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Formation of ring-expanded products from certain combinations of tetraphenyldisiloxanediolates $[(Ph_2SiOM')_2O]$ (M′ = Li or Na) and Group 4 metal chlorides MCl_4

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Experimental conditions and combinations of reagents have been varied in reactions between $[(Ph_2SiOM')_2O]$ (M′ = Li or Na) and Group 4 metal halides MCl_4, with the broad aim of assessing their affects on the formation of ring-expanded products. Lithium-7 NMR spectroscopy was used to monitor the reaction between $[(Ph_2SiOLi)_2O]$ and $MgCl_2{\cdot}2thf$ in thf (tetrahydrofuran) which gives a ring-expanded product. The reaction between $[(Ph_2SiONa)_2O]$, prepared *in situ* from sodium metal and $(Ph_2SiOH)_2O$, and $TiCl_4$ in a 3:1 molar ratio gave the sodium-bridged compound $[Ti\{O(SiPh_2O)_2\}_3\{Na(py)\}_2]{\cdot}py$, py = pyridine, the first example of a six-membered titanasiloxane ring. Further reaction with LiI gave the lithium-bridged analogue. The analogous reaction with $HfCl_4$ gave the ring-expanded compound $[Hf\{Ph_2Si(OSiPh_2O)_2\}_2(py)_2]{\cdot}2C_6H_5Me$, the first examples of eight-membered hafnasiloxane rings. Results of ^7Li, ^{29}Si, and ^{23}Na NMR, IR, and single-crystal X-ray diffraction studies are reported.

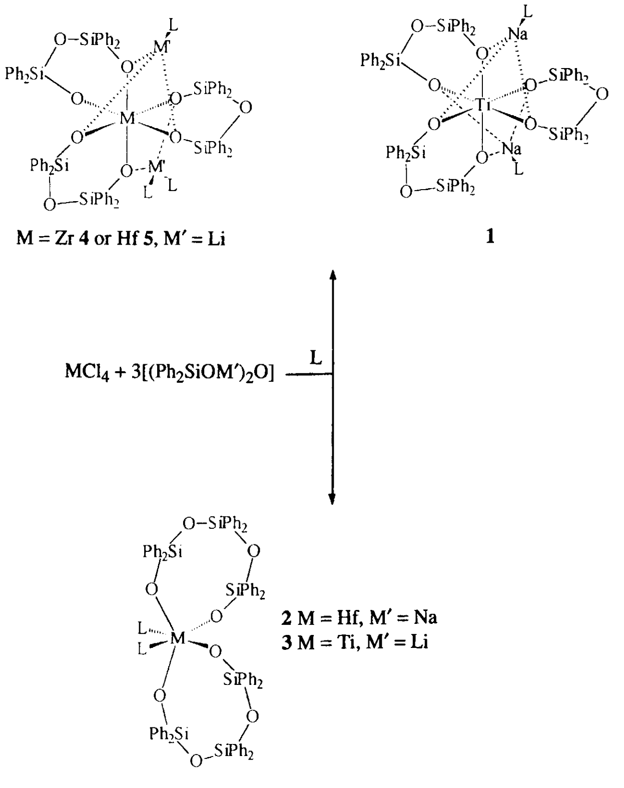
The number of metallasiloxanes incorporating tetraorganodisiloxanediolate ligands, $[(R_2SiO)_2O]^{2-}$, is growing and compounds wherein these ligands adopt chelate,[1] bridging[2] and chelate–bridging[3] co-ordination modes have been structurally characterised. The simple chelate mode is rarely seen; bridging or chelate–bridging is apparently preferred. We have reported on a number of compounds derived from the disiloxanediolates $[(Ph_2SiOM)_2O]$ (M = Li or Na) and metal halides where the ligand $[(Ph_2SiO)_2O]^{2-}$ adopts chelate–bridging co-ordination.[3] However it is now clear (from accumulated results reported herein and elsewhere[4–6]) that certain combinations of these reagents proceed instead to ring-expanded products.

