Phosphorus Donor Chemistry of $[W(CO)(Ph_2PC{\equiv}CPPh_2)(S_2CNEt_2)_2]$†

Anne K. Powell[a] **and Michael J. Went***[,b]
[a] *Department of Chemistry, University of East Anglia, Norwich NR4 7TJ, UK*
[b] *University Chemical Laboratory, Canterbury, Kent CT2 7NH, UK*

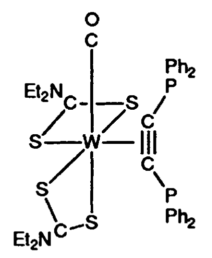
Reactions of $[W(CO)(Ph_2PC{\equiv}CPPh_2)(S_2CNEt_2)_2]$ with $[M(CO)_4(pip)_2]$ (M = Cr, Mo or W; pip = piperidine) afford $[W(CO)\{(Ph_2PC{\equiv}CPPh_2)M(CO)_4\}(S_2CNEt_2)_2]$. The molecular structures of all three compounds have been determined by X-ray diffraction studies and found to be isostructural. In all three cases the acetylenic bond of $Ph_2PC{\equiv}CPPh_2$ is co-ordinated to the tungsten(II) centre, which is also ligated by carbonyl and dithiocarbamate ligands, while both phosphorus atoms are co-ordinated to the metal tetracarbonyl fragment to form a five-membered chelate ring. The $^{13}C-\{^1H\}$ NMR data are discussed in relation to the molecular structures, and the barriers to alkyne rotation in these complexes have been established by variable-temperature $^{31}P-\{^1H\}$ NMR spectroscopy. Reactions of $[W(CO)(Ph_2PC{\equiv}CPPh_2)(S_2CNEt_2)_2]$ with $[Co_2(CO)_8]$ and $[Fe_2(CO)_9]$ afford $[W(CO)\{(Ph_2PC{\equiv}CPPh_2)Co_2(\mu\text{-}CO)_2(CO)_4\}(S_2CNEt_2)_2]$ and $[W(CO)(x)_4Fe(Ph_2PC{\equiv}CPPh_2)Fe(CO)_4\}(S_2CNEt_2)_2]$ respectively, which have been characterised by IR, NMR and mass spectroscopy.

The ability of bis(diphenylphosphino)acetylene ($Ph_2PC{\equiv}CPPh_2$) to act as a ligand to low-oxidation-state transition-metal centres has been extensively investigated.[1] It contains three potential donor sites, two phosphorus centres and the acetylenic bond, but co-ordination *via* the phosphorus atoms is the dominant bonding mode while acetylenic co-ordination is rarely observed. The linear nature of $Ph_2PC{\equiv}CPPh_2$ ensures that when the ligand acts as a bidentate phosphorus donor two separate metal–ligand fragments are co-ordinated. The ligand is not capable of chelating to a single metal centre or spanning a metal–metal bond.

Ward and Templeton[2] have shown that reaction of $[W(CO)_3(S_2CNEt_2)_2]$ with $Ph_2PC{\equiv}CPPh_2$ affords the complex $[W(CO)_2(Ph_2PC{\equiv}CPPh_2)(S_2CNEt_2)_2]$ in which the $Ph_2PC{\equiv}CPPh_2$ acts as a monodentate phosphorus donor. In solution this compound loses carbon monoxide and rearranges to $[W(CO)(Ph_2PC{\equiv}CPPh_2)(S_2CNEt_2)_2]$ **1**, which is a rare example of a complex containing $Ph_2PC{\equiv}CPPh_2$ co-ordinated through the C≡C linkage and in this case acts as a four-electron donor. Co-ordination of an alkyne to a transition metal results in a distortion of the skeleton of the alkyne to afford a *cis*-bent structure in which the substituents are bent back from linear 10–50°.[3] This paper describes how this distortion affects the donor chemistry of the phosphorus centres in compound **1**. A preliminary account has been made of some of the results.[4]

Results and Discussion

Reaction of compound **1** with $[M(CO)_4(pip)_2]$ (M = Cr, Mo or W; pip = piperidine) in CH_2Cl_2 at room temperature affords **2**, **3** and **4**, respectively, in which the alkyne ligand chelates *via* its phosphorus centres to a metal tetracarbonyl fragment, thereby utilising all three donor sites simultaneously. All three compounds gave satisfactory analytical data (see Table 1) and the fast atom bombardment (FAB) mass spectrum of **3** contains an isotope envelope centred at *m*/*z* 972 assigned to $[M - 5CO]^+$ which was fitted by MASPAN with $R = 3.7\%$. The IR and NMR spectra of **2**–**4** (see Tables 1 and 2) will be discussed after their crystal structures.



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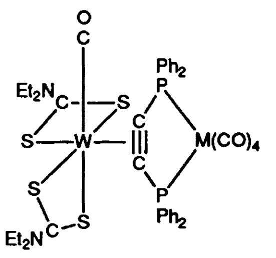
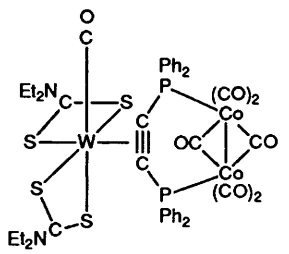


2 M = Cr
3 M = Mo
4 M = W



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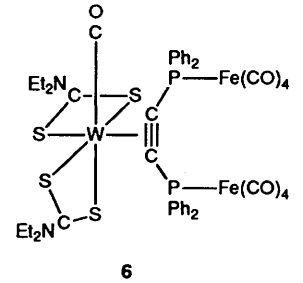

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Suitable crystals of all three compounds were obtained and the results of the X-ray diffraction studies are summarised in Table 3. The three compounds are isomorphous and crystallise

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Analytical[a] and physical data

Compound	Colour	Yield (%)	ν_{max}(CO)[b]/cm^{-1}	Analysis (%) C	H	N
2	Yellow-green	55	2008s, 1951m, 1917s, 1906vs, 1883m	46.8 (46.2)	4.4 (3.8)	2.5 (2.6)
3	Green	69	2020s, 1950m, 1923s, 1914vs, 1890m	43.9 (44.3)	3.6 (3.6)	2.5 (2.5)
4	Green	58	2016s, 1950m, 1916 (sh), 1905vs, 1885s	40.6 (41.1)	3.8 (3.4)	1.9 (2.3)
5	Yellow	46	2038s, 2003s, 1982vs, 1966m, 1938m, 1824m, 1814m, 1791w	42.9 (43.5)	3.1 (3.4)	2.3 (2.4)
6	Yellow	69	2047s, 1978 (sh), 1964s, 1947vs, 1933s	44.6 (43.6)	3.7 (3.3)	1.9 (2.3)

[a] Calculated values are in parentheses. [b] In toluene.

