Dilithium Tetra(t-butylimido)-molybdate(VI) and -tungstate(VI) and Some Reactions thereof. *X*-Ray Crystal Structures of $W[(\mu\text{-}NBu^t)_2AlX_2]_2$ (X = Cl or Me), $[W(NBu^t)_2(NH_2Bu^t)Cl(\mu\text{-}Cl)]_2$, and $[W_2Cu_5(NBu^t)_2(\mu\text{-}NBu^t)_6(NHBu^t)_2]BF_4$†

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The compounds $Li_2M(NBu^t)_4$ (M = Mo or W) have been made by deprotonation of $M(NBu^t)_2(NHBu^t)_2$ in diethyl ether by methyl-lithium. Interaction of $Li_2M(NBu^t)_4$ with $AlCl_3$, $GaCl_3$, and $AlMe_3$ gives rise to compounds of the type $M[(\mu\text{-}NBu^t)_2M'X_2]_2$ and the crystal structures of compounds where M = W, M′ = Al, X = Cl and Me have been determined. The $Li_2M(NBu^t)_4$ compounds are readily protonated by weak acids such as water or MeOH. Interaction with strong acids gives initially $M(NBu^t)_2(NHBu^t)_2$ and further protonation of the amido compound by CF_3SO_3H or CF_3CO_2H gives octahedral neutral species such as $M(NBu^t)_2(NH_2Bu^t)_2(OSO_2CF_3)_2$; $W(NBu^t)_2(NHBu^t)_2$ with HBF_4 gives only monoprotonation forming two species, $[W(NBu^t)_2(NHBu^t)(NH_2Bu^t)]BF_4$ and $W(NBu^t)_2(NHBu^t)(NH_2Bu^t)(F_2BF_2)$, depending on the conditions; HCl gives $[W(NBu^t)_2(NH_2Bu^t)Cl(\mu\text{-}Cl)]_2$. Interaction of $Li_2W(NBu^t)_4$ with $[Cu(MeCN)_4]BF_4$ gives a remarkable cation of stoicheiometry $[W^{VI}{}_2Cu^{I}{}_5(NBu^t)_2(\mu\text{-}NBu^t)_6(NHBu^t)_2]^+$ in which each W has one linear terminal NBu^t group and three NBu^t groups bridging to three copper(I) atoms in a triangle; two of these NBu^t groups are also bound to a $Cu^I(NHBu^t)$ unit thus being μ_3.

In a preliminary communication[1] we described the synthesis of the first homoleptic alkylimido compounds of transition metals, $Li_2W(NBu^t)_4$, $Li(tmen)Re(NBu^t)_4$ (tmen = tetramethylethylenediamine), and $[Re(NBu^t)_2(\mu\text{-}NBu^t)]_2$, and the *X*-ray crystal structures of the first two compounds. Details of the synthesis and n.m.r. spectra of the rhenium compounds and of the *X*-ray crystal structure of the dimeric bridged rhenium(VI) compound have been given.[2] The imidomolybdate $Li_2Mo(NBu^t)_4$ has been noted subsequently, together with protonation studies on $Li_2W(NBu^t)_4$.[3]

We now give details of the syntheses of $Li_2M(NBu^t)_4$, M = Mo and W, the reactions of these compounds with $AlMe_3$, $AlCl_3$, and $GaCl_3$, protonation studies on $Li_2W(NBu^t)_4$ and $W(NBu^t)_2(NHBu^t)_2$, and the reaction of $Li_2W(NBu^t)_4$ with $[Cu(MeCN)_4]BF_4$.

Analytical and physical data for new compounds are given in Table 1.

Results and Discussion

Synthesis of $Li_2M(NBu^t)_4$, [M = Mo, (**1**); *or* W (**2**)].—The t-butylimido analogues of the long known $MO_4{}^{2-}$ ions were made by deprotonation of the molybdenum and tungsten bis(imido)bis(amido) compounds, $M(NBu^t)_2(NHBu^t)_2$, by methyl-lithium in diethyl ether or by n-butyl-lithium in hexane, the former being more economical for large-scale syntheses.

The imidoamidotungsten compound was made by interaction of excess of t-butylamine and WCl_6 in hexane.[4] The molybdenum analogue was made by interaction of $Mo(NBu^t)_2Cl_2$, itself made by interaction of MoO_2Cl_2 with Bu^tNCO,[5] with a slight excess of $LiNHBu^t$. The imidoamido compound is readily isolated by sublimation in vacuum; it can be crystallised from concentrated solutions in hexane or hexamethyldisiloxane but, due to the high solubility, the yield is low and purification by sublimation is best. Attempts to prepare the compound from $Mo(NBu^t)_2(OSiMe_3)_2$[4] were unsuccessful.

The *X*-ray crystal structure[1] of $[Li_2W(NBu^t)_4]_2$ shows that the molecule is dimeric with a linear NBu^t group on each W atom and four lithium atoms in a square interacting with the NBu^t ligands. Although we have been unable to grow *X*-ray quality crystals of the molybdenum analogue, the structure would appear to be similar in view of the near identity of i.r. and n.m.r. spectra. Thus the ^1H n.m.r. spectra show two imido NBu^t resonances in a 1:3 ratio at δ 1.66 (9 H) and 1.47 (27 H) for the molybdenum and 1.67 and 1.48 for the tungsten compound. These correspond, respectively, to the linear MNC (downfield) and bent MNC groups found in the crystalline tungsten compound by *X*-ray diffraction.[1] For M^{VI} and an 18-electron configuration one linear and three bent groups are to be expected.[6a] The $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of $Li_2M(NBu^t)_4$ indicate differences in the electronic nature of bent and linear MNC groups following the suggestion[6a] that the chemical shift differences, Δ, between the α and β carbons of the $NCMe_3$ group provide a qualitative measure of the electron density on the nitrogen atom. For the bent imido groups, Δ = 24.6(Mo) and 23.6(W) p.p.m. while the linear groups have Δ = 14.67(Mo) and 13.18(W) p.p.m., indicating nucleophilic and electrophilic behaviour, respectively.

Both compounds $Li_2M(NBu^t)_4$ are non-conducting in tetrahydrofuran (thf) at 25 °C and they show no evidence for non-rigidity in the n.m.r. spectra up to 120 °C; there is evidently no linear-to-bent interconversion.

Deprotonation with other reagents. The use of $AlMe_3$ in hexane for deprotonation of $W(NBu^t)_2(NHBu^t)_2$ yields an air-sensitive compound whose mass i.r. and ^1H n.m.r. spectra are in agreement with the structure (**A**). Due to the high solubility in hexane and the presence of a minor impurity with similar solubility, we have been unable to isolate the compound

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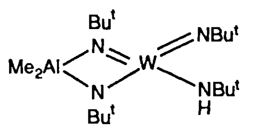
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Analytical and physical data for new compounds

Compound	Colour	M.p./°C	Analyses */% C	H	N
$Li_2Mo(NBu^t)_4$	Lemon	>280	48.9 (48.8)	9.2 (9.2)	14.2 (14.1)
$Li_2W(NBu^t)_4$	Colourless	decomp. > 270	38.9 (38.9)	7.3 (7.5)	11.9 (11.4)
$W[(\mu-NBu^t)_2AlCl_2]_2$	Purple-blue	260—262	29.0 (30.5)	5.5 (5.7)	8.5 (8.9)
$Mo[(\mu-NBu^t)_2AlCl_2]_2$	Yellow-green	160—165	33.2 (33.3)	6.2 (6.2)	9.7 (9.7)
$W[(\mu-NBu^t)_2AlMe_2]_2$	Orange-red	289—290	41.2 (41.2)	8.3 (8.3)	9.7 (9.6)
$Mo[(\mu-NBu^t)_2AlMe_2]_2$	Yellow-green	180—182	48.4 (48.6)	9.5 (9.7)	11.3 (11.3)
$W[(\mu-NBu^t)_2GaCl_2]_2$	Purple	>240	25.6 (25.6)	4.9 (4.8)	7.2 (7.5)
$W(NBu^t)_2(NH_2Bu^t)_2(O_3SCF_3)_2$	Yellow	>240	28.3 (28.1)	5.2 (5.2)	7.3 (7.3)
$Mo(NBu^t)_2(NH_2Bu^t)_2(O_3SCF_3)_2$	Orange	222	31.3 (31.6)	5.8 (5.9)	8.1 (8.2)
$W(NBu^t)_2(C_5H_5N)_2(O_3SCF_3)_2$	Orange	>270	30.7 (30.7)	3.5 (3.6)	7.3 (7.2)
$W(NBu^t)_2(4-BuC_5H_4N)_2(O_3SCF_3)_2$	Lemon	>250	37.4 (37.6)	4.3 (4.2)	6.0 (6.2)
$W(NBu^t)_2(NH_2Bu^t)_2(O_3SCF_3)_2$	Yellow	125—127	32.8 (34.4)	5.5 (5.7)	7.6 (8.0)
$[W(NBu^t)_2(NH_2Bu^t)Cl(\mu-Cl)]_2$	Yellow	169—170	33.5 (33.2)	6.5 (6.9)	9.3 (9.7)
$[W(NBu^t)_2(NHBu^t)(NH_2Bu^t)]BF_4$	Colourless		33.6 (34.4)	6.7 (7.0)	9.6 (9.5)
$W(NBu^t)_2(NHBu^t)(NH_2Bu^t)(F_2BF_2)$	Cream-white	108—110	32.8 (34.4)	7.6 (7.0)	10.0 (9.5)
$[W_2Cu_5(NBu^t)_2(\mu-NBu^t)_6(NHBu^t)_2]BF_4$	Yellow	>250	29.8 (30.3)	5.0 (5.8)	8.9 (9.8)

* Calculated values in parentheses. Mass spectral data are given in the Experimental section.



