

Synthesis of New Alkyne-bridged Ditungsten Complexes $[W_2(CO)_4(\mu-HC_2R)(\eta-C_5H_5)_2]$ ($R = Me$ or Ph) and the Reactions of these and Related Alkyne-bridged Complexes with Chlorodiphenylphosphine†

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The new ditungsten alkyne-bridged complexes $[W_2(CO)_4(\mu-R^1C_2R^2)(\eta-C_5H_5)_2]$ ($R^1 = H$, $R^2 = Ph$ **1c** or Me **1d**) have been prepared. These and the related complexes with $R^1 = R^2 = Ph$ **1a** or CO_2Me **1b** were treated with PPh_2Cl in refluxing xylene or toluene. The identity of the products depends on the nature of the R group but in general their formation involves the oxidative addition of one or more molecules of PPh_2Cl to **1**. From **1a** two species, $[W_2Cl(\mu-PPh_2)(\mu-PhC_2Ph)(CO)(\eta-C_5H_5)_2]$ **2a** and $[W_2(O)Cl(\mu-PPh_2)(\mu-PhC_2Ph)(\eta-C_5H_5)_2]$ **4a**, in which the alkyne bridge remains intact were isolated, along with a paramagnetic complex, $[W_2Cl(\mu-PPh_2)_2(CO)(\eta-C_5H_5)_2]$ **3a**, from which the alkyne bridge has been displaced by a diphenylphosphide group. Reaction of **1b** with PPh_2Cl gave $[W_2Cl(\mu-PPh_2)(\mu-C_2(CO_2Me)_2)(CO)(\eta-C_5H_5)_2]$ **2b**, an analogue of **2a**, together with two complexes involving phosphorus-carbon bond formation, $[W_2(\mu-Cl)\{\mu-PPh_2C(CO_2Me)=C(CO_2Me)\}(CO)_2(\eta-C_5H_5)_2]$ **6b** and $[W_2Cl_2(\mu-PPh_2)\{\mu-PPh_2C=CH(CO_2Me)\}(\eta-C_5H_5)_2]$ **5b**. The formation of **5b**, involves, in addition, cleavage of a carbon-carbon bond. From **1c**, both of the products, $[W_2Cl_2(\mu-PPh_2)\{\mu-PPh_2C=CHPh\}(\eta-C_5H_5)_2]$ **5c** and $[W_2Cl_2(\mu-Cl)(\mu-PPh_2C=CHPh)(\eta-C_5H_5)_2]$ **7c**, involve phosphorus-carbon bond formation. Finally from **1d** the only well characterised product is a terminal oxo species, $[W_2O(\mu-PPh_2)(\mu-CH=CHMe)(CO)(\eta-C_5H_5)_2]$ **8d**, in which a vinyl group and a phosphide fragment bridge the two metal centres. A complex related to **8d**, $[W_2O(\mu-PPh_2)\{\mu-C(CO_2Me)=CH(CO_2Me)\}(CO)(\eta-C_5H_5)_2]$ **8b**, is formed on treatment of **2b** with silica. Thermolysis of complex **6b** results in phosphorus-carbon bond cleavage to give **2b**. In contrast, photolysis of **6b** gives, as the only well characterised product, paramagnetic $[W_2Cl(\mu-Cl)\{\mu-PPh_2C(CO_2Me)=C(CO_2Me)\}(CO)(\eta-C_5H_5)_2]$ **9b**. The structures of complexes **2a**, **3a** and **9b** have been determined by X-ray crystallography.

In recent years the reactivity of alkyne-bridged dinuclear transition-metal carbonyl complexes towards organophosphines containing phosphorus-hydrogen, phosphorus-phosphorus, phosphorus-sulfur or phosphorus-carbon bonds has been the subject of a series of reports.¹⁻⁵ Such reactions can involve the cleavage of these bonds to give a wide variety of dinuclear transition-metal complexes which, in some cases, result from phosphorus-carbon or carbon-carbon bond formation subsequent to the initial cleavage step.

Studies on the reactivity of alkyne-bridged complexes towards halogenophosphines are less well documented. Cleavage of a phosphorus-chlorine bond has, however, been previously observed in the reactions of $[Mo_2(CO)_4(\mu-R^1C_2R^2)(\eta-C_5H_5)_2]$ ($R^1 = H$, $R^2 = H$, Me or Ph ; $R^1 = R^2 = CO_2Me$ or Me) with chlorodiphenylphosphine which afford products resulting from transformations of the bridging alkyne group.⁶

This report describes the synthesis of the new alkyne-bridged ditungsten complexes $[W_2(CO)_4(\mu-R^1C_2R^2)(\eta-C_5H_5)_2]$ ($R^1 = H$, $R^2 = Ph$ **1c** or Me **1d**) and presents a study of the reactivity of these and of related complexes towards PPh_2Cl with particular regard to any differences as compared to the molybdenum analogues. Some of the preliminary results of this work have been reported briefly elsewhere.⁷

Results and Discussion

(1) *Synthesis of $[W_2(CO)_4(\mu-R^1C_2R^2)(\eta-C_5H_5)_2]$ ($R^1 = H$, $R^2 = Ph$ **1c** or Me **1d**).*—The new ditungsten complexes were synthesised by a method similar to that used for related complexes.⁸ Heating a diglyme (2,5,8-trioxanonane) solution of $[W_2(CO)_6(\eta-C_5H_5)_2]$ under reflux for 5–7 h, whilst purging with nitrogen, affords the triply bonded complex $[W_2(CO)_4(\eta-C_5H_5)_2]$ which, on addition of $PhC\equiv CH$ or $MeC\equiv CH$, gives **1c** and **1d** respectively. Both **1c** and **1d** have been characterised on the basis of spectroscopic evidence (see Table 1 and Experimental section) and by a comparison of these data with those for other known transverse alkyne complexes.^{8,9}

The IR spectra of complexes **1c** and **1d** in hexane respectively show three and four absorption bands in the carbonyl region, the overall patterns being similar to the IR spectra of related complexes.⁸ An absorption due to a bridging carbonyl is seen in each case (at about 1835 cm^{-1}). The 1H NMR spectra of **1c** and **1d** both show a singlet resonance due to the two equivalent cyclopentadienyl ligands in each molecule. Signals due to the protons directly bonded to the bridging alkyne carbon atoms in **1c** and **1d** are seen respectively as a singlet at δ 4.72 and as a quartet at δ 4.76, the quartet splitting being due to coupling to the methyl group [$^3J(HH)$ 0.7 Hz]. Two upfield peaks seen in the $^{13}C\{-^1H\}$ NMR spectrum (at 293 K) of **1c**, at δ 53.3 and 45.7, may be attributed to the non-equivalent bridging alkyne carbon atoms.

(2) *Thermolysis of $[W_2(CO)_4(\mu-R^1CCR^2)(\eta-C_5H_5)_2]$ ($R^1 = R^2 = Ph$ **1a** or CO_2Me **1b**; $R^1 = H$, $R^2 = Ph$ **1c** or $R^2 = Me$*

† Reactivity of Halogenophosphines towards Transition-metal Complexes. Part 1.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 NMR data for the new complexes (cp = η -C₅H₅)

