry of tungsten–cobalt alkyne-bridged complexes **1** with phosphinoalkynes with particular regard to deviations from the chemistry observed for the molybdenum–cobalt family.

2 Results and discussion

2.1 Reaction of $[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}C_2(CO_2Me)_2\}Co(CO)_3]$ 1a with $Ph_2PC{\equiv}CPh$

Reaction of $[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}C_2(CO_2Me)_2\}Co(CO)_3]$ **1a** with $Ph_2PC{\equiv}CPh$ in toluene at 383 K affords $[(\eta^5\text{-}C_5H_5)$-

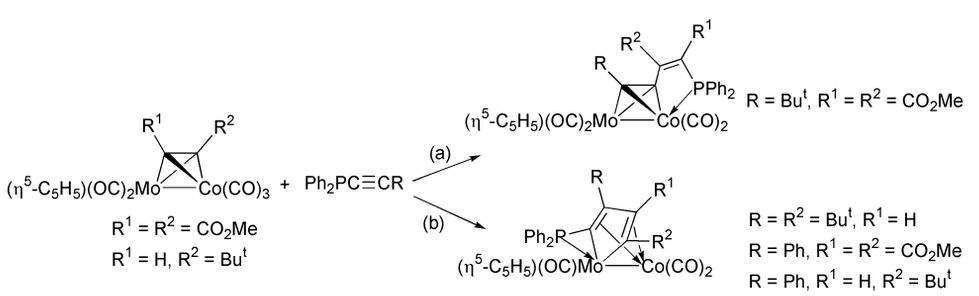
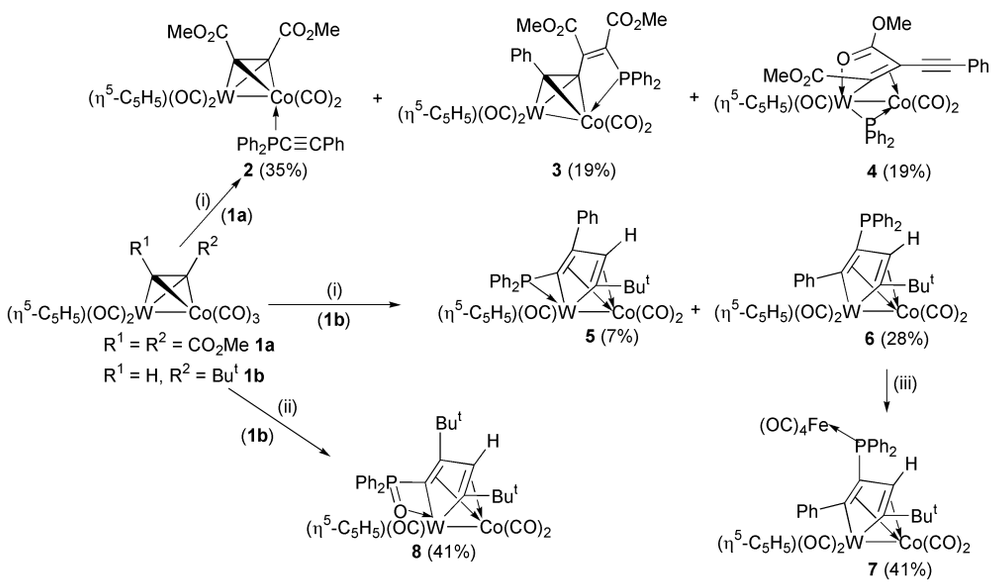


Fig. 1 Reactivity of phosphinoalkynes towards alkyne-bridged molybdenum–cobalt complexes.[4,5]

Table 1 Infrared, ^{1}H and ^{31}P NMR data for the new complexes **2**–**8**

Compound	ν(CO)[a]/cm^{-1}	^{1}H NMR (δ)[b]	^{31}P NMR (δ)[c]
2	2178w (C≡C), 2026m, 1993s, 1962s	7.7–7.2 [m, 15H, Ph], 5.30 [s, 5H, Cp], 3.30 [s, 6H, CO_2Me]	17.8 [s, $PPh_2C{\equiv}CPh$]
3	2010m, 1971vs, 1944s, 1705w	2178w (C≡C), 2026m, 1993s, 7.8–6.5 [m, 15H, Ph], 5.34 [s, 5H, Cp], 3.80 [s, 3H, CO_2Me], 3.40 [s, 3H, CO_2Me]	61.3 [s, μ-PhCCC(CO_2Me)=C(CO_2Me)PPh_2]
4	2010m, 1967vs, 1924sh, 1682w, 1546w	7.6–6.7 [m, 15H, Ph], 5.50 [d, ^{3}J(PH) 1.3, 5H, Cp], 3.60 [s, 3H, CO_2Me], 3.10 [s, 3H, CO_2Me]	118.4 [s, J(PW) 124.0, μ-PPh_2]
5	2002vs, 1950vs, 1828br	7.7–6.5 [m, 15H, Ph], 5.10 [s, 1H, CH], 5.00 [s, 5H, Cp], 1.28 [s, 9H, Bu^{t}]	−56.9 [s, J(PW) 53.6, μ-CBu^{t}=CHCPh=C(PPh_2)]
6	2016vs, 1961s, 1907m	7.8–6.5 [m, 15H, Ph], 5.10 [d, ^{3}J(PH) 2.0, 1H, CH], 4.90 [s, 5H, Cp], 1.06 [s, 9H, Bu^{t}]	−17.1 [s, μ-CBu^{t}=CHC(PPh_2)CPh]
7	2046s, 2024vs, 1968s, 1933s	7.4–6.6 [m, 15H, Ph], 6.10 [s, 1H, CH], 5.07 [s, 5H, Cp], 1.28 [s, 9H, Bu^{t}]	60.2 [s, μ-CBu^{t}=CHC(PPh_2Fe$(CO)_4$)CPh]
8	1982vs, 1930vs, 1116 (P–O)	7.8–7.1 [m, 10H, Ph], 6.20 [s, 1H, CH], 5.0 [s, 5H, Cp], 1.30 [s, 9H, Bu^{t}], 1.07 [s, 9H, Bu^{t}]	71.5 [s, μ-CBu^{t}=CHCBu^{t}=C(PPh_2O)]

[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 in $CDCl_3$ at 293 K. [c] ^{31}P chemical shifts (δ) in ppm relative to 85% external H_3PO_4 (0.0 ppm) (upfield shifts negative). Spectra were {^{1}H}-gated decoupled and measured in $CDCl_3$ at 293 K.



Scheme 1 *Reagents and conditions*: (i) $Ph_2PC{\equiv}CPh$, 383 K, C_6H_5Me; (ii) $Ph_2PC{\equiv}CBu^{t}$, 383 K, C_6H_5Me; (iii) $Fe_2(CO)_9$, 333 K, THF.

$(OC)_2W\{\mu\text{-}C_2(CO_2Me)_2\}Co(CO)_2(PPh_2C{\equiv}CPh)]$ **2**, $[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}PhCCC(CO_2Me){=}C(CO_2Me)PPh_2\}Co(CO)_2]$ **3** and $[(\eta^5\text{-}C_5H_5)(OC)W\{\mu\text{-}C(CO_2Me){=}C(C{\equiv}CPh)C(OMe)O\}(\mu\text{-}PPh_2)Co(CO)_2]$ **4** in yields between 19 and 35% (Scheme 1). All the complexes have been characterised spectroscopically (see Table 1 and Experimental section) and, in addition, the molecular structure of **4** has been determined by single crystal X-ray diffraction.

