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High oxidation state imido metallasiloxanes: synthesis and structural characterisation of novel bis-imido chromium(VI) and molybdenum(VI) compounds†

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For reactions between [M(NBu^t)$_2$Cl$_2$] (M = Cr or Mo) or [Mo(NAr)$_2$Cl$_2$]·dme, Ar = 2,6-Pr$^i_2$C$_6$H$_3$, dme = 1,2-dimethoxyethane, and tetraphenyldisiloxanediol, [O(Ph$_2$SiOH)$_2$] (2 : 1), in the presence of a nitrogen donor base, changing the nitrogen donor from pyridine, py, to triethylamine, NEt$_3$, inhibited the protonation of imido groups and facilitated the formation of bis-imido compounds. Thus the compounds [Cr(NBu^t)$_2$(O(Ph$_2$SiO)$_2$)]$_2$ **1**, [Mo(NBu^t)$_2$(O(Ph$_2$SiO)$_2$)$_2$] **2** and [Mo(NAr)$_2$(O(Ph$_2$SiO)$_2$)]$_2$ **3** were isolated when NEt$_3$ was used as base. Compound **3** was also formed when the dilithium reagent [O(Ph$_2$SiOLi)$_2$] was used. The pyridine adduct [Mo(NAr)$_2$Cl$_2$]·2py **4** was isolated from the reaction between [Mo(NAr)$_2$Cl$_2$] and O(Ph$_2$SiOH)$_2$ and py (1 : 1 : 2 molar ratio). Compounds **2**, **3**·C$_6$H$_6$ and **4**·0.5C$_6$H$_5$Me have been characterised by X-ray crystallography. The dimeric composition of **1** in the gas phase and in benzene was confirmed by mass spectroscopy and cryoscopic molecular weight determination respectively. All compounds were characterised by NMR spectroscopy.

Introduction

We are investigating routes to heteroleptic transition metal compounds incorporating the ligand type [(OSiR$_2$)$_n$O]$^{2-}$ (relatively few examples are available[1,2]) and our current focus is on Group 6 imido metallasiloxanes. We have discovered that reactions between the Group 6 bis-imido compounds [M(NBu^t)$_2$Cl$_2$], M = Cr or Mo and R = Bu^t, [Mo(N-2,6-Pr$^i_2$-C$_6$H$_3$)$_2$Cl$_2$]·dme and O(Ph$_2$SiOH)$_2$ in the presence of added amine proceed to markedly different products depending upon which of the amines py or NEt$_3$ is employed. We reported earlier[3] on the facile protonation of imido groups in compounds [M(NBu^t)$_2$X$_2$] (M = Cr or Mo, X = Cl; M = W, X = NHBu^t) by acidic protons in O(Ph$_2$SiOH)$_2$ even in the presence of py and on the role of the ligand (O(Ph$_2$SiO)$_2$)$^{2-}$ as an oxo-transfer reagent. The compounds [CrO(NBu^t)(O(Ph$_2$SiO)$_2$)]$_2$, [Mo(NBu^t)(py)(O(Ph$_2$SiO)$_2$)$_2$]·py and [W(NBu^t)(NH$_2$Bu^t)-(O(Ph$_2$SiO)$_2$)$_2$] were isolated revealing loss of one imido group from the starting metal reagents in the course of the reaction.

We now report on reactions between the compounds [M(NBu^t)$_2$Cl$_2$], M = Cr or Mo and R = Bu^t, or [Mo(N-2,6-Pr$^i_2$C$_6$H$_3$)$_2$Cl$_2$]·dme and tetraphenyldisiloxanediol in the presence of NEt$_3$.

Results and discussion

Synthesis

A simple strategy for the synthesis of bis-imido compounds [M(NR)$_2$(O(Ph$_2$SiO)$_2$)$_2$], M = Cr or Mo (isoelectronic analogues of [ZrCp$_2$(OSiPh$_2$OSiPh$_2$O)]$_2$),[4] from the corresponding bis-imido dichlorides was explored as illustrated in eqn. (1)

$$[\mathrm{M(NR)_2Cl_2}] + \mathrm{O(Ph_2SiOH)_2} + 2\mathrm{base} \xrightarrow[\text{r.t.}]{\text{toluene}} \tfrac{1}{2}[\mathrm{M(NR)_2(O(Ph_2SiO)_2)_2}]_2 + 2\mathrm{base{\cdot}HCl} \quad (1)$$

(base = py or NEt$_3$, M = Cr or Mo, R = Bu^t; M = Mo, R = 2,6-Pr$^i_2$C$_6$H$_3$). The base, py or NEt$_3$, was added to assist dehydrochlorination. The reactions involving added py proceeded[3] with initial protonation on an imido group. With the chromium compound the siloxanediolate also functioned as an oxo-transfer reagent. To account for the observed product [CrO(NBu^t)(O(Ph$_2$SiO)$_2$)]$_2$ the sequence of reactions shown in eqn. (2)

$$[\mathrm{Cr(NBu^t)_2Cl_2}] + \mathrm{O(Ph_2SiOH)_2} \longrightarrow \text{“}\mathrm{Cr(NHBu^t)(NBu^t)Cl_2(OSiPh_2OSiPH_2OH)}\text{”} \longrightarrow [\mathrm{Cr(NBu^t)(O)Cl_2}] + (\mathrm{Ph_2SiO})_n + \mathrm{Bu^tNH_2} \quad (2)$$