Table 2 Hydrogen-1, carbon-13 and phosphorus-31 NMR data[a]

Compound	^{1}H (δ)	^{13}C (δ)[b]	^{31}P (δ)[c]
2	[d]8.1–7.2 (m, 20 H, Ph), 3.7–3.4 (m, 8 H, CH$_2$), 1.32 [t, 3 H, Me, *J*(HH) 7], 1.20 [t, 6 H, 2 × Me, *J*(HH) 7], 1.11 [t, 3 H, Me, *J*(HH) 7]	[d]239.3 [d, C≡C, *J*(PC) 12], 233.9 [WCO, *J*(WC) 135], 229.0 [dd, *trans* Cr(CO)$_2$, *J*(PC) 2 and 12], 220.8 [t, *cis* Cr(CO)$_2$, *J*(PC) 11], 213.2, 199.7 (S$_2$*C*NEt$_2$), 135–127 (Ph), 46.4, 44.9, 44.6, 44.4 (CH$_2$), 13.1, 12.5, 12.4, 12.2 (Me)	[d,e] −19.5 [d, *J*(PP) 9], −23.7 [d, *J*(PP) 9]
3	[d]7.9–7.2 (m, 20 H, Ph), 3.7–3.4 (m, 8 H, CH$_2$), 1.26 [t, 3 H, Me, *J*(HH) 7], 1.18 (t, 6 H, 2 × Me, *J*(HH) 7], 1.10 [t, 3 H, Me, *J*(HH) 7]	[f]236.1 [d, C≡C, *J*(PC) 9, *J*(WC) 37], 233.3 [WCO, *J*(WC) 135], 217.5 [dd, *trans* Mo(CO)$_2$, *J*(PC) 7 and 29], 211.9 (S$_2$*C*NEt$_2$), 209.1 [t, *cis* Mo(CO)$_2$, *J*(PC) 9], 199.8 (S$_2$*C*NEt$_2$), 135–127 (Ph), 45.8 , 44.2, 44.0, 43.7 (CH$_2$), 12.1, 11.4, 11.3, 11.2 (Me)	[f,g] +48.5 [d, *J*(PP) 4], +44.2 [d, *J*(PP) 4]
4	[f] 8.0–6.9 (m, 20 H, Ph), 3.8–3.4 (m, 8 H, CH$_2$), 1.3–1.1 (m, 12 H, Me)	[f]238.1 (C≡C), 234.2 [WCO, *J*(WC), 135], 212.9 (S$_2$*C*NEt$_2$), 209.9 [dd, *trans* W(CO)$_2$, *J*(PC) 5 and 27], 203.1 [t, *cis* W(CO)$_2$, *J*(PC) 7], 199.7 (S$_2$*C*NEt$_2$), 139–128 (Ph), 47.0, 45.4, 45.1, 44.9 (CH$_2$), 13.3, 12.6, 12.5, 12.4 (Me)	[f,g] +34.0 [d, *J*(PP) 3, *J*(WP) 243], +29.8 [d, *J*(PP) 3, *J*(WP) 244]
5	[d]7.8–7.0 (m, 20 H, Ph), 3.8–3.1 (m, 8 H, CH$_2$), 1.4–0.9 (m, 12 H, Me)	[f]235.8 (WCO), 218.6 (C≡C), 215.2 (CoCO), 212.2, 200.0 (S$_2$*C*NEt$_2$), 136–128 (Ph), 46.4, 44.9, 44.7, 44.6 (CH$_2$), 13.1, 12.6 (× 2), 12.2 (Me)	[f,g] +31.4 [d, *J*(PP) 91], +21.3 [d, *J*(PP) 91]
6	[f]7.9–7.0 (m, 20 H, Ph), 3.7–3.3 (m, 8 H, CH$_2$), 1.5–1.0 (m, 12 H, Me)	[f]238.2 (WCO), 217.9 [d, C≡C, *J*(PC) 14], 214.8 [d, FeCO, *J*(PC) 15], 211.6, 199.4 (S$_2$*C*NEt$_2$), 138–128 (Ph), 46.4, 45.1, 44.9, 44.8 (CH$_2$), 13.3, 12.7 (× 2), 12.3 (Me)	[f,h] +81.9, +74.0

[a] Chemical shifts (δ) in ppm, coupling constants in Hz. [b] Hydrogen-1 decoupled. [c] Hydrogen-1 decoupled, chemical shifts (δ) to high frequency of 85% H_3PO_4 (external). [d] Measured in $CDCl_3$. [e] Measured at 223 K. [f] Measured in CD_2Cl_2. [g] Measured at 213 K. [h] Measured at 182 K.

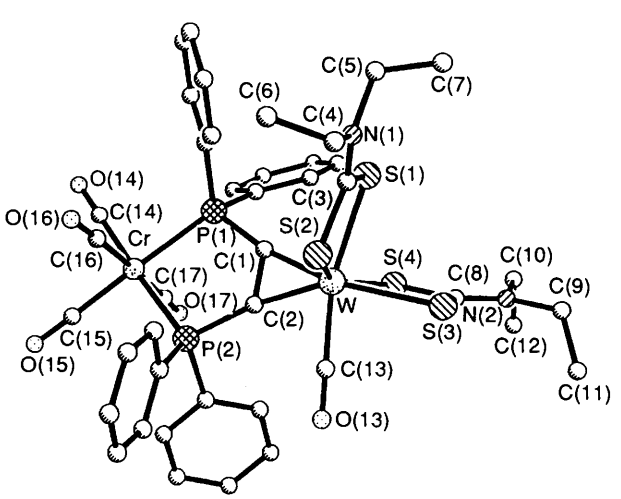

Fig. 1 The molecular structure of [W(CO){(Ph$_2$PC≡CPPh$_2$)Cr(CO)$_4$}(S$_2$CNEt$_2$)$_2$] **2** showing the atom labelling system

in space group $P2_1/n$ with one molecule of pentane per asymmetric unit which is reasonably ordered for **2** and **3** but disordered for **4**. They are isostructural and the molecular structure of **2** is shown in Fig. 1, while the molecular packing in the unit cell of **3** is shown in Fig. 2.

