

Evaluation of the 2,6-Diisopropylphenylimido Ligand as a Steric Force in d^1 and d^2 Monomeric Octahedral Complexes of Tungsten†

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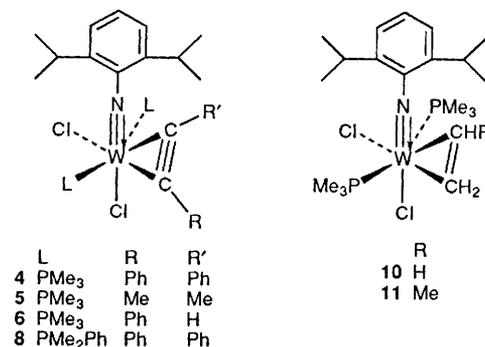
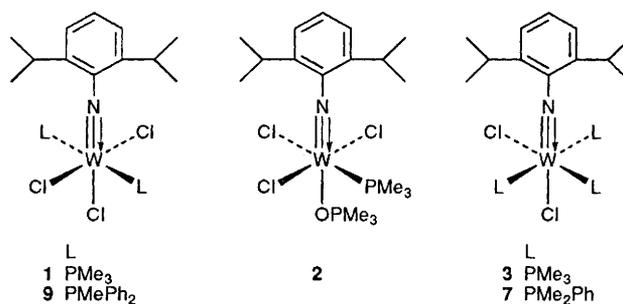
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Reduction of $[\{WCl_4(NC_6H_3Pr^i_2-2,6)\}_2]$ with 2 equivalents of Na–Hg amalgam in the presence of phosphines gave the d^1 complexes $[WCl_3(NC_6H_3Pr^i_2-2,6)L_2]$ ($L = PMe_3, PMe_2Ph$ or $PMePh_2$). The crystal structure of $[WCl_3(NC_6H_3Pr^i_2-2,6)(PMe_3)_2]$ **1** shows the 2,6-diisopropylphenylimido ligand exerts a greater *trans* influence than a phenylimido ligand but only slightly more steric pressure. Solutions of complex **1** react with air to give $[WCl_3(NC_6H_3Pr^i_2-2,6)(PMe_3)(OPMe_3)]$ **2** for which the crystal structure shows the $OPMe_3$ ligand lying *trans* to the imido ligand. Reduction of $[\{WCl_4(NC_6H_3Pr^i_2-2,6)\}_2]$ with 4 equivalents of Na–Hg amalgam in the presence of phosphines gave the d^2 complexes $[WCl_2(NC_6H_3Pr^i_2-2,6)L_3]$ ($L = PMe_3$ or PMe_2Ph). Complex $[WCl_2(NC_6H_3Pr^i_2-2,6)(PMe_3)_3]$ **3** reacts with alkynes L' to give the complexes $[WCl_2(NC_6H_3Pr^i_2-2,6)L'(PMe_3)_2]$ ($L' = PhC_2Ph, MeC_2Me$ or PhC_2H) for which 1H and ^{13}C - $\{^1H\}$ NMR spectral data were obtained. The crystal structure of $[WCl_2(NC_6H_3Pr^i_2-2,6)(PhC_2H)(PMe_3)_2]$ **6** shows *cis*-chloro ligands, *trans*-phosphines and mutually *cis*-imido and alkyne ligands. The C(6) isopropyl group rotates to minimise the isopropyl group and PhC_2H interaction. The complex $[WCl_2(NC_6H_3Pr^i_2-2,6)(PhC_2Ph)(PMe_2Ph)_2]$ can be prepared but not $[WCl_2(NC_6H_3Pr^i_2-2,6)(PhC_2Ph)(PMePh_2)_2]$. Reduction of $[WCl_3(NC_6H_3Pr^i_2-2,6)(PMe_3)_3]$ by Na–Hg amalgam in the presence of olefins gave the complexes $[WCl_2(NC_6H_3Pr^i_2-2,6)L'(PMe_3)_2]$ ($L' = CH_2CH_2$ or CH_2CHMe). A more bulky organoimido ligand or a large phosphine is needed to exert steric pressure in all the complexes prepared.

Use of the 2,6-diisopropylphenylimido ligand in the field of tungsten organoimido chemistry has led to a variety of interesting complexes containing bis- and tris-organoimido ligands.^{1–3} However, the chemistry of complexes containing only one of these sterically hindering ligands is less well developed although alkyl and alkylidene complexes are well established.^{1,4} We have shown that a variety of d^1 and d^2 phenylimido complexes of tungsten can be prepared containing phosphine ligands^{5,6} and that these complexes are useful precursors for the preparation of organoimido complexes which contain π -acceptor ligands.^{7–10} We report here the results of studies undertaken to ascertain how the steric properties of the 2,6-diisopropylphenylimido ligand affect the formation of phosphine, alkyne and olefin complexes of tungsten in d^1 and d^2 configurations.

Results and Discussion

Organoimido complexes of tungsten(v) containing ancillary phosphine ligands are easily prepared *via* phosphine reduction of tungsten(vi) organoimido complexes.^{5,6} However with the expectation that steric effects would hinder this reaction, reduction of $[\{WCl_4(NC_6H_3Pr^i_2-2,6)\}_2]$ was carried out in benzene using 2 equivalents of Na–Hg amalgam in the presence of 4 equivalents of PMe_3 . This procedure led to a high yield of $[WCl_3(NC_6H_3Pr^i_2-2,6)(PMe_3)_2]$ **1**. The complex has a solid-state magnetic moment ($\mu_{eff} = 1.49 \mu_B$) consistent with a d^1 configuration for this type of complex, and a far-IR spectrum (Table 1) similar to that obtained for $[WCl_3(NPh)(PMe_3)_2]$ ⁶ which has a *mer* arrangement of the three chloro ligands and *trans* phosphines. This geometry was confirmed in complex **1** by



a crystal-structure determination which shows one chloro ligand in the *mer* trichloro set lying *trans* to the imido ligand (Fig. 1). Atomic coordinates are contained in Table 2 and selected bond lengths and angles are listed in Table 3. The various bond lengths are similar to those found for

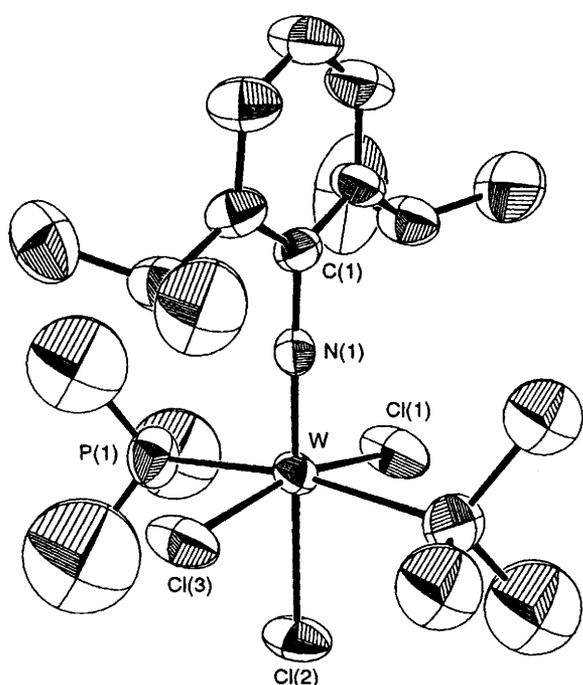
† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: $\mu_B \approx 9.274 \times 10^{-24} J T^{-1}$.

