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Disruption of the π-perpendicular component of a 4-electron donor alkyne ligand in a high-valent complex of tungsten by introduction of an organoimido ligand

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Addition of $Me_3SiNHCMe_3$ to the 4-electron donor alkyne complex $[\{WCl_4(PhC_2Ph)\}_2]$ gave $[\{WCl_2(NCMe_3)(PhC_2Ph)(NH_2CMe_3)\}_x]$ **1** for which the acetylenic carbon resonance position, δ 156.23, in the ^{13}C-$\{^1H\}$ NMR spectrum indicated a 2-electron donor alkyne. Small changes in δ for derivatives $[NEt_4][WCl_3(NCMe_3)(PhC_2Ph)(NH_2CMe_3)]$ **2** (161.28), *trans*-dichloro complexes $[WCl_2(NCMe_3)(PhC_2Ph)(bipy)]$ **3** (bipy = 2,2′-bipyridyl, δ 163.60) and $[WCl_2(NCMe_3)(PhC_2Ph)(dmbipy)]$ **4** (dmbipy = 4, 4′-dimethyl-2,2′-bipyridyl, δ 162.93) as well as *cis*-dichloro complexes $[WCl_2(NCMe_3)(PhC_2Ph)(py)_2]$ **5** (py = pyridine, δ 155.78), $[WCl_2(NCMe_3)(PhC_2Ph)(PMe_3)_2]$ **6** (δ 151.15) and $[WCl_2(NCMe_3)(PhC_2Ph)(PMe_2Ph)_2]$ **7** (δ 153.37) indicate small electronic differences in the alkyne–metal bonding. A crystal structure determination of **6** showed *trans*-phosphines, *cis*-chloro ligands and a *cis* arrangement of a 4-electron donor imido ligand [W–N 1.763(6) Å] and a 2-electron donor alkyne [W–C 2.131(6) and 2.111(7) Å]. The compound $Me_3SiNHCHMe_2$ added to $[\{WCl_4(PhC_2Ph)\}_2]$ followed by dmbipy gave $[WCl_2(NCHMe_2)(PhC_2Ph)(dmbipy)]$ **8** (δ 163.16), $Me_3SiNHCH_2Me$ and dmbipy formed *cis*- and *trans*-dichloro complexes $[WCl_2(NCH_2Me)(PhC_2Ph)(dmbipy)]$ **9** (δ 152.76 and 159.03) and **10** (δ 163.31) respectively. A crystal structure of determination **10** showed W–C bond lengths [2.085(8) Å] somewhat shorter than in **6**, consistent with the increase in alkyne $\pi_\perp$ donation for **10** indicated by δ. The compound $Me_3SiNHC_6H_3Pr^i_2$-2,6 and $[\{WCl_4(PhC_2Ph)\}_2]$ gave $[\{WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PhC_2Ph)(NH_2C_6H_3Pr^i_2\text{-}2,6)\}_x]$ **11** (δ 166.51) which with dmbipy gave *cis*-dichloro $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PhC_2Ph)(dmbipy)]$ **12** (δ 167.50). Other complexes prepared were $[WCl_2(NC_6H_3Me_2\text{-}2,6)(PhC_2Ph)(dmbipy)]$ **13** (δ 167.26), $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PhC_2Ph)(py)_2]$ **14** (δ 158.78) and $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PhC_2Ph)(PMe_3)_2]$ **15** (δ 154.40). The compound $Me_3SiNHC_6H_3Pr^i_2$ −2,6 and $[NEt_4][WCl_5(PhC_2Ph)]$ gave $[NEt_4][WCl_4(NHC_6H_3Pr^i_2\text{-}2,6)(PhC_2Ph)]$ **16** where δ (167.40) indicates an amido ligand allows conversion of the alkyne into a 2-electron donor.

We have reported that the complex $[\{WCl_4(PhC_2Ph)\}_2]$, which contains 4-electron donor alkyne ligands, may be regarded as a d^0 complex of tungsten as it exhibits chemistry similar to that of d^0 organoimido tungsten complexes.[1–3] This work arose from previous suggestions that alkynes could stabilise high oxidation states,[4] a concept which now has more acceptance.[5] We have also shown that a 2-electron donor alkyne is present in complexes of the type $[WCl_2(NR)(R'C_2R'')(PR_3)_2]$ (R = Ph or $CHMe_2$; R′, R″ = Ph or H; PR_3 = PMe_3 or PMe_2Ph) where there is a d^2 electron configuration.[6] An alkyne ligand can be regarded as a 2-electron donor if donation to the metal is from the $\pi\|$ (acetylene π-parallel) frontier orbital only, and a 4-electron donor if there is also donation from the $\pi_\perp$ (acetylene π-perpendicular) frontier orbital.[7] These two electronic types can be distinguished on the basis of the acetylenic carbon resonance position in ^{13}C-$\{^1H\}$ NMR spectra {for example δ 270.7 for $[NEt_4][WCl_5(PhC_2Ph)]$,[1] δ 155.77 for $[WCl_2(NPh)(PhC_2Ph)(PMe_3)_2]$[6]}. In view of the reaction between $[\{WCl_4(NPh)\}_2]$ and the silylamines Me_3SiNHR (R = Ph, C_6H_4Me-4, CMe_3, $CHMe_2$ or CH_2Me) which provides the means of introducing a second imido function,[8] it was of interest to establish if an imido ligand could be added to $[\{WCl_4(PhC_2Ph)\}_2]$ in a similar manner. We report here the results of these studies using ^{13}C-$\{^1H\}$ NMR spectroscopy in particular to probe the C≡C electronic environment. A preliminary account of some of this work has appeared.[9]

Results and discussion

Addition of $Me_3SiNHCMe_3$ to a suspension of $[\{WCl_4(PhC_2Ph)\}_2]$ in benzene gives rise to a red-brown solution which pales after several hours giving the colourless complex **1**, eqn. (1). After isolation the complex is not particularly soluble in benzene and decomposes slowly in chlorinated hydrocarbons. A ^{13}C-$\{^1H\}$ NMR spectrum accumulated rapidly in $CDCl_3$ showed quaternary carbon resonances in the vicinity of δ 70 and δ 54 which are characteristic of *tert*-butylimido and -butylamine ligands respectively which shows the complex is not the alternative bis-*tert*-butylamido complex $[\{WCl_2(NHCMe_3)_2(PhC_2Ph)\}_x]$. The IR spectrum shows a W–Cl stretch at 305 cm^{-1} and there is a weaker peak at 208 cm^{-1} (Table 1) which coupled with the insolubility of the complex suggests a chloro-bridged dimer or polymeric species. The ^{13}C-$\{^1H\}$ NMR spectrum shows the acetylenic carbon resonance at δ 156.23 and in the IR spectrum ν(C≡C) occurs at 1762 cm^{-1}. These features are similar to those found for the d^2 tungsten complex $[WCl_2(NPh)(PhC_2Ph)(PMe_3)_2]$ and compare with values of δ 244–283 and ν(C=C) 1590–1638 cm^{-1} found for complexes of the type

$$[\{WCl_4(PhC_2Ph)\}_2] + 4Me_3SiNHCMe_3 \longrightarrow \underset{\mathbf{1}}{[\{WCl_2(NCMe_3)(PhC_2Ph)(NH_2CMe_3)\}_x]} + 4Me_3SiCl \quad (1)$$

Table 1 Physical data

Complex	Colour	Analysis[a] (%)			IR (cm^{-1})	
		C	H	N	ν(C≡C)	ν(W–Cl)
1 $[WCl_2(NCMe_3)(PhC_2Ph)(NH_2CMe_3)]$ [b,c]	Colourless	47.2 (46.8)	5.8 (5.3)	5.2 (4.8)	1762	305, 208
3 $[WCl_2(NCMe_3)(PhC_2Ph)(bipy)]$ [c,d]	Yellow	53.3 (53.2)	4.9 (4.3)	6.3 (6.0)	1740	298
6 $[WCl_2(NCMe_3)(PhC_2Ph)(PMe_3)_2]$ [c,e]	Colourless	44.5 (44.4)	5.3 (5.7)	2.0 (2.1)	1770	265, 215
7 $[WCl_2(NCMe_3)(PhC_2Ph)(PMe_2Ph)_2]$	Colourless	52.0 (52.3)	5.4 (5.3)	1.9 (1.8)	1755	265, 235
8 $[WCl_2(NCHMe_2)(PhC_2Ph)(dmbipy)]$	Yellow	51.7 (51.7)	4.6 (4.3)	6.3 (6.2)	1765	295
9 *cis*-$[WCl_2(NCH_2Me)(PhC_2Ph)(dmbipy)]$	Yellow	49.6 (50.9)	4.8 (4.1)	6.9 (6.4)	1785	305, 212
10 *trans*-$[WCl_2(NCH_2Me)(PhC_2Ph)(dmbipy)]$ [c,f]	Yellow	55.1 (55.3)	4.7 (4.5)	5.7 (5.7)	1770	300
11 $[WCl_2(NC_6Pr^i_2\text{-}2,6)(PhC_2Ph)(NH_2C_6H_3Pr^i_2\text{-}2,6)]$	Orange	57.0 (58.1)	5.9 (5.9)	3.3 (3.6)	[g]	[g]
12 $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PhC_2Ph)(dmbipy)]$	Yellow	56.7 (57.6)	5.0 (4.9)	5.1 (5.3)	1790	300
16 $[NEt_4][WCl_4(NHC_6H_3Pr^i_2\text{-}2,6)(PhC_2Ph)]$ [c,h]	Colourless	49.4 (49.2)	6.0 (5.8)	3.3 (3.3)	1765	[g]

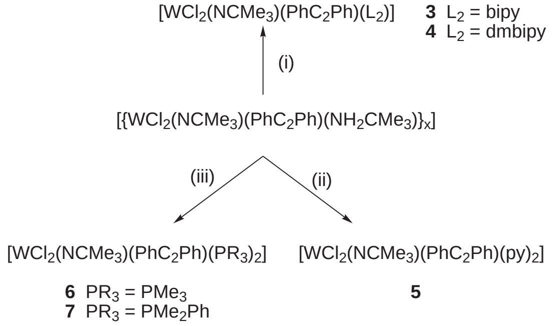
[a] Calculated values given in parentheses. [b] Calculated analytical data include $\frac{1}{6}C_6H_6$. [c] Solvent supported by NMR spectra. [d] Calculated analytical data include $0.5C_6JH_6$. [e] Calculated analytical data include $\frac{1}{12}C_6H_6$. [f] Calculated analytical data include C_6H_6. [g] Complex did not mull well in Nujol giving poorly resolved spectrum. [h] Calculated analytical data include $\frac{1}{3}CH_2Cl_2$.