The co-ordination geometry about the tungsten centre in all three cases is as expected by comparison with [W(CO)(C$_2$H$_2$)(S$_2$CNEt$_2$)$_2$][5] and can be described as pseudo-octahedral or pentagonal bipyramidal with sulfur atoms S(2) and S(4) at the apexes and the carbonyl carbon, both alkyne carbons and the two remaining sulfur atoms forming the equatorial plane. The longest W–S bond is *trans* to the alkyne while the mutually *trans* W–S bonds are the shortest in all three cases. The near coplanarity of the C≡O and C≡C bonds is as expected from bonding considerations.[6] The tungsten–alkyne carbon bond lengths are all in the range (2.03 ± 0.03) Å expected for four-electron-donor alkyne tungsten(II) systems.[6] The alkyne bond lengths, 1.328(16), 1.321(14) and 1.365 (18) Å, for complexes **2**, **3** and **4** respectively, are similar to that found in [W(CO)(C$_2$H$_2$)(S$_2$CNEt$_2$)$_2$], 1.29(1) Å.[5] The inadequacy of carbon–carbon bond distances as a probe of metal–alkyne bonding has been recognised for some time[5] and they are subject to considerable variation.[6] The two diethyldithiocarbamate ligands co-ordinated to the tungsten centres in **2**–**4** adopt different ethyl group conformations, one being cisoid and the other transoid with respect to the planes of the ligands. This has been observed previously and may well be a consequence of unit-cell packing.[7]

When considering the co-ordination of the metal tetracarbonyl fragment in complexes **2**–**4** it is useful to compare these complexes with those of other bidentate phosphines with unsaturated backbones. The similarity of dicobalt hexacarbonyl alkyne complexes to *ortho*-benzene systems has been noted previously.[8] For comparison with **2**–**4** particularly relevant examples are [Mo(CO)$_4$(*cis*-Ph$_2$PCH=CHPPh$_2$)][9] and [W(CO)$_4${*o*-(Pr$^i_2$P)$_2$C$_6$H$_4$}].[10] The unsaturated nature of the backbone ensures planarity of the two phosphorus centres and the backbone carbon atoms. For example, in **3** distances from the least-squares plane P(1), P(2), C(1), C(2) are +0.0146, −0.0155, −0.0375 and +0.0383 Å for the atoms listed. The tungsten and molybdenum atoms deviate from this plane by

Table 3 Selected internuclear distances (Å) and angles (°) for complexes **2**–**4**

	2 (M = Cr)	**3** (M = Mo)	**4** (M = W)
W–S(1)	2.543(3)	2.550(3)	2.547(4)
W–S(2)	2.387(3)	2.386(3)	2.381(4)
W–S(3)	2.580(4)	2.588(4)	2.582(5)
W–S(4)	2.515(3)	2.512(3)	2.514(4)
W–C(1)	2.033(13)	2.026(11)	2.033(14)
W–C(2)	2.025(13)	2.040(11)	2.041(14)
W–C(13)	2.006(16)	1.984(14)	1.957(17)
M–P(1)	2.380(4)	2.525(3)	2.512(4)
M–P(2)	2.375(4)	2.521(3)	2.507(4)
M–C(14)	1.868(15)	1.978(13)	1.955(18)
M–C(15)	1.867(14)	1.979(14)	1.971(16)
M–C(16)	1.920(14)	2.007(11)	2.026(16)
M–C(17)	1.913(13)	2.020(12)	2.016(17)
S(1)–W–S(2)	71.0(1)	71.0(1)	71.1(1)
S(1)–W–S(3)	83.6(1)	83.6(1)	83.4(2)
S(2)–W–S(3)	87.4(1)	87.4(1)	87.2(1)
S(1)–W–S(4)	88.7(1)	89.1(1)	89.2(2)
S(2)–W–S(4)	150.1(1)	150.5(1)	150.3(2)
S(3)–W–S(4)	68.2(1)	68.3(1)	68.1(1)
S(1)–W–C(1)	87.8(3)	88.2(3)	88.6(4)
S(2)–W–C(1)	107.8(3)	108.3(3)	108.3(4)
S(4)–W–C(1)	92.7(3)	92.1(3)	92.7(4)
S(1)–W–C(2)	124.8(4)	125.0(3)	126.6(4)
S(2)–W–C(2)	108.4(3)	109.2(3)	108.9(3)
S(4)–W–C(2)	101.2(3)	100.0(2)	100.6(3)
C(1)–W–C(2)	38.2(5)	37.9(4)	39.1(5)
S(1)–W–C(13)	157.6(4)	157.2(4)	157.6(4)
S(2)–W–C(13)	93.9(3)	92.9(3)	93.9(4)
S(3)–W–C(13)	79.2(5)	79.5(4)	79.2(6)
S(4)–W–C(13)	97.9(4)	98.7(4)	97.2(5)
C(2)–W–C(13)	75.0(5)	74.9(5)	73.4(6)
P(1)–M–P(2)	84.8(1)	82.2(1)	82.1(1)
P(1)–M–C(14)	92.0(5)	92.9(4)	91.8(5)
P(2)–M–C(15)	92.2(4)	92.7(4)	93.3(5)
C(14)–M–C(15)	91.0(6)	92.2(5)	92.9(7)
P(1)–M–C(16)	90.1(5)	90.8(4)	90.2(5)
P(2)–M–C(16)	93.7(4)	93.0(4)	93.1(5)
P(1)–C(1)	1.815(13)	1.826(11)	1.821(14)
P(2)–C(2)	1.818(13)	1.816(12)	1.796(15)
S(1)–C(3)	1.696(11)	1.695(10)	1.712(15)
S(2)–C(3)	1.747(12)	1.750(12)	1.758(16)
S(3)–C(8)	1.715(12)	1.687(11)	1.714(15)
S(4)–C(8)	1.710(16)	1.704(14)	1.701(19)
C(1)–C(2)	1.328(16)	1.321(14)	1.365(18)
C(3)–N(1)	1.317(16)	1.303(15)	1.300(20)
C(8)–N(2)	1.307(22)	1.322(21)	1.328(28)
C(13)–O(13)	1.129(19)	1.156(18)	1.155(22)
C(14)–O(14)	1.130(19)	1.141(17)	1.169 (23)
C(15)–O(15)	1.137(19)	1.156(17)	1.162(22)
C(16)–O(16)	1.122(18)	1.157(15)	1.136(20)
C(17)–O(17)	1.119(17)	1.131(15)	1.141(22)
C(14)–M–C(16)	88.7(6)	89.5(5)	88.7(6)
C(15)–M–C(16)	88.4(6)	87.1(5)	89.6(7)
P(1)–M–C(17)	92.4(5)	91.8(4)	92.6(6)
P(2)–M–C(17)	88.0(4)	88.1(4)	87.8(5)
C(14)–M–C(17)	89.7(6)	89.6(5)	90.7(7)
C(15)–M–C(17)	89.2(6)	90.3(5)	87.7(7)
M–P(1)–C(1)	106.6(4)	106.1(3)	106.1(5)
M–P(2)–C(2)	105.9(4)	104.8(4)	107.0(4)
W–S(1)–C(3)	86.1(4)	86.0(4)	86.5(5)
W–S(2)–C(3)	90.0(4)	90.1(3)	90.8(5)
W–S(3)–C(8)	88.2(6)	87.1(5)	88.0(7)
W–S(4)–C(8)	90.5(5)	89.2(5)	177.2(16)
W–C(1)–P(1)	169.6(7)	167.5(6)	90.5(6)
W–C(1)–C(2)	70.6(8)	71.6(7)	167.2(8)
P(1)–C(1)–C(2)	119.8(10)	120.9(9)	70.8(8)
W–C(2)–P(2)	164.7(6)	162.5(6)	122.0(11)
W–C(2)–C(1)	71.2(8)	70.5(7)	164.9(7)
P(2)–C(2)–C(1)	122.2(10)	125.4(9)	70.1(8)
S(1)–C(3)–S(2)	112.8(7)	112.9(6)	122.3(11)
S(3)–C(8)–S(4)	113.0(9)	115.2(9)	111.6(8)
W–C(13)–O(13)	178.4(11)	179.6(10)	113.4(12)
M–C(14)–O(14)	179.1(14)	178.9(12)	176.7(15)
M–C(15)–O(15)	178.5(12)	178.0(10)	177.7(14)
M–C(16)–O(16)	176.3(15)	177.6(12)	178.2(16)
M–C(17)–O(17)	177.8(15)	176.8(14)	177.9(19)