Table 1 Physical data

	Colour	Analysis ^a (%)			IR/cm ⁻¹ W-Cl
		C	H	N	
1 [WCl ₃ (NC ₆ H ₃ Pr ⁱ ₂ -2,6)(PMe ₃) ₂]	Brown	35.3 (35.0)	5.9 (5.8)	2.0 (2.3)	295, 255, 242
3 [WCl ₂ (NC ₆ H ₃ Pr ⁱ ₂ -2,6)(PMe ₃) ₃]	Purple	38.3 (38.3)	6.7 (6.7)	2.0 (2.1)	275, 230
4 [WCl ₂ (NC ₆ H ₃ Pr ⁱ ₂ -2,6)(Ph ₂ Ph)(PMe ₃) ₂] ^{b,c}	Yellow	53.0 (52.6)	6.1 (6.1)	1.7 (1.8)	275, 242
6 [WCl ₂ (NC ₆ H ₃ Pr ⁱ ₂ -2,6)(Ph ₂ H)(PMePh ₂) ₂] ^{c,d}	Yellow	46.4 (46.5)	6.1 (6.1)	1.2 (2.0)	275, 240
9 [WCl ₃ (NC ₆ H ₃ Pr ⁱ ₂ -2,6)(PMePh ₂) ₂]	Brown	52.7 (52.7)	5.1 (5.0)	1.3 (1.6)	302 (br), 265, 248
10 [WCl ₂ (NC ₆ H ₃ Pr ⁱ ₂ -2,6)(CH ₂ CH ₂)(PMe ₃) ₂]	Yellow	39.2 (39.4)	6.0 (6.4)	2.6 (2.3)	302, 260
11 [WCl ₂ (NC ₆ H ₃ Pr ⁱ ₂ -2,6)(CH ₂ CHMe)(PMe ₃) ₂] ^{c,e}	Yellow	45.2 (45.3)	6.7 (6.7)	2.1 (2.0)	305, 280

^a Calculated values given in parentheses. ^b Calculated analytical data include $\frac{1}{2}$ C₆H₆. ^c Solvent supported by NMR spectra. ^d Calculated analytical data includes $\frac{1}{2}$ C₇H₈. ^e Calculated data include $\frac{2}{3}$ C₆H₆.

**Fig. 1** Molecular structure of complex **1**; atoms are depicted as 50% probability surfaces

[WCl₃(NPh)(PMe₃)₂]⁶ except for the W-Cl(2) bond which is longer in complex **1** {2.490(2) versus 2.470(2) Å for [WCl₃(NPh)(PMe₃)₂]} showing that the 2,6-diisopropylimido ligand exerts a greater *trans* influence. In both complex **1** and [WCl₃(NPh)(PMe₃)₂] the aromatic ring and *trans* chloro ligands are essentially coplanar. The isopropyl group hydrogen atoms in complex **1** lie above and only slightly to either side of the *trans* chloro ligands so that the isopropyl groups are accommodated without significant twisting. However, as a result, the Cl(1)-W-Cl(3) bond angle in complex **1** is smaller than that observed for [WCl₃(NPh)(PMe₃)₂] [165.2(1) vs. 170.18(9)°⁶]. The isopropyl methyl groups exert a small influence on the phosphine ligands in complex **1** pushing the P(1)-W-P(2) bond angle to 169.5(1)° compared with 172.78(7)° in [WCl₃(NPh)(PMe₃)₂].⁶

The complex [WCl₃(NC₆H₃Prⁱ₂-2,6)(PMe₃)₂] **1** is a brown solid which is not particularly air sensitive. However crystallisations without protection from air gave in addition to

Table 2 Atomic coordinates for complex **1**

Atom	x	y	z
W	1501(1)	618(1)	1239(1)
Cl(1)	226(3)	288(2)	276(2)
Cl(2)	446(3)	2445(2)	1255(2)
Cl(3)	2520(3)	1395(2)	2215(1)
P(1)	2947(3)	1633(3)	471(2)
P(2)	-141(3)	-61(3)	2017(2)
N(1)	2234(4)	-669(5)	1214(3)
C(1)	2793(6)	-1723(6)	1198(4)
C(2)	2455(9)	-2550(6)	720(5)
C(3)	3015(11)	-3556(8)	735(6)
C(4)	3873(10)	-3800(8)	1214(5)
C(5)	4182(10)	-2995(8)	1702(5)
C(6)	3700(7)	-1936(8)	1705(4)
C(7)	1551(10)	-2305(8)	147(5)
C(8)	653(12)	-3211(15)	93(9)
C(9)	2198(18)	-2090(26)	-511(7)
C(10)	4083(10)	-1080(9)	2216(5)
C(11)	5409(11)	-893(13)	2172(8)
C(12)	3734(15)	-1346(17)	2955(7)
C(13)	2562(25)	1928(27)	-370(13)
C(14)	4342(23)	970(27)	515(15)
C(15)	3182(40)	3048(30)	711(18)
C(16)	71(16)	154(17)	2961(7)
C(17)	-1584(20)	502(19)	1805(12)
C(18)	-412(15)	-1550(13)	1909(8)

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

Cl(1)-W	2.387(3)	P(2)-W	2.516(3)
Cl(2)-W	2.490(2)	N(1)-W	1.750(6)
Cl(3)-W	2.382(3)	C(1)-N(1)	1.405(9)
P(1)-W	2.524(3)		
Cl(1)-W-Cl(2)	83.2(1)	P(2)-W-Cl(3)	91.0(1)
Cl(1)-W-Cl(3)	165.2(1)	P(1)-W-P(2)	169.5(1)
Cl(2)-W-Cl(3)	82.1(1)	N(1)-W-Cl(1)	97.7(2)
P(1)-W-Cl(1)	91.1(1)	N(1)-W-Cl(2)	179.0(2)
P(1)-W-Cl(2)	85.5(1)	N(1)-W-Cl(3)	97.1(2)
P(1)-W-Cl(3)	87.6(1)	N(1)-W-P(1)	95.0(2)
P(2)-W-Cl(1)	87.6(1)	N(1)-W-P(2)	95.5(2)
P(2)-W-Cl(2)	84.0(1)	C(1)-N(1)-W	178.0(5)

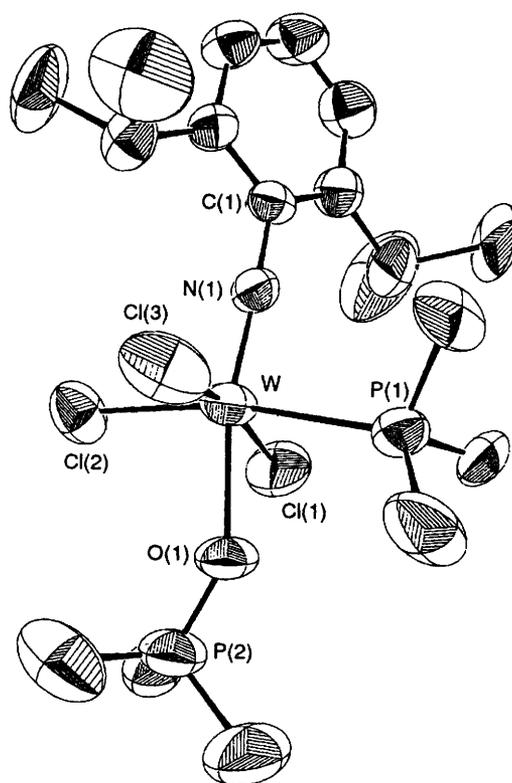
complex **1**, small quantities of green-brown crystals one of which was shown by X-ray crystallography to be [WCl₃(NC₆H₃Prⁱ₂-2,6)(PMe₃)(OPMe₃)] **2**. Atomic coordinates for complex **2** are listed in Table 4. In the crystal studied,