(A)

Table 2. Selected bond lengths (Å) and angles (°) for $W[(\mu-NBu^t)_2AlX_2]_2$ (X = Me or Cl)

	X = Me	X = Cl	
W–N	1.836(7)	1.857(13)	1.857(11)
	1.855(6)	1.862(12)	1.847(12)
Al–N	1.992(7)	1.893(14)	1.921(13)
	1.990(9)	1.936(11)	1.965(13)
Al–C/Cl	1.947(11)	2.094(9)	2.086(9)
	1.992(10)	2.101(8)	2.114(8)
N–C	1.480(9)		
	1.458(9)		
N–W–N (ring ends)	93.7(3)	91.0(6)	93.5(5)
N–W–N (ring *exo*)	117.8(3)	119.4(5)	123.2(5)
	118.1(3)	115.8(6)	116.1(6)
N–Al–N	85.1(5)	88.0(6)	87.6(5)
Al–N–W	90.0(3)	90.8(6)	89.9(5)
	90.2(3)	89.6(5)	89.2(5)
Al–N–C	125.7(6)	129.0(11)	128.4(9)
	126.7(5)	127.4(9)	127.7(9)
W–N–C	143.4(5)	140.3(10)	141.7(9)
	143.0(4)	142.7(8)	142.8(9)

completely pure and *X*-ray-quality crystals could not be obtained. The proposed structure (**A**) is, however, supported by structural studies on similar compounds discussed later.

Deprotonation of $W(NBu^t)_2(NHBu^t)_2$ using 'dibutylmagnesium'[7] in Et_2O gives a white microcrystalline solid that can be crystallised from hexane. Although no *X*-ray-quality crystals could be grown, the spectroscopic data suggest that it is probably $[Mg(\mu-NBu^t)_2W(NBu^t)(NHBu^t)]_2$ with a structure similar to (**A**). Thus there are W(NH) bands in the i.r. spectra of both aluminium and magnesium compounds, while ^1H n.m.r. spectra have a broad band, δ 4.64 (NH), and four bands at δ 1.58, 1.50, 1.49, and 1.32 in a 1:1:1:1 ratio indicating inequivalent t-butyl groups.

Deprotonation of $W(NBu^t)_2(NHBu^t)_2$ with dimethylzinc gave a compound,[4] considered on spectroscopic grounds to be $(Bu^tN)(Bu^tNH)_2MeW[(NBu^t)ZnMe]$.

Reactions of $Li_2M(NBu^t)_4$ *with Lewis and Protonic Acids.*—(*a*) *Lewis acids.* The imido compounds react with AlX_3 (X = Me or Cl) and $GaCl_3$ according to the stoicheiometry of equation (1). The reaction is best carried out in toluene; in hexane the reaction is slower.

$$Li_2M(NBu^t)_4 + 4M'X_3 \longrightarrow M[(\mu-NBu^t)_2M'X_2]_2 + 2LiM'X_4 \qquad (1)$$

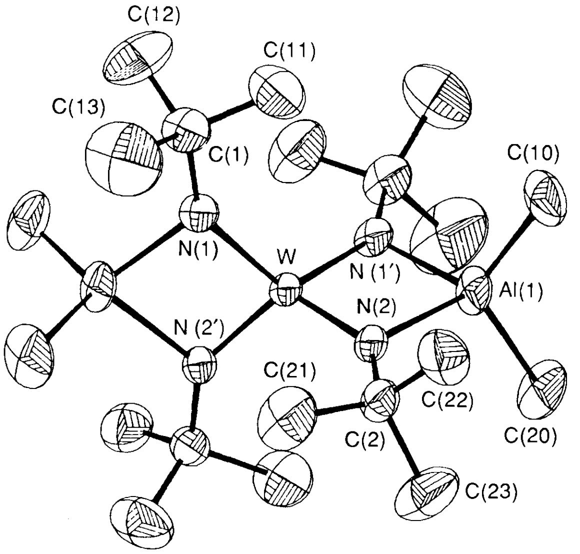


Figure 1. The structure of $W[(\mu\text{-}NBu^t)_2AlMe_2]_2$

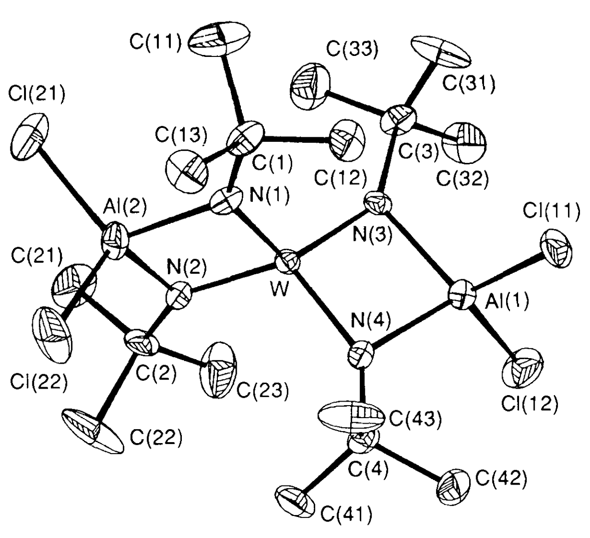


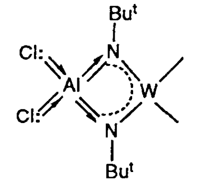
Figure 2. The structure of $W[(\mu\text{-}NBu^t)_2AlCl_2]_2$

The compounds (**3**) and (**4**) (M = Mo or W, M′ = Al, X = Cl), (**5**) and (**6**) (M = Mo or W, M′ = Al, X = Me), and (**7**) (M = W, M′ = Ga, X = Cl) are all extremely moisture-sensitive, but thermally stable, high-melting solids that can be sublimed without decomposition at *ca.* 220 °C in a stream of argon or N_2. Although the methyl compounds are orange the chlorides are intensely coloured; the Mo–Al compound is green, while the W–Al and W–Ga compounds are purple both in the solid state and in solution in non-co-ordinating organic solvents.

The tungsten compounds (**4**) and (**6**) have been structurally characterised. A diagram of the dimethylaluminium compound is given in Figure 1, and of the dichloroaluminium complex in Figure 2. Selected bond lengths and angles are given in Table 2. As might be expected the molecular geometries and configurations are very similar but the compounds are not crystallographically isostructural. The dimethyl complex lies on a two-fold axis. The main differences between the structures lie in the AlX_2 co-ordination to the nitrogen atoms with Al–N distances for the dimethyl slightly longer than for the dichloride. The WN_4 geometry is very similar in both with some deviation from ideal tetrahedral angles due to the N_2Al bridging. The W–N distances are very similar to those involved in bridging by Li in $Li_2W(NBu^t)_4$.

The spectroscopic data for the compounds are in accord with the structures determined. Thus the ^1H n.m.r. spectra of the chlorides show only a single band for the NBu^t groups at δ 1.37 (Mo–Al), 1.36 (W–Al), and 1.35 (W–Ga), while the methyls have NBu^t bands at 1.33 and Al–Me resonances at −0.24(Mo) and −0.18(W), respectively. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of the Me_2Al compounds have a broad band at −7.5 p.p.m. for tungsten but there is no observable band for the molybdenum analogue; the broadening is probably attributable to quadrupolar effects of the ^{27}Al ($I = \frac{5}{2}$) nucleus.

The ^{27}Al n.m.r. spectra of the $AlCl_2$ compounds of Mo and W show sharp resonances, $\Delta_{\frac{1}{2}}$ = 133 Hz, while the methyls have $\Delta_{\frac{1}{2}}$ = 2 930 Hz, in all four cases at *ca.* 52 p.p.m. The large difference in the linewidth can be attributed to the difference in the symmetry of the electronic environment around the aluminium atoms. Thus in the chlorides the electron density is more spherically symmetrical around the quadrupolar metal. The electronic spectrum of the $WAlCl_2$ complex in benzene shows two transitions: 570, ε = 55; 342 nm, ε = 470 dm^3 mol^{-1} cm^{-1}. The deep purple colour is presumably due to the 342-nm absorption and some type of charge-transfer interaction. The colour difference between the halide and methyl analogues may reflect the delocalisation of electron density in the lone pair of the halogen atoms over the W–N–Al–N ring, (**B**). It may be noted that WMe_6 is pale yellow while WCl_6 is dark red.



