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High oxidation state chromium, molybdenum and tungsten imido metallasiloxanes

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Reactions between the bis-imido compounds $[M(NBu^t)_2X_2]$ (M = Cr or Mo, X = Cl, M = W, X = NHBu^t) and tetraphenyldisiloxanediol (1 : 1) in the presence of two equivalents of added py where X = Cl gave the products $[\{CrO(NBu^t)(O(Ph_2SiO)_2)\}_2]$ **1**, $[Mo(NBu^t)(py)(O(Ph_2SiO)_2)_2]$ **2** and $[W(NBu^t)(NH_2Bu^t)(O(Ph_2SiO)_2)_2]$ **3** showing a marked variation from Cr to Mo and W. Single crystal X-ray studies of **1**·C_6H_5Me, **2**·py and **3**·C_6H_5Me were made. Compound **1** is the first chromium(VI) oxo-imido compound to be structurally characterised and the first example of a chromium(VI) monocyclic metallasiloxane. Compounds **2** and **3** incorporate the first examples of six-membered metallasiloxane rings for compounds of Mo or W. The compounds were also characterised by multinuclear NMR and mass spectroscopy.

Homoleptic compounds having ligands of the type $[(OSiR_2)_n\text{-}O]^{2-}$ are comparatively abundant with many examples of main-group, transition metal and recently lanthanide compounds known.[1,2] In contrast, very few heteroleptic systems incorporating the same class of ligand are known. Notable heteroleptic systems are the Group 4 cyclopentadienyl (η^5-C_5H_5, Cp) metallasiloxanes: $[\{ZrCp_2(OSiPh_2O)\}_2]$ and $[\{ZrCp_2(OSiPh_2\text{-}OSiPh_2O)\}_2]$.[3] We were interested in developing routes to the isoelectronic Group 6 compounds containing imido $[NR]^{2-}$ ligands. In recent years numerous synthetic entries into Group 6 imido chemistry have been described some of which have been used in this work. We report here on interesting results from reactions between $[M(NBu^t)_2X_2]$ (M = Cr or Mo, X = Cl; M = W, X = NHBu^t) and tetraphenyldisiloxanediol (1 : 1) in the presence of two equivalents of added py where X = Cl.[4–7]

Results and discussion

Synthesis

The air and moisture sensitive metallasiloxane compounds **1**, **2** and **3** were isolated from reactions (1)–(3) between the Group 6 bis-imido metal compounds and tetraphenyldisiloxane diol in 1 : 1 molar ratio in toluene at room temperature. In the reactions involving $[Cr(NBu^t)_2Cl_2]$ and $[Mo(NBu^t)_2Cl_2]$ two molar equivalents of pyridine were added to effect [Hpy]Cl formation which is subsequently separated from the products by filtration. However the expected bis-imidometallasiloxanes are *not* formed. The reaction with the chromium compound proceeds to a disiloxanediolato bridged dimer but with replacement of one of the imido groups at each chromium by an oxo group. In addition to the isolated red crystalline **1**·C_6H_5Me some toluene soluble colourless crystalline product (infrared features consistent with polysiloxane $(Ph_2SiO)_n$) is also formed. We have isolated similar polysiloxane type by-products in several other cases where the siloxanediolate has functioned as an oxo-transfer reagent.[8] Thus the reaction with the silanol may proceed by initial protonation of an imide group with subsequent transfer of oxygen and elimination of $(Ph_2SiO)_n$ and Bu^{t}NH$_2$ and formation of $[Cr(O)(NBu^t)Cl_2]$ from which compound **1** may be derived, *e.g.* eqn. (4). The recrystallised yield of

$$\begin{array}{l} [Cr(NBu^t)_2Cl_2] + O(Ph_2SiOH)_2 \longrightarrow \\ \qquad \text{“}Cr(NHBu^t)(NBu^t)Cl_2(OSiPh_2OSiPh_2OH)\text{”} \longrightarrow \\ \qquad\qquad [Cr(O)(NBu^t)Cl_2] + (Ph_2SiO)_n + Bu^tNH_2 \end{array} \quad (4)$$

