Imido and Oxo Compounds of Chromium-(V) and -(VI) and of Molybdenum- and Tungsten-(VI)†

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The interaction of 1,1,1,3,3,3-hexamethyldisilazane and CrO_2Cl_2 gives the amido complex $CrO_2[N(SiMe_3)_2]$ whereas MoO_2Cl_2 gives the imido complex $Mo(NSiMe_3)_2(OSiMe_3)_2$ and $WO_2Cl_2(dme)$ (dme = 1,2-dimethoxyethane) gives a red oil that reacts with pyridine (py) to give $WCl(NSiMe_3)(OSiMe_3)_3(py)$. Interaction of $CrO_2[N(SiMe_3)_2]$ with pyridine and 4-methylpyridine (L) leads to reduction to the chromium(V) species $[CrO(NSiMe_3)L]_2(\mu\text{-}OSiMe_3)_2$. Interaction of CrO_2Cl_2 with 2,2,6,6-tetramethylpiperidine gives the amido species $CrO_2Cl(NC_9H_{18})$ while $SiMe_2(NHBu^t)_2$ gives $Cr(NBu^t)_2Cl_2(NH_2Bu^t)$. The crystal structures of the compounds $[CrO(NSiMe_3)(py)]_2(\mu\text{-}OSiMe_3)_2$, $CrO_2Cl(NC_9H_{18})$ and $WCl(NSiMe_3)(OSiMe_3)_3(py)$ have been determined. In the centrosymmetric dimeric complex the Cr atom is five-co-ordinate with a geometry intermediate between trigonal bipyramidal and square pyramidal. The crystals of $CrO_2Cl(NC_9H_{18})$ contain two chemically equivalent tetrahedral molecules, while $WCl(NSiMe_3)(OSiMe_3)(py)$ is octahedral with the pyridine ligand *trans* to the imido group.

A well established[1] method for converting transition-metal species with M=O bonds into those with M=NR bonds is that using silylamines, which depends upon the high strength of the Si–O bond to give $(Me_3Si)_2O$ or $OSiMe_3^-$ in reactions of types (1) and (2). Although reactions of metal halides with 1,1,1,3,3,3-hexamethyldisilazane commonly give amido complexes with $N(SiMe_3)_2$ groups,[2] the silazane can also give imido compounds, $M(NSiMe_3)$ (M = V, Nb or Ta).[3] This paper describes the reactions of hexamethyldisilazane with MO_2Cl_2 (M = Cr, Mo or W) and some related chemistry.

$$MO + NR(SiMe_3)_2 \longrightarrow M(NR) + (Me_3Si)_2O \qquad (1)$$

$$MO + NHR(SiMe_3) \longrightarrow M(NR)(OSiMe_3)^- + H^+ \qquad (2)$$

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

Results and Discussion

Chromium Compounds.—The reaction of CrO_2Cl_2 with $NH(SiMe_3)_2$ might have been expected to give an imido complex since the reaction using $NH(Bu^t)(SiMe_3)$ produces $Cr(NBu^t)_2(OSiMe_3)_2$.[4] However, the Cr=O groups do not react and the product is the amido compound $CrO_2[N(SiMe_3)_2]_2$ **1**, formed according to equation (3). Compound **1** is a deep red oil at room temperature that gives yellow crystals (m.p. −33 °C) on cooling or on vacuum sublimation of the oil to a cold probe. The IR spectrum of the oil shows Cr=O stretches at 832 and 891 cm^{-1} (in hexane solution, 833 and 885 cm^{-1}). The ^1H NMR spectrum in C_6D_6 has a singlet at δ 0.36 for the four $SiMe_3$ groups that are equivalent on the NMR time-scale at 20 °C. Although the compound is both thermally unstable and light sensitive and slowly decomposes at room temperature, it is stable indefinitely in the dark at −20 °C. While we have been unable to obtain conventional microanalyses the mass spectrum (electron impact, EI) shows the molecular ion at $m/z = 404$.

$$CrO_2Cl_2 + 4NH(SiMe_3)_2 \longrightarrow CrO_2[N(SiMe_3)_2]_2 + 2[NH_2(SiMe_3)_2]Cl \qquad (3)$$

Interaction of compound **1** with tetrahydrofuran, 1,2-dimethoxyethane, 2- and 3-methylpyridine, 2,4-dimethylpyridine and quinuclidine does not give adducts, probably for steric reasons due to shielding of the Cr atom by the bulky $N(SiMe_3)_2$ groups. With an excess of pyridine and 4-methylpyridine (L) in CH_2Cl_2 at room temperature, reduction occurs to give the green, crystalline, five-co-ordinate chromium(V) dimers, $[CrO(NSiMe_3)L]_2(\mu\text{-}OSiMe_3)_2$, **2** and **3**. Both compounds are paramagnetic and give EPR (X-band) spectra at 20 °C in toluene: g = 1.965 (**2**) and 1.995 (**3**). The mechanism for the reduction and formation of **2** and **3** is not clear. Reduction to green chromium(V) species also occurs with PMe_3, PMe_2Ph and PPh_3, but the products are oils and intractable. The structure of **2** has been confirmed by X-ray diffraction study. A diagram of the molecule is shown in Fig. 1; selected bond lengths and angles are given in Table 2.