−0.1311 and −0.1213 Å respectively. The C≡C–P angles in **2**–**4** are similar [average 122(1)°] and are smaller than are normally found in alkyne complexes, which fall in the range 130–150°; this is due to the formation of the five-membered ring. For comparison the C=C–P angles in [$Mo(CO)_4$(*cis*-$Ph_2PCH{=}CHPPh_2$)] are 119.8(4) and 120.6(4)°.[9] The geometry around the tetracarbonyl fragments is that of a distorted octahedron with the equatorial plane being formed by two mutual *cis*-carbonyls and the two phosphorus centres. Distortions from the octahedral geometry are largely due to the formation of the five-membered chelate ring and also the differences between the M–P and M–CO bond lengths. As expected the M–C lengths for the mutually *cis*-carbonyl ligands (*trans* to the bidentate phosphine ligand) are shorter than the corresponding lengths for the mutually *trans*-carbonyl ligands. The bite angle P–M–P for complex **2** [84.8(1)°] is significantly larger than those in **3** [82.2(1)°] and **4** [82.1(1)°] due to the smaller covalent radius of chromium compared to molybdenum and tungsten.

The IR spectra of complexes **2**–**4** in the carbonyl stretching region (see Table 1) can be rationalised by considering the expected absorptions for the tungsten monocarbonyl and the metal tetracarbonyl moieties. For example, the absorptions in the spectrum of **2** at 2008s, 1917s, 1906vs and 1883m cm^{-1} can be compared with those reported in 1,2-dichloroethane for [$Cr(CO)_4$(dppe)][11] (dppe = $Ph_2PCH_2CH_2PPh_2$) at 2009s, 1914 (sh), 1899vs and 1877s cm^{-1}, while the absorption at 1951 cm^{-1} can be ascribed to the tungsten carbonyl by comparison with the absorption in the spectrum of **1** at 1931 cm^{-1}. The shift of approximately +20 cm^{-1} for all three compounds indicates that donation of the phosphorus lone pairs to the incoming metal–ligand fragment is making the alkyne a worse donor and/or a better electron acceptor as expected.

The ^{13}C NMR spectra of compounds **2**–**4** are also readily interpreted by comparison with those of **1** and other metal tetracarbonyl diphosphines. For example, the $^{13}C\text{-}\{^1H\}$ NMR spectrum of **3** contains resonances assigned to the *cis*- and *trans*-$Mo(CO)_2$ groups at δ 209.1 and 217.5 which compare closely with those observed for [$Mo(CO)_4$(dppe)] at δ 210.6 and 218.5 respectively.[12] Compounds **2**–**4** all have WCO resonances occurring at *ca.* δ 234, similar in position to the resonance at δ 237.9 for this group in **1**. The acetylenic resonances are shifted downfield to *ca.* δ 238 compared to δ 219 in the spectrum of **1**. A single resonance is observed at room temperature indicating that the alkyne is rotating relative to the tungsten–ligand fragment on the NMR time-scale at room temperature. This phenomenon is well known for this type of compound and was investigated further using ^{31}P NMR spectroscopy. At low temperature all three compounds display two resonances in their $^{31}P\text{-}\{^1H\}$ spectra (see Table 2) in accord with their solid-state structures, which coalesce to form one resonance upon warming. Coalescence temperatures for **2**, **3** and **4** are 298, 289 and 293 K, respectively, for spectra recorded at 109.25 MHz. The rotational activation barriers for the alkynes, $\Delta G^{\ddagger}_{T_c}$, were calculated from the Eyring equation after the Gutowsky–Holm equation was employed to calculate K_{ex} at the coalescence temperatures,[13] and found to be 55.6, 54.0 and 54.8 ± 2 kJ mol^{-1}. The variable-temperature behaviour of **3** was also modelled by band-shape analysis using a modified version of

