Preparation and Characterisation of Mononuclear Organoimido Complexes of Tungsten: *X*-Ray Crystal Structures of $[WCl_4(NC_6H_4Me\text{-}p)(thf)]$, $[P(CH_2Ph)Ph_3][WCl_5(NC_6H_4Me\text{-}p)]$, and $[WCl_2(NPh)_2(bipy)]$ †

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Some mononuclear organoimido complexes of W^{VI} and W^{V} have been prepared and the *X*-ray structures of $[WCl_4(NC_6H_4Me\text{-}p)(thf)]$ (thf = tetrahydrofuran) (**1**) and $[P(CH_2Ph)Ph_3][WCl_5(NC_6H_4Me\text{-}p)]$ (**2**) determined. In both species the octahedral W^{VI} centre is strongly bound to the tolylimido group [W$\equiv$N 1.711(7) for (**1**) and 1.709(11) Å for (**2**)] causing a bending down of the four equatorial W–Cl bonds [W–Cl 2.313(4)—2.349(6) Å] and a lengthening of the *trans* bond [W–O 2.237(6), W–Cl 2.464(5) Å]. The ^{14}N and ^{15}N n.m.r. spectra of the ethylimido compounds $[WCl_4(NEt)(thf)]$ and $[P(CH_2Ph)Ph_3][WCl_5(NEt)]$, and the t-butylimido compound $[W(NBu^t)_2(NHBu^t)_2]$ have been obtained. From reactions of the binuclear bis(organoimido) complexes $[\{WCl_2(NR)(NR')(NH_2R')\}_2]$ with neutral ligands [PMe_3 or 2,2′-bipyridyl (bipy)] the mononuclear bis(organoimido) complexes $[WCl_2(NR)(NR')(PMe_3)_2]$ and $[WCl_2(NR)(NR')(bipy)]$ were obtained. The *X*-ray crystal structure of $[WCl_2(NPh)_2(bipy)]$ has been determined and the distorted octahedral structure comprises *cis*-phenylimido groups and *trans*-dichloro ligands with the bipy nitrogens *trans* to the imido nitrogens. The phenylimido ligands are equivalent with mean W$\equiv$N bond lengths of 1.775(14) and 1.782(14) Å and mean W–N–C angles of 165.3(12) and 166.3(12)°.

The organoimido complexes $[\{WCl_4(NR)\}_n]$ (R = alkyl or aryl), which are readily available from the reactions of $WOCl_4$ and organic isocyanates (RNCO),[1–3] are useful starting materials for the synthesis of a range of organoimido tungsten complexes.[1–6] Crystal structure determinations[2] have shown the ethylimido and *p*-tolylimido compounds (R = Et or C_6H_4Me-*p*) to be binuclear (*n* = 2) with unsymmetrical μ-chloro bridges. Presumably the less soluble arylimido compounds are also dimeric. Addition of donor ligands cleaves the chloride bridges giving mononuclear neutral, $[WCl_4(NR)L]$, or anionic, $[WCl_5(NR)]^-$, complexes [R = Ph, C_6H_4Me-*p*, or Et; L = Et_2O, tetrahydrofuran (thf), MeCN, EtCN, or pyridine (py)]. With tertiary amines or phosphines (L′) reduction may occur, giving W^V complexes $[WCl_3(NR)L'_2]$. Further reduction to W^{IV} complexes without loss of the organoimido group can be accomplished using sodium amalgam. The crystal structures of $[WCl_3(NPh)L'_2]$ (L′ = PPh_3 or PMe_3) and $[WCl_2(NPh)(PMe_3)_3]$ have been described.[1,6]

During the course of our work we have been interested in comparing the *trans* influences of organoimido ligands in various tungsten complexes. However, only a few structural determinations of organoimido tungsten compounds have been reported.[1,3,4,6–8] We have now prepared and structurally characterised the thf and chloride adducts of tetrachloro(*p*-tolylimido)tungsten(VI). The corresponding ethylimido complexes are more soluble and we have been able to obtain ^{14}N and ^{15}N n.m.r. chemical shifts for these species as well as for the previously reported bis(t-butylamido)bis(t-butylimido)tungsten(VI) compound $[W(NBu^t)_2(NHBu^t)_2]$.[9] Also we report here the synthesis and characterisation of some mononuclear bis(organoimido)tungsten(VI) complexes $[WCl_2(NR)(NR')(bipy)]$ (bipy = 2,2′-bipyridyl), including the crystal structure of $[WCl_2(NPh)_2(bipy)]$, and $[WCl_2(NPh)(NBu^t)(PMe_3)_2]$ whose structure was deduced from i.r. and n.m.r. (^1H, ^{13}C, ^{31}P) spectra.

Table 1. Selected bond lengths (Å) and angles (°) for $[WCl_4(NC_6H_4Me\text{-}p)(thf)]$ (**1**)

W–Cl(1)	2.323(4)	N–W–Cl(1)	97.1(3)
W–Cl(2)	2.313(4)	N–W–Cl(2)	97.6(3)
W–Cl(3)	2.338(4)	N–W–Cl(3)	93.8(3)
W–Cl(4)	2.328(4)	N–W–Cl(4)	95.0(3)
W–N	1.711(7)	W–N–C	177.4(4)
W–O	2.237(6)	N–W–O	177.8(2)

Results and Discussion

Mono-organoimidotungsten(VI) *Compounds.*—Treatment of $[\{WCl_4(NC_6H_4Me\text{-}p)\}_2]$ with thf gave a green crystalline compound, (**1**). The i.r. spectrum of (**1**) contains bands at 1 005 and 814 cm^{-1} due to tetrahydrofuran and a strong band at 337 cm^{-1} due to ν(W–Cl). Microanalytical results and the ^1H n.m.r. spectrum are consistent with the formulation $[WCl_4(NC_6H_4Me\text{-}p)(thf)]$. Crystals grown by diffusion of hexane into a thf solution of (**1**) were suitable for a single-crystal *X*-ray diffraction study and the structure is shown in Figure 1. Relevant bond distances and angles are given in Table 1. The tungsten atom is almost octahedral, being displaced out of the plane of the four chlorines towards the nitrogen of the imido group. This is consistent with the imido group acting as a linear [WNC 177.4(4)°], four-electron donor, and the short W–N distance [1.711(7) Å] is similar to those found in other 16-electron

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† Tetrachloro(tetrahydrofuran)(*p*-tolylimido)tungsten(VI), benzyltriphenylphosphonium pentachloro(*p*-tolylimido)tungstate(VI), and (2,2′-bipyridyl)dichlorobis(phenylimido)tungsten(VI) respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

organoimidotungsten(VI) complexes.[8] The bond lengths and angles are also very similar to those reported for the molybdenum analogue of (1), $[MoCl_4(NC_6H_4Me\text{-}p)(thf)]$,[10] with the W–O(thf) bond showing some lengthening compared with normal octahedral W^{VI}–O bond lengths.

The anion, $[WCl_5(NC_6H_4Me\text{-}p)]^-$ was obtained as the benzyltriphenylphosphonium salt (2) by treatment of $[WCl_4(NC_6H_4Me\text{-}p)(OEt_2)]$ (prepared *in situ* from $[\{WCl_4(NC_6H_4Me\text{-}p)\}_2]$ and diethyl ether) with one equivalent of $[P(CH_2Ph)Ph_3]Cl$. The i.r. spectrum of (2) contained a very strong band at 322 cm^{-1} and a weak band at 255 cm^{-1} in the region for ν(W–Cl). ^1H N.m.r. and microanalytical results were in agreement with the formulation $[P(CH_2Ph)Ph_3][WCl_5(NC_6H_4Me\text{-}p)]$ and a crystal was selected for a single-crystal *X*-ray structure determination. The structure of (2) is shown in Figure 2 with relevant bond lengths and angles in Table 2. The tungsten atom is again displaced from the plane of the four 'equatorial' chlorines towards the imido nitrogen with a W-N distance of 1.709(11) Å. This molecule clearly displays the *trans*-lengthening influence of the linear *p*-tolylimido group, the average *cis*-equatorial W–Cl distance of 2.33 Å being 0.13 Å shorter than the *trans*-axial W–Cl distance.