Compound	NMR ^a
1c -0.5CH ₂ Cl ₂	¹ H: ^b 7.3–7.0 (m, 6 H, Ph), 5.35 (s, 10 H, cp), 5.25 (s, 1 H, CH ₂ Cl ₂), 4.72 (s, 1 H, HC ₂ Ph) ¹³ C- ¹ H: ^b 217.3 (s, CO), 217.1 (s, CO), 146.0 (s, C _{ipso} , Ph), 130.3 (s, C _{ortho} , Ph), 128.0 (s, C _{meta} , Ph), 125.2 (s, C _{para} , Ph), 89.5 (s, cp), 53.3 (s, CH ₂ Cl ₂ or HCCPh), 45.7 (s, HCCPh)
1d	¹ H: ^b 5.33 (s, 10 H, cp), 4.76 [q, ⁴ J(HH) 0.7, 1 H, HCCMe], 2.66 (d, 3 H, HC ₂ Me)
2a	¹ H: ^b 8.0–6.9 (m, 20 H, cp), 5.57 (s, 5 H, cp), 4.85 (s, br, 5 H, cp) ¹³ C- ¹ H: ^b 208.7 (s, CO), 131.6–125.6 (m, Ph), 94.8 (s, br, cp), 90.6 (s, cp) ³¹ P- ¹ H: ^c -59.6 [s, ¹ J(WP) 366.9, μ -PPh ₂]
2b	¹ H: ^b 8.1–6.4 (m, 10 H, Ph), 5.71 [d, ³ J(PH) 0.7, 5 H, cp], 5.23 [d, ³ J(PH) 1.1, 5 H, cp], 3.98 (s, 3 H, Me), 3.76 (s, 3 H, Me) ¹³ C- ¹ H: ^b 201.9 (s, CO), 177.2 (s, CO ₂ Me), 177.0 (s, CO ₂ Me), 147.9 [d, ¹ J(PC) 46.7, PC], 138.6 [d, ¹ J(PC) 53.0, PC], 135.2–127.5 (m, Ph), 96.0 (s, cp), 90.7 (s, cp), 52.5 (s, CO ₂ Me), 52.4 (s, CO ₂ Me) ³¹ P- ¹ H: ^c -46.4 [s, ¹ J(WP) 357.2, μ -PPh ₂]
3a	Paramagnetic
4a	¹ H: ^b 8.4–7.2 (m, 20 H, Ph), 5.35 [d, ³ J(PH) 1.0, 5 H, cp], 4.54 (s, 5 H, cp) ³¹ P- ¹ H: ^c -40.5 [s, ¹ J(WP) 305.9, μ -PPh ₂]
5b	¹ H: ^b 8.3–7.1 (m, 20 H, Ph), 4.43 [dd, ³ J(PH) 0.8, ³ J(P'H) 0.8, 5 H, cp], 4.39 [dd, ³ J(PH) 1.8, ³ J(P'H) 0.4, 5 H, cp], 3.94 (s, 3 H, Me), 2.05 [dd, ³ J(PH) 6.1, ³ J(P'H) 1.2, 1 H, CHCO ₂ Me] ¹³ C- ¹ H: ^b 178.2 (s, CO ₂ Me), 145.0 [d, ¹ J(PC) 43.8, μ -C], 143.4 [d, ¹ J(PC) 38.4, PC], 137.0–126.5 (m, Ph), 96.7 (s, cp), 92.8 (s, cp), 51.4 (s, CO ₂ Me), 47.2 [d, ² J(PC) 12.9, CHCO ₂ Me] ³¹ P- ¹ H: ^c -20.9 [d, ² J(PP) 60.8, ¹ J(WP) 280.3, μ -PPh ₂], -246.0 [d, ¹ J(WP) 244.6, μ -Ph ₂ PC=CHCO ₂ Me]
5c	¹ H: ^b 8.4–6.7 (m, 25 H, Ph), 4.35 [dd, ³ J(PH) 0.8, ³ J(P'H) 0.8, 5 H, cp], 4.00 [d, ³ J(PH) 1.6, 5 H, cp], 2.58 [dd, ³ J(PH) 8.0, ³ J(P'H) 2.0, 1 H, CHPh] ¹³ C- ¹ H: ^b 149.6 (s, PC), 147.1 (s, PC), 146.6 [d, ¹ J(PC) 12.1, μ -C], 136.7–123.9 (m, Ph), 96.5 (s, cp), 93.2 (s, cp), 62.9 [d, ² J(PC) 13.8, CHPh] ³¹ P- ¹ H: ^c -26.0 [dd, ² J(PP) 62.2, ¹ J(WP) 278.1, μ -PPh ₂], -238.9 [dd, ¹ J(WP) 121.8, μ -Ph ₂ PC=CHPh]
6b -CH ₂ Cl ₂	¹ H: ^b 8.0–7.2 (m, 10 H, Ph), 5.25 (s, 2 H, CH ₂ Cl ₂), 4.90 [d, ³ J(PH) 1.9, 5 H, cp], 4.86 (s, 5 H, cp), 3.80 (s, 3 H, Me), 3.61 (s, 3 H, Me) ¹³ C- ¹ H: ^b 240.3 [d, ² J(PC) 8.4, CO], 222.9 (s, CO), 182.1 [d, J(PC) 4.6, CO ₂ Me], 176.1 [d, J(PC) 5.3, CO ₂ Me], 140.2 [d, ¹ J(PC) 25.0, PC], 133.1 [d, ¹ J(PC) 46.7, PC], 130.9–128.2 (m, Ph), 99.6 (s, CCO ₂ Me), 91.6 (s, cp), 90.3 (s, cp), 53.4 (s, CH ₂ Cl ₂), 51.1 (s, Me), 50.7 (s, Me), 31.4 [d, J(PC) 45.8, CCO ₂ Me] ³¹ P- ¹ H: ^c -143.4 [s, ¹ J(WP) 239.0, μ -Ph ₂ PC(CO ₂ Me)=C(CO ₂ Me)]
7c	¹ H: ^b 8.2–6.9 (m, 15 H, Ph), 4.87 [d, ³ J(PH) 1.6, 5 H, cp], 4.53 (s, 5 H, cp), 2.84 [d, ³ J(PH) 6.1, 1 H, CHPh] ¹³ C- ¹ H: ^b 149.0 (s, μ -C), 136.7–124.4 (m, Ph), 96.9 (s, cp), 94.8 (s, cp), 29.7 (s, CHPh) ³¹ P- ¹ H: ^c -247.5 [s, ¹ J(WP) 161.0, μ -Ph ₂ PC=CHPh]
8b	¹ H: ^b 8.0–6.7 (m, 10 H, Ph), 5.64 [d, ³ J(PH) 0.9, 5 H, cp], 5.28 [d, ³ J(PH) 1.2, 5 H, cp], 3.95 (s, 3 H, Me), 3.68 (s, 3 H, Me), 2.93 [dd, ³ J(PH) 0.3, ² J(WH) 4.8, 1 H, CHCO ₂ Me] ¹³ C- ¹ H: ^b 216.6 (s, CO), 181.0 (s, CO ₂ Me), 176.4 (s, CO ₂ Me), 145.9 [d, ¹ J(PC) 47.5, PC], 134.9 [d, ¹ J(PC) 10.8, PC], 132.3–128.1 (m, Ph), 102.5 (s, cp), 89.9 (s, cp), 52.1 (s, CO ₂ Me), 51.1 (s, CO ₂ Me), 30.0 [s, C(CO ₂ Me)=CHCO ₂ Me] ³¹ P- ¹ H: ^c -17.6 [s, ¹ J(WP) 326.9, μ -PPh ₂]
8d	¹ H: ^b 8.0–7.1 (m, 10 H, Ph), 7.63 [d, ³ J(H ¹ H ²) 9.1, 1 H, H ¹], 5.19 [s, br, 5 H, cp], 4.77 [d, ³ J(PH) 1.6, 5 H, cp], 2.77 [dq, ³ J(H ² Me) 5.9, 1 H, H ²], 1.95 (d, 3 H, Me) ¹³ C- ¹ H: ^b 230.8 (s, CO), 146.6 [d, ¹ J(PC) 40.7, PC], 139.7 [d, ¹ J(PC) 50.3, PC], 135.8 [d, ² J(PC) 11.0, C _{ortho} , Ph], 133.7 [d, ² J(PC) 11.5, C _{ortho} , Ph], 132.7 (s, C _{para} , Ph), 129.7 (s, μ -C), 128.4 [d, ³ J(PC) 11.4, C _{meta} , Ph], 128.3 (s, C _{para} , Ph), 127.9 [d, ³ J(PC) 10.8, C _{meta} , Ph], 100.9 (s, cp), 87.6 (s, cp), 32.4 (s, Me), 28.6 (s, CH=CHMe) ³¹ P- ¹ H: ^c -18.3 [s, ¹ J(WP) 349.5, μ -PPh ₂]
9b	Paramagnetic

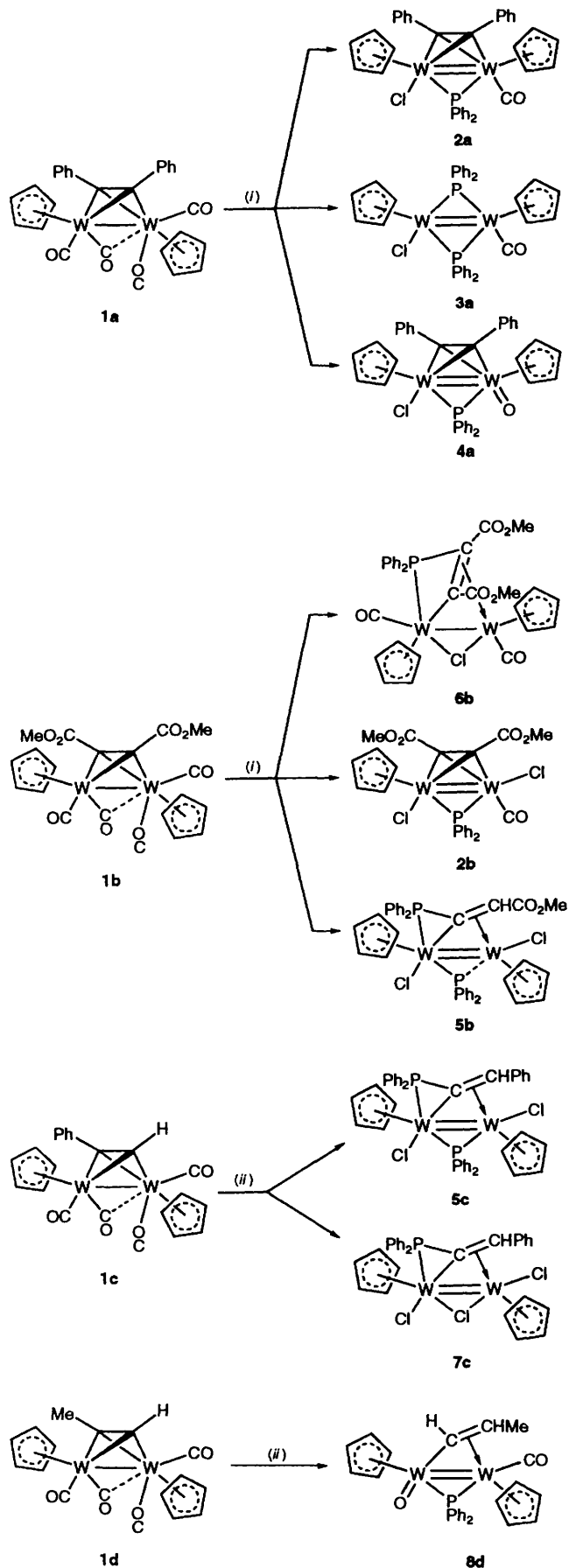
^a Data for ¹H given as: chemical shift (δ) [multiplicity (*J* in Hz), relative intensity, assignment], etc. ^b Recorded in CDCl₃ solution at 293 K. ^c Recorded in CDCl₃ solution, values relative to external P(OMe)₃ (0.0 ppm) (upfield shifts negative), measured at 293 K.

1d with PPh₂Cl.—Solutions of a number of transverse alkyne complexes of general formula [W₂(CO)₄(μ -R¹CCR²)(η -C₅H₅)₂] were heated with an excess of chlorodiphenylphosphine, the products from these reactions (Scheme 1) depending on the nature of R¹ and R².

Heating [W₂(CO)₄(μ -PhC₂Ph)(η -C₅H₅)₂] **1a** in xylene under reflux for 6 h with 2 equivalents of PPh₂Cl affords the complexes [W₂Cl(μ -PPh₂)(μ -PhC₂Ph)(CO)(η -C₅H₅)₂] **2a**, [W₂Cl(μ -PPh₂)₂(CO)(η -C₅H₅)₂] **3a** and [W₂O(Cl(μ -PPh₂)(μ -PhC₂Ph)(η -C₅H₅)₂)] **4a**. Complexes **2a** and **3a** migrate on a TLC plate as one band. The presence of the paramagnetic complex **3a** is only inferred from NMR studies on the mixture of **2a** and **3a**, its structure being revealed by single-crystal X-ray diffraction (see later and Fig. 2). Heating a xylene solution of [W₂(CO)₄(μ -C₂(CO₂Me)₂)(η -C₅H₅)₂] **1b** under reflux with 2 equivalents of PPh₂Cl for 60 h produces a number of new complexes: [W₂Cl₂(μ -PPh₂)(μ -PPh₂C=CH(CO₂Me))-(η -C₅H₅)₂] **5b**, [W₂(μ -Cl)(μ -PPh₂C(CO₂Me)=C(CO₂Me))-(CO)₂(η -C₅H₅)₂] **6b** (major product) and [W₂Cl(μ -PPh₂)(μ -C₂(CO₂Me)₂)(CO)(η -C₅H₅)₂] **2b**. Complex **2b** may also be synthesised by prolonged thermalolysis of **6b** in refluxing xylene

(see later). Heating a toluene solution of [W₂(CO)₄(μ -HC₂Ph)(η -C₅H₅)₂] **1c** under reflux for 24 h with 2 equivalents of PPh₂Cl affords a number of products, of which two were characterised. These are the new complexes [W₂Cl₂(μ -PPh₂)(μ -PPh₂C=CHPh)(η -C₅H₅)₂] **5c** and [W₂Cl₂(μ -Cl)(μ -PPh₂C=CHPh)(η -C₅H₅)₂] **7c**. Heating a toluene solution of [W₂(CO)₄(μ -HC₂Me)(η -C₅H₅)₂] **1d** to 373 K for 75 min with 2 equivalents of PPh₂Cl yields [W₂O(μ -PPh₂)(μ -CH=CHMe)(CO)(η -C₅H₅)₂] **8d** as the only product. The complexes **2**, **4a**, **5**, **6b**, **7c** and **8d** have been characterised spectroscopically (see Table 1 and Experimental section) and in addition complexes **2a** and **3a** by single-crystal X-ray diffraction studies.