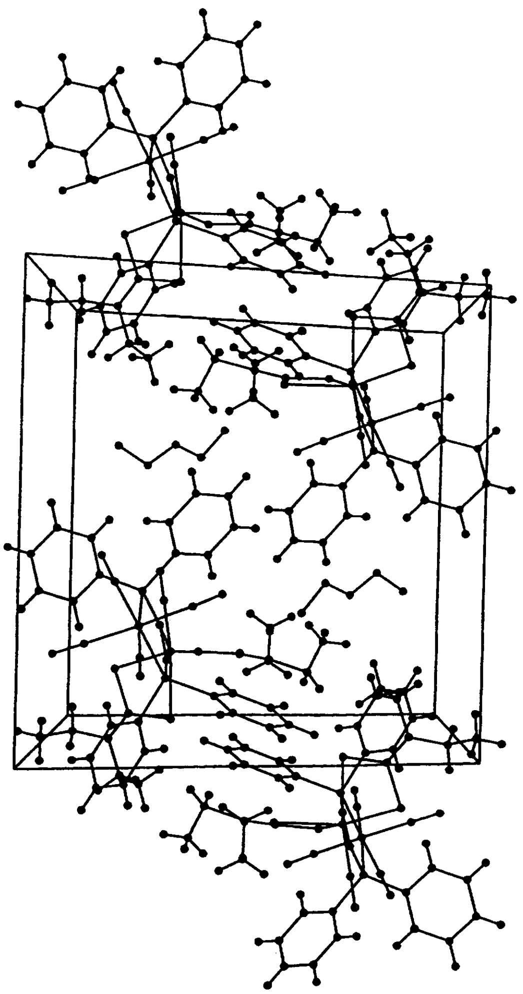

Fig. 2 Projection of the contents of the unit cell of complex **3** in the *ab* plane

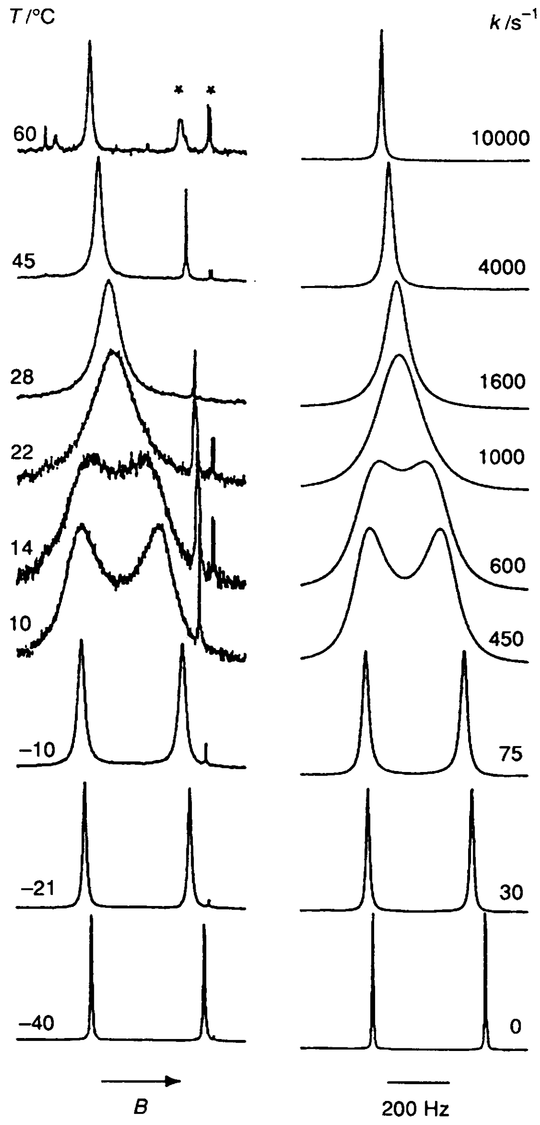

Fig. 3 Variable-temperature $^{31}P-\{^1H\}$ NMR spectra of complex $[W(CO)\{(Ph_2PC{\equiv}CPPh_2)Mo(CO)_4\}(S_2CNEt_2)_2]$ **3** and their computer syntheses; the asterisk indicates an impurity

DNMR 3.[14] The calculated and observed spectra are shown in Fig. 3. Recording spectra below −40 °C allowed an estimate of the temperature dependence to be made which was modelled in a linear fashion by 0.98 Hz K^{-1} for the downfield resonance and 2.52 Hz K^{-1} for the upfield resonance. An Erying plot of the data gave $\Delta H^{\ddagger} = 47.8 \pm 0.7$ kJ mol^{-1} and $\Delta S^{\ddagger} = -25.8 \pm 2.5$ J K^{-1} mol^{-1} corresponding to $\Delta G^{\ddagger}_{T_c} = 55.3 \pm 0.1$ kJ mol^{-1} and $\Delta G^{\ddagger}_{298} = 55.5 \pm 0.1$ kJ mol^{-1}. Ward and Templeton[2] report a $\Delta G^{\ddagger}_{T_c}$ value for **1** of 47.7 ± 0.4 kJ mol^{-1} and typically compounds of the type $[W(CO)(alkyne)(S_2CNR_2)_2]$ have alkyne rotational barriers in the range 43–50 kJ mol^{-1}, although barriers of up to 80 kJ mol^{-1} have been observed in some four-electron-donor alkyne systems.[6] It is possible that steric factors influence the magnitude of the barrier as addition of a metal tetracarbonyl moiety makes the alkyne bulkier and forces the aromatic rings close to the tungsten fragment as rotation about the phosphorus–alkyne carbon bonds is now prevented. As well as steric factors, both $\Pi^*_{\parallel}$ acceptance and $\Pi_{\perp}$ donation by the alkyne also influence the barrier making interpretation difficult.[6] Extended-Hückel molecular-orbital calculations performed by us using the model compound $[W(CO)(HC{\equiv}CH)(S_2CNH_2)_2]$ indicate that the magnitude of the barrier is affected little by the alkyne bend-back angle.