The identification of the terminal Me_3SiN and bridging Me_3SiO groups was made during the structure refinement process (see Experimental section). The chromium geometry is midway between trigonal bipyramidal and square pyramidal. In the former description, the oxygen of a bridging siloxy group and the pyridine define the axis with an O–Cr–N angle of 153.3°, whilst in the equatorial plane the angle between the bridging siloxy group and the imido nitrogen has opened up to 136.2°. In the alternative, square-pyramidal geometry, the Cr=O bond is axial and the two groupings mentioned above define the *trans* ligand pairs. The axial/basal angles from the oxo function then range between 99.1 and 106.9° (see Table 2).

The siloxide bridge is slightly unsymmetrical in terms of both lengths [Δ(Cr–O) = 0.066(6) Å], due perhaps to the *trans* influence of the oxo ligand, and angles [Δ(Cr–O–Si) = 6.5(4)°], due perhaps to steric interactions. The $NSiMe_3$ imido group may be considered to be bonding as a two-electron donor, giving a formal 17e count for the metal. The relevant Cr–N–Si

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Analytical and physical data for new compounds

Compound	Colour	M.p./°C	Analysis (%)		
			C	H	N
1 $CrO_2[N(SiMe_3)_2]_2$	Yellow	−33			
2 $[CrO(NSiMe_3)(py)]_2(\mu\text{-}OSiMe_3)_2$	Green	175	40.6 (40.9)	7.0 (7.1)	8.3 (8.7)
3 $[CrO(NSiMe_3)(4Me\text{-}py)]_2(\mu\text{-}OSiMe_3)_2$	Green	183	42.3 (42.7)	7.5 (7.4)	8.2 (8.3)
4 $CrO_2Cl(NC_9H_{18})$[a]	Red		42.9 (41.6)	7.3 (7.0)	5.6 (5.4)
5 $Cr(NBu^t)_2Cl_2(NH_2Bu^t)$	Red	155	42.6 (42.6)	8.3 (8.6)	12.2 (12.4)
6 $Mo(NSiMe_3)_2(OSiMe_3)_2$[b]	Yellow	−10	31.6 (32.1)	8.0 (8.0)	6.2 (6.3)
7 $WCl(NSiMe_3)(OSiMe_3)_3(py)$	Colourless	109	30.9 (31.3)	6.4 (6.3)	4.2 (4.3)

[a] O, 11.9 (12.3%). [b] O, 6.8 (7.1%).

Table 2 Selected bond lengths (Å) and angles (°) for compound **2** with estimated standard deviations (e.s.d.s) in parentheses

O(1)–Cr(1)	1.957(6)	N(2)–Cr(1)	1.875(6)
N(1)–Cr(1)	2.082(7)	O(3)–Cr(1)	1.541(7)
O(1a)–Cr(1)	2.008(7)		
Si(1)–O(1)	1.649(6)	C(111)–Si(1)	1.860(11)
C(112)–Si(1)	1.838(10)	C(113)–Si(1)	1.825(12)
Si(2)–N(2)	1.581(6)	C(211)–Si(2)	1.883(10)
C(212)–Si(2)	1.890(10)	C(213)–Si(2)	1.838(10)
C(11)–N(1)	1.340(9)	C(15)–N(1)	1.328(9)
C(12)–C(11)	1.362(11)	C(13)–C(12)	1.351(12)
C(14)–C(13)	1.360(12)	C(15)–C(14)	1.374(11)
N(2)–Cr(1)–O(1)	136.2(2)	N(1)–Cr(1)–O(1)	87.3(3)
N(1)–Cr(1)–N(2)	87.1(3)	O(3)–Cr(1)–O(1)	112.3(3)
O(3)–Cr(1)–N(2)	111.4(4)	O(3)–Cr(1)–N(1)	99.1(4)
O(1)–Cr(1)–O(1a)	77.1(2)	N(2)–Cr(1)–O(1a)	89.4(3)
N(1)–Cr(1)–O(1a)	153.3(3)	O(3)–Cr(1)–O(1a)	106.9(3)
Si(1)–O(1)–Cr(1)	133.9(3)	C(111)–Si(1)–O(1)	108.7(5)
C(112)–Si(1)–O(1)	111.2(4)	C(112)–Si(1)–C(111)	109.8(6)
C(113)–Si(1)–O(1)	109.6(5)	C(113)–Si(1)–C(111)	110.3(7)
C(113)–Si(1)–C(112)	102.7(7)	Si(2)–N(2)–Cr(1)	144.1(3)
C(211)–Si(2)–N(2)	111.8(5)	C(212)–Si(2)–N(2)	108.1(5)
C(212)–Si(2)–C(211)	107.7(5)	C(213)–Si(2)–N(2)	112.4(5)
C(213)–Si(2)–C(211)	108.0(6)	C(213)–Si(2)–C(212)	108.9(6)
C(11)–N(1)–Cr(1)	116.9(6)	C(15)–N(1)–Cr(1)	125.6(6)
C(15)–N(1)–C(11)	117.5(8)	C(12)–C(11)–N(1)	120.7(9)
C(13)–C(12)–C(11)	121.7(10)	C(14)–C(13)–C(12)	118.1(9)
C(15)–C(14)–C(13)	118.4(9)	C(14)–C(15)–N(1)	123.6(9)

Atom O(1a) is generated from O(1) *via* symmetry operation 1 − *x*, *y*, 0.5 − *z*.