(a) *Characterisation of* [W₂Cl(μ -PPh₂)(μ -R¹C₂R²)(CO)(η -C₅H₅)₂] (R¹ = R² = Ph **2a** or CO₂Me **2b**). The electron-impact (EI) mass spectra of complexes **2a** and **2b** show peaks due to the molecular ions and to the loss of one carbonyl ligand in each case. One band is seen in the terminal carbonyl region of the IR spectra of both **2a** and **2b** in CH₂Cl₂ solution (at 1960 and 1993 cm⁻¹ respectively) and in the case of **2b** an additional band is observed at 1694 cm⁻¹ due to the ν (C=O) stretch of the



Scheme 1 Products from the reactions of $[\text{W}_2(\text{CO})_4(\mu\text{-R}^1\text{C}_2\text{R}^2)(\eta\text{-C}_5\text{H}_5)_2]$ ($\text{R}^1 = \text{R}^2 = \text{Ph}$ **1a** or CO_2Me **1b**; $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Ph}$ **1c** or $\text{R}^2 = \text{Me}$ **1d**) with PPh_2Cl : (i) xylene, reflux; (ii) toluene, reflux

CO_2Me group. Two separate resonances are present in the ^1H NMR spectrum of **2a** and **2b** due to the two non-equivalent cyclopentadienyl groups in each complex (δ 5.57 and 4.85 **2a**, δ 5.71 and 5.23 **2b**). Both the cyclopentadienyl resonances in the spectrum of **2b** are coupled to phosphorus [$^3J(\text{PH})$ 0.7 and 1.1 Hz], whereas no such coupling is resolved in the spectrum of **2a**, presumably because of the broadening induced by the presence of the paramagnetic complex **3a**.

The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra of complexes **2a** and **2b** show resonances at δ -59.6 and -46.4 [relative to $\text{P}(\text{OMe})_3$, δ 0.0] respectively which are consistent with the phosphido groups bridging the metal centres. The latter signal is accompanied by clearly resolved ^{183}W satellites, $^1J(\text{WP})$ 357.2 Hz (**2b**), while the broadness of the signal for the former (**2a**) can be attributed to the presence of the paramagnetic **3a**.

Based on this spectroscopic data complexes **2a** and **2b** are assigned the structures shown in Scheme 1. Confirmation of the structure of **2a** and, in addition, the deduction of the structure of paramagnetic **3a** was achieved by a single-crystal X-ray analysis. It is noteworthy that no evidence for the presence of **3a** was obtained from the FAB or EI mass spectra or IR spectrum of **2a** and indeed the microanalysis seems more consistent with pure **2a** (see Experimental section). These observations may reflect the low concentration of **3a** in the bulk sample.

The molecular structures of complexes **2a** and **3a** are shown in Figs. 1 and 2 respectively, both species being found in one crystal. Suitable crystals were grown from a CH_2Cl_2 -hexane solution by means of the solvent-diffusion method. Two independent molecular units **A** and **B** are present in the cell, **A** being a 50:50 disorder of a molecule of **2a** and one of **3a** and **B** a molecule of **2a**. The structures of **2a** and **3a** in the disordered molecular unit **A** are superimposed, except for the two alkyne carbons in **2a** which are replaced by a second phosphorus atom in **3a**. Throughout the following discussion the bond lengths for **2a** are those of the single-component molecular unit **B**. The bond lengths and angles for the two components of molecular unit **A** (**2a** and **3a**) and of molecular unit **B** (**2a**) are listed in Table 2.

The two tungsten atoms in complex **2a** are bridged by a diphenylphosphide and a diphenylacetylene group with a cyclopentadienyl and a carbonyl ligand bonded to one tungsten atom and a cyclopentadienyl and a chloride to the other. The two cyclopentadienyl groups are in a *cis* arrangement, as are the chloride and carbonyl ligands. The 18-electron rule requires a double bond between the metal centres in **2a** and indeed the tungsten-tungsten bond distance [2.660(1) Å] is slightly shorter than the $\text{W}=\text{W}$ double bond [2.681(1) Å] in the phosphide-bridged species $[\text{W}_2\text{Cl}_4(\mu\text{-H})(\mu\text{-PHC}_2\text{H}_3)(\eta\text{-C}_5\text{Me}_5)_2]$,¹⁰ and is considerably shorter than the $\text{Mo}=\text{Mo}$ bond length [2.714(1) Å] in the dimolybdenum bis(phosphido) complex $[\text{Mo}_2(\mu\text{-PPh}_2)_2(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$.¹¹ The metal-metal bond is approximately symmetrically bridged by the diphenylphosphide group; however, a minor displacement towards $\text{W}(2)$ is observed, the $\text{W}(1)\text{-P}(1)$ bond length being 0.029 Å longer than $\text{W}(2)\text{-P}(1)$.

The bridging alkyne in complex **2a** is on the opposite side of the tungsten-tungsten bond from the phosphide group. In a perfect tetrahedrane structure (M_2C_2) the alkyne would lie in a plane which is perpendicular to the M-M bond and θ (the twist angle of the acetylenic carbon atoms away from this perpendicular plane) would equal 0° . However, in **2a** there is a significant twist of the alkyne ($\theta = 10.3^\circ$) away from this perpendicular orientation. As a result the $\text{W}(1)\text{-C}(3)$ and $\text{W}(2)\text{-C}(4)$ bonds [2.172(12) and 2.358(10) Å respectively] are longer than the $\text{W}(2)\text{-C}(3)$ and $\text{W}(1)\text{-C}(4)$ bonds [2.125(10) and 2.114(12) Å respectively]. The twist is probably the result of steric constraints imposed by the bulky bridging alkyne, and similar or even larger twist angles have been observed in other ditungsten transverse alkyne complexes.¹² The $\text{C}(3)\text{-C}(4)$ alkyne bond length [1.296(16) Å] is shorter than those previously observed in transverse alkyne complexes [1.329(6)-1.450(1) Å]^{12,13a,b} but the difference is of low significance.

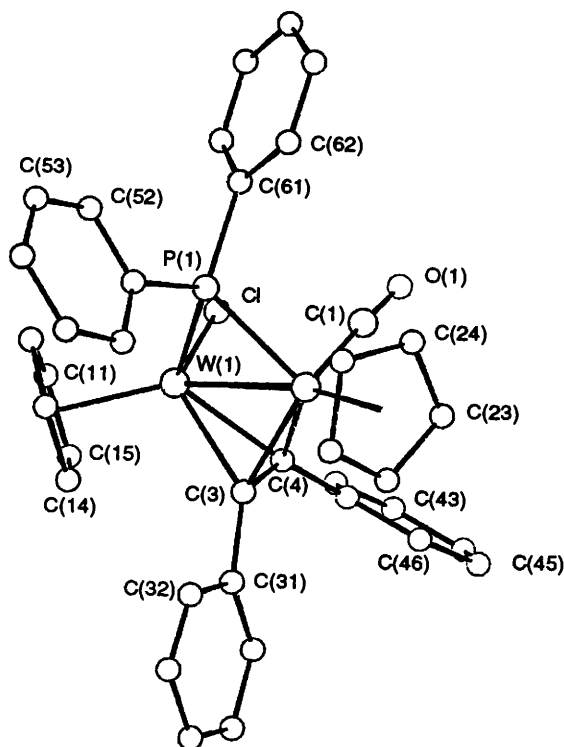


Fig. 1 Structure of one of the two independent molecules of $[\text{W}_2\text{Cl}(\mu\text{-PPh}_2)(\mu\text{-PhC}_2\text{Ph})(\text{CO})(\eta\text{-C}_5\text{H}_5)_2]$ **2a**. The molecule illustrated occurs in molecular unit A. Hydrogen atoms have been omitted for clarity

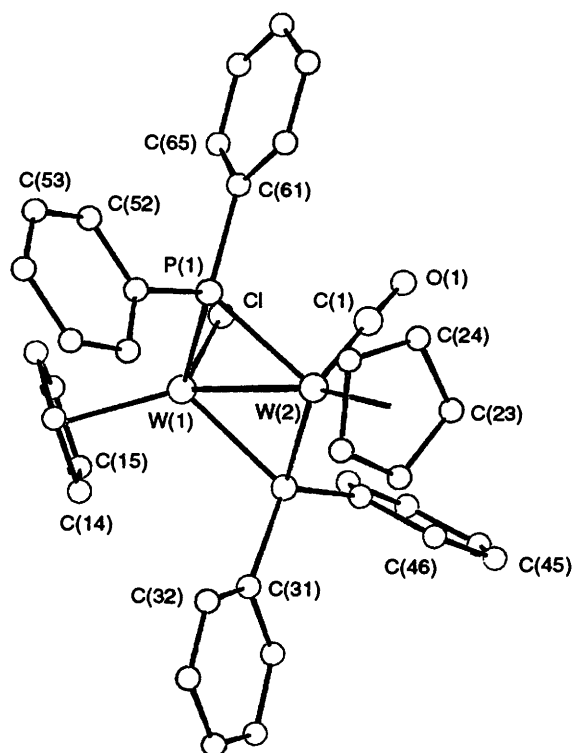


Fig. 2 Molecular structure of $[\text{W}_2\text{Cl}(\mu\text{-PPh}_2)_2(\text{CO})(\eta\text{-C}_5\text{H}_5)_2]$ **3a** disordered in a 50:50 ratio with **2a** in molecular unit A of crystal **2a/3a**. Hydrogen atoms have been omitted for clarity

(b) *Characterisation of $[\text{W}_2\text{Cl}(\mu\text{-PPh}_2)_2(\text{CO})(\eta\text{-C}_5\text{H}_5)_2]$ **3a**.* The molecular structure of complex **3a**, depicted in Fig. 2, shows that the tungsten atoms are bridged by two diphenylphosphide ligands. As in **2a**, a cyclopentadienyl and a carbonyl group are bonded to one tungsten [W(2)] and a

Table 2 Selected bond lengths (Å) and angles (°) for the two independent molecules of complex **2a** and the disordered molecule of **3a**

	Molecular unit A of 2a/3a	Molecule B 2a	
W(1)–W(2)	2.654(1)	2.660(1)	
W(1)–Cl	2.416(4)	2.412(4)	
W(1)–P(1)	2.298(5)	2.371(3)	
W(1)–C(3)	2.171(15)	2.172(12)	
W(1)–C(4)	2.115(18)	2.114(12)	
W(2)–P(1)	2.271(6)	2.342(4)	
W(2)–C(3)	2.129(11)	2.125(10)	
W(2)–C(4)	2.362(17)	2.358(10)	
W(2)–C(1)	1.974(14)	1.952(14)	
C(3)–C(4)	1.31(3)	1.293(16)	
C(1)–O(1)	1.137(18)	1.157(17)	
Unique to complex 3a			
W(1)–P(2)	2.282(10)	W(2)–P(2)	2.240(9)
Molecular unit A of 2a/3a			
Cl–W(1)–W(2)	107.7(1)	Molecule B 2a	108.0(1)
P(1)–W(1)–W(2)	54.0(1)		55.1(1)
P(1)–W(1)–Cl	101.8(2)		95.7(1)
C(3)–W(1)–W(2)	51.2(3)		51.0(3)
C(3)–W(1)–Cl	119.8(6)		124.1(3)
C(3)–W(1)–P(1)	101.3(4)		102.8(3)
C(4)–W(1)–W(2)	58.1(4)		57.9(3)
C(4)–W(1)–Cl	84.3(5)		89.1(3)
C(4)–W(1)–P(1)	110.2(4)		110.8(3)
P(1)–W(2)–W(1)	55.0(1)		56.2(1)
C(3)–W(2)–W(1)	52.6(4)		52.6(3)
C(3)–W(2)–P(1)	103.5(4)		105.3(3)
C(4)–W(2)–W(1)	49.4(4)		49.4(3)
C(4)–W(2)–P(1)	102.8(4)		103.6(3)
C(1)–W(2)–W(1)	85.0(4)		86.4(4)
C(1)–W(2)–P(1)	87.2(5)		86.5(5)
C(1)–W(2)–C(3)	107.3(7)		108.0(5)
C(1)–W(2)–C(4)	73.9(6)		75.0(5)
W(2)–P(1)–W(1)	71.0(2)		68.7(1)
O(1)–C(1)–W(2)	176(1)		178(1)
Unique to complex 3a			
W(2)–P(2)–W(1)	71.9(3)	P(2)–W(2)–W(1)	54.8(2)
P(2)–W(1)–W(2)	53.3(2)	P(2)–W(2)–P(1)	109.6(3)
P(2)–W(1)–P(1)	102.7(3)	C(1)–W(2)–P(2)	90.9(5)
P(2)–W(1)–P(1)	107.2(3)		

cyclopentadienyl and a chloride to the other [W(1)]. The two cyclopentadienyl ligands are in a *cis* arrangement as are the chloride and carbonyl ligands.