In the ring-expanded products characterised to date the trisiloxanediolate ligand $[Ph_2Si(OSiPh_2O)_2]^{2-}$ is formed and adopts either simple chelate or chelate–bridging co-ordination. In this paper we describe some attempts to probe the ring-expansion process and factors which might affect it. In addition the synthesis and solid-state structures of some new cyclometalasiloxane compounds $[Ti\{O(SiPh_2O)_2\}_3\{Na(py)\}_2]{\cdot}py$ **1** (py = pyridine) and $[Hf\{Ph_2Si(OSiPh_2O)_2\}_2(py)_2]{\cdot}2C_6H_5Me$ **2** isolated in the course of this work, are reported.

Results and Discussion

Synthesis

We have previously reported on the reactions between the dilithium disiloxanediolate $[(Ph_2SiOLi)_2O]$,[7] and the Group 4 transition-metal chlorides $TiCl_4$, $ZrCl_4$[4] and $HfCl_4$[8] which lead to the products **3**–**5** shown in Scheme 1. While the disiloxanediolate ligand was transferred intact with elimination of lithium chloride in reactions with $ZrCl_4$ and $HfCl_4$, the reaction with $TiCl_4$ gave the ring-expanded product **3**. We have also observed[5] that in reactions between $SnCl_4$ and $[(Ph_2SiONa)_2O]$ a dichelated ring-expanded product $[Sn\{Ph_2Si(OSiPh_2O)_2\}_2(thf)_2]{\cdot}C_6H_5Me$ (thf = tetrahydrofuran) was formed. Reactions between $SnCl_4$ and $[(Ph_2SiOLi)_2O]$ however proceeded without ring expansion to $[Sn\{O(SiPh_2O)_2\}_2Cl_2\{Li(thf)_2\}_2]$.[5] We decided to see whether changing the disiloxanediolate reagent from $[(Ph_2SiOLi)_2O]$ to $[(Ph_2SiONa)_2O]$ affected the nature of products formed in reactions with $TiCl_4$, $ZrCl_4$ and $HfCl_4$. It would appear from the results that converse sets of reaction products are preferred when the Group 4 metal chlorides react with the lithium and sodium reagents respectively. The reactions between $TiCl_4$ and $HfCl_4$ and the disodium disiloxanediolate $[(Ph_2SiONa)_2O]$ lead to the products **1** and **2** shown in the Scheme 1. In this case while the disiloxanediolate ligand is transferred intact with elimination of sodium chloride in the reaction with $TiCl_4$ giving **1**, the reaction with $HfCl_4$ gave product **2** incorporating ring expansion. The structures of compounds **1** and **2** were determined crystallographically. The reaction between $ZrCl_4$