$[\{WCl_4(RC_2R)\}_2]$[10] which are regarded as d^0 systems. Thus addition of the strongly π-donating imido ligand appears to convert the alkyne ligand from a 4- into a 2-electron donor.

To obtain further information on this process, the reaction between $Me_3SiNHCMe_3$ and $[\{WCl_4(PhC_2Ph)\}_2]$ was carried out in an NMR tube in $CDCl_3$ and the acetylenic carbon position monitored by $^{13}C\text{-}\{^1H\}$ NMR spectroscopy. A 10 min accumulation after mixing showed a spectrum consistent with the formation of $[WCl_4(PhC_2Ph)(Me_3SiNHCMe_3)]$ **A** as indicated by a shift in the silylamine CMe_3 group quaternary carbon compared with that of the free amine. The acetylenic carbon resonance appeared at δ 254.43 consistent with a 4-electron donor alkyne ligand. After a further 15 min accumulation the characteristics of **A** had disappeared but new features were present attributable to an amido species **B** (CMe_3 group quaternary carbon δ 56.20,[11] acetylenic carbon resonance δ 188) and an imido species **C** (CMe_3 group quaternary carbon δ 71.74,[11] acetylenic carbon resonances δ 161.62 and 161.77). After 50 min from mixing a 10 min accumulation showed essentially only **C** was present. The spectra thus show transformation of the diphenylacetylene ligand from a 4-electron donor in **A** to a 2-electron donor in **C**. This apparently occurs as the imido group is the stronger π donor and competes more successfully for the available tungsten d orbitals. Species **B** is of interest as the acetylenic carbon resonance at δ 188 may represent an intermediate competitive situation. A crystal structure determination of the molybdenum complex $[Mo(NC_6H_4Me\text{-}4)(MeO_2CC_2CO_2Me)(S_2CNEt_2)_2]$[12] suggests that the alkyne donates π-electron density to the molybdenum atom in competition with the imido ligand but $^{13}C\text{-}\{^1H\}$ NMR data are not available for this compound. However for $[\{WCl_2(PhC_2Ph)(MeOCH_2CH_2OMe)\}_2(\mu\text{-}N_2)]$,[13] where the crystal structure shows similar features, the acetylenic carbon resonance occurs at δ 184.4. In comparison, the complex $[WCl_2(PhC_2Ph)_2(PMe_3)_2]$[14] containing two alkyne ligands donating to the same metal orbital shows the resonance for the acetylenic carbons at δ 185.5.

A complex that is more stable after isolation than complex **1** can be formed if $[Et_4N]Cl$ in CH_2Cl_2 is added to the reaction mixture after the solution has lightened in colour. In this case the characteristics of an imido complex with a 2-electron donor diphenylacetylene ligand are present (CMe_3 quaternary carbon δ 69.7,[11] acetylenic carbon δ 150.89). This complex can also be formed if two equivalents of $Me_3SiNHCMe_3$ are added to $[NEt_4][WCl_5(PhC_2Ph)]$[2] generated in CH_2Cl_2. However we have not been able to obtain an analytically pure sample of this complex or grow crystals suitable for X-ray crystallography. The NMR spectra suggest the complex is $[NEt_4][WCl_3(NCMe_3)(PhC_2Ph)(NH_2CMe_3]$ **2**. The ^1H NMR spectrum shows a 1 : 1 : 1 ratio of diphenylacetylene, *tert*-butylimido and -butylamine ligands with the NH_2 protons at δ 3.96 while in the $^{13}C\text{-}\{^1H\}$ NMR spectrum the *tert*-butylimido and -butylamine ligand quaternary carbons appear at δ 69.84 and 52.46 respectively and the acetylenic carbons at δ 161.28.

Derivatives of complex **1** can be prepared with nitrogen donor ligands (Scheme 1). Refluxing the light coloured solution obtained after treating $Me_3SiNHCMe_3$ and $[\{WCl_4(PhC_2Ph)\}_2]$ with 2,2′-bipyridyl (bipy) gave $[WCl_2(NCMe_3)(PhC_2Ph)(bipy)]$ **3**. The $^{13}C\text{-}\{^1H\}$ NMR spectrum showed a single resonance for the *tert*-butyl methyl groups and resonances in the aromatic region which at 400 MHz were separated sufficiently to allow first-order analysis. For the diphenylacetylene ligand the *ortho* protons appear as a doublet (δ 7.83) and the *meta* and *para* protons as triplets (δ 7.44 and 7.25 respectively) indicating that the two phenyl groups are symmetrical. However there are 8 separate resonances for the bipy ligand indicating asymmetry for this part of the complex. The two C^6 protons (for the bipy numbering scheme see Table 2) appear at greater separation (δ 9.41 and 8.27) than the other proton pairs indicative of different environments. Similarly, the $^{13}C\text{-}\{^1H\}$ NMR spectrum



Scheme 1 (i) bipy or dmbipy in benzene, reflux 2–4 h; (ii) neat pyridine, stir 3 h; (iii) neat PMe_3, stir 3 h; neat PMe_2Ph, reflux 2 h.

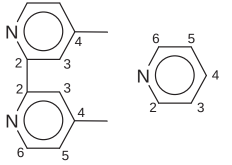
Table 2 NMR Spectroscopic data (δ, J/Hz)[a]