As the structures of complex **2a** (molecular unit A) and **3a** are superimposed, except for the replacement of the four-electron donor bridging alkyne in **2a** by a three-electron donor bridging phosphide group in **3a**, most of the bond lengths and angles in **3a** are the same as those of **2a** (molecular unit A). The tungsten–tungsten bond is bridged in an approximately symmetrical fashion by the two phosphide groups, with a slight displacement of both P atoms towards W(2). The W_2P_2 core is virtually planar (maximum deviation 0.04 Å), which may be compared with the exactly planar Mo_2P_2 core observed in $[\text{Mo}_2(\mu\text{-PPh}_2)_2(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$.¹¹

(c) *Characterisation of $[\text{W}_2(\text{O})\text{Cl}(\mu\text{-PPh}_2)(\mu\text{-PhC}_2\text{Ph})(\eta\text{-C}_5\text{H}_5)_2]$ **4a**.* Complex **4a** has been characterised on the basis of spectroscopic data. The EI mass spectrum shows parent peaks at 12 mass units less than those seen in the spectrum of **2a**, which indicates the replacement of a carbonyl ligand by an oxo group. No absorption bands are seen in the carbonyl region of the IR spectrum of **4a**. However, a comparison of the IR spectrum of a KBr disc of **4a** with that of **2a** shows an additional band in the spectrum of the former at 914 cm^{-1} , which is

attributed to a W=O absorption. The ^1H NMR spectrum shows resonances due to the phenyl groups and to two cyclopentadienyl resonances, of which one shows coupling [$^3J(\text{PH})$ 1.0 Hz] to phosphorus. The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum shows one peak at $\delta -40.5$ with ^{183}W satellites [$^1J(\text{WP})$ 305.9 Hz] and this is assigned to a phosphide bridge. The proposed structure of **4a** is shown in Scheme 1. The chloride ligand is assumed to adopt a terminal rather than a bridging position and hence a tungsten-tungsten double bond is invoked in order for the complex to obey the 18-electron rule. Although no transverse alkyne oxo complexes have been isolated from the analogous dimolybdenum system,⁶ oxo complexes of the type $[\text{M}_2\text{O}(\mu\text{-PPh}_2)_2(\text{CO})(\eta\text{-C}_5\text{H}_5)_2]$ ($\text{M} = \text{Mo}$ or W) have been obtained previously.^{11,14}

(d) *Characterisation of* $[\text{W}_2\text{Cl}_2(\mu\text{-PPh}_2)(\mu\text{-PPh}_2\text{C}=\text{CHR})(\eta\text{-C}_5\text{H}_5)_2]$ ($\text{R} = \text{CO}_2\text{Me}$ **5b** or Ph **5c**). Complexes **5b** and **5c**, prepared respectively from the reactions of **1b** and **1c** with PPh_2Cl , have been characterised on the basis of spectroscopic data. The EI mass spectra of **5b** and **5c** both show peaks due to their respective molecular ions. No terminal carbonyl absorptions are seen in the IR spectrum of either **5b** or **5c**.

In the ^1H NMR spectra of complexes **5b** and **5c** the inequivalence of the two cyclopentadienyl ligands results in separate resonances (δ 4.43 and 4.39 **5b**, δ 4.35 and 4.00 **5c**). The olefinic protons in **5b** and **5c** are seen as doublets of doublets at δ 2.05 [$^3J(\text{PH})$ 6.1, 1.2] and δ 2.58 [$^3J(\text{PH})$ 8.0, 2.0 Hz] respectively. Unequivocal assignment of the olefinic protons as being *cis* or *trans* to the phosphide group is not possible on the basis of the value of $^3J(\text{PH})$. However, by comparison with related complexes a *trans* configuration is tentatively suggested.^{6,15}

The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra of the two complexes **5b** and **5c** are most informative, both showing two doublets at very different chemical shifts ($\delta -20.9$ and -246.0 **5b**, $\delta -26.0$ and -238.9 **5c**), each with coupling constants [$^2J(\text{PP})$] of about 69 Hz. The downfield resonances are assigned to the phosphide bridges in each of the two complexes. The very high-field shifts of the other resonances are indicative of a phosphorus atom being in a strained three-membered metallacycle.^{6,15} The greater resolution of the ^{183}W satellites for the bridging phosphido phosphorus signals (bonded to two tungsten centres) as compared to those for a phosphide group incorporated in a three-membered metallacycle (bonded to one tungsten centre) further supports the assignment.

The $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum at 293 K of complex **5b** shows the presence of only one CO_2Me group in the complex. Resonances due to C^2 of the organophosphorus ligand ($\mu\text{-PPh}_2\text{C}^1=\text{C}^2\text{HR}$) are seen in the spectra of **5b** and **5c** at δ 47.2 and 62.9 respectively, both showing coupling constants of about 13 Hz to phosphorus. A singlet at δ 149.6 in the spectrum of **5c** can tentatively be assigned to C^1 whereas for **5b** no signal which could be assigned to C^1 was observed. The chemical shift values of C^1 and C^2 in complexes **5** are comparable to those found in related dimolybdenum and diiron complexes.^{6,15}

In view of the above spectroscopic data it is proposed that complexes **5b** and **5c** adopt the structures shown in Scheme 1. They are assumed to have two terminal chloride ligands and a $\text{M}=\text{M}$ double bond as found previously for the related dimolybdenum complex $[\text{Mo}_2\text{Cl}_2(\mu\text{-PPh}_2)(\mu\text{-PPh}_2\text{C}=\text{CHMe})(\eta\text{-C}_5\text{H}_5)_2]$,⁶ which has been characterised by X-ray crystallography.

(e) *Characterisation of* $[\text{W}_2(\mu\text{-Cl})\{\mu\text{-PPh}_2\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ **6b**. The type of product represented by **6b** was only isolated from the reaction of **1b** with PPh_2Cl . Its characterisation is based on spectroscopic evidence and on a comparison of this evidence with that for the related molybdenum complex $[\text{Mo}_2(\mu\text{-Cl})(\mu\text{-PPh}_2\text{CH}=\text{CH})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$, the structure of which has been determined by X-ray analysis.⁶ The EI mass spectrum of **6b** shows peaks corresponding to the molecular ion and to the loss of $n(\text{CO})$ ($n = 1$ or 2). The IR spectrum in CH_2Cl_2 solution

shows two terminal carbonyl absorptions and a band at 1669 cm^{-1} , which is attributed to $\nu(\text{C}=\text{O})$ of the CO_2Me groups. The ^1H NMR spectrum shows two separate cyclopentadienyl resonances at δ 4.90 and 4.86, the former being coupled [$^3J(\text{PH})$ 1.9 Hz] to a phosphorus atom. The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum shows one peak with ^{183}W satellites [$^1J(\text{WP})$ 239.0 Hz] at a chemical shift of $\delta -143.4$, and this is assigned to the phosphorus atom of the metallacyclic bridging ligand, $\mu\text{-PPh}_2\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})$.^{5a,6,16}

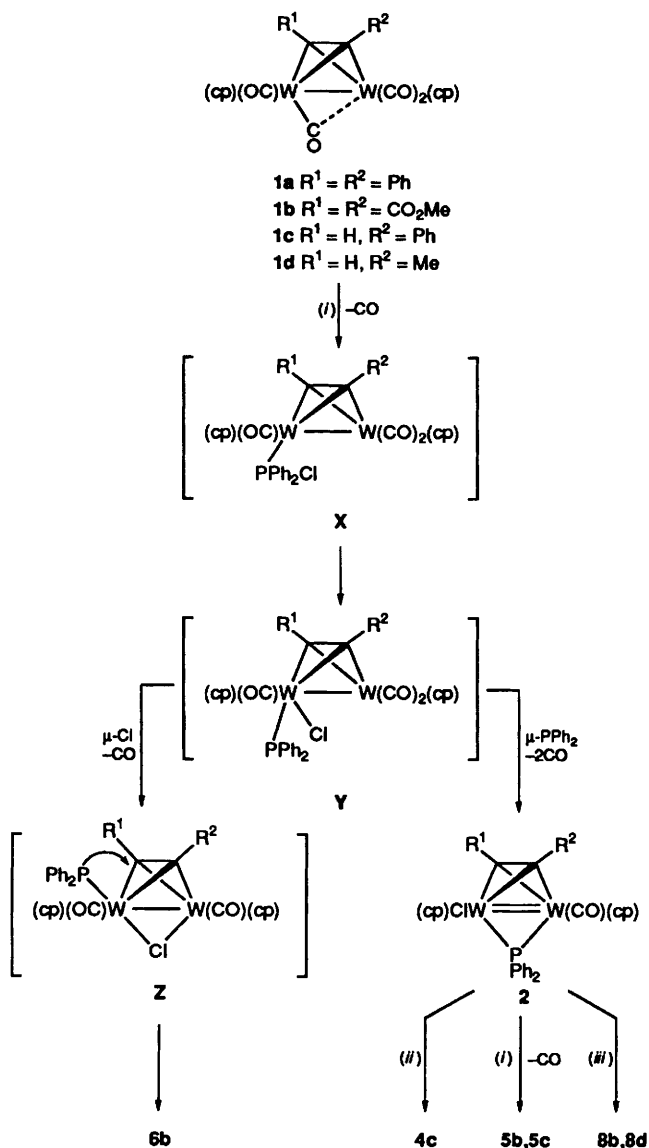
The $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum at 293 K of complex **6b** shows two distinct terminal carbonyl resonances at δ 240.3 and 222.9, the downfield signal being coupled to phosphorus [$^2J(\text{PC})$ 8.4 Hz]. A doublet is seen at δ 31.4 [$^1J(\text{PC})$ 45.8 Hz] and a singlet at δ 99.6 which are assigned to the olefinic carbons of the four-membered ring. The structure proposed for **6b** is shown in Scheme 1. The chloride ligand is assumed to bridge the two tungsten atoms, which are also bonded by a single metal-metal bond.