leading to [Cr(NBu^t)(O)Cl$_2$] was proposed.[3] In contrast reactions in the presence of added NEt$_3$ proceed cleanly to the expected products [M(NR)$_2$(O(Ph$_2$SiO)$_2$)]$_2$ (M = Cr, R = Bu^t **1**; Mo, R = Bu^t **2**; R = 2,6-Pr$^i_2$C$_6$H$_3$ **3**) without loss of imido groups or incorporation of oxo ligands. With added NEt$_3$, siloxanediolato bridged dimers are formed and the two imido groups at each metal centre adopt linear 6e donor co-ordination. We attributed the loss of the imido group in [Mo(NBu^t)(py)(O(Ph$_2$SiO)$_2$)$_2$]·py accompanied by oxo-transfer in [CrO(NBu^t)(O(Ph$_2$SiO)$_2$)]$_2$[3] to initial protonation of the imido group followed by elimination of amine. Use of the base NEt$_3$ inhibits this process by forming a stronger interaction with the silanol protons than is the case with pyridine. The relative basicities of py and NEt$_3$ as determined by gas-phase protonation are $\Delta H = -936.8$ and -985.6 kJ mol^{-1} respectively.[5] The general chemistry of silanols and their adducts was discussed by Lickiss.[6]

A further interesting point regarding the different outcomes with py and NEt$_3$ relating to our previously observed oxo-transfer to chromium, to give [CrO(NBu^t)(O(Ph$_2$SiO)$_2$)]$_2$, is that, whereas oxo-transfer to chromium occurs with loss of amine following protonation of an imido group,[3] we now see that it does not occur when protonation is inhibited and chloride is the only available leaving group; in other words reaction (2) above is favoured but the following reaction (3) apparently is

$$[\mathrm{Cr(NBu^t)_2Cl_2}] + \mathrm{O(Ph_2SiOH)_2} + 2\mathrm{NEt_3} \longrightarrow [\mathrm{Cr(NBu^t)_2(O)}] + (\mathrm{Ph_2SiO})_n + 2\mathrm{NEt_3HCl} \quad (3)$$

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† Dedicated to Professor Don Bradley on the occasion of his 75th birthday.

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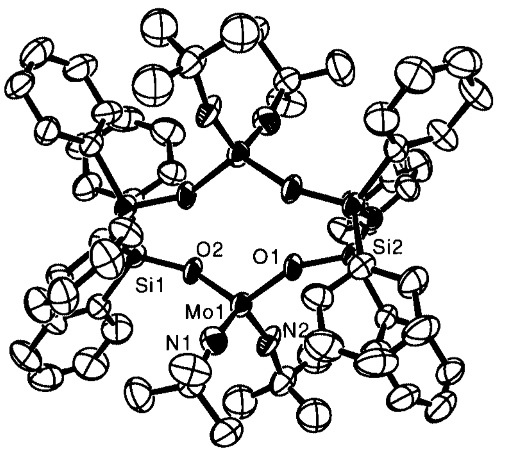

Fig. 1 Molecular structure of compound **2**. Thermal ellipsoids at the 50% probability level, hydrogen atoms omitted (in all figures).

not. This may reflect the relative thermodynamic stabilities of the known $[Cr(NBu^t)(O)Cl_2]$[7] *versus* unknown $[Cr(NBu^t)_2(O)]$.

We also investigated the extreme case where the silanol protons were removed by reaction with strong base BuLi prior to reaction with $[Mo(NBu^t)_2Cl_2]$. Once again with protonation of imide prevented, the reaction proceeded cleanly to the expected product $[Mo(NBu^t)_2O(Ph_2SiO)_2]_2$. The analogous reaction with $[Cr(NBu^t)_2Cl_2]$ however gave a mixture (both green and red powders were evident in the crude product suggesting formation of reduced chromium species) from which no single product could be isolated.

Changing the substituent on the imido ligand from Bu^t to aryl, Ar = $2,6\text{-}Pr^i_2C_6H_3$, did not affect the course of these reactions. Reactions between $O(Ph_2SiOH)_2$ and $[Mo(NAr)_2Cl_2]$ (in place of $[Mo(NBu^t)_2Cl_2]$) in the presence of NEt_3 (relative molar ratio 1 : 1 : 2) gave the expected dimeric product $[M(NAr)_2(O(Ph_2SiO)_2)]_2$ **3**. When pyridine was used as base in this reaction the proton NMR of the crude product indicated that a mixture of compounds was present. The only crystalline product isolated was $[Mo(NAr)_2Cl_2]\cdot 2py$ **4**. The isolation of **4** (36% yield) indicated that a substantial fraction of the molybdenum starting material was not consumed. This is in-keeping with the related reaction involving $[Mo(NBu^t)_2Cl_2]/O(Ph_2SiOH)_2/2py$ where only half the starting metal reagent is consumed and $[Mo(NBu^t)(py)(O(Ph_2SiO)_2)_2]\cdot py$ is formed.[3]

Compounds **1**–**3** were characterised by ^1H, ^{13}C and ^{29}Si NMR. The spectra were consistent with the structures observed in the solid state for **2** and **3** and assignments are given in the Experimental section. Compound **1** failed to give crystals suitable for structure determination. However the molecular weight of **1** determined by freezing point depression of benzene (1233 (for 8.586×10^{-3} mol dm^{-3} solution) and 1206 (for 8.404×10^{-3} mol dm^{-3} solution), calculated 1213.66 for $C_{64}H_{76}Cr_2N_4O_6Si_4$) was consistent with a dimeric structure in solution. The dimeric structure was also retained in the gas phase as evidenced by the mass spectrum (found *m*/*z* 1212.37, calculated for $C_{64}H_{76}N_4O_6Si_4Cr_2(M^+)$ 1212.37). The NMR spectra, ^1H and ^{13}C, for compound **4** were consistent with the solid state structure.