Reaction of complex **1** with $[Co_2(CO)_8]$ affords **5** in which the Co–Co bond is bridged in an analogous fashion to the known $[Co_2(\mu-L_2)(\mu-CO)_2(CO)_4]$ complexes $[L_2 = R_2M(CH_2)_nMR_2$; R = alkyl or aryl, M = P or As, $n \geqslant 1$].[15] This contrasts with the reaction of $Ph_2PC{\equiv}CPPh_2$ with $[Co_2(CO)_8]$ which forms $[\{Co_2(CO)_7\}_2(\mu-Ph_2PC{\equiv}CPPh_2)]$ in which two $Co_2(CO)_7$ moieties are linked by a linear $Ph_2PC{\equiv}CPPh_2$ and the acetylenic bond remains unco-ordinated.[16] The FAB mass spectrum of **5** contains isotope envelopes centred at *m*/*z* 1048, 1020 and 992 assigned to $[M - nCO]^+$ (n = 5–7). The cobalt carbonyl IR absorptions are similar to those of other $[Co_2(\mu-L_2)(\mu-CO)_2(CO)_4]$ complexes[15] and the extra absorption at 1938 cm^{-1} is assigned to the tungsten carbonyl. Again alkyne rotation is observed on the NMR time-scale at room temperature. Upon cooling, the resonance in the $^{31}P-\{^1H\}$ NMR spectrum at δ +23.7 broadens and then becomes two sharp doublets (see Table 2).

Reaction of complex **1** with $[Fe_2(CO)_9]$ affords **6** which decomposes slowly in solution at room temperature and is also light sensitive. The FAB mass spectrum contains an isotope envelope centred at *m*/*z* 1126 corresponding to $[M - 4CO]^+$ and five subsequent CO-loss peaks. Compound **6** was characterised by comparison of its spectroscopic characteristics with those of **1** and $[Fe_2(\mu-dppm)(CO)_8]$ (dppm = $Ph_2PCH_2PPh_2$).[17] The latter compound undergoes photolysis to form $[Fe_2(\mu-dppm)(\mu-CO)(CO)_6]$, containing an Fe–Fe bond.[17,18] Photolysis of **6** leads to decomposition without any evidence for the formation of an analogous compound.

In conclusion this paper presents a range of compounds in

Table 4 Crystal data and experimental parameters

	2	3	4
Compound	$C_{41}H_{40}CrN_2O_5P_2S_4W{\cdot}C_5H_{12}$	$C_{41}H_{40}MoN_2O_5P_4S_4W{\cdot}C_5H_{12}$	$C_{41}H_{40}N_2O_5P_2S_4W_2{\cdot}C_5H_{12}$
M	1120.9	1170.8	1258.7
Crystal system	Monoclinic	Monoclinic	Monoclinic
Crystal habit	Cuboid	Rhombohedral	Rhombohedral
Colour	Green	Green	Green
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	15.856(2)	15.981(5)	15.920(4)
b/Å	16.175(3)	16.349(5)	16.306(3)
c/Å	21.009(4)	21.106(6)	21.248(4)
β/°	111.50(10)	111.21(2)	111.09(2)
U/Å^3	5146(2)	5141(3)	5146(2)
Z	4	4	4
D_c/g cm^{-3}	1.447	1.513	1.625
F(000)	2236	2320	2448
μ(Mo-Kα)/mm^{-1}	2.743	2.781	4.823
Crystal size/mm	0.48 × 0.30 × 0.25	0.35 × 0.15 × 0.10	0.45 × 0.40 × 0.38
Minimum, maximum 2θ/°	2.0, 50.0	0.0, 50.0	2.0, 50.0
Data recorded	9983	7540	10 126
Data unique	8872	6936	9004
Data used [$F \geqslant 4\sigma(F)$]	6951	5515	6737
R(*R*′)	4.7 (4.7)	8.5 (5.0)	5.6 (5.6)

Table 5 Atomic coordinates (× 10^4), with estimated standard deviations (e.s.d.s) in parentheses, for complex **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	2876(1)	1922(1)	4288(1)	O(17)	4102(7)	3344(8)	7260(6)
Cr	2244(1)	2611(1)	6498(1)	C(20)	2230(8)	495(7)	5909(6)
P(1)	2841(2)	1481(2)	6071(2)	C(21)	2404(9)	−91(9)	6425(7)
P(2)	2227(2)	3311(2)	5500(2)	C(22)	1935(11)	−827(9)	6301(9)
S(1)	2895(2)	353(2)	4215(2)	C(23)	1283(11)	−980(9)	5666(9)
S(2)	1460(2)	1463(2)	3475(2)	C(24)	1090(9)	−403(10)	5160(8)
S(3)	3505(2)	1846(2)	3318(2)	C(25)	1553(9)	328(8)	5276(7)
S(4)	4580(2)	1905(3)	4745(2)	C(30)	4003(7)	1126(7)	6509(6)
C(1)	2826(8)	1791(7)	5236(6)	C(31)	4438(9)	1241(10)	7199(7)
C(2)	2631(8)	2567(7)	5029(6)	C(32)	5323(10)	959(11)	7530(8)
C(3)	1824(8)	437(8)	3633(6)	C(33)	5760(10)	558(11)	7176(10)
N(1)	1313(8)	−194(7)	3324(6)	C(34)	5345(10)	438(10)	6503(9)
C(4)	390(10)	−90(10)	2799(8)	C(35)	4463(9)	715(9)	6155(7)
C(5)	1619(12)	−1057(10)	3474(11)	C(40)	1135(8)	3635(8)	4841(6)
C(6)	−326(12)	−195(15)	3077(10)	C(41)	529(10)	3025(9)	4520(8)
C(7)	2034(16)	−1368(14)	3036(15)	C(42)	−327(10)	3246(12)	4054(8)
C(8)	4575(9)	1814(9)	3933(7)	C(43)	−553(11)	4033(11)	3904(8)
N(2)	5302(9)	1673(10)	3796(7)	C(44)	46(13)	4638(12)	4211(10)
C(9)	5266(11)	1595(11)	3084(8)	C(45)	904(11)	4439(10)	4681(9)
C(10)	6248(13)	1467(13)	4393(11)	C(50)	2973(8)	4216(7)	5638(6)
C(11)	5316(14)	2358(11)	2748(10)	C(51)	3724(10)	4216(9)	5459(7)
C(12)	6724(19)	2184(14)	4544(14)	C(52)	4297(11)	4899(11)	5613(8)
C(13)	2697(9)	3094(10)	3953(6)	C(53)	4114(12)	5579(10)	5940(8)
O(13)	2575(9)	3750(7)	3757(6)	C(54)	3382(12)	5579(9)	6125(8)
C(14)	2331(8)	2026(9)	7287(7)	C(55)	2814(10)	4904(8)	5982(7)
O(14)	2386(8)	1681(8)	7768(6)	C(60)*	1148	1886	1486
C(15)	1738(8)	3517(8)	6780(6)	C(61)*	1416	1378	1607
O(15)	1432(8)	4059(6)	6964(5)	C(62)*	2276	1703	1143
C(16)	1042(10)	2177(8)	6061(7)	C(63)*	2860	1149	1106
O(16)	332(7)	1930(8)	5837(6)	C(64)*	3562	1571	854
C(17)	3422(10)	3066(9)	6969(6)				

