Diphenylacetylene Complexes of Tungsten containing π-Acceptor Ligands†

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Reaction of PhC_2Ph with $[WCl_2(PhC_2Ph)(PMe_3)_3]$ gave $[WCl_2(PhC_2Ph)_2(PMe_3)_2]$ **1** for which IR and NMR spectral data indicated *cis*-chloro ligands, *trans* phosphines and mutually-*cis* diphenylacetylene ligands. This geometry was confirmed by X-ray crystallography. The average W–C bond lengths are 2.071(3) Å. The ^{13}C NMR spectrum showed the acetylenic carbon resonance at δ 185.45. The alkynes HC_2H and PhC_2H reacted with $[WCl_2(PhC_2Ph)(PMe_3)_3]$ giving $[WCl_2(PhC_2Ph)(HC_2H)(PMe_3)_2]$ **2** and $[WCl_2(PhC_2Ph)(PhC_2H)(PMe_3)_2]$ **3**. The phenylacetylene ligand gave rise to asymmetry in complex **3** leading to an AB system $^{31}P-\{^1H\}$ NMR spectrum. Different values of $^1J(PW)$ indicated small differences in the W–P bonding. Alkyl-substituted acetylenes did not react cleanly with $[WCl_2(PhC_2Ph)(PMe_3)_3]$. The complexes $[WCl_2(PhC_2Ph)(Pr^nC_2Me)(PMe_3)_2]$ **4** and $[WCl_2(PhC_2Ph)(MeC_2Me)(PMe_3)_2]$ **5** were prepared by sodium–mercury amalgam reduction of $[WCl_3(PhC_2Ph)(PMe_3)_2]$ with hex-2-yne or but-2-yne present but were not particularly stable in solution. Sodium–mercury amalgam reduction of $[WCl_3(PhC_2Ph)(PMe_3)_2]$ under ethylene or propene gave $[WCl_2(PhC_2Ph)(CH_2CH_2)(PMe_3)_2]$ **6** or $[WCl_2(PhC_2Ph)(MeCHCH_2)(PMe_3)_2]$ **9**. Complex **9** was unstable in solution and was characterised by NMR spectroscopy. The ^{13}C NMR acetylenic carbon resonances in complexes **6** and **9** are at δ 218.11 and 218.82. Reduction of $[WCl_3(PhC_2Ph)(PMe_3)_2]$ under *cis*- or *trans*-but-2-ene or 2-methylpropene afforded $[WCl_2(PhC_2Ph)(PMe_3)_3]$ and $[WCl_2(PhC_2Ph)(PMe_3)_2]_x$ **10** as characterised by NMR spectroscopy. Reduction of $[WCl_3(PhC_2Ph)L_2]$ (L = PMe_3 or $PMePh_2$) under CO gave $[WCl_2(PhC_2Ph)(CO)(PMe_3)_2]$ **11** and $[WCl_2(PhC_2Ph)(CO)(PMePh_2)_2]$ **12** for which X-ray crystal structure determinations showed *cis*-chloro ligands, *trans* phosphines and mutually-*cis* PhC_2Ph and CO ligands. The W–C and C–C bond lengths for complex **11** are 2.009(5), 2.024(5) and 1.341(6) Å, respectively. Overall the reactions showed that the diphenylacetylene ligand in these complexes acts like an organoimido or oxo ligand.

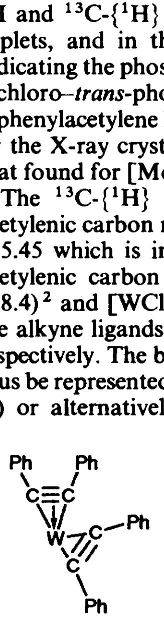
Although alkyne complexes of tungsten are traditionally prepared from low-valent precursors,[1] we have shown recently[2] that a variety of diphenylacetylene complexes of tungsten can also be prepared from $[\{WCl_4(PhC_2Ph)\}_2]$ which has significant high-valent character. The alkyne ligand in $[\{WCl_4(PhC_2Ph)\}_2]$ functions in a similar manner to an organoimido ligand so that the properties and reactions of the complex are similar to those of $[\{WCl_4(NPh)\}_2]$.[3] Correspondingly, the complexes $[WCl_3(PhC_2Ph)L_2]$ and $[WCl_2(PhC_2Ph)L_3]$ (L = PMe_3 or PMe_2Ph) have been prepared which are analogues of $[WCl_3(NPh)L_2]$ and $[WCl_2(NPh)L_3]$.[2] We have been interested in developing further this high-valent alkyne–tungsten chemistry, especially in preparing complexes analogous to known d^2 tungsten organoimido[3–6] or oxo compounds.[7] We report here the preparation of diphenylacetylene complexes of tungsten which contain a second alkyne, an olefin or a CO ligand as an ancillary ligand. A preliminary account of some of this work has appeared.[8]

Results and Discussion

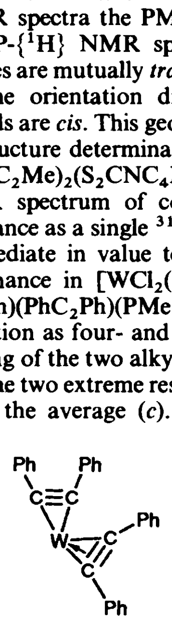
Reduction of $[\{WCl_4(PhC_2Ph)\}_2]$ by sodium–mercury amalgam in the presence of PMe_3 gives rise to $[WCl_2(PhC_2Ph)(PMe_3)_3]$.[2] This complex reacts with diphenylacetylene in benzene under reflux over a period of 18 h to give the bis(alkyne) complex $[WCl_2(PhC_2Ph)_2(PMe_3)_2]$ **1**. On determining the X-ray crystal structure of complex **1** we found that the crystal lattice incorporated a stacking fault. The stacking mechanism, and the requisite restrained refinement, have been described elsewhere.[9] We now outline the chemical and spectroscopic properties of complex **1** and describe in more detail the important features of its molecular geometry.

The IR spectrum of complex **1** shows alkyne absorptions at 1720 and 1702 cm^{-1}, and W–Cl stretches at 265 and 235 cm^{-1} (Table 1) consistent with *cis*-orientated chloro ligands.[10] In the ^1H and $^{13}C-\{^1H\}$ NMR spectra the PMe_3 ligands appear as triplets, and in the $^{31}P-\{^1H\}$ NMR spectrum as a singlet, indicating the phosphines are mutually *trans* (Table 2). This *cis*-dichloro–*trans*-phosphine orientation dictates that the two diphenylacetylene ligands are *cis*. This geometry was confirmed by the X-ray crystal structure determination and is similar to that found for $[Mo(MeC_2Me)_2(S_2CNC_4H_4)_2]$.[11]

The $^{13}C-\{^1H\}$ NMR spectrum of complex **1** shows the acetylenic carbon resonance as a single ^{31}P-coupled triplet at δ 185.45 which is intermediate in value to that found for the acetylenic carbon resonance in $[WCl_2(PhC_2Ph)(PMe_3)_3]$ (δ 228.4)[2] and $[WCl_2(NPh)(PhC_2Ph)(PMe_3)_2]$ (δ 155.8)[6] where the alkyne ligands function as four- and two-electron donors, respectively. The bonding of the two alkynes in complex **1** may thus be represented by the two extreme resonance forms (*a*) and (*b*) or alternatively by the average (*c*). A molecular-orbital



(*a*)