Scheme 1 L = py

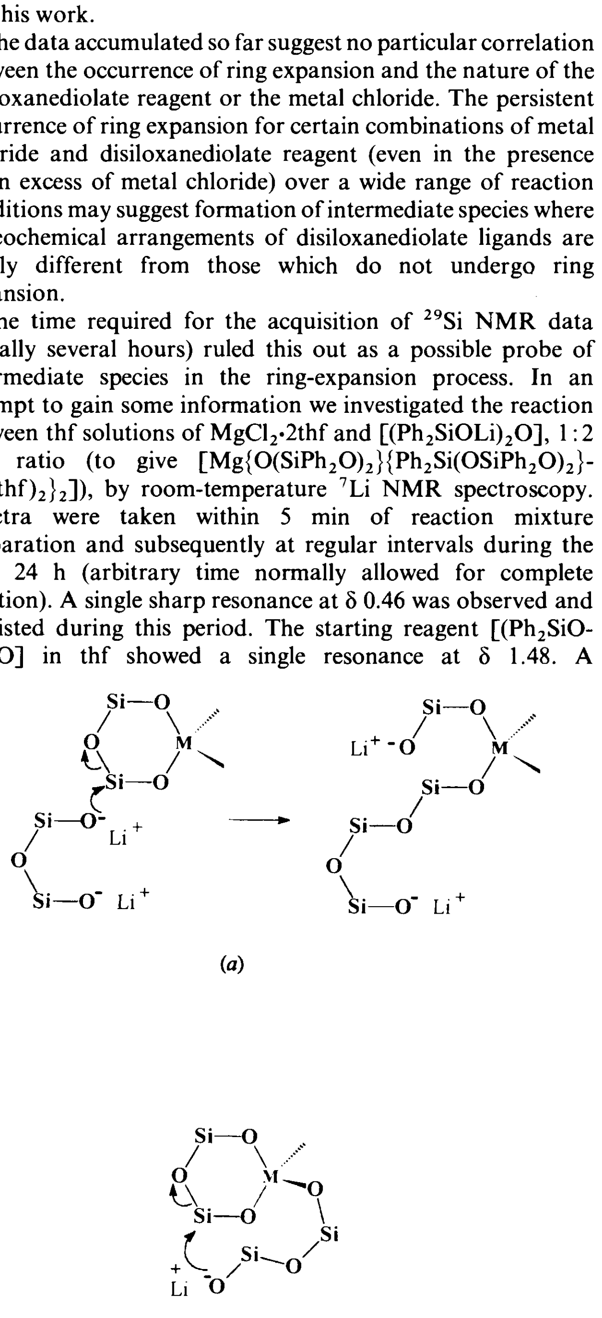
and $[(Ph_2SiONa)_2O]$ (1:3 molar ratio) gave a crystalline zirconium compound with an identical pattern of bands in its infrared spectrum to that of **2** and is therefore probably structurally similar to **2**. Compound **2** is isostructural (less than 1% difference in unit-cell dimensions) to the titanium compound **3**[4] in Scheme 1. The bridging sodium cations in **1** can be exchanged for lithium giving a compound with a similar pattern of bands in its infrared spectrum to that observed for **4** and **5**, and which by analogy might be formulated as $[Ti\{O(SiPh_2O)_2\}_3Li_2]\cdot 3py$ {the reaction between $TiCl_4$ and $[(Ph_2SiOLi)_2O]$ gave the ring-expanded product **3**}. Single resonances were observed in both the room-temperature ^{29}Si and ^{7}Li NMR spectra of $[Ti\{O(SiPh_2O)_2\}_3Li_2]\cdot 3py$ as was the case for **4** and **5**.