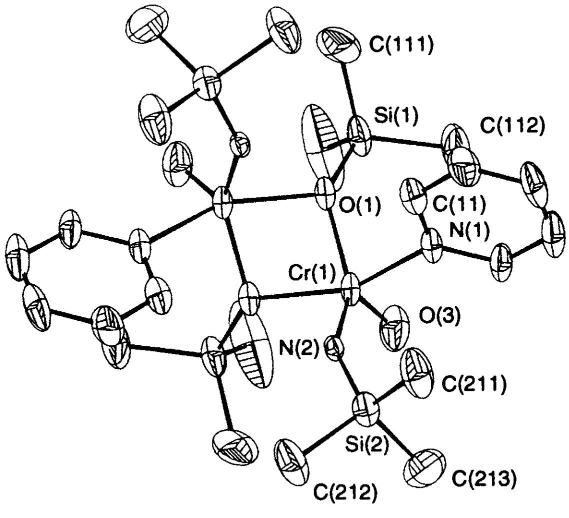


Fig. 1 The structure of $[CrO(NSiMe_3)(py)]_2(\mu\text{-}OSiMe_3)_2$

angle of 144° is consistent with this, although a value closer to 120° would be expected in an uncrowded co-ordination sphere.

The reaction of CrO_2Cl_2 with an excess of 2,2,6,6-tetramethylpiperidine that is bulky but without α-hydrogen atoms produces as the only isolable product the red dioxochloroamide **4**, equation (2). The IR spectrum has Cr=O stretches at 982 and 960 cm^{-1} while the ^1H NMR spectrum has three singlets at δ 1.10, 1.21 and 1.30 in a 6 : 1 : 2 ratio that can be assigned to the four CH_3, the 4-CH_2 and 3,5-CH_2 groups of the amide, respectively. The structure was confirmed by an X-ray study. The unit cell contains two independent molecules and a diagram of one of them is shown in Fig. 2; selected bond lengths and angles for both molecules are given in Table 3. The metal co-ordination geometry in each case is very close to tetrahedral, with all angles falling in the narrow range of 107.7–113.4(4)°. Analogous bond lengths both within and between molecules are equal within experimental error.

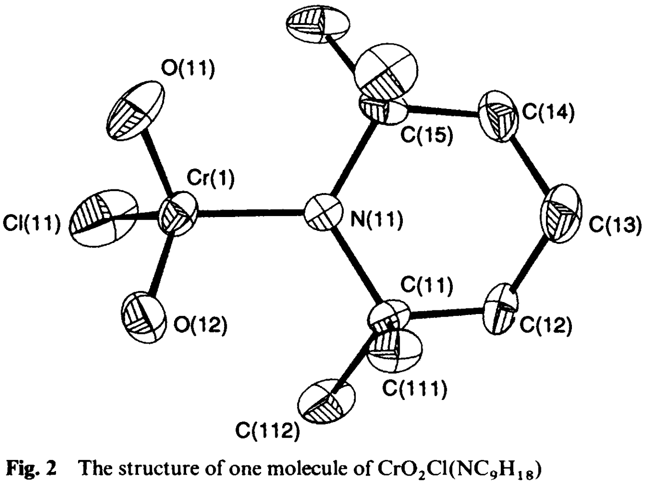
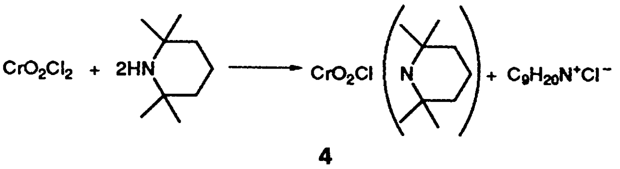


Fig. 2 The structure of one molecule of $CrO_2Cl(NC_9H_{18})$



(2)

4

The interaction of CrO_2Cl_2 with $SiMe_2(NHBu^t)_2$ [5] in hexane at −78 °C gives the bis(*tert*-butylimido) complex $Cr(NBu^t)_2Cl_2(NH_2Bu^t)$ **5**, as red crystals. The IR spectrum shows a $Cr(NBu^t)$ stretch at 1247 cm^{-1} while the ^1H NMR spectrum has singlets at δ 1.58 (NBu^t) and 1.40 (NH_2Bu^t) with a broad signal at 0.1 for the NH_2 group. The compound is thus presumed to be similar to the adducts [6] $Cr(NBu^t)_2Cl_2L$ (L = PMe_3, PMe_2Ph or Bu^tNC), with a structure similar to that determined by X-ray diffraction for $Cr(NBu^t)_2Cl_2(PMe_2Ph)$.[6]

Although some CrO_2X_2 species are known to oxidize alkenes [7] the present oxo species only decompose when refluxed with cyclohexene, 1-methylcyclohexene, *cis*-stilbene or 1,2-dichloroethene.

