2,6-Diisopropylphenylimido and Diphenylacetylene Complexes of Tungsten containing the Bidentate Ligands 4,4′-Dimethyl-2,2′-bipyridine and 1,2-Bis(diphenylphosphino)ethane†

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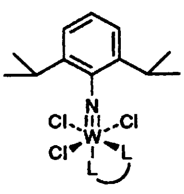
Sodium–mercury amalgam reduction of $[\{WCl_4(NC_6H_3Pr^i_2\text{-}2,6)\}_2]$ in the presence of 4,4′-dimethyl-2,2′-bipyridine (dmbipy) or 1,2-bis(diphenylphosphino)ethane (dppe) gave the d^1 complexes $[WCl_3(NC_6H_3Pr^i_2\text{-}2,6)(dmbipy)]$ **1** and $[WCl_3(NC_6H_3Pr^i_2\text{-}2,6)(dppe)]$ **2**. A crystal-structure determination of complex **2** shows the three chloro ligands in a *mer* arrangement and the dppe ligand phosphorus atoms lying *trans* to one chloro ligand and also the imido ligand. The W–P bond *trans* to the chloro ligand is normal [2.550(2) Å] whereas the W–P bond *trans* to the imido ligand is very long [2.765(2) Å]. One phenyl group of dppe rotates to accommodate an isopropyl group of the imido ligand. Sodium–mercury amalgam reduction of $[\{WCl_4(PhC_2Ph)\}_2]$ in the presence of dmbipy gave $[WCl_3(PhC_2Ph)(dmbipy)]$ which the W–Cl stretches suggest is the *mer* trichloride. However, an IR spectrum of the product of standing $[\{WCl_4(PhC_2Ph)\}_2]$ and dmbipy in tetrahydrofuran indicates the *fac* isomer. A reduction of $[\{WCl_4(PhC_2Ph)\}_2]$ in the presence of dppe gave $[WCl_3(PhC_2Ph)(dppe)]$ for which the *mer* isomer is preferred. The dppe complexes do not give characterisable complexes on further reduction in the presence of diphenylacetylene, ethylene or CO. Sodium–mercury amalgam reduction of **1** in the presence of diphenylacetylene gave $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PhC_2Ph)(dmbipy)]$ which IR and NMR spectra indicate has an asymmetric structure where the alkyne ligand is a two-electron donor. Reductions of complex **1** under ethylene or CO gave $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(CH_2CH_2)(dmbipy)]$ and $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(CO)(dmbipy)]$ both of which consist of several isomers.

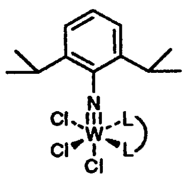
Recently we reported that a variety of complexes can be prepared from $[\{WCl_4(PhC_2Ph)\}_2]$ in which the diphenylacetylene ligand functions in a similar manner to an organoimido ligand.[1] For both these ligand systems, d^1 and d^2 complexes were prepared which contain phosphines as ancillary ligands.[1–4] These complexes have then been used to prepare d^2 complexes containing π-acceptor ligands such as alkynes,[5–8] olefins[5,8,9] or CO.[7,8] In view of the capability of both alkyne and organoimido ligands to stabilise high oxidation states,[1,10] we have carried out further studies to establish comparisons between the two ligand systems. We report here the results of work aimed at preparing organoimido and diphenylacetylene complexes of tungsten which contain bidentate nitrogen and phosphorus donors as ancillary ligands.

Results and Discussion

Attempts to obtain d^1 or d^2 complexes from the d^0 complexes $[\{WCl_4(NPh)\}_2]$[2] or $[\{WCl_4(PhC_2Ph)\}_2]$,[1,11] by reduction carried out in the presence of *N,N,N′,N′*-tetramethylethylenediamine were not successful. Reductions carried out in the presence of 2,2′-bipyridine did lead to products but low solubility precluded characterisation. However characterisable products were obtained when more soluble ligand systems were used. Reduction of $[\{WCl_4(NC_6H_3Pr^i_2\text{-}2,6)\}_2]$[12] in thf (tetrahydrofuran) using 1 equivalent of sodium–mercury amalgam per tungsten atom, in the presence of 4,4′-dimethyl-2,2′-bipyridine (dmbipy), gave $[WCl_3(NC_6H_3Pr^i_2\text{-}2,6)(dmbipy)]$ **1** (Table 1). The complex has a magnetic moment ($\mu_{eff} = 1.50\ \mu_B$) consistent with a d^1 configuration for tungsten but we have been unable to obtain more information about this complex. Recrystallisation from a variety of solvents has so far given crystals which are unsuitable for analysis by X-ray crystallography. The IR spectrum shows only a broadened band near 300 cm^{-1} which does not allow differentiation between *mer* or *fac* trichloro ligands in the two possible isomers **1a** and **1b** depending on the co-ordination mode of the dmbipy nitrogen atoms. Molecular models show no steric preference for **1a** or **1b** so that the broadened W–Cl stretching region may indicate a mixture of isomers.