Formation of ring-expanded products

From the range of compounds we have characterised to date {formed in reactions between the disiloxanediolates $[(Ph_2SiOM)_2O]$ (M = Li or Na) and metal chlorides} it is clear that formation of ring-expanded products is not simply dictated by single factors like the nature of cation in the reagent $[(Ph_2SiO)_2O]^{2-}$, or the size of the target metal centre. Both the lithium and sodium reagents, $[(Ph_2SiOM)_2O]$ (M = Li or Na), have in different cases given products where the disiloxanediolate ligand was transferred intact[4,5,8,9] or formed products incorporating ring expansion.[4–6] The diol, $(Ph_2SiOH)_2O$, also gave the ring-expanded product **3** when used in conjunction with $TiCl_4$ and pyridine to promote dehydrohalogenation.[4] There is no obvious correlation between the formation of ring-expanded reaction products and the size of the target metal in the metal chloride reagent (for example both product types have been structurally characterised for Ti **1** and **3**) and Hf (**2** and **5**). In addition we recently reported[6] on the structure of the compound $[Mg\{O(SiPh_2O)_2\}\{Ph_2Si(OSiPh_2O)_2\}\{Li(py)_2\}_2]$ having both six- and eight-membered metalasiloxane rings which was obtained from reactions between $MgCl_2\cdot 2thf$ and the dilithium disiloxanediolate. We report here that variation in reaction conditions such as temperature (reactions carried out at −78, 25 °C and solvent reflux temperature), dilution (siloxanolate reagent concentration between 0.06 and 0.6 mol dm^{-3}), or solvent (thf or toluene) had no apparent affect on the nature of the product isolated in reactions between $MgCl_2\cdot 2thf$ and the dilithium disiloxanediolate. Structurally similar products were isolated when reactions (*e.g.* leading to **3** or $[Mg\{O(SiPh_2O)_2\}\{Ph_2Si(OSiPh_2O)_2\}\{Li(py)_2\}_2]$) were carried out in toluene instead of thf. Changing L from pyridine to some other donor in a number of cases left the gross structure unchanged. *e.g.* $[Sn\{Ph_2Si(OSiPh_2O)_2\}L_2]$ (L = thf or py)[5] and $[Cr\{O(SiPh_2O)_2\}_2(NaL_2)_2]$ (L = thf,[10] py or $Me_2NCH_2CH_2NMe_2$[9]). Formation of ring-expanded metallasiloxane products was not affected by varying the reaction stoichiometry in a number of cases. For example, ring-expanded products were isolated from reactions between $SnCl_4$ or $TiCl_4$ and disiloxanediolates $[(Ph_2SiOM)_2O]$ (M = Na and Li)[4,5] in molar ratios 1:1, 1:2 and 1:3. The reaction between $MgCl_2\cdot 2thf$ and $[(Ph_2SiOLi)_2O]$ in molar ratio 1:2 gave the compound $[Mg\{O(SiPh_2O)_2\}\{Ph_2Si(OSiPh_2O)_2\}\{Li(py)_2\}_2]$[6] where there are both six- and eight-membered magnesium siloxane rings. We now report that the same magnesium compound is formed when a molar ratio of 1:1 or 1:3 is employed. The ideal stoichiometry, based on required silicon, for the formation of the magnesasiloxane $[Mg\{O(SiPh_2O)_2\}\{Ph_2Si(OSiPh_2O)_2\}\{Li(py)_2\}_2]$[6] is a 1:2.5 molar ratio of $MgCl_2:[(Ph_2SiOLi)_2O]$. We note here that the yields of $[Mg\{O(SiPh_2O)_2\}\{Ph_2Si(OSiPh_2O)_2\}\{Li(py)_2\}_2]$ calculated in each case on the basis of such a molar ratio of $MgCl_2\cdot 2thf:[(Ph_2SiOLi)_2O]$ (that is ignoring the excess of $MgCl_2\cdot 2thf$) were 75, 69 and 78% when the actual molar ratios employed were 1:1, 1:2 and 1:3 respectively. Thus the presence of an excess of $MgCl_2\cdot 2thf$ in the 1:1 and 1:2 reactions apparently had very little effect on the yield. This implies the preferred formation of intermediate species involving association of more than one disiloxanediolate ligand with one metal centre. The ring-expansion process may be initiated [by analogy with accepted mechanisms for base-catalysed ring-opening polymerisation of $(Ph_2SiO)_3$ and $(Ph_2SiO)_4$[11,12]] by (*a*) attack at silicon in a six-membered metalasiloxane ring by free siloxanediolate or (*b*) attack by disiloxanediolate coordinated at one end to the target metal centre (see Scheme 2). It is noteworthy that heating toluene solutions of the compounds did not effect the conversion of **1** and **5** to the ring-expanded species **3** and **2**. In our work ring expansions from expected six-membered metallasiloxane rings have to date consistently and reproducibly resulted in eight-membered metallasiloxane rings. The electrophilicity of silicon in an eight-membered ring is expected to be considerably less than that in a six-membered ring and thus further ring expansion may require more forcing reaction conditions than employed for this work.

The data accumulated so far suggest no particular correlation between the occurrence of ring expansion and the nature of the disiloxanediolate reagent or the metal chloride. The persistent occurrence of ring expansion for certain combinations of metal chloride and disiloxanediolate reagent (even in the presence of an excess of metal chloride) over a wide range of reaction conditions may suggest formation of intermediate species where stereochemical arrangements of disiloxanediolate ligands are subtly different from those which do not undergo ring expansion.

