# Evaluation of the 2,6-Diisopropylphenylimido Ligand as a Steric Force in d¹ and d² Monomeric Octahedral Complexes of Tungsten †

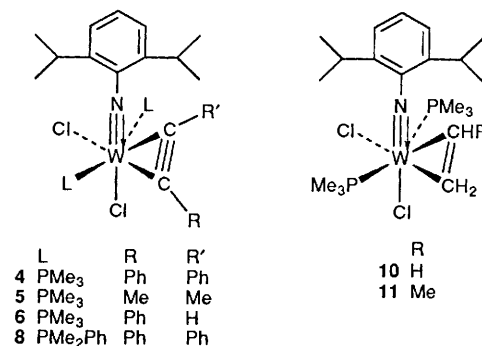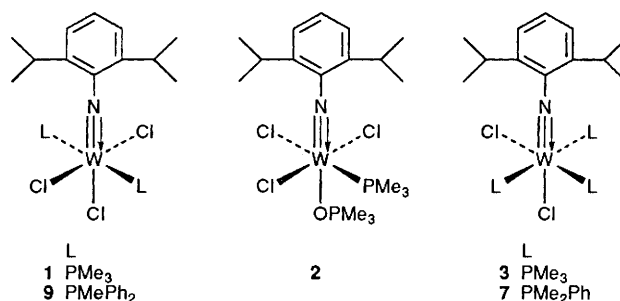George R. Clark, Alastair J. Nielson* and Clifton E. F. Rickard

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Reduction of [{WCl₄(NC₆H₃Pr$^i_2$-2,6)}₂] with 2 equivalents of Na–Hg amalgam in the presence of phosphines gave the d¹ complexes [WCl₃(NC₆H₃Pr$^i_2$-2,6)L₂] (L = PMe₃, PMe₂Ph or PMePh₂). The crystal structure of [WCl₃(NC₆H₃Pr$^i_2$-2,6)(PMe₃)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 [WCl₃(NC₆H₃Pr$^i_2$-2,6)(PMe₃)(OPMe₃)] 2 for which the crystal structure shows the OPMe₃ ligand lying *trans* to the imido ligand. Reduction of [{WCl₄(NC₆H₃Pr$^i_2$-2,6)}₂] with 4 equivalents of Na–Hg amalgam in the presence of phosphines gave the d² complexes [WCl₂(NC₆H₃Pr$^i_2$-2,6)L₃] (L = PMe₃ or PMe₂Ph). Complex [WCl₂(NC₆H₃Pr$^i_2$-2,6)(PMe₃)₃] 3 reacts with alkynes L′ to give the complexes [WCl₂(NC₆H₃Pr$^i_2$-2,6)L′(PMe₃)₂] (L′ = PhC₂Ph, MeC₂Me or PhC₂H) for which ¹H and ¹³C-{¹H} NMR spectral data were obtained. The crystal structure of [WCl₂(NC₆H₃Pr$^i_2$-2,6)(PhC₂H)(PMe₃)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 PhC₂H interaction. The complex [WCl₂(NC₆H₃Pr$^i_2$-2,6)(PhC₂Ph)(PMe₂Ph)₂] can be prepared but not [WCl₂(NC₆H₃Pr$^i_2$-2,6)(PhC₂Ph)(PMePh₂)₂]. Reduction of [WCl₃(NC₆H₃Pr$^i_2$-2,6)(PMe₃)₂] by Na–Hg amalgam in the presence of olefins gave the complexes [WCl₂(NC₆H₃Pr$^i_2$-2,6)L′(PMe₃)₂] (L′ = CH₂CH₂ or CH₂CHMe). 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 d¹ and d² 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 d¹ and d² 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 [{WCl₄(NC₆H₃Pr$^i_2$-2,6)}₂] was carried out in benzene using 2 equivalents of Na–Hg amalgam in the presence of 4 equivalents of PMe₃. This procedure led to a high yield of [WCl₃(NC₆H₃Pr$^i_2$-2,6)(PMe₃)₂] 1. The complex has a solid-state magnetic moment ($\mu_{eff}$ = 1.49 $\mu_B$) consistent with a d¹ configuration for this type of complex, and a far-IR spectrum (Table 1) similar to that obtained for [WCl₃(NPh)(PMe₃)₂][6] which has a *mer* arrangement of the three chloro ligands and *trans* phosphines. This geometry was confirmed in complex 1 by