Complex	^{1}H[b]	^{13}C-{^{1}H}[b,c]
2	0.99[t, ^3J(HH) 6.9, 12 H, Me]; 1.15 (s, 9 H, CMe$_3$); 1.58 (br, 9 H, CMe$_3$); 2.92 [q, ^3J(HH) 7.1, 8 H, CH$_2$], 3.96 (br, 2 H, NH$_2$); 7.11 [t, ^3J(HH) 7.3, 2 H, *p*-H, PhC$_2$Ph]; 7.31, [t, ^3J(HH) 7.6, 4 H, *m*-H, PhC$_2$Ph]; 7.71 [d, ^3J(HH) 7.5, 4 H, *o*-H, PhC$_2$Ph]	7.63 (Me, NEt$_4$); 29.44 (Me, NCMe$_3$); 31.33 (br, Me, NH$_2$CMe$_3$); 52.15 (CH$_2$); 52.46 (br, C, NH$_2$CMe$_3$); 69.84 (C, NCMe$_3$); 125.78 (*p*-C, PhC$_2$Ph); 127.25 (*m*-C, PhC$_2$Ph); 130.46 (*o*-C, PhC$_2$Ph); 142.30 (*ipso*-C, PhC$_2$Ph); 161.28 (C≡C)
3	1.32 (2, 9 H, Me); 7.21 (prt, 1 H, H^5, bipy); 7.25 [t, ^3J(HH) 7.4, 2 H, *p*-H, PhC$_2$Ph]; 7.28 (s, benzene); 7.44 [t, ^3J(HH) 7.7, 4 H, *m*-H, PhC$_2$Ph]; 7.65 [t, ^3J(HH) 6.5, 1 H, H^5, bipy]; 7.76 [t, ^3J(HH) 7.9, ^4J(HH), 1.4, 1 H, H^4, bipy]; 7.83 [d, ^3J(HH) 8.2, ^4J(HH) 1.2, 4 H, *o*-H, PhC$_2$Ph]; 7.93 [d, ^3J(HH) 8.1, 1 H, H^3, bipy], 8.00 [t, ^3J(HH) 7.8, ^4J(HH) 1.5, 1 H, H^4, bipy]; 8.08 [d, ^3J(HH) 8.0, 1 H, H^3, bipy]; 8.27 [d, ^3J(HH) 4.5, 1 H, H^6, bipy]; 9.41 [d, ^3J(HH) 5.2, 1 H, H^6, bipy]	29.76 (Me); 70.14 (C); 122.36 and 123.25 (C^3, bipy); 125.85 and 127.04 (C^5, bipy); 127.34 (*p*-C, PhC$_2$Ph); 128.08 (*m*-C, PhC$_2$Ph); 128.34 (benzene); 130.48 (*o*-C, PhC$_2$Ph); 139.41 and 139.46 (C^4, bipy); 139.74 (*ipso*-C, PhC$_2$Ph); 149.36 (C^6, bipy); 151.72 and 152.67 (C^2, bipy); 153.39 (C^6, bipy); 163.60 [t, ^1J(CW) 30.2, C≡C]
4	1.22 (s, 9 H, Me); 2.18 and 2.36 (2s, 6 H, Me); 6.90 [d, ^3J(HH) 4.8, 1 H, H^5, dmbipy]; 7.15 [t, ^3J(HH) 7.4, 2 H, *p*-H, PhC$_2$Ph]; 7.28 (s, benzene); 7.35 [t, ^3J(HH) 7.6, 5 H, *m*-H, PhC$_2$Ph and H^5, dmbipy (obscured)]; 7.73 [d, ^3J(HH) 7.6, 5 H, *o*-H, PhC$_2$Ph and H^3, dmbipy]; 7.83 (b, 1 H, H^3, dmbipy); 8.16 [d, ^3J(HH) 5.0, 1 H, H^6, dmbipy]; 9.42 [d, ^3J(HH) 5.0, 1 H, H^6, dmbipy]	21.28 and 21.44 (Me, dmbipy); 29.35 (Me, CMe$_3$); 69.52 (C, CMe$_3$); 123.32 and 123.93 (C^5, dmbipy); 125.94; (C^3, dmbipy); 126.74 (*p*-C, PhC$_2$Ph); 127.49 (C^3, dmbipy); 127.57 (*m*-C, PhC$_2$Ph); 127.98 (benzene); 129.98 (*o*-C, PhC$_2$Ph); 139.61 (*ipso*-C, PhC$_2$Ph); 148.41 (C^6, dmbipy); 151.03 (C^2 or C^4, dmbipy); 151.13 (C^6, dmbipy); 151.24 (C^4 or C^2, dmbipy); 162.93 [t, ^1J(CW) 31.4, C≡C]
5	1.28 (s, 9 H, Me); 6.89 [d, ^3J(HH) 7.6, 4 H, *o*-H, PhC$_2$Ph]; 6.99 [t, ^3J(HH) 7.1, 2 H, H^4, py]; 7.08 (m, 6 H, *m* and *p*-H, PhC$_2$Ph); 7.63 [t, ^3J(HH) 7.2, 4 H, H^3 and H^5 py]; 9.25 [d, ^3J(HH) 5.5, 4 H, H^2 and H^6, py]	29.50 (Me); 69.44 (C); 123.64 (C^3 and C^5, py); 126.35 (*p*-C, PhC$_2$Ph); 127.76 (*o*-C, PhC$_2$Ph); 128.12 (*m*-C, PhC$_2$Ph); 137.85 (C^4, py); 139.49 (*ipso*-C, PhC$_2$Ph); 155.24 (C≡C); 155.78 (C^2 and C^6, py)
6	1.26 (s, 9 H, Me); 1.58 [t, ^2J(HP)[d] 9.3, 18 H, PMe$_3$]; 7.12 [t, ^3J(HH) 7.3, 2 H, *p*-H, PhC$_2$Ph]; 7.21 [d, ^3J(HH) 7.3, 4 H, *o*-H, PhC$_2$Ph]; 7.29 [t, ^3J(HH) 7.3, 4 H, *m*-H, PhC$_2$Ph]	16.23 [t, ^1J(CP) 30.4, PMe$_3$]; 31.15 (Me); 69.38 (C); 126.09 (*p*-C, PhC$_2$Ph); 127.04 (*o*-C, PhC$_2$Ph); 128.10 (*m*-C, PhC$_2$Ph); 128.33 (benzene); 144.57 (*ipso*-C, PhC$_2$Ph); 151.15 [t, ^2J(CP) 24.0, C≡C]
7	0.74 (s, 9 H, CMe$_3$); 1.62 and 3.14 (prt, 12 H, PMe$_2$); 7.13 (m, 6 H, aromatic H); 7.26 (m, 4 H, aromatic H); 7.36 (br, 6 H, aromatic H); 7.79 (br, 4 H, *o*-H, PMe$_2$Ph)	12.77 [t, ^2J(HP) 31.9, PMe$_2$]; 17.38 [t, ^2J(HP) 35.4, PMe$_2$]; 29.81 (s, Me); 69.70 (C); 126.28 (*p*-C, PhC$_2$Ph); 128.0 (*m*- and *o*-C, PhC$_2$Ph); 128.11 (*m*-C, PMe$_2$Ph); 129.70 (*p*-C, PMe$_2$Ph); 131.36 (*o*-C, PMe$_2$Ph); 137.19 [t, ^1J(CP) 36.2, *ipso*-C, PMe$_2$Ph]; 143.56 (*ipso*-C, PhC$_2$Ph); 153.37 [t, ^2J(CP) 24.1, C≡C]
8	1.26 [d, ^3J(HH) 6.4, 6 H, Me$_2$]; 2.16 and 2.36 (2s, 6 H, Me); 4.36 [sept, ^3J(HH) 6.4, 1 H, CH]; 6.95 [d, ^3J(HH) 5.4, 1 H, H^5, dmbipy]; 7.22 [t, ^3J(HH) 7.4, 2 H, *p*-H, PhC$_2$Ph]; 7.38 (prd, 1 H, H^5, dmbipy); 7.42 [t, ^3J(HH) 7.7, 4 H, *m*-H, PhC$_2$Ph]; 7.77 (s, 1 H, H^3, dmbipy); 7.80 [d, ^3J(HH) 7.9, 4 H, *o*-H, PhC$_2$Ph]; 7.89 (s, 1 H, H^3, dmbipy); 8.09 [d, ^3J(HH) 5.5, 1 H, H^6, dmbipy], 9.35 [d, ^3J(HH) 5.6, 1 H, H^6, dmbipy]	20.79 and 21.13 (Me, dmbipy); 23.11 (Me, CHMe$_2$); 64.63 (CH, CHMe$_2$); 123.17 and 123.83 (C^5, dmbipy); 128.33 (C^3, dmbipy); 127.02 (*p*-C, PhC$_2$Ph); 127.61 (C^3, dmbipy); 127.83 (*m*-C, PhC$_2$Ph); 130.26 (*o*-C, PhC$_2$Ph); 139.99 (*ipso*-C, PhC$_2$Ph); 148.56 (C^6, dmbipy); 151.34, 151.40 and 151.55 (C^2 and C^4, dmbipy); 151.99 (C^6, dmbipy); 152.39 (C^2 or C^4, dmbipy); 163.16 [t, ^1J(CW) 30.2, C≡C]
9	1.30 [t, ^3J(HH) 7.1, 3 H, Me]; 2.40 and 2.42 (2s, 6 H, Me, dmbipy); 4.21 (obsq, 2 H, CH$_2$); 6.27 [d, ^3J(HH) 7.6, 2 H, *o*-H, PhC$_2$Ph]; 6.87 [t, ^3J(HH) 7.2, 1 H, *p*-H, PhC$_2$Ph]; 6.93 [t, ^3J(HH) 7.5, 2 H, *m*-H, PhC$_2$Ph]; 7.13 [d, ^3J(HH) 5.5, 1 H, H^5, dmbipy]; 7.26 [prt, ^3J(HH) 7.2, *p*-H, PhC$_2$Ph]; 7.27 [prd, ^3J(HH) 5.4, 1 H, H^5, dmbipy]; 7.39 (m, 2 H, *m*-H, PhC$_2$Ph); 7.68 (s, 1 H, H^3, dmbipy); 7.39 (s, 1 H, H^3, dmbipy); 7.80 [d, ^3J(HH) 8.2, 2 H, *o*-H, PhC$_2$Ph]; 8.72 [d, ^3J(HH) 5.6, 1 H, H^6, dmbipy]; 8.85 [d, ^3J(HH) 5.9, 1 H, H^6, dmbipy]	15.55 (Me, CH$_2$Me); 21.27 and 21.54 (Me, dmbipy); 58.33 (CH$_2$); 122.26 and 123.95 (C^5, dmbipy); 126.04 (C^3, dmbipy); 126.31 (*o*-C, PhC$_2$Ph); 126.92 (*p*-C, PhC$_2$Ph); 127.39 (C^3, dmbipy); 127.49 (*m*-C, PhC$_2$Ph); 128.01 (*m*-C, PhC$_2$Ph); 130.45 (*p*-C, PhC$_2$Ph); 131.06 (*o*-C, PhC$_2$Ph); 138.76 and 140.84 (*ipso*-C, PhC$_2$Ph); 148.59 (C^6, dmbipy); 150.45 and 150.88 (C^2 or C^4, dmbipy); 151.77 (C^6, dmbipy); 152.19 and 152.76 (C^4 or C^2, dmbipy); 159.02 (C≡C)
10	1.23 [t, ^3J(HH) 7.1, 3 H, Me]; 2.27 and 2.47 (2s, 6 H, Me, dmbipy]; 4.19 [q, ^3J(HH) 7.1, 2 H, CH$_2$]; 7.03 [d, ^3J(HH) 5.5, 1 H, H^5, dmbipy]; 7.23 [t, ^3J(HH) 7.4, 2 H, *p*-H, PhC$_2$Ph]; 7.28 (s, benzene); 7.43 [t, ^3J(HH) 7.7, 5 H, *m*-H, PhC$_2$Ph and H^5, dmbipy (obscured)]; 7.54 [d, ^3J(HH) 7.5, 5 H, *o*-H, PhC$_2$Ph and H^3, dmbipy (obscured)]; 7.92 (s, 1 H, H^3, dmbipy); 8.13 [d, ^3J(HH) 5.6, 1 H, H^6, dmbipy]; 9.26 [d, ^3J(HH) 5.7, 1 H, H^6, dmbipy]	15.55 (Me, CH$_2$Me); 21.37 and 21.62 (Me, dmbipy); 58.70 (CH$_2$); 123.15 and 123.83 (C^5, dmbipy); 126.61 (C^3, dmbipy); 127.20 (*p*-C, PhC$_2$Ph); 127.89 (C^3, dmbipy); 127.98 (*m*-C, PhC$_2$Ph); 128.32 (benzene); 130.43 (*o*-C, PhC$_2$Ph); 140.03 (*ipso*-C, PhC$_2$Ph); 149.04 (C^6, dmbipy); 151.46, 151.54 and 151.64 (C^2 and C^4, dmbipy); 151.89 (C^6, dmbipy); 152.58 (C^2 or C^4, dmbipy); 163.31 [t, ^1J(CW) 29.8, C≡C]
12	1.07 [d, ^{3}J(HH) 6.8, 12 H, Me]; 2.40 and 2.56 (2s, 6 H, Me); 4.16 [sept, ^3J(HH) 6.8, 2 H, CH]; 7.02 [d, ^3J(HH) 6.8, 1 H, H^5, dmbipy]; 7.10 [d, ^3J(HH) 7.9, 2 H, *m*-H, imido]; 7.25 [t, ^3J(HH), 6.8, 1 H, *p*-H, imido]; 7.26 [t, ^3J(HH) 6.3, 2 H, *p*-H, PhC$_2$Ph]; 7.36 (prd, 1 H, H^5, dmbipy); 7.40 [t, ^3J(HH) 7.9, 4 H, *m*-H, PhC$_2$Ph]; 7.86 (s, 1 H, H^3, dmbipy); 7.89 [d, J(HH) 7.6, 4 H, *o*-H, PhC$_2$Ph]; 7.98 (s, 1 H, H^3, dmbipy); 8.17 [d, ^3J(HH) 5.7, 1 H, H^6, dmbipy]; 9.15 [d, ^3J(HH) 5.7, 1 H, H^6, dmbipy]	21.47 and 21.67 (Me, dmbipy); 24.68 (Me, CHMe$_2$); 27.24 (CH); 122.77 (*m*-C, imido); 123.14 and 123.88 (C^5, dmbipy); 125.38 (*p*-C, imido); 126.91 (C^3, dmbipy); 127.47 (*p*-C, PhC$_2$Ph); 127.55 (C^3, dmbipy); 127.90 (*m*-C, PhC$_2$Ph); 130.66 (*o*-C, PhC$_2$Ph); 140.05 (*ipso*-C, PhC$_2$Ph); 146.47 (C^6, dmbipy); 149.21 (C^6, dmbipy); 151.24, 151.54, 151.61 and 151.67 (C^2, C^4, dmbipy and *o*-C, imido); 151.80 (*ipso*-C, imido); 167.50 (C≡C)
13	2.21 and 2.35 (2s, 6 H, Me, dmbipy); 2.43 (s, 6 H, Me, imido); 6.73 [t, ^3J(HH) 7.1, 1 H, *p*-H, imido]; 6.89 [d, ^3J(HH), 2 H, *m*-H, imido]; 6.94 [d, ^3J(HH) 5.4, 1 H, H^5, dmbipy]; 7.15 [t, ^3J(HH) 7.4, 2 H, *p*-H, PhC$_2$Ph]; 7.23 [d, ^3J(HH) 5.2, 1 H, H^5, dmbipy]; 7.33 [t, ^3J(HH) 7.6, 4 H, *m*-H, PhC$_2$Ph]; 7.74 [d, ^3J(HH) 7.4, 5 H, *o*-H, PhC$_2$Ph and H^3, dmbipy (obscured)]; 7.86 (s, 1 H, H^3, dmbipy); 8.05 [d, ^3J(HH) 5.4, 1 H, H^6, dmbipy]; 9.09 [d, ^3J(HH) 5.5, 1 H, H^6, dmbipy]	19.70 (Me, imido); 21.36 and 21.51 (Me, dmbipy); 121.36 (*m*-C, imido); 124.05 and 125.05 (C^5, dmbipy); 126.64 (C^3, dmbipy); 127.28 (*p*-C, imido); 127.36 (*p*-C, PhC$_2$Ph); 127.59 (C^3, dmbipy); 127.88 (*m*-C, PhC$_2$Ph); 130.19 (*o*-C, PhC$_2$Ph); 135.75 (*o*-C, imido); 139.86 (*ipso*-C, PhC$_2$Ph); 148.67 and 150.69 (C^6, dmbipy); 151.49 (C^4, dmbipy); 151.54 and 152.33 (C^2, dmbipy); 153.29 (*ipso*-C, imido); 167.27 (C≡C)
14	0.85 and 0.95 (br, 12 H, Me); 3.81 and 4.09 (br, 2 H, CH); 6.81 [d, ^3J(HH) 7.5, 4 H, *o*-H, PhC$_2$Ph]; 6.98–7.07 (m, 7 H, H^4, py, *p*-H, PhC$_2$Ph, *m*- and *p*-H, imido); 7.13 [t, ^3J(HH) 6.4, 4 H, *m*-H, PhC$_2$Ph]; 7.67 [t, ^3J(HH) 7.0, 4 H, H^3, py]; 9.10 (br, 4 H, H^2, py)	24.74 (Me); 26.84 (CH); 124.80 (C^3 and C^5, py); 126.73 (*p*-C, PhC$_2$Ph); 127.83 (*o*-C, PhC$_2$Ph); 127.92 (*m*-C, imido); 128.06 (*p*-C, imido); 128.24 (*m*-C, PhC$_2$Ph); 138.01 (C^4, py); 139.07 (*ipso*-C, PhC$_2$Ph); 147.73 (*ipso*-C, imido); 149.87 (*o*-C, imido); 154.42 (C^2 and C^6, py); 158.78 (C≡C)