The time required for the acquisition of ^{29}Si NMR data (usually several hours) ruled this out as a possible probe of intermediate species in the ring-expansion process. In an attempt to gain some information we investigated the reaction between thf solutions of $MgCl_2\cdot 2thf$ and $[(Ph_2SiOLi)_2O]$, 1:2 mol ratio (to give $[Mg\{O(SiPh_2O)_2\}\{Ph_2Si(OSiPh_2O)_2\}\{Li(thf)_2\}_2]$), by room-temperature ^{7}Li NMR spectroscopy. Spectra were taken within 5 min of reaction mixture preparation and subsequently at regular intervals during the next 24 h (arbitrary time normally allowed for complete reaction). A single sharp resonance at δ 0.46 was observed and persisted during this period. The starting reagent $[(Ph_2SiOLi)_2O]$ in thf showed a single resonance at δ 1.48. A



(*a*)

(*b*)

Scheme 2 Possible routes to eight-membered rings. Phenyl groups on silicon omitted

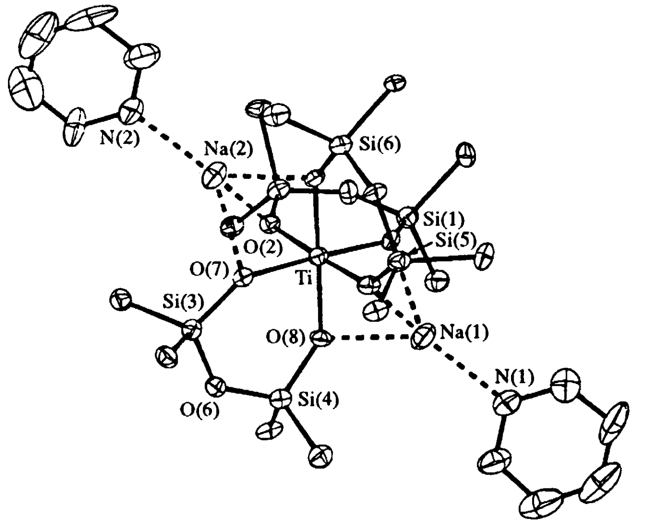


Fig. 1 Molecular structure of compound **1** (excluding phenyl rings) showing thermal ellipsoids at the 50% probability level

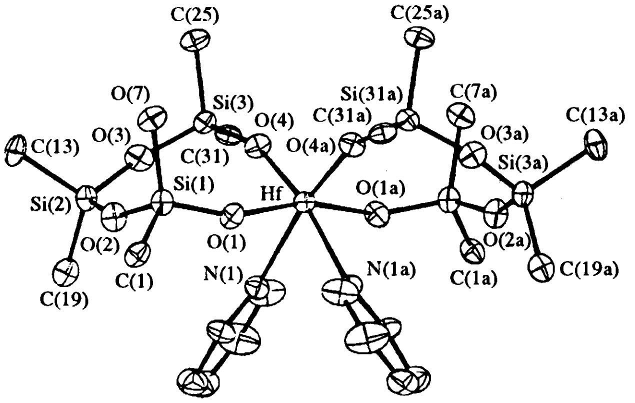


Fig. 2 Molecular structure of compound **2**. Details as in Fig. 1

single resonance for the reaction mixture {$MgCl_2$·2thf and [$(Ph_2SiOLi)_2O$], 1 : 2 mol ratio in thf} shows that there is rapid exchange between the lithium-containing species present. Lithium-containing final products expected include LiCl and [$Mg\{O(SiPh_2O)_2\}\{Ph_2Si(OSiPh_2O)_2\}\{Li(thf)_2\}_2$]. Since the chemical shift of the 'average signal' at δ 0.46 did not change during the 24 h of observation this suggests that the reaction had reached completion in the time required (less than 5 min) to acquire the first spectrum. This result places an upper limit on the time required for the reaction. However given the rapid exchange of lithium environments it is not possible to use ^{7}Li NMR spectroscopy to probe intermediates in the ring-expansion process (even at low temperature because of the difficulty of differentiating species involved in exchange processes from intermediates in the ring-expansion reaction). In comparison with this apparently rapid ring-expansion process, base (KOH, $KOSiMe_3$)-catalysed ring-opening polymerisation of $(Ph_2SiO)_4$ at 140 °C [as measured by residual $(Ph_2SiO)_4$ or weight of polymer formed] was 95% complete after 18 h (k = 0.017 min^{-1}).[12] However polymerisation of $(Ph_2SiO)_3$ occurs 50 times faster (*i.e.* complete within 21 min).[11]