(B)

(*b*) *Weak protonic acids.* Both the compounds $Li_2M(NBu^t)_4$ are moisture sensitive giving $MO_3{\cdot}nH_2O$ and Bu^tNH_2. In excess of dry methanol, $Li_2W(NBu^t)_4$ gives Bu^tNH_2 and white, air- and water-sensitive crystals of a compound formulated on the basis of n.m.r. spectra as $W(NBu^t)(OMe)_4$: δ 1.33(9) (NBu^t); 4.75(12) (OMe). Similarly, with excess of Bu^tOH in thf a 1 : 1 mixture of $W(NBu^t)(OBu^t)_4$ and $W(NBu^t)_2(OBu^t)_2$ is formed. These alkoxides were identified from previous n.m.r. data.[4] The formation of a mixture with Bu^tOH suggests that initial protonation occurs to give $W(NBu^t)_2(NHBu^t)_2$ which reacts further as previously reported[4] to give $W(NBu^t)_2(OBu^t)_2$. On the other hand, attack by Bu^tOH on the third, nucleophilic, imido group of $Li_2(NBu^t)_4$ could give an intermediate $[W(NBu^t)(NHBu^t)_3]^+$, which in a second step is converted into $W(NBu^t)(OBu^t)_4$. Methanol, with the less bulky methyl group, is likely to react faster giving $[W(NBu^t)(NHBu^t)_3]^+$ and predominantly $W(NBu^t)(OMe)_4$.

Both $Li_2M(NBu^t)_4$ compounds act as strong bases deprotonating acetone which undergoes further aldol reactions, while acetonitrile undergoes Thorpe-type reactions.[8]

(*c*) *Strong protonic acids.* The first product from interaction of $Li_2M(NBu^t)_4$ (M = Mo and W) with strong protonic acids is the amido complex, $M(NBu^t)_2(NHBu^t)_2$, but further reaction with excess of HX gives complexes whose nature depends on the nature of the acid. We have used the tungsten imidoamido complex for these protonation studies, which result in the preferential protonation of the amido nitrogen atom to give the co-ordinated amino complex, as well as the co-ordinated conjugate anion of the acid.

The simplest cases are CF_3SO_3H and CF_3CO_2H which react

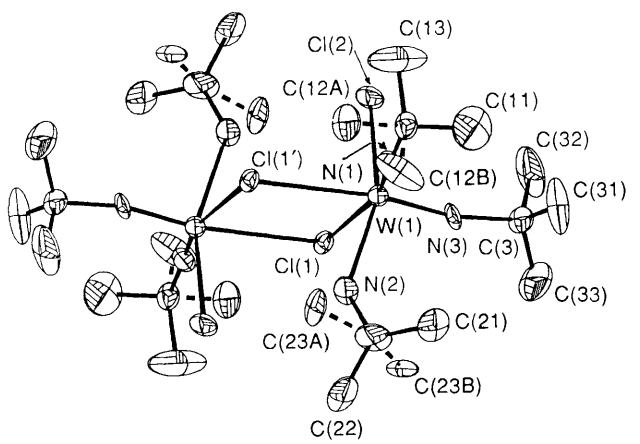
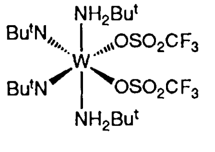


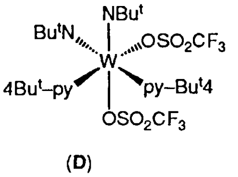
Figure 3. The structure of $[W(NBu^t)_2(NH_2Bu^t)Cl(\mu\text{-}Cl)]_2$; thermal ellipsoids are drawn at the 30% probability level

Table 3. Selected bond lengths (Å) and angles (°) for $[W(NBu^t)_2(NH_2Bu^t)Cl(\mu\text{-}Cl)]_2$

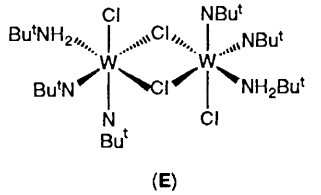
Cl(1)–W(1)	2.657(6)	Cl(2)–W(1)	2.395(6)
Cl(1')–W(1)	2.722(10)	N(1)–W(1)	1.715(15)
N(2)–W(1)	2.202(15)	N(3)–W(1)	1.726(14)
C(1)–N(1)	1.470(22)	C(2)–N(2)	1.436(22)
C(3)–N(3)	1.471(22)		
Cl(2)–W(1)–Cl(1)	83.6(2)	N(1)–W(1)–Cl(1)	162.7(5)
N(1)–W(1)–Cl(2)	95.7(6)	N(2)–W(1)–Cl(1)	76.3(5)
N(2)–W(1)–Cl(2)	155.3(4)	N(2)–W(1)–N(1)	99.2(7)
N(3)–W(1)–Cl(1)	91.1(5)	N(3)–W(1)–Cl(2)	96.1(5)
N(3)–W(1)–N(1)	106.1(7)	N(3)–W(1)–N(2)	98.6(6)
W(1)–Cl(1)–W(1')	106.2(3)	Cl(1)–W(1)–Cl(1')	73.8(3)
Cl(2)–W(1)–Cl(1')	84.2(3)	N(1)–W(1)–Cl(1')	88.0(6)
N(2)–W(1)–Cl(1')	76.6(7)	N(1)–W(1)–Cl(1')	165.0(4)
C(1)–N(1)–W(1)	170.1(12)	C(2)–N(2)–W(1)	132.9(14)
C(3)–N(3)–W(1)	166.5(12)		



(C)



(D)



(E)

at low temperatures with $W(NBu^t)_2(NHBu^t)_2$ in diethyl ether to give the neutral monomeric complex with *cis*-NBu^t, *cis*-OSO_2CF_3, and *trans*-NH_2Bu^t ligands as in diagram (C). The structure was confirmed for the triflate by an *X*-ray crystallographic study.[3] For CF_3SO_3 this is the only isomer present; the complex is non-conducting in CH_2Cl_2 or thf and the i.r. spectrum shows the shift to higher wavenumbers compared to $CF_3SO_3^-$ characteristic of O bonding.[9]

The co-ordinated amine can be substituted by strong nitrogen bases but bidentate ligands, *e.g.* 2,2'-bipyridyl gives oligomers, while there is no reaction with tertiary phosphines. The substitution by 4-t-butylpyridine leads to isomerisation by a dissociative route, as shown by the ^{13}C n.m.r. spectrum which indicates inequivalent imido and pyridine groups and hence the structure (**D**).

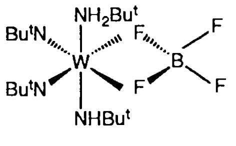
The non-conducting trifluoroacetate is similar to the triflate with O bonding of the ligand, according to the ν_{asym} and ν_{sym} absorptions in the i.r. spectrum.[10]

Interaction of $W(NBu^t)_2(NHBu^t)_2$ with HCl in Et_2O gives the dimer (**E**) which probably arises from loss of Bu^tNH_2 from the unisolable intermediate, $W(NBu^t)_2(NH_2Bu^t)Cl_2$, on dimerisation to give the chloride-bridged species. Since NBu^t could be a better bridging group than Cl the formation of this dimer is presumably kinetically controlled. A compound with the same stoicheiometry[11] obtained by interaction of WCl_6 with $Bu^tNHSiMe_3$ in benzene differs spectroscopically from our product and we assume that the structure is that proposed with μ-NBu^t.

The structure of the chlorine-bridged dimer, which lies on a centre of symmetry, is shown in Figure 3 and selected bond lengths and angles in Table 3. The tungsten(VI) centres now have a very distorted octahedral geometry, the distortions arising from the dichloro bridging (Cl–W–Cl ≈ 74°) and steric interactions between the t-butyl-imido and -amine ligands. The two imido ligands have near linear geometries and normal W=N distances (*ca.* 1.72 Å). The W–N(2) (amine) bond is long [2.20(1) Å] and the Bu^t carbons show considerable disorder. The amine nitrogen N(2) is in close contact with both bridging chlorines (3.02, 3.07 Å) and the nearest terminal chlorine (3.35 Å), and it is likely that hydrogen bonding is present. The disorder in the Bu^t group of this ligand may reflect different modes of connectivity $\begin{array}{l}\mathrm{N{-}H\cdots Cl}\\ \mathrm{|}\\ \mathrm{H\cdot\cdot Cl}\end{array}$. The W_2Cl_2W bridge system is slightly asymmetric with W–Cl distances of *ca.* 2.72 and 2.66 Å.

The nature of the product from interaction of $W(NBu^t)_2(NHBu^t)_2$ with HBF_4 in Et_2O depends on the conditions. Slow addition of acid at −78 °C gives the monoprotonated species $[W(NBu^t)_2(NHBu^t)(NH_2Bu^t)]BF_4$. This formulation is inferred from spectroscopic and analytical data since we have been unable to grow *X*-ray-quality crystals. Thus the ^1H n.m.r. spectrum shows three t-butyl resonances at δ 1.39, 1.41, and 1.49 assignable to Bu^tNH_2, Bu^{t}N, and Bu^{t}NH, respectively, and two broad NH resonances. The ^{19}F n.m.r. spectrum has only a singlet at −177.7 p.p.m. as expected for unco-ordinated BF_4^-; this is confirmed by the conductivity in nitromethane which is that for a 1 : 1 electrolyte (70 ohm^{-1} cm^2 mol^{-1} at 10^{-3} mol dm^{-3}).