1·C_6H_5Me increased from 14 to 25% when a 1 : 2 molar ratio of reagents $[Cr(NBu^t)_2Cl_2]:O(Ph_2SiOH)_2$ was employed. Oxo–imido exchange in the compounds $[Cr(NBu^t)_2Cl_2]$[9] and $[Cr(NBu^t)_2(OSiMe_3)_2]$[10] has been reported to occur on addition of stoichiometric quantities of aqueous HCl and a red oil believed to be $[Cr(O)(NBu^t)Cl_2]$ has been reported. To our knowledge **1** is the first example of a chromium(VI) monocyclicmetallasiloxane (the cage compound $[(c\text{-}C_5H_{11})_7Si_7O_{11}(OSiMe_3)\text{-}CrO_2]$[11] and the mononuclear compound $[CrO_2(Ph_3SiO)_2]$[12] are known). There are no other structurally characterised chromium(VI) oxo-imido or monoimido compounds although an oxo-imido chromium(V) species is known.[13]

Treatment of the molybdenum compound $[Mo(NBu^t)_2Cl_2]$ with a solution of $O(Ph_2SiOH)_2$ and 2 equivalents of pyridine in toluene gives the mononuclear monoimido bis-chelate product **2**·py. This indicates a 1 : 2 rather than 1 : 1 stoichiometric reaction between $[Mo(NBu^t)_2Cl_2]$ and $O(Ph_2SiOH)_2$. When the stoichiometric ratio was changed to 1 : 2 the yield of **2**·py increased from 28 to 40%. In the reaction leading to compound **2** there is elimination of both HCl and the amine Bu^{t}NH$_2$, but no oxo–imido exchange as found for **1**. Instead the relatively large co-ordination sphere of the metal accommodates two mutually *trans*-disiloxanediolato ligands in chelate co-ordination mode with *tert*-butylimido, Bu^{t}N, and pyridine occupying the fifth and sixth co-ordination sites so that the metal centre is both electronically and sterically saturated. We observed a similar result in the product from reaction of $O(Ph_2SiOH)_2$ with the tungsten compound $[W(NBu^t)_2(NHBu^t)_2]$. Once again there is a 1 : 2 stoichiometric reaction

$$\begin{array}{lll} [Cr(NBu^t)_2Cl_2] + O(Ph_2SiOH)_2 + 2py\ (\text{r.t.}) \longrightarrow & [\{CrO(NBu^t)(O(Ph_2SiO)_2)\}_2]\ \mathbf{1}\ 14\%. & \\ & \text{Red crystals } \mathbf{1}\cdot C_6H_5Me \text{ from toluene at } -20\ ^\circ C, \text{ mp } 169\text{–}171\ ^\circ C & (1) \\ [Mo(NBu^t)_2Cl_2] + O(Ph_2SiOH)_2 + 2py\ (\text{r.t.}) \longrightarrow & [Mo(NBu^t)(py)(O(Ph_2SiO)_2)_2]\ \mathbf{2}\ 31\%. & \\ & \text{Yellow crystals } \mathbf{2}\cdot py \text{ from toluene at } -20\ ^\circ C, \text{ mp } 165\text{–}167\ ^\circ C & (2) \\ [W(NBu^t)_2(NHBu^t)_2] + O(Ph_2SiOH)_2\ (\text{r.t.}) \longrightarrow & [W(NBu^t)(NH_2Bu^t)(O(Ph_2SiO)_2)_2]\ \mathbf{3}\ 49\%. & \\ & \text{Cream crystals } \mathbf{3}\cdot C_6H_5Me \text{ from } CH_2Cl_2 \text{ at } -20\ ^\circ C; \text{ mp } 186\text{–}188\ ^\circ C & (3) \end{array}$$