* Solvent molecule.

which $Ph_2PC{\equiv}CPPh_2$ bonds to metal centres using all three donor sites and illustrates the dramatic effect that the structural distortion caused by co-ordination of the acetylenic bond can have on the subsequent chemistry.

Experimental

The experimental techniques used and the instrumentation employed have been described previously.[19] The compound $[W(CO)(Ph_2PC{\equiv}CPPh_2)(S_2CNEt_2)_2]$ was prepared by a literature method.[2] Analytical and other data for the new compounds are given in Tables 1 and 2. Compounds **2**–**4** were prepared by similar procedures and will only be described in detail for **3**.

Preparations.—$[W(CO)\{(Ph_2PC{\equiv}CPPh_2)Mo(CO)_4\}(S_2CNEt_2)_2]$ **3**. A solution of $[W(CO)(Ph_2PC{\equiv}CPPh_2)(S_2CNEt_2)_2]$ (0.14 g, 0.16 mmol) and $[Mo(CO)_4(pip)_2]$ (0.06 g, 0.16 mmol) in CH_2Cl_2 (20 cm^3) was stirred for 2 h, after which time the solvent was removed *in vacuo*. Chromatography of the residue on an alumina column (1.5 × 15 cm) eluting with light petroleum (40–60 °C)–CH_2Cl_2 (1:1) afforded a green eluate

Table 6 Atomic coordinates (× 10^4), with e.s.d.s in parentheses, for complex **3**

Atom	*x*	*y*	*z*
W	2850(1)	1906(1)	4292(1)
Mo	2217(1)	2609(1)	6547(1)
P(1)	2830(2)	1439(2)	6065(1)
P(2)	2215(2)	3316(2)	5485(1)
S(1)	2883(2)	350(2)	4220(2)
S(2)	1456(2)	1442(2)	3484(2)
S(3)	3486(2)	1840(2)	3327(1)
S(4)	4536(2)	1912(3)	4750(2)
C(1)	2806(6)	1782(6)	5235(5)
C(2)	2613(6)	2549(7)	5039(5)
C(3)	1824(7)	429(7)	3644(6)
N(1)	1321(7)	−180(7)	3325(6)
C(4)	410(9)	−62(9)	2807(7)
C(5)	1626(10)	−1031(10)	3455(9)
C(6)	−324(9)	−159(11)	3076(8)
C(7)	2056(11)	−1301(11)	3008(12)
C(8)	4517(9)	1830(9)	3940(6)
N(2)	5254(8)	1707(8)	3806(5)
C(9)	5242(9)	1614(9)	3102(7)
C(10)	6212(14)	1465(13)	4417(12)
C(11)	5275(10)	2386(10)	2767(8)
C(12)	6592(16)	2185(15)	4506(11)
C(13)	2642(8)	3048(9)	3954(6)
O(13)	2523(6)	3712(6)	3754(5)
C(14)	2313(7)	1989(8)	7375(6)
O(14)	2365(6)	1642(7)	7857(5)
C(15)	1683(8)	3566(8)	6833(6)
O(15)	1395(6)	4129(6)	7016(5)
C(16)	961(8)	2188(7)	6092(6)
O(16)	232(6)	1949(7)	5851(5)
C(17)	3459(8)	3066(8)	7033(6)
O(17)	4137(6)	3349(7)	7318(6)
C(20)	2216	476	5894
C(21)	2413(5)	−113(5)	6406(3)
C(22)	1937	−848	6287
C(23)	1265	−993	5657
C(24)	1069	−405	5145
C(25)	1544	330	5264
C(30)	3982	1091	6484
C(31)	4421(6)	1221(5)	7179(4)
C(32)	5297	941	7504
C(33)	5735	531	7133
C(34)	5296	401	6438
C(35)	4419	681	6113
C(40)	1164	3639	4838
C(41)	544(6)	3026(4)	4527(4)
C(42)	−299	3232	4057
C(43)	−523	4051	3898
C(44)	96	4664	4209
C(45)	940	4458	4679
C(50)	2985	4173	5618
C(51)	3733(6)	4141(5)	5426(4)
C(52)	4333	4796	5573
C(53)	4186	5482	5912
C(54)	3438	5513	6104
C(55)	2838	4858	5957
C(60)*	988(17)	2065(19)	1550(15)
C(61)*	1553(21)	1397(21)	1432(17)
C(62)*	2169(17)	1658(15)	1205(12)
C(63)*	2833(23)	1156(23)	1156(17)
C(64)*	3522(27)	1577(29)	891(24)

* Solvent molecule.