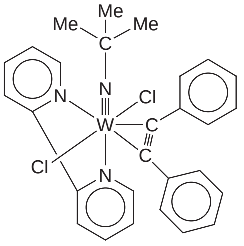
Table 2 (*Contd.*)

Complex	^{1}H ^{b}	^{13}C-{^{1}H} ^{b,c}
16	1.06 (prt, 12 H, Me, NEt$_4$); 1.38 (prd, 12 H, Me); 2.90 (prq, 8 H, CH$_2$, NEt$_4$); 3.55 (br, 2 H, CH); 5.28 (CH$_2$Cl$_2$); 6.95–7.45 (m, aromatic H); 7.45–7.95 (m, aromatic H); 9.82 (br, 1 H, NH)	8.78 (Me, NEt$_4$); 23.37 and 23.89 (CHMe$_2$); 26.69 and 27.24 (CH); 55.30 (CH$_2$); 88.77 (CH$_2$Cl$_2$); 123.63, 127.26, 127.79, 130.40 and 130.97 (aromatic C); 141.88 (*ipso*-C, PhC$_2$Ph); 150.52 (*o*-C, imido); 151.23 (*ipso*-C, imido); 167.40 (C≡C)

[a] Spectra obtained in CDCl$_3$ solution. [b] t = Triplet s = singlet, br = broad, q = quartet, d = doublet, pr = partially resolved, m = multiplet; sept = septet, obs = obscured. [c] Aromatic ring resonance assignments: *ortho*-carbons shift from δ 128.5, *meta*-carbons based on δ 128.5, *para*-carbons from relative peak height. [d] For virtual HP spin coupling ^2J(HP) quoted as $\frac{1}{2}[^2J(\mathrm{HP}) + {}^6J(\mathrm{HP}')]$ where ^6J(HP′) is very small.

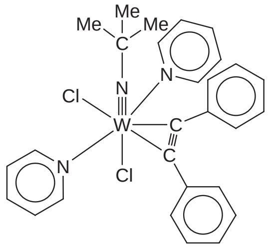


shows one set of resonances for each of the diphenylacetylene ligand *ortho*, *meta* and *para* carbons and 10 resonances for the bipy carbons with the two C^6 carbons showing the greatest separation (δ 153.39 and 149.36). The *tert*-butylimido quaternary carbon appears at δ 70.14 and the acetylenic carbons at δ 163.60 which is further downfield than the parent complex **1** (δ 156.23) and may represent a small electronic change. From the symmetry of the diphenylacetylene ligand and asymmetry of the bipy ligand in the NMR spectra and also a single W–Cl stretch in the IR spectrum, complex **3** has *trans*-chloro ligands and the bipy nitrogen atoms lying *trans* to the imido and diphenylacetylene ligands (structure **I**). Evidence for the complex being a d^2 tungsten species comes from a preliminary X-ray photoelectron spectral (XPS) study where the tungsten(4f$_{7/2}$) binding energy (33.84 eV) is well below that found for [{WCl$_4$(PhC$_2$Ph)}$_2$] (35.1 eV)[1] and falls in the range considered to be of tungsten(IV).[15] A fuller XPS study of imido and η^2-acetylene complexes of tungsten will be reported in the future. That the diphenylacetylene ligand in **3** is a 2-electron donor is verified by the position of ν(C≡C) (1740 cm^{-1})[6] in the IR spectrum and the position of the acetylenic carbon resonance (δ 163.60) in the ^{13}C-{^{1}H} NMR spectrum.



Structure **I**

We have also prepared the 4,4′-dimethylbipyridyl (dmbipy) analogue to increase solubility and decrease the complexity of the NMR spectra. With the C^4 protons of bipy replaced by methyl groups in [WCl$_2$(NCMe$_3$)(PhC$_2$Ph)(dmbipy)] **4** the ^{1}H NMR spectrum shows two methyl group resonances, two singlets for the C^3 protons [^4J(HH) coupling was not resolved at 400 MHz] and two doublets each for the C^5 and C^6 protons. The doublets have ^3J(HH) coupling constants of about 5 Hz which distinguishes them from the diphenylacetylene protons where ^3J(HH) is 7–8 Hz.† The ^{13}C-{^{1}H} NMR spectrum now contains two dmbipy methyl group resonances and shows C^4 tertiary carbon resonances which simplifies the diphenylacetylene *ipso*-carbon region (δ 139.61). The acetylenic carbon resonance is at δ 162.93. Addition of pyridine (py) to a solution of complex **1** gave [WCl$_2$(NCMe$_3$)(PhC$_2$Ph)(Py)$_2$] **5** which was characterised by NMR spectroscopy. Both the ^{1}H and ^{13}C-{^{1}H} NMR spectra show a single resonance for the diphenylacetylene ligand *ortho*, *meta* and *para* positions as well as the pyridine α and β positions indicating that the pyridines are symmetrically ligated. The complex thus has a *trans*-(bis)pyridine, *cis*-dichloro structure (structure **II**). For this complex the acetylenic carbon resonance occurs at δ 155.78 in the ^{13}C-{^{1}H} NMR spectrum which is upfield to that of dmbipy complex **4** (δ 162.93) but similar to that of the parent complex **1** (δ 156.23).