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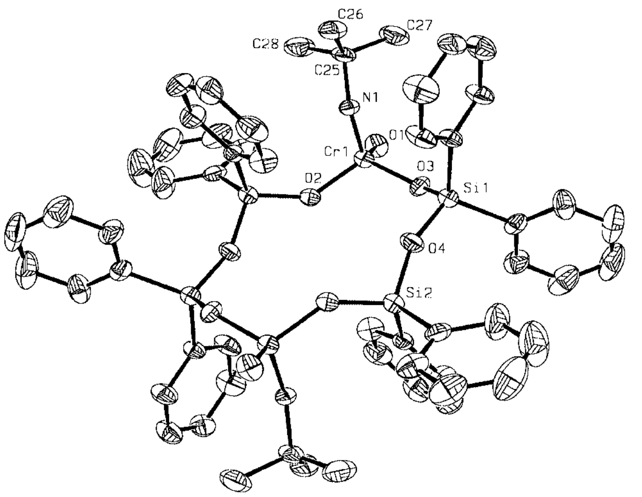

Fig. 1 Molecular structure of compound **1**·C_6H_5Me (thermal ellipsoids at the 50% probability level).

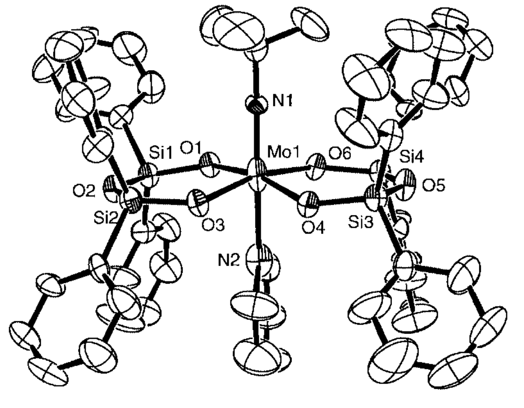

Fig. 2 Molecular structure of compound **2**·py, as in Fig. 1.

(although a 1 : 1 molar ratio was employed). The reaction is virtually quantitative in terms of available silicon reagent. As with the molybdenum compound **2**·py, elimination of both HCl and the amine Bu^tNH_2 occurs without oxo–imido exchange and the product $[W(NBu^t)(NH_2Bu^t)(O(Ph_2SiO)_2)_2]\cdot C_6H_5Me$, **3**·toluene, is formed. Roesky and co-workers[14] have previously reported on formation of the bis-imido tungsten dimer compound $[(NBu^t)_2W(OBu^t_2SiO)]_2$ from the reaction between $[W(NBu^t)_2(NHBu^t)_2]$ and the silanediol $Bu^t_2Si(OH)_2$, so it may be inferred that the acidity of the silanol proton is an important factor in determining whether or not protonation of the imido group occurs. Silanol acidity is discussed extensively in a recent review by Lickiss.[15]

The pattern of reactivity which resulted in the present series of compounds is largely consequent upon the fact that the imido groups are readily protonated by an acidic disiloxanediol even in the presence of pyridine. Also the ligand $(O(Ph_2SiO)_2)^{2-}$ can function as an oxo-transfer reagent particularly when associated with oxophilic metal centres.

Table 1 Bond lengths [Å] and angles [°] for compound **1**·C_6H_5Me

Cr(1)–O(1)	1.573(5)	Si(1)–O(3)	1.630(6)
Cr(1)–N(1)	1.624(7)	Si(2)–O(4)	1.611(6)
Cr(1)–O(2)	1.767(5)	Si(2)–O(2)	1.625(5)
Cr(1)–O(3)	1.769(5)	Si(3)–O(8)	1.617(5)
Cr(2)–O(5)	1.574(5)	Si(3)–O(7)	1.629(5)
Cr(2)–N(2)	1.621(7)	Si(4)–O(8)	1.623(5)
Cr(2)–O(6)	1.769(5)	Si(4)–O(6)^2	1.625(5)
Cr(2)–O(7)	1.772(5)	O(4)–Si(1)^1	1.621(6)
Si(1)–O(4)^1	1.621(6)	O(6)–Si(4)^2	1.625(5)
O(1)–Cr(1)–N(1)	107.0(3)	O(4)^1–Si(1)–O(3)	108.1(3)
O(1)–Cr(1)–O(2)	110.6(3)	O(4)–Si(2)–O(2)	106.7(3)
N(1)–Cr(1)–O(2)	107.2(3)	O(8)–Si(3)–O(7)	108.5(3)
O(1)–Cr(1)–O(3)	109.6(3)	O(8)–Si(4)–O(6)^2	106.4(3)
N(1)–Cr(1)–O(3)	109.9(3)	Si(2)–O(2)–Cr(1)	140.3(3)
N(2)–Cr(1)–O(3)	112.4(3)	Si(1)–O(3)–Cr(1)	141.0(3)
O(5)–Cr(2)–N(2)	107.1(3)	Si(2)–O(4)–Si(1)^1	154.2(4)
O(5)–Cr(2)–O(6)	110.4(3)	Si(4)^2–O(6)–Cr(2)	140.0(3)
N(2)–Cr(2)–O(6)	107.0(3)	Si(3)–O(7)–Cr(2)	139.2(3)
O(5)–Cr(2)–O(7)	109.8(3)	Si(3)–O(8)–Si(4)	151.8(4)
N(2)–Cr(2)–O(7)	110.0(3)	C(25)–N(1)–Cr(1)	145.6(6)
O(6)–Cr(2)–O(7)	112.5(2)	C(53)^2–N(2)–Cr(2)	146.4(6)

