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 $1 \cdot C_6H_5Me$, 2·py and $3 \cdot C_6H_5Me$ were made. Compound 1 is the first chromium(v1) oxo-imido compound to be structurally characterised and the first example of a chromium(v1) 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 $[(OSiR_2)_n O]^{2-}$ are comparatively abundant with many examples of maingroup, 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 -C₅H₅, Cp) metallasiloxanes: $[{ZrCp_2(OSiPh_2O)}_2]$ and $[{ZrCp_2(OSiPh_2 OSiPh_2O)}_2]$.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)₂Cl₂] and [Mo(NBu^t)₂Cl₂] 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 $1 \cdot C_6 H_5 Me$ some toluene soluble colourless crystalline product (infrared features consistent with polysiloxane (Ph₂SiO)_n) is also formed. We have isolated similar polysiloxane type by-products in several other cases where the siloxanediolate has functioned as an oxotransfer 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^tNH_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

$$[Cr(NBu^{t})_{2}Cl_{2}] + O(Ph_{2}SiOH)_{2} \longrightarrow$$

$$"Cr(NHBu^{t})(NBu^{t})Cl_{2}(OSiPh_{2}OSiPh_{2}OH)" \longrightarrow$$

$$[Cr(O)(NBu^{t})Cl_{2}] + (Ph_{2}SiO)_{n} + Bu^{t}NH_{2} \quad (4)$$

1•C₆H₅Me increased from 14 to 25% when a 1:2 molar ratio of reagents [Cr(NBu^t)₂Cl₂]:O(Ph₂SiOH)₂ was employed. Oxoimido exchange in the compounds [Cr(NBu^t)₂Cl₂]⁹ and [Cr-(NBu^t)₂(OSiMe₃)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)Cl₂] has been reported. To our knowledge **1** is the first example of a chromium(v1) monocyclicmetallasiloxane (the cage compound [(c-C₅H₁₁)₇Si₇O₁₁(OSiMe₃)-CrO₂]¹¹ and the mononuclear compound [CrO₂(Ph₃SiO)₂]¹² are known). There are no other structurally characterised chromium(v1) oxo-imido or monoimido compounds although an oxo-imido chromium(v) species is known.¹³

Treatment of the molybdenum compound [Mo(NBu^t)₂Cl₂] with a solution of O(Ph₂SiOH)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)₂Cl₂] and O(Ph₂SiOH)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^tNH₂, 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 coordination mode with tert-butylimido, ButN, 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(Ph₂SiOH)₂ with the tungsten compound [W(NBu^t)₂(NH-Bu^t)₂]. Once again there is a 1:2 stoichiometric reaction

| (1) |
|-----|
| |
| (2) |
| |
| (3) |
| |

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Fig. 1 Molecular structure of compound $1{\cdot}C_6H_5Me$ (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 $2 \cdot py$, elimination of both HCl and the amine Bu^tNH₂ occurs without oxo-imido exchange and the product [W(NBu^t)(NH₂Bu^t)(O(Ph₂SiO)₂)₂]·C₆H₅Me, $3 \cdot tolu$ ene, is formed. Roesky and co-workers¹⁴ have previously reported on formation of the bis-imido tungsten dimer compound [(NBu^t)₂W(OBu^t₂SiO)]₂ from the reaction between [W(NBu^t)₂(NHBu^t)₂] and the silanediol Bu^t₂Si(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.

Crystal structures

The structures of one of two crystallographically distinct molecules of compound $1 \cdot C_6 H_5 Me$ 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

Table 1 Bond lengths [Å] and angles $[\degree]$ for compound $1 \cdot C_6 H_5 Me$

| 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 transfo -x + 1, -y, -z + | rmations used 1; $2 - x$, $-y - y$ | to generate equivalent $1, z + 1$. | atoms: 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) |
| | | | · · · |

 $[(c-C_5H_{11})_7Si_7O_{11}(OSiMe_3)CrO_2]$ 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 d⁰ complexes).

X-Ray data collected on a crystal of compound $3 \cdot C_6 H_5 Me$ at 180 K failed to distinguish clearly between a centrosymmetric $P\bar{1}$ and non-centrosymmetric P1 structure. The solution in P1started off with two different tungsten-nitrogen distances within the *trans*-Bu'N–W–NBu'H₂ unit. With further refinement cycles the nitrogen positions became non-positive definite and

Table 3 Bond lengths [Å] and angles $[\circ]$ for compound $3 \cdot C_6 H_5 Me$

| 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 $3 \cdot C_6 H_5 Me$, as in Fig. 1.