Structure **II**

Phosphine derivatives of complex **1** can also be prepared. Addition of PMe$_3$ gave [WCl$_2$(NCMe$_3$)(PhC$_2$Ph)(PMe$_3$)$_2$] **6** which has a *trans*-phosphine *cis*-dichloro structure based on an apparent triplet for the PMe$_3$ ligand in both the ^{1}H and ^{13}C-{^{1}H} NMR spectra and W–Cl stretches at 265 and 215 cm^{-1} in the IR spectrum. The ^{13}C-{^{1}H} NMR spectrum shows the *tert*-butylimido quaternary carbon at δ 69.38 and the acetylenic carbons as a ^{31}P-coupled triplet at δ 151.15. This resonance is further upfield than for pyridine complex **5** (δ 155.78) which has a similar molecular geometry and considerably upfield of that of the dmbipy complex **4** (δ 162.93) where the geometry is different.

The *trans*-(bis)phosphine *cis*-dichloro structure for complex **6** was confirmed by a crystal structure determination. The molecular structure is shown in Fig. 1, and selected bond lengths and angles are contained in Table 3. The structure is essentially the same as that found for [WCl$_2$(NPh)(PhC$_2$Ph)(PMe$_3$)$_2$][5] with similar W–N bond lengths [1.763(6) and 1.770(14) Å respectively], no lengthening of the W–Cl bond *trans* to the imido function [W–Cl(1) and W–Cl(2) 2.520(2) and 2.519(2) Å compared with 2.503(8) and 2.515(8) Å], similar W–C(1) [2.131(6) and 2.128(20) Å respectively] and W–C(2) [2.111(7) and 2.123(21) Å respectively] as well as similar C(1)–C(2) bond lengths [1.267(9) and 1.26(2) Å respectively]. Data for the acetylene part of the molecule are consistent with this ligand being a 2-electron donor to tungsten. The major

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† NMR Spectra were run as concentrated CDCl$_3$ solutions to facilitate ^{13}C-{^{1}H} NMR spectra accumulation times. As a result ^3J(HH′) and ^3J(H′H) coupling constants reported in Table 2 are not always exactly equal.

Table 3 Selected bond lengths (Å) and angles (°) for complex **6**

W–N(1)	1.763(6)	W–P(2)	2.562(2)
W–Cl(1)	2.520(2)	N(1)–C(3)	1.400(1)
W–Cl(2)	2.519(2)	C(1)–C(2)	1.267(9)
W–C(1)	2.131(6)	C(1)–C(31)	1.460(9)
W–C(2)	2.111(7)	C(2)–C(21)	1.471(10)
W–P(1)	2.574(2)		
N(1)–W–C(1)	99.4(3)	C(2)–W–P(2)	116.9(2)
N(1)–W–C(2)	96.0(3)	Cl(1)–W–P(1)	76.98(7)
N(1)–W–Cl(1)	169.4(2)	Cl(1)–W–P(2)	79.46(8)
N(1)–W–Cl(2)	86.0(2)	Cl(2)–W–P(1)	78.95(7)
N(1)–W–P(1)	102.9(2)	Cl(2)–W–P(2)	82.10(8)
N(1)–W–P(2)	97.3(2)	Cl(2)–W–Cl(1)	83.58(8)
C(1)–W–Cl(1)	90.2(2)	C(2)–W–C(1)	34.7(2)
C(1)–W–Cl(2)	163.9(2)	P(2)–W–P(1)	151.15(7)
C(1)–W–P(1)	114.2(2)	C(3)–N(1)–W	173.7(6)
C(1)–W–P(2)	82.2(2)	C(1)–C(2)–C(21)	136.3(6)
C(2)–W–Cl(1)	94.4(2)	C(2)–C(1)–C(31)	136.7(7)
C(2)–W–Cl(2)	160.4(2)	C(1)–C(2)–W	73.5(4)
C(2)–W–P(1)	81.6(2)	C(2)–C(1)–W	71.8(4)

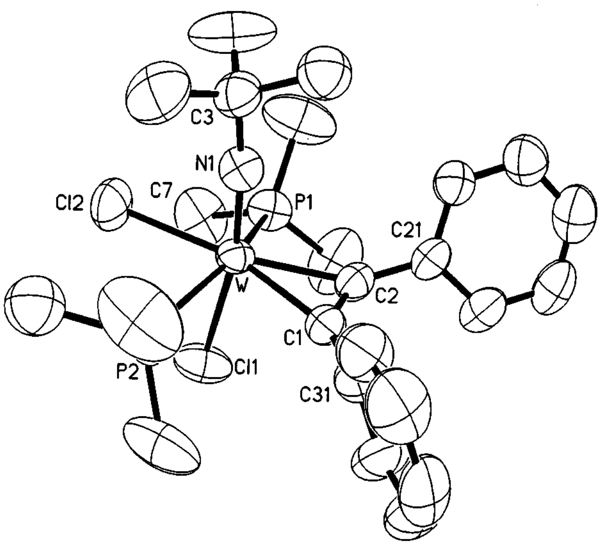
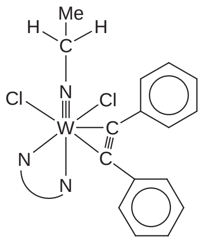


Fig. 1 Molecular structure of complex **6**; atoms are represented at 50% probability surfaces.

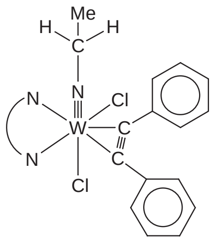
structural difference between the two molecules is that in complex **6** a small twist of the diphenylacetylene ligand about the tungsten–acetylene axis [N–W–C(1) and N–W–C(2) bond angles 99.4(2) and 96.0(3)°] allows the phenyl rings to sit above the plane of the two PMe_3 ligands whereas in $[WCl_2(NPh)(PhC_2Ph)(PMe_3)_2]$ a larger twist occurs [N–W–C(1) and N–W–C(2) bond angles 104.6(7) and 94.9(7)° respectively] with the phenyl rings sitting above and below the two phosphines. The reason for this is not clear but may be related to the π-donor strength of the two different imido ligands. While the PMe_3 ligands bend away from the diphenylacetylene ligand in **6** and $[WCl_2(NPh)(PhC_2Ph)(PMe_3)_2]$ to similar extents [P(1)–W–P(2) angles 151.15(7) and 151.9(2)° respectively] the P–W–P pushback angle from the imido ligand is greater for the more electron donating *tert*-butylimido ligand [relevant angles 200.3(2) and 186.9(5)° respectively].

We have also investigated the effect of increasing phosphine ligand size in complexes similar to **6**. Reaction of PMe_2Ph with complex **1** gives $[WCl_2(NCMe_3)(PhC_2Ph)(PMe_2Ph)_2]$ **7** which also has the *trans*-(bis)phosphine *cis*-dichloro structure based on a pair of triplets for the PMe_2Ph methyl groups in the ^1H and $^{13}C-\{^1H\}$ NMR spectra, a triplet for the aromatic ring *ipso* carbon of the phosphine and W–Cl stretches at 265 and 235 cm^{-1} in the IR spectrum. The $^{13}C-\{^1H\}$ NMR spectrum shows the *tert*-butylimido ligand quaternary carbon at a similar position to that of the PMe_3 complex (δ 69.70 for **7** compared to δ 69.38 for **6**), whereas there is a small downfield shift of the acetylenic carbon triplet (δ 153.37 for **7** compared with δ 151.15 for **6**). Attempts to form a similar complex with $PMePh_2$ were not successful.

Additions of the silylamines Me_3SiNHR containing less sterically demanding R groups ($R = CHMe_2$ or Et) to $[\{WCl_4(PhC_2Ph)\}_2]$ also give light coloured solutions. We have not characterised the complexes (expected to be of the form $[\{WCl_2(NR)(PhC_2Ph)(NH_2R)\}_x]$) directly, other than to check the position of the acetylenic carbon resonance in the $^{13}C-\{^1H\}$ NMR spectra (for example $[\{WCl_2(NCHMe_2)(PhC_2Ph)(NH_2CH_2Me_2)\}_x]$ δ 151.99). Instead the light coloured solutions were treated directly with dmbipy. The NMR spectra of $[WCl_2(NCHMe_2)(PhC_2Ph)(dmbipy)]$ **8** are similar to those of $[WCl_2(NCMe_3)(PhC_2Ph)(dmbipy)]$ except for the characteristic isopropylimido group resonances (^1H NMR septet at δ 4.36, $^{13}C-\{^1H\}$ NMR, CH resonance δ 64.63). On crystallising the ethylimido complex $[WCl_2(NCH_2Me)(PhC_2Ph)(dmbipy)]$ a small quantity of a less soluble form **9** was obtained which had different spectral characteristics to those of the remaining sample **10**. The IR spectrum showed *cis*-chloro ligands for **9** [ν(W–Cl) 305 and 212 cm^{-1}] and exhibited ν(C≡C) at 1785 cm^{-1} while for **10** *trans*-chloro ligands were apparent [ν(W–Cl) 300 cm^{-1}] and ν(C≡C) was at 1770 cm^{-1}. The two dmbipy methyl group resonances in the ^1H NMR of **9** are closer together than in **10** (δ 2.40 and 2.42 compared with δ 2.27 and 2.47) as are the dmbipy C^6 protons (δ 8.72, 8.85 and δ 8.13, 9.26 respectively) while there are two sets of diphenylacetylene phenyl ring resonances for **9** and only one for **10**. In the $^{13}C-\{^1H\}$ NMR spectra complex **9** showed two sets of resonances for the diphenylacetylene ligand phenyl groups and two acetylenic carbon resonances (δ 152.76 and 159.03) while complex **10** has only a single set for the respective carbons (δ 163.31). The asymmetry in **9** can be explained by two *cis*-chloro structures, **9a** and **9b**, but **9a** is preferred on the basis of similarities of the dmbipy resonances in the NMR spectra to those of $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PhC_2Ph)(dmbipy)]^3$ prepared by reduction of $[WCl_3(NC_6H_3Pr^i_2\text{-}2,6)(dmbipy)]$ by Na/Hg amalgam in the presence of diphenylacetylene where steric factors do not favour the type **b** isomer. NMR spectra show that **9** does not turn into **10** on refluxing in benzene and similarly **10** does not turn into **9**.