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

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

Mo(1)–N(1)	1.804(5)	Si(2)–O(3)	1.619(5)
Mo(1)–O(1)	1.912(5)	Si(2)–O(2)	1.632(5)
Mo(1)–O(6)	1.928(5)	Si(3)–O(4)	1.626(5)
Mo(1)–O(3)	1.939(5)	Si(3)–O(5)	1.641(5)
Mo(1)–O(4)	1.942(5)	Si(4)–O(6)	1.621(5)
Mo(1)–N(2)	2.270(5)	Si(4)–O(5)	1.624(5)
Si(1)–O(2)	1.631(5)	N(1)–C(54)	1.401(11)
Si(1)–O(1)	1.639(5)		
N(1)–Mo(1)–O(1)	94.4(2)	O(4)–Mo(1)–N(2)	83.70(19)
N(1)–Mo(1)–O(6)	95.1(2)	O(2)–Si(1)–O(1)	108.4(3)
O(1)–Mo(1)–O(6)	90.0(2)	O(3)–Si(2)–O(2)	109.0(3)
N(1)–Mo(1)–O(3)	99.6(2)	O(4)–Si(3)–O(5)	107.9(3)
O(1)–Mo(1)–O(3)	90.1(2)	O(6)–Si(4)–O(5)	108.3(3)
O(6)–Mo(1)–O(3)	165.2(2)	C(54)–N(1)–Mo(1)	170.3(5)
N(1)–Mo(1)–O(4)	99.9(2)	Si(1)–O(1)–Mo(1)	139.2(3)
O(1)–Mo(1)–O(4)	165.7(2)	Si(2)–O(2)–Si(1)	132.1(3)
O(6)–Mo(1)–O(4)	88.61(19)	Si(2)–O(3)–Mo(1)	136.8(3)
O(3)–Mo(1)–O(4)	87.6(2)	Si(3)–O(4)–Mo(1)	136.5(3)
N(1)–Mo(1)–N(2)	174.9(2)	Si(4)–O(5)–Si(3)	132.4(3)
O(1)–Mo(1)–N(2)	82.04(18)	Si(4)–O(6)–Mo(1)	140.4(3)
O(6)–Mo(1)–N(2)	81.37(19)	C(49)–N(2)–Mo(1)	120.7(2)
O(3)–Mo(1)–N(2)	83.99(19)	C(53)–N(2)–Mo(1)	119.3(2)

Crystal structures

The structures of one of two crystallographically distinct molecules of compound **1**·C_6H_5Me and **2** are shown in Figs. 1 and 2. Selected bond distances and angles are given in Tables 1 and 2. There is a slightly puckered 12-membered dichromiahexasiloxane ring in **1** (deviations from the plane described by the ligating oxygens O(2) and O(3) are Cr(1) −0.4575, Si(1) −0.4806, Si(2) −0.6270, O(4) 0.2423 Å). The distances and angles associated with the disiloxanediolate ligand are within the normal ranges while the geometry at chromium is tetrahedral. The Cr=O distance in **1** 1.573(5) Å is close to those in $[(c\text{-}C_5H_{11})_7Si_7O_{11}(OSiMe_3)CrO_2]$ 1.557(5),1.574(5) Å.[11] The Cr–N distance in **1** 1.624(7) Å is slightly longer and the Cr–N–C angle 145.6(6)° bent compared to Cr–N 1.548(15) Å and Cr–N–C 160.7(13) and 174.3(13)° in $[Cr(NBu^t)_2(OSiPh_3)_2]$.[16]