| | L | R | R′ |
|---|---|---|---|
| 1 | PMe₃ | | |
| 9 | PMePh₂ | | |

| | 2 |
|---|---|

| | L | |
|---|---|---|
| 3 | PMe₃ | |
| 7 | PMe₂Ph | |

| | L | R | R′ |
|---|---|---|---|
| 4 | PMe₃ | Ph | Ph |
| 5 | PMe₃ | Me | Me |
| 6 | PMe₃ | Ph | H |
| 8 | PMe₂Ph | Ph | Ph |

| | R |
|---|---|
| 10 | H |
| 11 | Me |

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

**Table 1** Physical data

| | Colour | Analysis[a] (%) | | | IR/cm⁻¹ W–Cl |
| | | C | H | N | |
|---|---|---|---|---|---|
| **1** [WCl₃(NC₆H₃Pr^i₂-2,6)(PMe₃)₂] | Brown | 35.3 (35.0) | 5.9 (5.8) | 2.0 (2.3) | 295, 255, 242 |
| **3** [WCl₂(NC₆H₃Pr^i₂-2,6)(PMe₃)₃] | Purple | 38.3 (38.3) | 6.7 (6.7) | 2.0 (2.1) | 275, 230 |
| **4** [WCl₂(NC₆H₃Pr^i₂-2,6)(PhC₂Ph)(PMe₃)₂][b,c] | Yellow | 53.0 (52.6) | 6.1 (6.1) | 1.7 (1.8) | 275, 242 |
| **6** [WCl₂(NC₆H₃Pr^i₂-2,6)(PhC₂H)(PMePh₂)₂][c,d] | Yellow | 46.4 (46.5) | 6.1 (6.1) | 1.2 (2.0) | 275, 240 |
| **9** [WCl₃(NC₆H₃Pr^i₂-2,6)(PMePh₂)₂] | Brown | 52.7 (52.7) | 5.1 (5.0) | 1.3 (1.6) | 302 (br), 265, 248 |
| **10** [WCl₂(NC₆H₃Pr^i₂-2,6)(CH₂CH₂)(PMe₃)₂] | Yellow | 39.2 (39.4) | 6.0 (6.4) | 2.6 (2.3) | 302, 260 |
| **11** [WCl₂(NC₆H₃Pr^i₂-2,6)(CH₂CHMe)(PMe₃)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 ½C₆H₆. [c] Solvent supported by NMR spectra. [d] Calculated analytical data includes ⅐C₇H₈. [e] Calculated data include ⅚C₆H₆.
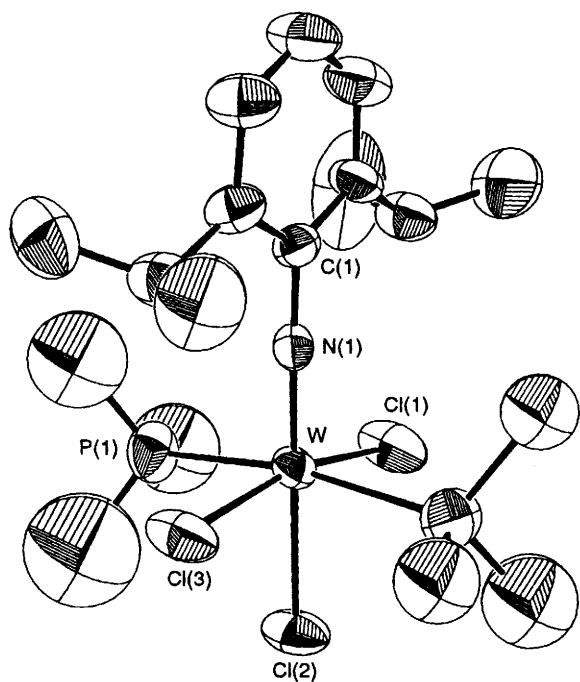