Crystal structures of $[Mo(NBu^t)_2(O(Ph_2SiO)_2)]_2$ 2, $[Mo(N\text{-}2,6\text{-}Pr^i_2C_6H_3)_2(O(Ph_2SiO)_2)]$ 3 and $[Mo(N\text{-}2,6\text{-}Pr^i_2C_6H_3)_2Cl_2]\cdot 2py$ 4

The structures of compounds **2** and **3** are shown in Figs. 1 and 2 with selected bond lengths and angles in Tables 1 and 2. Dimeric 12-membered rings are indicated. The Mo atoms in centrosymmetric **2** possess distorted tetrahedral geometry emphasised by the wide O(1)–Mo(1)–O(2) angle 118.1(3)°. There is no such distortion of geometry at Si where the angles are close to tetrahedral. The Si–O–Si and Si–O–Mo angles are fairly similar in the range 138.5(4)–144.6(4). Approximately linear bonding modes are adopted by the imido groups C(25)–N(1)–Mo(1) 163.9(9) and C(29)–N(2)–Mo(1) 165.9(9)°. Substantial puckering is evident within the 12-membered ring; deviations from the plane of the disiloxanolato oxyanions O(1),O(2) O(1a),O(2a) are Si(1) 0.2069, O(3) −0.9399, Si(2) −0.7614, Mo(1) 0.8137°; the symmetry related set in the second ligand deviates in the opposite direction. In compound **3** the

Table 1 Bond lengths [Å] and angles [°] for compound **2**

Mo(1)–N(2)	1.698(9)	Si(1)–C(1)	1.877(6)
Mo(1)–N(1)	1.701(8)	Si(2)–O(1)	1.618(6)
Mo(1)–O(1)	1.873(6)	Si(2)–O(3)	1.654(7)
MO(1)–O(2)	1.899(6)	Si(2)–C(13)	1.863(6)
Si(1)–O(3^I)	1.605(7)	Si(2)–C(19)	1.879(6)
Si(1)–O(2)	1.630(6)	O(3)–Si(1^I)	1.605(7)
Si(1)–C(7)	1.863(6)		
N(2)–Mo(1)–N(1)	110.2(5)	O(1)–Si(2)–O(3)	110.0(4)
N(2)–Mo(1)–O(1)	106.2(4)	O(1)–Si(2)–C(13)	112.1(3)
N(1)–Mo(1)–O(1)	107.6(4)	O(3)–Si(2)–C(13)	107.1(3)
N(2)–Mo(1)–O(2)	104.8(4)	O(1)–Si(2)–C(19)	107.6(3)
N(1)–Mo(1)–O(2)	109.6(4)	O(3)–Si(2)–C(19)	109.1(3)
O(1)–Mo(1)–O(2)	118.1(3)	C(13)–Si(2)–C(19)	110.9(3)
O(3^I)–Si(1)–O(2)	113.2(4)	Si(2)–O(1)–Mo(1)	144.6(4)
O(3^I)–Si(1)–C(7)	110.4(4)	Si(1)–O(2)–Mo(1)	142.0(4)
O(2)–Si(1)–C(7)	105.9(3)	Si(1^I)–O(3)–Si(2)	138.5(4)
O(3^I)–Si(1)–C(1)	107.0(3)	C(25)–N(1)–Mo(1)	163.9(9)
O(2)–Si(1)–C(1)	109.9(4)	C(29)–N(2)–Mo(1)	165.9(9)
C(7)–Si(1)–C(1)	110.6(4)		

Symmetry transformation used to generate equivalent atoms: I $-x + 1, -y + 1, -z + 1$.

Table 2 Bond lengths [Å] and angles [°] for compound **3**

Mo(1)–N(2)	1.740(4)	Si(1)–C(31)	1.877(3)
Mo(1)–N(1)	1.745(4)	Si(2)–O(3^I)	1.612(4)
Mo(1)–O(3)	1.883(4)	Si(2)–O(2)	1.614(4)
Mo(1)–O(1)	1.884(4)	Si(2)–C(43)	1.868(3)
Si(1)–O(2)	1.617(4)	Si(2)–C(37)	1.884(4)
Si(1)–O(1)	1.627(4)	O(3)–Si(2^I)	1.612(4)
Si(1)–C(25)	1.869(3)		
N(2)–Mo(1)–N(1)	110.15(19)	O(3^I)–Si(2)–O(2)	110.3(2)
N(2)–Mo(1)–O(3)	109.1(2)	O(3^I)–Si(2)–C(43)	107.7(2)
N(1)–Mo(1)–O(3)	108.37(19)	O(2)–Si(2)–C(43)	108.01(19)
N(2)–Mo(1)–O(1)	108.61(19)	O(3^I)–Si(2)–C(37)	110.3(2)
N(1)–Mo(1)–O(1)	108.77(19)	O(2)–Si(2)–C(37)	105.9(2)
O(3)–Mo(1)–O(1)	111.84(17)	C(43)–Si(2)–C(37)	114.66(19)
O(2)–Si(1)–O(1)	108.8(2)	Si(1)–O(1)–Mo(1)	174.9(3)
O(2)–Si(1)–C(25)	108.00(19)	Si(2)–O(2)–Si(1)	161.7(3)
O(1)–Si(1)–C(25)	109.1(2)	Si(2^I)–O(3)–Mo(1)	174.7(3)
O(2)–Si(1)–C(31)	108.0(2)	C(1)–N(1)–Mo(1)	161.1(4)
O(1)–Si(1)–C(31)	111.5(2)	C(13)–N(2)–Mo(1)	167.8(4)
C(25)–Si(1)–C(31)	111.30(19)		