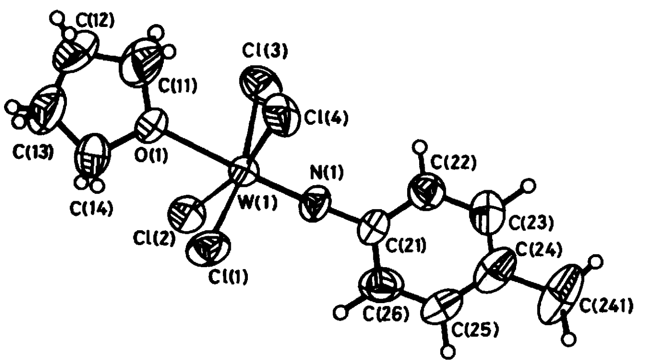


Figure 1. Structure of $[WCl_4(NC_6H_4Me\text{-}p)(thf)]$ (1)

Table 2. Selected bond lengths (Å) and angles (°) for the anion $[WCl_5(NC_6H_4Me\text{-}p)]^-$ of (2)

W–Cl(1)	2.349(6)	N–W–Cl(1)	95.2(5)
W–Cl(2)	2.341(6)	N–W–Cl(2)	94.4(4)
W–Cl(3)	2.317(7)	N–W–Cl(3)	93.8(5)
W–Cl(4)	2.328(6)	N–W–Cl(4)	92.7(5)
W–Cl(5)	2.464(5)	N–W–Cl(5)	176.4(4)
W–N	1.709(11)	W–N–C	173.5(12)

We have also been interested in obtaining ^{14}N or ^{15}N n.m.r. chemical shifts of organoimidotungsten complexes, since they should reflect any change in the bonding mode of the imido group. A change from linear to bent geometry should be accompanied by a decrease in the amount of deshielding, *i.e.* a decrease in the chemical shift of the ^{14}N or ^{15}N nucleus. In order to obtain mononuclear organoimidotungsten compounds which were sufficiently soluble for n.m.r. studies, we prepared the ethylimido complexes $[WCl_4(NEt)(thf)]$[1] (3) and $[P(CH_2Ph)Ph_3][WCl_5(NEt)]$ (4). A saturated solution of (3) in C_6D_6–thf gave a resonance at δ 437.3 in the inverse-gated decoupled ^{15}N spectrum. In the ^{14}N n.m.r. spectrum of this solution after several days, as well as the major peak at δ 437.3 there were also minor peaks at δ 430.0 and 409.0 which were probably due to decomposition products. A saturated solution of (4) in $CDCl_3$ gave ^{15}N and ^{14}N resonances at δ 412.9. Other organoimidotungsten(VI) complexes have been found to have similar medium-field nitrogen chemical shifts (see Table 3).

One tungsten(VI) compound containing both imido and amido ligands, $[W(NBu^t)_2(NHBu^t)_2]$, has been reported.[9] We found two resonances in both the ^{15}N and ^{14}N n.m.r. spectra of this compound. The low-field resonance at δ 365.1 in the ^{15}N spectrum was assigned to the t-butylimido groups and the higher field resonance at δ 143.5 to the t-butylamido groups. Thus the presence of other potential π-donor ligands in $[W(NBu^t)_2(NHBu^t)_2]$ increases the electron density on the t-butylimido nitrogen compared with the ethylimido ligand in (3) and (4). These values for imido and amido ligands compare with

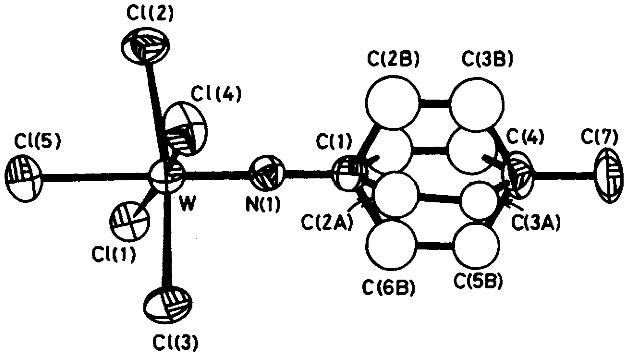


Figure 2. Structure of the anion $[WCl_5(NC_6H_4Me\text{-}p)]^-$ of (2)

Table 3. Nitrogen-14 and ^{15}N chemical shifts for organoimido complexes (dmpe = $Me_2PCH_2CH_2PMe_2$)

Complex	δ (nucleus)[a]	Solvent	Ref.
$[TaCl_3(NPh)(thf)_2]$	347.4 (^{15}N)	thf	*b*
$[TaCl_3(NPh)(PEt_3)_2]$	331.4 (^{15}N)	thf	
$[TaCl(NPh)(dmpe)_2]$	281.4 (^{15}N)	PhCl	
$[TaCl(NPh)(PMe_3)_4]$	282.4 (^{15}N)	thf	
$[WF_4(NMe)(NCMe)]$	379.1 (^{14}N)	MeCN	*c*
$[WF_4(NMe)\{MeC(O)(OEt)\}]$	370.1 (^{14}N)	MeC(O)(OEt)	
$[WF_4(NMe)\{OS(OMe)_2\}]$	370.4 (^{14}N)	$OS(OMe)_2$	
$[WCl_4(NEt)(thf)]$	437.3 (^{14}N, ^{15}N)	C_6D_6–thf	*d*
$[P(CH_2Ph)Ph_3][WCl_5(NEt)]$	412.9 (^{14}N, ^{15}N)	$CDCl_3$	
$[W(NBu^t)_2(NHBu^t)_2]$	365.8, 143 (^{14}N) 365.1, 143.5 (^{15}N)	$C_6D_5CD_3$	
$[\{WCl_2(\mu\text{-}NPh)(NBu^t)(NH_2Bu^t)\}_2]$	404.0 (^{14}N, NBu^t) 52.5 (^{15}N, NH_2Bu^t)	$CDCl_3$	12

[a] δ To low field of NH_4^+ in NH_4NO_3. [b] S. M. Rocklage and R. R. Schrock, *J. Am. Chem. Soc.*, 1982, **104**, 3077. [c] O. R. Chambers, M. E. Harman, D. S. Rycroft, D. W. A. Sharp, and J. M. Winfield, *J. Chem. Res.*, (*M*) 1849, 1977. [d] This work.

Table 4. Physical data for the organomido complexes of tungsten

			Analysis[b] (%)						
Compound[a]	Colour	M.p. (°C)	C	H	N	Cl	I.r. ν(W–Cl)/cm^{-1}	^{1}H N.m.r.[c,d]	^{13}C N.m.r.[d,e,f]
[$WCl_4(NC_6H_4Me$-*p*)(thf)] (**1**)[g]	Green		26.5 (26.3)	3.0 (3.0)	2.8 (2.8)	28.0 (28.2)	337	7.54, 7.21 [4 H, AB, *J*(AB) 8, C_6H_4]; 4.78 [4 H, m, $O(CH_2)_2$]; 3.11 (3 H, s, Me); 2.18 [4 H, m, $O(CH_2)_2$]	
[$P(CH_2Ph)Ph_3$][$WCl_5(NC_6H_4Me$-*p*)]·$0.7CH_2Cl_2$ (**2**)[g]	Green		44.0 (44.7)	3.4 (3.5)	1.6 (1.6)	25.3 (25.8)	322, 255	[h] 7.5 [24 H, m, aromatic]; 4.97 [2 H, d, ^2J(PH) 14, PCH_2]; 3.05 (3 H, s, Me)	
[WCl_4(NEt)(thf)] (**3**)[g]	Yellow							6.12 [2 H, q, ^3J(HH) 7.2, ^3J(WH) 11.1, NCH_2]; 4.38 [4 H, m, $O(CH_2)_2$]; 1.35 [4 H, m, $O(CH_2)_2$]; 1.06 [3 H, t, ^3J(HH) 7.2, Me]	
[$P(CH_2Ph)Ph_3$][WCl_5(NEt)] (**4**)[g]	Orange							7.9—6.9 [20 H, m, Ph]; 7.21 [2 H, q, ^3J(HH) 7.0, ^3J(WH) 11.2, NCH_2]; 4.64 [2 H, d, ^2J(PH) 14, PCH_2]; 1.57 [3 H, t, ^3J(HH) 7.0, Me]	[i] 54.02 (NCH_2); 12.80 (Me)
[$WCl_2(NPh)_2$(bipy)] (**5**)[g]	Red	211 (decomp.)	44.4 (44.5)	3.1 (3.1)	9.2 (9.5)		295 (*trans*)	6.57—8.36 (several m, 16 H, Ph and bipy); 9.31—9.46 (d br, 2 H, α-CH of bipy)	123.1 (*p*-Ph); 123.7 (*o*-Ph); 125.1, 127.3 (β-CH of bipy); 128.6 (*m*-Ph); 140.7 (γ-CH of bipy); 151.3 (*i*-C of bipy); 153.2 (α-CH of bipy); 156.6 (*i*-Ph)
[$WCl_2(NCHMe_2)_2$(bipy)] (**6**)[g]	Yellow	130—133 (decomp.)	35.6 (35.6)	4.3 (4.1)	10.8 (10.8)		302 (*trans*)	1.60 (d, 12 H, Me_2); 5.35 (s, 2 H, NCH); 7.38—7.75 (m, 2 H, γ-CH of bipy); 7.80—8.18 (m, 4 H, β-CH of bipy); 9.48 (d, 2 H, α-CH of bipy)	25.4 (Me_2); 64.5 (NCH); 122.1, 126.1 (β-CH of bipy); 139.4 (γ-CH of bipy); 150.8 (*i*-C of bipy); 153.6 (α-CH of bipy)
[WCl_2(NPh)(NEt)(bipy)]·$\frac{1}{3}C_6H_6$ (**7**)[g]	Red	[a]110 (decomp.)	41.2 (42.0)	4.2 (3.5)	10.3 (9.8)		308 (*trans*)	1.16—1.76 (t, 3 H, Me); 4.92—5.41 (q, 2 H, NCH_2); 6.57—7.82 (several m, 7 H, Ph and γ-CH of bipy); 8.10—8.32 (m, 4 H, β-CH of bipy); 9.52 (d, 2 H, α-CH of bipy)	18.5 (Me); 59.1 (NCH_2); 122.2 (*o,p*-Ph); 123.4, 126.5 (β-CH of bipy); 128.1 (*m*-Ph); 139.8 (γ-CH of bipy); 151.7 (*i*-C of bipy); 153.6 (α-CH of bipy); 156.2 (*i*-Ph)
[WCl_2(NMe)(NBu^t)(bipy)] (**8**)[g]	Yellow	>135 (decomp.)	34.9 (35.3)	3.5 (3.9)	11.1 (11.0)		305 (*trans*)	1.54, 1.58 (2s, 9 H, Me_3); 5.00 (s, 3 H, NMe); 7.25—8.89 (several m, 6 H, γ-CH and β-CH of bipy); 9.43 (d, 2 H, α-CH of bipy)	32.2 (Me_3); 67.8 (NMe); 69.3 (NC); 122.2 (β-CH of bipy); 139.5 (γ-CH of bipy); 150.9 (*i*-C of bipy); 152.9 (α-CH of bipy)
[WCl_2(NPh)(NBu^t)$(PMe_3)_2$] (**9**)[g]	Red	128—130	33.5 (33.8)	5.9 (5.7)	5.5 (4.9)		345, 250 (*cis*)	1.39 (s, 9 H, Me_3); 1.85 [virtual coupling t, 18 H, *J*(PH) = 20, *trans*-PMe_3]; 6.75—7.55 (m, 5 H, Ph)	14.9, 15.9, 17.0 [virtual coupling t, *J*(PC) 42.9, *trans*-PMe_3]; 32.6 (Me_3); 69.4 (NC); 121.7 (*o*-Ph); 124.5 (*p*-Ph); 128.2 (*m*-Ph); 156.9 (*i*-Ph)