A quite different product is obtained when $HBF_4\cdot Et_2O$ is added to the tungsten compound rapidly at room temperature. In this case the compound isolated has a ^{19}F n.m.r. spectrum consisting of an AB pattern centred at −163 p.p.m. This suggests two magnetically inequivalent groups of F nuclei coupled to give the observed spectrum. The relatively broad lines might be responsible for the absence of ^{10}B isotopomers. Since the complex is non-conducting in $MeNO_2$ the structure (**F**) seems likely. Similar bonding has been proposed for BF_4 in



(F)

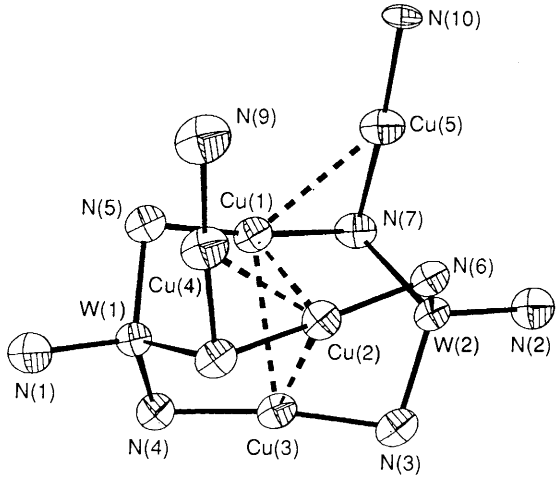


Figure 4. The structure of $[W_2Cu_5(NBu^t)_2(\mu\text{-}NBu^t)_6(NHBu^t)_2]^+$ in the BF_4^- salt

a uranium compound.[12] Again, we have been unable to grow *X*-ray-quality crystals.

The F_2BF_2 compound is slowly isomerised to the cationic species on heating in $CDCl_3$ at 70 °C as shown by ^1H and ^{19}F n.m.r. spectra. Presumably the formation of the ionic species in the protonation reaction is thermodynamically controlled, while that of the bridged species is kinetically controlled. There is no evidence for a second protonation with $HBF_4 \cdot Et_2O$ using an excess of acid.

(*d*) $Li_2W(NBu^t)_4$ *and* $[Cu(MeCN)_4]BF_4$. This interaction in acetonitrile affords a remarkable copper(I)–tungsten(VI) heterobimetallic cation, $[W_2Cu_5(NBu^t)_2(\mu\text{-}NBu^t)_6(NHBu^t)_2]^+$ with NBu^t bridges, as the tetrafluoroborate salt. The compound is extremely air and moisture sensitive although it is thermally stable. It is the first of its type. There are numerous anionic complexes[13a] between various transition metals, including copper, with chalcogenide ions of Mo^{VI} and W^{VI}, MX_4^{2-} (X = S or Se). Examples of Cu^I–M^{VI} anions include $[MoO(\mu\text{-}S)_3(CuCl)_3]^{2-}$ (ref. 14*a*) and $[M_2Cu_5S_8(S_2CNMe_2)_3]^{2-}$ (M = Mo or W).[14b]

In the t-butylimido complex cation the tungsten retains the tetrahedral arrangement of NBu^t groups with one linear $WNBu^t$ group (18e) as in $LiW(NBu^t)_4$. The amido group on copper(I) probably arises by protonation of strongly basic $Li_2W(NBu^t)_4$ by acetonitrile (see earlier).

The structure of the cation is shown in Figure 4 and selected bond lengths and angles are given in Table 4. The structure comprises an essentially equilateral triangle of Cu atoms with Cu $\cdots$ Cu contacts of 2.732—2.748(8) Å. This is sandwiched between two $W(NBu^t)_4$ units *via* one N_3 triangle of each N_4 tetrahedron. To one of the three W $\cdots$ Cu bridging imido functions on each side is also co-ordinated a $Cu(NHBu^t)$ unit. The Cu atoms in each of these units each interact with one of two Cu atoms in the central triangle, with Cu $\cdots$ Cu distances of 2.547(8) and 2.590(7) Å, *i.e.* shorter than the distances in the Cu_3 triangle. The co-ordination of the $Cu(NHBu^t)$ units has an influence on the W–W–Cu bridging. Whilst the four 'normal' W–NBu^t–Cu bridges are symmetrical, with little difference between the W–N distances [1.828—1.837(8) Å] and the N–Cu distances [1.825—1.846(8) Å], the $Cu(NHBu^t)$ co-ordinated bridges are unsymmetrical, with lengthened W–N distances of 2.012(10) Å but unchanged N–Cu distances [1.830 and 1.833(8) Å]. The shorter W–N distances fall into the range found for the bridging nitrogens in the other structures (see above and ref. 1).

Table 4. Selected bond lengths (Å) and angles (°) for $[W_2Cu_5(NBu^t)_2(\mu\text{-}NBu^t)_6(NHBu^t)_2]BF_4$

N(2)–W(1)	1.650(8)	N(3)–W(1)	1.837(8)
N(6)–W(1)	1.833(10)	N(7)–W(1)	2.012(9)
N(1)–W(2)	1.658(8)	N(4)–W(2)	1.833(10)
N(5)–W(2)	1.828(9)	N(8)–W(2)	2.012(10)
Cu(2)–Cu(1)	2.748(8)	Cu(3)–Cu(1)	2.734(7)
Cu(3)–Cu(2)	2.732(8)	Cu(4)–Cu(2)	2.547(8)
Cu(5)–Cu(1)	2.590(7)	N(5)–Cu(1)	1.823(9)
N(7)–Cu(1)	1.833(8)	N(6)–Cu(2)	1.831(8)
N(8)–Cu(2)	1.830(8)	N(3)–Cu(3)	1.858(8)
N(4)–Cu(3)	1.846(8)	N(8)–Cu(4)	1.884(9)
N(9)–Cu(4)	1.915(11)	N(7)–Cu(5)	1.912(9)
N(10)–Cu(5)	1.931(10)	C(1)–N(1)	1.427(11)
C(2)–N(2)	1.456(11)	C(3)–N(3)	1.516(13)
C(4)–N(4)	1.517(15)	C(5)–N(5)	1.490(12)
C(6)–N(6)	1.484(14)	C(7)–N(7)	1.474(14)
C(8)–N(8)	1.496(13)	C(9)–N(9)	1.468(17)
C(10)–N(10)	1.490(14)		

N(3)–W(1)–N(2)	107.3(4)	N(6)–W(1)–N(2)	109.0(5)
N(6)–W(1)–N(3)	111.5(4)	N(7)–W(1)–N(2)	109.9(4)
N(7)–W(1)–N(3)	112.7(4)	N(7)–W(1)–N(6)	106.5(4)
N(4)–W(2)–N(1)	107.8(4)	N(5)–W(2)–N(1)	107.5(4)
N(5)–W(2)–N(4)	111.5(4)	N(8)–W(2)–N(1)	110.7(5)
N(8)–W(2)–N(4)	113.8(4)	N(8)–W(2)–N(5)	105.3(4)
Cu(3)–Cu(1)–Cu(2)	59.8(2)	Cu(3)–Cu(2)–Cu(1)	59.9(2)
Cu(2)–Cu(3)–Cu(1)	60.4(2)	Cu(2)–Cu(1)–Cu(5)	90.4(2)
Cu(3)–Cu(1)–Cu(5)	122.5(2)	Cu(1)–Cu(2)–Cu(4)	89.6(2)
Cu(3)–Cu(2)–Cu(4)	121.4(2)	N(6)–Cu(2)–Cu(4)	126.7(3)
N(8)–Cu(2)–Cu(4)	77.8(4)	N(8)–Cu(4)–Cu(2)	45.8(2)
N(9)–Cu(4)–Cu(2)	131.7(2)	N(7)–Cu(5)–Cu(1)	45.2(2)
N(10)–Cu(5)–Cu(1)	134.0(3)	N(5)–Cu(1)–Cu(2)	91.0(4)
N(5)–Cu(1)–Cu(3)	101.7(3)	N(7)–Cu(1)–Cu(2)	96.1(3)
N(7)–Cu(1)–Cu(3)	85.2(3)	N(7)–Cu(1)–Cu(5)	47.5(2)
N(7)–Cu(1)–N(5)	172.0(3)	N(6)–Cu(2)–Cu(1)	91.2(3)
N(6)–Cu(2)–Cu(3)	104.2(4)	N(8)–Cu(2)–Cu(1)	95.9(3)
N(8)–Cu(2)–Cu(3)	84.5(4)	N(8)–Cu(2)–N(6)	170.7(4)
N(3)–Cu(3)–Cu(1)	105.1(3)	N(3)–Cu(3)–Cu(2)	80.8(4)
N(4)–Cu(3)–Cu(1)	83.0(3)	N(4)–Cu(3)–Cu(2)	106.9(4)
N(4)–Cu(3)–N(3)	171.1(3)	N(9)–Cu(4)–N(8)	174.7(3)
N(10)–Cu(5)–N(7)	174.3(3)	C(1)–N(1)–W(2)	179.1(8)
C(2)–N(2)–W(1)	179.4(7)	Cu(3)–N(3)–W(1)	99.6(4)
C(3)–N(3)–W(1)	139.9(5)	C(3)–N(3)–Cu(3)	119.8(6)
Cu(3)–N(4)–W(2)	98.0(4)	C(4)–N(4)–W(2)	141.9(5)
C(4)–N(4)–Cu(3)	120.0(7)	Cu(1)–N(5)–W(2)	97.6(4)
C(5)–N(5)–W(2)	140.1(5)	C(5)–N(5)–Cu(1)	120.1(6)
Cu(2)–N(6)–W(1)	95.8(4)	C(6)–N(6)–W(1)	143.4(5)
C(6)–N(6)–Cu(2)	119.8(7)	Cu(1)–N(7)–W(1)	102.3(4)
Cu(5)–N(7)–W(1)	98.3(4)	Cu(5)–N(7)–Cu(1)	87.5(4)
C(7)–N(7)–W(1)	126.0(6)	C(7)–N(7)–Cu(1)	116.0(6)
C(7)–N(7)–Cu(5)	118.9(6)	Cu(2)–N(8)–W(2)	103.1(5)
Cu(4)–N(8)–W(2)	99.1(4)	Cu(4)–N(8)–Cu(2)	86.6(4)
C(8)–N(8)–W(2)	124.6(6)	C(8)–N(8)–Cu(2)	115.0(6)
C(8)–N(8)–Cu(4)	120.9(8)	C(9)–N(9)–Cu(4)	119.2(7)
C(10)–N(10)–Cu(5)	115.2(8)		