Table 3 Selected bond lengths (Å) and angles (°) for compound **4** with e.s.d.s in parentheses

Molecule	1	2
Cr(*n*)–Cl(*n*1)	2.185(4)	2.190(4)
Cr(*n*)–O(*n*1)	1.581(7)	1.582(6)
Cr(*n*)–O(*n*2)	1.574(6)	1.581(6)
Cr(*n*)–N(*n*1)	1.802(6)	1.812(7)
N(*n*1)–C(*n*1)	1.53(1)	1.52(9)
N(*n*1)–C(*n*5)	1.55(1)	1.54(1)
C(*n*1)–C(*n*2)	1.51(1)	1.52(1)
C(*n*2)–C(*n*3)	1.49(1)	1.51(1)
C(*n*3)–C(*n*4)	1.49(1)	1.51(1)
C(*n*4)–C(*n*5)	1.52(1)	1.52(1)
C(*n*1)–C(*n*11)	1.54(1)	1.54(1)
C(*n*1)–C(*n*12)	1.53(1)	1.56(1)
C(*n*5)–C(*n*51)	1.52(1)	1.52(1)
C(*n*5)–C(*n*52)	1.53(1)	1.54(1)
O(*n*1)–Cr(*n*)–Cl(*n*)	108.4(3)	108.4(3)
O(*n*2)–Cr(*n*)–Cl(*n*)	108.3(3)	108.2(3)
O(*n*2)–Cr(*n*)–O(*n*1)	113.4(4)	110.7(3)
N(*n*1)–Cr(*n*)–Cl(*n*)	108.2(3)	107.7(3)
N(*n*1)–Cr(*n*)–O(*n*1)	111.0(4)	111.1(3)
N(*n*1)–Cr(*n*)–O(*n*2)	109.6(4)	110.6(3)
C(*n*1)–N(*n*1)–Cr(*n*)	119.8(5)	120.3(4)
C(*n*5)–N(*n*1)–Cr(*n*)	119.6(5)	118.8(5)
C(*n*1)–N(*n*1)–C(*n*5)	119.4(6)	120.0(6)
C(*n*2)–C(*n*1)–N(*n*1)	113.2(6)	112.8(5)
C(*n*11)–C(*n*1)–N(*n*1)	108.1(6)	107.7(7)
C(*n*12)–C(*n*1)–N(*n*1)	108.6(7)	108.8(6)
C(*n*11)–C(*n*1)–C(*n*12)	110.1(6)	110.8(6)
C(*n*11)–C(*n*1)–C(*n*2)	110.2(7)	106.8(6)
C(*n*12)–C(*n*1)–C(*n*2)	106.7(7)	109.9(7)
C(*n*3)–C(*n*2)–C(*n*1)	113.7(7)	115.1(6)
C(*n*4)–C(*n*3)–C(*n*2)	108.3(8)	106.3(8)
C(*n*5)–C(*n*4)–C(*n*3)	114.7(6)	116.7(7)
C(*n*4)–C(*n*5)–N(*n*1)	111.8(6)	111.7(6)
C(*n*51)–C(*n*5)–C(*n*4)	108.7(6)	108.1(7)
C(*n*52)–C(*n*5)–C(*n*4)	111.5(8)	110.1(7)
C(*n*51)–C(*n*5)–C(*n*52)	109.6(7)	110.9(7)
C(*n*51)–C(*n*5)–N(*n*1)	108.1(7)	108.8(7)
C(*n*52)–C(*n*5)–N(*n*1)	107.2(6)	107.3(6)

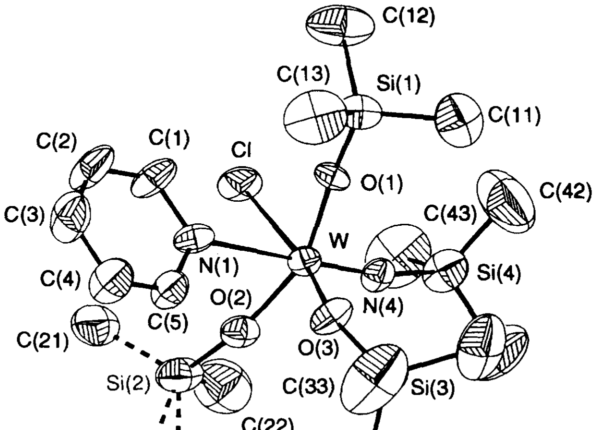


Fig. 3 The structure of WCl(NSiMe$_3$)(OSiMe$_3$)$_3$(py)

Table 4 Selected bond lengths (Å) and angles (°) for compound **7** with e.s.d.s in parentheses