**Fig. 1** Molecular structure of complex **1**; atoms are depicted as 50% probability surfaces

[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(NC₆H₃Pr^i₂-2,6)(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(NC₆H₃Pr^i₂-2,6)(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 PMe₃ and OPMe₃ 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) |
| C(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 (°) 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 PMe₃ and OPMe₃ orientations is shown; atoms are represented as 50% probability surfaces
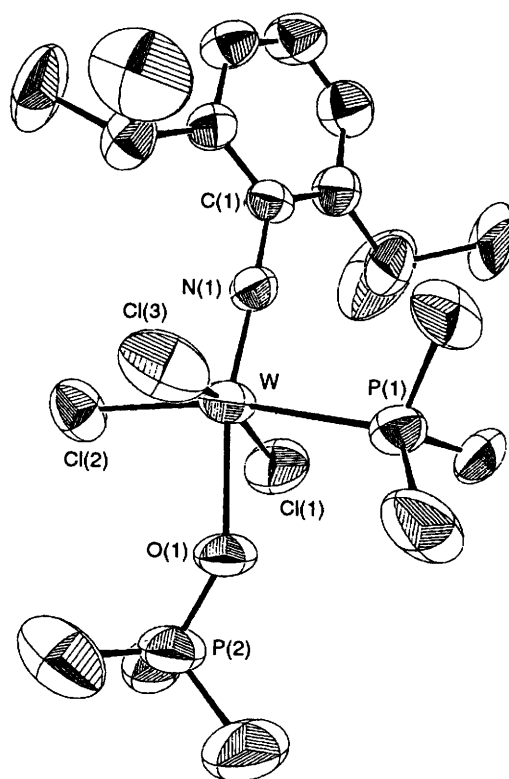
the PMe₃ and OPMe₃ groups could each be resolved into two separate molecules occupying the same co-ordination sites, with equal occupancy, but oriented slightly differently. The two sets of atoms are labelled with and without primes. The structure (Fig. 2) consists of a distorted octahedral array with three chloro ligands in the equatorial plane. The PMe₃ and OPMe₃ 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 PMe₃. 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)°] compared with complex **1** [N(1)–W–P(1) 95.0(2), N(1)–W–P(2) 95.5(2)°]. 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)°] 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)°.

The Me₃PO ligand orientates with its Me₃P 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)°] [P(2)–O(1')–W 144(1)°] is

larger than expected for electron donation from an oxygen sp² orbital (120°).

Reduction of [{WCl₄(NC₆H₃Pr$^i$₂-2,6)}₂] with 4 equivalents of Na–Hg amalgam in the presence of 6 equivalents of PMe₃, proceeded smoothly giving [WCl₂(NC₆H₃Pr$^i$₂-2,6)(PMe₃)₃] **3**. The complex has a *cis*-dichloro, *mer*-phosphine structure based on two W–Cl stretches in the far-IR spectrum [11] and a triplet and doublet for the PMe₃ ligands in the ¹H and ¹³C-{¹H} NMR spectra [12] (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<sup>a</sup>