(f) *Characterisation of* $[\text{W}_2\text{Cl}_2(\mu\text{-Cl})(\mu\text{-PPh}_2\text{C}=\text{CHPh})(\eta\text{-C}_5\text{H}_5)_2]$ **7c**. Complex **7c**, formed in low yield from the reaction of **1c** with PPh_2Cl , is formulated on the basis of a comparison of spectroscopic data with those obtained for the related dimolybdenum complex $[\text{Mo}_2\text{Cl}_2(\mu\text{-Cl})(\mu\text{-PPh}_2\text{C}=\text{CH}_2)(\eta\text{-C}_5\text{H}_5)_2]$, which was isolated as a major product from a similar reaction.⁶ Peaks due to the molecular ion are clearly seen in the mass spectrum of **7c**. However, peaks due to the loss of carbonyl ligands are not seen, nor are there any absorption bands in the terminal carbonyl region of the IR spectrum. The ^1H NMR spectrum shows a doublet at δ 2.84 [$^3J(\text{PH})$ 6.1 Hz] which is attributed to the single proton on the organophosphorus bridge. The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum shows a single peak at $\delta -247.5$ with ^{183}W satellites [$^1J(\text{WP})$ 161.0 Hz]. As for **5**, a negative chemical shift of this magnitude is indicative of the phosphide group being present in a strained three-membered metallacycle. On the basis of these data the structure shown in Scheme 1 is postulated for **7c**.

(g) *Synthesis and characterisation of* $[\text{W}_2\text{O}(\mu\text{-PPh}_2)(\mu\text{-CR}^1=\text{CHR}^2)(\text{CO})(\eta\text{-C}_5\text{H}_5)_2]$ ($\text{R}^1 = \text{R}^2 = \text{CO}_2\text{Me}$ **8b**; $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Me}$ **8d**). Heating $[\text{W}_2(\text{CO})_4(\mu\text{-HC}_2\text{Me})(\eta\text{-C}_5\text{H}_5)_2]$ **1d** with PPh_2Cl in toluene to 373 K for 75 min affords complex **8d** in low yield. Alternatively, **8d** can be prepared by reaction of **1d** with P_2Ph_4 in xylene under reflux for 18 h. Good yields of complex **8b** can be obtained by the action of silica on $[\text{W}_2\text{Cl}(\mu\text{-PPh}_2)\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}(\text{CO})(\eta\text{-C}_5\text{H}_5)_2]$ **2b**. Similar dimolybdenum complexes containing vinyl and bridging phosphide ligands have been previously synthesised¹⁷ and the characterisation of **8** is based on a comparison of the spectroscopic data.

The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra for complexes **8b** and **8d** are very similar, both showing a singlet at about $\delta -18$, with well defined ^{183}W satellites [$^1J(\text{WP})$ 326.9 **8b** and 349.5 Hz **8d**]. Both the chemical shift and high resolution of the signals suggest the phosphide group is bridging the metal centres. The $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum at 293 K of **8d** shows singlet peaks at δ 32.4 and 28.6 which are attributed to the methyl group and the β -carbon atom of the bridging vinyl group ($\mu\text{-CH}=\text{CHMe}$). A resonance at δ 129.7 is assigned to the α -carbon atom on the basis of poorly resolved ^{183}W satellites. The $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum at 293 K of **8b** shows, in addition, resonances due to the two CO_2Me groups. In the ^1H NMR spectrum of **8d** a coupling constant of 9.1 Hz is observed between the olefinic protons, which is closely comparable to the value of 10.3 Hz observed for the structurally characterised $[\text{Mo}_2\text{O}(\mu\text{-PPh}_2)(\mu\text{-CH}=\text{CHPh})(\text{CO})(\eta\text{-C}_5\text{H}_5)_2]$.¹⁷ The proposed structures of **8b** and **8d** (Scheme 1) thus assume a similar arrangement involving *trans* configurations of the olefinic protons.

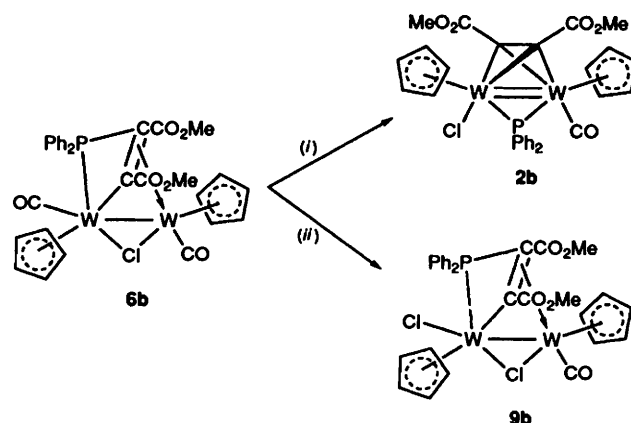
(3) *Reaction Pathways for Formation of Complexes obtained from the PPh_2Cl Reactions.*—Pathways for the reactions of analogous dimolybdenum transverse alkyne complexes with PPh_2Cl have been previously proposed.⁶ A similar scheme for the formation of the various products derived from the



Scheme 2 Possible pathways for the reactions of $[W_2(CO)_4(\mu-R^1C_2R^2)(\eta-C_5H_5)_2]$ **1** with PPh_2Cl . cp = $\eta-C_5H_5$. (i) PPh_2Cl ; (ii) O_2 ; (iii) silica, OH^- . Complex **2** was isolated where $R^1 = R^2 = Ph$ or CO_2Me **b**

ditungsten systems can be postulated (Scheme 2). Initial substitution of a carbonyl ligand in **1** by PPh_2Cl to form X is followed by oxidative addition at one of the tungsten centres to form terminal PPh_2 and Cl ligands as in Y. At this stage bridging by either the PPh_2 or Cl ligand leads to the formation of intermediates **2** (isolable for $R^1 = R^2 = Ph$ or CO_2Me) or Z respectively. Scheme 2 illustrates the further pathways leading to products derived from the intermediates **2** and Z.

(4) *Thermolysis and Photolysis Reactions of $[W_2(\mu-Cl)\{\mu-PPh_2C(CO_2Me)=C(CO_2Me)\}(CO)_2(\eta-C_5H_5)_2]$ **6b**.*—Thermolysis of complex **6b** in refluxing xylene results in partial conversion into **2b** while irradiation of a toluene solution of **6b** with UV light affords the complex $[W_2Cl(\mu-Cl)\{\mu-PPh_2C(CO_2Me)=C(CO_2Me)\}(CO)(\eta-C_5H_5)_2]$ **9b** along with several other uncharacterised complexes in low yield (Scheme 3). Complex **9b** has been characterised by mass spectrometry, microanalysis, IR and 1H and ^{13}C NMR spectroscopy. In addition its structure has been elucidated by X-ray crystallography. The paramagnetic nature of the complex was revealed by the broadening of the peaks in its 1H NMR spectra and confirmed by ESR spectroscopy in the solid state.



Scheme 3 Products from the thermolysis and photolysis of $[W_2(\mu-Cl)\{\mu-PPh_2C(CO_2Me)=C(CO_2Me)\}(CO)_2(\eta-C_5H_5)_2]$ **6b**. (i) Heat, xylene, 3.5 d; (ii) irradiate, toluene, 14 h

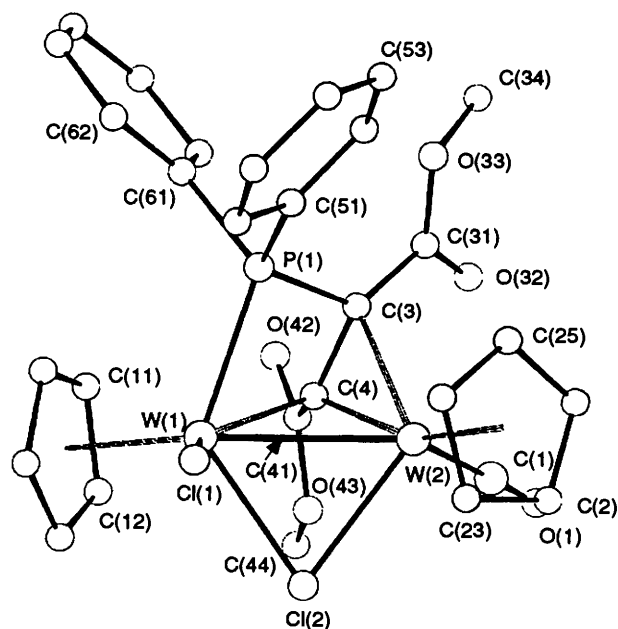


Fig. 3 Molecular structure of $[W_2Cl(\mu-Cl)\{\mu-PPh_2C(CO_2Me)=C(CO_2Me)\}(CO)(\eta-C_5H_5)_2]$ **9b**. Hydrogen atoms have been omitted for clarity

The molecular structure of complex **9b** is shown in Fig. 3 and Table 3 lists selected bond lengths and angles. Two independent molecules were found in the unit cell (molecules C and D) but these are fundamentally the same, and in the following discussion only the mean values of the relevant structural parameters will be used. The two tungsten atoms in **9b** are bridged by a chloride and by a four-membered metallacyclic ring, $\overline{W-P-C=C}$. In addition, a cyclopentadienyl group and a chloride are bonded to one tungsten atom and a cyclopentadienyl group and a carbonyl group to the other. The chloride and the carbonyl ligands are in a transoid arrangement as are the two cyclopentadienyl groups. The tungsten-tungsten bond length [2.846(1) Å] is substantially longer than those seen in complexes **2a** and **3a** [2.654(1)–2.660(1) Å] which contain tungsten-tungsten double bonds, while close to that in the similar dimolybdenum complex $[Mo_2(\mu-Cl)\{\mu-PPh_2C(CO_2Me)=C(CO_2Me)\}(CO)_2(\eta-C_5H_5)_2]$ [2.871(1) Å] which contains a single metal-metal bond.⁶ Complex **9b** contains a terminal chloride in place of one of the carbonyl ligands present in either this dimolybdenum complex or in **6b**. The replacement of a two-electron donor CO ligand in **6b** by a one-electron donor chlorine explains the observed paramagnetism. The ESR spectrum confirms the paramagnetic nature of **9b**

Table 3 Selected bond distances (Å) and angles (°) for complex **9b** in the two independent molecules **C** and **D**

	Molecule C	Molecule D
W(1)–W(2)	2.842(1)	2.850(1)
W(1)–Cl(1)	2.422(4)	2.431(5)
W(1)–Cl(2)	2.437(4)	2.441(4)
W(1)–P(1)	2.467(4)	2.478(4)
W(1)–C(4)	2.184(17)	2.196(13)
W(2)–Cl(2)	2.470(5)	2.468(4)
W(2)–C(3)	2.206(14)	2.200(15)
W(2)–C(4)	2.071(12)	2.125(16)
W(2)–C(1)	1.985(21)	1.955(14)
P(1)–C(3)	1.783(17)	1.795(11)
C(3)–C(4)	1.450(22)	1.542(21)
C(1)–O(1)	1.12(3)	1.16(2)
range W(1)–C(cp)	2.279(14)–2.383(15)	2.311(18)–2.408(15)
range W(2)–C(cp)	2.281(15)–2.370(16)	2.289(19)–2.354(18)
Cl(1)–W(1)–W(2)	91.9(1)	90.9(1)
Cl(2)–W(1)–W(2)	55.2(1)	55.0(1)
P(1)–W(1)–W(2)	72.4(1)	72.4(1)
C(4)–W(1)–W(2)	46.4(3)	47.7(4)
Cl(1)–W(1)–Cl(2)	84.1(2)	84.9(1)
Cl(1)–W(1)–P(1)	94.8(2)	93.8(1)
C(4)–W(1)–Cl(1)	136.5(3)	136.6(4)
P(1)–W(1)–Cl(2)	127.4(1)	127.3(1)
C(4)–W(1)–P(1)	64.7(4)	65.1(4)
C(3)–W(2)–W(1)	69.1(4)	70.5(3)
C(4)–W(2)–W(1)	49.8(5)	49.8(3)
C(4)–W(2)–Cl(2)	80.4(4)	81.1(4)
Cl(2)–W(2)–W(1)	54.1(1)	54.1(1)
C(3)–W(2)–Cl(2)	117.8(4)	119.3(4)
C(4)–W(2)–Cl(2)	81.8(4)	81.1(4)
O(1)–C(1)–W(2)	178.0(10)	177.0(20)
C(4)–C(3)–P(1)	101.0(10)	98.0(8)
W(2)–Cl(2)–W(1)	70.8(1)	71.0(1)

with a signal being seen in the range 4–293 K. At 77 K, three g tensors are observed: $g_1 = 1.96$, $g_2 = 1.94$ and $g_3 = 1.89$ which gives $g_{av} = 1.92$. No hyperfine coupling is observed and power-saturation measurements show the presence of only one type of radical.¹⁸