Table 4 Atomic coordinates for complex **2**. Primed atoms are for the second of the two orientationally disordered PMe_3 and OPMe_3 groups

Atom	x	y	z
W	2136(1)	1457(1)	3404(1)
Cl(1)	580(2)	1085(2)	3910(2)
Cl(2)	1168(1)	1461(1)	1941(1)
Cl(3)	3588(2)	2250(1)	2955(2)
P(1)	2950(8)	1753(8)	4994(8)
Cl(13)	4115(13)	1069(22)	5220(23)
C(14)	3320(30)	3023(18)	5271(21)
C(15)	2333(30)	1345(15)	5823(17)
P(1')	3254(8)	1947(9)	4794(8)
C(13')	4486(14)	1240(21)	5053(25)
C(14')	3658(31)	3286(19)	4916(19)
C(15')	2565(30)	1854(20)	5698(20)
P(2)	911(2)	3863(2)	3302(1)
O(1)	1499(16)	2921(18)	3633(15)
C(16)	1052(25)	4773(20)	4122(18)
C(17)	1296(19)	4409(18)	2429(15)
C(18)	-404(15)	3524(25)	3045(12)
O(1')	1782(16)	3078(18)	3379(15)
C(16')	558(27)	4215(25)	4293(18)
C(17')	1401(23)	5002(14)	2896(18)
C(18')	-262(17)	3544(27)	2567(14)
N(1)	2591(3)	200(4)	3456(3)
C(1)	2940(4)	-811(4)	3457(4)
C(2)	2704(5)	-1510(5)	4067(4)
C(3)	3055(6)	-2507(5)	4020(5)
C(4)	3589(6)	-2813(5)	3409(5)
C(5)	3806(5)	-2123(5)	2819(5)
C(6)	3487(4)	-1116(4)	2815(4)
C(7)	2057(8)	-1209(8)	4725(6)
C(8)	2701(46)	-1355(33)	5692(19)
C(8')	2659(40)	-1317(34)	5554(27)
C(9)	1101(9)	-1858(12)	4640(8)
C(10)	3727(6)	-353(5)	2165(4)
C(11')	3156(46)	-667(37)	1309(25)
C(11)	3639(49)	-771(32)	1248(30)
C(12)	4863(8)	-115(8)	2338(8)

Table 5 Selected bond lengths (Å) and angles ($^\circ$) for complex **2**

Cl(1)-W	2.386(2)	P(2)-O(1')	1.52(2)
Cl(2)-W	2.419(2)	O(1)-W	2.15(2)
Cl(3)-W	2.398(2)	O(1')-W	2.17(2)
P(1)-W	2.568(18)	N(1)-W	1.743(5)
P(1')-W	2.483(13)	N(1)-C(1)	1.398(7)
P(2)-O(1)	1.49(2)		
Cl(1)-W-Cl(2)	89.69(8)	Cl(3)-W-O(1)	91.4(4)
Cl(1)-W-Cl(3)	166.13(7)	Cl(3)-W-O(1')	75.7(4)
Cl(1)-W-P(1)	85.6(2)	N(1)-W-Cl(1)	95.8(2)
Cl(1)-W-P(1')	98.9(2)	N(1)-W-Cl(2)	99.2(2)
Cl(1)-W-O(1)	74.7(4)	N(1)-W-Cl(3)	97.7(2)
Cl(1)-W-O(1')	90.6(4)	N(1)-W-P(1)	91.2(3)
Cl(2)-W-Cl(3)	90.98(7)	N(1)-W-P(1')	93.6(3)
Cl(2)-W-P(1)	169.0(2)	N(1)-W-O(1)	166.5(5)
Cl(2)-W-P(1')	163.9(2)	N(1)-W-O(1')	172.5(6)
Cl(2)-W-O(1)	90.5(7)	P(2)-O(1)-W	150.0(2)
Cl(2)-W-O(1')	84.8(7)	P(2)-O(1')-W	144.5(12)
Cl(3)-W-P(1)	91.2(2)	C(1)-N(1)-W	177.4(4)
Cl(3)-W-P(1')	77.4(2)		

**Fig. 2** Molecular structure of complex **2**. Only one of the alternative PMe_3 and OPMe_3 orientations is shown; atoms are represented as 50% probability surfaces

the PMe_3 and OPMe_3 groups could each be resolved into two separate molecules occupying the same co-ordination sites, with equal occupancy, but oriented slightly differently. The two sets of atoms are labelled with and without primes. The structure (Fig. 2) consists of a distorted octahedral array with three chloro ligands in the equatorial plane. The PMe_3 and OPMe_3 ligands lie *cis* to each other, the former lying in the equatorial plane *trans* to a chloro ligand and the latter *trans* to the imido ligand. In complex **1** rotation of the imido ligand is constrained by the *trans*-phosphine ligands but the new geometry of complex **2** is such that the isopropyl C-H atoms lie nearly midway between the Cl(1)-W-P(1) [or Cl(1)-W-P(1')] and Cl(2)-W-Cl(3) vectors.

Selected bond lengths and angles for complex **2** are contained in Table 5. The W-P(1), W-Cl(2) and W-Cl(3) bond lengths are not significantly different to those found for complex **1**. The W-Cl(2) bond length [2.419(2) Å] is slightly longer than for the *trans*-chloro ligands [W-Cl(1) 2.386(2), W-Cl(3) 2.398(2) Å] due to the *trans* ligand now being PMe_3 . This phosphine ligand does not push away significantly from the imido ligand [N(1)-W-P(1) 91.2(3), N(1)-W-P(1') 93.6(3) $^\circ$] compared with complex **1** [N(1)-W-P(1) 95.0(2), N(1)-W-P(2) 95.5(2) $^\circ$]. However, the three equatorial chloro ligands of complex **2** do push away. The N(1)-W-Cl(1) and N(1)-W-Cl(3) bond angles [95.8(2) and 97.7(2) $^\circ$] are similar to those found for complex **1** and the N(1)-W-Cl(2) bond angle is larger than these at 99.2(2) $^\circ$.

The Me_3PO ligand orientates with its Me_3P group below Cl(2) more than Cl(1) and the methyl groups are rotated to minimise C-H interactions with Cl(2). As a result the P(2)-O(1)-W bond angle [150(0) $^\circ$] [P(2)-O(1')-W 144(1) $^\circ$] is

larger than expected for electron donation from an oxygen sp^2 orbital (120 $^\circ$).