Isomer a



Isomer b

L–L
1 dmbipy
2 dppe

When the sodium–mercury amalgam reduction of $[\{WCl_4(NC_6H_3Pr^i_2\text{-}2,6)\}_2]$ was carried out in thf with 1,2-bis(diphenylphosphino)ethane (dppe) present, $[WCl_3(NC_6H_3Pr^i_2\text{-}2,6)(dppe)]$ **2** was obtained as a crystalline solid. The complex has a very low magnetic moment ($\mu_{eff} = 1.1\ \mu_B$) and there are three W–Cl stretches near 300 cm^{-1} in the IR spectrum which suggest a *mer* arrangement of the three chloro ligands[13] (isomer **1a**). This was confirmed by X-ray crystallography (Fig. 1, atomic coordinates Table 2), which showed a distorted octahedral array with meridional chloro ligands and the phosphorus atoms of dppe lying *trans* to one chloro

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

Non-SI unit employed: $\mu_B = 9.27 \times 10^{-24}\ J\ T^{-1}$.

ligand and the imido ligand. This ligand geometry is different from that of $[WCl_3(O)(dppe)]$[14] for which EPR studies indicate equatorial phosphorus atoms (*i.e. cis* to the terminal oxo group) and thus *fac* chloro ligands.

Selected bond lengths and angles for complex **2** are contained in Table 3. The W–N, W–Cl(1) and W–Cl(3) bond lengths are not significantly different from those found for the complexes $[WCl_3(NPh)L_2]$ (L = PPh_3[2] or PMe_3[3]). The W–P(2) bond length in complex **2** [2.550(2) Å] is similar to that found for $[WCl_3(NPh)(PMe_3)_2]$ but shorter than that found for $[WCl_3(NPh)(PPh_3)_2]$ [2.590(3) Å].[2] The W–Cl(2) bond length [2.391(2) Å] in **2** is significantly longer than the W–Cl bond lengths for the mutually *trans* chloro ligands [2.373(2) and 2.367(2) Å] when Cl(2) lies *trans* to the P(2) phosphine atom. The main feature of complex **2** is the W–P(1) bond length [2.765(2) Å] which is much longer than the W–P(2) bond [2.550(2) Å]. It is also much longer than the W–P bond length in $[W(C_2Ph)_2(NPh)(PhC_2Ph)(PMe_3)_2]$ [2.727(4) Å][6] where one phosphine ligand also lies *trans* to the imido ligand.

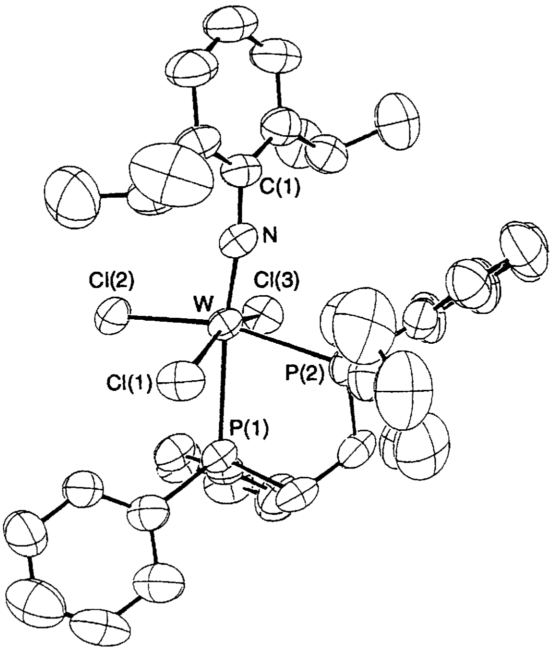


Fig. 1 Molecular structure of complex **2**

The N–W–P(2) bond angle [94.9(2)°] in complex **2** is similar to that found for the $[WCl_3(NPh)L_2]$ complexes[2,3] but the equatorial chloro ligands are pushed further away from the imido ligand in complex **2** where the N–W–Cl bond angles open out by about 6°. The Cl(1)–W–Cl(3) bond angle [158.2(1)°] is thus much smaller than in the other complexes (equivalent angle *ca.* 170°). The isopropyl group C–H protons of the imido ligand lie above and slightly to either side of Cl(1) and Cl(3) and are accommodated without significant twisting of this group. The small twist of the phenylimido ring is facilitated by rotation of one of the P(2) phenyl groups to an angle of nearly 90° with respect to the plane of the other P(2) phenyl group. This rotation does not occur for the P(1) phenyl groups where the molecule is less crowded. The observed structure shows that the interactions are easily accommodated when P(1) co-ordinates *trans* to the imido ligand but the molecule must suffer a long W–P bond. Molecular models indicate little steric relief for the dppe phenyl groups and the imido ligand if both phosphorus atoms co-ordinate in the equatorial plane (isomer **2b**).