Cl–W	2.448(7)	O(1)–W	1.885(11)
O(2)–W	1.873(11)	O(3)–W	1.883(13)
N(1)–W	1.707(13)	N(10)–W	2.440(15)
Si(1)–O(1)	1.620(12)	Si(2)–O(2)	1.632(12)
Si(3)–O(3)	1.631(13)	Si(4)–N(1)	1.781(15)
C(10)–N(10)	1.345(19)	C(40)–N(10)	1.366(22)
C(20)–C(10)	1.377(21)	C(30)–C(20)	1.358(31)
C(50)–C(30)	1.403(28)	C(50)–C(40)	1.354(21)
C(11)–Si(1)	1.838(18)	C(12)–Si(1)	1.854(23)
C(13)–Si(1)	1.780(21)	C(21)–Si(2)	1.790(19)
C(22)–Si(2)	1.879(22)	C(23)–Si(2)	2.078(57)
C(23B)–Si(2)	1.792(45)	C(31)–Si(3)	1.833(21)
C(32)–Si(3)	1.802(24)	C(33)–Si(3)	1.805(24)
C(41)–Si(4)	1.796(23)	C(42)–Si(4)	1.769(23)
C(43)–Si(4)	1.836(26)		
O(1)–W–Cl	85.7(5)	O(2)–W–Cl	85.2(5)
O(2)–W–O(1)	157.1(4)	O(3)–W–Cl	164.9(3)
O(3)–W–O(1)	91.9(6)	O(3)–W–O(2)	91.4(6)
N(1)–W–Cl	94.5(6)	N(1)–W–O(1)	100.1(6)
N(1)–W–O(2)	101.6(6)	N(1)–W–O(3)	100.6(6)
N(10)–W–Cl	82.7(5)	N(10)–W–O(1)	80.1(5)
N(10)–W–O(2)	77.9(5)	N(10)–W–O(3)	82.2(5)
N(10)–W–N(1)	177.2(6)	Si(1)–O(1)–W	169.9(9)
Si(2)–O(2)–W	162.1(8)	Si(3)–O(3)–W	146.8(7)
Si(4)–N(1)–W	165.6(9)	C(10)–N(10)–W	126.0(13)
C(40)–N(10)–W	119.6(11)	C(40)–N(10)–C(10)	114.4(16)
C(20)–C(10)–N(10)	124.4(20)	C(30)–C(20)–C(10)	120.9(21)
C(50)–C(30)–C(20)	115.3(19)	C(50)–C(40)–N(10)	123.4(19)
C(40)–C(50)–C(30)	121.3(21)	C(11)–Si(1)–O(1)	108.5(9)
C(12)–Si(1)–O(1)	107.6(10)	C(12)–Si(1)–C(11)	107.2(11)
C(13)–Si(1)–O(1)	109.5(10)	C(13)–Si(1)–C(11)	111.2(12)
C(13)–Si(1)–C(12)	112.7(12)	C(21)–Si(2)–O(2)	110.4(8)
C(22)–Si(2)–O(2)	105.5(9)	C(22)–Si(2)–C(21)	111.1(12)
C(23)–Si(2)–O(2)	101.8(16)	C(23)–Si(2)–C(21)	100.3(16)
C(23)–Si(2)–C(22)	127.0(16)	C(23B)–Si(2)–O(2)	114.2(15)
C(23B)–Si(2)–C(21)	119.7(15)	C(23B)–Si(2)–C(22)	94.0(16)
C(23B)–Si(2)–C(23)	31.1(15)	C(31)–Si(3)–O(3)	109.4(10)
C(32)–Si(3)–O(3)	108.0(11)	C(32)–Si(3)–C(31)	112.1(13)
C(33)–Si(3)–O(3)	108.8(10)	C(33)–Si(3)–C(31)	107.2(13)
C(33)–Si(3)–C(32)	111.3(15)	C(41)–Si(4)–N(1)	110.8(10)
C(42)–Si(4)–N(1)	107.3(10)	C(42)–Si(4)–C(41)	108.6(13)
C(43)–Si(4)–N(1)	107.3(10)	C(43)–Si(4)–C(41)	109.3(13)
C(43)–Si(4)–C(42)	113.6(15)		

Molybdenum and Tungsten Compounds.—The interaction of MoO_2Cl_2 and $NH(SiMe_3)_2$ in CH_2Cl_2 at −78 °C gives the complex Mo(NSiMe$_3$)$_2$(OSiMe$_3$)$_2$ **6** in contrast to the reaction with CrO_2Cl_2 described above. This compound is also a low-melting (−10 °C) solid; it is both thermally and light stable. Its spectra are in accord with the formulation. The mass spectrum shows the molecular ion at m/z = 450, the IR has an Mo=N stretch at 1171 cm^{-1} (in hexane), while the ^{1}H NMR spectrum shows two singlets in a 1 : 1 ratio at δ 0.20 and 0.28 (in C_6D_6) that can be assigned to OSiMe$_3$ and NSiMe$_3$, respectively, by comparison with data for Mo(NBu^t)$_2$(OSiMe$_3$)$_2$[4] and the tungsten compound described below. It is likely that an oxoamido species similar to **1** is an intermediate: transfer of Me$_3$Si groups from this amido species to the Mo=O moieties would lead to **6**.