Reduction of [$\{\text{WCl}_4(\text{NC}_6\text{H}_3\text{Pr}^i_2-2,6)\}_2$] with 4 equivalents of Na-Hg amalgam in the presence of 6 equivalents of PMe_3 , proceeded smoothly giving [$\text{WCl}_2(\text{NC}_6\text{H}_3\text{Pr}^i_2-2,6)(\text{PMe}_3)_3$] **3**. The complex has a *cis*-dichloro, *mer*-phosphine structure based on two W-Cl stretches in the far-IR spectrum¹¹ and a triplet and doublet for the PMe_3 ligands in the ^1H and $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra¹² (Table 6). The ^1H NMR spectrum shows only one isopropyl CH resonance and one doublet for the methyl groups even though the expected equatorial arrangement of phosphine ligands gives rise to different isopropyl group environments on either side of the imido ligand aromatic ring. Similarly, the

Table 6 NMR spectral data^a

Complex	¹ H ^b	¹³ C- ¹ H ^{b,c}
3	1.18 [d, ³ J(HH) 6.7, 12 H, CHMe ₂], 1.62 [t, ² J(HP) ^d 3.5, 18 H, PMe ₃], 1.77 [d, ² J(HP) 8.0, 9 H, PMe ₃], 3.89 (spt, 2 H, CHMe ₂), 6.99 [d, ³ J(HH) 7.6, 2 H, <i>m</i> -H], 7.20 [t, ³ J(HH) 7.6, 1 H, <i>p</i> -H]	16.8 [t, ¹ J(CP) 13.5, PMe ₃], 23.8 (Me), 26.0 (CH), 26.0 and 26.3 [d, ¹ J(CP) 29.3, PMe ₃], 122.3 (<i>m</i> -C) 124.1 (<i>p</i> -C), 143.7 (<i>o</i> -C), 149.7 (<i>ipso</i> -C)
4	0.95 and 1.18 [2d, ³ J(HH) 6.6, 12 H, CHMe ₂], 1.42 [t, ² J(HP) ^d 4.4, 18 H, PMe ₃], 3.25 [spt, 1 H, CHMe ₂], 4.36 (spt, 1 H, CHMe ₂), 7.00, 7.24 and 7.42 (m, aromatic C-H)	14.2 [t, ¹ J(CP) 15.2, PMe ₃], 23.3 and 23.7 (Me), 25.2 and 25.3 (CH), 125.1, 126.2, 126.4, 126.6, 126.8, 126.9 and 130.1 (aromatic CH), 141.7 (<i>ipso</i> -C _{acet}), 146.8 (<i>ipso</i> -C _{imido}), 147.9 (<i>o</i> -C _{imido}), 154.4 [t, ² J(CP) 12.3, C≡C]
5	0.92 [d, ³ J(HH) 6.8, CHMe ₂], 1.16 [dd, ³ J(HH) 6.8, CHMe ₂], 1.75 [t, ² J(HP) ^d 5.2, 18 H, PMe ₃], 2.78 (s, 6 H, Me), 3.05 (br spt 1 H, CHMe ₂) 4.43 (br spt, 1 H, CHMe ₂), 6.95 (d, 1 H, <i>p</i> -H), 7.05 (m, 2 H, <i>m</i> -H)	14.8 [t, ¹ J(CP) 14.9, PMe ₃], 16.9 (Me), 23.4 and 24.3 (CHMe ₂) 26.3 and 26.4 (CHMe ₂), 126.9 (<i>m</i> -C), 127.9 (<i>p</i> -C), 146.7 [t, ² J(CP) 12.9, C≡C], 147.9, 148.9 and 149.8 (<i>ipso</i> - and <i>o</i> -C _{imido})
6 ^e	0.82 [d, ³ J(HH) 6.6, 3 H, Me], 1.03 [d, ³ J(HH) 6.7, 3 H, Me], 1.12 [d, ³ J(HH) 6.7, 3 H, Me], 1.16 [d, ³ J(HH) 6.6, 3 H, Me], 1.37 and 1.72 [2d, ² J(HP) 9.3, 18 H, PMe ₃], 2.83 (spt, 1 H, CHMe ₂), 4.46 (spt, 1 H, CHMe ₂), 6.89–7.40 (m, 3 H, imido H), 7.16 [t, ³ J(HH) 7.3, 1 H, <i>p</i> -H _{acet}], 7.31 [t, ³ J(HH) 7.7, 2 H, <i>m</i> -H _{acet}], 7.70 [d, ³ J(HH) 7.80, 2 H, <i>o</i> -H _{acet}]	14.1 and 14.2 [2d, ¹ J(CP) 31.2 and 31.4, PMe ₃] 22.2, 24.3, 25.1 and 25.2 (Me), 26.4 and 26.6 (CH), 122.6, 123.7, 126.7, 127.2, 127.6 and 128.0 (aromatic CH), 140.7 [dd, ² J(CP) _{cis} 5.6, ² J(CP) _{trans} 22.8, ≡CH], 143.3 [t, ³ J(CP) 3.2, <i>ipso</i> -C _{acet}], 148.7 (<i>o</i> -C _{imido}) 149.3 (prt, <i>ipso</i> -C _{imido}), 149.8 (<i>o</i> -C _{imido}), 152.6 [dd, ² J(CP) _{cis} 5.2, ² J(CP) _{trans} 16.0, PhC≡]
8	0.95 [obsc d, ³ J(HH) 6.8, 12 H, CHMe ₂], 1.65 and 1.78 [2t, ² J(HP) ^d 3.2, 12 H, PMe ₃], 3.15 (spt, 1 H, CHMe ₂), 4.48 (spt, 1 H, CHMe ₂), 6.74 (d), 6.92 (m), 7.10 (m), 7.24 (s) and 7.45 (m), (aromatic H)	12.9 and 15.0 [2t, ¹ J(CP) 15.2 and 15.4, PMe ₂], 24.2 and 24.6 (Me), 26.6 and 26.8 (CH), 122.5, 123.0, 124.0, 125.6, 127.2, 127.4, 127.5 [t, ¹ J(CP) 4.5], 128.0, 128.1, 129.2, 131.2 [t, ¹ J(CP) 4.4] and 131.3 (aromatic CH), 134.8 [t, ¹ J(CP) 21.6, <i>ipso</i> -C of PMe ₂ Ph], 142.3 (<i>ipso</i> -C _{acet}), 149.6, 150.2 and 150.3 (<i>ipso</i> - and <i>o</i> -C _{imido}), 154.8 [t, ² J(CP) 12.1, C≡C]
10	1.12 [d, ³ J(HH) 6.7, 12 H, CHMe ₂], 1.12 (obsc, 2 H, CH ₂), 1.69 [t, ² J(HP) ^d 4.3, 18 H, PMe ₃], 2.10 (spt, 2 H, CHMe ₂), 2.14 (m, 2 H, CH ₂), 6.97 [d, ³ J(HH) 7.5, 2 H, <i>m</i> -H], 7.07 [t, ³ J(HH) 7.5, 1 H, <i>p</i> -H]	13.7 [t, ¹ J(CP) 15, PMe ₃], 24.4 (Me ₂), 26.4 (CH), 39.7 [t, ² J(CP) 3.6, CH ₂ CH ₂], 123.4 (<i>m</i> -C), 126.5 (<i>p</i> -C), 148.5 (<i>o</i> -C), 149.3 (<i>ipso</i> -C)
11 ^f	1.05–1.24 (m, 12 H, CHMe ₂), 1.65 and 1.74 [2d, ³ J(HH) 9.2, 9 H, PMe ₃], 2.22 [d, ³ J(HH) 5.8, Me], 2.35 (m), 2.47 [d, ³ J(HH) 5.3, Me], 2.52 (m), 2.61 (m), 2.82 (m), 2.93 (m), 3.82 (m), 6.92–7.15 (m, aromatic H)	13.8 and 14.5 [2d, ¹ J(CP) 28.8 and 28.2, PMe ₃] 24.6, 25.0 and 26.5 (Me), 27.1 and 27.2 (CH), 45.7 [d, ² J(CP) 8.2, CH ₂], 47.8 [d, ² J(CP) 4.5, CH ₂], 48.9 [d, ² J(CP) 7.7, CH], 51.5 [d, ² J(CP) 6.3, CH], 123.5 and 123.8 (<i>m</i> -C), 126.5 and 126.6 (<i>p</i> -C) 128.3 (benzene), 148.2 and 148.4 (br, <i>o</i> -C) 149.2 (br, <i>ipso</i> -C)