Solid-state structures of compounds 1 and 2

Single crystals of the compounds **1** and **2** were obtained when toluene solutions containing pyridine were allowed to stand at room temperature for several days. The molecular structures are shown in Figs. 1 and 2. Selected bond lengths and angles are given in Tables 1 and 2 with fractional atomic coordinates in Tables 3 and 4. Both **1** and **2** have distorted-octahedral geometry at the transition-metal centres. The solvated sodium-capped tris(chelated) octahedral structure **1** differs from the previously described[4] lithium-bridged zirconium compound **4** and hafnium compound **5**[8] in that both sodiums are face bridging in **1** while one of the lithium cations is edge bridging in **4** and **5**. The sodium ions are in a very distorted tetrahedral environment where the O–Na–O angles are some 39° less than the tetrahedral value while the O–Na–N angles are considerably widened. Similar distortions were observed at the face-bridging lithium site in **5**.[8] The Na–O(Si) distances in **1** are slightly longer than those in [$Cr\{O(SiPh_2O)_2\}_2\{Na(thf)_2\}_2$].[10] Compound **1** is the first example of a titanasiloxane compound having six-membered rings to be structurally characterised. The M–O(Si) distances are shorter than the Si–O(Si) in both **1** and **2** as is generally the case. The difference in M–O(Si) distances between compounds **1**, **4** and **5** and between **3** and **2** is in keeping with differences in covalent radii of the metals. This suggests that the M–O(Si) bond character does not change significantly within these groups. The transition metal–oxygen distances are slightly shorter in the ring-expanded titanium and hafnium compounds **3** and **2** compared to the alkali-metal-bridged titanium and hafnium tris(chelates) **1** and **5**. The six-membered rings in **1** are relatively planar and the average Si–O–Si angles are close to those previously found in [$VO\{O(SiPh_2O)_2\}_2\{Li(thf)_2\}_2$][13] and [$Cr\{O(SiPh_2O)_2\}_2\{Na(thf)_2\}_2$].[9] The eight-membered rings in the hafnium compound **2** are also relatively planar as was found for the isostructural titanium compound **3** but in contrast to the puckered arrangement found in related *trans*-Sn{$Ph_2Si(OSiPh_2O)_2$}·2thf.[5] The Si–O–Si angles in **2** [149.6.(4), 156.6(4)°] are close to those in **3** [146.4(3), 156.0(3)°].

The ^{29}Si NMR spectra of toluene solutions of the hafnium compound **2** showed five resonances (see Experimental section). This might be rationalised on the basis of *cis* and *trans* isomers (where three resonances might be expected for the *cis* and two for the *trans*). The isostructural titanium analogue **3** displayed only two ^{29}Si NMR resonances[4] and thus probably adopts the *trans* configuration in solution.

Experimental

All manipulations were carried out in an atmosphere of purified nitrogen using standard Schlenk techniques. The chemicals $TiCl_4$, $ZrCl_4$, $HfCl_4$ and LiI (Aldrich) were used as supplied. Crystalline samples for elemental analyses were dried under vacuum (0.001 Torr, *ca.* 0.133 Pa) for several hours prior to submission. Spectrometers used were as follows: IR, Perkin-Elmer 1720X; NMR, Bruker WH80 and AMX600. Standard reference compounds used in NMR analysis were $SiMe_4$ (^{29}Si), LiCl in D_2O (^{7}Li) and NaCl in D_2O (^{23}Na).

Preparations

[$Ti\{O(SiPh_2O)_2\}_3\{Na(py)\}_2$]·py 1. A solution of [$(Ph_2SiONa)_2O$] [from sodium metal and $(Ph_2SiOH)_2O$] (7.24 mmol) in thf (30 cm^3) was added to a solution of $TiCl_4$ (2.41 cm^3 of a 1.0 mol dm^{-3} solution in toluene, 2.41 mmol) in benzene (20 cm^3) at 0 °C. After the mixture was stirred overnight at ambient temperature the volatiles were removed under vacuum and toluene (30 cm^3) was added to the white residue. The toluene-insoluble products were filtered off and the resulting clear, colourless solution was concentrated to 15 cm^3. Pyridine (3 cm^3) was added until the solution became turbid. On heating the solution became clear and colourless crystals (2.46 g, 68.5%), m.p. 183–185 °C, were deposited on cooling to room temperature (Found: C, 66.90; H, 5.05; N, 2.60. Calc. for $C_{87}H_{75}N_3Na_2O_9Si_6Ti$: C, 66.60; H, 4.80; N, 2.70%) IR (Nujol): 1592m, 1428s, 1309m, 1186m, 1121s, 1070s, 1054s, 1026s, 1010s, 997s, 926vs, 742m, 716s, 700vs, 679m, 631m,