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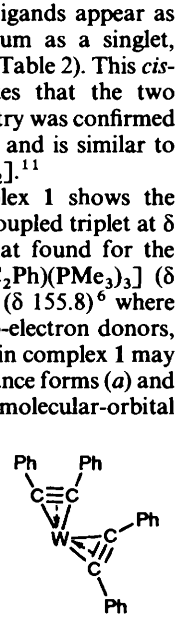

(*c*)

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Physical data

Complex	Colour	Analysis (%)[a] C	H	N	IR ṽ/cm⁻¹ ν(C≡C)	ν(W–Cl)
1 $[WCl_2(PhC_2Ph)_2(PMe_3)_2]$	Yellow	53.6 (53.5)	4.9 (5.0)	8.1 (8.1)	1720, 1702	265, 235
2 $[WCl_2(PhC_2Ph)(HC_2H)(PMe_3)_2]$	Colourless	42.1 (42.2)	5.5 (5.0)	9.0 (10.1)	1720 (br)	264, 240
3 $[WCl_2(PhC_2Ph)(PhC_2H)(PMe_3)_2]$[b]	Colourless	50.5 (50.5)	5.1 (5.1)	8.6 (8.7)	1680 (br)	264, 235
6 $[WCl_2(PhC_2Ph)(CH_2CH_2)(PMe_3)_2]$	Yellow	42.4 (43.1)	4.9 (5.3)	9.8 (10.1)	1640	290, 250
11 $[WCl_2(PhC_2Ph)(CO)(PMe_3)_2]$	Blue	40.9 (41.1)	4.4 (4.6)	10.2 (10.1)	Not observed	290, 240
12 $[WCl_2(PhC_2Ph)(CO)(PMePh_2)_2]$	Blue	57.3 (57.2)	4.1 (4.2)	7.1 (7.2)	Not observed	290, 245

[a] Calculated values given in parentheses. [b] Contains $\frac{1}{3}C_6H_6$ solvent molecules.

description of the *cis*-alkyne fragment in $MoL_4(RC_2R)_2$ complexes allows for both filled π-perpendicular alkyne orbitals to overlap with unfilled metal *d* orbitals resulting in a three-centre, four-electron bonding scheme.[12]

The X-ray crystal structure determination of $[WCl_2(PhC_2Ph)_2(PMe_3)_2]$ **1** afforded the structure depicted in Fig. 1. Bond lengths and angles are listed in Table 3. The phosphines push away equally from the two acetylene ligands [P(1)–W–P(2) 144.3(1)°], as do the chloro ligands but to a lesser extent [Cl(1)–W–Cl(2) 85.0(1)°]. Both acetylene ligands straddle the P(1) ··· P(2) vector and no significant twists are observed. The two W–Cl bonds are of equal length as are the two W–P bonds. Similarly, the four W–C bond lengths are not significantly different, nor are the two C–C bond lengths. The average W–C bond length [2.071(6) Å] is intermediate in value between those found in $[WCl_2(PhC_2Ph)(PMe_3)_3]$ [2.013(11) Å] and $[WCl_2(NCMe_3)(PhC_2Ph)(PMe_3)_2]$ [2.128(15) Å][13] where the alkyne ligands are four- and two-electron donors, respectively. The intermediate value for $[WCl_2(PhC_2Ph)_2(PMe_3)_2]$ **1** further reflects the use of both alkyne π-perpendicular orbitals in bonding to the metal which was apparent from the $^{13}C-\{^1H\}$ NMR spectrum. The acetylene C≡C bond lengths and C≡C–Ph angles are not significantly different from those found for $[WCl_2(PhC_2Ph)(PMe)_3]$[13] and $[WCl_2(NPh)(PhC_2Ph)(PMe_3)_2]$.[14]

Phenylacetylene and acetylene both react with $[WCl_2(PhC_2Ph)(PMe_3)_3]$ in a similar manner to diphenylacetylene but the reaction time needed is much shorter. IR and NMR spectra indicate that $[WCl_2(PhC_2Ph)(HC_2H)(PMe_3)_2]$ **2** has the *cis*-chloro–*trans*-phosphine structure of complex **1**. In the $^{13}C-\{^1H\}$ NMR spectra the acetylenic carbons of PhC_2Ph and HC_2H occur as triplets at δ 187.16 and 168.31, respectively. For $[WCl_2(PhC_2Ph)(PhC_2H)(PMe_3)_2]$ **3** the ^1H and $^{13}C-\{^1H\}$ NMR spectra show doublets of doublets for the phosphine ligands, suggesting *cis* phosphines, but the $^{31}P-\{^1H\}$ NMR spectrum shows an AB system with a ^{31}P coupling constant, $^2J(PP)$, of 103.71 Hz which is consistent with non-equivalent *trans*-PMe_3 ligands in an asymmetric molecule.[5] The two W–P coupling constants are dissimilar (123.10 and 130.16 Hz) which may represent small differences in the W–P bond lengths.[5,14] The $^{13}C-\{^1H\}$ NMR spectrum shows two ^{31}P-coupled doublet of doublet sets for the diphenylacetylene acetylenic carbons (δ 188.9, 185.6) suggesting slight bonding differences in the presence of the *cis* PhC≡CH ligand for which the expected two acetylenic resonances appear. In addition there are three *ipso* carbon signals for the three phenyl rings present.

Phosphine replacement reactions of $[WCl_2(PhC_2Ph)(PMe_3)_3]$ by alkyl-substituted acetylenes were not successful. However, $[WCl_2(PhC_2Ph)(Pr^nC_2Me)(PMe_3)_2]$ **4** was prepared by reduction of $[WCl_3(PhC_2Ph)(PMe_3)_2]$[2] in benzene using 1 equivalent of sodium–mercury amalgam and with 1 equivalent of hex-2-yne present. Although this alkyne ligand is asymmetric, this was not reflected in the NMR spectra where a virtually coupled triplet was found for the PMe_3 ligands in the ^1H NMR spectrum and the PMe_3 and acetylenic carbons in the $^{13}C-\{^1H\}$ NMR spectrum were ^{31}P-coupled triplets. The complex is a single entity, as shown by a singlet in the $^{31}P-\{^1H\}$ NMR spectrum, but further peaks develop with time (4 h) indicating the complex is not stable for longer periods in solution.

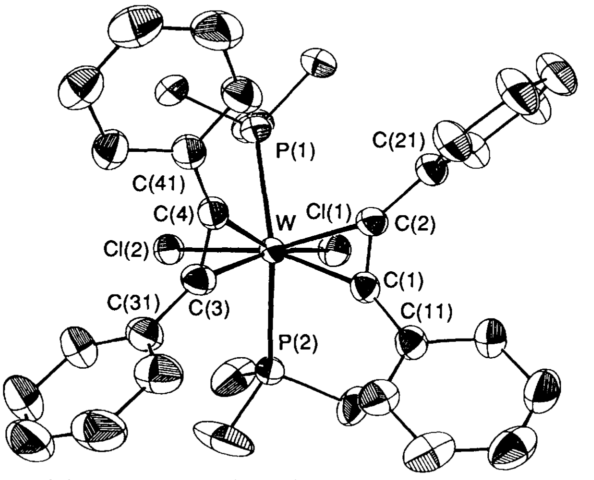
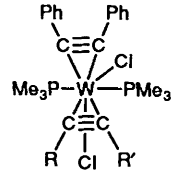
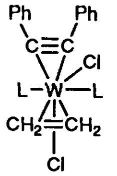


Fig. 1 Molecular structure of complex **1**



1 R = R′ = Ph
2 R = R′ = H
3 R = Ph, R′ = H
4 R = Prⁿ, R′ = Me
5 R = R′ = Me



	L
6	PMe_3
7	PMe_2Ph
8	$PMePh_2$

Complex **5**, $[WCl_2(PhC_2Ph)(MeC_2Me)(PMe_3)_2]$, prepared by a similar reduction to that above, was characterised by IR and NMR spectroscopy which showed the usual *cis*-chloro–*trans*-phosphine geometry. The reaction also gives rise to about 15% of $[WCl_2(MeC_2Me)(PMe_3)_3]$ as evidenced by the NMR spectra. By way of comparison, reduction of $[WCl_3(PhC_2Ph)(PMe_3)_2]$ in the presence of PhC_2Ph leads primarily to complex **1** but also to $[WCl_2(PhC_2Ph)(PMe_3)_3]$ (33% by ^1H NMR).