Symmetry transformation used to generate equivalent atoms: I $-x + 2, -y + 1, -z$.

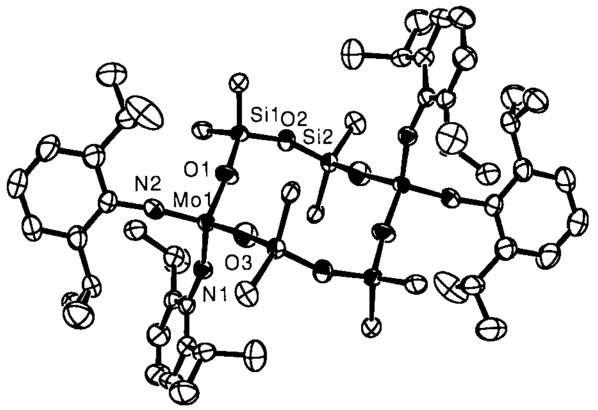

Fig. 2 Molecular structure of compound **3**.

Table 3 Bond lengths [Å] and angles [°] for compound **4**. Comparable data for [Mo(NBu^t)$_2$Cl$_2$(py)$_2$] in parentheses

Mo(1)–N(2)	1.758(9)	(1.706)	Mo(1)–Cl(2)	2.397(3)	(2.418)
Mo(1)–N(1)	1.773(10)	(1.735)	Mo(1)–N(4)	2.422(6)	(2.450)
Mo(1)–Cl(1)	2.395(3)	(2.422)	N(1)–C(1)	1.374(12)	(1.450)
Mo(1)–N(3)	2.396(5)	(2.430)	N(2)–C(10)	1.370(11)	(1.456)
N(2)–Mo(1)–N(1)	102.1(4)	(107.8)	N(1)–Mo(1)–N(4)	169.1(4)	(164.1)
N(2)–Mo(1)–Cl(1)	96.2(3)	(93.9)	Cl(1)–Mo(1)–N(4)	80.9(2)	(82.7)
N(1)–Mo(1)–Cl(1)	96.4(3)	(96.2)	N(3)–Mo(1)–N(4)	79.2(2)	(75.5)
N(2)–Mo(1)–N(3)	167.8(3)	(163.4)	Cl(2)–Mo(1)–N(4)	82.2(2)	(82.2)
N(1)–Mo(1)–N(3)	90.0(4)	(88.6)	Cl(1)–N(1)–Mo(1)	157.2(7)	(163.9)
Cl(1)–Mo(1)–N(3)	82.0(2)	(81.9)	C(10)–N(2)–Mo(1)	166.1(7)	(173.4)
N(2)–Mo(1)–Cl(2)	96.9(3)	(96.3)	C(25)–N(3)–Mo(1)	117.3(3)	
N(1)–Mo(1)–Cl(2)	97.7(3)	(95.3)	C(29)–N(3)–Mo(1)	122.5(3)	
Cl(1)–Mo(1)–Cl(2)	158.37(12)	(161.5)	C(30)–N(4)–Mo(1)	116.8(3)	
N(3)–Mo(1)–Cl(2)	81.6(2)	(84.0)	C(34)–N(4)–Mo(1)	123.1(3)	
N(2)–Mo(1)–N(4)	88.6(3)	(88.0)			

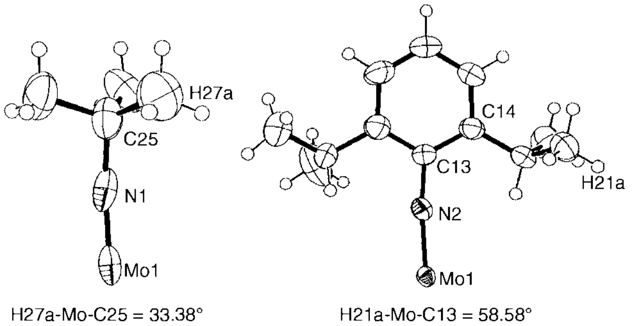

Fig. 3 Imido groups from compounds **2** and **3** used for calculation of cone angles.