| Complex | $^1$H$^b$ | $^{13}$C-$\{^1$H$\}^{b,c}$ |
|---|---|---|
| **3** | 1.18 [d, $^3J$(HH) 6.7, 12 H, CHMe$_2$], 1.62 [t, $^2J$(HP)$^d$ 3.5, 18 H, PMe$_3$], 1.77 [d, $^2J$(HP) 8.0, 9 H, PMe$_3$], 3.89 (spt, 2 H, CHMe$_2$), 6.99 [d, $^3J$(HH) 7.6, 2 H, m-H], 7.20 [t, $^3J$(HH) 7.6, 1 H, p-H] | 16.8 [t, $^1J$(CP) 13.5, PMe$_3$], 23.8 (Me), 26.0 (CH), 26.0 and 26.3 [d, $^1J$(CP) 29.3, PMe$_3$], 122.3 (m-C) 124.1 (p-C), 143.7 (o-C), 149.7 (ipso-C) |
| **4** | 0.95 and 1.18 [2d, $^3J$(HH) 6.6, 12 H, CHMe$_2$], 1.42 [t, $^2J$(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, $^1J$(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 (ipso-C$_{acet}$), 146.8 (ipso-C$_{imido}$), 147.9 (o-C$_{imido}$), 154.4 [t, $^2J$(CP) 12.3, C≡C] |
| **5** | 0.92 [d, $^3J$(HH) 6.8, CHMe$_2$], 1.16 [dd, $^3J$(HH) 6.8, CHMe$_2$], 1.75 [t, $^2J$(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, p-H), 7.05 (m, 2 H, m-H) | 14.8 [t, $^1J$(CP) 14.9, PMe$_3$], 16.9 (Me), 23.4 and 24.3 (CHMe$_2$) 26.3 and 26.4 (CHMe$_2$), 126.9 (m-C), 127.9 (p-C), 146.7 [t, $^2J$(CP) 12.9, C≡C], 147.9, 148.9 and 149.8 (ipso- and o-C$_{imido}$) |
| **6**$^e$ | 0.82 [d, $^3J$(HH) 6.6, 3 H, Me], 1.03 [d, $^3J$(HH) 6.7, 3 H, Me], 1.12 [d, $^3J$(HH) 6.7, 3 H, Me], 1.16 [d, $^3J$(HH) 6.6, 3 H, Me], 1.37 and 1.72 [2d, $^2J$(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, $^3J$(HH) 7.3, 1 H, p-H$_{acet}$], 7.31 [t, $^3J$(HH) 7.7, 2 H, m-H$_{acet}$], 7.70 [d, $^3J$(HH) 7.80, 2 H, o-H$_{acet}$] | 14.1 and 14.2 [2d, $^1J$(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, $^2J$(CP)$_{cis}$ 5.6, $^2J$(CP)$_{trans}$ 22.8, ≡CH], 143.3 [t, $^3J$(CP) 3.2, ipso-C$_{acet}$], 148.7 (o-C$_{imido}$) 149.3 (prt, ipso-C$_{imido}$), 149.8 (o-C$_{imido}$), 152.6 [dd, $^2J$(CP)$_{cis}$ 5.2, $^2J$(CP)$_{trans}$ 16.0, PhC≡] |
| **8** | 0.95 [obsc d, $^3J$(HH) 6.8, 12 H, CHMe$_2$], 1.65 and 1.78 [2t, $^2J$(HP)$^d$ 3.2, 12 H, PMe$_2$], 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, $^1J$(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, $J$(CP) 4.5], 128.0, 128.1, 129.2, 131.2 [t, $J$(CP) 4.4] and 131.3 (aromatic CH), 134.8 [t, $^1J$(CP) 21.6, ipso-C of PMe$_2$Ph], 142.3 (ipso-C$_{acet}$), 149.6, 150.2 and 150.3 (ipso- and o-C$_{imido}$), 154.8 [t, $^2J$(CP) 12.1, C≡C] |
| **10** | 1.12 [d, $^3J$(HH) 6.7, 12 H, CHMe$_2$], 1.12 (obsc, 2 H, CH$_2$), 1.69 [t, $^2J$(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, $^3J$(HH) 7.5, 2 H, m-H], 7.07 [t, $^3J$(HH) 7.5, 1 H, p-H] | 13.7 [t, $^1J$(CP) 15, PMe$_3$], 24.4 (Me$_2$), 26.4 (CH), 39.7 [t, $^2J$(CP) 3.6, CH$_2$CH$_2$], 123.4 (m-C), 126.5 (p-C), 148.5 (o-C), 149.3 (ipso-C) |
| **11**$^f$ | 1.05–1.24 (m, 12 H, CHMe$_2$), 1.65 and 1.74 [2d, $^3J$(HH) 9.2, 9 H, PMe$_3$], 2.22 [d, $^3J$(HH) 5.8, Me], 2.35 (m), 2.47 [d, $^3J$(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, $^1J$(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, $^2J$(CP) 8.2, CH$_2$], 47.8 [d, $^2J$(CP) 4.5, CH$_2$], 48.9 [d, $^2J$(CP) 7.7, CH], 51.5 [d, $^2J$(CP) 6.3, CH], 123.5 and 123.8 (m-C), 126.5 and 126.6 (p-C) 128.3 (benzene), 148.2 and 148.4 (br, o-C) 149.2 (br, ipso-C) |