The spectroscopic properties of **2** show it has a structure analogous to that of $[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}C_2(CO_2Me)_2\}Co(CO)_2(PPh_2C{\equiv}CBu^{t})]$.[4] Thus in the IR spectrum three ν(CO) bands assigned to the terminal carbonyls are observed in the region 2030–1950 cm^{-1} and a weak absorption at 2178 cm^{-1} which is assigned to the C≡C stretch of the non-coordinated alkyne. In the $^{31}P\text{-}\{^{1}H\}$ NMR spectrum there is a single peak at δ 17.8, in the normal range for coordinated phosphines.

The structure of **3** is assigned on the basis of the close similarity in spectroscopic properties with $[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}Bu^{t}CCC(CO_2Me){=}C(CO_2Me)PPh_2\}Co(CO)_2]$.[4] In the IR spectrum three terminal carbonyl absorptions are observed along with a band at 1705 cm^{-1} which is ascribed to the non-coordinated methyl carboxylate groups. The $^{31}P\text{-}\{^{1}H\}$ NMR spectrum reveals a broad singlet resonance at δ 61.3 which can be assigned to the PPh_2 fragment incorporated into a five-membered metallacycle.[4] The broadness of the resonance can be attributed to the proximity of the quadrupolar ^{59}Co centre and is further evidence that the phosphorus atom is bound to cobalt.

The molecular structure of **4** is shown in Fig. 2 while Table 2 lists selected bond distances and angles. Crystals of **4** were grown by slow evaporation of a CH_2Cl_2–hexane solution at 273 K. The structure of **4** consists of two independent molecules (*A* and *B*) within the unit cell with the only appreciable difference between them being the orientation of the phenylacetylide and methyl carboxylate groups. The bond parameters for *A* and *B* are essentially the same but only *A* will be discussed throughout the following; bond lengths and angles are listed separately for the two molecules *A* and *B* in Table 2.

The structure reveals a $(\eta^5\text{-}C_5H_5)(OC)W\text{–}Co(CO)_2$ skeleton bridged by a diphenylphosphido group and by a vinyl group which σ-bonds to tungsten [W(1)–C(10) 2.142(7) Å] and π-bonds to cobalt [C(10)–Co(1) 1.968(7), C(9)–Co(1) 2.102(6) Å]. The β-carbon of the vinyl group has two substituents namely phenylacetylide and methyl carboxylate, the latter of

Table 2 Selected bond distances (Å) and angles (°) for **4**

	Molecule *A*	Molecule *B*
W(1)–Co(1)	2.651(2)	2.653(2)
W(1)–O(4)	2.210(4)	2.203(4)
W(1)–C(10)	2.142(7)	2.167(6)
W(1)–$(C_5H_5)_{centroid}$	1.991(7)	1.988(7)
W(1)–P(1)	2.400(3)	2.394(2)
Co(1)–C(10)	1.968(7)	1.962(7)
Co(1)–C(9)	2.102(6)	2.089(6)
Co(1)–P(1)	2.197(2)	2.186(2)
C(4)–C(7)	1.444(9)	1.431(9)
C(7)–C(8)	1.199(9)	1.188(8)
C(8)–C(9)	1.441(9)	1.450(8)
C(9)–C(13)	1.437(8)	1.450(8)
C(13)–O(4)	1.352(7)	1.318(7)
C(9)–C(10)	1.457(8)	1.470(8)
C(10)–W(1)–O(4)	76.2(2)	75.4(2)
O(4)–W(1)–P(1)	129.6(1)	131.8(1)
O(4)–W(1)–Co(1)	78.8(1)	81.2(1)
P(1)–W(1)–Co(1)	51.3(1)	51.0(1)
C(10)–Co(1)–P(1)	82.5(2)	84.6(2)
C(10)–Co(1)–W(1)	52.8(2)	53.5(2)
P(1)–Co(1)–W(1)	58.5(1)	58.4(1)
C(8)–C(7)–C(4)	176.2(6)	172.2(7)
C(7)–C(8)–C(9)	169.1(7)	176.9(6)
C(8)–C(9)–C(10)	121.2(5)	124.4(5)
C(9)–C(10)–C(11)	117.4(6)	115.9(5)
Co(1)–C(10)–W(1)	80.2(2)	79.8(2)
Co(1)–W(1)–$(C_5H_5)_{centroid}$	166.4(2)	165.5(2)
W(1)–P(1)–Co(1)	70.3(1)	70.6(1)

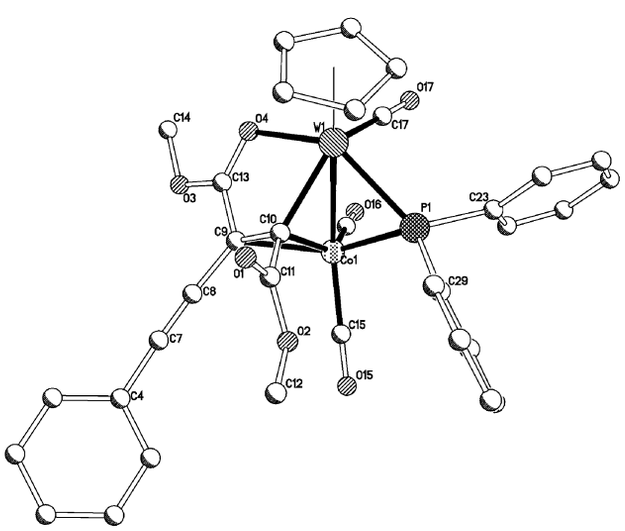


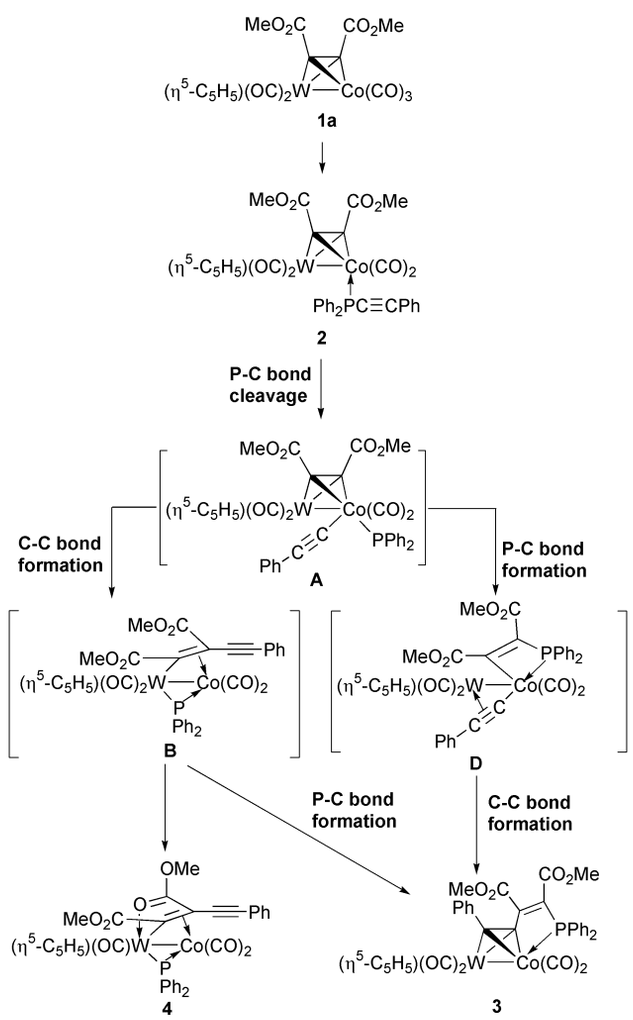
Fig. 2 Molecular structure of $[(\eta^5\text{-}C_5H_5)(OC)W\{\mu\text{-}C(CO_2Me)=C(C{\equiv}CPh)C(OMe)O\}(\mu\text{-}PPh_2)Co(CO)_2]$ **4** including the atom numbering scheme. All hydrogen atoms have been omitted for clarity.