Conclusion

The reactions of the ditungsten complexes $[\text{W}_2(\text{CO})_4(\mu\text{-R}^1\text{C}_2\text{R}^2)(\eta\text{-C}_5\text{H}_5)_2]$ ($\text{R}^1 = \text{R}^2 = \text{Ph}$ **1a** or CO_2Me **1b**; $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Ph}$ **1c** or Me **1d**) with PPh_2Cl are similar to those of the corresponding reactions of the dimolybdenum complexes $[\text{Mo}_2(\text{CO})_4(\mu\text{-R}^1\text{C}_2\text{R}^2)(\eta\text{-C}_5\text{H}_5)_2]$ ($\text{R}^1 = \text{H}$, $\text{R}^2 = \text{H}$, Me or Ph ; $\text{R}^1 = \text{R}^2 = \text{CO}_2\text{Me}$ or Me)⁶ and the reaction products **2a**, **2b**, **5c**, **6b** and **7c** are closely related to those obtained in the molybdenum system. However, some notable differences in the outcome of reactions of the tungsten complexes are observed. In particular the formation of the paramagnetic bis(phosphido) complex $[\text{W}_2\text{Cl}(\mu\text{-PPh}_2)_2(\text{CO})(\eta\text{-C}_5\text{H}_5)_2]$ **3a**, the oxo complexes $[\text{W}_2(\text{O})\text{Cl}(\mu\text{-PPh}_2)(\mu\text{-PhC}_2\text{Ph})(\eta\text{-C}_5\text{H}_5)_2]$ **4a** and $[\text{W}_2\text{O}(\mu\text{-PPh}_2)(\mu\text{-CR}^1=\text{CHR}^2)(\text{CO})(\eta\text{-C}_5\text{H}_5)_2]$ ($\text{R}^1 = \text{R}^2 = \text{CO}_2\text{Me}$ **8b**; $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Me}$ **8d**) and a species in which C–C bond scission has occurred, $[\text{W}_2\text{Cl}_2(\mu\text{-PPh}_2)\{\mu\text{-PPh}_2\text{C}=\text{CH}(\text{CO}_2\text{Me})\}(\eta\text{-C}_5\text{H}_5)_2]$ **5b** are all unique to tungsten. The additional products in the ditungsten system are perhaps the result of the longer reaction times and higher temperatures which are needed to induce the reactions to take place.

Experimental

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use. Preparative thin-layer chromatography (TLC) was

carried out on commercial Merck plates 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 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.¹⁹ All reagents were obtained from commercial suppliers and used without further purification. The compounds $[\text{W}_2(\text{CO})_4(\mu\text{-R}_2\text{C}_2)(\eta\text{-C}_5\text{H}_5)_2]$ ($\text{R} = \text{Ph}$ **1a**, or CO_2Me **1b**)⁸ and P_2Ph_4 ²⁰ were prepared by literature methods.

(i) *Synthesis of $[\text{W}_2(\text{CO})_4(\mu\text{-HC}_2\text{R})(\eta\text{-C}_5\text{H}_5)_2]$ ($\text{R} = \text{Ph}$ **1c** or Me **1d**).*—(a) **1c**. The complex $[\text{W}_2(\text{CO})_6(\eta\text{-C}_5\text{H}_5)_2]$ (0.60 g, 0.090 mmol) was heated to reflux in diglyme for 7 h, whilst the solution was purged with a steady stream of N_2 , to give a deep red solution of $[\text{W}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$. The reaction was allowed to cool and $\text{PhC}\equiv\text{CH}$ (1.0 cm^3 , excess) added. After stirring for 2 h at room temperature the solvent was removed under reduced pressure. Column separation eluting with hexane– CH_2Cl_2 (3:2) gave red crystalline $[\text{W}_2(\text{CO})_4(\mu\text{-HC}_2\text{-Ph})(\eta\text{-C}_5\text{H}_5)_2]$ **1c** (0.440 g, 69%) as the major product. Complex **1c**–0.5 CH_2Cl_2 (Found: C, 35.6; H, 2.3. $\text{C}_{22.5}\text{H}_{17}\text{ClO}_4\text{W}_2$ requires C, 35.8; H, 2.3%); EI mass spectrum, m/z 712 (M^+) and $M^+ - n\text{CO}$ ($n = 1-4$); IR (hexane) ν_{CO} 1993s, 1926s and 1839s cm^{-1} .

(b) **1d**. The complex $[\text{W}_2(\text{CO})_6(\eta\text{-C}_5\text{H}_5)_2]$ (3.60 g, 5.41 mmol) was used as in (a) above, except that diglyme was heated to reflux for 5 h only. Methylacetylene was bubbled through the cooled solution for 15 min followed by stirring for 2 h. Column separation eluting with hexane– CH_2Cl_2 (3:2) gave red crystalline $[\text{W}_2(\text{CO})_4(\mu\text{-HC}_2\text{Me})(\eta\text{-C}_5\text{H}_5)_2]$ **1d** (1.942 g, 55%) (Found: C, 31.5; H, 2.0. $\text{C}_{17}\text{H}_{14}\text{O}_4\text{W}_2$ requires C, 31.4; H, 2.2%); EI mass spectrum, m/z 650 (M^+) and $M^+ - n\text{CO}$ ($n = 1$ or 2); IR (hexane) ν_{CO} 1988s, 1921s, 1913s and 1834s cm^{-1} .

(ii) *Thermolytic Reaction of $[\text{W}_2(\text{CO})_4(\mu\text{-R}^1\text{C}\equiv\text{CR}^2)(\eta\text{-C}_5\text{H}_5)_2]$ **1a**–**1d** with PPh_2Cl .*—(a) Chlorodiphenylphosphine (0.30 cm^3 , 1.69 mmol) was added to a solution of $[\text{W}_2(\text{CO})_4(\mu\text{-PhC}_2\text{Ph})(\eta\text{-C}_5\text{H}_5)_2]$ **1a** (0.666 g, 0.85 mmol) in xylene (300 cm^3) and the mixture heated to reflux for 8 h. The solvent was removed under reduced pressure and the residue dissolved in the minimum volume of CH_2Cl_2 and separated by preparative TLC. Elution using hexane– CH_2Cl_2 (4:1) gave a trace of the starting material (0.01 g) followed by green crystalline $[\text{W}_2\text{Cl}(\mu\text{-PPh}_2)(\mu\text{-PhC}_2\text{Ph})(\text{CO})(\eta\text{-C}_5\text{H}_5)_2]$ **2a** and $[\text{W}_2\text{Cl}(\mu\text{-PPh}_2)_2(\text{CO})(\eta\text{-C}_5\text{H}_5)_2]$ **3a** (which were inseparable by TLC) (combined mass 0.292 g). Further elution gave green crystalline $[\text{W}_2(\text{O})\text{Cl}(\mu\text{-PPh}_2)(\mu\text{-PhC}_2\text{Ph})(\eta\text{-C}_5\text{H}_5)_2]$ **4a** (0.040 g, 5%). Complex **2a/3a** (Found: C, 48.5; H, 3.5; Cl, 4.2; P, 3.2. $\text{C}_{73}\text{H}_{60}\text{Cl}_2\text{O}_2\text{P}_2\text{W}_4$ 1.5 **2a** 0.5 **3a** requires C, 47.3; H, 3.3; Cl, 3.8; P, 4.2. $\text{C}_{37}\text{H}_{30}\text{ClOPW}_2$ **2a** requires C, 48.1; H, 3.3; Cl, 3.8; P, 3.4%); EI mass spectrum, m/z 924 (M^+) and $M^+ - \text{CO}$; IR (CH_2Cl_2) ν_{CO} 1960s cm^{-1} . Complex **4a** (Found: C, 47.7; H, 3.5. $\text{C}_{36}\text{H}_{30}\text{ClOPW}_2$ requires C, 47.4; H, 3.3%); EI mass spectrum, m/z 912 (M^+); IR (KBr disc) $\nu(\text{W}=\text{O})$ 914w cm^{-1} (no peaks in ν_{CO} region).

(b) Chlorodiphenylphosphine (0.48 cm^3 , 1.69 mmol) was added to a solution of $[\text{W}_2(\text{CO})_4(\mu\text{-C}_2(\text{CO}_2\text{Me})_2)(\eta\text{-C}_5\text{H}_5)_2]$ **1b** (1.00 g, 1.33 mmol) in xylene (300 cm^3) and the mixture heated to reflux for 60 h. After removal of the solvent at reduced pressure the residue was added to the top of a chromatography column. Elution with CH_2Cl_2 –acetone (98:2) gave brown crystalline $[\text{W}_2\text{Cl}_2(\mu\text{-PPh}_2)\{\mu\text{-PPh}_2\text{C}=\text{CH}(\text{CO}_2\text{Me})\}(\eta\text{-C}_5\text{H}_5)_2]$ **5b** (0.100 g, 7%) followed by an uncharacterised brown compound. Further elution with CH_2Cl_2 –acetone (95:5) gave red crystalline $[\text{W}_2(\mu\text{-Cl})\{\mu\text{-PPh}_2\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ **6b** (0.510 g, 42%). Finally, elution with CH_2Cl_2 –acetone (92:8) gave green crystalline $[\text{W}_2\text{Cl}(\mu\text{-PPh}_2)\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}(\text{CO})(\eta\text{-C}_5\text{H}_5)_2]$ **2b** (0.066 g, 6%). Complex **5b** (Found: C, 44.3; H, 3.2; P, 6.9.