Complex $[WCl_3(PhC_2Ph)(dmbipy)]$ **3**, can be prepared by sodium–mercury amalgam reduction of $[\{WCl_4(PhC_2Ph)\}_2]$ in benzene in the presence of dmbipy or by adding dmbipy to $[\{WCl_4(PhC_2Ph)\}_2]$ in thf and allowing a reduced volume solution to stand for several weeks. The former reaction gives rise to a green microcrystalline solid which has a magnetic moment consistent with a d^1 configuration. The complex is slightly soluble but multiple recrystallisations did not yield crystals suitable for X-ray analysis. The far IR spectrum contains W–Cl stretches at 320, 300 and 255 cm^{-1} which are consistent with a *mer* configuration of the three chloro ligands[13] (isomer **3a**). The latter reaction gives rise to an insoluble paramagnetic crystalline solid which has W–Cl stretches at 325 and 225 cm^{-1} consistent with a *fac* arrangement of the three chloride ligands

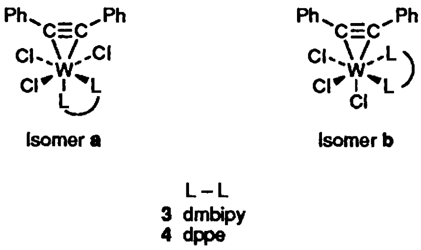


Table 1 Physical data

Complex	Colour	Analysis (%) [a] C	H	N	μ_{eff}/μ_B
1 $[WCl_3(NC_6H_3Pr^i_2\text{-}2,6)(dmbipy)]$	Purple	44.1	4.9	6.3	1.50
		(44.2)	(4.8)	(6.5)	
2 $[WCl_3(NC_6H_3Pr^i_2\text{-}2,6)(dppe)]$	Green	50.5	5.1	1.6	1.10
		(52.8)	(4.8)	(1.6)	
3 $[WCl_3(PhC_2Ph)(dmbipy)]$					
mer Isomer [b]	Green	51.6	3.9	4.1	1.88
		(51.1)	(3.7)	(4.0)	
fac Isomer [c]	Green	49.3	4.0	4.3	1.56
		(48.8)	(3.8)	(4.1)	
4 $[WCl_3(PhC_2Ph)(dppe)]$	Brown	55.1	4.4	—	0.75
		(55.4)	(4.0)	—	
5 $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PhC_2Ph)(dmbipy)]$ [d]	Lime green	58.8	5.0	4.5	—
		(58.7)	(5.1)	(5.1)	
6 $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(CH_2CH_2)(dmbipy)]$ [e]	Red-purple	50.8	5.2	6.5	—
		(50.4)	(4.9)	(6.5)	
7 $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(CO)(dmbipy)]$ [e]	Purple	48.5	5.2	6.6	—
		(48.5)	(4.7)	(6.3)	

[a] Calculated values in parentheses. [b] Contains $\frac{2}{3}$ C_6H_6 solvent molecules. [c] Contains $\frac{1}{2}$ thf solvent molecules. [d] Contains $\frac{2}{7}$ C_7H_8 solvent molecules, supported by NMR spectra. [e] Contains $\frac{1}{3}$ C_6H_6 solvent molecules, supported by NMR spectra.

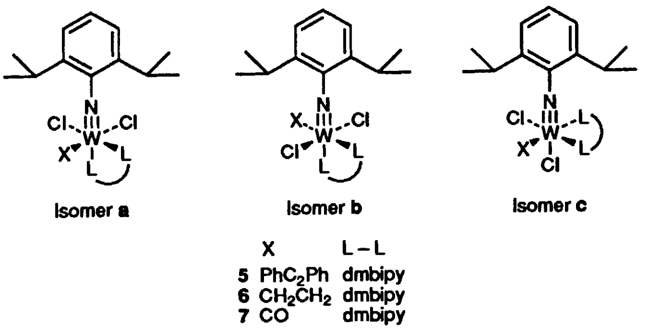
Table 2 Atomic coordinates (× 10^4) for complex **2**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
W	819(1)	1664(1)	1752(1)
Cl(1)	2909(2)	1230(2)	1512(1)
Cl(2)	1771(3)	3099(2)	2103(1)
Cl(3)	−886(2)	1784(2)	2239(1)
P(1)	2103(2)	672(2)	2496(1)
P(2)	57(2)	−63(2)	1581(1)
N	−3(7)	2140(5)	1238(2)
C(1)	−588(9)	2625(6)	849(3)
C(2)	217(10)	3015(7)	542(3)
C(3)	−360(13)	3616(8)	202(4)
C(4)	−1737(13)	3826(9)	157(4)
C(5)	−2548(12)	3371(8)	450(4)
C(6)	−1997(10)	2779(7)	795(3)
C(7)	1685(12)	2792(9)	575(3)
C(8)	2062(15)	2399(14)	122(5)
C(9)	2540(15)	3627(12)	776(7)
C(10)	−2900(10)	2298(8)	1094(4)
C(11)	−3466(14)	3002(10)	1421(5)
C(12)	−4086(14)	1806(10)	803(6)
C(20)	1894(10)	−599(6)	2319(3)
C(40)	513(11)	−792(6)	2100(3)
C(21)	3907(9)	807(7)	2673(3)
C(22)	4672(11)	37(9)	2864(4)
C(23)	6045(14)	202(12)	3017(5)
C(24)	6633(14)	1041(14)	2950(5)
C(25)	5895(13)	1804(11)	2768(6)
C(26)	4530(11)	1672(8)	2617(5)
C(31)	1436(9)	772(6)	3042(3)
C(32)	1581(11)	1640(7)	3270(3)
C(33)	1066(14)	1760(9)	3688(4)
C(34)	399(14)	1020(10)	3866(4)
C(35)	249(12)	160(9)	3646(4)
C(36)	745(10)	26(8)	3236(3)
C(41)	−1724(10)	−308(7)	1429(4)
C(42)	−2574(11)	−189(9)	1755(4)
C(43)	−3904(12)	−387(11)	1648(5)
C(44)	−4426(15)	−718(11)	1215(7)
C(45)	−3558(14)	−818(11)	883(6)
C(46)	−2211(12)	−615(9)	996(4)
C(51)	866(10)	−615(7)	1119(3)
C(52)	1384(12)	−1534(8)	1166(4)
C(53)	1950(15)	−1887(10)	782(6)
C(54)	2034(16)	−1398(13)	394(5)
C(55)	1528(17)	−499(13)	365(4)
C(56)	918(13)	−79(9)	725(4)
Cl(4)	5302(18)	6827(12)	907(7)
Cl(5)	5302(14)	5420(10)	343(5)
C(13)	5823(31)	5607(19)	912(10)