9a



9b

Crystals of complex **9** suitable for X-ray crystallography have not been obtained but a structural determination of **10** has been carried out. The complex (Fig. 2) has a distorted octahedral geometry with *trans*-orientated chloro ligands and mutually *cis* ethylimido and diphenylacetylene ligands which are both *trans* to the dmbipy nitrogen ligand atoms. The geometry is that predicted on the basis of the spectral data for complex **10** as well as the other dmbipy complexes. The structure shows that the dmbipy C^6 protons will have different environments with one pointing towards the equatorial C(1)–C(2) multiple bond of diphenylacetylene and the other towards the longitudinally orientated W–N multiple bond, which will result in different effects in relation to the ^1H NMR spectrum, as is observed. Selected bond lengths and angles for complex **10** are contained in Table 4. The W–N(1) bond length [1.733(6) Å] is not significantly different to that found for $[WCl_2(NCMe_3)(PhC_2Ph)(PMe_3)_2]$ **6** [1.763(6) Å]. For the dmbipy ligand the

Table 4 Selected bond lengths (Å) and angles (°) for complex **10**

W–N(1)	1.733(6)	W–C(2)	2.085(8)
W–N(2)	2.233(7)	N(1)–C(3)	1.420(10)
W–N(3)	2.331(6)	C(1)–C(2)	1.271(11)
W–Cl(1)	2.447(2)	C(1)–C(17)	1.461(12)
W–Cl(2)	2.448(2)	C(2)–C(23)	1.463(11)
W–C(1)	2.086(8)		
N(1)–W–C(1)	99.9(3)	C(2)–W–N(3)	89.8(3)
N(1)–W–C(2)	102.7(3)	Cl(2)–W–Cl(1)	153.32(8)
N(1)–W–Cl(1)	94.3(3)	N(2)–W–Cl(1)	77.2(2)
N(1)–W–Cl(2)	97.9(3)	N(2)–W–Cl(2)	78.0(2)
N(1)–W–N(2)	96.0(3)	N(3)–W–Cl(1)	81.3(2)
N(1)–W–N(3)	166.2(3)	N(3)–W–Cl(2)	81.3(2)
C(1)–W–Cl(1)	118.8(2)	N(3)–W–N(2)	70.3(2)
C(1)–W–Cl(2)	82.3(2)	C(3)–N(1)–W	178.1(7)
C(1)–W–N(2)	156.2(3)	C(23)–C(2)–C(1)	139.6(8)
C(1)–W–N(3)	93.7(3)	C(17)–C(1)–C(2)	141.6(8)
C(2)–W–Cl(1)	83.4(2)	C(1)–C(2)–W	72.3(5)
C(2)–W–Cl(2)	116.5(2)	C(2)–C(1)–W	72.2(5)
C(2)–W–N(2)	153.9(3)	C(2)–W–C(1)	35.5(3)

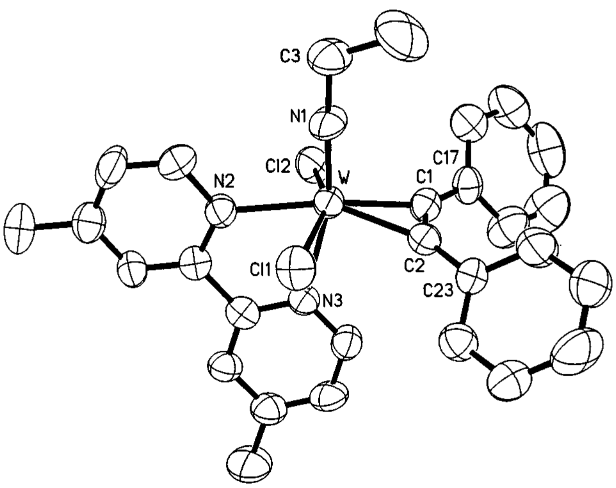


Fig. 2 Molecular structure of complex **10**; atoms are represented as 50% probability surfaces.

W–N(3) bond length [2.331(6) Å] is significantly longer than the W–N(2) bond length [2.233(7) Å] apparently to remove interaction of the C11 proton with the diphenylacetylene C(1)–C(2) multiple bond. The W–Cl bond lengths [2.447(2) and 2.448(2) Å] are considerably shorter than the two *cis*-orientated W–Cl bonds in complex **6** [2.519(2) and 2.520(2) Å] where imido and diphenylacetylene ligands are the *trans* ligands. The W–C bond lengths in complex **10** [2.086(8) and 2.085(8) Å] are outside the 3σ limit for the W–C(1) bond length [2.131(6) Å] in complex **6** and just inside the 3σ limit for the WC(2) bond length [2.111(7) Å] indicating that these bonds in the dmbipy complex are becoming shorter. This may involve the acetylene $\pi_\perp$ orbitals donating to the same metal orbital as one of the imido donors, resulting in a competitive π-donor situation which is reflected in the $^{13}C\text{-}\{^1H\}$ NMR spectrum where there is an 11.8 ppm shift to lower field for the acetylenic carbon of complex **10** (δ 163.31) compared to that of **6** (δ 151.15). However this effect is small and the diphenylacetylene ligand can still be regarded as a nett 2-electron donor. The chloro ligands in complex **10** push further away from the diphenylacetylene ligand than the imido ligand [relevant angles 215.8(4) and 192.2(4)°] while there is only a very small twist of the C≡C bond about the tungsten–acetylene axis [N–W–C(1) and N–W–C(2) bond angles 99.9(3) and 102.7(3)° respectively].

We have also investigated the reaction of $Me_3SiNHC_6H_3Pr^i_2$-2,6 with $[\{WCl_4(PhC_2Ph)\}_2]$ as a route to complexes of the type $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PhC_2Ph)(L)_2]$.[16] This reaction is best carried out in diethyl ether and requires refluxing to give $[\{WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PhC_2Ph)(NH_2C_6H_3Pr^i_2\text{-}2,6)\}_x]$ **11**. The NMR spectra are complex and individual assignments have not been attempted other than again to note the position of the acetylenic carbon resonance in the $^{13}C\text{-}\{^1H\}$ NMR spectrum at δ 166.51 which compares with the alkylimido complexes at *ca.* δ 155.00. Reaction of complex **11** with dmbipy gave $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PhC_2Ph)(dmbipy)]$ **12** which has IR and NMR spectral characteristics for the dmbipy and diphenylacetylene ligands similar to those of dmbipy complexes **4** and **8**. The complex thus has a *trans*-dichloro structure and not the *cis*-dichloro structure (similar to complex **9**) found for $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PhC_2Ph)(dmbipy)]$ produced by the reduction of $[WCl_3(NC_6H_3Pr^i_2\text{-}2,6)(dmbipy)]$ in the presence of diphenylacetylene.[3] The $^{13}C\text{-}\{^1H\}$ NMR spectrum of complex **12** shows the acetylenic carbon resonance at δ 167.50 which is higher than those of all the other complexes and may represent some acetylene ligand $\pi_\perp$ orbital donation in a competitive manner to the tungsten orbital involved in the imido π-donor system. An XPS spectrum shows the tungsten($4f_{7/2}$) binding energy at 33.97 eV which is slightly higher than that found for $[WCl_2(NCMe_3)(PhC_2Ph)(bipy)]$ **3** (33.84 eV) where the acetylenic carbon resonance in the $^{13}C\text{-}\{^1H\}$ NMR spectrum occurs at δ 163.60. For a further comparison of this resonance position, $[WCl_2(NC_6H_3Me_2\text{-}2,6)(PhC_2Ph)(dmbipy)]$ **13** prepared by reaction of $Me_3SiNHC_6H_3Me_2$-2,6 with $[\{WCl_4(PhC_2Ph)\}_2]$ and characterised by NMR spectroscopy, has the acetylenic carbons at δ 167.26 which is not significantly different to those of complex **12** (δ 167.50).