[a] Inclusion of solvent molecules supported by n.m.r. spectra. [b] Calculated values given in parentheses. [c] Spectra obtained in $CDCl_3$. [d] br = Broad, m = multiplet, s = singlet, d = doublet, t = triplet, q = quartet; *J* values in Hz. [e] C_6H_6 assignments: *ortho,meta*, tentative (*meta* based on δ 128.5) *para* made from relative peak height. [f] Bipyridyl assignments made by comparison with free ligand. [g] Yields >80%. [h] Spectrum obtained in CD_2Cl_2. [i] Spectrum obtained in $C_6D_6CD_3$.

the co-ordinated t-butylamine ^{15}N resonances in [{$WCl_2(NHBu^t)(NH_2Bu^t)$}$_2$] (δ 66.1)[11] and [{WCl_2(μ-NPh)(NBu^t)(NH_2Bu^t)}$_2$] (δ 52.5)[12] and fit in with the previously observed trend for nitrido, imido, and amine chemical shifts.[13]

In the ^{1}H n.m.r. spectra of ethylimido complexes, (**3**) and (**4**), one noteworthy feature is the presence of ^{183}W–H coupling in the NCH_2– resonances, with $^3J(^{183}WH)$ values of 11.1 and 11.2 Hz respectively. When the 400-MHz ^{1}H n.m.r. spectrum of [$W(NBu^t)_2(NHBu^t)_2$] was examined, the N*H*Bu^t resonance showed coupling to ^{15}N, with a $^1J(^{15}NH)$ value of 70.8 Hz.

In an attempt to obtain a compound containing both oxo and organoimido ligands, as in the trinuclear compound [{W(NPh)(μ-O)$Me_2(PMe_3)$}$_3$],[7] we treated [{WCl_4(NPh)}$_2$] with water and trimethylphosphine. The product of the reaction, however, was shown to be [$WCl_3(NPh)(PMe_3)_2$] which has been prepared and structurally characterised previously.[6] Reduction to W^V also occurred when [{WCl_4(NPh)}$_2$] was treated with bipy in refluxing toluene. The resulting insoluble green compound was formulated as [WCl_3(NPh)(bipy)] on the basis of its i.r. spectrum and the accurate mass determination of

Table 5. Selected bond lengths (Å) and angles (°) for [WCl$_2$(NPh)$_2$(bipy)] (**5**)

	Molecule A	Molecule B
W–Cl(1)	2.386(5)	2.394(5)
W–Cl(2)	2.386(5)	2.384(5)
W–N(1)	1.781(11)	1.783(14)
W–N(2)	1.787(14)	1.762(12)
W–N(3)	2.309(12)	2.328(11)
W–N(4)	2.319(13)	2.311(11)
N(1)–C(11)	1.36(2)	1.36(4)
N(2)–C(21)	1.36(2)	1.38(2)
W–N(1)–C(11)	165.6(12)	165.0(12)
W–N(2)–C(21)	164.4(11)	168.1(12)
N(1)–W–N(2)	103.6(6)	105.0(6)
N(1)–W–N(3)	164.3(5)	162.2(5)
N(1)–W–N(4)	95.2(5)	92.8(5)
N(2)–W–N(3)	91.4(5)	92.4(5)
N(2)–W–N(4)	161.2(5)	162.2(5)
N(3)–W–N(4)	69.8(4)	69.8(4)
Cl(1)–W–Cl(2)	159.5(2)	159.0(1)
Cl(1)–W–N(1)	98.1(4)	96.0(5)
Cl(1)–W–N(2)	98.1(4)	94.9(5)
Cl(1)–W–N(3)	84.1(4)	80.4(3)
Cl(1)–W–N(4)	80.9(3)	83.2(4)
Cl(2)–W–N(1)	93.0(4)	96.8(5)
Cl(2)–W–N(2)	96.0(5)	97.7(5)
Cl(2)–W–N(3)	80.7(3)	81.8(3)
Cl(2)–W–N(4)	81.0(3)	80.3(4)

its molecular ion in the mass spectrum, but microanalytical results suggested that it was impure. The e.s.r. spectrum showed that it was paramagnetic but further analysis of the spectrum was not attempted.

Bis(organoimido)tungsten(VI) *Compounds*.—Treatment of the binuclear bis(organoimido) compounds [{WCl$_2$(NR)(NR′)(NH$_2$R′)$_2$}][12] with bipy gave crystalline products [WCl$_2$(NR)(NR′)(bipy)] (**5**, R = R′ = Ph; **6**, R = R′ = Pr^i; **7**, R = Ph, R′ = Et; **8**, R = Bu^t, R′ = Me) for which analytical and spectroscopic data are given in Table 4.

In the ^{13}C n.m.r. spectra of [WCl$_2$(NPh)$_2$(bipy)] (**5**) and [WCl$_2$(NPh)(NEt)(bipy)] (**7**) the *ipso*-carbon resonances of the phenylimido ligands appear at δ 156.6 and 156.2 respectively, compared with the bridging and terminal ligand *ipso*-carbons at δ 163.4 and 145.6 in the binuclear complex [{WCl$_2$(NPh)(μ-NPh)(NH$_2$Ph)}$_2$][12] suggesting that in the mononuclear species the organoimido groups may not be linear. In the i.r. spectrum a single W–Cl stretching vibration at *ca.* 310 cm^{-1} in the bipy complexes suggested a *trans*-dichloro configuration. The configuration of the organoimido ligands in the mononuclear [WCl$_2$(NR)(NR′)(bipy)] complexes is especially interesting because the 18-electron configuration requires one linear (four-electron donor) and one 'bent' (two-electron donor) imido ligand. In view of the results of the ^{13}C n.m.r., which suggests equivalent ligands but does not rule out the one-linear/one-bent configuration because the system may be fluxional, we determined the *X*-ray crystal structure of [WCl$_2$(NPh)$_2$(bipy)] (**5**). This confirmed that the complex is mononuclear and gave an asymmetric unit containing crystallographically distinct molecules A and B. In each molecule the tungsten atom has a distorted octahedral geometry comprising two *cis*-oriented phenylimido groups, two *trans*-chloro ligands, and the nitrogens of the bipy ligand. The overall geometry of molecule A is depicted in Figure 3 and the bond lengths and bond angles for A and B are given in Table 5.