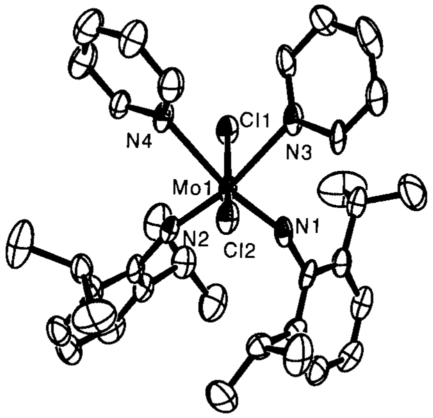

Fig. 4 Molecular structure of compound **4**. Solvent molecule omitted.

geometry at Mo and Si is almost perfectly tetrahedral and consequently the 12-membered ring conformation is rather different from that observed for **2**. The Si–O–Si and Si–O–Mo units are approaching linear arrangements with angles Si(1)–O(1)–Mo(1) 174.9(3), Si(2)–O(2)–Si(1) 161.7(3), Si(2^I)–O(3)–Mo(1) 174.7(3)°. Compared to **2** the ring is less puckered; deviations from the plane of the disiloxanolato oxyanions O(1),O(3) O(1a),O(3a) are Si(1) 0.5594, O(2) 0.2000, Si(2) −0.5060, Mo(1) −0.6140 Å; the symmetry related set in the second ligand deviates in the opposite direction.

As for **2**, the Mo–imido groups in compound **3** are also approximately linear C(1)–N(1)–Mo(1) 161.1(4) and C(13)–N(2)–Mo(1) 167.8(4)°. The different conformations observed for **2** and **3** result from the different steric requirements of the two imido groups. Given that the Mo–imido groups were approximately linear in both cases it seemed reasonable to compare their Tolman-type[8] cone angles (see Fig. 3). The values 67 (NBu^t) and 117.2° (NAr), Ar = 2,6-$Pr^iC_6H_3$, based on the metrical parameters of the two compounds provide a comparative measure of the steric demands of the two ligands in these compounds. The widened Si–O–Si angles and generally more planar conformation in **3** prevent unfavourable steric interactions between the sterically demanding aryl substituents on silicon and nitrogen.

The structure of compound **4** is shown in Fig. 4 with bond lengths and angles in Table 3. A database search revealed that other simple adducts [Mo(NR)$_2$Cl$_2$L$_2$] have been structurally characterised, for example [Mo(NBu^t)(N-3,5-Pr$^i_2$C$_6$H$_3$)Cl$_2$]·dme, dme = 1,2-dimethoxyethane,[9] and of particular interest to the present work [Mo(NBu^t)$_2$Cl$_2$]·2py which is the only direct analogue of **4**.[10] One structural feature of interest of adducts [Mo(NR)$_2$Cl$_2$]·L$_2$ concerns the stereochemistries they might prefer to adopt. As found for [Mo(NBu^t)$_2$Cl$_2$]·2py the two chloride groups in **4** take up relative *trans* orientation, the imido groups are approximately linear and have a *cis* relationship to each other and *trans* relationship to the *cis*-pyridines. This configuration of course maximises the imido ligand to metal π interaction. The Mo-N (py) distances in [Mo(NBu^t)$_2$Cl$_2$(py)$_2$] are very similar to those in **4**, see Table 3. Thus the solid state data indicate that the two ligands NBu^t and NAr exhibit similar *trans* influence. We note however that a recent theoretical study of isolated molecular titanium compounds, *mer*-[Ti(NR)Cl$_2$(NH$_3$)$_3$],[11] found the *trans* influence of imido ligands showed marked substituent effects, although these effects were not evident from the experimentally determined solid state structures of these compounds. Similar structural features are evident in both analogues **4** and [Mo(NBu^t)$_2$Cl$_2$(py)$_2$] with both showing significant bending for one of the two imido groups NBu^t or NAr. The imido groups exhibit very similar structural influences in these molecules. The most obvious effect is the narrowing of the *trans*-Cl–Mo–Cl, *cis*-(py)N–Mo–N(py) and *cis*-Cl–Mo–N(py) angles. The degree of narrowing is similar in both cases which suggests that the large difference in the cone angles of the imido ligands has apparently little impact on the central co-ordination sphere.

Conclusion

The disiloxanediol O(Ph$_2$SiOH)$_2$ will protonate the imido groups in [M(NBu^t)$_2$Cl$_2$] (M = Cr or Mo) and [Mo(NAr)$_2$Cl$_2$]·dme, Ar = 2,6-Pr$^i_2$C$_6$H$_3$, even in the presence of pyridine, leading to the corresponding mono-imido complexes. However this is avoided for reactions employing the stronger base NEt_3 in-keeping with the expected stronger interaction between NEt_3 and the silanol proton; bis-imido complexes are formed. Use of the dilithium reagent [O(Ph$_2$SiOLi)$_2$] has the same effect with the compound [Mo(NBu^t)$_2$Cl$_2$] but this reagent is reducing for [Cr(NBu^t)$_2$Cl$_2$]. Imido group cone angles are influential in dictating ring conformation in dimers **2** and **3**. Conversely these imido groups exhibit very similar structural effects in the analogous monomeric octahedral complexes [Mo(NBu^t)$_2$Cl$_2$(py)$_2$] and **4** despite the difference in cone angles. Further studies on the chemistry of these and related heteroleptic metallasiloxanes are in-hand.

Experimental

General

All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk/cannula techniques and a conventional nitrogen filled glove-box. Solvents were refluxed over an appropriate drying agent and degassed prior to use. Melting points were recorded on samples sealed in capillaries under nitrogen. Molecular weight determinations were made under a purified nitrogen atmosphere in an all glass cryoscopic cell. The NMR spectra were recorded on Bruker WH250 (^{1}H, ^{13}C) and AMX600 (^{29}Si) spectrometers, IR spectra on a PE 1720X FT instrument with a solid-state ATR attachment. Microanalyses were obtained from the service at University College London, and mass spectra from the EPSRC Mass Spectroscopy Service, Swansea, Wales using LSIMS (liquid secondary ion mass spectrometry): caesium ion bombardment was used at 25 kV, with the sample dissolved in matrix liquid, 3-nitrobenzyl alcohol (NOBA), and polyethylene glycol (PEG) as a mass reference.