Tungsten gives a different product; interaction of WO_2Cl_2(dme) (dme = 1,2-dimethoxyethane) and $NH(SiMe_3)_2$ at room temperature gives a deep red oil which we have not been able to characterize directly. However, with an excess of pyridine (py) this gives a crystalline product, which proved to be the octahedral tungsten(VI) complex WCl(NSiMe$_3$)(OSiMe$_3$)$_3$(py) **7**. A diagram of the structure as determined by an X-ray study is shown in Fig. 3; bond lengths and angles are given in Table 4.

Although the identification of the one NSiMe$_3$ imido group and the three OSiMe$_3$ groups *via* comparison of thermal parameters for the alternative assignments was not completely unequivocal, the distinction can be made quite confidently on structural grounds. Thus, as chosen, the W–N (imido) bond length is 1.71(1) Å and is *trans* to the co-ordinating pyridine, whilst the three W–O (siloxo) bond lengths are 1.873–1.885(12) Å. The distances to the Si atoms are also indicative of atom type

Table 5 Crystal data and details of data collection and refinement

Compound	**2**	**4**	**7**
Formula	$C_{26}H_{48}Cr_2N_6O_2Si_4$	$C_9H_{18}ClCrNO_2$	$C_{17}H_{44}ClN_5Si_4W$
M	693.04	259.70	650.22
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	*C*2/*c*	$P\bar{1}$	$P2_1/a$
a/Å	19.775(1)	7.848(1)	17.661(2)
b/Å	9.679(1)	12.040(1)	10.779(1)
c/Å	20.129(2)	14.416(2)	17.330(2)
α/°	90	66.16(2)	90
β/°	111.73(2)	79.09(2)	103.28(2)
γ/°	90	88.87(1)	90
U/Å^3	3579	1223	3211
Z	4	4	4
D_c/g cm^{-3}	1.286	1.411	1.345
F(000)	1464	544	1312
μ/cm^{-1}	7.54	11.12	39.17
Total reflections	6483	8156	11 413
Total unique	3146	5394	6298
R_{int}	0.045	0.048	0.041
Total observed [$F_o > 3\sigma(F_o)$]	1637	1842	2077
No. refined parameters	190	288	299
Final *R*	0.0516	0.041	0.041
Final *R'*	0.0612	0.051	0.048

Weighting scheme: $w = 1/\sigma^2(F_o)$.

Table 6 Fractional atomic coordinates (× 10^4) for compound **2**

Atom	*x*	*y*	*z*
Cr(1)	4210(1)	3080(1)	2168(1)
O(1)	4939(2)	2522(4)	3089(2)
Si(1)	4934(1)	1451(2)	3724(1)
N(2)	4058(2)	4607(5)	1557(2)
Si(2)	3455(1)	5535(2)	998(1)
N(1)	3719(3)	4225(6)	2741(3)
C(11)	4136(4)	5153(8)	3207(4)
C(12)	3851(5)	5983(10)	3584(5)
C(13)	3146(5)	5893(10)	3512(5)
C(14)	2718(5)	4949(10)	3043(5)
C(15)	3029(4)	4123(8)	2679(4)
O(3)	3617(3)	1973(6)	1853(3)
C(111)	5588(6)	2092(14)	4597(5)
C(112)	4020(5)	1316(12)	3758(5)
C(113)	5193(8)	−275(11)	3541(8)
C(211)	3188(6)	7038(9)	1443(5)
C(212)	3846(6)	6260(11)	345(5)
C(213)	2626(5)	4554(12)	500(6)

with Si–N(imido) 1.78(2) and Si–O 1.62–1.63(1) Å. The W–N–Si angle is 166(1)°, and the W–O–Si angles are 147–170(1)°. The siloxo group with the smallest angle is that which is *trans* to the chloride ligand, although there is no significant difference between any of the three W–O bond lengths.

Experimental

Microanalyses by Pascher, Remagen, Medac plc, Brunel University and University College, London. The general methods and instrumentation were as described.[6] Infrared spectra were recorded in Nujol unless otherwise specified; ^1H NMR spectra are at 270 MHz, in δ *vs.* $SiMe_4$; EPR spectra, X-band.

Chromyl chloride and general chemicals were from Aldrich. Standard methods were used for MoO_2Cl_2[8] and WO_2Cl_2(dme).[9] All operations were carried out under purified N_2 or Ar or under vacuum; solvents were dried and degassed before use.

Bis[*bis*(*trimethylsilyl*)*amido*]*dioxochromium*(VI) **1**.—To a rapidly stirred solution of CrO_2Cl_2 (1.0 g, 6.5 mmol) in hexane (15 cm^3) was added a solution in hexane (30 cm^3) of hexamethyldisilazane (4.15 g, 25.8 mmol), when an exothermic reaction occurred. After stirring for 2 h at room temperature, volatiles were removed in vacuum and the residue extracted with hexane (2 x 25 cm^3). The extract was filtered, concentrated to *ca.* 3 cm^3 and cooled at −78 °C. The pale yellow crystals collected at −78 °C melted to a red oil on warming to room temperature. The product can be purified by sublimation [80 °C, 0.1 mmHg (*ca.* 13.3 Pa)] to a probe at −78 °C giving yellow needles. Yield: 2.0 g, 77%. Mass spectrum (EI); *m*/*z* 404, M^+; 243, $[M - NH(SiMe_3)_2]^+$. ^1H NMR ($CDCl_3$) δ 0.37; (C_6D_6) δ 0.36 (s, 36 H, $SiMe_3$). IR: 1252s, 832s (br) and 891s (br) cm^{-1}. The compound should be kept in the dark and stored at low temperature.