Reduction of $[WCl_3(PhC_2Ph)(PMe_3)_2]$ with sodium–mercury amalgam in benzene under ethylene gave $[WCl_2(PhC_2Ph)(CH_2CH_2)(PMe_3)_2]$ **6**. IR and NMR spectra, and an X-ray crystal structure determination[8] show the complex has a *cis*-chloro–*trans*-phosphine geometry with the diphenylacetylene and ethylene ligands mutually *cis*. The $^{13}C-\{^1H\}$ NMR spectrum places the ethylene carbons at δ 39.24 which is similar to that found for the organoimido analogue $[WCl_2(NPh)$-

Table 2 NMR spectral data[a]

	^{31}P-{^{1}H}				
Complex	δ	^{2}J(PP)/ Hz	^{1}J(PW)/ Hz	^{1}H[b]	^{13}C-{^{1}H}[b,c]
1	−21.96	—	124.84	1.41 [t, ^{2}J(HP) 4.59, 18 H, PMe$_3$], 7.10 [d, ^{3}J(HH) 7.34, 4 H, *o*-H], 7.15 [t, ^{3}J(HH) 7.37, 2 H, *p*-H], 7.30 [t, ^{3}J(HH) 7.55, 4 H, *m*-H]	15.77 [t, ^{1}J(CP) 14.44, PMe$_3$], 126.44 (*o*-C), 127.07 (*p*-C), 127.95 (*m*-C), 143.38 (*ipso*-C), 185.45 [t, ^{2}J(CP) 13.00, C≡C]
2	−20.08	—	131.20	1.69 [t, ^{2}J(HP) 4.50, 18 H, PMe$_3$], 6.93 [d, ^{3}J(HH) 7.66, 4 H, *o*-H], 7.16 [t, ^{3}J(HH) 7.19, 2 H, *p*-H], 7.29 [t, ^{3}J(HH) 7.58, 4 H, *m*-H], 8.13 [t, ^{3}J(HP) 4.29, 2 H, HC≡CH]	15.12 [t, ^{1}J(CP) 15.13, PMe$_3$], 125.59 (*o*-C), 127.36 (*p*-C), 128.10 (*m*-C), 143.20 (*ipso*-C), 168.31 [t, ^{2}J(CP) 12.80, HC≡CH], 187.16 [t, ^{2}J(CP) 12.7, Ph*C*≡*C*Ph]
3	−12.94 −16.97	103.71	123.10 130.16	1.84 and 2.15 [d, ^{2}J(HP) 9.50 and 9.66, 18 H, PMe$_3$], 6.95 [t, ^{2}J(HP) 6.88, 4 H, *o*-H], 7.10 [d, ^{2}J(HP) 7.38, 2 H, *o*-H], 7.15–7.21 (m, 3 H, aromatic H), 7.24–7.32 (m, 3 H, aromatic H), 7.34–7.38 (m, 3 H, aromatic H), 7.90 and 7.94 [d, ^{3}J(HP) 5.67, 1 H, C≡CH]	15.20 and 15.48 [d, ^{1}J(CP) 28.39 and 26.43, PMe$_3$], 125.70 and 125.74 (*o*-C), 126.98, 127.04 and 127.5 (*p*-C), 127.83, 127.94 and 128.12 (*m*-C), 143.04 and 143.67 (*ipso*-C, PhC≡CPh), 144.32 and 144.36 [d, ^{3}J(CP) 3.57 and 3.61, *ipso*-C, PhC≡CH], 171.00 and 172.01 [d, ^{2}J(CP) 5.8, ≡CH], 181.57 and 181.74 [d, ^{2}J(CP) 5.1, Ph*C*≡], 185.55 and 185.75 [d, ^{2}J(CP) 5.4, Ph*C*≡*C*Ph], 188.81 and 189.00 [d, ^{2}J(CP) 5.5, Ph*C*≡*C*Ph]
4	−20.33	—	122.78	0.90 [t, ^{3}J(HH) 7.32, 3 H, Me], 1.47–1.56 (m, 2 H, CH$_2$), 1.62 [t, ^{2}J(HP) 4.40, 18 H, PMe$_3$], 1.71 [t, ^{3}J(HH) 3.89, 2 H, CH$_2$], 2.98 (s, 3 H, Me), 6.87 (br, 4 H, *o*-H), 7.08 [t, ^{3}J(HH) 7.41, 2 H, *p*-H], 7.23 [t, ^{3}J(HH) 7.55, 4 H, *m*-H]	14.38 (Me), 16.64 [t, ^{1}J(CP) 14.01, PMe$_3$], 21.82 (CH$_2$), 22.47 (CH$_2$), 38.36 (Me), 125.38 (*o*-C), 126.31 (*p*-C), 127.80 (*m*-C), 145.16 (*ipso*-C), 179.92 (br m, CH$_2$*C*≡*C*Me), 184.05 and 186.25 [t, ^{2}J(CP) 13.30 and 13.50, Ph*C*≡*C*Ph]
5	−19.71	—	120.71	1.63 [t, ^{2}J(HP), 4.46, 18 H, PMe$_3$], 2.82 (Me), 6.86 [d, ^{3}J(HH) 7.55, 4 H, *o*-C], 7.08 [t, ^{3}J(HH) 7.18, 2 H, *p*-C], 7.23 [t, ^{3}J(HH) 7.41, 4 H, *m*-C]	16.49 [t, ^{1}J(CP) 14.28, PMe$_3$], 20.67 (Me), 125.43 (*o*-C), 126.33 (*p*-C), 127.78 (*m*-C), 145.06 (*ipso*-C), 179.25 [t, ^{2}J(CP) 12.20, Me*C*≡*C*Me], 185.05 [t, ^{2}J(CP) 14.10, Ph*C*≡*C*Ph]
6	−22.75	—	148.70	1.60 [t, ^{2}J(HP) 4.42, 18 H, PMe$_3$], 1.65 (m, 2 H, CH$_2$), 1.96 (m, 2 H, CH$_2$), 6.89 [d, ^{3}J(HH) 7.53, 4 H, *o*-H], 7.14 [t, ^{3}J(HH) 6.99, 2 H, *p*-H], 7.28 [t, ^{3}J(HH) 7.51, 4 H, *m*-H]	14.51 [t, ^{1}J(CP) 14.34, PMe$_3$], 39.24 (CH$_2$CH$_2$), 124.34 (*o*-C), 127.13 (*p*-C), 127.94 (*m*-C), 144.75 (*ipso*-C), 218.11 [t, ^{2}J(CP) 13.85, PhC≡CPh]
7	−7.55	—	175.83	1.59 (m, 2 H, CH$_2$), 1.78 [t, ^{2}J(HP) 3.52, 6 H, PMe$_2$], 19.5 [t, ^{2}J(HP) 3.89, 6 H, PMe$_2$], 2.02 (m, 2 H, CH$_2$), 6.78 [d, ^{3}J(HH) 7.38, 4 H, *o*-H], 7.12–7.23 (m, 6 H, aromatic H), 7.23–7.29 (m, 6 H, aromatic H), 7.30–7.37 (m, 4 H, aromatic H)	12.33 [t, ^{1}J(CP) 14.34, PMe$_2$], 13.97 [t, ^{1}J(CP) 15.71, PMe$_2$], 44.62 (CH$_2$CH$_2$), 125.56 (*o*-C), 127.67 [t, ^{2}J(CP) 3.80, *o*-C], 127.77 (*p*-C), 127.87 (*m*-C), 129.01 (*p*-C), 130.58 [t, ^{3}J(CP) 3.20, *m*-C], 137.02 [t, ^{1}J(CP) 19.05, *ipso*-C], 143.32 (*ipso*-C), 226.56 [t, ^{2}J(CP) 10.02, Ph*C*≡*C*Ph]
9	−11.23 −14.71	166.70	[d]	1.50 and 1.64 (prd, 18 H, PMe$_3$), 1.86 (m, 3 H, Me), 2.45 (m, 1 H, CH), 2.81 (m, 2 H, CH$_2$), 7.01 (br, 4 H, *o*-H), 7.22 (br, 2 H, *p*-H), 7.38 (br, 4 H, *m*-H)	14.36 and 15.15 [d, ^{1}J(CP) 27.27 and 28.53, PMe$_3$], 27.89 (Me), 46.66 (CH$_2$), 55.42 (CH), 124.59 (*o*-C), 126.04 (*p*-C), 128.17 (*m*-C), 145.01 (*ipso*-C), 218.55 and 218.82 [prd, Ph*C*≡*C*Ph]
10[e]	−12.87 −14.94	169.95	204.37 198.15	1.37 and 1.64 [d, ^{2}J(HP) 9.03 and 8.88, 18 H, PMe$_3$], 7.11 [d, ^{3}J(HH) 7.7, 4 H, *o*-H], 7.15–7.30 (obs, 2 H, *p*-H), 7.34–7.42 (m, 4 H, *m*-H)	15.00 and 15.85 [d, ^{1}J(CP) 27.54 and 27.85, PMe$_3$], 127.39 (*o*-C), 127.52 (*p*-C), 128.26 (*m*-C), 143.59 (*ipso*-C), 186.43 and 186.54 [d, ^{2}J(CP) 7.43 and 7.79, Ph*C*≡*C*Ph]
11	−19.34	—	271.33	1.39 [t, ^{2}J(HP) 4.28, 18 H, PMe$_3$], 7.42 [d, ^{3}J(HH) 7.39, 2 H, *p*-H], 7.49 [t, ^{3}J(HH) 7.61, 4 H, *m*-H], 7.70 [d, ^{3}J(HH) 7.35, 4 H, *o*-H]	15.62 [t, ^{1}J(CP) 14.92, 18 H, PMe$_3$], 128.64 (*m*-C), 128.81 (*o*-C), 129.97 (*p*-C), 139.22 (*ipso*-C), 226.88 [t, ^{2}J(CP) 5.39, Ph*C*≡*C*Ph], 227.38 [t, ^{2}J(CP) 4.04, C≡O]
12	1.16	—	273.62	2.21 [t, ^{2}J(HP) 4.34, 6 H, PMe], 6.94 [t, ^{3}J(HH) 7.21, 4 H, *o*-H], 7.00 [t, ^{3}J(HH) 7.16, 2 H, *p*-H], 7.12–7.21 (m, 10 H, aromatic H), 7.21–7.28 (m, 3 H, aromatic H), 7.28–7.38 (m, 7 H, aromatic H), 7.48–7.60 (m, 4 H, aromatic H)	14.12 [t, ^{1}J(CP) 16.06, PMe], 127.64 [t, J(CP) 4.4, aromatic C], 128.00 (aromatic C), 128.20 [t, J(CP) 4.6, aromatic C] 128.80 (br, aromatic C), 129.48 (*m*-C), 129.60 (*p*-C), 130.18 (*o*-C), 131.80 [t, J(CP) 4.8, aromatic C], 132.54 [t, J(CP) 5.0, aromatic C], 133.97 [t, ^{1}J(CP) 20.30, *ipso*-C], 134.17 [t, J(CP) 22.20, *ipso*-C], 139.67 (*ipso*-C), 226.82 [t, ^{2}J(CP) 5.1, PhC≡CPh], 228.17 (br, C≡O)