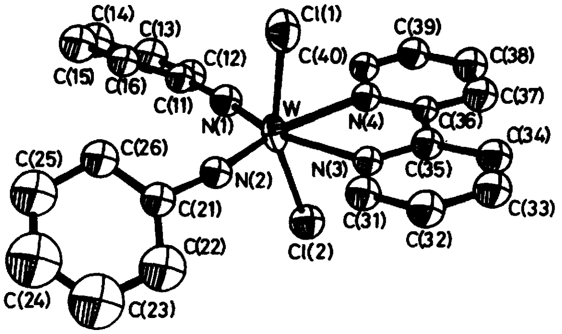


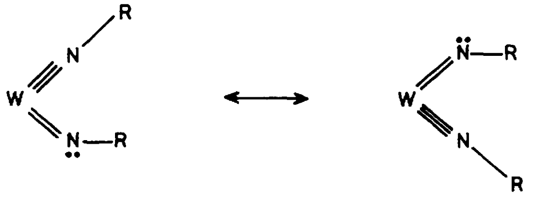
Figure 3. Structure of [WCl$_2$(NPh)$_2$(bipy)] (**5**)

The W–N(1) and W–N(2) bond lengths of 1.781(11) and 1.787(14) Å in molecule A and 1.783(14) and 1.762(12) Å in molecule B are not significantly different but they are longer than predicted for a W≡N triple bond involving a four-electron donor nitrogen (1.71 Å)[8] and lie slightly outside the range observed [1.67(3)—1.757(12) Å][1,4,8,15] for terminal mono-organoimido complexes of tungsten(VI). However, they are shorter than the bond length [1.890(6) Å] found in the bridging phenylimido ligand acting as a two-electron donor in [{WCl$_2$(μ-NPh)(NBu^t)(NH$_2$Bu^t)}$_2$].[4] The mean W–N(1)–C(11) and W–N(2)–C(21) bond angles of 165.3 and 166.3 ° are significantly smaller than those observed for terminal organoimido ligands bonded to tungsten(VI) (171–174 °)[15] but not sufficiently to suggest that they are behaving as two-electron donors. Tungsten–chlorine bond lengths lie within the range observed for other complexes of tungsten(VI)[15,16] while the W–N(bipy) bond lengths are similar to those found in [MoO$_2$Me$_2$(bipy)][17] where a small lengthening occurs due to the strong *trans* influence of the terminal oxo ligands.

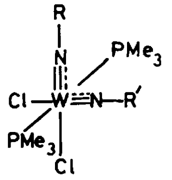
Distortion away from regular octahedral geometry in the molecule is shown by the wide N(1)–W–N(2) bond angle (mean 104.3°) and a decrease in the Cl(1)–W–Cl(2) bond angle (mean 159.2°) whereby the chloro ligands are bent away from the *cis*-bis(imido) ligands. These features are similarly found in the related *cis*-dioxo complexes, [MoO$_2$X$_2$(bipy)] (X = Br or Me).[17] The mean non-bonding N(1) ··· N(2) distance is 2.81 Å which is less than twice the van der Waals radius of nitrogen (1.5 Å). The bite angle made by the bipy nitrogens (mean 69.8°) is not significantly different from that found in other bipy complexes.[14,17]

Whereas the phenylimido nitrogen atoms are bent away from each other the sense of the bend at N(1) and N(2) is such that the *ipso*-carbon atoms C(11) and C(21) are drawn inwards towards each other, apparently to relieve strain imposed by an otherwise close contact of the bipy α-hydrogens with C(11) and C(21). The phenyl rings are twisted from the N(1)N(2)N(3)N(4) plane, again to minimise interaction between *ortho*-hydrogens on the phenyl and bipy rings. The imido nitrogens are essentially coplanar with the nitrogens of the bipy ligand, the maximum displacement being 0.03 Å from the plane of best fit for N(1)—N(4). The rings of each bipy ligand are twisted relative to each other by angles of 5.2 and 7.2° for molecules A and B respectively.

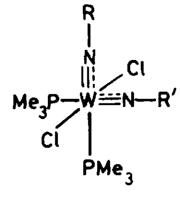
Several features arise from this crystal structure determination which relate to the bonding in *cis*-bis(imido) complexes. An 18-electron count for [WCl$_2$(NPh)$_2$(bipy)] requires the two imido ligands to donate collectively a total of six electrons. Organoimido ligands can act formally as four- or two-electron donors[8] but the two-electron donor formalism has yet to be observed for a terminal imido ligand. For example, the structure determined for [Mo(NPh)$_2$(S$_2$CNEt$_2$)$_2$] at −130 °C[18] showed a Mo–N bond length of 1.789(4) Å and a Mo–N–C bond angle of 139.4(4)° but this M–N bond length lies between those of the



(a) (b)



(c)



(d)

terminal butylimido and bridging phenylimido ligands in $[\{WCl_2(\mu\text{-}NPh)(NBu^t)(NH_2Bu^t)\}_2]$[W–N 1.736(7) and 1.890(6) Å][12] where the phenylimido nitrogen lone pair donates to the adjacent tungsten atom. The similarity of bond lengths and angles in $[WCl_2(NPh)_2(bipy)]$ [average values 1.778(12) Å and 165.8°] indicates that the six electrons are essentially delocalised over the two imido W–N bonds. If bond orders of *ca.* 2.5 are apparent, the structure is thus best represented by something between the two canonical forms (a) and (b).

The W–Cl bond lengths [mean values 2.390(5) and 2.385(5) Å] indicate that the chloro ligands participate in minimal π-bonding to the metal which contrasts with the case of WCl_6 (W–Cl bond length 2.24)[19] where W–Cl π-bonding is neccessary to obtain an 18-electron count. In solution, the spread of electrons over the imido N–W–N system is clearly shown by the phenyl *ipso*-carbon resonance at δ 156.6 which is intermediate between those observed for the essentially four- and two-electron donors in $[\{WCl_2(NPh)(\mu\text{-}NPh)(NH_2Ph)\}_2]$.[12] It is noteworthy that in $[WCl_2(NPh)_2(bipy)]$ the phenylimido ligands are *trans* to the bipy nitrogens which can act only as very weak π donors and in principle could actually be π acceptors using π* antibonding molecular orbitals.

The structural implications also indicate why *trans*-dichloro ligands are found in the complex. In d^0 complexes only lone-pair donation from a ligand has been observed *trans* to a single terminal organoimido four-electron donor[3,7,8,15] while for the bridging two-electron donor in $[\{WCl_2(\mu\text{-}NPh)(NBu^t)(NH_2Bu^t)\}_2]$, chlorine binds *trans* but is subject to a *trans* lengthening.[4,12] In the limiting case where both imido functions may act as four-electron donors in $[WCl_2(NPh)_2(bipy)]$, chloro ligands *trans* to either imido function will not be preferred.

In the bis(isopropylimido) complex (**6**) the ^{13}C resonance of the α-carbons is at δ 64.5 which is close to that observed (δ 64.8) for the same ligands in the dimer $[\{WCl_2(NPr^i)_2(NH_2Pr^i)\}_2]$ where it is presumed that one isopropylimide is linear and the other bridging.[12]

Among the bipy complexes isolated was $[WCl_2(NPh)(NCOMe)(bipy)]$ which was obtained by treating $[\{WCl_4(NPh)\}_2]$ with $Me_3SiNHCOMe$ followed by the addition of bipy. Attempts to prepare the alkoxo derivatives $[W(NR)(NR')(OEt)_2(bipy)]$ to study the effects of the potentially π-donating alkoxo ligands[20] were less successful. Reaction of $[WCl_2(NR)(NR')(bipy)]$ complexes with $EtOH–NH_2Bu^t$[3] or LiOEt failed to produce tractable products but the reaction of $[\{WCl_2(NPh)(OEt)_2\}_2]$ with $Me_3SiNHBu^t$ gave a product whose ^1H and ^{13}C n.m.r. spectra indicated the presence of t-butylimido and t-butylamine groups and which upon addition of bipy gave a non-crystalline complex $[W(NPh)(NBu^t)(OEt)_2(bipy)]$ that appeared from its spectra to contain a mixture of isomers.

From the reaction of $[\{WCl_2(\mu\text{-}NPh)(NBu^t)(NH_2Bu^t)\}_2]$ with PMe_3 in light petroleum a non-crystalline product, $[WCl_2(NPh)(NBu^t)(PMe_3)_2]$ (**9**), was obtained in which the phenylimido *ipso*-carbon resonance appeared at δ 156.9 but the quaternary carbon of the t-butylimido group showed no change from the parent dimer. The PMe_3 methyl groups gave triplet resonances in both ^1H and ^{13}C n.m.r. spectra suggesting a *trans* configuration of phosphines as in (c), although there remained the possibility that accidental overlapping of the two doublets for the *cis* configuration (d) could produce a pseudo-triplet.[21] However, the ^{31}P n.m.r. spectrum showed a singlet at δ −9.89 with ^{183}W satellites [*J*(WP) 316 Hz] thus showing that the PMe_3 ligands are in the *trans* configuration (c). The i.r. spectrum contained bands at 345 and 250 cm^{-1} which could well be due to *cis*-WCl_2 stretching vibrations. Attempts to grow a single crystal of (**9**) have so far proved unsuccessful.