The molybdenum compound **2** crystallises with one pyridine solvent molecule per unit cell and adopts the classic py solvated vanadyl acetate type structure. The six-coordinated Mo atom sits slightly below the equatorial plane described by the chelating disiloxanolate ligands. The structural parameters of the planar molybdadisiloxane rings are within the ranges seen for other six-membered metallasiloxane rings. The imido function displays the linear co-ordination of the 6e-donor ligand. The Mo–N(1) distance is 1.804(5)Å (there are no structures with comparable geometry having the NBu^t group but values between 1.704(8) and 1.733(7) Å are reported for other linear $Mo–NBu^t$ fragments in d^0 complexes).

X-Ray data collected on a crystal of compound **3**·C_6H_5Me at 180 K failed to distinguish clearly between a centrosymmetric $P\bar{1}$ and non-centrosymmetric $P1$ structure. The solution in $P1$ started off with two different tungsten-nitrogen distances within the *trans*-$Bu^tN–W–NBu^tH_2$ unit. With further refinement cycles the nitrogen positions became non-positive definite and

Table 3 Bond lengths [Å] and angles [°] for compound **3**·C_6H_5Me

W(1)–O(1)	1.919(5)	Si(1)–O(1)	1.617(5)
W(1)–O(1)^1	1.919(5)	Si(1)–O(2)	1.640(5)
W(1)–O(3)^1	1.932(5)	Si(2)–O(3)	1.617(5)
W(1)–O(3)	1.932(5)	Si(2)–O(2)	1.636(5)
W(1)–N(1)	2.013(7)	N(1)–C(25)	1.456(11)
W(1)–N(1)^1	2.013(7)		
O(1)–W(1)–O(1)^1	180.0(3)	O(1)^1–W(1)–N(1)^1	90.2(2)
O(1)–W(1)–O(3)^1	90.0(2)	O(3)^1–W(1)–N(1)^1	89.7(3)
O(1)^1–W(1)–O(3)^1	90.0(2)	O(3)–W(1)–N(1)^1	90.3(3)
O(1)–W(1)–O(3)	90.0(2)	N(1)–W(1)–N(1)^1	180.0(6)
O(1)^1–W(1)–O(3)	90.0(2)	O(1)–Si(1)–O(2)	109.5(3)
O(3)^1–W(1)–O(3)	180.0(3)	O(3)–Si(2)–O(2)	108.9(3)
O(1)–W(1)–N(1)	90.2(2)	Si(1)–O(1)–W(1)	138.2(3)
O(1)^1–W(1)–N(1)	89.8(2)	Si(2)–O(2)–Si(1)	131.2(3)
O(3)^1–W(1)–N(1)	90.3(3)	Si(2)–O(3)–W(1)	139.0(3)
O(3)–W(1)–N(1)	89.7(3)	C(25)–N(1)–W(1)	161.9(7)
O(1)–W(1)–N(1)^1	89.8(2)		

Symmetry transformations used to generate equivalent atoms: 1 $-x, -y, -z$; 2 $-x-1, -y-1, -z-1$.

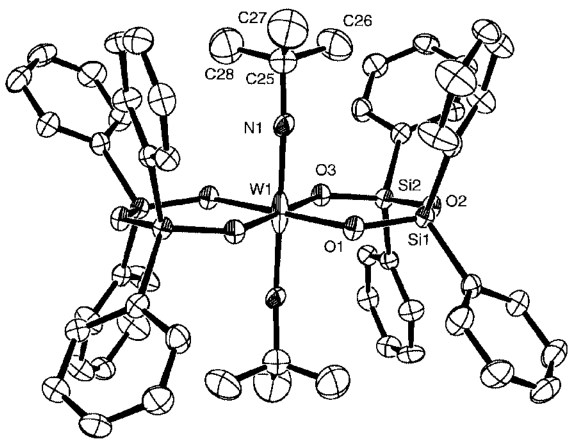

Fig. 3 Molecular structure of compound **3**·C_6H_5Me, as in Fig. 1.