Starting reagents $[\mathrm{Cr(NBu^t)_2Cl_2}]$, $[\mathrm{Mo(NBu^t)_2Cl_2}]$ and $[\mathrm{Mo(NAr)_2Cl_2}]\cdot$dme were synthesized according to standard literature procedures.[12–14] Dilithium tetraphenyldisiloxanediolate, $[\mathrm{(Ph_2SiOLi)_2O}]$, was generated and used *in situ* by treatment of $\mathrm{(Ph_2SiOH)_2O}$ with 2 equivalents of n-BuLi. Triethylamine was distilled over KOH and stored over molecular sieves.

Preparations

$[\mathrm{Cr(NBu^t)_2(O(Ph_2SiO)_2)}]_2$ 1. To a solution of $[\mathrm{Cr(NBu^t)_2Cl_2}]$ (0.62 g, 2.34 mmol) in toluene (25 cm^3) was added dropwise, with stirring, a mixture of $\mathrm{(Ph_2SiOH)_2O}$ (0.97 g, 2.34 mmol) and $\mathrm{Et_3N}$ (0.65 cm^3, 4.7 mmol) in toluene (40 cm^3). Following the addition of the siloxanediol the red solution lightened slightly accompanied by the formation of a fine precipitate. After 4 h at room temperature the solution was filtered and the mother-liquor reduced *in vacuo* to yield a dark brown oil. Dissolution of the oil in the minimum quantity of $\mathrm{CH_2Cl_2}$ followed by cooling at −20 °C afforded chocolate brown needles of $[\mathrm{Cr(NBu^t)_2(OSiPh_2OSiPh_2O)}]_2$ (3 crops, 0.8 g, 28%), mp 175–177 °C (with decomposition). IR: 3044w, 2972w, 1591w, 1428m, 1193m, 1114s, 1016m, 997m, 930vs, 756m, 739m, 715s, 696vs, 518s and 489vs cm^{-1}. NMR: ^{1}H ($\mathrm{C_6D_6}$, 250 MHz, 298 K), δ 1.05 (s, 36H, $\mathrm{C(CH_3)_3}$), 7.2–7.35 (m, *m*-, *p*-H of $\mathrm{C_6H_5}$ and $\mathrm{C_6D_6}$ solvent) and 8.0–8.1 (m, 16H, *o*-H of $\mathrm{C_6H_5}$); ^{13}C ($\mathrm{CDCl_3}$, 62.9 MHz, 298K), δ 30.7 ($\mathrm{NC(}\mathit{C}\mathrm{H_3)_3}$), 79.5 ($\mathrm{N}\mathit{C}\mathrm{(CH_3)_3}$), 127.1 (*m-C* of $\mathrm{C_6H_5}$), 128.9 (*p-C* of $\mathrm{C_6H_5}$), 135.2 (*o-C* of $\mathrm{C_6H_5}$) and 138.1 (*ipso-C* of $\mathrm{C_6H_5}$); ^{29}Si ($\mathrm{CDCl_3}$, 119.2 MHz, 300K), δ −38.2 (s). Found: C, 60.24; H, 6.50; N, 4.09. Calculated for $\mathrm{C_{32}H_{38}CrN_2O_3Si_2}$: C, 63.3; H, 6.3; N, 4.6%. Found: mol. wt. 1233.00 (for 8.586 × 10^{-3} mol dm^{-3} solution) and 1206.99 (for 8.404 × 10^{-3} mol dm^{-3} solution). Calculated for $\mathrm{C_{64}H_{76}Cr_2N_4O_6Si_4}$: 1213.66. Accurate mass FAB (LSIMS, PEG/NOBA Matrix): found *m*/*z* 1212.37; calculated for $\mathrm{C_{64}H_{76}N_4O_6Si_4Cr_2(M^+)}$ 1212.37.

$[\mathrm{Mo(NBu^t)_2(O(Ph_2SiO)_2)}]_2$ 2. To a solution of $[\mathrm{Mo(NBu^t)_2Cl_2}]$ (1.39 g, 4.5 mmol) in toluene (30 cm^3) was added dropwise, with stirring, a mixture of $\mathrm{(Ph_2SiOH)_2O}$ (1.85 g, 4.5 mmol) and $\mathrm{Et_3N}$ (1.3 cm^3, 9.0 mmol) in toluene (40 cm^3). Following the addition of the diol the solution changed slowly from yellow to green, accompanied by the formation of a fine precipitate. After 4 h at room temperature the solution was filtered and the mother-liquor reduced *in vacuo* to yield a green oil. Dissolution of the oil in the minimum quantity of toluene followed by cooling at −20 °C afforded a small quantity of $[\mathrm{Mo(NBu^t)_2(OSiPh_2OSiPh_2O)}]_2$ (0.4 g, 7%), as colourless cubes. The crystal structure determination was performed on a crystal from this sample.