<sup>a</sup> Spectra obtained in CDCl$_3$ solution. <sup>b</sup> br = Broad, spt = septet, d = doublet, dd = doublet of doublets, m = multiplet, obsc = obscured, prt = poorly resolved triplet, s = singlet, t = triplet. <sup>c</sup> 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. <sup>d</sup> For virtual HP spin coupling $^2J$(HP) quoted as $\frac{1}{2}$ [$^2J$(HP) + $^6J$(HP′)] where $^6J$(HP′) is very small. <sup>e</sup> $^{31}$P-$\{^1$H$\}$ 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]. <sup>f</sup> $^{31}$P-$\{^1$H$\}$ 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].

$^{13}$C-$\{^1$H$\}$ NMR spectrum shows one methyl resonance and one isopropyl carbon resonance.

Complex 3 reacts readily with diphenylacetylene under reflux in toluene to give [WCl$_2$(NC$_6$H$_3$Pr$^i_2$-2,6)(PhC$_2$Ph)(PMe$_3$)$_2$] 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 PMe$_3$ ligands in the $^1$H and $^{13}$C-$\{^1$H$\}$ 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 $^1$H NMR spectrum and two sets of resonances in the $^{13}$C-$\{^1$H$\}$ NMR spectrum for each of the appropriate carbons.

Complex 5 [WCl$_2$(NC$_6$H$_3$Pr$^i_2$-2,6)(MeC$_2$Me)(PMe$_3$)$_2$] was prepared by reduction of [WCl$_3$(NC$_3$H$_6$Pr$^i_2$-2,6)(PMe$_3$)$_2$] 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 [WCl$_2$(NC$_6$H$_3$Pr$^i_2$-2,6)(PhC$_2$H)(PMe$_3$)$_2$] 6 which has a cis-chloro, trans-phosphine geometry based on IR and NMR spectra. Co-ordination of PhC$_2$H leads to asymmetry in the molecule which is reflected in the NMR spectra of the phosphine ligands. The $^1$H and $^{13}$C-$\{^1$H$\}$ NMR spectra each show the PMe$_3$ ligands as a pair of doublets and in the $^{31}$P-$\{^1$H$\}$ 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 $^1$H 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 PhC$_2$H ligand. Similarly, in the $^{13}$C-$\{^1$H$\}$ 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 [WCl$_2$(NPh)(PhC$_2$Ph)(PMe$_3$)$_2$][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 $^{31}$P-$\{^1$H$\}$ NMR spectrum by the difference in
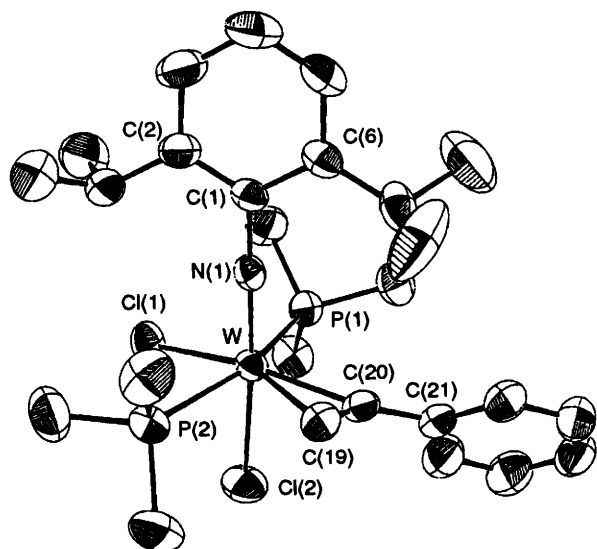
**Fig. 3** Molecular structure of complex **6**; atoms are depicted as 50% probability surfaces