Table 3 Selected bond lengths (Å) and angles (°) for complex **2**

W–N	1.758(7)	W–Cl(3)	2.367(2)
W–Cl(1)	2.373(2)	W–P(1)	2.765(2)
W–Cl(2)	2.391(2)	W–P(2)	2.550(2)
N–W–Cl(1)	100.7(2)	Cl(2)–W–Cl(1)	90.9(1)
N–W–Cl(2)	100.2(2)	Cl(1)–W–P(2)	87.7(1)
N–W–Cl(3)	100.9(2)	Cl(3)–W–P(2)	87.8(1)
N–W–P(2)	94.9(2)	P(1)–W–P(2)	77.7(1)
N–W–P(1)	172.0(2)	P(1)–W–Cl(1)	76.13(8)
Cl(1)–W–Cl(3)	158.2(1)	P(1)–W–Cl(2)	87.20(8)
Cl(2)–W–P(2)	164.8(1)	P(1)–W–Cl(3)	82.12(8)
Cl(2)–W–Cl(3)	87.9(1)	W–N–C(1)	172.9(1)

(isomer **3b**). However an unequivocable isomer assignment cannot be made on the basis of W–Cl stretches alone when low symmetry is inherent in the molecule.[15] Both isomers of complex **3** show a possible ν(C≡C) stretch near 1820 cm^{-1} which is high in comparison to four-electron donor alkyne complexes.[16] If this stretch relates to a two-electron donor alkyne ligand, then it is clear that π loading from the chloro ligands would be needed to maximise the overall electron count.



	X	L–L
5	PhC_2Ph	dmbipy
6	CH_2CH_2	dmbipy
7	CO	dmbipy

Reduction of $[\{WCl_4(PhC_2Ph)\}_2]$ by 1 equivalent-per-metal of sodium–mercury amalgam in the presence of dppe, gave $[WCl_3(PhC_2Ph)(dppe)]$ **4**. The magnetic moment for this complex was again low (μ_{eff} = 0.75 μ_B) while the IR spectrum in the vicinity of 300 cm^{-1} was complicated making isomer characterisation difficult. However by analogy to complex **2** where the crystal structure showed phosphorus *trans* to the imido function, isomer **4a** is expected as the dppe and diphenylacetylene ligands are congested in **4b**. The IR spectrum did not show a band attributable to ν(C≡C) but this complex also requires π loading from the alkyne or chloro ligands to maximise the electron count.

The potential of these d^1 complexes to act as precursors to d^2 complexes containing π-acceptor ligands was assessed. Attempted reductions of the organoimido or diphenylacetylene complexes containing dppe (complexes **2** and **4**) by sodium–mercury amalgam in the presence of diphenylacetylene, ethylene or CO, failed to give characterisable complexes. However the reduction of $[WCl_3(NC_6H_3Pr^i_2\text{-}2,6)(dmbipy)]$ **1** in the presence of diphenylacetylene gave $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PhC_2Ph)(dmbipy)]$ **5** which consistently formed feather-like crystals which were unsuitable for X-ray crystallography. The IR spectrum of this complex showed two W–Cl stretches consistent with mutually *cis* dichloro ligands and in the ^1H NMR spectrum the isopropyl methyl resonances of the imido ligand appeared as two unequal intensity doublets characteristic of an asymmetric molecule.[17] These IR and NMR spectral features indicate that isomers **5a** and **5c** are likely contenders since isomer **5b** is symmetrical and contains mutually *trans* chloro ligands.