the refinement became unstable. The presence of *trans* imido–amine ligation, *trans*-Bu^{t}N–W–NBu^{t}H$_2$, is confirmed by ^{1}H and ^{13}C NMR spectra of **3**. The refinement in $P\bar{1}$ on the other hand was stable and the residual electron density in the difference map relatively low. In this solution the bond distances and angles in the *trans*-Bu^{t}N–W–NBu^{t}H$_2$ unit given in Table 3 are an average of those expected for the isomeric bis-amide and imide–amine systems, *e.g.* compare values for compound **3** W–N,W–N–C [W(NHBu^t)$_2$] 2.013(7) Å,161.9(7)° with those in BzpW(NBu^t)(NHBu^t)$_2$[17] W–N, W–N–C[W(NHBu^t)$_2$] 1.924(5) Å, 139.5(4) and 1.931(4) Å, 140.6(4)° and W–N,W–N–C-[W(NBu^t)] 1.753(4) Å, 161.0(4)° or those in [W(NBu^t)(OBu^t)$_3$-Cl(NH$_2$Bu^t)][18] W–N,W–N–C [W(NBu^t)]1.740(9) Å, 171.9(5)°, W–N,W–N–C[W(NH$_2$Bu^t)] 2.429(5) Å, 130.8(4)°. Despite the averaging within the *trans*-Bu^{t}N–W–NBu^{t}H$_2$ unit the structure does provide confirmation that the gross structural features of the molecule, shown in Fig. 3, are similar to those of the molybdenum compound **2**·py. The latter and **3** are examples of the class of compounds [M(NR)X$_4$L$_n$],[4] *e.g.* [W(NBu^t)(OBu^t)$_3$-Cl(NH$_2$Bu^t)][18] and [Mo(NC$_6$H$_4$Me)Cl$_4$]thf.[19] However there are no other examples of compounds of Mo or W having six-membered metallasiloxane rings ([WO(O(Ph$_2$SiO)$_3$)$_2$] with eight-membered tungstasiloxane rings was recently reported).[20]

Further investigations of the chemistry of the compounds **1**–**3** and modifications to the sequence of reactions in which they were formed are in progress.

Experimental

All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk 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. 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, Wales, Pyridine was distilled over KOH and stored over 4 Å molecular sieves.

Syntheses

[{CrO(NBu^t)(OSiPh$_2$OSiPh$_2$O)}$_2$] 1. To a solution of [Cr(NBu^t)$_2$Cl$_2$] (0.32 g, 1.2 mmol) in toluene (25 cm^3) was added dropwise, with stirring, a mixture of (Ph$_2$SiOH)$_2$O (0.50 g, 1.2 mmol) and pyridine (0.2 cm^3, 2.4 mmol) in toluene (25 cm^3). Following the addition of the siloxanediol the dark red solution immediately lightened and a fine precipitate was deposited. After 4 h at room temperature the solution was filtered and the mother-liquor reduced in *vacuo* to yield a red oil. Dissolution of the oil in the minimum quantity of toluene (*ca.* 15 cm^3), followed by the addition of an excess of hexane (*ca.* 50 cm^3), precipitated halide salts and siloxane (Ph$_2$SiO)$_n$. Filtration of the solution followed by reduction *in vacuo* afforded the crude product as a red oil. X-Ray quality crystals of [{CrO(NBu^t)-(OSiPh$_2$OSiPh$_2$O)}$_2$] were grown in low yield (0.20 g, 14%) from a concentrated toluene solution at −20 °C, mp 169–171 °C. IR (cm^{-1}): 3045w, 2978w, 1591w, 1568w, 1429m, 1116s, 1062s, 1026s, 998s, 966s, 911vs, 742s, 718vs, 697vs, 496s and 481s. NMR: ^{1}H (CDCl$_3$, 250 MHz, 298 K), δ 1.0 (s, 18 H, NBu^t), 7.15–7.4 (m, *m*-, *p*-H of Ph, CDCl$_3$ solvent) and 7.55–7.7 (m, 16 H, *o*-H of Ph); ^{13}C (C$_6$D$_6$, 62.9 MHz, 298 K), δ 28.5 (C(*C*H$_3$)$_3$), 69.0 (*C*(CH$_3$)$_3$), 127.6 (*m*-C of Ph), 129.8 (*p*-C of Ph), 134.9, 135.0 (*o*-C of Ph) and 135.5(*ipso*-C of Ph); ^{29}Si (CDCl$_3$, 119.2 MHz, 300 K), δ −35.97 (s). Accurate mass FAB (liquid secondary ion mass spectroscopy) (polyethylene glycol)–3-nitrobenzyl alcohol matrix): found *m*/*z* 1103.2088, calculated for $C_{56}H_{59}Cr_2N_2O_8Si_4(MH^+)$ 1103.215875.