[a] Spectra obtained in CDCl$_3$ solution. [b] br = Broad, d = doublet, m = multiplet, prd = poorly resolved doublet, t = triplet, J in Hz. [c] Aromatic ring resonance assignments: *ortho*-carbons shift from δ 128.5, *meta*-carbons based on δ 128.5, *para*-carbons made from relative peak height, δ in ppm. [d] ^{1}J(PW) values not observed. Complex decomposes in solution. [e] Sample contains [WCl$_2$(PhC$_2$Ph)(PMe$_3$)$_3$]. Tentative ^{1}H and ^{13}C NMR aromatic assignments.

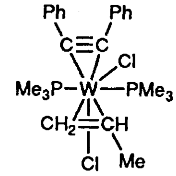
(CH$_2$CH$_2$)(PMe$_3$)$_2$].[5] For complex **6** the acetylenic carbons appear at δ 218.11 which is close to that observed for [WCl$_2$(PhC$_2$Ph)(PMe$_3$)$_3$].[2]

Complex **7**, [WCl$_2$(PhC$_2$Ph)(CH$_2$CH$_2$)(PMe$_2$Ph)$_2$], was characterised by NMR spectroscopy. The ^{13}C-{^{1}H} NMR spectrum shows the ethylenic carbons at δ 44.62 and the acetylenic carbons at δ 226.56 both of which are downfield from the relative resonances in complex **6**. The complex [WCl$_2$(PhC$_2$Ph)(CH$_2$CH$_2$)(PMePh$_2$)$_2$] **8** can also be prepared but the reaction is less clean. The ^{13}C-{^{1}H} NMR spectrum shows the ethylenic and acetylenic carbons at δ 47.8 and 228.5, respectively. The increase in the downfield shift for the ethylenic carbons in complexes **7** and **8** compared with **6** may represent a decrease in π back-bonding to the olefin π* orbital.[15]

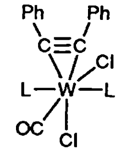
Reduction of [$WCl_3(PhC_2Ph)(PMe_3)_2$] by sodium–mercury amalgam under propene gave mainly [$WCl_2(PhC_2Ph)(PMe_3)_3$] and a small quantity of [$WCl_2(PhC_2Ph)(MeCHCH_2)(PMe_3)_2$] **9** which was unstable in solution after isolation. The ^1H NMR spectrum was broad but the $^{13}C\text{-}\{^1H\}$ NMR spectrum was more informative showing *trans* phosphines based on the PMe_3 doublet of doublets in the $^{13}C\text{-}\{^1H\}$ NMR spectrum and an AB quartet in the $^{31}P\text{-}\{^1H\}$ NMR spectrum with $^2J(PP)_{trans}$ 166.70 Hz. The spectra indicate only one isomer is present which is in contrast to [$WCl_2(NPh)(MeCHCH_2)(PMe_3)_2$] where two isomers exist resulting from the propene methyl group lying above or below the equatorial plane.[5] The $^{13}C\text{-}\{^1H\}$ NMR spectrum of complex **9** shows a single set of propene resonances and a single acetylenic carbon resonance (δ 218.82).