Experimental

Preparations and manipulations were carried out under dry, oxygen-free nitrogen using standard Schlenk-tube techniques. Hydrocarbon and ether solvents were distilled from sodium diphenylketyl or sodium dihydronaphthylide and stored over 4 Å molecular sieves. Dichloromethane was distilled from P_4O_{10} and stored over 4Å molecular sieves. The imido complexes $[\{WCl_4(NR)\}_2]$ were prepared from $WOCl_4$ and RNCO (R = Ph,[1] C_6H_4Me-*p*, or Et); $WOCl_4$ was prepared from WO_3 and $SOCl_2$[22] and sublimed *in vacuo*; $[W(NBu^t)_2(NHBu^t)_2]$ was prepared from WCl_6 and NH_2Bu^t.[9] Trimethylphosphine was prepared by a literature method.[23] Infrared spectra were obtained from Nujol mulls between CsI plates and recorded on Perkin-Elmer 577 or 597 spectrometers. N.m.r. spectra were recorded on Bruker WP-80 and WH-400 or JEOL FX60 spectrometers. Elemental analyses were carried out either at University College London, Microanalytical Department or by Dr. A. C. Campbell and associates at the University of Otago, New Zealand.

*Tetrachloro(tetrahydrofuran)(*p*-tolylimido)tungsten*(VI), (**1**).—The complex $[\{WCl_4(C_6H_4Me\text{-}p)\}_2]$ (1.41 g, 3.30 mmol) was dissolved in thf (15 cm^3) with heating. The solvent was removed under reduced pressure to give a quantitative yield of the green crystalline adduct (**1**). I.r.: 1 588s, 1 365w, 1 355m, 1 308w, 1 292w, 1 261w, 1 216w, 1 175m, 1 118w, 1 005m, 945w, 830w, 814s, 721w, 533w, 436m, 378m, 364s, 337s, 330 (sh), 281w, 260w cm^{-1}.

*Benzyltriphenylphosphonium Pentachloro(*p*-tolylimido)tungstate*(VI), (**2**).—The complex $[\{WCl_4(C_6H_4Me\text{-}p)\}_2]$ (3.07 g, 7.13 mmol) was dissolved in diethyl ether (70 cm^3) and the solvent removed under reduced pressure. The diethyl ether adduct was dissolved in dichloromethane (30 cm^3) and $[P(CH_2Ph)Ph_3]Cl$ (2.80 g, 7.20 mmol) added with stirring. The volume of the deep green solution was reduced to *ca.* 15 cm^3 and hexane (30 cm^3) added slowly with stirring. The green, crystalline precipitate was filtered off, washed with hexane, and pumped to dryness. Yield 5.18 g, 89%. Crystals suitable for a single-crystal *X*-ray diffraction study were obtained by slow diffusion of a hexane layer into a dichloromethane solution of (**2**). I.r.: 3 031w, 1 732w, 1 590w, 1 486w, 1 444m, 1 265w, 1 191w, 1 171w, 1 167w, 1 113s, 1 106 (sh), 1 074w, 1 019w, 1 000m, 975w, 930w, 846w, 836 (sh), 825m, 770m, 753 (sh), 749s, 745 (sh), 723s, 705m, 692s, 653w, 586m, 581 (sh), 576s, 570s, 500s, 444m, 361m, 322vs, 255m cm^{-1}.

Tetrachloro(ethylimido)(tetrahydrofuran)tungsten(VI), (**3**).—This compound was prepared *in situ* by dissolving $[\{WCl_4(NEt)\}_2]$[1] in thf and removing the solvent under reduced pressure. The residue was then dissolved in the appropriate deuteriated solvent for n.m.r. studies (data in Table 4).

Benzyltriphenylphosphonium Pentachloro(ethylimido)tungstate(VI), (**4**).—A mixture of $[\{WCl_4(NEt)\}_2]$ (2.50 g, 3.29 mmol) and $[P(CH_2Ph)Ph_3]Cl$ (2.56 g, 6.58 mmol) was stirred in dichloromethane (20 cm^3) for 30 min. Slow removal of the solvent under reduced pressure gave an orange crystalline product which was used without further purification for n.m.r. studies (data in Table 4).

Trichloro(phenylimido)bis(trimethylphosphine)tungsten(V).[6]—Water (45 μl, 2.5 mmol) was added to $[\{WCl_4(NPh)\}_2]$ (0.97 g, 2.33 mmol) in toluene (20 cm^3) with stirring. The mixture was frozen in liquid nitrogen and PMe_3 (7.2 mmol) was condensed into the flask from a calibrated gas manifold. The mixture was warmed to *ca.* 25 °C and stirred for 16 h. The green-brown solution was filtered from a pale green solid and the solvent removed under reduced pressure to give a yellow-brown crystalline solid (0.80 g) which was recrystallised from toluene–hexane (Found: C, 27.2; H, 4.15; Cl, 20.2; N, 2.75. $C_{12}H_{23}Cl_3NP_2W$ requires C, 27.0; H, 4.35, Cl 19.95; N, 2.65%). I.r. 3 080w, 3 050w, 1 580w, 1 478m, 1 446m, 1 425w, 1 420w, 1 416m, 1 354m, 1 310w, 1 305w, 1 286m, 1 170w, 1 106br w, 1 070w, 1 023w, 1 008w, 990w, 952vs, 926w, 860w, 850w, 781s, 750m, 695m, 674w, 555w, 546w, 386w, 316w, 299s, 290 (sh), 282w, 247w cm^{-1}.

(2,2′-*Bipyridyl)trichloro(phenylimido)tungsten*(V).—A mixture of $[\{WCl_4(NPh)\}_2]$ (1.17 g, 2.81 mmol) and bipy (0.48 g, 3.09 mmol) in toluene (40 cm^3) was heated to reflux for 6 h and stirred for a further 16 h at 25 °C. A green solid was filtered off from the brown-green solution, washed with toluene and dried *in vacuo* (1.32 g) (Found: C, 32.15; H, 2.30; Cl, 24.05; N, 7.05%; M^+, 535.970 456. $C_{16}H_{13}Cl_3N_3W$ requires C, 35.75; H, 2.45; Cl, 19.8; N, 7.80%; M^+, 535.968 238). I.r.: 3 145w, 3 115w, 3 065w, 1 627w, 1 617w, 1 599m, 1 585w, 1 525w, 1 356w, 1 323w, 1 319w, 1 314w, 1 280w, 1 220w, 1 177w, 1 159w, 1 065w, 1 022w, 990w, 915w, 850 (sh), 840s, 768vs, 760s, 729w, 725w, 684w, 561w, 393w, 356w, 317s br, 280w, 252w cm^{-1}.

(2,2′-*Bipyridyl)dichlorobis(phenylimido)tungsten*(VI), (**5**).—2,2′-Bipyridyl (0.14 g, 0.90 mmol) in dichloromethane (30 cm^3) was added to $[\{WCl_2(NPh)_2(NH_2Ph)\}_2]$[12] (0.46 g, 0.43 mmol) in dichloromethane (30 cm^3) and the mixture stirred for 3 h. The red solution was filtered and the solvent removed to give a red crystalline solid which was dissolved in chloroform (30 cm^3), the solution filtered and the volume reduced to *ca.* 10 cm^3. On standing at −20 °C the complex formed as dark red crystals which were filtered off, washed with diethyl ether (10 cm^3), and dried *in vacuo*. I.r.: 1 595s, 1 580m, 1 570s, 1 560m, 1 540m, 1 530w, 1 520w, 1 510w, 1 330s, 1 300s, 1 275s, 1 265w, 1 245w, 1 215w, 1 120w, 1 105m, 1 065s, 1 045w, 1 020s, 1 000s, 985m, 975s, 905m, 900s, 825m, 800m, 790w, 760s, 730s, 670w, 650s, 630m, 620m, 560m, 550m, 540m, 530m, 510w, 480s, 460w, 445w, 410m, 395m, 370m, 365w, 350s, 330s, 325w, 295s, 270m cm^{-1}.

(2,2′-*Bipyridyl)dichlorobis(isopropylimido)tungsten*(VI), (**6**).—2,2′-Bipyridyl (0.56 g, 3.6 mmol) in dichloromethane (30 cm^3) was added to $[\{WCl_2(NPr^i)_2(NH_2Pr^i)\}_2]$[12] (1.51 g, 1.75 mmol) in dichloromethane (40 cm^3) and the mixture was stirred for 3 h followed by refluxing for 1 h. The orange solution was filtered and the solvent volume reduced to *ca.* 10 cm^3. On standing, orange crystals of the complex were formed which were filtered off and washed with light petroleum (10 cm^3). On drying *in vacuo* the product lost crystallinity, giving a yellow solid. I.r.: 1 585s, 1 560s, 1 535m, 1 510w, 1 500w, 1 280s, 1 230s, 1 210m, 1 140m, 1 110m, 1 105s, 1 095s, 1 065m, 1 055m, 1 035w, 1 015m, 1 010s, 925w, 890w, 880w, 850m, 800w, 760s, 650s, 630s, 610s, 605m, 550s, 525s, 500w, 460m, 440s, 410s, 355m, 345s, 320w, 302s, 290m, 275m, 265m cm^{-1}.