the refinement became unstable. The presence of trans imidoamine ligation, trans-Bu^tN-W-NBu^tH₂, is confirmed by ¹H and ¹³C NMR spectra of **3**. The refinement in $P\overline{1}$ 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^tN-W-NBu^tH₂ 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)₂¹⁷ 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(NH₂Bu^t)]¹⁸ W–N,W–N–C [W(NBu^t)]1.740(9) Å, 171.9(5)°, W-N,W-N-C[W(NH₂Bu^t)] 2.429(5) Å, 130.8(4)°. Despite the averaging within the trans-Bu^tN-W-NBu^tH₂ 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 $[M(NR)X_4L_n]$, $e.g. [W(NBu^t)(OBu^t)_3$ -Cl(NH₂Bu^t)]¹⁸ and [Mo(NC₆H₄Me)Cl₄]thf.¹⁹ However there are no other examples of compounds of Mo or W having sixmembered metallasiloxane rings ([WO(O(Ph₂SiO)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 (¹H, ¹³C) and AMX600 (²⁹Si) 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)(OSiPh₂OSiPh₂O)}₂] 1. To a solution of [Cr-(NBu^t)₂Cl₂] (0.32 g, 1.2 mmol) in toluene (25 cm³) was added dropwise, with stirring, a mixture of (Ph₂SiOH)₂O (0.50 g, 1.2 mmol) and pyridine (0.2 cm³, 2.4 mmol) in toluene (25 cm³). 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 cm³), followed by the addition of an excess of hexane (*ca.* 50 cm^3), precipitated halide salts and siloxane (Ph₂SiO)_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)-(OSiPh₂OSiPh₂O)}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: ¹H (CDCl₃, 250 MHz, 298 K), δ 1.0 (s, 18 H, NBu^t), 7.15-7.4 (m, m-, p-H of Ph, CDCl₃ solvent) and 7.55-7.7 (m, 16 H, o-H of Ph); ¹³C (C₆D₆, 62.9 MHz, 298 K), δ 28.5 (C(CH₃)₃), 69.0 (C(CH₃)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); ²⁹Si (CDCl₃, 119.2 MHz, 300 K), δ –35.97 (s). Accurate mass FAB (liquid secondary ion mass spectroscopy) (polyethylene glycol)-3nitrobenzyl 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 $1 \cdot C_{6}H_{5}Me$ increased to 25%.

[Mo(NBu^t)(py)(OSiPh₂OSiPh₂O)₂] 2. To a solution of $[Mo(NBu^t)_2Cl_2]$ (0.52 g, 1.7 mmol) in toluene (25 cm³) was added dropwise, with stirring, a mixture of (Ph₂SiOH)₂O (0.69 g, 1.7 mmol) and pyridine (0.27 cm³, 3.3 mmol) in toluene (50 cm³). 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 cm³), followed by filtration and reduction in vacuo then cooling to -20 °C afforded yellow crystals of [Mo(NBu^t)(py)(OSiPh₂OSiPh₂O)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: 1H (CDCl₃, 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, CDCl₃ 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); ¹³C (CDCl₃, 62.9 MHz, 298 K), δ 28.7 (C(CH₃)₃), 75.0 (C(CH₃)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); ²⁹Si (CDCl₃, 119.2 MHz, 300 K), δ -38.73 (s). Found: C, 63.3; H, 5.4; N, 2.8. Calc. for C₅₇H₅₄MoN₂O₆Si₄: C, 63.8; H, 5.1; N, 2.6%.

When the reaction was repeated using a 1:2 molar ratio of $[Mo(NBu^t)_2Cl_2]$ and $(Ph_2SiOH)_2O$ the yield of compound **2**·py increased to 40%.

[W(NBu^t)₂(NH₂Bu^t)(OSiPh₂OSiPh₂O)₂] 3. To a solution of

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 $[W(NBu^t)_2(NHBu^t)_2]$ (0.50 g, 1.1 mmol) in toluene (25 cm³) was added dropwise, with stirring, a solution of (Ph₂SiOH)₂O (0.44 g, 1.1 mmol) in toluene (25 cm³). 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 CH₂Cl₂ 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-d⁸, 250 MHz, 298 K), δ 0.4 (s, 9 H, NBu^tH₂), 0.6 (s, 9 H, NBu^t), 2.05 (s, 2 H, NBu^tH₂), 7.0–7.3 (m, m-, p-H of Ph, C₇D₈ solvent), 7.92 (dd, 8 H, o-H of Ph) and 8.1 (dd, 8 H, o-H of Ph); ¹³C (CDCl₃, 62.9 MHz, 298 K), δ 30.8 (C(CH₃)₃ of NH₂Bu^t), 31.5 (C(CH₃)₃ of NBu^t), 49.0 (C(CH₃)₃ of NH₂Bu^t), 70.1 (C(CH₃)₃ of NBut), 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); ²⁹Si (CDCl₃, 119.2 MHz, 300 K), δ – 36.9.

X-Ray crystallography

Data were collected on a CAD4 diffractometer using Mo-Ka $(\lambda = 0.71069 \text{ Å})$ radiation and corrected for absorption using ψ scans and DIFABS²¹ for compound 3·C₆H₅Me (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 A]. 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 $3 \cdot C_6 H_5 Me$ in P1 and $P\overline{1}$ were discussed above. For the toluene molecule in the $P\overline{1}$ 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.

CCDC reference number 186/1600.

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

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