which adopts a *trans* position with respect to the other CO_2Me group and wraps around to coordinate *via* the ketonic group to tungsten [W(1)–O(4) 2.210(4) Å] so as to form a five-membered W–C=C–C–O metallacycle. Related metallacyclic rings have been reported for $[(\eta^5\text{-}C_5H_5)(OC)W\{\mu\text{-}C(CO_2Me)=C(C{\equiv}CBu^t)C(OMe)O\}(\mu\text{-}PPh_2)Co(CO)_2]$[4] and for a range of other homo- and hetero-bimetallic complexes $[Fe_2$,[10] Mo_2,[11] Ru_2,[12] Mn_2,[13] Co_2,[14] FeCo,[15] MoCo,[6] WCo[8]]. The carbon–carbon bond [C(8)–C(9)] formed by the linking of the acetylide to the β-carbon of the vinyl group of the metallacyclic ring has a distance of 1.441(9) Å indicating some conjugation between the acetylide group and the ring. The C_α–C_β bond distance in the vinyl group is 1.457(8) Å [C(9)–C(10)] identical within experimental error to the corresponding distances in $[(\eta^5\text{-}C_5H_5)(OC)W\{\mu\text{-}C(CO_2Me)=C(C{\equiv}CBu^t)C(OMe)O\}(\mu\text{-}PPh_2)Co(CO)_2]$[4] and $[(\eta^5\text{-}C_5H_5)(OC)W\{\mu\text{-}C(CO_2Me)=CHC(OMe)O\}(\mu\text{-}SPh)Co(CO)\{PPh_2(SPh)\}]$.[8] The uncoordinated alkyne C≡C bond distance of 1.199(9) Å lies in the normal range for free alkynes. The metal–metal bond is asymmetrically bridged by the phosphido group [W(1)–P(1) 2.400(3), Co(1)–P(1) 2.197(2) Å] in keeping with the larger atomic radius of tungsten as compared to cobalt. The observed W–Co bond distance [2.651(2) Å] is similar to that found in other structurally characterised W–Co complexes.[16]

The IR spectrum of complex **4**, recorded in hexane, shows in addition to terminal carbonyl absorptions, two absorptions due to the carbonyl bands of the ester group at 1682 and 1546 cm^{-1}. That at lower frequency is indicative of oxygen coordination and suggests that the solid state structure of **4** is maintained in solution. The $^{31}P\text{-}\{^1H\}$ NMR spectrum displays a singlet at δ 118.4 with ^{183}W satellites [J(PW) 124 Hz], the chemical shift of which is consistent with the phosphido group bridging a tungsten–cobalt single bond.[8,9]

In the $^{13}C\text{-}\{^1H\}$ NMR spectrum, in addition to phenyl and cyclopentadienyl resonances, there are signals corresponding to metal-bound carbonyl ligands, at δ 237.0, typical of a tungsten-bound terminal carbonyl and broad singlets at δ 210.0 and 207.0, typical of cobalt-bound terminal carbonyl groups. All three carbonyl ligands give rise to distinct resonances showing that there is no carbonyl fluxionality at this temperature (293 K).

A plausible pathway for the formation of **3** and **4** is shown in Scheme 2. Initial displacement of a cobalt-bound carbonyl group in **1a** by the phosphinoalkyne (coordinated through phosphorus) gives **2** which is followed by oxidative addition of



Scheme 2 Possible reaction pathways for the formation of complexes **3** and **4**.

the phosphinoalkyne at the cobalt centre to yield **A**. Migration of the acetylide ligand in **A** to the bridging alkyne gives the vinyl-bridged species **B** which can then form **4** by displacement of a tungsten carbonyl group by coordination through oxygen of one of the CO_2Me groups in **B**. Related P–C bond cleavage in organophosphines and migration of the resultant organic group to a bridging alkyne ligand has been previously observed in dimolybdenum systems,[11] while acetylide–alkyne coupling and C–C bond formation at the α-carbon atom of the acetylide has been reported for related diiron[17] and dicobalt[18] systems. Conversely, P–C bond formation at the tungsten centre in **B** and displacement of the coordinated alkene by the alkyne moiety gives **3**. Scheme 2 also shows an alternative pathway for the formation of **3** involving P–C bond formation at the cobalt centre in **A** to give **C**, followed by acetylide–alkene coupling to afford **3**.

2.2 Reaction of $[(\eta^5\text{-}C_5H_5)(OC)_2W(\mu\text{-}HCCBu^t)Co(CO)_3]$ 1b with $Ph_2PC{\equiv}CPh$

Reaction of $[(\eta^5\text{-}C_5H_5)(OC)_2W(\mu\text{-}HCCBu^t)Co(CO)_3]$ **1b** with $Ph_2PC{\equiv}CPh$ in toluene at 383 K affords the complexes $[(\eta^5\text{-}C_5H_5)(OC)W\{\mu\text{-}CBu^tCHCPhC(PPh_2)\}Co(CO)_2]$ **5** and $[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}CBu^tCHC(PPh_2)CPh\}Co(CO)_2]$ **6** in moderate yield (Scheme 1). The complexes have been characterised by ^1H, ^{31}P, ^{13}C NMR, IR spectroscopy and mass spectrometry and, in addition, **6** has been the subject of a single crystal X-ray diffraction study.

The assignment of the structure of **5** has been made on the basis of the close similarity of its spectroscopic properties to those of $[(\eta^5\text{-}C_5H_5)(OC)Mo\{\mu\text{-}CBu^tCHCPhC(PPh_2)\}Co(CO)_2]$.[5] Thus three terminal carbonyl bands are seen in the IR spectrum between 2002 and 1828 cm^{-1}. The $^{31}P\text{-}\{^1H\}$ NMR spectrum shows a peak at δ –56.9 with satellites due to coupling to ^{183}W [J(PW) 54 Hz] and consistent with the phosphorus atom being bound to tungsten rather than to cobalt. In the ^1H NMR a singlet is observed for the CH proton of the bridging butadiene ligand at δ 5.1 in addition to resonances for the phenyl, *tert*-butyl and cyclopentadienyl groups.

The molecular structure of **6** is shown in Fig. 3; Table 3 lists selected bond distances and angles. The molecule consists of a tungsten and cobalt atom singly bonded to each other [W(1)–Co(1) 2.689(1) Å][16] and bridged by a $\mu\text{-}C_4$ ligand derived from coupling of the bridging alkyne in **1b** with the α-carbon of $Ph_2PC_\alpha{\equiv}C_\beta Ph$. The C_4 fragment is incorporated into a tungstacyclopentadienyl ring with C(5) and C(8) unsymmetrically σ-bonded to the tungsten atom [W(1)–C(5) 2.224(7), W(1)–C(8) 2.154(8) Å] while the carbon–carbon double bonds are both π-bonded to the cobalt atom [Co(1)–C(5) 2.096(8), Co(1)–C(6) 2.117(7), Co(1)–C(7) 2.078(8), Co(1)–C(8) 2.056(8) Å]. Each substituent on the C_4 unit is different, with the terminal carbon atoms bearing Bu^t and Ph groups while the internal carbon atoms possess H and Ph_2P substituents. The similar carbon–carbon bond distances within the tungstacyclopentadienyl ring [C(5)–C(6) 1.411(11), C(6)–C(7) 1.415(11), C(7)–C(8) 1.424(1) Å] coupled with coplanarity of the four carbon atoms implies some delocalisation in the ring. The coordination sphere of the tungsten atom is completed by a η^5-cyclopentadienyl and two carbonyl ligands while on cobalt it is completed by two carbonyl groups. Three other crystallographically characterised W–Co complexes bridged by butadiene ligands have been reported namely $[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}C(CF_3)C(CF_3)C(CF_3)C(CF_3)\}Co(CO)_2]$,[16c] $[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}C(C_6H_4Me\text{-}4)CEtCEtC(C_6H_4Me\text{-}4)\}Co(CO)_2]$[19] and $[(Ph_3P)(OC)_2Co\{\mu\text{-}CPhCMeCMeC(OH)\}W(CO)_4][BF_4]$,[20] the last of which is unique in that it differs from all other examples in that the butadiene ligand is η^4-coordinated to tungsten rather than cobalt.