^a Spectra obtained in CDCl₃ solution. ^b br = Broad, spt = septet, d = doublet, dd = doublet of doublets, m = multiplet, obsc = obscured, prt = poorly resolved triplet, s = singlet, t = triplet. ^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. ^d For virtual HP spin coupling ²J(HP) quoted as $\frac{1}{2} [^2J(HP) + ^0J(HP)]$ where ⁰J(HP) is very small. ^e ³¹P-¹H NMR spectrum: δ –12.3 [d, ²J(PP)_{trans} 168.1, ¹J(PW) 210.3], –17.7 [d, ²J(PP)_{trans} 168.1, ¹J(PW) 222.7 Hz]. ^f ³¹P-¹H NMR spectrum: δ –16.0 [d, ²J(PP)_{trans} 176.0, ¹J(PW) 242.1], –20.0 [d, ²J(PP)_{trans} 176.0, ¹J(PW) 225.6], –19.0 [d, ²J(PP)_{trans} 161.0], –20.1 [d, ²J(PP)_{trans} 161.0 Hz].

¹³C-¹H NMR spectrum shows one methyl resonance and one isopropyl carbon resonance.

Complex 3 reacts readily with diphenylacetylene under reflux in toluene to give [WCl₂(NC₆H₃Prⁱ₂-2,6)(PhC₂H)(PMe₃)₂] 4. The complex has a *cis*-chloro, *trans*-phosphine geometry based on two W–Cl stretches in the IR spectrum and a virtually coupled triplet for the PMe₃ ligands in the ¹H and ¹³C-¹H NMR spectra. In comparison with complex 3, complex 4 exhibits two isopropyl group C–H proton resonances and two isopropyl group methyl doublets in the ¹H NMR spectrum and two sets of resonances in the ¹³C-¹H NMR spectrum for each of the appropriate carbons.

Complex 5 [WCl₂(NC₆H₃Prⁱ₂-2,6)(MeC₂Me)(PMe₃)₂] was prepared by reduction of [WCl₃(NC₃H₆Prⁱ₂-2,6)(PMe₃)₂] with 1 equivalent of Na–Hg amalgam in the presence of but-2-yne. The complex was characterised by NMR spectroscopy which showed essentially the same spectra as for the diphenylacetylene complex except that the acetylenic carbons appear at δ146.7 for co-ordinated but-2-yne compared with δ154.4 for the diphenylacetylene ligand.

Reaction of phenylacetylene with complex 3 under reflux in benzene gave [WCl₂(NC₆H₃Prⁱ₂-2,6)(PhC₂H)(PMe₃)₂] 6 which has a *cis*-chloro, *trans*-phosphine geometry based on IR and NMR spectra. Co-ordination of PhC₂H leads to asymmetry in the molecule which is reflected in the NMR spectra of the phosphine ligands. The ¹H and ¹³C-¹H NMR spectra each show the PMe₃ ligands as a pair of doublets and in the ³¹P-¹H NMR spectrum there is an AB system with ²J(PP) 168.1 Hz which is consistent with *trans*-phosphines.¹³ The two

W–P coupling constants are dissimilar (210.3 and 222.7 Hz) which suggests that in solution the two W–P bond lengths are slightly different.¹⁴ In the ¹H NMR spectrum there are two resonances for the isopropyl C–H protons and four methyl resonances of equal intensity showing that these groups have become diastereotopic in the presence of the asymmetric PhC₂H ligand. Similarly, in the ¹³C-¹H NMR spectrum there are two isopropyl CH resonances and four methyl group resonances.

The overall geometry of complex 6 was obtained from an X-ray crystal structure determination. The molecule (Fig. 3) consists of a distorted octahedral array with *trans*-phosphines, *cis*-chloro ligands and mutually *cis*-orientated 2,6-diisopropylphenylimido and phenylacetylene ligands. Atomic coordinates are contained in Table 7 and selected bond lengths and angles are listed in Table 8.

The bond lengths within the molecule are generally similar to those found for [WCl₂(NPh)(PhC₂H)(PMe₃)₂]⁷ apart from two exceptions. First, the W–Cl(2) bond length for the chloro ligand lying *trans* to the imido function [2.541(1) Å] is considerably longer than in the phenylimido complex [2.503(8) Å]. This may be a result of increased electron density in the tungsten–nitrogen multiple bond, arising from the electron donating isopropyl groups. There is however no difference in the W–N bond lengths in both complexes. Secondly, the W–P(2) bond length [2.533(2) Å], is significantly shorter than the W–P(1) bond length [2.553(2) Å] when the P(1) phosphine ligand lies adjacent to the alkyne phenyl group. In solution this is reflected in the ³¹P-¹H NMR spectrum by the difference in

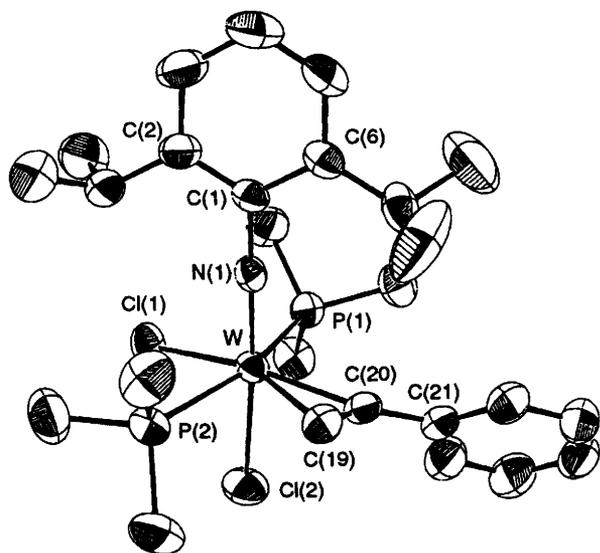


Fig. 3 Molecular structure of complex **6**; atoms are depicted as 50% probability surfaces

Table 7 Atomic coordinates for complex **6**

Atom	x	y	z
W	1766(1)	1410(1)	1061(1)
P(1)	329(1)	854(1)	1279(1)
P(2)	3179(1)	1705(1)	499(1)
Cl(2)	1101(1)	2148(1)	109(1)
Cl(1)	1677(1)	598(1)	64(1)
N(1)	2206(2)	833(2)	1664(2)
C(1)	2524(3)	362(2)	2144(2)
C(2)	2998(3)	-196(2)	1907(3)
C(3)	3278(4)	-652(3)	2403(3)
C(4)	3092(4)	-573(3)	3116(3)
C(5)	2642(4)	-30(3)	3349(3)
C(6)	2350(3)	453(3)	2879(2)
C(7)	3197(4)	-301(3)	1129(3)
C(8)	2724(5)	-910(3)	835(3)
C(9)	4150(4)	-388(3)	998(4)
C(10)	1904(3)	1068(3)	3157(3)
C(11)	2546(5)	1596(4)	3365(4)
C(12)	1298(6)	921(5)	3765(4)
C(13)	-444(4)	968(3)	583(3)
C(14)	-251(4)	1023(3)	2092(3)
C(15)	453(4)	-47(3)	1348(3)
C(16)	3295(4)	2544(3)	170(4)
C(17)	3558(4)	1203(3)	-240(3)
C(18)	4030(4)	1626(3)	1135(3)
C(19)	2113(4)	2285(3)	1606(3)
C(20)	1361(4)	2203(2)	1744(3)
C(21)	648(4)	2552(2)	2112(3)
C(22)	-74(4)	2729(3)	1744(4)
C(23)	-720(4)	3096(3)	2068(4)
C(24)	-639(5)	3274(3)	2777(4)
C(25)	68(4)	3099(3)	3148(3)
C(26)	714(4)	2739(3)	2820(3)

magnitude of the two $^1J(\text{PW})$ values (10 Hz). The two W–C bond lengths [2.095(5) and 2.132(5) Å] are just significantly different and lie in the range of values found for two-electron donor alkynes.¹⁵