Olefin complexes are not formed when the reduction of [$WCl_3(PhC_2Ph)(PMe_3)_2$] is carried out under *cis*- or *trans*-but-2-ene or 2-methylpropene. Instead, these reactions produce [$WCl_2(PhC_2Ph)(PMe_3)_3$] and varying amounts of a product which NMR spectra suggest is [$WCl_2(PhC_2Ph)(PMe_3)_2$]$_x$ **10** on the basis of the phosphine resonances being similar to those observed for [$WCl_2(NPh)(PMe_3)_2$]$_x$.[5] The PMe_3 ligands appear in the ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra as doublets of doublets and the $^{31}P\text{-}\{^1H\}$ NMR spectrum shows an AB system with $^2J(PP)$ 169.95 Hz which is consistent with *trans* phosphines. The product has so far been obtained only as a non-crystalline coprecipitate with [$WCl_2(PhC_2Ph)(PMe_3)_3$].

Sodium–mercury amalgam reductions of [$WCl_3(PhC_2Ph)L_2$] (L = PMe_3 or $PMePh_2$) under carbon monoxide lead to the complexes [$WCl_2(PhC_2Ph)(CO)(PMe_3)_2$] **11** and [$WCl_2(PhC_2Ph)(CO)(PMePh_2)_2$] **12** which IR and NMR spectra show have the usual *cis*-chloro-*trans*-phosphine geometry. The acetylenic carbon resonances in both complexes are found at a position similar to that of [$WCl_2(PhC_2Ph)(CH_2CH_2)(PMe_3)_2$] **6**.



9



L
11 PMe_3
12 $PMePh_2$

Table 3 Selected bond lengths (Å) and angles (°) for complex **1**

Cl(1)–W	2.504(2)	C(4)–W	2.068(6)
Cl(2)–W	2.503(1)	C(2)–C(1)	1.296(8)
P(1)–W	2.594(2)	C(4)–C(3)	1.295(7)
P(2)–W	2.581(2)	C(11)–C(1)	1.470(4)
C(1)–W	2.075(4)	C(21)–C(2)	1.471(4)
C(2)–W	2.066(5)	C(31)–C(3)	1.470(5)
C(3)–W	2.076(7)	C(41)–C(4)	1.470(5)
Cl(1)–W–Cl(2)	85.0(1)	C(2)–C(1)–C(11)	133.0(6)
Cl(1)–W–P(1)	79.0(1)	W–C(2)–C(1)	72.1(2)
Cl(1)–W–P(2)	75.3(1)	W–C(2)–C(21)	153.1(4)
P(1)–W–P(2)	144.3(1)	C(1)–C(2)–C(21)	134.8(4)
C(1)–W–C(2)	36.5(2)	W–C(3)–C(4)	71.4(4)
C(1)–W–C(3)	93.5(6)	W–C(3)–C(31)	151.2(5)
C(1)–W–C(4)	98.0(8)	C(4)–C(3)–C(31)	137.0(7)
C(2)–W–C(3)	109.3(3)	W–C(4)–C(3)	72.1(4)
W–C(1)–C(2)	71.4(3)	W–C(4)–C(41)	152.4(4)
W–C(1)–C(11)	154.4(3)	C(3)–C(4)–C(41)	135.4(6)

Structures of complexes **11** and **12** were determined by X-ray crystallography. Both molecules contain *cis*-chloro ligands, *trans* phosphines and the CO ligand lies *cis* to the diphenylacetylene ligand. The structure of complex **11** is shown in Fig. 2. Selected bond lengths and angles are contained in Tables 4 and 5, and atomic coordinates in Tables 6 and 7, respectively. Both complexes have similar bond lengths and angles. The W–$C_{acetylene}$ and C–$C_{acetylene}$ bond lengths and the Ph–C≡C bond angles are similar to those found for [$WCl_2(PhC_2Ph)(PMe_3)_3$][13] where the alkyne ligand acts as a four-electron donor. In this complex the acetylene ligand straddles the P(1) ··· P(2) vector (*trans* phosphines) whereas in

Table 4 Selected bond lengths (Å) and angles (°) for complex **11**

Cl(1)–W	2.508(1)	C(3)–W	1.968(6)
Cl(2)–W	2.494(1)	C(3)–O(1)	1.142(7)
P(1)–W	2.519(2)	C(2)–C(1)	1.341(6)
P(2)–W	2.530(2)	C(11)–C(1)	1.457(7)
C(1)–W	2.009(5)	C(21)–C(2)	1.469(7)
C(2)–W	2.024(5)		
Cl(2)–W–Cl(1)	81.7(1)	C(3)–W–P(1)	93.5(2)
P(1)–W–Cl(1)	83.4(1)	C(3)–W–P(2)	95.2(2)
P(1)–W–Cl(2)	85.7(1)	C(2)–C(1)–W	71.2(3)
P(2)–W–Cl(1)	84.4(1)	C(11)–C(1)–W	153.1(4)
P(2)–W–Cl(2)	85.2(1)	C(11)–C(1)–C(2)	135.5(5)
P(2)–W–P(1)	165.7(1)	C(1)–C(2)–W	70.0(3)
C(2)–W–C(1)	38.8(2)	C(21)–C(2)–W	148.6(3)
C(3)–W–Cl(1)	158.9(2)	C(21)–C(2)–C(1)	141.4(4)
C(3)–W–Cl(2)	77.3(2)	O(1)–C(3)–W	178.4(5)

Table 5 Selected bond lengths (Å) and angles (°) for complex **12**

Cl(1)–W	2.473(2)	C(3)–W	1.964(7)
P(1)–W	2.539(2)	C(3)–O(3)	1.148(8)
P(2)–W	2.557(2)	C(2)–C(1)	1.342(10)
Cl(2)–W	2.507(2)	C(21)–C(1)	1.469(10)
C(1)–W	2.028(6)	C(11)–C(2)	1.477(9)
C(2)–W	2.022(6)		
P(1)–W–Cl(1)	87.6(1)	C(3)–W–P(2)	94.9(2)
P(2)–W–Cl(1)	86.0(1)	C(3)–W–Cl(2)	158.9(2)
P(2)–W–P(1)	168.4(1)	C(2)–C(1)–W	70.4(4)
Cl(2)–W–Cl(1)	81.1(1)	C(21)–C(1)–W	151.2(5)
Cl(2)–W–P(1)	87.3(1)	C(21)–C(1)–C(2)	138.4(6)
Cl(2)–W–P(2)	82.1(1)	C(1)–C(2)–W	70.9(4)
C(2)–W–C(1)	38.7(3)	C(11)–C(2)–W	147.3(5)
C(3)–W–Cl(1)	77.9(2)	C(11)–C(2)–C(1)	141.8(6)
C(3)–W–P(1)	93.3(2)	O(3)–C(3)–W	179.7(3)