Table 6. Crystal data and details of structure analysis for compounds (**1**), (**2**), and (**5**)

Compound	(**1**)	(**2**)	(**5**)
	$C_{11}H_{15}Cl_4NW$	$[C_{22}H_{22}P][C_7H_7Cl_5W]\cdot 0.5CH_2Cl_2$	$C_{22}H_{18}Cl_6N_4W$
M	498.88	862.10	593.15
Crystal system	Monoclinic	Monoclinic	Triclinic
a/Å	6.986(6)	17.756(6)	14.616(6)
b/Å	17.954(5)	20.207(4)	17.778(6)
c/Å	12.915(5)	10.071(2)	8.532(2)
α/°	90	90	94.71(2)
β/°	96.90(5)	88.49(2)	100.41(3)
γ/°	90	90	84.31(3)
U/Å^3	1 608.4	3 612.2	2 165.1
Space group	$P2_1/n$	$P2_1/a$	$P\bar{1}$
Z	4	4	4
D_c/g cm^{-3}	2.06	1.58	1.82
μ/cm^{-1}	74.9	37.8	64.2
F(000)	952	1 692	1 144
ω scan width/°	a	a	a
$\theta_{min.}$, $\theta_{max.}$/°	2.0, 27.0	1.5, 27.0	2.0, 22.0
Total data	4 034	8 359	4 481
Total unique	3 497	7 880	3 357
Total observed	2 707	4 272	3 357
$[I > n\sigma(I)]$	(n = 1.5)	(n = 1.5)	(n = 3.0)
No. of parameters	157	373	263
Weighting scheme coefficient g[b]	0.0003	0.0003	0.003
Final R[c]	0.0335	0.0644	0.048
Final R'[d]	0.0325	0.0553	0.051

[a] $(0.8 + 0.35 \tan \theta)°$. [b] $w = [\sigma^2(F_o) + gF_o^2]^{-1}$. [c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $R' = \Sigma w^{\frac{1}{2}}||F_o| - |F_c||/\Sigma w^{\frac{1}{2}}|F_o|$.

(2,2′-*Bipyridyl)diethoxy(phenylimido)(t-butylimido)tungsten*(VI).—A solution of $Me_3SiNHBu^t$ (0.8 cm^3, 4.1 mmol) in benzene (30 cm^3) was added to $[\{WCl_2(NPh)(OEt)_2\}_2]$[24] (0.9 g, 1.0 mmol) in benzene (30 cm^3) and the mixture was stirred for 12 h. The red solution was filtered and the solvent removed to give a red gum which failed to solidify. ^1H N.m.r. ($CDCl_3$): δ 1.1—1.2 (m, Me), 4.3—5.2 (m, CH_2), 6.5—7.2 (m, Ph). ^{13}C N.m.r. ($CDCl_3$): δ 18.93, ($OCH_2\mathit{C}H_3$); 30.77, 31.75, 32.53 ($\mathit{C}Me_3$); 53.14, 54.54, 55.06 ($NH_2\mathit{C}Me_3$); 68.70, 69.12 ($N\mathit{C}Me_3$); 72.69, 73.18 ($O\mathit{C}H_2CH_3$); 121.19, 123.43, 123.72, 127.69, 128.73 (*o*-, *m*-, *p*-Ph); 151.22, 154.0, 156.50, 158.27, 166.67 (*i*-Ph).

The red gum was dissolved in light petroleum (30 cm^3) and a solution of 2,2′-bipyridyl (0.3 g) dissolved in light petroleum (30 cm^3) was added. The mixture was allowed to stand for several days whereupon the complex formed as a red-brown solid (Found: C, 46.1; H, 5.8, N; 4.2. $C_{24}H_{32}N_4O_2W$ requires C, 48.6; H, 5.4; N, 9.5%). I.r.: 1 595m, 1 575s, 1 470s, 1 325s, 1 305s, 1 248s, 1 210w, 1 160w, 1 150w, 1 090m, 1 050s, 1 018m, 995m, 970m, 890m, 755s, 730m, 720w, 690m, 650w, 590w, 550w, 520w, 485w, 415w, 340w, 290w cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ 0.8—1.75 (several m, 15 H, Me and Bu^t); 4.18—4.80 and 4.72—5.30 (m, 4 H, OCH_2); 6.50—7.40 (m, 7 H, Ph and γ-CH of bipy); 7.60—8.32 (m, 4 H, β-CH of bipy); 9.35 (d, 2 H, α-CH of bipy). ^{13}C

Table 7. Fractional atomic co-ordinates (× 10^4) for (**1**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W(1)	1 680	1 359	−1 992	C(14)	1 169(13)	1 678(9)	10 461(7)
Cl(1)	3 514(3)	2 375(1)	8 649(1)	N(1)	2 700(8)	1 252(3)	6 877(4)
Cl(2)	3 725(3)	574(1)	9 042(1)	C(241)	5 544(13)	867(5)	2 991(6)
Cl(3)	−432(3)	359(1)	7 658(1)	C(21)	3 431(5)	1 172(2)	5 949(2)
Cl(4)	−743(3)	2 161(1)	7 290(1)	C(22)	2 171(5)	1 231(2)	5 029(2)
O(1)	239(6)	1 488(2)	9 453(3)	C(23)	2 854(5)	1 130(2)	4 067(2)
C(11)	−1 697(12)	1 447(10)	9 545(8)	C(24)	4 797(5)	970(2)	4 025(2)
C(12)	−2 059(11)	1 583(6)	10 605(6)	C(25)	6 057(5)	911(2)	4 945(2)
C(13)	−223(12)	1 665(6)	11 183(6)	C(26)	5 374(5)	1 012(2)	5 907(2)

Table 8. Fractional atomic co-ordinates (× 10^4) for (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W(1)	2 706	4 582	3 029(1)	C(31)	5 820(8)	2 096(6)	4 327(17)
Cl(1)	2 795(2)	3 751(1)	4 649(3)	C(32)	6 388(8)	2 532(8)	3 986(19)
Cl(2)	2 650(2)	3 746(2)	1 424(3)	C(33)	6 278(10)	3 171(8)	4 196(19)
Cl(3)	2 586(2)	5 355(2)	4 720(4)	C(34)	5 593(13)	3 396(8)	4 720(24)
Cl(4)	2 439(2)	5 375(2)	1 431(4)	C(35)	5 023(9)	2 965(7)	5 089(22)
Cl(5)	1 325(2)	4 488(2)	3 249(4)	C(40)	4 786(6)	922(5)	5 796(11)
N(1)	3 657(5)	4 695(4)	2 834(9)	C(41)	5 192(7)	946(5)	7 103(15)
C(1)	4 405(6)	4 858(7)	2 626(12)	C(42)	5 955(7)	1 034(5)	7 106(14)
C(4)	5 922(7)	5 205(7)	2 233(12)	C(43)	6 310(8)	1 028(8)	8 337(18)
C(7)	6 736(8)	5 412(9)	2 014(16)	C(44)	5 902(10)	906(8)	9 471(17)
				C(45)	5 134(9)	843(9)	9 453(15)
P(1)	4 412(2)	1 714(1)	5 242(3)	C(46)	4 792(7)	841(6)	8 274(14)
C(10)	3 779(6)	2 059(5)	6 481(11)				
C(11)	3 027(7)	2 012(7)	6 342(13)	C(2B)	4 809(16)	4 629(18)	1 513(24)
C(12)	2 519(8)	2 265(9)	7 339(16)	C(3B)	5 580(17)	4 773(16)	1 360(32)
C(13)	2 791(10)	2 586(7)	8 387(14)	C(5B)	5 580(14)	5 278(14)	3 479(19)
C(14)	3 540(12)	2 629(9)	8 505(17)	C(6B)	4 835(14)	5 079(16)	3 684(23)
C(15)	4 055(9)	2 349(8)	7 534(15)	C(2A)	4 593(17)	5 515(9)	2 395(36)
C(20)	3 917(6)	1 577(5)	3 732(10)	C(3A)	5 356(14)	5 678(14)	2 297(43)
C(21)	3 897(7)	954(6)	3 138(11)	C(5A)	5 714(17)	4 545(10)	2 398(41)
C(22)	3 510(8)	869(7)	1 992(13)	C(6A)	4 960(14)	4 372(13)	2 640(37)
C(23)	3 157(7)	1 392(7)	1 393(12)				
C(24)	3 170(7)	1 999(7)	1 989(14)	Cl(10)	4 984(6)	2 528(5)	1 157(10)
C(25)	3 554(7)	2 093(6)	3 155(12)	Cl(11)	5 934(8)	3 133(7)	−441(14)
C(30)	5 148(6)	2 297(5)	4 880(12)	C(100)	5 874(17)	2 528(15)	608(31)

N.m.r. ($CDCl_3$): δ 19.1 (Me); 32.8 (Bu^t); 71.6 (NC); 73.2 (OCH_2); 122.7 (β-CH of bipy); 122.9 (*p*-Ph); 123.7 (*o*-Ph); 126.5 (β-CH of bipy); 128.1 (*m*-Ph); 140.0 (γ-CH of bipy); 150.9 (α-CH of bipy); 152.1 (*i*-C of bipy); 156.9 (*i*-Ph).