The phosphine ligands push back significantly from the acetylene ligand [P(1)–W–P(2) 161.2(1)°], but very little from the organoimido ligand [P–W–P 182.0(0)°]. The P(1)–W–Cl(1) bond angle [77.7(1)°] is similar to that found for the two P–W–Cl bond angles in [WCl₂(NPh)(PhC₂Ph)(PMe₃)₂] [78.8(3) and 79.9(3)°] while the P(2)–W–Cl(1) bond angle opens out [83.5(1)°] where the P(2) phosphine lies adjacent to the acetylene C–H bond. As the two N–W–P bond angles and

Table 8 Selected bond lengths (Å) and angles (°) for complex **6**

Cl(1)–W	2.479(1)	N(1)–W	1.757(4)
Cl(2)–W	2.541(1)	C(19)–W	2.095(5)
P(1)–W	2.553(2)	C(20)–W	2.132(5)
P(2)–W	2.533(2)	C(19)–C(20)	1.223(7)
Cl(1)–W–Cl(2)	79.9(1)	N(1)–W–P(2)	94.2(1)
Cl(1)–W–P(1)	77.7(1)	C(1)–N(1)–W	177.7(3)
Cl(1)–W–P(2)	83.5(1)	C(19)–W–N(1)	97.4(2)
Cl(2)–W–P(1)	89.9(1)	C(20)–W–N(1)	102.5(2)
Cl(2)–W–P(2)	86.3(1)	C(19)–W–C(20)	33.6(2)
P(1)–W–P(2)	161.2(1)	C(9)–C(14)–W	71.5(4)
N(1)–W–Cl(1)	94.6(1)	C(20)–C(19)–W	74.8(4)
N(1)–W–Cl(2)	174.4(1)	C(21)–C(20)–C(19)	139.8(5)
N(1)–W–P(1)	87.8(1)		

the P(1)–W–Cl(1) bond angle are similar to those found for the phenylimido complex, it is apparent that the isopropyl substituents on the phenyl ring of complex **6** have little steric effect on the phosphine ligands.

The phenylacetylene ligand in complex **6** is twisted about the P(2)–W–P(1) vector to about the same extent found for the diphenylacetylene ligand in [WCl₂(NPh)(PhC₂Ph)(PMe₃)₂]. In complex **6** both the imido ligand phenyl group and one isopropyl group rotate to minimise the C(6) isopropyl group interaction with the acetylene ligand. The phenyl ring rotation is such that the C(2) isopropyl group does not need to rotate to minimise interaction of the C(H) proton and the phosphine ligand. The rotations observed give rise to different environments for the four isopropyl methyl groups so that they become diastereotopic as both the ¹H and ¹³C–{¹H} NMR spectra show.

We have attempted to form diphenylacetylene complexes similar to complex **3** which contain more sterically hindering phosphine ligands. The complex [(WCl₄(NC₆H₃Prⁱ₂-2,6))₂] was reduced with Na–Hg amalgam in the presence of PMe₂Ph to give a green solid expected to be [WCl₂(NC₆H₃Prⁱ₂-2,6)(PMe₂Ph)₃] **7**. This complex was not characterised but reacted directly with PhC₂Ph in benzene under reflux to give [WCl₂(NC₆H₃Prⁱ₂-2,6)(PhC₂Ph)(PMe₂Ph)₂] **8**. Characterised by NMR spectroscopy, the complex showed two triplets in the ¹H and ¹³C–{¹H} NMR spectra characteristic of *trans* PMe₂Ph ligands. In the ¹H NMR there were two isopropyl group C–H protons (δ 3.15 and 4.48) and two broadened doublets for the isopropyl methyl groups. In the ¹³C–{¹H} NMR spectrum both the isopropyl methyl and C–H protons appeared as two sets of resonances each and the acetylenic carbon resonance at a normal position of δ 154.8.

When a one-electron reduction per metal of [(WCl₄(NC₆H₃Prⁱ₂-2,6))₂] was carried out in the presence of PMePh₂, [WCl₃(NC₆H₃Prⁱ₂-2,6)(PMePh₂)₂] **9** was formed. This tungsten(v) complex (μ_{eff} = 1.34 μ_B) did not give identifiable products when further reductions were carried out in the presence of PMePh₂ or PhC₂Ph. The complex [(WCl₄(NC₆H₃Prⁱ₂-2,6))₂] can also be reduced by 1 equivalent of Na–Hg amalgam in the absence of other ligands to give a diamagnetic solid containing at least three complexes for which separation has not been successful.

We have also been able to prepare d² 2,6-diisopropylphenylimido complexes containing olefin ligands. Sodium–mercury amalgam reduction of [WCl₃(NC₆H₃Prⁱ₂-2,6)(PMe₃)₂] **1** under ethylene gave rise to [WCl₂(NC₆H₃Prⁱ₂-2,6)(CH₂–CH₂)(PMe₃)₂] **10** which has the usual *cis*-chloro, *trans*-phosphine structure based on two W–Cl stretches in the far-IR spectrum and triplets in the ¹H and ¹³C–{¹H} NMR spectrum for the PMe₃ ligands.¹⁰ There is apparently little steric interaction between the olefin and imido ligand as the CH protons occur as a broad peak in the ¹H NMR spectrum and there is only one isopropyl methyl group resonance. In the

$^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum there is only one resonance for the two primary and secondary carbons of the isopropyl groups.

Reduction of $[\text{WCl}_3(\text{NC}_6\text{H}_3\text{Pr}^1_2\text{-2,6})(\text{PMe}_3)_2]$ with Na–Hg amalgam under propene gave some $[\text{WCl}_2(\text{NC}_6\text{H}_3\text{Pr}^1_2\text{-2,6})(\text{PMe}_3)_3]$ **3** but mainly $[\text{WCl}_2(\text{NC}_6\text{H}_3\text{Pr}^1_2\text{-2,6})(\text{CH}_2\text{CH-Me})(\text{PMe}_3)_2]$ **11**. The olefin complex has two isomeric forms in the approximate ratio of 2:1. The ^1H NMR spectrum contains several overlapping resonances making analysis difficult, but in the $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum the PMe_3 ligands of the major isomer show as an AB quartet and the olefin CH_2 and CH carbons as ^{31}P -coupled doublets. In the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum there is an AB quartet for which the coupling constant of 176.0 Hz is consistent with *trans* phosphines.¹³ In the $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum of the minor isomer, overlapping of PMe_3 resonances precluded analysis but the olefin CH_2 and CH carbon resonances were well defined as ^{31}P -coupled doublets with some evidence of further coupling to ^{31}P . The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum shows an AB quartet consistent with *trans*-phosphine [$^2J(\text{PP})$ 161 Hz] but the inner lines are close together (27.6 compared with 472.9 Hz for the other isomer) so that the phosphine ligands are nearly equivalent in this isomer. The spectra of the complex clearly indicate that the phosphine ligands of the two isomers have different environments but the exact nature is complicated as the methyl group of the co-ordinated propene can lie above or below the equatorial plane¹⁰ and both the phenyl ring and isopropyl groups of the organoimido ligand can rotate.