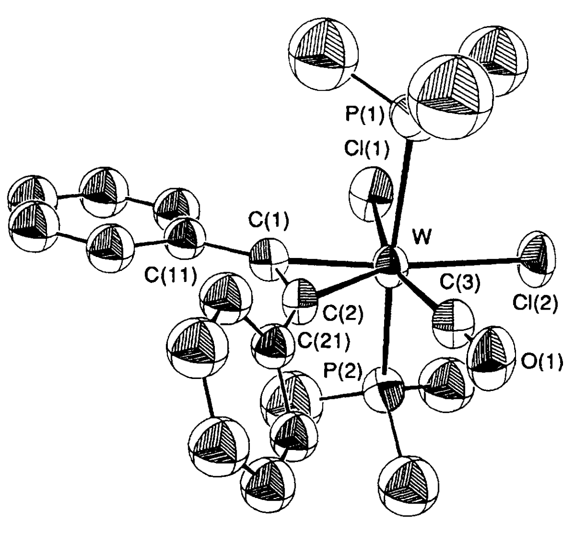


Fig. 2 Molecular structure of complex **11**

Table 6 Atomic coordinates for complex **11**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
W	0.268 12(2)	0.501 52(2)	0.228 35(2)	C(12)	−0.132 6(6)	0.304 0(7)	0.199 3(5)
Cl(1)	0.134 42(17)	0.628 97(19)	0.236 72(17)	C(13)	−0.271 3(8)	0.229 8(9)	0.191 5(6)
Cl(2)	0.457 93(17)	0.737 72(17)	0.242 70(17)	C(14)	−0.329 4(7)	0.095 6(8)	0.198 9(6)
P(1)	0.316 82(19)	0.636 69(19)	0.438 05(14)	C(15)	−0.250 0(7)	0.042 4(8)	0.213 8(5)
P(2)	0.218 19(17)	0.421 71(18)	0.021 03(13)	C(16)	−0.112 0(6)	0.116 3(7)	0.219 2(5)
O	0.518 4(4)	0.455 4(5)	0.233 2(5)	C(21)	0.224 4(5)	0.181 8(5)	0.212 1(4)
C(1)	0.095 5(4)	0.329 0(5)	0.220 9(4)	C(22)	0.200 9(6)	0.135 1(6)	0.293 0(5)
C(2)	0.196 7(4)	0.297 6(5)	0.217 1(4)	C(23)	0.235 1(7)	0.024 8(9)	0.286 8(6)
C(3)	0.426 9(5)	0.472 7(6)	0.230 1(4)	C(24)	0.286 0(7)	−0.037 0(8)	0.199 9(6)
C(4)	0.164 5(14)	0.584 1(17)	0.486 1(12)	C(25)	0.306 0(6)	0.012 5(7)	0.125 8(5)
C(5)	0.430 3(18)	0.625 7(19)	0.519 2(15)	C(26)	0.277 5(6)	0.121 0(6)	0.127 2(5)
C(6)	0.389 6(15)	0.833 7(14)	0.497 3(11)	O(30)	0.922 9(14)	1.034 4(16)	0.475 8(12)
C(7)	0.040 5(14)	0.299 4(15)	−0.046 6(12)	C(31)	0.952(2)	0.912(2)	0.458 4(18)
C(8)	0.255 6(11)	0.569 4(11)	−0.018 3(9)	C(32)	0.869(3)	0.763(3)	0.389(2)
C(9)	0.302 9(11)	0.336 9(12)	−0.060 5(9)	C(33)	0.838(3)	0.870(3)	0.406(2)
C(11)	−0.050 7(5)	0.249 9(5)	0.213 4(4)	C(34)	0.980(3)	0.838(3)	0.458(2)

Table 7 Atomic coordinates for complex **12**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
W	0.212 59(2)	0.086 57(1)	0.231 65(1)	C(32)	0.118 0(8)	0.096 2(4)	0.016 8(5)
Cl(1)	−0.019 28(17)	0.079 31(10)	0.180 46(11)	C(33)	0.038 7(9)	0.093 2(4)	−0.046 6(5)
P(1)	0.272 16(16)	0.158 86(8)	0.123 58(9)	C(34)	0.003 8(9)	0.149 9(5)	−0.081 4(6)
P(2)	0.115 82(18)	0.031 41(9)	0.345 20(10)	C(35)	0.042 6(10)	0.210 2(5)	−0.055 6(5)
Cl(2)	0.113 5(2)	0.187 36(10)	0.289 51(11)	C(36)	0.125 5(8)	0.214 2(5)	0.007 5(5)
O(3)	0.226 2(5)	−0.042 6(3)	0.140 4(3)	C(41)	0.438 3(7)	0.140 6(4)	0.084 5(4)
C(1)	0.395 3(7)	0.110 7(3)	0.275 2(4)	C(42)	0.452 3(11)	0.097 8(5)	0.026 7(6)
C(2)	0.401 9(6)	0.050 5(4)	0.244 8(4)	C(43)	0.575 2(13)	0.082 6(6)	−0.001 4(7)
C(3)	0.221 1(6)	0.004 9(3)	0.174 2(4)	C(44)	0.688 2(12)	0.109 4(6)	0.027 7(7)
C(4)	0.286 8(9)	0.245 5(4)	0.148 3(5)	C(45)	0.681 5(11)	0.150 9(6)	0.082 6(6)
C(5)	−0.063 8(8)	0.049 7(5)	0.358 0(5)	C(46)	0.554 9(9)	0.168 7(5)	0.113 1(6)
C(11)	0.495 9(7)	−0.005 0(4)	0.233 3(4)	C(51)	0.117 9(7)	−0.058 8(4)	0.347 3(4)
C(12)	0.454 2(8)	−0.068 8(4)	0.252 1(4)	C(52)	0.052 4(8)	−0.091 2(4)	0.290 4(5)
C(13)	0.539 9(9)	−0.122 8(5)	0.237 8(5)	C(53)	0.044 3(9)	−0.158 7(5)	0.288 8(5)
C(14)	0.661 7(10)	−0.113 0(5)	0.206 1(6)	C(54)	0.107 0(11)	−0.196 1(6)	0.341 8(6)
C(15)	0.703 1(10)	−0.049 9(5)	0.186 6(5)	C(55)	0.174 0(10)	−0.164 5(6)	0.398 5(6)
C(16)	0.620 4(8)	0.004 2(4)	0.200 2(5)	C(56)	0.180 0(9)	−0.095 7(4)	0.401 8(5)
C(21)	0.484 4(8)	0.156 3(4)	0.315 1(5)	C(61)	0.201 3(8)	0.056 1(4)	0.429 9(4)
C(22)	0.625 0(10)	0.155 8(5)	0.303 4(6)	C(62)	0.127 3(10)	0.083 0(5)	0.487 8(6)
C(23)	0.707 9(14)	0.202 2(7)	0.342 3(7)	C(63)	0.194 7(12)	0.102 5(6)	0.550 9(7)
C(24)	0.651 0(13)	0.243 2(7)	0.392 0(7)	C(64)	0.327 1(13)	0.093 9(6)	0.557 3(7)
C(25)	0.512 2(11)	0.246 0(6)	0.400 2(6)	C(65)	0.405 4(13)	0.071 8(6)	0.499 9(7)
C(26)	0.429 4(9)	0.202 7(5)	0.361 5(5)	C(66)	0.339 0(10)	0.049 9(5)	0.435 1(6)
C(31)	0.161 6(6)	0.157 0(4)	0.044 3(4)				

complexes **11** and **12** the acetylene has rotated 90° to straddle the Cl(2)···CO vector. Theoretical studies of complexes containing the *cis*-Mo(PhC$_2$Ph)(CO) core show the alkyne ligand must adopt this orientation to optimise alkyne bonding when the strongly back-bonding CO ligand is present.[11] In complexes **11** and **12** the Cl and CO ligands are distorted away from the diphenylacetylene ligand with this orientation [**11**, Cl(1)–W–C(3) 158.9(2)°; [WCl$_2$(PhC$_2$Ph)(PMe$_3$)$_3$], Cl(2)–W–P(1) 163.1°].