Of the two asymmetric complexes isomer **5c** is not preferred on steric grounds. Molecular models indicate that a severe clash between the dmbipy α proton and the adjacent acetylenic carbon would only be relieved if the acetylenic C–C bond rotated significantly out of the equatorial plane which is not the orientation preferred for an organoimido ligand and an alkyne.[5–7] This clash is not present in isomer **5a** where the acetylenic C–C bond lies in the equatorial plane. However for this isomer, the *ortho* hydrogens of one phenyl ring of diphenylacetylene would lie near to the face of the dmbipy rings. This is reflected in the ^1H NMR spectrum where the *ortho* protons of one phenyl ring shift upfield to δ 6.29. The ^1H NMR spectrum also shows there are differences associated with the two dmbipy rings. The two α protons shift downfield to δ 8.72 and 8.78, while there are two resonances for the β hydrogens adjacent to the α ring linkage which suggests the two rings do not have the same planarity.

The ^{13}C-$\{^1H\}$ NMR spectrum also reflects the asymmetric nature of complex **5**. There are two distinct resonances for the α-protonated carbons (C^6 and $C^{6'}$) of the dmbipy ligand (δ 148.24 and 150.74) and separate resonances for the eight remaining carbons. The spectrum clearly shows that the two sides of the diphenylacetylene ligand have different environments, there being four resonances for the two sets of *ortho* and *meta* carbons, one set of which is shifted downfield from the remainder. In addition, there are two resonances for the acetylene *ipso* carbons and two for the acetylenic carbons.

Complex $[WCl_2(NC_6H_3Pr^i{}_2\text{-}2,6)(CH_2CH_2)(dmbipy)]$ **6** was prepared by sodium–mercury amalgam reduction of $[WCl_3(NC_6H_3Pr^i{}_2\text{-}2,6)(dmbipy)]$ in benzene under ethylene. The IR spectrum shows several absorbances in the vicinity of 300 cm^{-1} suggesting a mixture of isomers and the ^{1}H NMR spectrum shows two sets of isopropyl group methyl resonances characteristic of molecular asymmetry. The region containing the ethylene protons, the imido ligand, isopropyl C–H protons and the dmbipy methyl protons, shows a variety of overlapping resonances complicating individual assignments. However, the ^{13}C-{^{1}H} NMR spectrum shows clearly that three isomers are present in the mixture. The major isomer shows a single resonance for the dmbipy methyl groups and also for the imido ligand isopropyl methyl groups but there are two isopropyl C–H carbon resonances. The ethylene carbons appear as a single resonance at δ 58.48 which is downfield of the region found for oxo and organoimido phosphine complexes containing ethylene.[9,18] The shift to lower field may represent a decrease in π back-bonding to the olefin π* orbital[19] where nitrogen makes up the ancillary donor ligands rather than phosphorus. The complex crystallises with solvent present which is very easily lost and this has so far precluded analysis of single crystals by X-ray crystallography. However where the molecule is asymmetric and there is a clash of the ethylene group and the dmbipy α C–H proton, when these ligands lie in the same plane (isomer **6c**), then isomer **6a** is preferred.

Reduction of $[WCl_3(NC_6H_3Pr^i{}_2\text{-}2,6)(dmbipy)]$ by sodium–mercury amalgam under CO gave $[WCl_2(NC_6H_3Pr^i{}_2\text{-}2,6)(CO)(dmbipy)]$ **7** which was only slightly soluble in organic solvents after isolation. The IR spectrum showed at least three CO stretches and there were IR bands near 300 cm^{-1} attributable to both *cis* and *trans* dichloro ligands. However insolubility has precluded further characterisation of this complex.

Conclusion

The results of this work show that the chemistry of organoimido and alkyne complexes is comparable for d^1 complexes of tungsten when the chelate nitrogen or phosphorus donors dmbipy or dppe are used. However the dppe complexes do not give characterisable products on further reduction in the presence of π-acceptor ligands. Solubility is a problem for reductions of the d^1 dmbipy–diphenylacetylene complexes while asymmetric or isomeric products containing π-accceptor ligands result on reduction of the more soluble d^1 dmbipy–organoimido complex.

Experimental

The complex $[\{WCl_4(NC_6H_3Pr^i{}_2\text{-}2,6)\}_2]$ was prepared from $[\{WCl_4(O)\}_x]$ and 2,6-diisopropylphenyl isocyanate in refluxing octane,[12] and $[\{WCl_4(PhC_2Ph)\}_2]$ was prepared by refluxing WCl_6 and diphenylacetylene in CH_2Cl_2 containing tetrachloroethylene.[11] Commercial ethylene and carbon monoxide were used as supplied as were dmbipy and dppe (Aldrich). Light petroleum (b.p. 40–60 °C) and benzene were distilled from sodium wire, thf from sodium benzophenone and dichloromethane from finely ground calcium hydride. All distillations and bench-top manipulations were carried out under N_2 treated to remove traces of oxygen and water. Infrared spectra were recorded on a Perkin-Elmer 597 spectrometer and ^{1}H NMR (400.14 MHz) and ^{13}C-{^{1}H} NMR (100.6 MHz) spectra were obtained on a Bruker AM400 spectrometer. Magnetic susceptibility measurements were made on a Sherwood Scientific magnetic susceptibility balance. Analytical data were obtained by Dr. R. G. Cunninghame and associates, University of Otago, New Zealand.