Bis(μ-*trimethylsiloxo*)-*bis*[*oxo*(*pyridine*)(*trimethylsilylimido*)-*chromium*(V)] **2**.—To a stirred solution of compound **1** (1.0 g, 2.5 mmol) in CH_2Cl_2 (20 cm^3) was added pyridine (2 cm^3) and the mixture stirred at room temperature (4 h). After removal of volatiles the residue was extracted with hexane (2 x 15 cm^3) and the extract filtered, reduced to *ca.* 5 cm^3 and cooled at −20 °C to give green rod-like crystals that were collected, washed with cold hexane (3 cm^3) and dried in vacuum. Yield: 0.4 g, 30%. IR: 1610m, 957s, 900s, 867s and 833s cm^{-1}. EPR (X-band in toluene, 293 K): *g* = 1.965.

Bis(μ-*trimethylsiloxo*)-*bis*[(4-*methylpyridine*)*oxo*(*trimethylsilylimido*)*chromium*(V)] **3**.—This was prepared as for compound **2** but using 4-methylpyridine (2 cm^3). Yield: 0.76 g, 50%. IR: 1619m, 966s, 905s, 875s and 829s cm^{-1}. EPR (X-band in toluene, 293 K): *g* = 1.995.

Chlorodioxo-(2,2,6,6-*tetramethylpiperidine*)*chromium*(VI)**4**.—To CrO_2Cl_2 (1.0 g, 6.5 mmol) in hexane (20 cm^3) at −78 °C was added 2,2,6,6-tetramethylpiperidine (4.4 cm^3, 26 mmol). After warming to room temperature the volatiles were removed and the residue extracted with hexane (50 cm^3). The extract was filtered, concentrated (*ca.* 5 cm^3) and cooled (−20 °C) to give deep red rod-shaped crystals. Yield: 0.3 g, 18%. IR: 1231s, 1189m, 1153s, 1115s, 982vs, 960vs, 802w (br) and 722m cm^{-1}. ^1H NMR (C_6D_6, 25 °C): δ 1.10 (s, 12 H, Me), 1.21 (s, 2 H, CH_2) and 1.30 (s, 4 H, CH_2).

(tert-*Butylamine*)*bis*(tert-*butylimido*)*dichlorochromium*(VI) **5**.—A hexane (20 cm^3) solution of CrO_2Cl_2 (1.0 g, 6.5 mmol) was slowly added to a solution of $SiMe_2(NHBu^t)_2$[5] (2.6 g, 13

Table 7 Fractional atomic coordinates (× 10^4) for compound **4**

Atom	*x*	*y*	*z*
Cr(1)	504(2)	1838(1)	657(1)
Cr(2)	5786(2)	6609(1)	5352(1)
Cl(11)	1540(3)	3085(2)	1152(2)
Cl(21)	6739(3)	7202(2)	6404(2)
O(11)	2077(7)	1235(4)	142(5)
O(12)	−551(7)	854(4)	1627(4)
O(21)	7378(6)	6500(4)	4533(4)
O(22)	4932(7)	5335(3)	6001(3)
N(21)	4187(6)	7736(4)	4738(3)
N(11)	−929(6)	2694(4)	−248(4)
C(11)	−2874(8)	2761(5)	125(5)
C(12)	−3812(9)	3788(6)	−627(5)
C(13)	−3326(11)	3886(7)	−1710(6)
C(14)	−1433(11)	4127(7)	−2043(6)
C(15)	−246(9)	3138(6)	−1415(5)
C(111)	−3630(10)	1538(6)	337(6)
C(112)	−3148(10)	2986(7)	1112(6)
C(151)	1541(10)	3652(6)	−1619(6)
C(152)	−86(11)	2029(7)	−1692(6)
C(21)	2267(8)	7566(5)	5172(5)
C(22)	1184(9)	8741(6)	4789(5)
C(23)	1563(11)	9479(7)	3650(6)
C(24)	3449(11)	9795(6)	3412(5)
C(25)	4764(9)	8735(5)	3672(5)
C(211)	2069(11)	7142(7)	6350(5)
C(212)	1600(10)	6596(7)	4883(7)
C(251)	6484(10)	9215(7)	3671(6)
C(252)	4968(12)	8153(7)	2879(5)

mmol) in hexane (30 cm^3) at −78 °C. Work-up as for compound **1** extracting the residue with hexane (2 × 30 cm^3), concentrating to *ca.* 20 cm^3 and cooling at −20 °C gave red crystals which were collected, washed with chilled hexane (5 cm^3) and dried in vacuum. Yield: 1.0 g, 47%. IR: 2710s, 2601m, 1326m, 1247m, 1200s, 1070m, 1033m, 825m, 797m, 729s, 699w, 611m and 502w cm^{-1}. ^1H NMR ($CDCl_3$, 25 °C): δ 0.10 (br, 2 H, NH_2), 1.40 (s, 9 H, Bu^tNH_2) and 1.58 (s, 18 H, NBu^t).