The complexes $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PhC_2Ph)(py)_2]$ **14** and $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PhC_2Ph)(PMe_3)_2]$ **15** were also prepared from $[\{WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PhC_2Ph)(NH_2C_6H_3Pr^i_2\text{-}2,6)\}_x]$ **11** with characterisation made by NMR spectroscopy. The ^1H and $^{13}C\text{-}\{^1H\}$ spectral characteristics of the py and diphenylacetylene ligands for complex **14** are similar to those found for $[WCl_2(NCMe_3)(PhC_2Ph)(py)_2]$ **5** with the respective acetylenic carbon resonances in the $^{13}C\text{-}\{^1H\}$ NMR spectra at δ 158.78 and 155.78. Phosphine complex **15** has identical NMR spectra to those of $[WCl_2(NC_6H_3Pr^i\text{-}2,6)(PhC_2Ph)(PMe_3)_2]$[16] prepared by the reaction of $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PMe_3)_3]$ and diphenylacetylene [$^{13}C\text{-}\{^1H\}$ NMR spectrum, $\delta_{C\equiv C}$ 154.40].[3]

Finally, we have found that addition of one equivalent of $Me_3SiNHC_6H_3Pr^i_2$-2,6 to $[NEt_4][WCl_5(PhC_2Ph)]$ generated in CH_2Cl_2 gives the amido complex $[NEt_4][WCl_4(NHC_6H_3Pr^i_2\text{-}2,6)(PhC_2Ph)]$ **16** but it is not particularly stable. The ^1H NMR spectrum shows the NH proton at δ 9.82 with poorly resolved peaks for the isopropyl methyl groups and those of the NEt_4 cation. The $^{13}C\text{-}\{^1H\}$ NMR spectrum accumulated over a longer period shows resonances consistent with this formulation although some decomposition is evident. However the main feature is the acetylenic carbon resonance at δ 167.40 and in the IR spectrum ν(C≡C) occurs at 1765 cm^{-1} indicating that a single amido ligand (1σ and 1π donor interactions) is sufficient to convert the acetylene ligand into a 2-electron donor. The crystal structure of the 2,6-diisopropylphenylimido analogue, $[NH_3C_6H_3Pr^i_2\text{-}2,6][WCl_4(NC_6H_3Pr^i_2\text{-}2,6)(NHC_6H_3Pr^i_2\text{-}2,6)]$, has been described.[17]

Conclusion

The results of these studies show that the 4-electron donor alkyne ligands in $[\{WCl_4(PhC_2Ph)\}_2]$ are converted into 2-electron donors when an imido ligand is added to the complex. This occurs as the imido ligand is a stronger π donor (2π donor interactions) compared with the alkyne (1π donor interaction). This complex exhibits properties and chemistry consistent with it being a d^0 tungsten complex whereas the imido complexes are d^2 so that in formal terms a change in oxidation state has occurred. The position of the acetylenic carbon resonance in the $^{13}C\text{-}\{^1H\}$ NMR spectra is an important indicator of this change with the downfield shifts observed for some of the imido complexes suggesting increasing involvement of the alkyne $\pi_\perp$ component (π-donor interaction). Our initial studies aimed at converting the alkyne back into a 4-electron donor *via* such species as a five-co-ordinate cation, $[WCl(NR)(PhC_2Ph)(L)_2]^+$, or neutral five-co-ordinate complex $[WCl_2(NR)(PhC_2Ph)(L)]$ where L is a bulky ligand, have so far been unsuccessful. This approach has been taken in view of the 4-electron donor nature of the alkyne ligand in the tantalum complex $[TaCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PhC_2Ph)(py)_2]$ ($\delta_{C\equiv C}$ 195.9).[18] Such reactions are important as the alkyne ligand has the potential to act as an electron sink so that cycling through the d^0/d^2 system would provide a reversible redox system. The synthetic strategy outlined in this work also allows the preparation of a variety of d^2 imido-alkyne complexes which we have otherwise found difficult to prepare.[3]

Experimental

General procedures and instrumentation have been described. The IR spectra were obtained as Nujol mulls and ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra were recorded at 400 and 100 MHz respectively. Analytical data were obtained by Dr A. Cunningham and associates, University of Otago, New Zealand. The trimethylsilylalkylamines (Me_3SiNHR, R = CMe_3 or $CHMe_2$) were prepared by reaction of the alkylamine with Me_3SiCl and the substituted trimethylsilylanilines by reaction of the lithium amide with Me_3SiCl. The complex $[\{WCl_4(PhC_2Ph)\}_2]$ was prepared by treating WCl_6 with PhC_2Ph in the presence of tetrachloroethylene.[19] Trimethylphosphine was prepared by reaction of MgMeI with $P(OPh)_3$ in di-*n*-butyl ether[20] and PMe_2Ph by reaction of MgMeI on PCl_2Ph. Pyridine was dried over and distilled from freshly ground calcium hydride and $[Et_4N]Cl$ was dried at 100 °C under vacuum for 2 h prior to use. The bipy and dmbipy were obtained from Aldrich and used without further purification. Benzene, light petroleum (bp range 40–60 °C) and diethyl ether were distilled over sodium wire, tetrahydrofuran from sodium–benzophenone and dichloromethane from freshly ground calcium hydride.

Syntheses

$[\{WCl_2(NCMe_3)(PhC_2Ph)(NH_2CMe_3)\}_x]$ 1. A solution of $Me_3SiNHCMe_3$ (1.1 cm^3, 5.7 mmol) in benzene (30 cm^3) was added to a suspension of $[\{WCl_4(PhC_2Ph)\}_2]$ (1.30 g, 1.6 mmol) in benzene and the mixture stirred for 18 h. The solution was filtered and the solvent removed to small volume (*ca.* 5 cm^3) and allowed to stand. The colourless solid was filtered off, washed with cold benzene (10 cm^3, 5 °C), and dried under vacuum. Yield 0.95 g (63%). IR spectrum: 3254w, 3252w, 2752w, 2605w, 2502w, 1762w, 1590w, 1562m, 1515w, 1396w, 1340w, 1302m, 1250s, 1210m, 1185m, 1158w, 1075w, 1028w, 925w, 770m, 695m, 600w, 535w, 455w, 350w, 305w and 208w cm^{-1}.

$[NEt_4][WCl_3(NCMe_3)(PhC_2Ph)(NH_2CMe_3)]$ 2. The salt $[Et_4N]Cl$ (0.33 g, 2.0 mmol) in CH_2Cl_2 (20 cm^3) was added to $[\{WCl_4(PhC_2Ph)\}_2]$ (1.0 g, 0.95 mmol) suspended in CH_2Cl_2 (40 cm^3) and the mixture stirred for 10 min giving a red-brown solution which was filtered from a small amount of solid. A solution of $Me_3SiNHCMe_3$ (0.8 cm^3, 4.1 mmol) in CH_2Cl_2 was added and the mixture stirred for 2.5 h. The solution was filtered and the solvent removed to give a colourless solid. Yield 1.23 g. The complex could not be obtained analytically pure by recrystallisation and was characterised tentatively on the basis of NMR spectra.

$[WCl_2(NCMe_3)(PhC_2Ph)(bipy)]$ 3. A solution of $Me_3SiNHCMe_3$ (0.5 cm^3, 2.6 mmol) in benzene (30 cm^3) was added to a suspension of $[\{WCl_4(PhC_2Ph)\}_2]$ (0.6 g, 0.6 mmol) in benzene (50 cm^3) and the mixture stirred for 16 h and filtered. A solution of 2,2′-bipyridyl (0.2 g, 1.3 mmol) in benzene (20 cm^3) was added and the mixture refluxed for 2 h and then filtered while hot. The volume was reduced while keeping the solution hot and on standing yellow crystals of the complex formed. Yield: 0.6 g (72%). IR spectrum: 1740w, 1600m, 1575w, 1515w, 1405w, 1360m, 1310m, 1275s, 1220m, 1175m, 1158m, 1108w, 1076w, 1045w, 1030m, 1020m, 970w, 920w, 905w, 848w, 808w, 770s, 738m, 700s, 680s, 655w, 640w, 595w, 560w, 540w, 505w, 455w, 355w and 298m cm^{-1}.

$[WCl_2(NCMe_3)(PhC_2Ph)(dmbipy)]$ 4. A solution of $Me_3SiNHCMe_3$ (2.0 cm^3, 10.3 mmol) in benzene (35 cm^3) was added to $[\{WCl_4(PhC_2Ph)\}_2]$ (2.4 g, 2.4 mmol) suspended in benzene (40 cm^3). The solution was stirred for 16 h, filtered, 4,4′-dimethyl-2,2′-bipyridyl (0.90 g, 4.9 mmol) in benzene (25 cm^3) added and the mixture refluxed for 4 h. The solution was filtered and the product cropped successively by reducing the amount of solvent. Yield: 2.67 g (81%). The complex was characterised by NMR spectroscopy.

$[WCl_2(NCMe_3)(PhC_2Ph)(py)_2]$ 5. A solution of $Me_3SiNHCMe_3$ (0.8 cm^3, 4.1 mmol) in benzene (10 cm^3) was added to $[\{WCl_4(PhC_2Ph)\}_2]$ (1.0 g, 1.0 mmol) suspended in benzene. The mixture was stirred for 18 h, neat pyridine added (1 cm^3) and the solution stirred for 3 h. The yellow solid obtained on removing the solvent and washing the residue with light petroleum (100 cm^3) was characterised by NMR spectroscopy.

$[WCl_2(NCMe_3)(PhC_2Ph)(PMe_3)_2]$ 6. A solution of $Me_3SiNHCMe_3$ (0.7 cm, 3.6 mmol) in benzene (15 cm^3) was added to a suspension of $[\{WCl_4(PhC_2Ph)\}_2]$ (0.9 g, 0.9 mmol) in benzene (50 cm^3) and the mixture stirred for 20 h. The solution was filtered, PMe_3 (0.5 cm^3, 4.6 mmol) added, and the mixture stirred for 3 h. After filtering and removal of the volatiles the complex was obtained as a colourless crystalline solid. Yield 0.8 g (67%). IR spectrum: 1770w, 1685w, 1415m, 1305w, 1280m, 1255s, 1212w, 1065w, 1020w, 940s, 850w, 780w, 730w, 700w, 580w, 560w, 500w, 265w and 215w cm^{-1}.