When the reaction was repeated using a 1 : 2 molar ratio of [Cr(NBu^t)$_2$Cl$_2$] and (Ph$_2$SiOH)$_2$O the yield of compound **1**·C$_6$H$_5$Me increased to 25%.

[Mo(NBu^t)(py)(OSiPh$_2$OSiPh$_2$O)$_2$] 2. To a solution of [Mo(NBu^t)$_2$Cl$_2$] (0.52 g, 1.7 mmol) in toluene (25 cm^3) was added dropwise, with stirring, a mixture of (Ph$_2$SiOH)$_2$O (0.69 g, 1.7 mmol) and pyridine (0.27 cm^3, 3.3 mmol) in toluene (50 cm^3). Upon addition of the siloxanediol the solution turned orange, and a fine precipitate was deposited. After 4 h at room temperature the solution was filtered and the mother-liquor reduced *in vacuo* to yield a yellow oil. Dissolution of the oil in toluene (*ca.* 20 cm^3), followed by filtration and reduction *in vacuo* then cooling to −20 °C afforded yellow crystals of [Mo(NBu^t)(py)(OSiPh$_2$OSiPh$_2$O)$_2$]·py (0.55 g, 28%), mp 165–167 °C. IR (cm^{-1}): 3048w, 2973w, 1603w, 1591w, 1486w, 1446w, 1429m, 1216w, 1115s, 1070s, 1033s, 1006s, 990s, 879vs, 743s, 715s, 695vs, 513s, 503s, and 473s. NMR: ^{1}H (CDCl$_3$, 250 MHz, 298 K), δ 0.7 (s, 9 H, NBu^t), 6.25 (t, 2 H, py), 7.0–7.35 (m, *m*-, *p*-H of Ph, CDCl$_3$ solvent), 7.55–7.61 (m, 8 H), 7.9–8.0 (s, 1 H, py), 8.1–8.2 (m, 8 H) and 8.7–8.8 (m, 2 H, py); ^{13}C (CDCl$_3$, 62.9 MHz, 298 K), δ 28.7 (C(*C*H$_3$)$_3$), 75.0 (*C*(CH$_3$)$_3$), 122.4(py), 127.3, 127.5 (*m*-C of Ph), 129.1(py) 129.3, 129.7 (*p*-C of Ph), 134.5, 134.9 (*o*-C of Ph), 136.5, 137.0 (*ipso*-C of Ph) and 149.5(py); ^{29}Si (CDCl$_3$, 119.2 MHz, 300 K), δ −38.73 (s). Found: C, 63.3; H, 5.4; N, 2.8. Calc. for $C_{57}H_{54}MoN_2O_6Si_4$: C, 63.8; H, 5.1; N, 2.6%.

When the reaction was repeated using a 1 : 2 molar ratio of [Mo(NBu^t)$_2$Cl$_2$] and (Ph$_2$SiOH)$_2$O the yield of compound **2**·py increased to 40%.