Conclusion

The results of this work show that the 2,6-diisopropylphenylimido ligand will tolerate a variety of ligands in the equatorial plane of a six-co-ordinate monomeric complex. The structural studies indicate that for the d^1 complexes an isopropyl group is easily accommodated above the equatorial chloro ligands and exerts only a small steric influence. For the d^2 complexes, the isopropyl group rotates to remove interaction with the phenylacetylene ligand and the synthetic work indicates that complexes are not formed when the large PMePh_2 ligand is used. It is thus clear that a bulky organoimido ligand or a large phosphine ligand is needed to bring steric pressure to bear in these molecules.

Experimental

General procedures and instrumentation have been described.¹⁰ The IR spectra were obtained as Nujol mulls, and ^1H and $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra were recorded at 400 and 100 MHz, respectively. Analytical data were obtained by Dr A. G. Cunninghame and associates, University of Otago, New Zealand. Magnetic susceptibility measurements were obtained using a Sherwood Scientific magnetic susceptibility balance. The compound $[\{\text{WCl}_4(\text{NC}_6\text{H}_3\text{Pr}^1_2\text{-2,6})\}_2]$ was prepared from $[\{\text{WCl}_4\text{O}\}_x]$ and 2,6-diisopropylphenyl isocyanate in octane.¹ Trimethylphosphine was prepared by reaction of MgMeI with $\text{P}(\text{OPh})_3$ in di-*n*-butyl ether¹⁶ and PMe_2Ph and PMePh_2 by reaction of MgMeI on PCl_2Ph and PClPh_2 . Light petroleum had a b.p. range of 40–60 °C.

Syntheses.— $[\text{WCl}_3(\text{NC}_6\text{H}_3\text{Pr}^1_2\text{-2,6})(\text{PMe}_3)_2]$ **1**. A solution of $[\{\text{WCl}_4(\text{NC}_6\text{H}_3\text{Pr}^1_2\text{-2,6})\}_2]$ (1.0 g, 2.0 mmol) in benzene (50 cm^3) was added to Na–Hg amalgam (50 mg Na, 2.17 mmol; 30 g Hg) under benzene (25 cm^3) containing PMe_3 (0.5 cm^3 , 4.6 mmol) and the mixture stirred vigorously for 1 h. The solution was filtered and the spent amalgam washed with benzene (2 \times 5 cm^3). Removal of the volatiles from the combined filtrate and washings gave a brown solid. Crude yield: 1.1 g (89%). Recrystallisation from toluene at –20 °C gave the complex as brown crystals 0.82 g (66%). $\mu_{\text{eff}} = 1.49 \mu_{\text{B}}$. IR spectrum: 1580w, 1440s, 1410s, 1370m, 1355m, 1325w, 1280m,

1255w, 1230w, 1175w, 1160w, 1050w, 930s, 845w, 798w, 760m, 740m, 730m, 450w, 295s, 255m and 242m cm^{-1}

$[\text{WCl}_3(\text{NC}_6\text{H}_3\text{Pr}^1_2\text{-2,6})(\text{PMe}_3)(\text{OPMe}_3)]$ **2**. The complex $[\text{WCl}_3(\text{NC}_6\text{H}_3\text{Pr}^1_2\text{-2,6})(\text{PMe}_3)_2]$ was dissolved in toluene in a glass tube and the solution was layered with light petroleum. The tube was stoppered with a plastic cap and allowed to stand for several weeks during which time the solvent volume reduced to one third. Brown crystals of $[\text{WCl}_3(\text{NC}_6\text{H}_3\text{Pr}^1_2\text{-2,6})(\text{PMe}_3)_2]$ were formed along with a small quantity of green-brown crystals one of which was characterised by X-ray crystallography.

$[\text{WCl}_2(\text{NC}_6\text{H}_3\text{Pr}^1_2\text{-2,6})(\text{PMe}_3)_3]$ **3**. A solution of $[\{\text{WCl}_4(\text{NC}_6\text{H}_3\text{Pr}^1_2\text{-2,6})\}_2]$ (1.1 g, 1.1 mmol) in benzene (50 cm^3) was added to Na–Hg amalgam (0.12 g Na, 5.2 mmol, 40 g Hg) under benzene (20 cm^3) containing PMe_3 (0.75 cm^3 , 6.8 mmol) and the mixture was stirred for 3 h. The solution was filtered, the spent amalgam washed with benzene (2 \times 5 cm^3) and the volatiles removed from the combined filtrate and washings to give a blue solid. Crude yield 1.5 g (100%). The complex is essentially pure at this point. The analytical sample was obtained by dissolving the solid (0.8 g) in toluene and layering with light petroleum which gave the complex as small blue crystals (0.44 g). IR spectrum: 1425s, 1375s, 1365s, 1330s, 1320s, 1280s, 1260m, 1235w, 1175w, 1112w, 1060w, 935s, 850m, 805w, 765w, 725m, 710m, 670w, 345w, 275m and 230m cm^{-1} .

$[\text{WCl}_2(\text{NC}_6\text{H}_3\text{Pr}^1_2\text{-2,6})(\text{PhC}_2\text{Ph})(\text{PMe}_3)_2]$ **4**. A mixture of $[\text{WCl}_2(\text{NC}_6\text{H}_3\text{Pr}^1_2\text{-2,6})(\text{PMe}_3)_3]$ (0.8 g, 1.2 mmol) and diphenylacetylene (0.23 g 1.3 mmol) was refluxed in benzene (35 cm^3) for 3 h. The solution was filtered and the volatiles removed leaving a gum which was repeatedly extracted with light petroleum until the extracts were no longer coloured. The combined solutions were filtered and the volatiles removed leaving a gum which solidified on further pumping. Crude yield 0.28 g. The analytical sample was obtained by dissolving the solid in benzene (5 cm^3), reducing the volume and allowing to stand. Yield 0.46 g (49%). IR spectrum: 1760m, 1690m, 1460s, 1325s, 1282s, 1100m, 1075m, 1030m, 940s, 850w, 800w, 740m, 730m, 695m, 570w, 460w, 340w, 275m and 242m cm^{-1}

$[\text{WCl}_2(\text{NC}_6\text{H}_3\text{Pr}^1_2\text{-2,6})(\text{MeC}_2\text{Me})(\text{PMe}_3)_2]$ **5**. A solution of $[\{\text{WCl}_4(\text{NC}_6\text{H}_3\text{Pr}^1_2\text{-2,6})\}_2]$ (0.8 g, 0.8 mmol) and but-2-yne (0.2 cm^3 , 2.6 mmol) in benzene (50 cm^3) was added to Na–Hg amalgam (30 mg Na, 1.3 mmol; 25 g Hg) under benzene (10 cm^3) and the mixture was stirred vigorously for 2 h. The solution was filtered, the spent amalgam washed with benzene (2 \times 5 cm^3) and the volatiles removed from the combined filtrate and washings giving the complex as a yellow-brown crystalline solid. Crude yield 0.82 g (99%). Characterisation was made on the basis of ^1H and $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra (Table 6).