The spectroscopic properties of **6** are consistent with the solid-state structure being maintained in solution. The IR spectrum shows absorptions in the terminal carbonyl region and this evidence is supported by the $^{13}C\text{-}\{^1H\}$ NMR spectrum which identifies four separate terminal carbonyl resonances at δ 224.3, 222.6, 203.8 and 202.8, the broadness and chemical shift of the last two signals being consistent with cobalt-bound carbonyls. In the ^1H NMR spectrum of **6** the proton on the C_4 unit is seen, as in **5**, at δ 5.1 but in the case of **6** the resonance takes the form of a doublet with ^3J(PH) 2 Hz. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **6** shows a singlet for the uncoordinated diphenylphosphino group at δ −17.1.

Table 3 Selected bond distances (Å) and angles (°) for **6**

W(1)–Co(1)	2.689(1)	W(1)–C(8)	2.154(8)
W(1)–C(5)	2.224(7)	$W(1)\text{–}(C_5H_5)_{centroid}$	1.980(8)
Co(1)–C(5)	2.096(8)	Co(1)–C(6)	2.117(7)
Co(1)–C(7)	2.078(8)	Co(1)–C(8)	2.056(8)
P(1)–C(7)	1.847(8)	C(5)–C(6)	1.411(11)
C(6)–C(7)	1.415(11)	C(7)–C(8)	1.424(1)
C(8)–W(1)–C(5)	74.5(3)	C(8)–W(1)–Co(1)	48.7(2)
C(5)–W(1)–Co(1)	49.4(2)	C(8)–Co(1)–W(1)	51.9(2)
C(7)–Co(1)–W(1)	79.4(2)	C(5)–Co(1)–W(1)	53.7(2)
C(7)–C(6)–C(5)	116.8(7)	C(6)–C(7)–C(8)	114.7(7)
C(6)–C(7)–P(1)	122.2(6)	C(8)–C(7)–P(1)	123.0(6)
$Co(1)\text{–}W(1)\text{–}(C_5H_5)_{centroid}$	158.0(5)	Co(1)–C(8)–W(1)	79.4(3)

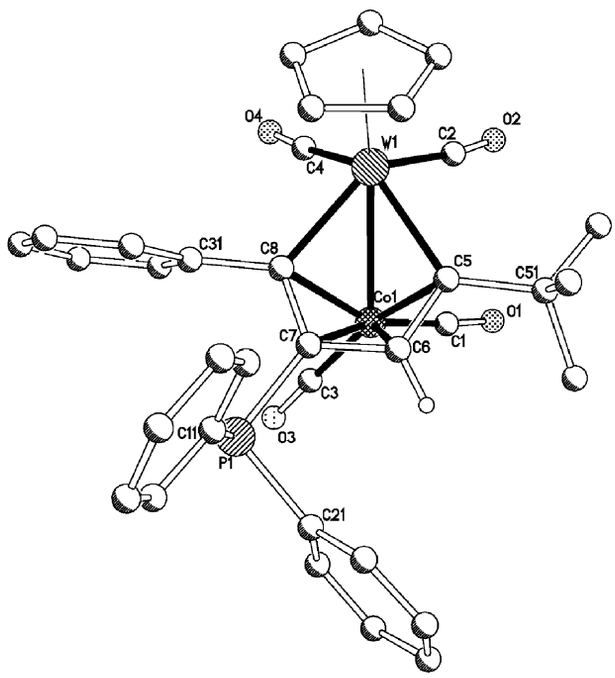


Fig. 3 Molecular structure of $[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}CBu^tCHC(PPh_2)CPh\}Co(CO)_2]$ **6**, including the atom numbering scheme. All hydrogen atoms except for H6 have been omitted for clarity.

The anticipated reactivity of the pendant diphenylphosphino group in **6** was realised during its reaction with $[Fe_2(CO)_9]$ (Scheme 1) in THF at 333 K. The complex $[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}CBu^tCHC(PPh_2Fe(CO)_4)CPh\}Co(CO)_2]$ **7** was isolated in 41% yield and has been characterised spectroscopically (see Table 1 and Experimental section) and in addition, the molecular structure has been determined by single crystal X-ray diffraction.

The molecular structure of **7** is depicted in Fig. 4; bond lengths and angles are collected in Table 4. The structure is essentially the same as that of **6** with the C_4 unit bridging a W–Co vector but having the diphenylphosphino substituent coordinated to an axial site of an $Fe(CO)_4$ unit. The presence of the coordinated $Fe(CO)_4$ fragment has little effect on the

Table 4 Selected bond distances (Å) and angles (°) for **7**

W(1)–Co(1)	2.682(2)	W(1)–C(9)	2.181(6)
Co(1)–C(9)	2.070(6)	Co(1)–C(12)	2.108(6)
Co(1)–C(10)	2.106(6)	C(9)–C(10)	1.437(9)
Fe(1)–P(1)	2.263(2)	W(1)–C(12)	2.201(7)
C(10)–C(11)	1.408(9)	Co(1)–C(11)	2.103(7)
W(1)–$(C_5H_5)_{centroid}$	1.987(6)	C(11)–C(12)	1.414(9)
P(1)–C(10)	1.842(6)		
C(9)–W(1)–Co(1)	49.1(2)	C(9)–Co(1)–C(11)	69.6(3)
C(9)–W(1)–C(12)	74.6(2)	C(12)–W(1)–Co(1)	50.0(2)
C(11)–Co(1)–C(12)	39.2(2)	C(9)–Co(1)–W(1)	52.7(2)
C(12)–Co(1)–W(1)	53.1(2)	C(11)–C(10)–C(9)	113.8(6)
C(9)–C(10)–Co(1)	68.5(3)	C(9)–C(10)–P(1)	130.2(5)
Co(1)–W(1)–$(C_5H_5)_{centroid}$	159.1(4)	C(12)–C(11)–C(10)	118.1(6)
C(10)–C(11)–Co(1)	70.6(4)	C(11)–C(12)–Co(1)	70.2(4)
C(11)–C(12)–W(1)	114.8(4)	Co(1)–C(12)–W(1)	76.9(2)
C(9)–Co(1)–C(12)	78.9(2)	C(9)–Co(1)–C(10)	40.2(2)
C(12)–Co(1)–C(10)	70.1(2)	C(11)–Co(1)–W(1)	78.9(2)
C(10)–Co(1)–W(1)	79.9(2)	C(10)–P(1)–Fe(1)	113.8(2)
C(10)–C(9)–Co(1)	71.2(4)	C(10)–C(9)–W(1)	116.9(4)
Co(1)–C(9)–W(1)	78.2(2)		