The Cu_3 triangle is almost equilateral, with the Cu(1) $\cdots$ Cu(2) distance between the two Cu atoms involved in interactions with the co-ordinating Cu atoms only slightly larger than the Cu(1) $\cdots$ Cu(3) and Cu(2) $\cdots$ Cu(3) distances, 2.748(8) *vs.* 2.734(7) and 2.732(8) Å. The N–Cu–N groupings at all Cu atoms are essentially linear, with angles of 170.7—174.7(3)°. The terminal amido functions are also linear, with W–N–C angles of 179.1(8) and 179.4(7)°.

Experimental

The methods and techniques used were similar to those described previously.[15] The compounds $W(NBu^t)_2(NHBu^t)_2$,[4]

Table 5. Crystal data, details of intensity measurements and structure refinement

	$W[(\mu\text{-}NBu^t)_2AlMe_2]_2$	$W[(\mu\text{-}NBu^t)_2AlCl_2]_2$	$[W(NBu^t)_2(NH_2Bu^t)\text{-}Cl(\mu\text{-}Cl)]_2$	$[W_2Cu_5(NBu^t)_2(\mu\text{-}NBu^t)_6\text{-}(NHBu^t)_2]BF_4$
M	528.484	664.148	940.36	1 485.50
Crystal system	Monoclinic	Orthorhombic	Triclinic	Triclinic
a/Å	18.673(3)	10.660(1)	12.936(2)	13.927(3)
b/Å	9.187(1)	15.387(3)	8.806(2)	18.939(2)
c/Å	20.168(3)	16.990(6)	8.765(3)	11.748(2)
α/°	90.0	90.0	102.28(3)	92.34(1)
β/°	121.95(1)	90.0	95.13(3)	110.81(2)
γ/°	90.0	90.0	101.46(3)	86.96(1)
U/Å^3	2 935.67	2 792.02	946.97	2 755.20
Space group	$C2/c$	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$
Z	4	4	1	2
D_c/g cm^{-3}	1.32	1.579	1.648	1.79
μ/cm^{-1}	38.60	46.83	60.99	62.37
F(000)	1 184	1 312	462	1 528
h, *k*, *l* range	0—22 0—10 −24 to 24	0—11 0—16 0—18	−14 to 14 −9 to 9 0—9	−15 to 15 −20 to 20 0—12
Total no. of reflections	2 848	2 234	2 843	8 480
No. of unique reflections	2 582	2 213	2 636	8 014
No. of reflections used [$F > 3\sigma(F)$]	2 351	1 733	2 001	6 599
No. of parameters	125	244	163	559
Weighting scheme parameters *g* in $w = 1/[\sigma^2(F) + gF_o^2]$	0.000 393	0.000 67	0.0009	0.000 05
Final *R*	0.0331	0.0294	0.0501	0.0365
Final *R′*	0.0326	0.0308	0.0494	0.0353

Table 6. Fractional atomic co-ordinates ($\times 10^4$) for $W[(\mu\text{-}NBu^t)_2\text{-}AlMe_2]_2$

Atom	*x*	*y*	*z*
W	5 000	3 128(1)	2 500
Al(1)	5 050(1)	3 115(3)	1 172(1)
N(1)	4 378(3)	2 095(5)	2 802(3)
N(2)	4 420(3)	4 166(5)	1 572(3)
C(2)	3 774(5)	5 278(8)	1 162(4)
C(1)	3 712(5)	975(9)	2 543(5)
C(10)	4 344(7)	1 846(10)	287(6)
C(20)	5 837(6)	4 470(12)	1 098(5)
C(21)	3 401(8)	5 682(14)	1 636(7)
C(22)	3 116(7)	4 779(12)	354(6)
C(23)	4 216(10)	6 638(13)	1 056(9)
C(11)	3 439(9)	434(14)	1 743(8)
C(12)	4 028(11)	−276(16)	3 065(9)
C(13)	3 013(12)	1 658(18)	2 619(13)

$Mo(NBu^t)_2Cl_2$,[5] and $[Cu(MeCN)_4]BF_4$[16] were prepared as described. Deprotonation of t-butylamine with $LiBu^n$ (Aldrich) in hexane gave $LiNHBu^t$.

N.m.r. spectra (in C_6D_6 unless otherwise stated) are given in p.p.m.: ^1H and ^{13}C *vs.* $SiMe_4$; ^{19}F *vs.* $CFCl_3$ external, at 84.27 MHz; ^{27}Al *vs.* external $[Al(H_2O)_6]^{3+}$, at 23.26 MHz. I.r. spectra in Nujol mulls.

Di(t-butylamido)di(t-butylimido)molybdenum(VI).—To a solution of $LiNHBu^t$ (0.31 g, 3.83 mmol) in diethyl ether (20 cm^3) at −78 °C was slowly (4 min) added *via* a cannula a solution of $Mo(NBu^t)_2Cl_2$ (0.50 g, 1.92 mmol) in Et_2O (30 cm^3) and the mixture stirred at −78 °C for 15 min. On slow warming the colour changed from yellow to yellow-brown; after stirring at room temperature (2 h) the volatiles were removed and the residue extracted with hexane (30 cm^3). Filtration and evaporation of the solution left a solid which was sublimed [100—120 °C at 0.05 mmHg (*ca.* 6.65 Pa)]. Yield: 0.38 g (51.8%). M.p. 78—81 °C. Mass spectrum: *m/z* 310 (M^+, isotopic cluster computer-simulated), 295 (M^+ − Me), and 239 (M^+ − NBu^t).

Table 7. Fractional atomic co-ordinates ($\times 10^4$) for $W[(\mu\text{-}NBu^t)_2\text{-}AlCl_2]_2$

Atom	*x*	*y*	*z*
W	1 082.9(4)	13.6(4)	8 601.2(2)
N(1)	292(10)	757(6)	9 304(7)
N(2)	−292(8)	44(8)	7 933(6)
Al(1)	−1 184(4)	737(3)	8 688(3)
Cl(1)	−2 666(4)	78(6)	9 232(4)
Cl(2)	−1 732(6)	1 953(3)	8 271(3)
Al(2)	3 267(4)	−833(3)	8 709(3)
Cl(11)	4 386(4)	−707(3)	9 719(3)
Cl(12)	4 038(5)	−1 692(3)	7 868(4)
N(3)	2 707(9)	262(5)	8 272(6)
N(4)	1 515(10)	−1 065(7)	8 993(7)
C(1)	557(17)	1 258(10)	10 075(9)
C(2)	−731(14)	−271(8)	7 145(9)
C(3)	3 498(13)	959(9)	7 909(9)
C(4)	997(14)	−1 844(8)	9 424(8)
C(11)	745(21)	2 251(9)	9 844(12)
C(12)	1 800(17)	929(12)	10 428(9)
C(13)	−576(16)	1 137(12)	10 630(10)
C(31)	4 166(19)	1 448(12)	8 531(11)
C(32)	4 484(16)	548(12)	7 343(11)
C(33)	2 617(18)	1 542(13)	7 458(15)
C(21)	−1 245(21)	459(13)	6 716(11)
C(22)	−1 871(23)	−926(17)	7 308(13)
C(23)	332(21)	−757(16)	6 696(13)
C(41)	−57(15)	−2 205(10)	8 953(10)
C(42)	1 995(16)	−2 567(10)	9 442(13)
C(43)	657(26)	−1 604(13)	10 225(13)

I.r.: 3 354 cm^{-1} (N–H). N.m.r.: ^1H (90 MHz), δ 5.71 (2 H, NH), 1.41 [18 H, $NHC(CH_3)_3$], and 1.30 [18 H, $NC(CH_3)_3$]. $^{13}C\text{-}\{^1H\}$, δ 67.21 ($NCMe_3$), 53.42 ($HNCMe_3$), 33.71 [$NHC(CH_3)_3$], and 32.86 [$NC(CH_3)_3$].