Conclusion

This work further demonstrates the ability of π-acid ligands to co-ordinate *cis* to a four-electron-donating alkyne ligand.[1] In addition, it illustrates synthetic procedures leading to the formation of bis(alkyne) complexes containing dissimilar alkyne ligands. In particular, the reduction reaction enables kinetic control of the product for the alkyl-substituted acetylenes even though the complexes are not particularly stable in bis(alkyne) form.

Overall, the reactions outlined are similar to those used to obtain organoimido or oxo complexes containing alkyne, olefin and CO ligands[3–6] and this gives further evidence that the strongly π-donating alkyne ligand acts in a similar manner to an organoimido or oxo ligand. Initial results of studies using X-ray photoelectron spectroscopy indicate that the $4f_{\frac{7}{2}}$ binding energies of the present complexes are similar to those obtained for d^2 organoimido complexes. This further reflects the ability of an alkyne ligand to stabilise high oxidation states in the earlier transition metals.

Experimental

General procedures and instrumentation have been described.[5] IR spectra were obtained as Nujol mulls, ^{1}H, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} NMR spectra were recorded at 400, 100 and 162 MHz, respectively. Analytical data were obtained by Dr. A. G. Cunninghame and associates, University of Otago, New Zealand. The complex [{WCl$_4$(PhC$_2$Ph)}$_2$] was prepared by refluxing WCl$_6$ and diphenylacetylene in CH$_2$Cl$_2$ containing tetrachloroethylene.[16] Specific details for the preparations of the complexes [WCl$_3$(PhC$_2$Ph)L$_2$] (L = PMe$_3$, PMe$_2$Ph or PMePh$_2$) and [WCl$_2$(PhC$_2$Ph)(PMe$_3$)$_3$] as outlined in ref. 2 will be reported at a later date. Commercial grade acetylenes and carbon monoxide were used as supplied.

Preparation of the Complexes.—[WCl$_2$(PhC$_2$Ph)$_2$(PMe$_3$)$_2$] **1**. A solution of [WCl$_2$(PhC$_2$Ph)(PMe$_3$)$_3$] (0.8 g, 1.2 mmol) and diphenylacetylene (0.24 g, 1.35 mmol) in benzene (40 cm^3) was refluxed for 18 h. The solution was filtered and the volatiles removed under reduced pressure giving a gum which on washing with light petroleum (b.p. 40–60 °C, 50 cm^3) to remove excess diphenylacetylene gave a yellow solid. Crude yield 0.86 g, 88%. Recrystallisation of the residue from toluene at −20 °C gave the complex as yellow crystals. Yield: 0.58 g (60%). IR spectrum: 1720w, 1702w, 1600m, 1568w, 1480s, 1450s, 1418m, 1374m, 1300m, 1282m, 1180w, 1100w, 1068w, 1024w, 458s, 864w, 780s, 760s, 730s, 702s, 570w, 265w and 235w cm^{-1}.

$[WCl_2(PhC_2Ph)(HC_2H)(PMe_3)_2]$ **2**. A solution of $[WCl_2(PhC_2Ph)(PMe_3)_3]$ (0.6 g, 0.9 mmol) in benzene (40 cm^3) was refluxed under a slight positive pressure of acetylene gas for 2 h. The solution was filtered and the volatiles removed to give a colourless gum. On washing with light petroleum (50 cm^3) the complex was obtained pure as a colourless solid. Yield: 0.5 g (90%). IR spectrum: 1720w (br), 1595m, 1575w, 1460s, 1442s, 1418s, 1370s, 1300w, 1282m, 1150w, 1070w, 935vs, 850w, 770m, 730m, 680s (br), 590m, 562m, 480w, 264m and 240m cm^{-1}.

$[WCl_2(PhC_2Ph)(PhC_2H)(PMe_3)_2]\cdot\frac{1}{3}C_6H_6$ **3**. A solution of $[WCl_2(PhC_2Ph)(PMe_3)_3]$ (0.5 g, 0.76 mmol) and phenylacetylene (0.1 g, 0.97 mmol) in benzene (30 cm^3) was refluxed for 2 h. The solution was filtered, the volatiles removed and the resulting gum stored under light petroleum (5 cm^3) giving the complex as a colourless solid. Yield: 0.48 g (92%). IR spectrum: 1680w (br), 1595m, 1570w, 1440s, 1370s, 1300w, 1280m, 1260w, 1100w, 1072w, 1020w, 940s, 852w, 775w, 755m, 730m, 695m, 680m, 590w, 562w, 264w and 235w cm^{-1}.

$[WCl_2(PhC_2Ph)(Pr^nC_2Me)(PMe_3)_2]\cdot\frac{1}{6}C_6H_6$ **4**. A solution of $[WCl_3(PhC_2Ph)(PMe_3)_2]$ (0.8 g, 1.3 mmol) and hex-2-yne (0.12 g, 1.5 mmol) in benzene (35 cm^3) was added to sodium–mercury amalgam (Na, 32 mg, 1.4 mmol; Hg, 25 g) under benzene (15 cm^3). The mixture was stirred rapidly for 1.5 h, filtered and the spent amalgam extracted with benzene (2 × 20 cm^3). The extracts and filtrate were combined and the volatiles removed leaving a gum which gave the complex as a colourless solid on standing under light petroleum (10 cm^3). Yield: 0.72 g (83%) (Found: C, 47.8; H, 5.5; N, 8.8. $C_{27}H_{39}Cl_2P_2W$ requires C, 47.7; H, 5.8; N, 9.1%). Attempted recrystallisation of the solid from toluene at −20 °C gave a solid which NMR spectra showed to contain several products.

$[WCl_2(PhC_2Ph)(MeC_2Me)(PMe_3)_2]$ **5**. A solution of $[WCl_3(PhC_2Ph)(PMe_3)_2]$ (0.8 g, 1.3 mmol) in benzene (35 cm^3) was reduced with sodium–mercury amalgam as for complex **4** in the presence of but-2-yne (75 mg, 1.4 mmol). Filtration and removal of the volatiles gave a gum which on standing under light petroleum (10 cm^3) gave a solid which was not obtained analytically pure. Crude yield 0.8 g. Attempts to recrystallise the material gave a solid which ^{1}H, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} NMR spectra showed to contain several compounds. Characterisation of the original crude product was made by NMR spectroscopy.