Table 4 Fractional coordinates for complex 2a/3a

Atom	Molecular unit A			Molecule B		
	x	y	z	x	y	z
W(1)	0.042 84(2)	0.176 65(5)	0.373 83(3)	0.692 79(2)	0.164 20(5)	0.528 15(3)
W(2)	0.023 22(2)	0.219 21(5)	0.243 82(3)	0.681 52(2)	0.202 79(5)	0.398 41(3)
Cl	0.011 7(1)	-0.023 6(3)	0.390 1(2)	0.649 7(1)	-0.020 2(3)	0.541 9(2)
P(1a)	-0.024 7(2)	0.273 4(5)	0.312 4(2)	0.625 9(1)	0.265 2(3)	0.458 7(2)
P(2) ^a	0.091 8(3)	0.137 2(12)	0.303 7(4)			
C(1)	-0.008 8(5)	0.057 9(13)	0.235 6(7)	0.646 7(5)	0.047 6(13)	0.385 3(7)
O(1)	-0.027 6(4)	-0.034 6(10)	0.227 5(6)	0.626 7(4)	-0.045 3(10)	0.375 8(6)
C(11)	0.058 0(8)	0.162 8(19)	0.493 4(10)	0.690 7(6)	0.182 8(16)	0.644 3(8)
C(12)	0.101 0(6)	0.165 0(17)	0.476 2(9)	0.738 2(6)	0.142 2(16)	0.639 8(8)
C(13)	0.105 9(6)	0.272 9(17)	0.447 1(9)	0.755 0(6)	0.242 1(15)	0.609 2(8)
C(14)	0.061 0(6)	0.341 9(17)	0.443 0(9)	0.720 2(5)	0.334 1(15)	0.592 8(8)
C(15)	0.030 6(7)	0.268 8(18)	0.474 1(9)	0.678 6(5)	0.292 9(14)	0.615 9(7)
C(21)	0.043 2(6)	0.379 3(16)	0.178 4(8)	0.705 6(6)	0.367 8(16)	0.339 1(8)
C(22)	0.061 1(7)	0.270 4(18)	0.160 8(9)	0.728 5(5)	0.257 6(14)	0.324 2(8)
C(23)	0.023 0(8)	0.186 0(20)	0.132 2(11)	0.693 2(6)	0.166 6(15)	0.290 0(8)
C(24)	-0.020 6(8)	0.254 1(20)	0.135 3(10)	0.647 2(6)	0.231 7(16)	0.285 5(8)
C(25)	-0.009 5(6)	0.371 5(16)	0.165 0(8)	0.652 2(6)	0.348 4(16)	0.313 0(8)
C(3) ^b	0.092 4(4)	0.197 8(22)	0.309 7(7)	0.747 2(4)	0.175 0(11)	0.470 8(5)
C(31)	0.144 2(5)	0.247 0(13)	0.312 8(6)	0.795 3(4)	0.229 1(11)	0.480 3(6)
C(32)	0.147 1(5)	0.373 3(14)	0.314 2(8)	0.802 2(5)	0.357 2(13)	0.482 1(8)
C(33)	0.189 3(6)	0.433 0(14)	0.321 2(8)	0.847 1(5)	0.407 0(14)	0.494 7(9)
C(34)	0.230 8(5)	0.368 2(16)	0.323 8(8)	0.887 4(5)	0.335 4(15)	0.501 7(8)
C(35)	0.229 5(6)	0.244 4(17)	0.321 9(8)	0.881 2(5)	0.211 2(15)	0.499 7(8)
C(36)	0.186 3(6)	0.180 8(15)	0.317 3(8)	0.837 1(4)	0.157 6(13)	0.490 0(7)
C(4) ^b	0.078 9(7)	0.083 3(18)	0.310 3(7)	0.731 6(4)	0.063 9(10)	0.470 6(5)
C(41)	0.101 4(5)	-0.031 1(14)	0.285 7(7)	0.747 9(4)	-0.062 3(12)	0.454 0(7)
C(42)	0.103 1(5)	-0.132 6(14)	0.324 6(8)	0.749 6(5)	-0.156 7(13)	0.498 6(8)
C(43)	0.119 2(5)	-0.245 5(16)	0.307 2(8)	0.766 3(5)	-0.267 9(14)	0.484 2(9)
C(44)	0.134 0(5)	-0.253 9(15)	0.249 0(8)	0.781 2(5)	-0.287 1(14)	0.426 3(9)
C(45)	0.132 1(5)	-0.154 4(14)	0.207 2(8)	0.778 4(5)	-0.193 7(13)	0.381 8(9)
C(46)	0.116 9(6)	-0.041 9(15)	0.225 8(8)	0.761 8(5)	-0.082 2(12)	0.394 8(8)
C(51)	-0.031 4(5)	0.439 4(13)	0.329 0(7)	0.617 5(5)	0.424 4(12)	0.476 6(6)
C(52)	-0.070 2(6)	0.466 6(13)	0.356 2(8)	0.579 9(5)	0.463 0(11)	0.503 5(7)
C(53)	-0.078 3(6)	0.587 8(15)	0.369 0(8)	0.574 6(5)	0.582 7(13)	0.520 2(7)
C(54)	-0.050 6(6)	0.681 6(14)	0.356 9(7)	0.606 4(5)	0.670 6(13)	0.508 4(8)
C(55)	-0.011 9(6)	0.654 0(13)	0.329 7(8)	0.643 5(5)	0.637 3(12)	0.482 2(8)
C(56)	-0.002 6(6)	0.531 6(13)	0.315 3(8)	0.648 7(5)	0.515 0(14)	0.466 7(8)
C(61)	-0.084 5(5)	0.192 4(15)	0.299 4(7)	0.564 2(4)	0.211 8(10)	0.435 0(6)
C(62)	-0.117 6(5)	0.229 6(15)	0.242 9(9)	0.537 7(4)	0.234 7(12)	0.371 0(7)
C(63)	-0.163 7(6)	0.185 9(20)	0.227 8(10)	0.488 6(4)	0.207 1(15)	0.353 7(7)
C(64)	-0.176 0(6)	0.104 1(18)	0.271 5(10)	0.466 6(5)	0.160 3(12)	0.398 6(8)
C(65)	-0.144 4(7)	0.065 8(21)	0.324 5(11)	0.491 3(5)	0.136 4(12)	0.462 0(8)
C(66)	-0.098 9(6)	0.107 7(20)	0.338 6(9)	0.541 4(5)	0.157 8(12)	0.481 2(7)

^a Atom present only in 0.5 occupancy corresponding to complex 3a. ^b Atom present only in 0.5 occupancy corresponding to complex 2a.

$C_{38}H_{34}Cl_2O_2P_2W_2$ requires C, 44.6; H, 3.3; P, 6.1%): EI mass spectrum, m/z 1023 (M^+) and $M^+ - PPh_2$; IR (hexane) ν_{CO} 1674s cm^{-1} . Complex 6b. CH_2Cl_2 (Found: C, 37.4; H, 2.7; P, 3.0. $C_{31}H_{28}Cl_3O_6PW_2$ requires C, 37.1; H, 2.8; P, 3.0%): EI mass spectrum, m/z 916 (M^+) and $M^+ - nCO$ ($n = 1$ or 2); IR (CH_2Cl_2) ν_{CO} 1924s, 1880s and 1669s cm^{-1} . Complex 2b (Found: C, 39.1; H, 2.9. $C_{29}H_{26}ClO_5PW_2$ requires C, 39.2; H, 2.9%): EI mass spectrum, m/z 888 (M^+) and $M^+ - CO$; IR (CH_2Cl_2) ν_{CO} 1993s and 1694s cm^{-1} .

(c) Chlorodiphenylphosphine (0.96 cm^3 , 5.34 mmol) was added to a solution of $[W_2(CO)_4(\mu-HC_2Ph)(\eta-C_5H_5)_2]$ 1c (1.90 g, 2.67 mmol) in toluene (300 cm^3) and heated under reflux for 24 h. After removal of the solvent at reduced pressure the residue was added to the top of a chromatography column. Elution with hexane- CH_2Cl_2 (1:1) gave brown $[W_2Cl_2(\mu-PPh_2)(\mu-PPh_2C=CHPh)(\eta-C_5H_5)_2]$ 5c (0.740 g, 27%) as the first band. A weak second band consisting of green and orange compounds was obtained on elution with 100% CH_2Cl_2 but remains uncharacterised. Thin-layer chromatography using CH_2Cl_2 -acetone (95:5) as eluent on the third band gave three uncharacterised compounds and red crystalline $[W_2Cl_2(\mu-Cl)(\mu-PPh_2C=CHPh)(\eta-C_5H_5)_2]$ 7c (0.070 g, 3%). Elution of the fourth band with CH_2Cl_2 -acetone (95:5) gave an

uncharacterised green product. Complex 5c (Found: C, 48.8; H, 3.5; P, 6.3. $C_{42}H_{36}Cl_2P_2W_2$ requires C, 48.4; H, 3.5; P, 6.0%): EI mass spectrum, m/z 1041 (M^+); IR (hexane) no peaks in ν_{CO} region. Complex 7c (Found: C, 40.6; H, 2.9; P, 2.6. $C_{30}H_{26}Cl_3PW_2$ requires C, 40.4; H, 2.9; P, 3.5%): EI mass spectrum, m/z 892 (M^+); IR (hexane) no peaks in ν_{CO} region.

(d) Chlorodiphenylphosphine (0.07 cm^3 , 0.37 mmol) was added to a solution of $[W_2(CO)_4(\mu-HC_2Me)(\eta-C_5H_5)_2]$ 1d (0.120 g, 0.18 mmol) in toluene (200 cm^3) and heated to 373 K for 75 min. The solvent was removed under reduced pressure and the residue dissolved in the minimum volume of CH_2Cl_2 and separated by preparative TLC. Elution with hexane- CH_2Cl_2 (1:1) gave orange crystalline $[W_2O(\mu-PPh_2)(\mu-CH=CHMe)(CO)(\eta-C_5H_5)_2]$ 8d (0.021 g, 15%) as the only product (Found: C, 40.9; H, 3.2. $C_{26}H_{25}O_2PW_2$ requires C, 40.6; H, 3.3%): EI mass spectrum, m/z 768 (M^+) and $M^+ - CO$; IR (hexane) ν_{CO} 1851s, (KBr disc) $\nu(W=O)$ 918w cm^{-1} .

(iii) Conversion of $[W_2Cl(\mu-PPh_2)\{\mu-C_2(CO_2Me)_2\}(CO)(\eta-C_5H_5)_2]$ 2b into $[W_2O(\mu-PPh_2)\{\mu-C(CO_2Me)=CH(CO_2Me)\}(CO)(\eta-C_5H_5)_2]$ 8b.—Complex 2b (0.035 g, 0.04 mmol) was absorbed onto the base of a TLC plate and left standing in the