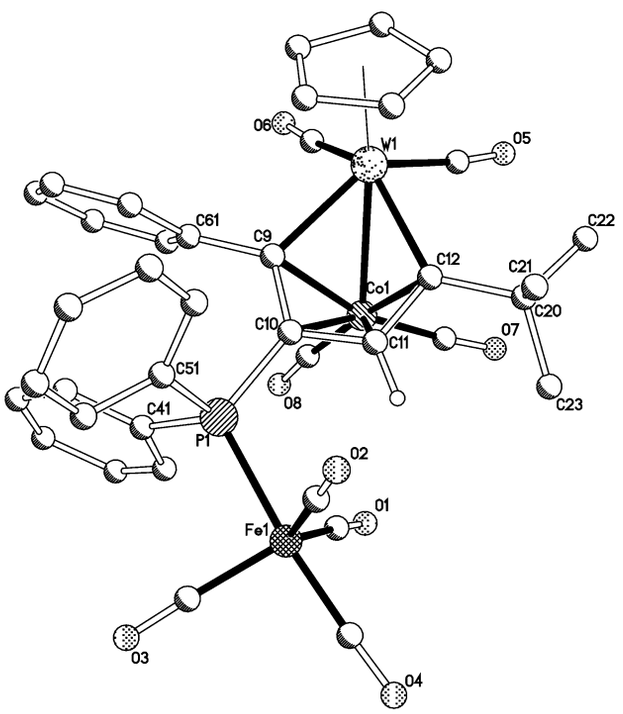
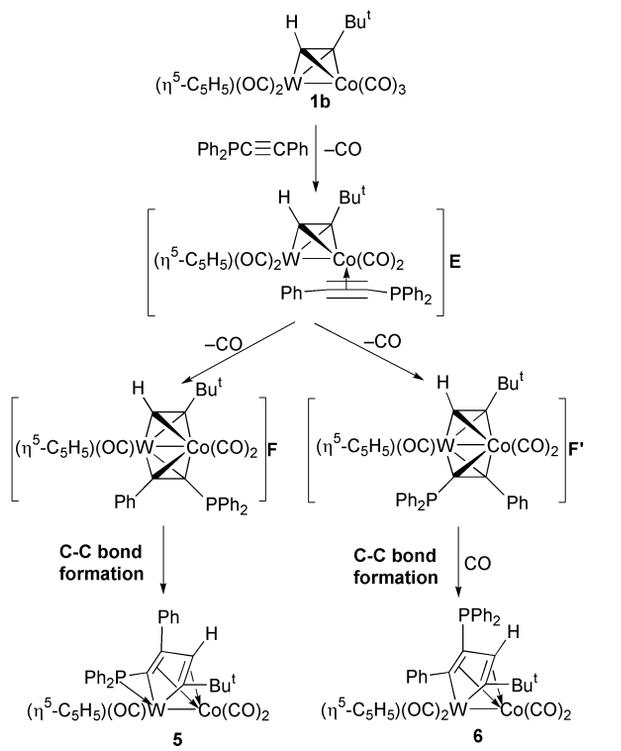


Fig. 4 Molecular structure of [$(\eta^5$-$C_5H_5)(OC)_2W\{\mu$-CBu^{t}CHC(PPh_2-$Fe(CO)_4$)CPh}$Co(CO)_2$] **7**. Details as in Fig. 3.

carbonyl region. The ^{31}P-{^1H} NMR spectrum shows a peak at δ 60.2 which is assigned to the coordinated diphenylphosphino group in the complex, being shifted downfield by *ca*. 77 ppm compared to that of **6**. In the ^{13}C-{^1H} NMR spectrum of **7** in addition to phenyl, cyclopentadienyl and *tert*-butyl signals, four upfield resonances are seen in the terminal carbonyl region and four downfield resonances are observed for the inequivalent carbon atoms of the bridging C_4 unit [δ 179.2, 168.4, 150.4, 119.0]. The upfield carbonyl resonances at δ 221.9 and 220.4 are attributed to inequivalent tungsten-bound carbonyls, the doublet at δ 213.8 with ^2J(PC) 17 Hz to the equivalent iron-bound carbonyls and the broad resonances at δ 202.3 to the cobalt-bound carbonyls. It is noteworthy that the cobalt-bound carbonyls in **6** are inequivalent in the ^{13}C-{^1H} NMR spectrum [δ 203.8 and 202.8] whereas in **7** they lie at the same chemical shift. Given the similarity in the structure of **6** and **7** it is unlikely that a fluxional process is operative for **7** and not **6** at this temperature (293 K) and more likely that the cobalt carbonyl resonances coincide.

The mechanism for the formation of **5** and **6** is uncertain but a possible pathway is shown in Scheme 3. It is proposed that



Scheme 3 Possible reaction pathways for the formation of complexes **5** and **6**.

bond parameters within the tungstacyclopentadiene ring when compared with **6**, the only slight variation being the W–C bond distances which in **7** are closer in length [W(1)–C(9) 2.181(6), W(1)–C(12) 2.201(7) Å] than the corresponding distances in **6** [W(1)–C(5) 2.224(7) Å, W(1)–C(8) 2.154(8) Å]. W(1) is also linked to Co(1) *via* a metal–metal bond of 2.682(2) Å, which is similar to the W(1)–Co(1) distance of 2.689(1) Å in **6**, and to the distances reported for other W–Co complexes.[16] The magnitude of the Co(1)···Fe(1) [4.687 Å] and W(1)···Fe(1) [6.410 Å] distances in **7** precludes any metal–metal bonding interactions. The Fe(1)–P(1) bond distance of 2.263(2) Å indicates a dative bond to the iron atom. The P–C bond distance of 1.842(6) Å is almost the same as in **6** [1.847(8) Å] and consistent with a single bond.

The spectroscopic properties of **7** in solution are in accordance with the solid-state structure. In the IR spectrum four strong carbonyl bands are observed in the terminal

displacement of carbonyl group on cobalt in **1b** by the phosphinoalkyne, coordinating as a two electron donor *via* one π bond of the alkyne moiety to the cobalt centre, gives **E**. Coordination of the second π bond of the alkyne to tungsten with displacement of a carbonyl group gives the bis(alkyne)–bridged species **F** or **F′** depending on the relative disposition of the substituents on the two perpendicularly bridged alkynes. *cis* Coupling of the less bulky CH terminus of the coordinated *t*-butylacetylene with the β-carbon atom of the coordinated $Ph_2PC_\alpha{\equiv}C_\beta Ph$ ligand in **F**, with concomitant coordination of the phosphino group, gives **5**. Conversely, *cis* coupling of the CH terminus with the α-carbon atom of the coordinated $Ph_2PC_\alpha{\equiv}C_\beta Ph$ ligand in **F′** affords, on carbonylation, **6**. Similar coupling of bis(alkyne)-bridged Group 6–Group 9 complexes has been reported by Davidson *et al*. in which the presence of CO has been shown to promote the coupling reaction.[16e]

Table 5 Selected bond distances (Å) and angles (°) for **8**

W(1)–Co(1)	2.685(1)	W(1)–P(1)	2.867(2)
W(1)–C(25)	2.172(6)	P(1)–C(28)	1.745(5)
Co(1)–C(26)	2.086(5)	W(1)–C(28)	2.151(5)
C(26)–C(27)	1.455(7)	W(1)–$(C_5H_5)_{centroid}$	2.005(5)
W(1)–O(4)	2.250(4)	Co(1)–C(27)	2.107(5)
Co(1)–C(28)	2.070(5)	C(25)–C(26)	1.418(7)
P(1)–O(4)	1.546(4)	C(27)–C(28)	1.405(7)
Co(1)–C(25)	2.110(5)		
C(28)–W(1)–C(25)	75.7(2)	C(28)–W(1)–O(4)	68.9(1)
C(25)–W(1)–Co(1)	50.1(1)	C(28)–W(1)–P(1)	37.4(1)
O(4)–W(1)–Co(1)	86.9(1)	Co(1)–W(1)–P(1)	71.0(1)
C(25)–W(1)–O(4)	136.4(2)	C(28)–W(1)–Co(1)	49.2(2)
Co(1)–W(1)–$(C_5H_5)_{centroid}$	157.7(2)	O(4)–W(1)–Co(1)	86.9(1)
C(25)–W(1)–P(1)	111.7(2)	C(28)–Co(1)–W(1)	51.8(2)
O(4)–P(1)–W(1)	51.3(1)	P(1)–O(4)–W(1)	96.3(2)
O(4)–P(1)–C(28)	98.1(2)		