Compound **2**$\cdot\mathrm{CH_2Cl_2}$ was obtained in a more satisfactory yield upon reaction of $[\mathrm{Mo(NBu^t)_2Cl_2}]$ with dilithium tetraphenyldisiloxanediolate, $[\mathrm{(Ph_2SiOLi)_2O}]$, as follows. To a solution of $[\mathrm{Mo(NBu^t)_2Cl_2}]$ (1.30 g, 4.2 mmol) in THF (25 cm^3) at 0 °C was added dropwise, with stirring, a solution of $[\mathrm{(Ph_2SiOLi)_2O}]$ (4.2 mmol) in THF (30 cm^3). Following the addition of the diolate the solution was allowed to reach room temperature and stirred for 18 h. No colour change was observed during this time, although the formation of a precipitate (LiCl) was apparent. Filtration of the solution followed by removal of the solvent *in vacuo* afforded a yellow waxy solid of low solubility. Addition of $\mathrm{CH_2Cl_2}$ followed by cooling afforded the compound **2**$\cdot\mathrm{CH_2Cl_2}$ as a pale yellow crystalline material (1.44 g, 50%), mp 199–201 °C. IR: 3067w, 2968w, 1591w, 1428m, 1203m, 1126m, 1115s, 1036m, 1021m, 996m, 923vs, 737m, 718s, 695vs, 521s and 479s cm^{-1}. NMR: ^{1}H ($\mathrm{CDCl_3}$, 250 MHz, 298 K), δ 1.0 (s, 36H, $\mathrm{NC(CH_3)_3}$), 5.2 (s, $\mathrm{CH_2Cl_2}$), 7.2–7.4 (m, *m*-, *p*-H of $\mathrm{C_6H_5}$ and $\mathrm{CDCl_3}$ solvent), 7.6–7.7 (m, 16H, *o*-H of $\mathrm{C_6H_5}$); ^{13}C ($\mathrm{CDCl_3}$, 62.9 MHz, 298K), δ 31.5 ($\mathrm{NC(}\mathit{C}\mathrm{H_3)_3}$), 69.9 ($\mathrm{N}\mathit{C}\mathrm{(CH_3)_3}$), 127.4 (*m-C* of $\mathrm{C_6H_5}$), 129.4 (*p-C* of $\mathrm{C_6H_5}$), 134.9 (*o-C* of $\mathrm{C_6H_5}$) and 136.6 (*ipso-C* of $\mathrm{C_6H_5}$); ^{29}Si ($\mathrm{CDCl_3}$, 119.2 MHz, 300 K), δ −38.6 (s). Found: C, 57.4; H, 5.8; N, 4.1. Calculated for $\mathrm{C_{64}H_{76}Mo_2N_4O_6Si_4\cdot CH_2Cl_2}$: C, 56.3; H, 5.7; N, 4.0%.

$[\mathrm{Mo(NAr)_2(O(Ph_2SiO)_2)}]_2$ 3. To a solution of $[\mathrm{Mo(NAr)_2Cl_2}]\cdot$dme in toluene (1.00 g, 1.6 mmol) in $\mathrm{Et_2O}$ (25 cm^3) was added dropwise, with stirring, a mixture of $\mathrm{(Ph_2SiOH)_2O}$ (0.68 g, 1.6 mmol) and $\mathrm{Et_3N}$ (0.46 cm^3, 3.2 mmol) in $\mathrm{Et_2O}$ (40 cm^3). Following the addition of the siloxanediol the dark red solution immediately lightened accompanied by the formation of a fine precipitate. After 18 h at room temperature the solution was filtered and reduced *in vacuo* to *ca.* ≈ 20 cm^3. Treatment of the mother-liquor with light petroleum (bp 40–60 °C)–benzene (9 : 1, *ca.* 60 cm^3) precipitated any unwanted halide salt. Filtration of the solution followed by further reduction *in vacuo* and addition of light petroleum (bp 40–60 °C)–benzene (30 cm^3) led to the deposition of complex **3**$\cdot\mathrm{C_6H_6}$ as orange, diamond-shaped plates (0.8 g, 56%), mp 186–188 °C. IR: 3055w, 2958w, 1592w, 1427m, 1116s, 1097s, 1028m, 950vs, 742s, 716vs, 696vs, 527s and 481vs cm^{-1}. NMR: ^{1}H ($\mathrm{CDCl_3}$, 250 MHz, 298 K), δ 0.65–0.75 (d, 48H, $\mathrm{CH(C}\mathit{H}_3\mathrm{)_2}$), 3.15–3.3 (sept, 8H, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$), 6.9 (s, 12H, $\mathrm{2,6\text{-}Pr^i{}_2C_6}\mathit{H}_3$), 7.0–7.1 (t, 16H, *m*-H of $\mathrm{C_6H_5}$), 7.2–7.3 (m, 8H, *p*-H of $\mathrm{C_6H_5}$) and 7.55–7.65 (d, 16H, *o*-H of $\mathrm{C_6H_5}$); ^{13}C ($\mathrm{CDCl_3}$, 62.9 MHz, 298 K), δ 23.1 ($\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$), 28.5 ($\mathit{C}\mathrm{H(CH_3)_2}$), 122.1 (*m-C* of $\mathrm{2,6\text{-}Pr^i{}_2C_6H_3}$), 125.9 (*p-C* of $\mathrm{2,6\text{-}Pr^i{}_2C_6H_3}$), 127.6 (*m-C* of $\mathrm{C_6H_5}$), 129.8 (*p-C* of $\mathrm{C_6H_5}$), 134.7 (*o-C* of $\mathrm{C_6H_5}$), 135.2 (*ipso-C* of $\mathrm{C_6H_5}$), 142.8 (*o-C* of $\mathrm{2,6\text{-}Pr^i{}_2C_6H_3}$) and 153.4 (*ipso-C* of $\mathrm{2,6\text{-}Pr^i{}_2C_6H_3}$); ^{29}Si ($\mathrm{CDCl_3}$, 119.2 MHz, 300K), δ −39.9 (s). Found: C, 68.1; H, 6.6; N, 3.1. Calculated for $\mathrm{C_{96}H_{108}Mo_2N_4O_6Si_4\cdot C_6H_6}$: C, 68.2; H, 6.4; N, 3.1%.