[W(NBu^t)$_2$(NH$_2$Bu^t)(OSiPh$_2$OSiPh$_2$O)$_2$] 3. To a solution of

Table 4 X-Ray data for compounds **1**·C_6H_5Me, **2**·py and **3**·C_6H_5Me

	1·C_6H_5Me	**2**·py	**3**·C_6H_5Me
Empirical formula	$C_{63}H_{66}Cr_2N_2O_8Si_4$	$C_{62}H_{59}MoN_3O_6Si_4$	$C_{63}H_{66}N_2O_6Si_4W$
Formula weight	1195.54	1150.42	1243.39
T/K	220(2)	293(2)	180(2)
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	13.931(7)	13.655(9)	10.333(4)
b/Å	15.948(9)	14.524(10)	10.733(8)
c/Å	16.469(8)	16.072(12)	14.149(7)
α/°	68.08(6)	102.67(8)	110.88(6)
β/°	111.08(5)	87.75(6)	90.08(4)
γ/°	89.96(7)	107.62(6)	99.91(4)
V/Å^3	3129(3)	2963(4)	1440.9(14)
Z	2	2	2
μ/mm^{-1}	0.477	0.354	2.140
Reflections collected	9964	10403	5351
Independent reflections	9614 [R(int) = 0.3003]	10401 [R(int) = 0.0000]	5054 [R(int) = 0.0173]
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0716, 0.1543	0.1150, 0.2584	0.0638, 0.1566
(all data)	0.2487, 0.2077	0.2366, 0.3001	0.0696, 0.1619

[$W(NBu^t)_2(NHBu^t)_2$] (0.50 g, 1.1 mmol) in toluene (25 cm^3) was added dropwise, with stirring, a solution of $(Ph_2SiOH)_2O$ (0.44 g, 1.1 mmol) in toluene (25 cm^3). No visible changes were observed following the diol addition. After 18 h at room temperature the solution was reduced *in vacuo* to yield a yellow oil. Recrystallisation from a concentrated CH_2Cl_2 solution at −20 °C, afforded compound **3** (0.62 g, 49%) as colourless cubes, mp 186–188 °C. IR (cm^{-1}): 3314w, 3047w, 2974w, 1591w, 1429m, 1274m, 1215w, 1114s, 1032m, 1005s, 989s, 883vs, 744s, 715s, 696vs, 517s, 505s, and 472vs. NMR: ^1H (toluene-d^8, 250 MHz, 298 K), δ 0.4 (s, 9 H, NBu^tH$_2$), 0.6 (s, 9 H, NBu^t), 2.05 (s, 2 H, NBu^tH_2), 7.0–7.3 (m, *m*-, *p*-H of Ph, C_7D_8 solvent), 7.92 (dd, 8 H, *o*-H of Ph) and 8.1 (dd, 8 H, *o*-H of Ph); ^{13}C ($CDCl_3$, 62.9 MHz, 298 K), δ 30.8 (C(CH$_3$)$_3$ of NH$_2$Bu^t), 31.5 (C(CH$_3$)$_3$ of NBu^t), 49.0 (C(CH$_3$)$_3$ of NH$_2$Bu^t), 70.1 (C(CH$_3$)$_3$ of NBu^t), 127.7 (*m*-C of Ph), 129.9, 130.0 (*p*-C of Ph), 134.4, 134.7 (*o*-C of Ph), 135.8, 136.3 (*ipso*-C of Ph); ^{29}Si ($CDCl_3$, 119.2 MHz, 300 K), δ −36.9.

X-Ray crystallography

Data were collected on a CAD4 diffractometer using Mo-Kα (λ = 0.71069 Å) radiation and corrected for absorption using ψ scans and DIFABS[21] for compound **3**·C_6H_5Me (see Table 4 for details of data collection and refinement). The structures were solved by standard heavy atom techniques (SHELXS 86)[22] and refined by full-matrix least squares (on F^2, SHELXL 97).[23] 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]. The lattice held pyridine in compound **2**·py showed positional disorder which was modelled (as a rigid hexagon) using a 60/40 two site occupation. Hydrogens were included at fixed positions. The high residual factor for it may in part be due to this disorder. Solutions for **3**·C_6H_5Me in $P1$ and $P\bar{1}$ were discussed above. For the toluene molecule in the $P\bar{1}$ four of the carbon sites including the methyl group and its 3 nearest neighbours were modelled for 2-site occupancy about the centre of symmetry.

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See http://www.rsc.org/suppdata/dt/1999/3225/ for crystallographic files in .cif format.

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