$[WCl_2(PhC_2Ph)(CH_2CH_2)(PMe_3)_2]$ **6**. A solution of $[WCl_3(PhC_2Ph)(PMe_3)_2]$ (0.7 g, 1.13 mmol) in benzene (40 cm^3) was added to a pressure bottle containing sodium–mercury amalgam (Na, 30 mg, 1.3 mmol; Hg, 25 g) and the vessel was vented twice with ethylene gas. The mixture was stirred rapidly and ethylene gas added until a constant pressure of 16.6 kPa was obtained in the pressure bottle. The mixture was stirred for 1 h, filtered and the spent amalgam extracted with benzene (2 × 10 cm^3). The volatiles were removed from the combined filtrate and extracts giving a yellow-brown crystalline solid. Crude yield 0.65 g. The complex was recrystallised from toluene at −20 °C to give yellow crystals. Yield: 0.4 g (58%). IR spectrum: 1640w, 1590w, 1568w, 1460s, 1445s, 1420s, 1375m, 1305m, 1285m, 1180m, 1150w, 1070w, 1028w, 940s, 855m, 780m, 760m, 730m, 705m, 675w, 600w, 570w, 518w, 480w, 360w, 290m and 250m cm^{-1}.

$[WCl_2(PhC_2Ph)(CH_2CH_2)(PMe_2Ph)_2]$ **7**. *Reduction of* $[WCl_3(PhC_2Ph)(PMe_2Ph)_2]$ *under ethylene*. A solution of $[WCl_3(PhC_2Ph)(PMe_2Ph)_2]$ (0.6 g, 0.81 mmol) in benzene (50 cm^3) was reduced with sodium–mercury amalgam (Na, 20 mg, 0.87 mmol; Hg, 20 g) under ethylene using the method employed for complex **6**. Characterisation of complex **7** was made on the basis of NMR spectra only (Table 2).

Table 8 Crystallographic data for complexes **11** and **12**

	11	**12**
Formula	$C_{21}H_{28}ClOP_2W$	$C_{41}H_{36}Cl_2OP_2W$
M	577.24	861.46
Crystal size/mm	0.57 × 0.26 × 0.23	0.54 × 0.15 × 0.09
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	11.306(2)	9.885(1)
b/Å	11.421(3)	20.287(4)
c/Å	13.466(5)	18.333(10)
α/°	113.81(2)	
β/°	90.35(2)	90.52(2)
γ/°	117.09(1)	
U/Å^3	1377.7	3676.3
Z	2	4
D_c/g cm^{-3}	1.392	1.556
$F(000)$	536	1712
μ/cm^{-1}	45.6	34.3
2θ range/°	2–55	2–57
No. of measured reflections	8323	9831
No. of unique reflections	7634	8346
R_{int}	0.035	0.014
No. of observed reflections	6776 [$I > 3\sigma(I)$]	6517
A range	1.00–0.82	0.60–1.00
Least-squares weights	$1.0/[\sigma(F^2) + 0.006F^2]$	$1.0/[\sigma(F^2) + 0.014F^2]$
No. of variables	193	252
R^a, R'^b	0.042, 0.050	0.046, 0.051

[a] $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. [b] $R' = \Sigma(w^{\frac{1}{2}}\|F_o| - |F_c\|)/\Sigma(w^{\frac{1}{2}}|F_o|)$.

$[WCl_2(PhC_2Ph)(MeCHCH_2)(PMe_3)_2]$ **9**. *Reduction of* $[WCl_3(PhC_2Ph)(PMe_3)_2]$ *under propene*. A solution of $[WCl_3(PhC_2Ph)(PMe_3)_2]$ (0.8 g, 1.3 mmol) in benzene (30 cm^3) was reduced with sodium–mercury amalgam (Na, 32 mg, 14 mmol; Hg, 26 g) under propene as for the preparation of complex **6**. Filtration and removal of the volatiles gave a green-brown solid which on recrystallisation gave $[WCl_2(PhC_2Ph)(PMe_3)_3]$. Yield: 0.15 g. Characterisation of complex **9** was carried out by NMR spectra obtained rapidly on the crude green-brown solid and using spectral comparisons with the known complex $[WCl_2(NPh)(MeCHCH_2)(PMe_3)_2]$.[5] Complex **9** decomposes in solution and is present in small quantities only after removal of volatiles from the recrystallisation mother liquors.

$[WCl_2(PhC_2Ph)(PMe_3)_2]_x$ **10**. *Reductions of* $[WCl_3(PhC_2Ph)(PMe_3)_2]$ *under* cis- *or* trans-*but-2-ene or 2-methylpropene*. These reactions were carried out using the method employed for complex **6**. Removal of the volatiles gave a dark brown solid which NMR analysis showed to be a mixture of $[WCl_2(PhC_2Ph)(PMe_3)_3]$ and a complex tentatively characterised as $[WCl_2(PhC_2Ph)(PMe_3)_2]_x$ **10** (see Table 2). The latter complex forms as a purple-brown solid on recrystallisation but the samples obtained were contaminated with $[WCl_2(PhC_2Ph)(PMe_3)_3]$.

$[WCl_2(PhC_2Ph)(CO)(PMe_3)_2]$ **11**. A solution of $[WCl_3(PhC_2Ph)(PMe_3)_2]$ (0.9 g, 1.45 mmol) in benzene (65 cm^3) was added to a pressure bottle containing sodium–mercury amalgam (Na, 35 mg, 1.5 mmol; Hg, 28 g) and the vessel was vented twice with carbon monoxide and then run up to a pressure of 12.45 kPa. The mixture was stirred rapidly for 3 h, filtered and the spent amalgam washed with benzene (2 × 5 cm^3). The filtrate and washings were combined and the volatiles removed to give a blue solid (crude yield 0.9 g). Recrystallisation from diethyl ether (100 cm^3) and successive reduction of solution volume gave the complex as dark blue crystals. Yield: 0.64 g (72%). IR spectrum: 1940s (br), 1598w, 1572w, 1450s, 1418s, 1378s, 1305w, 1285s, 1180w, 1160w, 1110w, 1078w, 1030w, 950s, 850w, 770m, 740m, 710m, 695m, 600w, 580w, 560w, 542w, 518w, 460w, 385w, 342w, 290m and 240w cm^{-1}.

[$WCl_2(PhC_2Ph)(CO)(PMePh_2)_2$] **12**. The complex [$WCl_3(PhC_2Ph)(PMePh_2)_2$] (1.0 g, 1.15 mmol) in benzene (80 cm^3) was reduced with sodium–mercury amalgam (Na, 30 mg, 1.3 mmol; Hg, 30 g) under carbon monoxide as for complex **11**. Recrystallisation from diethyl ether gave the complex as blue crystals. Yield: 0.6 g (61%). IR spectrum: 1940s, 1595w, 1568w, 1450s, 1435s, 1375s, 1315w, 1280w, 1190w, 1160w, 1095m, 1070w, 1028w, 1000w, 940w, 890s, 780m, 740s, 695s, 600w, 580w, 555w, 538w, 505s, 480m, 450m, 405w, 350w, 290m and 245w cm^{-1}.

Crystallography.—Crystal data for complexes **11** and **12** are given in Table 8, together with information on instrumentation, data collection and structure determination. Data collection on a Nonius CAD-4 diffractometer used graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) and ω–2θ scans at room temperature. Lorentz and polarisation corrections were applied using locally written programs and absorption corrections applied from empirical psi scans.[17] The structures were solved from Patterson and heavy-atom electron-density syntheses and refined by full-matrix least squares on F using the program SHELX 76.[18] The heavier atoms were assigned anisotropic thermal parameters, the light atoms were refined isotropically. Hydrogen atoms were included in calculated positions and allowed to ride on the atom to which they were attached with a common thermal parameter.

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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