(*Acetylimido*)(*2,2′-bipyridyl*)*dichloro*(*phenylimido*)*tungsten*(VI).—A solution of $Me_3SiNHCOMe$ (0.63 g, 4.8 mmol) in benzene (30 cm^3) was added slowly to $[\{WCl_4(NPh)\}_2]$ (1.0 g, 2.4 mmol) suspended in benzene and the mixture was stirred for 14 h. The yellow-brown solution was filtered and the solvent removed to yield a dark brown flaky solid. I.r.: 3 075w, 2 560m, 2 460w, 2 400w, 2 350w, 1 720m, 1 700m, 1 680m, 1 630s, 1 530s, 1 310w, 845w, 800m, 740m, 710w, 680m, 520w, 500w, 470s, 400s, 340s, 320w, 270m cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ 2.10 (s, 6 H, 2 Me); 6.70—8.0 (m, 5 H, Ph); 8.85 (s br, 2 H, NH_2).

The brown solid (0.3 g) was dissolved in dichloromethane (30 cm^3) and 2,2-bipyridyl (0.11 g) in dichloromethane (20 cm^3) was added to it. The mixture was stirred for 14 h, during which time the complex was deposited as a brown precipitate. The product was filtered off, washed with dichloromethane (2 cm^3) and dried *in vacuo* (Found: C, 33.5; H, 3.0; N, 7.3. $C_{18}H_{16}Cl_2N_4OW$ requires C, 33.4; H, 2.8; N, 7.8%). I.r.: 2 675w, 2 600w, 1 976w, 1 650w, 1 605m, 1 595s, 1 570w, 1 560w, 1 260w, 1 240w, 1 220w, 1 040w, 1 025m, 1 020m, 1 000w, 950s, 910s, 900s, 800w, 775s, 770s, 740m, 730s, 690m, 660m, 650m, 640m, 600w, 560w, 520w, 475m, 445w, 420m, 400w, 390w, 370w, 340s, 330s, 320m, 305w, 270w cm^{-1}. The complex was insoluble in common organic solvents which precluded n.m.r. spectral characterisation.

(*2,2′-Bipyridyl*)*dichloro*(*ethylimido*)(*phenylimido*)*tungsten*(VI), (**7**).—2,2′-Bipyridyl (0.1 g, 0.64 mmol) in dichloromethane (20 cm^3) was added to $[\{WCl_2(NEt)(NPh)(NH_2Ph)\}_2]$[12] (0.27 g, 0.31 mmol) and the solution stirred overnight. After filtering, the solvent was removed to yield a flaky solid which was washed with benzene (2 cm^3) and dried *in vacuo*. I.r.: 1 600s, 1 580m, 1 560m, 1 305m, 1 280m, 1 260m, 1 100m, 1 066m, 1 040m, 1 020s, 1 010m, 1 000w, 930w, 890s, 760m, 730m, 720w, 690w, 650w, 630w, 530w, 510w, 440m, 410m, 360m, 320m, 308s cm^{-1}.

(*2,2′-Bipyridyl*)*dichloro*(*methylimido*)(*t-butylimido*)*tungsten*(VI), (**8**).—2,2′-Bipyridyl (0.1 g, 0.64 mmol) in dichloromethane (30 cm^3) was added to $[\{WCl_2(NMe)(NBu^t)(NH_2Bu^t)\}_2]$[12] (0.24 g, 0.28 mmol) and the mixture was stirred for 6 h. The solution was filtered and the solvent removed to yield a pale yellow solid. Recrystallisation from dichloromethane–light petroleum (1:1) gave the complex as yellow microcrystals. I.r.: 1 600s, 1 575w, 1 560w, 1 510m, 1 490m, 1 400w, 1 255s, 1 210s, 1 120w, 1 090m, 1 040w, 1 020m, 960m, 890m, 840w, 800m, 760s, 650m, 630w, 580w, 445s, 410w, 380w, 345s, 320w, 305s, 280w cm^{-1}.

Table 9. Fractional atomic co-ordinates for (**5**)

Atom	Molecule A			Molecule B		
	x	*y*	*z*	*x*	*y*	*z*
W	0.296 80(5)	0.100 24(2)	0.289 33(6)	0.847 23(5)	0.341 08(3)	0.138 47(6)
Cl(1)	0.141 3(3)	0.079 0(2)	0.312 6(5)	0.945 8(3)	0.428 7(2)	0.070 6(4)
Cl(2)	0.449 9(3)	0.076 3(2)	0.225 7(5)	0.768 3(3)	0.275 4(2)	0.229 5(5)
N(1)	0.339 8(8)	0.122 5(7)	0.495 1(13)	0.895 8(9)	0.260 2(8)	0.034 1(16)
N(2)	0.272 1(9)	0.190 8(7)	0.207 3(14)	0.747 1(9)	0.374 3(7)	0.006 1(15)
N(3)	0.260 2(8)	0.039 1(7)	0.039 6(14)	0.825 5(8)	0.439 2(6)	0.329 8(13)
N(4)	0.316 1(8)	−0.030 0(7)	0.308 0(14)	0.962 7(8)	0.329 1(7)	0.361 1(13)
C(11)	0.376 3(10)	0.156 3(8)	0.638 4(17)	0.921 5(10)	0.208 1(9)	0.079 8(18)
C(12)	0.442 6(12)	0.114 6(10)	0.741 9(20)	0.962 7(12)	0.136 4(10)	0.038 0(19)
C(13)	0.481 4(14)	0.148 2(12)	0.885 2(23)	0.986 5(15)	0.084 2(12)	0.149 8(25)
C(14)	0.454 2(16)	0.218 8(14)	0.926 1(26)	0.964 3(15)	0.099 9(12)	0.311 7(24)
C(15)	0.385 8(16)	0.260 4(13)	0.824 7(27)	0.919 7(14)	0.168 1(12)	0.356 9(23)
C(16)	0.352 4(12)	0.227 6(10)	0.681 0(21)	0.901 5(11)	0.223 3(9)	0.239 4(18)
C(21)	0.272 8(10)	0.264 7(9)	0.177 2(17)	0.675 2(11)	0.388 9(9)	0.119 7(18)
C(22)	0.194 4(11)	0.299 9(9)	0.087 7(19)	0.587 9(16)	0.407 2(13)	0.079 0(27)
C(23)	0.198 4(14)	0.376 6(11)	0.052 6(22)	0.510 9(20)	0.425 6(16)	0.209 0(34)
C(24)	0.272 5(14)	0.410 3(12)	0.102 8(25)	0.530 7(20)	0.422 0(16)	0.360 3(33)
C(25)	0.351 1(14)	0.376 2(12)	0.193 2(24)	0.612 3(16)	0.406 5(13)	0.394 1(25)
C(26)	0.351 0(12)	0.302 1(10)	0.235 7(20)	0.693 4(12)	0.393 2(10)	0.268 4(20)
C(31)	0.235 3(12)	0.075 0(10)	−0.093 1(21)	0.758 6(11)	0.495 0(9)	0.299 0(18)
C(32)	0.210 2(12)	0.040 8(11)	−0.242 6(21)	0.748 4(12)	0.556 4(10)	0.407 2(20)
C(33)	0.208 9(15)	−0.033 6(13)	−0.254 0(24)	0.808 4(11)	0.560 0(10)	0.549 0(19)
C(34)	0.234 1(14)	−0.076 0(11)	−0.119 4(23)	0.879 5(11)	0.499 9(9)	0.589 8(19)
C(35)	0.259 7(12)	−0.036 2(10)	0.027 5(19)	0.884 7(10)	0.441 1(9)	0.467 3(18)
C(36)	0.293 5(11)	−0.075 6(9)	0.178 6(18)	0.959 2(10)	0.379 5(8)	0.489 5(17)
C(37)	0.299 9(12)	−0.155 3(10)	0.186 0(20)	1.022 1(11)	0.370 1(9)	0.634 9(19)
C(38)	0.336 3(15)	−0.181 9(12)	0.329 0(25)	1.090 3(12)	0.311 2(10)	0.637 5(20)
C(39)	0.360 1(12)	−0.137 5(10)	0.458 6(20)	1.096 2(12)	0.259 2(10)	0.510 0(20)
C(40)	0.349 6(12)	−0.061 3(10)	0.446 1(19)	1.031 1(11)	0.274 2(9)	0.370 7(18)