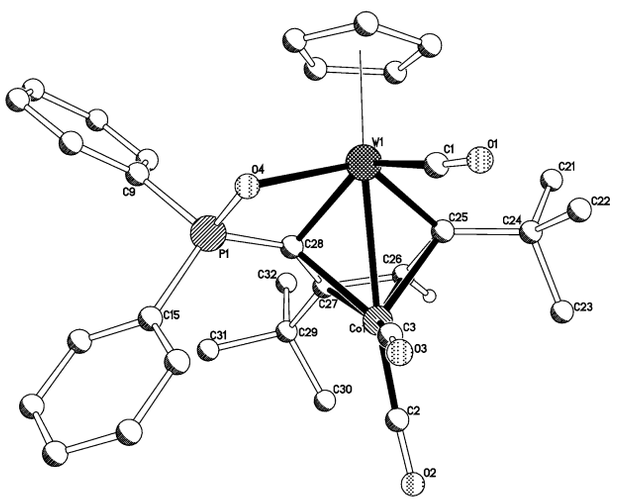


Fig. 5 Molecular structure of $[(\eta^5\text{-}C_5H_5)(OC)W\{\mu\text{-}CBu^t{=}CH\text{-}CBu^t{=}C(PPh_2O)\}Co(CO)_2]$ **8**, including the atom numbering scheme. All hydrogen atoms except for H28 have been omitted for clarity.

2.3 Reaction of $[(\eta^5\text{-}C_5H_5)(OC)_2W(\mu\text{-}HCCBu^t)Co(CO)_3]$ 1b with $Ph_2PC{\equiv}CBu^t$

The reaction of $[(\eta^5\text{-}C_5H_5)(OC)_2W(\mu\text{-}HCCBu^t)Co(CO)_3]$ **1b** with $Ph_2PC{\equiv}CBu^t$ in toluene at 383 K affords the complex $[(\eta^5\text{-}C_5H_5)(OC)W\{\mu\text{-}CBu^tCHCBu^tC(PPh_2O)\}Co(CO)_2]$ **8** in good yield (Scheme 1). The complex has been characterised by ^1H, ^{31}P, ^{13}C NMR, IR spectroscopy and mass spectrometry and in addition has been the subject of a single crystal X-ray diffraction study.

The molecular structure of **8** is shown in Fig. 5 while selected bond distances and angles are given in Table 5. The molecule consists of $(\eta^5\text{-}C_5H_5)(OC)W$ and $Co(CO)_2$ units linked by a single metal–metal bond [W(1)–Co(1) 2.685(1) Å][16] and bridged by a butadiene ligand which σ-bonds to tungsten *via* C(25) [W(1)–C(25) 2.172(6) Å] and C(28) [W(1)–C(28) 2.151(5) Å] and π-bonds to cobalt *via* the butadiene C–C double bonds [Co(1)–C(25) 2.110(5), Co(1)–C(26) 2.086(5), Co(1)–C(27) 2.107(5), Co(1)–C(28) 2.070(5) Å]. The substituents on the terminal carbon atoms C(25) and C(28) of the butadiene ligand are *t*-Bu and Ph_2PO the latter of which wraps around and coordinates to tungsten through O(4) so as to form a four-membered metallacyclic ring W(1)–C(28)–P(1)–O(4). The W(1)–O(4) and O(4)–P(1) bond distances within the four-membered ring of 2.250(4) and 1.546(4) Å are slightly longer than those in related tungsten structures [range (W–O): 2.038–2.200, range (P–O), 1.488–1.537 Å][21,22] and, due to the constraints of the four-membered ring, the W–O–P angle is unusually small [96.3(2) *vs.* 121.2–168.5°].[21,22] The smaller W–O–P has the result of bringing the phosphorus atom closer to the tungsten and allows some W–P bonding interactions [W(1)–P(1) 2.867(2) Å]. Similar structural parameters have been observed for the molybdenum analogue of **8**, $[(\eta^5\text{-}C_5H_5)(OC)Mo\{\mu\text{-}CBu^tCH\text{-}CBu^tC(PPh_2O)\}Co(CO)_2]$[5] although the M–O–P angle is marginally larger in **8** [96.3(1) (**8**) *vs.* 95.7(1)°].

The IR spectrum of **8** shows two terminal carbonyl bands (1982, 1930 cm^{-1}) and an intense band at 1116 cm^{-1} which is assigned to the P–O stretching frequency. The $^{31}P\text{-}\{^1H\}$ NMR spectrum shows a downfield signal at δ 71.5. In the ^1H NMR spectrum resonances for the phenyl, cyclopentadienyl and *tert*-butyl resonances are observed along with a singlet at δ 6.2 integrating as one proton and corresponding to the butadiene CH proton. The $^{13}C\text{-}\{^1H\}$ NMR spectrum shows, in addition to phenyl, cyclopentadienyl and *tert*-butyl resonances, a singlet at δ 236.7 assigned to a tungsten-bound carbonyl, and a broad singlet at δ 208.5 due to the cobalt-bound carbonyl groups. Only three of the inequivalent carbon atoms of the bridging C_4 unit can clearly be seen in the $^{13}C\text{-}\{^1H\}$ NMR spectrum (the fourth presumably masked by the phenyl resonances) at δ 175.3, 171.2 and 108.7. Notably, the first of these signals is assigned to the α-carbon of the $\mu\text{-}CBu^tCHCBu^tC(PPh_2O)$ ligand since the signal takes the form of a doublet with $^3J(PC)$ 3 Hz and is flanked by ^{183}W satellites with $J(WC)$ 41 Hz.

As with the analogous molybdenum–cobalt complex $[(\eta^5\text{-}C_5H_5)(OC)Mo\{\mu\text{-}CBu^tCHCBu^tC(PPh_2O)\}Co(CO)_2]$[5] the source of the oxygen atom in **8** is uncertain but could either be a carbonyl group, molecular oxygen or water. Insertion of an oxygen atom into a phosphorus–iron bond in the complex $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(PPh_2C{\equiv}CR)][BF_4]$ (R = C_6H_4Me-4 or Ph) during the reaction with $Me_3NO{\cdot}2H_2O$ has recently been reported.[23] Notably, oxidation occurs only when there are two tertiary butyl groups on the metallacyclopentadiene ring regardless of the Group 6 metal centre. The high electron density on the metallacyclopentadiene ring as a consequence of the electron donating capability of the *tert*-butyl substituents may result in increased oxophilicity of the phosphorus centre.

2.4 Comparisons of the reactivity of 1 towards $Ph_2PC{\equiv}CR$ with the reactivity of Mo–Co analogues

As was the case in the reactions of $[(\eta^5\text{-}C_5H_5)(OC)_2Mo\text{-}(\mu\text{-alkyne})Co(CO)_3]$ with phosphinoalkynes,[4,5] two reaction pathways can also operate for the tungsten analogues (**1a** and **1b**) namely one involving scission of the P–C(alkyne) bond of the phosphinoalkyne to give **3** and **4** (Scheme 2) or one involving coupling of the intact phosphinoalkyne with the bridging alkyne in **1** to give **5** and **6** (Scheme 3). In our earlier studies on the reactivity of $[(\eta^5\text{-}C_5H_5)(OC)_2Mo(\mu\text{-}R^1CCR^2)\text{-}Co(CO)_3]$ towards $Ph_2PC{\equiv}CR$ the nature of the substituent R on the phosphinoalkyne and the substituents R^1 and R^2 on the bridging alkyne have been shown to affect the course of the reaction. In this work a similar trend is observed; however, the effect of having tungsten in place of molybdenum introduces a number of significant differences in reactivity.