Dilithium Tetra(t-butylimido)molybdate(VI).—To a solution of LiMe in Et_2O (6.1 cm^3 of 0.52 mol dm^{-3} solution, 3.16 mmol) and hexane (20 cm^3) at −40 °C was added $Mo(NBu^t)_2$-

Table 8. Fractional atomic co-ordinates ($\times 10^4$) for $[\mathrm{W(NBu^t)_2(NH_2Bu^t)Cl(\mu\text{-}Cl)}]_2$

Atom	x	y	z
W(1)	3 370(1)	4 051(1)	215(1)
Cl(1)	5 028(3)	6 437(4)	1 503(4)
Cl(2)	3 042(4)	5 739(6)	−1 500(6)
N(1)	2 573(10)	2 337(15)	−967(17)
N(2)	4 366(12)	2 992(17)	1 671(18)
N(3)	2 616(9)	4 759(13)	1 617(16)
C(2)	4 118(20)	1 846(28)	2 606(28)
C(1)	1 775(14)	1 050(21)	−2 055(22)
C(3)	1 768(16)	5 221(19)	2 501(21)
C(11)	802(25)	814(48)	−1 445(45)
C(13)	1 485(37)	1 655(55)	−3 432(45)
C(21)	3 026(19)	1 193(22)	2 687(26)
C(22)	4 924(25)	1 423(33)	3 436(28)
C(31)	856(20)	3 945(31)	2 129(47)
C(32)	1 544(24)	6 667(32)	1 996(47)
C(33)	2 148(36)	5 657(65)	4 154(39)
C(23A)	4 388(32)	375(34)	905(45)
C(23B)	4 357(34)	3 745(42)	4 203(40)
C(12A)	2 371(35)	−22(50)	−3 040(50)
C(12B)	1 903(46)	−520(43)	−1 597(94)

All occupancies 1.0 except: C(12A), 0.611; C(12B), 0.389; C(23A), 0.532; C(23B), 0.468.

$(\mathrm{NHBu^t})_2$ (0.52 g, 1.36 mmol) in hexane (30 cm^3). After stirring at −40 °C (10 min), warming to room temperature, and stirring (30 min) the solution was gently refluxed (2 h). Removal of volatiles in vacuum gave a residue, which was extracted into toluene (30 cm^3), and the solution filtered and concentrated to give, after cooling (−20 °C), lemon yellow crystals. Yield: 0.25 g (48.9%). I.r.: 1 243 (linear $\mathrm{MoNBu^t}$) and 1 181 cm^{-1} (bent $\mathrm{MoNBu^t}$). N.m.r.: ^{1}H, δ 1.66 (s, 9 H, linear $\mathrm{NBu^t}$) and 1.47 (s, 27 H, bent $\mathrm{NBu^t}$); ^{13}C-{^{1}H}, δ 60.62 (bent $C\mathrm{Me_3}$), 36.58 [bent $\mathrm{C(}C\mathrm{H_3)_3}$], 48.5 (linear $C\mathrm{Me_3}$), and 33.83 [linear $\mathrm{C(}C\mathrm{H_3)_3}$].

Dilithium Tetra(t-butylimido)tungstate(VI).—As above from $\mathrm{W(NBu^t)_2(NHBu^t)_2}$ (0.73 g, 1.55 mmol) in hexane (30 cm^3) and LiMe (7.5 cm^3 of 0.52 mol dm^{-3} $\mathrm{Et_2O}$ solution, 3.9 mmol) in hexane (30 cm^3). On warming a white crystalline precipitate is formed between −20 and 0 °C. After removal of volatiles the solid was extracted with hot hexane (3 × 40 cm^3), the solution filtered through Celite, and concentrated until crystallisation began. Cooling at −20 °C (12 h) gave colourless needles. Yield: 0.5 g (65%). I.r.: 1 276 (linear $\mathrm{WNBu^t}$) and 1 181 cm^{-1} (bent $\mathrm{WNBu^t}$). N.m.r.: ^{1}H, δ 1.67 (s, 9 H, linear $\mathrm{NBu^t}$) and 1.48 (s, 27 H, bent $\mathrm{NBu^t}$); ^{13}C-{^{1}H}, δ 60.78 (bent $C\mathrm{Me_3}$), 47.8 (linear $C\mathrm{Me_3}$), 37.15 [bent $\mathrm{C(}C\mathrm{H_3)_3}$], and 34.62 [linear $\mathrm{C(}C\mathrm{H_3)_3}$].

Tetrachloro-1κ^2,3κ^2-*tetra*-μ-t-*butylimido*-1:2κ^{2}N;2:3κ^{2}N-1,3-*dialuminium-2-tungsten and the Molybdenum Analogue*.—To a mixture of $\mathrm{Li_2W(NBu^t)_4}$ (1.25 g, 2.6 mmol) and $\mathrm{AlCl_3}$ (freshly sublimed; 1.42 g, 10.6 mmol) was added toluene (40 cm^3) at room temperature. The initially white suspension turned black-purple after stirring for *ca.* 15 min; after *ca.* 8 h the toluene was removed and the residue extracted with hexane (3 × 30 cm^3). After filtration and concentration the purple extracts were cooled at −20 °C (12 h) to give purple-blue crystals. Yield: 1.45 g [84.5% based on $\mathrm{Li_2W(NBu^t)_4}$]. Mass spectrum: m/z 664 (M^+, isotopic cluster), 649 ($M^+ - \mathrm{CH_3}$), 593 ($M^+ - \mathrm{NBu^t}$), and 537 ($M^+ - \mathrm{NBu^t{-}Bu^t}$). I.r.: 1 046s cm^{-1} [$\mathrm{Al(\mu\text{-}NBu^t)W}$, *cf.* ref. 6*a*, p. 123]. N.m.r.: ^{1}H, δ 1.36 (s, $\mathrm{NBu^t}$); ^{13}C-{^{1}H}, δ 70.2 ($C\mathrm{Me_3}$) and 34.7 [$\mathrm{C(}C\mathrm{H_3)_3}$]; ^{27}Al, δ 51.25, $\Delta_{\frac{1}{2}}$ 133 Hz.

The molybdenum analogue was made similarly from $\mathrm{Li_2Mo(NBu^t)_4}$ (0.1 g, 0.25 mmol) and $\mathrm{AlCl_3}$ (0.15 g, 1.12 mmol) in toluene (10 cm^3) as yellow-green crystals from hexane (−20 °C). Yield: 0.1 g (69.5%). Mass spectrum: m/z 561 ($M^+ - \mathrm{CH_3}$, isotopic cluster) and 501 ($M^+ - \mathrm{NBu^t}$). I.r.: 1 021s cm^{-1} [$\mathrm{Al(\mu\text{-}NBu^t)Mo}$]. N.m.r.: ^{1}H, δ 1.37 (s, $\mathrm{NBu^t}$); ^{13}C-{^{1}H}, δ 73.07 ($C\mathrm{Me_3}$) and 34.14 [$\mathrm{C(}C\mathrm{H_3)_3}$]; ^{27}Al, δ 58.0.

Tetramethyl-1κ^2,3κ^2-*tetra*-μ-*t-butylimido*-1:2κ^{2}N;2:3κ^{2}N-1,3-*dialuminium-2-tungsten and the Molybdenum Analogue*.—To a solution of $\mathrm{Li_2W(NBu^t)_4}$ (1.69 g, 3.5 mmol) in toluene (30 cm^3) was added a hexane solution of $\mathrm{AlMe_3}$ (15.8 cm^3 of 1 mol dm^{-3} solution, 0.016 mmol) at ambient temperature. After *ca.* 1 min the colourless solution became orange-red and was stirred for 12 h when volatiles were removed in vacuum. The residue was extracted with hexane (3 × 20 cm^3) which was filtered and concentrated. A small initial precipitate of $\mathrm{Li_2W(NBu^t)_4}$ was removed and the solution cooled (−20 °C, 12 h) to give two crops of orange-red prisms. Yield: 1.16 g (56.8%). Mass spectrum: m/z 567 (M^+, isotopic cluster), 552 ($M^+ - \mathrm{CH_3}$), 511 ($M^+ - \mathrm{NBu^t}$), and 495 ($M^+ - \mathrm{AlMe_3}$). I.r.: 1 065 cm^{-1} ($\mathrm{\mu\text{-}NBu^t}$). N.m.r.: ^{1}H, δ 1.33 (s, 36 H, $\mathrm{NBu^t}$) and −0.18 (s, 12 H, Me); ^{13}C-{^{1}H}, δ 65.75 ($C\mathrm{Me_3}$), 35.37 [$\mathrm{C(}C\mathrm{H_3)_3}$], and −7.5 (br, $\mathrm{Al}C\mathrm{H_3}$); ^{27}Al, δ 53.86, $\Delta_{\frac{1}{2}}$ 2 900 Hz.