**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) |

**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) | | |
| N(1)–W–Cl(1) | 94.6(1) | C(9)–C(14)–W | 71.5(4) |
| N(1)–W–Cl(2) | 174.4(1) | C(20)–C(19)–W | 74.8(4) |
| N(1)–W–P(1) | 87.8(1) | C(21)–C(20)–C(19) | 139.8(5) |

magnitude of the two $^1J$(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 [WCl$_2$(NPh)(PhC$_2$Ph)(PMe$_3$)$_2$] [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

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 [WCl$_2$(NPh)(PhC$_2$Ph)(PMe$_3$)$_2$]. 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 $^1$H and $^{13}$C-$\{^1$H$\}$ NMR spectra show.

We have attempted to form diphenylacetylene complexes similar to complex **3** which contain more sterically hindering phosphine ligands. The complex [{WCl$_4$(NC$_6$H$_3$Pr$^i_2$-2,6)}$_2$] was reduced with Na–Hg amalgam in the presence of PMe$_2$Ph to give a green solid expected to be [WCl$_2$(NC$_6$H$_3$Pr$^i_2$-2,6)(PMe$_2$Ph)$_3$] **7**. This complex was not characterised but reacted directly with PhC$_2$Ph in benzene under reflux to give [WCl$_2$(NC$_6$H$_3$Pr$^i_2$-2,6)(PhC$_2$Ph)(PMe$_2$Ph)$_2$] **8**. Characterised by NMR spectroscopy, the complex showed two triplets in the $^1$H and $^{13}$C-$\{^1$H$\}$ NMR spectra characteristic of trans PMe$_2$Ph ligands. In the $^1$H 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 $^{13}$C-$\{^1$H$\}$ 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 δ154.8.

When a one-electron reduction per metal of [{WCl$_4$(NC$_6$H$_3$Pr$^i_2$-2,6)}$_2$] was carried out in the presence of PMePh$_2$, [WCl$_3$(NC$_6$H$_3$Pr$^i_2$-2,6)(PMePh$_2$)$_2$] **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 PMePh$_2$ or PhC$_2$Ph. The complex [{WCl$_4$(NC$_6$H$_3$Pr$^i_2$-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 d$^2$ 2,6-diisopropylphenylimido complexes containing olefin ligands. Sodium–mercury amalgam reduction of [WCl$_3$(NC$_6$H$_3$Pr$^i_2$-2,6)(PMe$_3$)$_2$] **1** under ethylene gave rise to [WCl$_2$(NC$_6$H$_3$Pr$^i_2$-2,6)(CH$_2$-CH$_2$)(PMe$_3$)$_2$] **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 $^1$H and $^{13}$C-$\{^1$H$\}$ NMR spectrum for the PMe$_3$ 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 $^1$H NMR spectrum and there is only one isopropyl methyl group resonance. In the