Preparation of the Complexes.—$[WCl_3(NC_6H_3Pr^i{}_2\text{-}2,6)(dmbipy)]$ **1**. A solution of $[\{WCl_4(NC_6H_3Pr^i{}_2\text{-}2,6)\}_2]$ (2.2 g, 2.2 mmol) in thf (50 cm^3) was added to sodium–mercury amalgam (Na, 0.11 g, 4.8 mmol; Hg, 45 g) under thf (30 cm^3) containing dmbipy (0.82 g, 4.5 mmol) and the mixture was stirred for 2 h with periodic vigorous shaking of the flask. The solution was filtered and the spent amalgam extracted with thf (2 × 20 cm^3). The volatiles were removed from the combined filtrate and extracts, giving a purple crystalline solid (crude yield 2.4 g, 84%) which was recrystallised from thf (30 cm^3). Successive cropping by reducing the solvent volume, gave purple microcrystals. Yield, 2.1 g (73%). IR spectrum: 1610s, 1585w, 1540w, 1375s, 1345m, 1300w, 1280w, 1240w, 1025w, 995w, 925w, 825w, 804w, 760w, 730w, 550w, 518w, 425w and 318s (br) cm^{-1}.

$[WCl_3(NC_6H_3Pr^i{}_2\text{-}2,6)(dppe)]$ **2**. A solution of $[\{WCl_4(NC_6H_3Pr^i{}_2\text{-}2,6)\}_2]$ (0.9 g, 0.9 mmol) in thf (50 cm^3) was reduced with sodium–mercury amalgam (Na, 41 mg, 1.8 mmol; Hg, 40 g) under thf (30 cm^3) containing dppe (0.71 g, 1.8 mmol) using the conditions employed for complex **1**. The solution was filtered, the volatiles removed and the yellow-green solid washed with light petroleum (2 × 50 cm^3). Crude yield, 1.45 g (93%). Recrystallisation of the product from toluene gave the complex as green crystals. Yield: 1.1 g (76%). IR spectrum: 1465s, 1340w, 1307w, 1261w, 1190w, 1159w, 1099m, 1066m, 1026m, 999w, 952w, 868w, 800m, 742s, 604s, 522s, 490m, 473w, 418w, 371w, 354w, 340w, 327m, 318m, 297m and 276w cm^{-1}.

$[WCl_3(PhC_2Ph)(dmbipy)]$ **3**, mer-*isomer*. A solution of $[\{WCl_4(PhC_2Ph)\}_2]$ (0.6 g, 0.6 mmol) was obtained by heating in benzene (60 cm^3) until all the solid had dissolved. The solution was cooled to room temperature and added to sodium–mercury amalgam (Na, 30 mg, 1.3 mmol; Hg, 25 g) under benzene (50 cm^3) containing dmbipy (0.22 g, 1.2 mmol) and the solution was stirred for 2 h with periodic vigorous shaking of the flask. The solution was filtered and the spent amalgam extracted with CH_2Cl_2 (2 × 30 cm^3). The volatiles were removed from the combined filtrate and extracts to give a green solid. Crude yield 0.6 g (77%). The complex was dissolved in hot benzene (60 cm^3) and the volume reduced while keeping the solution hot, to give green microcrystals which lost crystallinity on drying under vacuum. Yield 0.38 g (49%). IR spectrum: 1825w, 1618s, 1555w, 1480s, 1305w, 1280w, 1245w, 1220w, 1070w, 1030m, 945s, 930m, 835m, 770m, 700m, 565w, 525w, 425w, 320m, 300m and 255m cm^{-1}.

$[WCl_3(PhC_2Ph)(dmbipy)]$ **3**, fac-*isomer*. A solution of dmbipy (0.27 g, 1.5 mmol) in thf (20 cm^3) was added to $[\{WCl_4(PhC_2Ph)\}_2]$ (0.7 g, 0.7 mmol) dissolved in thf (50 cm^3) and the mixture was stirred for 2 h. The red-brown solution was filtered, the solvent reduced to *ca.* 10 cm^3, and allowed to stand for 3 w whereupon a green crystalline mass was obtained. The complex was filtered off, washed with thf (2 × 20 cm^3) and dried *in vacuo*. Yield 0.74 g (82%). IR spectrum: 1810w, 1618s, 1570w, 1550w, 1480s, 1305w, 1245w, 1105w, 1070w, 1030m, 950s, 920m, 900w, 835m, 770m, 750m, 700m, 585w, 555w, 520w, 450w, 420w, 325m and 255m cm^{-1}.

$[WCl_3(PhC_2Ph)(dppe)]$ **4**. A solution of $[\{WCl_4(PhC_2Ph)\}_2]$ (1.0 g 1.0 mmol) in thf (50 cm^3) was added to sodium–mercury amalgam (Na, 50 mg, 2.2 mmol) under thf (40 cm^3) containing dppe (0.84 g, 2.1 mmol) and the mixture was stirred, with periodic shaking, for 2 h. The solution was filtered and the volatiles removed to give a gum which solidified on standing under light petroleum giving a brown solid. Yield, 1.5 g (88%). IR spectrum: 1575w, 1555w, 1470s, 1420s, 1320w, 1300w, 1290w, 1260w, 1180w, 1150w, 1120m, 1098s, 1075m, 1040w, 995w, 960w, 930m, 860w, 760w, 740m, 690s, 660m, 560w, 527s, 490w, 470w, 325w, 308m, 303m, 281w, 258w, and 234w cm^{-1}.