$[WCl_2(NCMe_3)(PhC_2Ph)(PMe_2Ph)_2]$ 7. A solution of $Me_3SiNHCMe_3$ (0.7 cm^3, 4.8 mmol) in benzene (30 cm^3) and $[\{WCl_4(PhC_2Ph)\}_2]$ (0.9 g, 1.8 mmol) suspended in benzene (20 cm^3) were treated in the usual manner. After filtering, PMe_2Ph (0.5 cm^3, 4.1 mmol) was added and the mixture refluxed for 2 h. The volatiles were removed from the filtered solution giving a gum which solidified on standing under light petroleum for several hours. Crude yield 1.1 g (79%). Recrystallisation of the solid from toluene at −20 °C gave colourless crystals. Yield: 0.8 g (57%). IR spectrum: 1755m, 1590m, 1565w, 1460s, 1415s, 1450s, 1290w, 1245s, 1210w, 1108w, 1075w, 1012w, 1000w, 945m, 905s, 845m, 778m, 740s, 695s, 585w, 555w, 490s, 410m, 350w, 318w, 265m and 235w cm^{-1}.

$[WCl_2(NCHMe_2)(PhC_2Ph)(dmbipy)]$ 8. A solution of $Me_3SiNHCHMe_2$ (0.75 cm^3, 4.2 mmol) in benzene (10 cm^3) was added to a suspension of $[\{WCl_4(PhC_2Ph)\}_2]$ (1.0 g, 1.0 mmol) in benzene (30 cm^3) and the mixture was stirred for 5 h and filtered. 4,4′-Dimethyl-2,2′-bipyridyl (0.4 g, 2.2 mmol) in benzene (10 cm^3) was added and the solution refluxed for 2 h, filtered and the volatiles were removed. The residue was washed with cold benzene (5 × 1 cm^3) leaving a yellow solid (0.8 g) which was extracted with hot benzene (120 cm^3), the solution filtered and the volume reduced to give yellow microcrystals. Yield 0.5 g (37%). IR spectrum: 1765w, 1610s, 1595m, 1480m, 1410s, 1370m, 1280s, 1235w, 1220w, 1155w, 1110w, 1070w, 1018m, 918w, 895w, 835w, 822m, 770m, 765m, 695m, 590w, 545w, 522w, 500w, 455w, 420w and 295s cm^{-1}.

$[WCl_2(NCH_2Me)(PhC_2Ph)(dmbipy)]$ *cis*-chloro isomer 9. A solution of $Me_3SiNHEt$ (0.4 cm^3, 2.5 mmol) in benzene (25 cm^3) was added to a suspension of $[\{WCl_4(PhC_2Ph)\}_2]$ (0.6 g, 0.6 mmol) in benzene (35 cm^3) and the mixture stirred for 16 h. The solution was filtered, 4,4′-dimethyl-2,2′-bipyridyl (0.25 g, 1.36 mmol) in benzene (15 cm^3) added and the mixture refluxed for 1 h. The solution was filtered while hot, the solvent reduced to *ca.* 45 cm^3 and on standing the complex formed as a non-crystalline solid. Yield 0.24 g (30%). IR spectrum: 1785w, 1618s, 1595m, 1410m, 1325w, 1295s, 1258w, 1240w, 1065w, 1020m, 925m, 840w, 835w, 765m, 700m, 585w, 560w, 550w, 522w, 305m and 212w cm^{-1}.

$[WCl_2(NCH_2Me)(PhC_2Ph)(dmbipy)]$ *trans*-chloro isomer 10. The solution remaining after isolation of complex **9** was reduced in volume to *ca.* 20 cm^3 and on standing the complex formed as yellow crystals. Yield 0.46 g (52%). IR spectrum: 1770w, 1618s, 1595w, 1410w, 1330w, 1305s, 1285m, 1265w, 1242w, 1075w, 1025m, 928w, 910w, 835m, 775m, 745w, 690s, 550w, 520w, 420w and 300m cm^{-1}.

$[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PhC_2Ph)(NH_2C_6H_3Pr^i_2\text{-}2,6)]$ 11. The compound $Me_3SiNHC_6H_3Pr^i_2$-2,6 (3.8 g, 15.3 mmol) in diethyl ether (30 cm^3) was added to $[\{WCl_4(PhC_2Ph)\}_2]$ (3.8 g, 3.8 mmol) suspended in diethyl ether (120 cm^3) and the mixture stirred for 24 h followed by a gentle reflux for 1 h. The solution was filtered, the solvent removed and the solid washed with light petroleum (60 cm^3, 0 °C) and dried under vacuum. Yield 5.7 g (96%). The complex did not mull well in Nujol giving a poorly resolved spectrum.

$[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PhC_2Ph)(dmbipy)]$ 12. Complex **11** (0.9 g, 1.2 mmol) and dmbipy (0.25 g, 1.4 mmol) were mixed and degassed. Tetrahydrofuran (25 cm^3) was added and the mixture refluxed for 2 h. The solution was filtered and the solvent reduced to *ca.* 8 cm^3 giving the complex as a yellow microcrystalline solid. Yield 0.48 g (53%). IR spectrum: 1790w, 1615s, 1590w, 1360s, 1340s, 1300w, 1240w, 1070w, 1020w, 900w, 830w, 802w, 760m, 730m, 695m, 580w, 560w, 518w, 455w and 300w cm^{-1}.

$[WCl_2(NC_6H_3Me_2\text{-}2,6)(PhC_2Ph)(dmbipy)]$ 13. The compound $Me_3SiNHC_6H_3Me_2$-2,6 (0.8 g, 4.2 mmol) in benzene (15 cm^3) was added to a suspension of $[\{WCl_4(PhC_2Ph)\}_2]$ (1.0 g, 1.0 mmol) in benzene (35 cm^3) and the mixture stirred for 18 h. The yellow-brown solution was filtered and the solvent removed to give a yellow crystalline solid. Yield 1.3 g (98%). The complex (1.0 g, 1.5 mmol) and 4,4′-dimethyl-2,2′-bipyridyl (0.3 g, 1.6 mmol) were refluxed in benzene (35 cm^3) for 2 h. The solution was filtered, the solvent removed and the yellow solid washed with light petroleum (60 cm^3). Yield 1.0 g (99%). The complex was characterised by NMR spectroscopy.

$[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PhC_2Ph)(py)_2]$ 14. Neat pyridine (1 cm^3) was added to complex **11** (0.8 g, 1.0 mmol) in diethyl ether (30 cm^3) and the mixture was stirred for 2 h. The solution was filtered and the solvent removed to give a yellow gum which solidified on standing under light petroleum (50 cm^3). The solid was dissolved in toluene (20 cm^3), the solution filtered and light petroleum (60 cm^3) added to precipitate the complex. Yield 0.45 g (58%). This procedure failed to give an analytically pure sample [Found: C, 52.6; H, 4.6; N, 4.6. $C_{36}H_{37}Cl_2N_3W$ requires C, 56.4; H, 4.9; N, 5.5%] and the sample would not crystallise from other solvents so it was characterised by NMR spectroscopy.

$[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PhC_2Ph)(PMe_3)_2]$ 15. Complex **11** (0.8 g, 1.0 mmol) was dissolved in diethyl ether (45 cm^3) and an excess of PMe_3 (0.25 cm^3) added. The mixture was stirred for 3 h, the solution filtered and the solvent removed to give a gum which solidified on standing under light petroleum (50 cm^3). Yield 0.75 g (97%). The complex had identical NMR spectra to those of an authentic sample.[3]

$[NEt_4][WCl_4(NHC_6H_3Pr^i_2\text{-}2,6)(PhC_2Ph)]$ 16. The salt $[Et_4N]Cl$ (0.33 g, 2.0 mmol) in CH_2Cl_2 (25 cm^3) was added to $[\{WCl_4(PhC_2Ph)\}_2]$ (1.0 g, 1.0 mmol) suspended in CH_2Cl_2 (25 cm^3) and the mixture stirred for 1 h. The compound $Me_3SiNHC_6H_3Pr^i_2$-2,6 (0.5 g, 2.0 mmol) in CH_2Cl_2 (15 cm^3) was added and the solution stirred for 20 h. The solution was filtered, the solvent removed and the solid held under vacuum for several hours. Yield 1.6 g (94%). The complex did not mull well in Nujol giving a poorly resolved spectrum.

Crystallography

Data collection was performed on a Nonius CAD-4 diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å). The intensities were reduced to F^2 and an empirical absorption correction applied based on ψ scan data.[21] The structures were solved by Patterson and Fourier methods followed by full-matrix refinement on F^2 using programs SHELXS 86[22] and SHELXL 93.[23] Hydrogen atoms were introduced in calculated positions and allowed to ride on the carrier atom. The thermal parameters of the methyl groups in complex **6** show large thermal motion indicative of some disorder. With C4 and C12 the electron density could be resolved into two peaks and these atoms have been allowed to refine as two half-weighted atoms with isotropic thermal parameters.

Crystal data for complex 6. $C_{24}H_{37}Cl_2NP_2W$, $M = 656.24$, monoclinic, space group $P2_1/c$, $a = 16.674(2)$, $b = 10.159(4)$, $c = 17.196(2)$ Å, $\beta = 106.63(2)°$, $U = 2791.0(12)$ Å^3, $T = 173$ K, $Z = 4$, μ(Mo-Kα) = 4.45 mm^{-1}, 3969 observed reflections. Final $wR(F^2)$ was 0.0942; $R1 = 0.0334$.

Crystal data for complex 10. C_6H_6. $C_{34}H_{33}Cl_2N_3W$, $M = 738.38$, triclinic, space group $P\bar{1}$, $a = 10.091(2)$, $b = 11.584(4)$, $c = 14.098(2)$ Å, $\alpha = 87.00(2)$, $\beta = 100.68(1)$, $\gamma = 97.31(2)°$, $U = 1605.6(2)$ Å^3, $T = 173$ K, $Z = 2$, μ(Mo-Kα) = 3.79, 4143 observed reflections. Final $wR(F^2)$ was 0.1080; $R1 = 0.0429$.

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