Bis(trimethylsiloxo)bis(trimethylsilylimido)molybdenum(VI) **6**.—Hexamethyldisilazane (3.2 g, 20 mmol) was slowly added to a stirred suspension of MoO_2Cl_2 (1.0 g, 5.0 mmol) in hexane (30 cm^3) at room temperature. After 24 h volatiles were removed, the residue was extracted with hexane (2 × 50 cm^3) and the filtered extract reduced to *ca.* 3 cm^3 and cooled (−20 °C) to give yellow needles which were collected at −78 °C. These melted to a red oil on warming. Mass spectrum (EI): *m*/*z* 450, M^+. ^1H NMR: ($CDCl_3$) δ 0.15 (s, 18 H, $SiMe_3$) and 0.23 (s, 18 H, $SiMe_3$); (C_6D_6) δ 0.20 and 0.28.

Chloro(pyridine)tris(trimethylsiloxo)(trimethylsilylimido)-tungsten(VI) **7**.—Hexamethyldisilazane (0.85 g, 5.3 mmol) was added to a stirred solution of WO_2Cl_2(dme) (0.5 g, 1.3 mmol) in CH_2Cl_2 (20 cm^3). After 6 h, pyridine (0.5 cm^3) was added and the mixture stirred for 24 h. Evaporation and extraction of the residue with hot hexane (30 cm^3) followed by filtration, concentration (*ca.* 10 cm^3) and cooling (−20 °C) gave colourless plates that can be recrystallized from hexane. Yield: 0.2 g (40%). IR: 1602s, 1249s, 1167s, 1072m, 1012m, 913s, 752m, 698w and 627m cm^{-1}. ^1H NMR (C_6D_6, 25 °C): δ 0.28 (s, 27 H, $OSiMe_3$), 0.38 (s, 9 H, $NSiMe_3$) and 6.5–6.9 (m, 5 H, py).

X-Ray Crystallography.—Crystals of the three compounds were sealed in thin-walled glass capillaries for the X-ray work. Unit-cell and intensity data were obtained using a FAST TV area detector diffractometer following previously described procedures.[6] The structures were solved *via* the heavy-atom method and refined using full-matrix least squares. Non-hydrogen atoms were assigned anisotropic displacement factors except for two partial atom methyl components of a disordered $SiMe_3$ group in complex **2**. In all three structures hydrogens were included in idealized positions and refined with group U_{iso} values. For **2** the distinction between $OSiMe_3$ and $NSiMe_3$ could be made confidently on the basis of refinement with interchanged U_{iso} values at the isotropic refinement stage. For compound **7** this normal procedure was not indicative but fortunately bond length differences were quite conclusive.

Table 8 Fractional atomic coordinates (× 10^4) for compound **7**

Atom	*x*	*y*	*z*
W	2197	953(1)	2676
Cl	1666(3)	1255(4)	3850(3)
O(1)	1804(7)	2549(9)	2372(7)
O(2)	2837(7)	−241(9)	3289(6)
O(3)	2821(7)	971(9)	1930(5)
N(1)	1435(8)	66(11)	2188(7)
N(1)	3257(8)	2217(12)	3432(8)
C(1)	2190(11)	3126(15)	3944(10)
C(2)	3805(13)	3810(19)	4368(12)
C(3)	4532(13)	3667(20)	4246(14)
C(4)	4616(11)	2710(20)	3723(12)
C(5)	3998(10)	2027(17)	3345(11)
Si(1)	1565(4)	3911(5)	2001(3)
Si(2)	3202(5)	−1218(5)	3997(3)
Si(3)	2974(4)	397(6)	1108(3)
Si(4)	526(4)	−705(6)	1861(4)
C(11)	988(12)	3722(19)	981(10)
C(12)	922(14)	4636(19)	2581(13)
C(13)	2421(13)	4795(19)	2024(13)
C(21)	3460(12)	−432(18)	4931(10)
C(22)	2417(14)	−2396(19)	3990(13)
C(31)	2071(14)	454(25)	336(12)
C(32)	3329(17)	−1166(21)	1305(16)
C(33)	3675(16)	1359(24)	779(15)
C(41)	611(14)	−1976(20)	1217(14)
C(42)	−138(14)	388(23)	1320(18)
C(43)	242(15)	−1301(23)	2746(14)
C(23)	4300(31)	−1541(42)	3794(30)
C(23B)	3861(26)	−2324(36)	3739(24)

Atoms C(23) and C(23B) were refined isotropically with partial occupancies of 0.47 and 0.53 respectively.

Crystal data and details of the structure refinement are given in Table 5, fractional atomic coordinates in Tables 6–8. Programs and sources of scattering data were as previously referenced.[6]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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