The molybdenum analogue was made similarly from $\mathrm{Li_2Mo(NBu^t)_4}$ (0.1 g), $\mathrm{AlMe_3}$ solution (1.14 cm^3), and toluene (10 cm^3). The solution became green on stirring and work-up as above, but with cooling at −78 °C gave green crystals. Yield: 0.03 g (24.3%). Mass spectrum: m/z 475 (M^+ − Me, isotopic cluster) and 419 ($M^+ - \mathrm{NBu^t}$). I.r.: 1 045 cm^{-1} ($\mathrm{\mu\text{-}NBu^t}$). N.m.r.: ^{1}H, δ 1.33 (s, 36 H, $\mathrm{NBu^t}$) and −0.24 (s, 12 H, Me); ^{13}C-{^{1}H}, δ 67.40 ($C\mathrm{Me_3}$) and 45.90 [$\mathrm{C(}C\mathrm{H_3)_3}$]; ^{27}Al, δ 59.0, $\Delta_{\frac{1}{2}}$ 2 930 Hz.

Tetrachloro-1κ^2,3κ^2-*tetra*-μ-t-*butylimido*-1:2κ^{2}N;2:3κ^{2}N-1,3-*digallium-2-tungsten*.—A solution of $\mathrm{Li_2W(NBu^t)_4}$ (0.33 g, 0.7 mmol) in toluene (20 cm^3) was added to a solution of $\mathrm{GaCl_3}$ (0.49 g, 2.55 mmol) in toluene (20 cm^3) at −78 °C. The colour changed from yellow to green and eventually, after warming to 0 °C, to purple. After stirring for *ca.* 8 h at room temperature the toluene was removed and the residue extracted into hexane (2 × 20 cm^3), which was filtered, concentrated (10 cm^3), and cooled at −20 °C for 4 d to give purple prisms. Yield: 0.2 g (38%). N.m.r.: ^{1}H, δ 1.35 (s, $\mathrm{NBu^t}$); ^{13}C-{^{1}H}, δ 70.0 ($C\mathrm{Me_3}$) and 34.5 [$\mathrm{C(}C\mathrm{H_3)_3}$].

Di(t-butylamine)di(t-butylimido)bis(trifluoromethanesulphonato)tungsten(VI) *and the Molybdenum Analogue*.—To a solution of $\mathrm{W(NBu^t)_2(NHBu^t)_2}$ (3.5 g, 7.45 mmol) in $\mathrm{Et_2O}$ (30 cm^3) at −78 °C was added dropwise over 30 min a solution of $\mathrm{CF_3SO_3H}$ (37.3 cm^3, 0.44 mol dm^{-3} solution in $\mathrm{Et_2O}$). After stirring at −78 °C (30 min) and slow warming to ambient temperature the solution was evaporated in vacuum, the yellow residue washed with $\mathrm{Et_2O}$ (2 × 20 cm^3) and extracted into $\mathrm{CH_2Cl_2}$ (3 × 20 cm^3). The filtered extracts were concentrated (*ca.* 20 cm^3), $\mathrm{Et_2O}$ (20 cm^3) added, and the solution cooled (−20°, 12 h) to yield yellow prisms. Yield: 3.3 g (57.5%). I.r.: 3 287, 3 238, 3 185, 3 121 (N–H); 1 214 ($\mathrm{NBu^t}$); and 1 317 cm^{-1} ($\mathrm{CF_3SO_3}$). N.m.r. ($\mathrm{CDCl_3}$): ^{1}H, δ 1.40 (18 H, s, $\mathrm{NBu^t}$), 1.52 (18 H, s, $\mathrm{H_2N}Bu^t$), and 4.25 (4 H, br s, $H_2\mathrm{NBu^t}$); ^{13}C-{^{1}H}, δ 30.56 [$(C\mathrm{H_3})_3\mathrm{CNH_2}$], 32.34 [$(C\mathrm{H_3})_3\mathrm{CN}$], 54.49 ($\mathrm{Me_3}C\mathrm{NH_2}$), 70.63 ($\mathrm{Me_3}C\mathrm{N}$), and 124.0 (s, $\mathrm{CF_3SO_3}$, $J_{\mathrm{C-F}}$ 317 Hz); ^{19}F, δ −79.65.

The molybdenum analogue was made similarly from $\mathrm{Mo(NBu^t)_2(NHBu^t)_2}$ (0.3 g, 0.78 mmol) and $\mathrm{CF_3SO_3H}$ (3.9 cm^3, 0.44 mol solution, 1.73 mmol). Yield: 0.15 g (36%). I.r.: 3 287, 3 238, 3 185, 3 121 (N–H); 1 211 ($\mathrm{NBu^t}$); and 1 308 cm^{-1} ($\mathrm{CF_3SO_3}$). N.m.r. ($\mathrm{CDCl_3}$): ^{1}H, δ 1.38 (18 H, s, $\mathrm{NBu^t}$), 1.63 (18 H, s, $\mathrm{H_2N}Bu^t$), and 4.18 (4 H, br s, $H_2\mathrm{NBu^t}$); ^{13}C-{^{1}H}, δ 30 [s, $(C\mathrm{H_3})_3\mathrm{CNH_2}$], 31.0 [s, $(C\mathrm{H_3})_3\mathrm{CN}$], and 53.32 (s, $\mathrm{Me_3}C\mathrm{NH_2}$); ^{19}F, δ −83.12.

Table 9. Fractional atomic co-ordinates (× 10^4) for $[W_2Cu_5(NBu^t)_2(\mu\text{-}NBu^t)_6(NHBu^t)_2]BF_4$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W(1)	5 242.8(3)	1 752.2(2)	2 699.6(3)	C(53)	9 180(7)	4 163(5)	5.386(10)
W(2)	8 811.3(3)	2 282.9(2)	5 188.3(3)	N(6)	5 818(5)	2 071(4)	1 618(7)
Cu(1)	6 703(1)	2 787(1)	4 421(1)	C(6)	5 568(7)	2 222(5)	315(9)
Cu(2)	7 222(1)	2 017(1)	2 659(1)	C(61)	4 393(8)	2 446(6)	−288(10)
Cu(3)	7 137(1)	1 362(1)	4 650(1)	C(62)	6 199(8)	2 866(6)	213(10)
Cu(4)	8 685(1)	2 878(1)	2 842(1)	C(63)	5 830(9)	1 575(7)	−365(11)
Cu(5)	4 992(1)	3 318(1)	2 775(1)	N(7)	5 282(5)	2 558(4)	3 883(6)
N(1)	10 085(1)	2 425(4)	6 034(7)	C(7)	4 768(7)	2 584(5)	4 809(8)
C(1)	11 185(7)	2 547(6)	6 746(10)	C(71)	4 796(8)	1 840(5)	5 314(9)
C(11)	11 248(8)	3 007(6)	7 899(10)	C(72)	3 627(7)	2 835(6)	4 195(10)
C(12)	11 723(9)	1 807(7)	7 096(12)	C(73)	5 332(8)	3 103(6)	5 868(10)
C(13)	11 649(8)	2 934(7)	5 949(11)	N(10)	4 692(6)	4 149(4)	1 788(7)
N(2)	3 983(5)	1 543(4)	1 952(7)	C(10)	3 956(7)	4 698(5)	2 058(9)
C(2)	2 867(7)	1 363(6)	1 301(9)	C(102)	3 887(8)	5 379(6)	1 340(11)
C(21)	2 272(8)	2 040(6)	835(11)	C(103)	2 884(8)	4 361(6)	1 650(11)
C(22)	2 821(8)	812(6)	266(11)	C(101)	4 394(9)	4 878(6)	3 426(10)
C(23)	2 484(8)	1 027(6)	2 247(10)	N(8)	8 682(5)	1 983(4)	3 481(6)
N(3)	5 976(5)	951(4)	3 454(6)	C(8)	9 279(7)	1 359(5)	3 162(9)
C(3)	5 970(7)	155(5)	3 268(8)	C(81)	10 400(8)	1 569(6)	3 456(11)
C(31)	6 800(8)	−200(5)	4 386(10)	C(82)	8 790(9)	1 196(7)	1 778(11)
C(33)	4 915(8)	−105(5)	3 137(10)	C(83)	9 259(9)	715(6)	3 886(11)
C(32)	6 201(9)	−12(6)	2 085(11)	N(9)	8 645(6)	3 747(5)	2 046(8)
N(4)	8 314(5)	1 639(4)	5 965(7)	C(9)	9 476(8)	3 861(6)	1 524(10)
C(4)	8 526(7)	1 340(5)	7 211(9)	C(91)	10 536(10)	3 747(8)	2 624(14)
C(41)	9 214(11)	665(8)	7 311(13)	C(92)	9 354(10)	4 595(7)	1 007(13)
C(42)	9 106(12)	1 861(8)	8 235(14)	C(93)	9 404(12)	3 254(9)	605(14)
C(43)	7 546(10)	1 124(8)	7 366(12)	F(4)	3 445(6)	4 289(4)	7 134(8)
N(5)	8 054(5)	3 130(4)	5 039(7)	F(3)	3 377(5)	5 260(4)	8 258(6)
C(5)	8 207(7)	3 876(5)	5 502(9)	F(2)	1 993(5)	4 654(4)	7 317(8)
C(51)	7 244(8)	4 347(5)	4 759(10)	F(1)	3 243(6)	4 173(4)	8 902(7)
C(52)	8 304(8)	3 895(6)	6 865(9)	B(1)	3 021(10)	4 573(7)	7 903(13)

Di(pyridine)di(t-butylimido)bis(trifluoromethanesulphonato)tungsten(VI).—To a solution of $W(NBu^t)_2(NH_2Bu^t)_2(O_3SCF_3)_2$ (0.3 g, 0.39 mmol) in CH_2Cl_2 (10 cm^3) was added excess of pyridine (0.2 cm^3) when the colour changed from yellow to orange. After stirring for 0.5 h the solution was evaporated under vacuum and the residue washed with Et_2O (2 × 20 cm^3) and crystallized from CH_2Cl_2–Et_2O (1:1). Yield: 0.1 g (32.7%). I.r.: 1 615 (aromatic CH), 1 239 (NBu^t), and 1 308 cm^{-1} (CF_3SO_3). N.m.r. (C_5D_5N): ^1H, δ 1.45 (18 H, s, NBu^t) and 8.2—8.5 (10 H, m, py); ^{19}F, δ −80.0.