When the substituents on the bridging alkyne are electron withdrawing (**1a**) products are isolated in which P–C(alkyne) bond cleavage invariably occurs (**5** and **6**) irrespective of whether the R group on the phosphinoalkyne is Ph or Bu^t (see Scheme 1 and ref. 4). In contrast, for the reactions of the molybdenum analogue of **1a** the nature of the R substituent on the phosphinoalkyne controls the pathway. That is P–C(alkyne) bond scission occurs when R = Bu^t but coupling of the intact phosphinoalkyne with the bridging alkyne takes place when R = Ph.[4,5]

Having an electron donating (**1b**) substituent on the bridging alkyne results in products (**5**, **6**, **8**) which are exclusively the result of coupling of the intact phosphinoalkyne with the bridging alkyne for both $Ph_2PC{\equiv}CPh$ and $Ph_2PC{\equiv}CBu^t$, a reactivity pattern that is mirrored in the corresponding

molybdenum–cobalt chemistry.[5] However, the coupling reaction does not exhibit regiospecificity in the case of $Ph_2PC{\equiv}CPh$, with the carbon–carbon coupling occurring at both the α- (**6**) and β-carbon (**5**) atoms of the phosphinoalkyne in a ratio of respectively 4 : 1. In contrast, for the molybdenum analogue the coupling takes place uniquely with the β-carbon. With $Ph_2PC{\equiv}CBu^t$ regiospecific coupling (**8**) with the β-carbon occurs in the tungsten case as well along with oxidation of the phosphino moiety as also observed for the molybdenum–cobalt analogue. Notably, in this study, **8** is the only product isolated and there is no evidence for the non-oxidised species although this is obtained as a product in the reaction of $[(\eta^5\text{-}C_5H_5)(OC)_2Mo(\mu\text{-}Bu^tCCH)Co(CO)_3]$ with $Ph_2PC{\equiv}CBu^t$.[5]

The explanation as to the different reactivity patterns is unclear but may stem from the initial mode of coordination of the phosphinoalkyne to the tungsten–cobalt framework which is dictated by the electronic demands of the particular bimetallic system. When the alkyne bridge has electron withdrawing substituents (**1a**) the bimetallic framework is electron deficient so the phosphinoalkyne binds to the cobalt centre through the phosphorus (good σ-donor) atom (see **2** in Scheme 2). Conversely, when the alkyne bridge has electron donating substituents (**1b**) the metal framework is electron rich causing the phosphinoalkyne to bind to the cobalt centre through the alkyne moiety (good π acceptor) of the phosphinoalkyne (see **E** in Scheme 3).

3 Experimental section

3.1 General techniques

All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen, using standard Schlenk techniques. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use.[24] Infrared spectra were recorded in hexane solution in 0.5 mm NaCl cells, using a Perkin-Elmer 1710 Fourier-transform spectrometer, fast atom bombardment (FAB) mass spectra on a Kratos MS 890 instrument using 3-nitrobenzyl alcohol as a matrix, proton (reference to $SiMe_4$), ^{31}P and ^{13}C NMR spectra on either a Bruker WM250 or AM400 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 with a 0.25 mm layer of silica, or on 1 mm silica plates prepared at the Department of Chemistry, Cambridge. Column chromatography was performed on Kieselgel 60 (70–230 or 230–400 mesh). Products are given in order of decreasing R_f values. Elemental analyses were performed at the Department of Chemistry, Cambridge.

Unless otherwise stated all reagents were obtained from commercial suppliers and used without further purification. The syntheses of $[(\eta^5\text{-}C_5H_5)(OC)_2W(\mu\text{-}R^1CCR^2)Co(CO)_3]$ ($R^1 = R^2 = CO_2Me$ **1a**; $R^1 = H$, $R^2 = Bu^t$ **1b**)[25,26] and $Ph_2PC{\equiv}CR$ ($R = Bu^t$ or Ph)[27] have been reported previously.

3.2 Syntheses

2, 3 and 4. To a solution of $[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}C_2(CO_2Me)_2\}Co(CO)_3]$ **1a** (0.70 g, 1.1 mmol) in toluene (70 cm^3) was added $Ph_2PC{\equiv}CPh$ (0.35 g, 1.1 mmol). The solution was stirred at 383 K for 8 h. After removal of the solvent under reduced pressure, the mixture was absorbed onto the minimum quantity of silica, added to the top of a chromatography column and purified with hexane–ethyl acetate (4 : 1) as eluent. This gave, in addition to a small amount of starting material, the complexes $[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}PhCCC(CO_2Me){=}C(CO_2Me)PPh_2\}Co(CO)_2]$ **3** (0.10 g, 19%), $[(\eta^5\text{-}C_5H_5)(OC)W\{\mu\text{-}C(CO_2Me){=}C(C{\equiv}CPh)C(OMe)O\}(\mu\text{-}PPh_2)Co(CO)_2]$ **4** (0.16 g, 19%) and $[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}C_2(CO_2Me)_2\}Co(CO)_2(PPh_2C{\equiv}CPh)]$ **2** (0.30 g, 35%). Complex **2**: FAB mass spectrum, *m*/*z* 848 (M^+) and $M^+ - nCO$ (n = 1–4); ^{13}C (^1H composite pulse decoupled), NMR ($CDCl_3$, 293 K): δ 235.0 [s, W–*C*O], 210.0 [s, Co–*C*O], 174.2 [s, *C*O_2Me], 135–128 [m, Ph], 88.0 [s, C_5H_5] and 60.5 [s, CO_2*Me*]. Complex **3**: FAB mass spectrum, *m*/*z* 848 (M^+) and $M^+ - nCO$ (n = 1–4); ^{13}C (^1H composite pulse decoupled) NMR ($CDCl_3$, 293 K): δ 206.0 [s, Co–*C*O], 136–127 [m, Ph], 87.0 [s, C_5H_5], 53.4 [s, CO_2*Me*] and 52.7 [s, CO_2*Me*]. Complex **4** (Found: C, 50.1; H, 4.0. $C_{34}H_{26}CoO_7PW$ requires C, 49.5; H, 3.8%). FAB mass spectrum, *m*/*z* 820 (M^+) and $M^+ - nCO$ (n = 1–3); ^{13}C (^1H composite pulse decoupled) NMR ($CDCl_3$, 293 K): δ 237.0 [s, W–*C*O], 210.0 [s, Co–*C*O], 207.0 [s, Co–*C*O], 187.4 [s, *C*O_2Me], 178.8 [s, *C*O_2Me], 143.0 [d, ^2J(PC) 38.2 Hz, μ-*C*(CO_2Me)C(C≡CPh)C(OMe)], 133–127 [m, Ph], 90.5 [s, μ-C(CO_2Me)C(C≡*C*Ph)C(OMe)], 90.0 [s, C_5H_5], 85.3 [s, μ-C(CO_2Me)C(C≡CPh)C(OMe)], 52.8 [s, CO_2*Me*] and 51.1 [s, CO_2*Me*].