$[WCl_2(NC_6H_3Pr^i{}_2\text{-}2,6)(PhC_2Ph)(dmbipy)]$ **5**. A solution of

Table 4 Crystallographic data for complex **2**

Formula	$C_{38}H_{41}Cl_3NP_2W{\cdot}0.5CH_2Cl_2$
M	905.97
Crystal size/mm	0.42 × 0.32 × 0.30
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	10.063(2)
b/Å	13.8976(14)
c/Å	29.298(7)
β/°	96.91(2)
U/Å^3	4067.6
Z	4
D_c/g cm^{-3}	1.479
F(000)	1808
μ/mm^{-1}	3.37
T/K	291
Scan technique	ω
2θ/°	2.0–50.0
h,k,l ranges	−11 to 0, 0–14, −34 to 34
No. of unique reflections	6624
R_{int}	0.027
No. observed reflections [$I > 2\sigma(I)$]	4793
A range	1.00–0.89
Least-squares weights	$1.0[\sigma^2(F^2) + 0.0086\{(F_o{}^2 + 2F_c{}^2)/3\}^2]$
No. of variables	422
Function minimised	$\Sigma w(F_o{}^2 - F_c{}^2)^2$
Goodness of fit on F^2	1.057
R[a] and $wR2$[b]	0.049, 0.130
Max., min. peak heights in final difference map/e Å^{-3}	+1.62, −1.80

[a] $R = \Sigma|F_o - F_c|/\Sigma F_o$. [b] $wR2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{\frac{1}{2}}$.

$[\{WCl_4(NC_6H_3Pr^i{}_2\text{-}2,6)\}_2]$ (0.9 g 0.9 mmol) dissolved in benzene (50 cm^3) was reduced with sodium–mercury amalgam (Na, 45 mg, 2.0 mmol; Hg, 30 g) under benzene (30 cm^3) containing dmbipy (0.35 g, 1.9 mmol) using the conditions employed for complex **1**. The solution containing complex **1** was filtered, diphenylacetylene (0.35 g 1.9 mmol) in benzene (20 cm^3) added, and the mixture was reduced with further sodium–mercury amalgam (Na, 45 mg, 2.0 mmol; Hg, 30 g) for 4 h. The resulting solution was filtered and discarded. The spent amalgam was extracted with CH_2Cl_2 (40 cm^3 and 20 cm^3) and the volatiles removed from the combined extracts to give the complex as a lime green solid. Crude yield 0.6 g (42%). The solid was extracted with boiling toluene (60 cm^3) and the solution allowed to stand giving the complex as feather-like crystals which lost crystallinity on drying *in vacuo*. IR spectrum: 1790w, 1615s, 1590w, 1360s, 1340s, 1300w, 1240w, 1070w, 1020w, 900w, 830w, 802w, 760m, 730m, 695m, 580w, 560w, 518w, 455w, 300m (br), and 230m cm^{-1}. NMR ($CDCl_3$): δ_H 0.98 and 1.21 [br d, (ratio 60:40), 12 H, isopropyl Me], 2.33 (s, 3 H, dmbipy Me), 2.35 (s, $C_6H_5CH_3$), 2.40 (s, 3 H, dmbipy Me), 4.20 (br, 2 H, isopropyl CH), 6.29 [dd, ^3J(HH) 7.8, ^4J(HH) 1.41, 2 H, *o*-H, PhC_2Ph], 6.84–6.94 (m, 3 H, *m*- and *p*-H, $NC_6H_3Pr^i{}_2$-2,6), 7.07–7.20 (m, 2 H, PhC_2Ph), 7.14–7.20 (m, $C_6H_5CH_3$), 7.21–7.27 (m, 4 H, PhC_2Ph), 7.32–7.37 (m, 2 H, PhC_2Ph), 7.61 and 7.75 (s, 2 H, H^3 and $H^{3'}$, dmbipy), 7.86 [dd, ^3J(HH) 8.31, ^4J(HH) 1.25, H^5 and $H^{5'}$, dmbipy], 8.72 [d, ^3J(HH) 5.56, 1 H, H^6 or $H^{6'}$, dmbipy], 8.78 [d, ^3J(HH) 5.87 Hz, 1 H, $H^{6'}$ or H^6, dmbipy]; δ_C 21.30 and 21.45 (2 Me, dmbipy), 24.25 (br, 4 Me, $CHMe_2$), 27.52 (2 CH, $CHMe_2$), 122.53 (*p*-C, $NC_6H_3Pr^i{}_2$-2,6) 122.89 (*m*-C, $NC_6H_3Pr^i{}_2$-2,6), 124.26 and 125.25 (CH), 126.41 (*o*-C, PhC_2Ph), 126.65, 126.75, 126.87 and 127.14 (CH), 127.61 (*m*-C, PhC_2Ph), 127.78 (CH), 127.9 (*m*-C, PhC_2Ph), 128.18 and 128.99 (CH), 131.49 (*o*-C, PhC_2Ph), 138.5 and 139.75 (*ipso*-C, PhC_2Ph), 148.24 (C^6 or $C^{6'}$, dmbipy), 148.65, 149.59, 150.12 and 150.60 (quaternary C), 150.74 [C^6 or $C^{6'}$, dmbipy], 150.80 and 152.75 (quaternary C), 155.86 and 164.39 (acetylenic C, PhC_2Ph).