Table 7 Atomic coordinates (× 10^4), with e.s.d.s in parentheses, for complex **4**

Atom	*x*	*y*	*z*
W(1)	2853(1)	1903(1)	4307(1)
W(2)	2213(1)	2612(1)	6540(1)
P(1)	2840(2)	1448(2)	6071(2)
P(2)	2220(3)	3312(2)	5492(2)
S(1)	2887(3)	345(3)	4237(2)
S(2)	1448(3)	1440(3)	3521(2)
S(3)	3460(3)	1830(3)	3333(2)
S(4)	4545(3)	1914(3)	4732(2)
C(1)	2825(8)	1790(8)	5252(6)
C(2)	2625(8)	2579(8)	5037(6)
C(3)	1807(11)	414(10)	3669(8)
N(1)	1310(10)	−200(9)	3358(7)
C(4)	385(13)	−84(12)	2825(10)
C(5)	1621(13)	−1047(12)	3501(11)
C(6)	−305(14)	−213(17)	3115(12)
C(7)	2067(17)	−1317(17)	2973(17)
C(8)	4526(11)	1824(11)	3930(8)
N(2)	5263(11)	1704(13)	3787(8)
C(9)	5218(14)	1590(14)	3081(9)
C(10)	6252(19)	1449(18)	4432(16)
C(11)	5261(17)	2386(14)	2739(11)
C(12)	6632(29)	2204(19)	4485(18)
C(13)	2670(12)	3036(11)	3981(7)
O(13)	2517(10)	3697(8)	3777(6)
C(14)	2298(10)	1975(11)	7341(8)
O(14)	2363(9)	1623(10)	7835(6)
C(15)	1708(11)	3574(9)	6840(8)
O(15)	1382(9)	4128(8)	7011(6)
C(16)	952(11)	2166(10)	6079(8)
O(16)	236(8)	1935(9)	5823(7)
C(17)	3443(12)	3094(11)	7025(8)
O(17)	4133(9)	3369(10)	7316(8)
C(20)	2252(9)	471(9)	5922(7)
C(21)	2408(11)	−112(9)	6419(8)
C(22)	1958(12)	−843(11)	6305(10)
C(23)	1301(13)	−987(11)	5689(11)
C(24)	1102(12)	−417(12)	5187(9)
C(25)	1549(10)	334(10)	5269(8)
C(30)	4011(9)	1115(8)	6493(7)
C(31)	4431(11)	1234(11)	7181(8)
C(32)	5299(13)	965(15)	7513(10)
C(33)	5737(13)	556(14)	7160(11)
C(34)	5339(12)	428(12)	6475(11)
C(35)	4454(11)	703(10)	6141(9)
C(40)	1168(11)	3640(10)	4852(7)
C(41)	532(12)	3073(12)	4524(9)
C(42)	−298(13)	3279(15)	4050(10)
C(43)	−522(13)	4052(15)	3911(10)
C(44)	88(17)	4629(15)	4226(12)
C(45)	938(13)	4433(11)	4683(10)
C(50)	2971(10)	4188(9)	5626(7)
C(51)	3718(13)	4172(12)	5447(9)
C(52)	4305(16)	4832(14)	5583(11)
C(53)	4163(15)	5497(13)	5925(11)
C(54)	3422(15)	5506(12)	6119(10)
C(55)	2848(12)	4854(10)	5984(9)
C(60)*	1696	563	1767
C(61)*	903	2065	1057
C(62)*	3566	1628	175
C(63)*	3513	1161	1430
C(64)*	1004	1997	1604
C(65)*	3169	1364	859
C(66)*	1887	1194	1238
C(67)*	2676	997	1077
C(68)*	1504	1658	986
C(69)*	1425	1326	1771

* Solvent molecule.

which upon removal of the solvent *in vacuo* gave complex **3** (0.12 g, 0.11 mmol).

$[W(CO)\{(Ph_2PC{\equiv}CPPh_2)Co_2(\mu\text{-}CO)_2(CO)_4\}(S_2CNEt_2)_2]$ **5**. A solution of $[W(CO)(Ph_2PC{\equiv}CPPh_2)(S_2CNEt_2)_2]$ (0.50 g, 0.55 mmol) and $[Co_2(CO)_8]$ (0.19 g, 0.55 mmol) was stirred for 36 h, after which time the solvent was removed *in vacuo*. The residue was chromatographed on an alumina column (1.5 × 10 cm) eluting with light petroleum (40–60 °C)–CH_2Cl_2 (1 : 1). The yellow eluate was collected and removal of the solvent *in vacuo* afforded complex **5** (0.30 g, 0.25 mmol).

$[W(CO)\{(OC)_4Fe(Ph_2PC{\equiv}CPPh_2)Fe(CO)_4\}(S_2CNEt_2)_2]$ **6**. A solution of $[W(CO)(Ph_2PC{\equiv}CPPh_2)(S_2CNEt_2)_2]$ (0.65 g, 0.72 mmol) and $[Fe_2(CO)_9]$ (0.79 g, 2.17 mmol) was stirred for 2 h, after which time the solvent was removed *in vacuo*. The residue was chromatographed on an alumina column (2.4 × 15 cm) eluting with light petroleum (40–60 °C)–CH_2Cl_2 (2 : 1). The yellow eluate was collected and removal of the solvent *in vacuo* afforded complex **6** (0.62 g, 0.50 mmol).

Crystal Structure Determinations.—Crystals of complexes **2**–**4** were obtained by solvent diffusion from CH_2Cl_2–light petroleum (40–60 °C). Crystal and other experimental data are summarised in Table 4. Data were collected at 294 K using a Siemens R3m/V diffractometer and corrected for Lorentz, polarisation and X-ray absorption (empirical) effects.[20,21] The asymmetric units of all three compounds contain a molecule of pentane. The structures were solved by conventional heavy-atom methods and successive Fourier difference syntheses were used to locate all non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters apart from the solvent molecule. The phenyl rings were treated as rigid groups. All hydrogen atoms were included in calculated positions (C–H 0.96 Å) with fixed isotropic thermal parameters. A weighting scheme $w^{-1} = [\sigma^2(F) + 0.0001|F|^2]$ gave a satisfactory analysis of variance for **3** while unit weights were used for **2** and **4**. Refinements were by full-matrix least squares using a Digital Micro Vax computer with the SHELXTL PLUS system of programs.[20] Scattering factors with corrections for anomalous dispersion were taken from ref. 22. Atomic coordinates for **2**–**4** are listed in Tables 5–7.

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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