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

Reduction of [WCl$_3$(NC$_6$H$_3$Pr$^i_2$-2,6)(PMe$_3$)$_2$] with Na–Hg amalgam under propene gave some [WCl$_2$(NC$_6$H$_3$Pr$^i_2$-2,6)(PMe$_3$)$_3$] **3** but mainly [WCl$_2$(NC$_6$H$_3$Pr$^i_2$-2,6)(CH$_2$CH-Me)(PMe$_3$)] **11**. The olefin complex has two isomeric forms in the approximate ratio of 2:1. The $^1$H NMR spectrum contains several overlapping resonances making analysis difficult, but in the $^{13}$C-$\{^1$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 $^{31}$P-$\{^1$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 $^{13}$C-$\{^1$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 $^{31}$P-$\{^1$H$\}$ NMR spectrum shows an AB quartet consistent with *trans*-phosphine [$^2J$(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 plane[10] and both the phenyl ring and isopropyl groups of the organomido 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 $^1$H and $^{13}$C-$\{^1$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 [$\{$WCl$_4$(NC$_6$H$_3$Pr$^i_2$-2,6)$\}_2$] was prepared from [$\{$WCl$_4$O$\}_x$] and 2,6-diisopropylphenyl isocynate in octane.[1] Trimethylphosphine was prepared by reaction of MgMeI with P(OPh)$_3$ in di-*n*-butyl ether[16] and PMe$_2$Ph and PMePh$_2$ by reaction of MgMeI on PCl$_2$Ph and PClPh$_2$. Light petroleum had a b.p. range of 40–60 °C.

*Syntheses.*—[WCl$_3$(NC$_6$H$_3$Pr$^i_2$-2,6)(PMe$_3$)$_2$] **1**. A solution of [$\{$WCl$_4$(NC$_6$H$_3$Pr$^i_2$-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 × 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%). $\mu_{eff} = 1.49$ $\mu_B$. 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$^{-1}$.

[WCl$_3$(NC$_6$H$_3$Pr$^i_2$-2,6)(PMe$_3$)(OPMe$_3$)] **2**. The complex [WCl$_3$(NC$_6$H$_3$Pr$^i_2$-2,6)(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 [WCl$_3$(NC$_6$H$_3$Pr$^i_2$-2,6)(PMe$_3$)$_2$] were formed along with a small quantity of green–brown crystals one of which was characterised by X-ray crystallography.

[WCl$_2$(NC$_6$H$_3$Pr$^i_2$-2,6)(PMe$_3$)$_3$] **3**. A solution of [$\{$WCl$_4$(NC$_6$H$_3$Pr$^i_2$-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 × 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$^{-1}$.

[WCl$_2$(NC$_6$H$_3$Pr$^i_2$-2,6)(PhC$_2$Ph)(PMe$_3$)$_2$] **4**. A mixture of [WCl$_2$(NC$_6$H$_3$Pr$^i_2$-2,6)(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$^{-1}$.

[WCl$_2$(NC$_6$H$_3$Pr$^i_2$-2,6)(MeC$_2$Me)(PMe$_3$)$_2$] **5**. A solution of [$\{$WCl$_4$(NC$_6$H$_3$Pr$^i_2$-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 × 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 $^1$H and $^{13}$C-$\{^1$H$\}$ NMR spectra (Table 6).

[WCl$_2$(NC$_6$H$_3$Pr$^i_2$-2,6)(PhC$_2$H)(PMe$_3$)$_2$] **6**. A solution of [WCl$_2$(NC$_6$H$_3$Pr$^i_2$-2,6)(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$^{-1}$.

[WCl$_2$(NC$_6$H$_3$Pr$^i_2$-2,6)(PhC$_2$Ph)(PMe$_2$Ph)$_2$] **8**. A solution of [$\{$WCl$_4$(NC$_6$H$_3$Pr$^i_2$-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$_2$Ph (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 $^1$H and $^{13}$C-$\{^1$H$\}$ NMR spectroscopy.