$[WCl_2(NC_6H_3Pr^i{}_2\text{-}2,6)(CH_2CH_2)(dmbipy)]$ **6**. A solution of $[\{WCl_4(NC_6H_3Pr^i{}_2\text{-}2,6)\}_2]$ (1.0 g, 1.0 mmol) dissolved in benzene (70 cm^3) was reduced with sodium–mercury amalgam (Na, 48 mg, 2.1 mmol; Hg, 35 g) under benzene (30 cm^3) containing dmbipy (0.38 g, 2.1 mmol) as for complex **1**. The solution was filtered, transferred to a pressure bottle containing sodium–mercury amalgam (Na, 48 mg, 2.1 mmol; Hg, 35 g) and stirred vigorously for 2 h, under ethylene gas maintained at 16.5 kPa. The volatiles were removed from the filtered solution to give a red-purple solid, crude yield 0.9 g (71%). Recrystallisation from benzene and reduction of solution volume gave red-purple microcrystals which lost crystallinity on drying under vacuum. Yield 0.6 g (47%). IR spectrum: 1618s, 1360m, 1340m, 1285w, 1270w, 1264w, 1240w, 1165w, 1090m, 1060m, 1020s, 760m, 745m 695w, 550w, 520w, 400w, 295m, 290m, 280w, 250w and 220m cm^{-1}. The ^{1}H NMR contains many overlapping peaks precluding assignment. The ^{13}C-{^{1}H} NMR spectrum indicates the presence of three isomers. The region δ 0–70 contains the following peaks attributable to the major isomer: 20.68 (dmbipy, Me), 22.82 ($CHMe_2$), 25.43 and 26.11 ($CHMe_2$), and 58.48 (CH_2CH_2). A complex with similar spectral characteristics to complex **6** was obtained when $[WCl_3(NC_6H_3Pr^i{}_2\text{-}2,6)(dmbipy)]$ **1** was reduced in benzene with 1 equivalent of sodium–mercury amalgam under ethylene.

$[WCl_2(NC_6H_3Pr^i{}_2\text{-}2,6)(CO)(dmbipy)]$ **7**. A solution of $[WCl_3(NC_6H_3Pr^i{}_2\text{-}2,6)(dmbipy)]$ **1** (0.75 g, 1.2 mmol) in benzene (80 cm^3) was reduced with sodium–mercury amalgam (Na, 30 mg, 1.3 mmol; Hg, 25 g) in a pressure bottle under CO at a constant pressure of 16.5 kPa for 2 h. The solution was filtered, the spent amalgam extracted with hot thf (2 × 50 cm^3) and the volatiles removed from the combined filtrate and extracts. Crude yield 0.5 g (66%). The solid was extracted with boiling benzene (80 cm^3), the hot solution filtered and the volume reduced. On standing, the complex formed purple microcrystals which lost crystallinity on drying under vacuum. Yield 0.25 g, (32%). IR spectrum: 1930s, 1885m (br), 1820m, 1618s, 1540w, 1360m, 1350m, 1340m, 1300w, 1258m, 1240w, 1180w, 1100, 1080m, 1060m (br), 1025s, 930w, 890w, 830m, 820m, 800s, 770m, 754w, 630w, 560w, 522w, 420w, 380w, 318m (br), 280w, and 255w cm^{-1}

Crystallography.—Crystals of complex **2** were grown from dichloromethane and light petroleum solution. Crystal data for the complex are given in Table 4 together with details of the data collection and structure determination. Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). Intensity data collection used ω scans with scan width 0.80 + 0.35 tan θ. Reflections were scanned until $\sigma(I)/I$ was 0.022 or for a maximum of 60 s. The data were corrected for Lorentz and polarisation effects and an absorption correction applied using empirical ψ scans.[20] The structure was solved by conventional Patterson and Fourier-difference techniques and refined by full-matrix least squares on F^2. Non-hydrogen atoms were assigned anisotropic thermal parameters. Hydrogen atoms were included in calculated positions and allowed to ride on the atom to which they were attached with thermal parameters 20% greater. Difference maps indicated the presence of some solvent which has been modelled as a half-weighted dichloromethane molecule. The final difference map contains some residual electron density in the vicinity of the solvent molecule indicative of some disorder in this molecule. Programs for data reduction and absorption corrections were written locally. SHELXS 86[21] was used for initial structure solution and SHELXL 93[22] for refinement.

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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