Di(4-butylpyridine)di(t-butylimido)bis(trifluoromethanesulphonato)tungsten(VI).—To $W(NBu^t)_2(NH_2Bu^t)_2(O_3SCF_3)_2$ (0.35 g, 0.45 mmol) in CH_2Cl_2 (10 cm^3) was added excess of 4-t-butylpyridine (0.05 cm^3) and the solution refluxed for *ca.* 10 h. After removal of volatiles the oily residue was washed with Et_2O (2 × 20 cm^3) and crystallised from CH_2Cl_2–Et_2O at −20 °C to give lemon crystals. Yield: 0.24 g (60%). I.r.: 1 618 (aromatic CH) and 1 218 cm^{-1} (NBu^t). N.m.r. ($CDCl_3$): ^1H, δ 1.27 (18 H, s, Bu^tpy), 1.40 (18 H, s, NBu^t), 7.7 and 8.5 (8 H, py H); ^{13}C-{^1H}, δ 28.3, 32.7 [$(CH_3)_3CN$], 30.2, 30.4 [$(CH_3)_3C$ of py], 52.1 and 75.5 (Me_3CN); ^{19}F, δ −79.3.

Di(t-butylamine)di(t-butylimido)bis(trifluoroacetato)tungsten(VI).—As for the triflate, from $W(NBu^t)_2(NHBu^t)_2$ (1 g, 2.13 mmol) and CF_3CO_2H (0.38 cm^3 in Et_2O, 50 cm^3). Crystallisation (twice) from hexane gave yellow crystals. Yield: 0.4 g (26.5%). I.r.: 3 327, 3 261 (NH); ν_{sym} 1 705, ν_{asym} 1 428 cm^{-1} (O_2CCF_3). N.m.r. (C_6D_6): ^1H, δ 1.28 (8 H, s, NBu^t), 1.52 (18 H, s, NH_2Bu^t), and 4.08 (4 H, br s, NH_2Bu^t); ^{19}F, δ −164.0.

Di-μ-chloro-bis[chloro(t-butylamine)di(t-butylimido)tungsten].—To $W(NBu^t)_2(NHBu^t)_2$ (0.5 g, 1.05 mmol) in Et_2O (30 cm^3) at −78 °C was added a solution of HCl in Et_2O (4.6 cm^3, 0.46 mol dm^{-3}) and the mixture allowed to warm to room temperature with stirring (2 h). After evaporation the yellow residue was washed with hexane (2 × 20 cm^3) and extracted into Et_2O (2 × 20 cm^3). Filtration, concentration, and washing (−20 °C) gave yellow plates. Yield: 0.1 g. I.r.: 3 294, 3 177 (NH) and 1 278 cm^{-1} (NBu^t). N.m.r. (C_6D_6): ^1H, δ 1.10 (18 H, s, Bu^tNH_2), 1.45 (36 H, s, NBu^t), and 2.60 (4 H, s, Bu^tNH_2); ^{13}C-{^1H}, δ 30.84 [s, $(CH_3)_3CNH_2$] and 3.57 [s, $(CH_3)_3CN$].

(t-Butylamido)(t-butylamine)di(t-butylimido)tungsten(VI) *Tetrafluoroborate*.—(*a*) *Reaction at low temperature: isomer* (**A**). To $W(NBu^t)_2(NHBu^t)_2$ (1 g, 2.13 mmol) in Et_2O (50 cm^3) at −78 °C was added dropwise with vigorous stirring a pre-cooled solution of $HBF_4{\cdot}Et_2O$ (2.55 mmol of 85% solution) over *ca.* 0.5 h, after which the solution was stirred for 2 h and allowed to warm to room temperature over 4 h. The precipitated solid was collected, washed with Et_2O (3 × 30 cm^3), and crystallised from boiling toluene as colourless plates. Yield: 0.4 g (37%). I.r.: 3 446, 3 265, 3 209, 3 168 (NH), 1 299 ($WNBu^t$), and 1 026 (br) cm^{-1} (BF_4^-). N.m.r.: ^1H, δ 1.39 (9 H, s, Bu^tNH_2), 1.41 (18 H, s, Bu^tN), 1.49 (9 H, s, Bu^tNH), 4.33 (1 H, br s, Bu^tNH), and 6.33 (2 H, s, Bu^tNH_2); ^{19}F, δ −177.7.

(*b*) *Reaction at room temperature: isomer* (**B**). In a similar way but at room temperature $HBF_4{\cdot}Et_2O$ (0.45 cm^3, 85% solution, 2.23 mmol) was added to $W(NBu^t)_2(NHBu^t)_2$ (0.7 g) in Et_2O (30 cm^3) to give an immediate white precipitate which, after stirring the mixture for *ca.* 20 min, becomes oily. After stirring for *ca.* 1 h the volatiles were removed in vacuum and the residue washed with hexane (3 × 50 cm^3), dissolved in toluene (*ca.* 20 cm^3) which was filtered and the product precipitated by addition of hexane. The solid was crystallised from boiling Et_2O (*ca.* 50 cm^3) as creamy white plates on cooling at −20 °C overnight. Yield: 0.29 (24%). I.r.: 3 276, 3 245, 3 153 (NH), 1 238 (NBu^t), 1 097, 598, and 360 cm^{-1} (BF_4). N.m.r. ($CDCl_3$): ^1H, δ 1.38 (18 H, s, NBu^t), 1.40 (18 H, *Bu^t*NH, *Bu^t*NH_2), 3.99 (2 H, br s, *H_2*NBu^t), and 6.30 (1 H, s, *H*NBu^t); ^{19}F, δ −163.0 (AB pattern), J_{AB} = 14.7 Hz.

Interaction of $Li_2W(NBu^t)_4$ *with* $[Cu(MeCN)_4]BF_4$.—To a suspension of $[Cu(MeCN)_4]BF_4$ (0.73 g, 2.34 mmol) in toluene (30 cm^3) at −78 °C was added a solution of $Li_2W(NBu^t)_4$ (0.5 g, 1.05 mmol) in toluene (20 cm^3). The white suspension turned yellow as the mixture warmed and stirring was continued for 12 h at room temperature when the volatiles were removed in vacuum and the residue extracted with hexane (5 × 30 cm^3). The hexane extracts were filtered, concentrated (to *ca.* 50 cm^3), filtered again, and cooled slowly at −20 °C to give yellow crystals. Yield: 0.2 g, 21%. *X*-Ray-quality crystals were obtained by slow vapour diffusion of hexane into toluene solutions. I.r.: 3 287, 3 250 (NH), 1 258 ($WNBu^t$), 1 215 [$W(\mu$-$NBu^t)Cu$], 1 033 and 780 cm^{-1} (BF_4^-). N.m.r. (C_6D_6): ^1H, δ 1.73 [$W(\mu$-$NBu^t)Cu$], 1.62 ($WNBu^t$), 1.54 (μ_3-NBu^t), and 1.29 (CuNH-*Bu^t*).

X-Ray Crystallography.—Measurements for all compounds were made on crystals sealed under argon in thin-walled glass capillaries. Following preliminary photography, unit-cell dimensions and intensity data were measured using standard procedures and software on an Enraf-Nonius CAD4 diffractometer operating with graphite-monochromated Mo-K_α radiation in the ω—2θ scan mode. Intensity data were corrected for absorption empirically and the structures solved *via* Patterson or direct methods. Refinement was accomplished by full-matrix least squares with anisotropic displacement factors for all non-hydrogen atoms. Hydrogen atoms were not included in any of the structures. Disorder occurs in the orientations of t-butyl groups in one imido and the amine ligands in the chloride-bridged dimer. It was not possible to identify the Me_3 sets in either case and so each group was modelled by including partial carbons (normalised to total 3) at the major sites, of which there were four in each (see Figure 3). Standard weighting schemes were applied to give acceptable agreement analyses. Details of the crystal data and experimental parameters are given in Table 5. Fractional atomic co-ordinates are listed in Tables 6—9.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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