5 and 6. To a solution of $[(\eta^5\text{-}C_5H_5)(OC)_2W(\mu\text{-}HCCBu^t)Co(CO)_3]$ **1b** (1.20 g, 2.3 mmol) in toluene (50 cm^3) was added $Ph_2PC{\equiv}CPh$ (0.70 g, 2.4 mmol). The solution was stirred at 383 K for 6 h and after removal of all volatiles under reduced pressure the residue was purified by preparative TLC with hexane–ethyl acetate (3 : 1) as eluent. This gave, in addition to a small amount of starting material, the orange complexes $[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}CBu^tCHCPhC(PPh_2)\}Co(CO)_2]$ **5** (0.12 g, 7%) and $[(\eta^5\text{-}C_5H_5)(OC)W\{\mu\text{-}CBu^tCHC(PPh_2)CPh\}Co(CO)_2]$ **6** (0.50 g, 28%). Complex **5**: FAB mass spectrum, *m*/*z* 760 (M^+) and $M^+ - nCO$ (n = 1–3); ^{13}C (^1H composite pulse decoupled) NMR ($CDCl_3$, 298 K): δ 222.0 [s, W–*C*O], 214.0 [s, Co–*C*O], 210.7 [s, Co–*C*O], 132–128 [m, Ph], 91.9 [s, μ-CBu^t=*C*HCPh=C(PPh_2)], 87.7 [s, C_5H_5], 37.0 [s, *C*Me_3] and 33.9 [s, C*Me*$_3$]. Complex **6**: FAB mass spectrum, *m*/*z* 788 (M^+) and $M^+ - nCO$ (n = 1–4); ^{13}C (^1H composite pulse decoupled) NMR ($CDCl_3$, 293 K): δ 224.3 [s, W–*C*O], 222.6 [s, W–*C*O], 203.8 [s, Co–*C*O], 202.8 [s, Co–*C*O], 171.1 [s, μ-*C*Bu^t=CHC(PPh_2)=CPh], 168.9 [d, ^1J(PC) 27, μ-CBu^t=CH*C*(PPh_2)=CPh], 152.6 [d, ^2J(PC) 9, μ-CBu^t=CHC(PPh_2)=*C*Ph], 139–123 [m, Ph], 111.3 [d, ^2J(PC) 22, μ-CBu^t=*C*HC(PPh_2)=CPh], 88.4 [s, C_5H_5], 43.5 [s, *C*Me_3] and 34.5 [s, C*Me*$_3$].

7. To a solution of $[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}CBu^tCHC(PPh_2)CPh\}Co(CO)_2]$ **6** (0.45 g, 0.57 mmol) in THF (50 cm^3) was added $[Fe_2(CO)_9]$ (0.28 g, 0.76 mmol). The solution was stirred at 333 K for 5 h and after removal of the volatiles under reduced pressure the residue was purified by preparative TLC using hexane–ethyl acetate (3 : 1) as eluent. This gave in addition to a small amount of starting material, the orange complex $[(\eta^5\text{-}C_5H_5)(OC)_2W\{\mu\text{-}CBu^tCHC(PPh_2Fe(CO)_4)CPh\}Co(CO)_2]$ **7** (0.23 g, 41%). FAB mass spectrum: *m*/*z* 956 (M^+) and $M^+ - nCO$ (n = 1–8). ^{13}C (^1H composite pulse decoupled) NMR ($CDCl_3$, 293 K): δ 221.9 [s, W–*C*O], 220.4 [s, W–*C*O], 213.8 [d, ^2J(PC) 17, Fe–*C*O], 202.3 [s, Co–*C*O], 179.2 [s, μ-*C*Bu^t=CHC($PPh_2Fe(CO)_4$)=CPh], 168.4 [d, ^1J(PC) 21, μ-CBu^t=CH*C*($PPh_2Fe(CO)_4$)=CPh], 150.4 [d, ^2J(PC) 9, μ-CBu^t=CHC($PPh_2Fe(CO)_4$)=*C*Ph], 137–124 [m, Ph], 119.0 [d, ^2J(PC) 12, μ-CBu^t=*C*HC($PPh_2Fe(CO)_4$)=*C*Ph], 89.3 [s, C_5H_5], 45.9 [s, *C*Me_3] and 34.5 [s, C*Me*$_3$].

8. To a solution of $[(\eta^5\text{-}C_5H_5)(OC)_2W(\mu\text{-}HCCBu^t)Co(CO)_3]$ **1b** (1.0 g, 1.88 mmol) in toluene (50 cm^3) was added $Ph_2PC{\equiv}CBu^t$ (0.50 g, 1.88 mmol). The solution was stirred at 383 K for 6 h and after removal of solvent under reduced pressure the residue was purified by preparative TLC using hexane–ethyl acetate (3 : 1) as eluent. This gave, in addition to starting material, the orange complex $[(\eta^5\text{-}C_5H_5)(OC)W\{\mu\text{-}CBu^tCHCBu^tC(PPh_2O)\}Co(CO)_2]$ **8** (0.64 g, 34%). FAB mass spectrum: *m*/*z* 776 (M^+) and $M^+ - nCO$ (n = 1–3). ^{13}C (^1H composite pulse decoupled) NMR ($CDCl_3$, 293 K): δ 236.7 [s, W–*C*O], 208.5 [s, Co–*C*O], 175.3 [d, ^3J(PC) 3, *J*(WC) 41, μ-*C*Bu^t=CHCBu^t=C(PPh_2O)], 171.2 [s, μ-CBu^t=CH*C*Bu^t=C(PPh_2O)], 138–127 [m, Ph and μ-CBu^t=CHCBu^t=*C*(PPh_2O)], 108.7 [d, ^2J(PC) 18,

Table 6 Crystallographic and data processing parameters for complexes **4**, **6**, **7** and **8**

	4	**6**	**7**	**8**
Empirical formula	$C_{34}H_{26}CoO_7PW$	$C_{35}H_{30}CoO_4PW{\cdot}CH_2Cl_2$	$C_{39}H_{30}CoFeO_8PW$	$C_{32}H_{34}CoO_4PW$
Formula weight	820.30	873.27	956.23	756.34
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P21/n$
a/Å	15.501(16)	9.451(5)	11.688(6)	10.990(5)
b/Å	12.623(14)	9.870(5)	17.919(9)	12.809(5)
c/Å	31.390(14)	35.91(2)	17.359(9)	21.080(5)
β/°	91.95(6)	91.59(3)	103.54(2)	102.81(4)
U/Å^3	6138(10)	3348(2)	3535(3)	2894(1)
Z	8	4	4	4
μ(Mo-Kα)/mm^{-1}	4.386	4.174	4.214	4.636
Reflections collected	32480	5886	4644	23089
Independent reflections	10491 (R_{int} = 0.069)	5875 (R_{int} = 0.038)	4605 (R_{int} = 0.029)	4999 (R_{int} = 0.063)
Parameters/restraints	793/0	364/0	463/0	359/0
Final R indices $I > 2\sigma(I)$[a]	$R1$ = 0.0476	$R1$ = 0.0462	$R1$ = 0.0308	$R1$ = 0.0352
	$wR2$ = 0.1017	$wR2$ = 0.0974	$wR2$ = 0.0780	$wR2$ = 0.0663
All data	$R1$ = 0.0592	$R1$ = 0.0656	$R1$ = 0.0404	$R1$ = 0.0583
	$wR2$ = 0.1150	$wR2$ = 0.1178	$wR2$ = 0.0864	wR_2 = 0.0709

Data in common: graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å, 180(2) K.

μ-CBu^t=*C*HCBu^t=C(PPh$_2$O)], 90.2 [s, C_5H_5], 45.7 [s, *C*Me$_3$], 37.0 [s, *C*Me$_3$], 34.9 [s, C*Me*$_3$] and 32.1 [s, C*Me*$_3$].

3.3 Crystal structure determinations of complexes 4, 6, 7 and 8

X-Ray intensity data was collected using a Siemens STOE AED four-circle diffractometer (compounds **6** and **7**) and a Rigaku RAXIS-IIC image plate system (**4** and **8**). Both instruments were equipped with an Oxford Cryosystems Cryostream. Details of data collection, refinement and crystal data are listed in Table 6. All data were corrected for Lorentz-polarisation factors. Semi-empirical absorption corrections based on ψ scans[28] were applied to the data for **6** and **7**, a spherical absorption correction was applied to the data for **8** and no absorption correction was applied to the data for **4**. Structures were solved and refined with the programs SHELXS 97[29] and SHELXL 97[30] respectively. Refinement was based on F^2. Hydrogen atoms were placed in idealised positions and refined using either a riding model or as rigid methyl groups.

CCDC reference numbers 154853–154856.

See http://www.rsc.org/suppdata/dt/b0/b009396n/ for crystallographic data in CIF or other electronic format.

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