$[\text{WCl}_2(\text{NC}_6\text{H}_3\text{Pr}^1_2\text{-2,6})(\text{PhC}_2\text{H})(\text{PMe}_3)_2]$ **6**. A solution of $[\text{WCl}_2(\text{NC}_6\text{H}_3\text{Pr}^1_2\text{-2,6})(\text{PMe}_3)_3]$ (0.8 g, 1.2 mmol) and phenylacetylene (0.4 g, 3.92 mmol) in benzene (40 cm^3) was refluxed for 5 h. The solution was filtered and the solvent removed to give a yellow crystalline solid which was washed with cold light petroleum (5 cm^3). Crude yield 0.8 g. The solid was recrystallised from toluene. Yield 0.5 g (60%). IR spectrum: 1715m, 1595w, 1420s, 1355s, 1335s, 1305s, 1284s, 1255w, 1174, 1115w, 1100w, 935s, 852w, 812w, 765m, 735s, 705m, 684m, 560w, 532m, 512w, 462w, 350w, 275m and 240m cm^{-1} .

$[\text{WCl}_2(\text{NC}_6\text{H}_3\text{Pr}^1_2\text{-2,6})(\text{PhC}_2\text{Ph})(\text{PMe}_2\text{Ph})_2]$ **8**. A solution of $[\{\text{WCl}_4(\text{NC}_6\text{H}_3\text{Pr}^1_2\text{-2,6})\}_2]$ (1.3 g, 1.3 mmol) in benzene (30 cm^3) was added to Na–Hg amalgam (0.12 g Na, 5.2 mmol; 40 g Hg) under benzene (35 cm^3) containing PMe_2Ph (1.2 cm^3 , 8.4 mmol) and the mixture was stirred for 6 h. The solution was filtered and the volatiles removed to give a green gum which solidified on standing under light petroleum (10 cm^3). The solid (1.0 g) and diphenylacetylene (0.25 g) were refluxed in benzene (50 cm^3) for 4 h and the solution filtered and the volatiles removed. The resulting gum was left to stand under light petroleum for 3 d giving the complex as a green solid. Yield 0.82 g. Characterisation was carried out by ^1H and $^{13}\text{C}\{-^1\text{H}\}$ NMR spectroscopy.

$[\text{WCl}_3(\text{NC}_6\text{H}_3\text{Pr}^1_2\text{-2,6})(\text{PMePh}_2)_2]$ **9**. A solution of

Table 9 Crystallographic data

Complex	1	2	6
Formula	C ₁₈ H ₃₅ Cl ₃ NP ₂ W	C ₁₈ H ₃₅ Cl ₃ NOP ₂ W	C ₂₆ H ₄₁ Cl ₂ NP ₂ W
<i>M</i>	617.61	633.61	684.29
<i>T</i> /K	293	293	293
λ /Å	0.710 69	0.710 69	0.710 69
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>Pbca</i>
<i>a</i> /Å	11.332(2)	13.1534(12)	15.745(6)
<i>b</i> /Å	11.954(3)	13.0579(12)	19.951(2)
<i>c</i> /Å	19.214(3)	15.836(3)	18.764(3)
β /°		101.107(12)	
<i>U</i> /Å ³	2602.8(9)	2669.0(3)	5894(3)
<i>Z</i>	4	4	8
<i>D</i> _c /g cm ⁻³	1.576	1.577	1.542
<i>F</i> (000)	1220	1252	2736
μ /mm ⁻¹	4.87	4.75	4.22
Crystal size/mm	0.31 × 0.26 × 0.26	0.22 × 0.20 × 0.17	0.28 × 0.16 × 0.15
<i>A</i> _{min. max}	0.99, 0.79	1.00, 0.86	0.99, 0.91
θ /°	2–33	1–26	1–26
Measured reflections	4917	5419	4000
Independent reflections	4903	5220	4000
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	3896	3584	3170
No. of variables	206	343	304
Weights (<i>a</i> , <i>b</i>)	0.076, 0.00	0.021, 7.06	0.088, 35.8
Goodness-of-fit on <i>F</i> ²	1.008	1.028	1.057
<i>R</i> 1, <i>wR</i> 2 (obs. data)*	0.042, 0.059	0.036, 0.068	0.026, 0.058

* $w = 1/[\sigma^2(F^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$; $R1 = \Sigma|F_o - F_c|/\Sigma(F_o)$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

[{WCl₄(NC₆H₃Prⁱ₂-2,6)}₂] (0.9 g, 0.9 mmol) in benzene (40 cm³) was reduced with Na–Hg amalgam (41 mg Na, 1.8 mmol; 30 g Hg) under benzene (20 cm³) containing PMePh₂ (0.72 g, 3.6 mmol) as for complex **1**. Removal of the volatiles gave a gum which was dissolved in hot toluene (50 cm³) and filtered. Reduction of the volume gave the complex as brown crystals, 0.95 g (61%). $\mu_{\text{eff}} = 1.34 \mu_{\text{B}}$. IR spectrum: 1330s, 1310s, 1280s, 1230w, 1150w, 1080m, 1050m, 1022m, 995w, 905m, 890m, 840w, 805w, 750w, 730m, 680m, 485s, 440s, 302m (br), 265m and 248m cm⁻¹.

[WCl₂(NC₆H₃Prⁱ₂-2,6)(CH₂CH₂)(PMe₃)₂] **10**. A solution of [WCl₃(NC₆H₃Prⁱ₂-2,6)(PMe₃)₂] (0.8 g, 1.3 mmol) in benzene (60 cm³) was added to a pressure bottle containing Na–Hg amalgam (30 mg Na, 1.3 mmol; 30 g Hg) and the vessel was vented twice with ethylene gas. The mixture was stirred rapidly and ethylene gas added until a constant pressure of 16.5 kPa was obtained in the pressure bottle. The mixture was stirred for 2 h, filtered and the spent amalgam extracted with benzene (2 × 5 cm³). The volatiles were removed from the combined filtrate and extracts giving a yellow-brown crystalline solid. Crude yield: 0.7 g (89%). IR spectrum: 1595w, 1420s, 1365m, 1350w, 1325m, 1315m, 1285s, 1260w, 1234w, 1165m, 1115w, 1055w, 1040w, 945s, 850w, 805w, 765w, 740m, 680w, 540w, 470w, 350w, 302m and 260m cm⁻¹.

[WCl₂(NC₆H₃Prⁱ₂-2,6)(CH₂CHMe)(PMe₃)₂] **11**. A solution of [WCl₃(NC₆H₃Prⁱ₂-2,6)(PMe₃)₂] (1.2 g, 1.9 mmol) in benzene (70 cm³) was reduced with Na–Hg amalgam (50 mg Na, 2.2 mmol; 35 g Hg) under propene, as for the preparation of complex **10**. Work-up and recrystallisation from benzene gave the complex as yellow crystals which lost surface crystallinity on drying under vacuum. Yield 0.86 g (71%). IR spectrum: 1590w, 1410s, 1360m, 1330w, 1285s, 1250w, 1235w, 1175w, 1140m, 1060m, 1030m, 950s, 860m, 805m, 765m, 740m, 475w, 340w, 305m and 280m cm⁻¹.

Crystallography.—Crystal data for complexes **1**, **2** and **6** are given in Table 9, together with information on instrumentation, data collection and structure determination. Data collection on a Nonius CAD-4 diffractometer used graphite-monochromated Mo-K α radiation ($\lambda = 0.710 69 \text{ \AA}$) and ω -2 θ scans. Lorentz and polarization corrections were applied using locally written

programs and absorption corrections applied from empirical ψ scans.¹⁷ The structures were solved from Patterson and heavy-atom electron-density syntheses and refined by full-matrix least squares on *F*² using the program SHELXL 93.¹⁸ 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. The atomic coordinates are for the correct absolute structure as determined by calculations of the Flack *x* parameter.¹⁹

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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