Table 5 Fractional coordinates for complex 9b

Atom	Molecule C			Molecule D		
	x	y	z	x	y	z
W(1)	0.391 12(3)	0.100 67(5)	0.158 90(6)	0.125 31(3)	0.870 93(5)	0.468 30(6)
W(2)	0.467 55(3)	0.293 78(5)	0.178 95(6)	0.0778 6(3)	0.743 36(5)	0.209 22(6)
Cl(1)	0.436 4(2)	0.119 3(4)	0.385 9(4)	0.217 7(2)	0.970 4(3)	0.404 4(4)
Cl(2)	0.514 6(2)	0.139 7(3)	0.150 9(4)	0.046 7(2)	0.906 0(3)	0.295 6(4)
P(1)	0.312 5(2)	0.218 9(3)	0.200 8(4)	0.183 5(2)	0.726 6(3)	0.450 3(4)
C(1)	0.495 4(9)	0.327 7(11)	0.026 3(18)	-0.018 0(8)	0.664 3(12)	0.147 7(15)
O(1)	0.512 8(8)	0.347 5(11)	-0.058 4(14)	-0.074 9(6)	0.618 8(9)	0.105 5(11)
C(11)	0.298 7(9)	-0.006 1(11)	0.005 3(16)	0.101 2(11)	0.853 6(14)	0.664 1(16)
C(12)	0.363 4(9)	-0.035 6(12)	-0.018 9(16)	0.056 1(9)	0.916 1(13)	0.615 4(15)
C(13)	0.393 2(8)	-0.071 3(11)	0.083 1(17)	0.098 6(8)	1.007 6(12)	0.614 0(15)
C(14)	0.350 0(9)	-0.063 4(10)	0.172 1(17)	0.169 8(9)	1.006 2(13)	0.665 1(16)
C(15)	0.292 1(9)	-0.021 7(11)	0.125 3(17)	0.171 9(9)	0.916 0(13)	0.691 5(16)
C(21)	0.512 7(10)	0.464 0(13)	0.268 3(20)	0.085 9(8)	0.649 5(11)	0.009 3(15)
C(22)	0.566 9(9)	0.408 8(12)	0.292 6(17)	0.070 8(9)	0.746 2(14)	-0.003 9(14)
C(23)	0.549 9(9)	0.347 8(14)	0.373 4(17)	0.133 1(9)	0.814 4(12)	0.076 1(16)
C(24)	0.485 2(9)	0.366 1(12)	0.406 0(16)	0.182 1(9)	0.771 8(12)	0.134 4(15)
C(25)	0.462 0(9)	0.435 3(14)	0.337 1(19)	0.153 5(8)	0.665 8(12)	0.092 5(14)
C(3)	0.354 9(7)	0.278 3(11)	0.099 8(14)	0.103 6(7)	0.653 5(10)	0.341 1(12)
C(31)	0.330 8(11)	0.352 6(16)	0.036 4(22)	0.078 0(8)	0.545 4(11)	0.298 0(14)
O(32)	0.351 3(7)	0.366 5(11)	-0.058 2(15)	0.017 1(5)	0.501 9(8)	0.258 3(10)
O(33)	0.287 6(8)	0.398 5(11)	0.089 6(14)	0.130 5(5)	0.496 9(8)	0.295 6(10)
C(34)	0.253 1(17)	0.445 3(25)	-0.005 8(33)	0.109 9(9)	0.389 5(12)	0.247 1(17)
C(34')	0.333 0(29)	0.466 5(39)	-0.068 6(54)			
C(4)	0.386 0(7)	0.199 1(11)	0.034 0(14)	0.054 4(7)	0.723 6(11)	0.385 3(14)
C(41)	0.372 4(9)	0.156 3(12)	-0.109 0(16)	-0.006 5(8)	0.699 7(12)	0.433 3(15)
O(42)	0.316 6(7)	0.147 9(10)	-0.180 9(13)	-0.015 1(7)	0.642 4(10)	0.498 8(13)
O(43)	0.425 7(6)	0.127 0(9)	-0.154 2(12)	-0.058 3(6)	0.743 0(8)	0.393 9(11)
C(44)	0.422 4(12)	0.084 2(17)	-0.292 9(22)	-0.125 5(10)	0.715 0(16)	0.430 3(21)
C(51)	0.307 6(7)	0.293 3(12)	0.361 9(15)	0.267 0(7)	0.724 7(10)	0.398 8(13)
C(52)	0.290 2(8)	0.386 7(12)	0.377 8(17)	0.281 4(8)	0.640 5(12)	0.320 9(15)
C(53)	0.282 7(10)	0.438 5(14)	0.503 1(21)	0.347 0(9)	0.642 4(14)	0.288 5(17)
C(54)	0.290 9(9)	0.397 5(14)	0.603 9(20)	0.398 4(8)	0.728 5(13)	0.339 8(19)
C(55)	0.307 0(9)	0.303 0(13)	0.583 2(16)	0.384 3(8)	0.811 2(13)	0.417 1(17)
C(56)	0.315 9(8)	0.252 7(13)	0.465 3(18)	0.319 5(8)	0.812 7(12)	0.447 1(15)
C(61)	0.217 4(7)	0.172 8(10)	0.127 5(14)	0.199 3(8)	0.681 3(11)	0.592 7(13)
C(62)	0.171 5(8)	0.140 3(11)	0.198 5(17)	0.263 2(8)	0.715 8(12)	0.680 7(14)
C(63)	0.100 4(9)	0.109 3(12)	0.142 7(19)	0.274 7(10)	0.687 6(14)	0.795 5(18)
C(64)	0.076 2(8)	0.109 8(13)	0.015 3(18)	0.221 0(11)	0.625 3(14)	0.820 8(15)
C(65)	0.120 7(8)	0.142 6(13)	-0.051 0(17)	0.157 7(10)	0.587 0(13)	0.729 4(19)
C(66)	0.193 2(8)	0.176 0(12)	-0.001 0(15)	0.145 7(9)	0.617 9(12)	0.619 6(16)

light for 36 h. The product was eluted using CH_2Cl_2 -acetone (95:5). Orange crystalline **8b** (0.025 g, 70%) was isolated as the only product (Found: C, 40.1; H, 3.1; P, 4.5. $\text{C}_{29}\text{H}_{27}\text{O}_6\text{PW}_2$ requires C, 40.0; H, 3.1; P, 4.6%); EI mass spectrum, m/z 870 (M^+) and $M^+ - \text{CO}$; IR (CH_2Cl_2) ν_{CO} 1916s and 1697s cm^{-1} .

(iv) *Thermolysis of* $[\text{W}_2(\text{CO})_4(\mu\text{-HC}_2\text{Me})(\eta\text{-C}_5\text{H}_5)_2]$ **1d** with P_2Ph_4 .—Complex **1d** (0.250 g, 0.38 mmol) was added to a flask containing P_2Ph_4 (0.38 mmol) dissolved in xylene (250 cm^3). The reaction mixture was heated under reflux for 18 h, after which time TLC separation gave **8d** (0.044 g, 15%) as the only major product.

(v) *Thermolysis of* $[\text{W}_2(\mu\text{-Cl})\{\mu\text{-PPh}_2\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ **6b**.—Complex **6b** was heated in xylene under reflux for 3.5 d to give unreacted **6b** and $[\text{W}_2\text{Cl}(\mu\text{-PPh}_2)\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}(\text{CO})(\eta\text{-C}_5\text{H}_5)_2]$ **2b** in approximately equal amounts, as the only products.

(vi) *Photolysis of Complex 6b*.—The complex (0.690 g, 0.75 mmol) was dissolved in toluene (150 cm^3) and irradiated with UV light for 14 h. After removal of the solvent under reduced pressure, separation by TLC using CH_2Cl_2 -acetone (9:1) gave an uncharacterised brown band (0.020 g), followed by dark green-brown crystalline paramagnetic $[\text{W}_2\text{Cl}(\mu\text{-Cl})\{\mu\text{-PPh}_2\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\}(\text{CO})(\eta\text{-C}_5\text{H}_5)_2]$ **9b** (0.100 g,

14%), unreacted **6b** (0.200 g) and a bottom band which on subsequent TLC separation using CH_2Cl_2 -acetone (4:1) gave a red band (0.050 g) and a yellow band (0.100 g) both of which remained uncharacterised. Complex **9b** (Found: C, 37.9; H, 2.8. $\text{C}_{29}\text{H}_{26}\text{Cl}_2\text{O}_5\text{PW}_2$ requires C, 37.7; H, 2.8%); EI mass spectrum, m/z 923 (M^+) and $M^+ - \text{CO}$; IR (CH_2Cl_2) ν_{CO} 1912s and 1676 cm^{-1} .

(vii) *Crystal Structure Determinations*.—Crystal data for complex 1.5 (**2a**)/0.5 (**3a**). $\text{C}_{73}\text{H}_{60}\text{Cl}_2\text{O}_2\text{P}_{2.5}\text{W}_4$, $M = 1852.82$, monoclinic, space group $P2_1/n$, $a = 28.556(5)$, $b = 10.924(2)$, $c = 20.684(4)$ Å, $\beta = 103.77(2)^\circ$, $U = 6267.45$ Å³, $Z = 4$, $D_c = 1.96$ g cm^{-3} , $\mu = 72.2$ cm^{-1} , $F(000) = 3526$.

Crystal data for complex **9b**: $\text{C}_{29}\text{H}_{26}\text{Cl}_2\text{O}_5\text{PW}_2$, $M = 923.71$, triclinic, space group $P\bar{1}$ (no. 2), $a = 19.768(4)$, $b = 14.143(3)$, $c = 10.915(2)$ Å, $\alpha = 104.74(2)$, $\beta = 99.56(2)$, $\gamma = 104.74(2)^\circ$, $U = 2845.65$, $Z = 4$, $D_c = 2.16$, $\mu = 83.0$ cm^{-1} , $F(000) = 1740$.

Data collection. Data ($\pm h, k, l$, **2a/3a** and $\pm h, \pm k$, **19b**) were collected in the range θ 3–25° (2009 **2a/3a** and 10645 **9b**), with a scan width of 0.90° using the technique described previously.²¹ For both structures Lorentz and polarisation corrections were applied, and equivalent reflections were merged to give 6620 data for **2a/3a** and 6153 for **9b** with $I/\sigma(I) > 3.0$.

Structure solution and refinement.²² The coordinates of the metal atoms in the structures of complexes **2a/3a** and **9b** were deduced from Patterson syntheses, and the remaining non-

hydrogen atoms located from subsequent Fourier-difference syntheses. Both crystals have two molecular units per equivalent position. In the case of **2a/3a**, three electron-density maxima (*ca.* 3, 8 and 3 e Å⁻³) were found in the region where the two alkyne C atoms had been expected in the first molecular unit **A**. These were interpreted as due to a 50:50 occupation of this region in the crystal by molecules of **2a** and **3a** with all the atoms, except the alkyne carbons of **2a** and the phosphorus atoms of **3a**, superimposed. The three maxima were assigned as two alkyne carbon atoms and one phosphorus atom all of half occupancy and this model gave a good overall geometry for both species and satisfactory refinement. In refinement the bond lengths involving the alkyne of half occupancy of molecular unit **A** (in the composite crystal **2a/3a**) were constrained to be equal within experimental error to the equivalent bonds in molecular unit **B**. In **9b** the methyl carbon atom C(34) in molecule **C** is disordered over two sites of 0.4:0.6 occupancy. The hydrogen atoms in both structures were included in geometrically idealised positions and constrained to ride on the relevant carbon atoms with group isotropic thermal parameters. The phenyl groups in both structures were refined as rigid hexagons (C–C 1.395 Å). After initial refinement with isotropic thermal parameters assigned to all atoms, empirical absorption corrections were applied to both structures.²³

Blocked full-matrix refinement was used with the parameters of the two crystallographically independent molecular units, for each crystal, refining in separate blocks (except for the 'tied' parameters of the alkyne groups in **2a/3a**), and anisotropic thermal parameters were assigned to all non-hydrogen atoms except the cyclopentadiene and alkyne carbons in **2a/3a** and the ten atoms of the bridging alkyne substituents of P(1) in molecules **C** and **D** of **9b**. For both complexes **2a/3a** and **9b** weights of $w = 1/\sigma^2 F_o$ were assigned to individual reflections. Refinement converged at $R = 0.0452$ and $R' = 0.0454$ for **2a/3a** and $R = 0.0475$ and $R' = 0.0460$ for **9b**.²² The fractional atomic coordinates for **2a/3a** and **9b** are in Tables 4 and 5 respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

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