[WCl$_3$(NC$_6$H$_3$Pr$^i_2$-2,6)(PMePh$_2$)$_2$] **9**. A solution of

**Table 9** Crystallographic data

| Complex | 1 | 2 | 6 |
|---|---|---|---|
| Formula | $C_{18}H_{35}Cl_3NP_2W$ | $C_{18}H_{35}Cl_3NOP_2W$ | $C_{26}H_{41}Cl_2NP_2W$ |
| $M$ | 617.61 | 633.61 | 684.29 |
| $T/K$ | 293 | 293 | 293 |
| $\lambda/\text{Å}$ | 0.710 69 | 0.710 69 | 0.710 69 |
| Crystal system | Orthorhombic | Monoclinic | Orthorhombic |
| Space group | $P2_12_12_1$ | $P2_1/c$ | $Pbca$ |
| $a/\text{Å}$ | 11.332(2) | 13.1534(12) | 15.745(6) |
| $b/\text{Å}$ | 11.954(3) | 13.0579(12) | 19.951(2) |
| $c/\text{Å}$ | 19.214(3) | 15.836(3) | 18.764(3) |
| $\beta/°$ | | 101.107(12) | |
| $U/\text{Å}^3$ | 2602.8(9) | 2669.0(3) | 5894(3) |
| $Z$ | 4 | 4 | 8 |
| $D_c/\text{g cm}^{-3}$ | 1.576 | 1.577 | 1.542 |
| $F(000)$ | 1220 | 1252 | 2736 |
| $\mu/\text{mm}^{-1}$ | 4.87 | 4.75 | 4.22 |
| Crystal size/mm | $0.31 \times 0.26 \times 0.26$ | $0.22 \times 0.20 \times 0.17$ | $0.28 \times 0.16 \times 0.15$ |
| $A_{\text{min, max}}$ | 0.99, 0.79 | 1.00, 0.86 | 0.99, 0.91 |
| $\theta/°$ | 2–33 | 1–26 | 1–26 |
| Measured reflections | 4917 | 5419 | 4000 |
| Independent reflections | 4903 | 5220 | 4000 |
| Observed reflections $[I > 2\sigma(I)]$ | 3896 | 3584 | 3170 |
| No. of variables | 206 | 343 | 304 |
| Weights $(a,b)$ | 0.076, 0.00 | 0.021, 7.06 | 0.088, 35.8 |
| Goodness-of-fit on $F^2$ | 1.008 | 1.028 | 1.057 |
| $R1$, $wR2$ (obs. data)* | 0.042, 0.059 | 0.036, 0.068 | 0.026, 0.058 |

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

[{WCl$_4$(NC$_6$H$_3$Pr$^i_2$-2,6)}$_2$] (0.9 g, 0.9 mmol) in benzene (40 cm$^3$) was reduced with Na–Hg amalgam (41 mg Na, 1.8 mmol; 30 g Hg) under benzene (20 cm$^3$) containing PMePh$_2$ (0.72 g, 3.6 mmol) as for complex **1**. Removal of the volatiles gave a gum which was dissolved in hot toluene (50 cm$^3$) and filtered. Reduction of the volume gave the complex as brown crystals, 0.95 g (61%). $\mu_{\text{eff}} = 1.34$ $\mu_B$. 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$^{-1}$.

[WCl$_2$(NC$_6$H$_3$Pr$^i_2$-2,6)(CH$_2$CH$_2$)(PMe$_3$)$_2$] **10**. A solution of [WCl$_3$(NC$_6$H$_3$Pr$^i_2$-2,6)(PMe$_3$)$_2$] (0.8 g, 1.3 mmol) in benzene (60 cm$^3$) 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 cm$^3$). 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$^{-1}$.

[WCl$_2$(NC$_6$H$_3$Pr$^i_2$-2,6)(CH$_2$CHMe)(PMe$_3$)$_2$] **11**. A solution of [WCl$_3$(NC$_6$H$_3$Pr$^i_2$-2,6)(PMe$_3$)$_2$] (1.2 g, 1.9 mmol) in benzene (70 cm$^3$) 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$\alpha$ radiation ($\lambda = 0.710\ 69$ Å) and $\omega$–2$\theta$ scans. Lorentz and polarization 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 $F^2$ 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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