Reaction between $[\mathrm{Mo(NAr)_2Cl_2}]\cdot$dme and $\mathrm{(Ph_2SiOH)_2O}$ in the presence of pyridine. Isolation of $[\mathrm{Mo(NAr)_2Cl_2}]\cdot 2\mathrm{py}\cdot 0.5\mathrm{C_6H_5Me}$ 4$\cdot$0.5$\mathrm{C_6H_5Me}$. To a solution of $[\mathrm{Mo(NAr)_2Cl_2}]\cdot$dme (0.75 g, 1.2 mmol) in $\mathrm{Et_2O}$ (25 cm^3) was added dropwise, with stirring, a mixture of $\mathrm{(Ph_2SiOH)_2O}$ (0.51 g, 1.2 mmol) and pyridine (0.20 cm^3, 2.4 mmol) in $\mathrm{Et_2O}$ (30 cm^3). Upon addition of the siloxanediol the red solution darkened slightly accompanied by the formation of a fine precipitate. After 18 h at room temperature the solution was filtered and reduced *in vacuo* to afford a dark red oil. Treatment of the oil with toluene (*ca.* 15 cm^3) followed by the addition of light petroleum (bp 40–60 °C) (*ca.* 60 cm^3) precipitated any unwanted halide salt. The solution was re-filtered and the mixture reduced *in vacuo* to yield a dark red oil. Addition of toluene (15 cm^3) followed by cooling (−20 °C) afforded dark red diamond-shaped crystals of $[\mathrm{Mo(NAr)_2Cl_2}]\cdot 2\mathrm{py}\cdot 0.5\mathrm{C_6H_5Me}$ (0.30 g, 36%). ^{1}H NMR: ($\mathrm{CDCl_3}$, 250 MHz, 298 K): δ 0.9 (d, 28H, $\mathrm{CH(C}\mathit{H}_3\mathrm{)_2}$), 3.8 (sept, 4H, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$), 9.0 (dd, 4H, py *o*-H), 7.8 (t, 2H, py *p*-H), 7.3 (m, 4H, py *m*-H) and 7.0 (m, 6H, $\mathrm{2,6\text{-}Pr^i{}_2C_6H_3}$).

Table 4 X-Ray data for compounds **2**–**4**

	2	**3**·C_6H_6	**4**·0.5C_6H_5Me
Empirical formula	$C_{64}H_{76}Mo_2N_4O_6Si_4$	$C_{102}H_{114}Mo_2N_4O_6Si_4$	$C_{37.50}H_{47.50}Cl_2MoN_4$
Formula weight	1301.53	1796.21	721.14
T/K	293(2)	220(2)	220(2)
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a/Å	12.395(2)	17.106(6)	9.689(6)
b/Å	15.831(3)	13.531(8)	37.658(8)
c/Å	17.246(3)	13.128(7)	10.246(4)
α/°		116.83(5)	
β/°	100.07(3)	112.58(3)	95.62(5)
γ/°		90.83(5)	
V/Å^3	3332.0(10)	2438(2)	3720.5(28)
Z	2	1	4
μ/mm^{-1}	0.498	0.359	0.526
Reflections collected	5846	8869	6378
Independent reflections	5846 [R(int) = 0.3290]	8552 [R(int) = 0.0573]	6378 [R(int) = 0.0000]
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0867, 0.2059	0.0559, 0.1340	0.1067, 0.2893
(all data)	0.2106, 0.2454	0.1229, 0.1564	0.1639, 0.3358

X-Ray crystallography

Data were collected on a CAD4 diffractometer using Mo-Kα (λ = 0.71069 Å) radiation and corrected for absorption (see Table 4 for details of data collection and refinement). The structures were solved by standard heavy atom techniques (SHELXS 97)[15] and refined by full matrix on F^2 (SHELXL 97).[16] The phenyl groups were treated as rigid hexagons [C–C 1.395 Å, C–C–C 120°, with inclusion of hydrogen atoms at fixed positions C–H 0.93 Å (riding model)]. The methyls in one of the *tert*-butyl groups in compound **2** were treated for disorder and the refinement includes modelling for 2-site occupancy in the ratio 61:39. The diagram for compound **2** shown in Fig. 1 displays the highest occupancy sites only. Some deterioration of the crystal during data collection affected the quality of data for **4** however the bond length and angle esds are reasonable despite the high residual electron density on the difference map and the stereochemistry of the molecule is well defined.

CCDC reference number 186/1863.

See http://www.rsc.org/suppdata/dt/a9/a909712k/ for crystallographic files in .cif format.

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