Dichloro(phenylimido)(t-butylimido)bis(trimethylphosphine)-tungsten(VI), (**9**).—Trimethylphosphine (0.4 cm^3, 3.6 mmol) was added to $[\{WCl_2(\mu\text{-}NPh)(NBu^t)(NH_2Bu^t)\}_2]$[12] (0.4 g, 0.41 mmol) suspended in light petroleum (50 cm^3). The mixture was stirred for 2 d during which time the suspended solid changed in colour from yellow to red. The complex was filtered off, washed with light petroleum (40 cm^3) and dried *in vacuo*. I.r.: 1 600w, 1 575m, 1 508w, 1 470s, 1 415m, 1 350s, 1 338s, 1 300s, 1 280s, 1 250s, 1 210m, 1 162w, 1 144w, 1 065w, 1 018w, 990w, 955s, 880w, 855w, 844w, 800w, 745s, 720w, 688m, 580w, 495w, 445w, 345w, 250 cm^{-1}.

X-*Ray Crystal Structures of* (**1**) and (**2**).—Crystals of (**1**) and (**2**) were sealed under argon in a thin-walled glass capillary and crystallographic measurements were made at 293 K using a CAD4 diffractometer, operating in the ω–2θ scan mode, with graphite-monochromatized Mo-K_α radiation (λ = 0.710 69 Å) in a manner previously described in detail.[25] Both sets of data were corrected for absorption.[26]

The structures were solved and refined using routine procedures and standard computer programs.[25] In the case of compound (**2**), the phenyl ring of the *p*-tolylimido group was found to be seriously disordered. Although we have modelled this in terms of two almost perpendicular orientations, with occupancy factors of 0.333 and 0.667, it was only possible to achieve any kind of convergent refinement by using isotropic thermal parameters for the atoms C(2), C(3), C(5), and C(6) at the two partially occupied sites A (population 0.333) and B (population 0.667) and constraining the relevant C–C distances to standard values. This strongly suggests that the disorder is likely to be more complex than this simple model. In addition, the structure appears to contain methylene chloride of crystallisation, but the relevant site is only partially occupied (population fixed at 0.5). Otherwise, non-hydrogen atoms were refined anisotropically and hydrogen atoms were included with group isotropic thermal coefficients in idealised positions. Crystal data and details of the data collection and refinement are given in Table 6. Final atomic fractional co-ordinates are given in Tables 7 and 8.

X-*Ray Crystal Structure of* (**5**).—A single crystal was sealed in a capillary under dry nitrogen. All measurements were made using a CAD4 diffractometer and graphite monochromatised Mo-K_α radiation. Accurate unit-cell dimensions were derived from a least-squares fit to the setting angles of 25 reflections widely dispersed throughout reciprocal space. Intensity data were collected to the practical crystal limit of θ = 22°, and processed in the normal manner. There were no non-statistical variations in the intensities of three standard reflections monitored periodically throughout the data collection. Absorption corrections employed empirical absorption curves derived from azimuthal scan data, and ranged from 1.000 to 1.213. The structure was solved *via* the heavy-atom method. The crystallographic asymmetric unit contains two monomers of complex. Refinement of atomic parameters was by full-matrix least-squares methods, minimising the function $\Sigma w(|F_o| - |F_c|)^2$, with weights being proportional to $1/[\sigma^2(F_o) + gF_o^2]$. The tungsten and chlorine atoms were assigned anisotropic thermal parameters; hydrogen atoms were placed in geometrically-derived positions (C–H 0.95 Å) with fixed isotropic thermal parameters of U = 0.08 $Å^2$, but not refined. Crystal data and details of the data collection and refinement are given in Table 6. Final atomic positions are given in Table 9.

Acknowledgements

We are grateful to the S.E.R.C. for supporting this research. We also thank Mr. P. Cook (mass spectra), Mr. G. Coumbarides

(80-MHz ^{1}H n.m.r. spectra) and the U.L.I.R.S. 400-MHz multinuclear n.m.r. facility at Q.M.C. (Dr. G. E. Hawkes) for their assistance.

References

1 D. C. Bradley, M. B. Hursthouse, K. M. A. Malik, A. J. Nielson, and R. L. Short, *J. Chem. Soc., Dalton Trans.*, 1983, 2651.

2 D. C. Bradley, R. J. Errington, M. B. Hursthouse, and R. L. Short, unpublished work; W. Clegg, R. J. Errington, and C. Redshaw, unpublished work.

3 A. J. Nielson, J. M. Waters, and D. C. Bradley, *Polyhedron*, 1985, **2**, 285.

4 D. C. Bradley, R. J. Errington, M. B. Hursthouse, A. J. Nielson, and R. L. Short, *Polyhedron*, 1983, **2**, 843.

5 S. F. Pederson and R. R. Schrock, *J. Am. Chem. Soc.*, 1982, **104**, 7483.

6 A. J. Nielson and J. M. Waters, *Aust. J. Chem.*, 1983, **36**, 243.

7 D. C. Bradley, M. B. Hursthouse, K. M. A. Malik, and A. J. Nielson, *J. Chem. Soc., Chem. Commun.*, 1981, 103.

8 W. A. Nugent and B. L. Haymore, *Coord. Chem. Rev.*, 1980, **31**, 123; W. A. Nugent, *Inorg. Chem.*, 1983, **22**, 965.

9 W. A. Nugent and R. L. Harlow, *Inorg. Chem.*, 1980, **19**, 777.

10 C. Y. Chou, J. C. Huffman, and E. A. Maata, *J. Chem. Soc., Chem. Commun.*, 1984, 1184.

11 D. C. Bradley, R. J. Errington, M. B. Hursthouse, and R. L. Short, *J. Chem. Soc., Dalton Trans.*, 1986, 1305.

12 B. R. Ashcroft, A. J. Nielson, D. C. Bradley, R. J. Errington, M. B. Hursthouse, and R. L. Short, preceding paper.

13 S. Donovan-Mtunzi, R. L. Richards, and J. Mason, *J. Chem. Soc., Dalton Trans.*, 1984, 1329; J. Mason, *Chem. Rev.*, 1981, **81**, 205.

14 R. H. Fenn, *J. Chem. Soc., A*, 1969, 1764; G. A. Barclay, B. F. Hoskins, and C. H. L. Kennard, *ibid.*, 1963, 5691.

15 P. A. Bates, A. J. Nielson, and J. M. Waters, *Polyhedron*, 1985, **4**, 999; F. A. Cotton and E. S. Shamshoum, *J. Am. Chem. Soc.*, 1984, **106**, 3222; D. Fenske, R. Kujanek, and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1983, **507**, 51; K. W. Chiu, R. A. Jones, G. Wilkinson, A. M. R. Galas, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1981, 2088.

16 V. W. Eichler and Y. H. J. Seiffert, *Z. Anorg. Allg. Chem.*, 1977, **431**, 123; M. G. B. Drew, G. W. A. Fowles, E. M. Page, and D. A. Rice, *J. Chem. Soc., Dalton Trans.*, 1981, 2409.

17 G. N. Schrauzer, L. A. Hughes, N. Strampach, P. R. Robinson, and E. O. Schliuper, *Organometallics*, 1982, **1**, 44.

18 B. L. Haymore, E. A. Maata, and R. A. D. Wentworth, *J. Am. Chem. Soc.*, 1979, **101**, 2063.

19 J. A. A. Ketelar and G. W. Van Oosterhout, *Recl. Trav. Chim. Pays-Bas*, 1943, **62**, 197.

20 G. V. Goeden and B. L. Haymore, *Inorg. Chem.*, 1983, **22**, 157; M. H. Chisholm, *Polyhedron*, 1981, **2**, 681.

21 C. A. McAuliffe and W. Levason, 'Studies in Inorganic Chemistry 1: Phosphine, Arsine, and Stibine Complexes of the Transition Elements,' Elsevier, New York, 1979, p. 51.

22 R. Colton and I. B. Tomkins, *Aust. J. Chem.*, 1965, **18**, 447.

23 W. Wolfsberger and H. Schmidbaur, *Synth. React. Inorg. Metal-Org. Chem.*, 1974, **4**, 149.

24 P. A. Bates, A. J. Nielson, and J. M. Waters, *Polyhedron*, in the press.

25 M. B. Hursthouse, R. A. Jones, K. M. A. Malik, and G. Wilkinson, *J. Am. Chem. Soc.*, 1979, **101**, 4128.

26 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

Received 14*th August* 1987; *Paper* 6/1660