Table 1 Selected bond lengths (Å) and angles (°) for compound **1**

Na(1)–O(4)	2.319(5)	Ti–O(4)	1.943(4)	Si(1)–O(3)	1.616(4)	Si(4)–O(8)	1.606(4)
Na(1)–O(8)	2.347(5)	Ti–O(3)	1.943(4)	Si(1)–O(1)	1.629(4)	Si(4)–O(6)	1.635(4)
Na(1)–N(1)	2.398(7)	Ti–O(5)	1.945(4)	Si(2)–O(2)	1.615(4)	Si(5)–O(4)	1.607(4)
Na(1)–O(3)	2.408(5)	Ti–O(2)	1.944(4)	Si(2)–O(1)	1.623(4)	Si(5)–O(9)	1.653(4)
Na(2)–O(5)	2.338(5)	Ti–O(7)	1.951(4)	Si(3)–O(7)	1.610(4)	Si(6)–O(5)	1.615(4)
Na(2)–N(2)	2.381(7)	Ti–O(8)	1.952(4)	Si(3)–O(6)	1.638(5)	Si(6)–O(9)	1.627(4)
Na(2)–O(2)	2.393(5)						
Na(2)–O(7)	2.444(5)						
O(4)–Na(1)–O(8)	70.3(2)	O(2)–Ti–O(7)	86.5(2)	O(7)–Si(3)–C(25)	110.2(2)	Si(2)–O(1)–Si(1)	131.4(3)
O(4)–Na(1)–N(1)	138.6(2)	O(4)–Ti–O(8)	87.2(2)	O(6)–Si(3)–C(25)	107.7(2)	Si(2)–O(2)–Ti	139.6(2)
O(8)–Na(1)–N(1)	137.7(3)	O(3)–Ti–O(8)	86.1(2)	C(31)–Si(3)–C(25)	107.9(2)	Si(2)–O(2)–Na(2)	118.8(2)
O(4)–Na(1)–O(3)	69.3(2)	O(5)–Ti–O(8)	175.6(2)	O(8)–Si(4)–O(6)	110.8(2)	Ti–O(2)–Na(2)	86.8(2)
O(8)–Na(1)–O(3)	68.0(2)	O(2)–Ti–O(8)	95.6(2)	O(8)–Si(4)–C(37)	108.7(2)	Si(1)–O(3)–Ti	136.6(2)
N(1)–Na(1)–O(3)	140.8(3)	O(7)–Ti–O(8)	89.6(2)	O(6)–Si(4)–C(37)	109.0(2)	Si(1)–O(3)–Na(1)	122.3(2)
O(5)–Na(2)–N(2)	135.6(2)	O(3)–Si(1)–O(1)	111.8(2)	O(8)–Si(4)–C(43)	111.2(2)	Ti–O(3)–Na(1)	85.1(2)
O(5)–Na(2)–O(2)	69.3(2)	O(3)–Si(1)–C(1)	111.5(2)	O(6)–Si(4)–C(43)	108.2(3)	Si(5)–O(4)–Ti	140.0(2)
N(2)–Na(2)–O(2)	146.0(2)	O(1)–Si(1)–C(1)	107.6(2)	C(37)–Si(4)–C(43)	108.9(2)	Si(5)–O(4)–Na(1)	122.6(2)
O(5)–Na(2)–O(7)	68.6(2)	O(3)–Si(1)–C(7)	110.8(2)	O(4)–Si(5)–O(9)	109.6(2)	Ti–O(4)–Na(1)	87.6(2)
N(2)–Na(2)–O(7)	136.6(2)	O(1)–Si(1)–C(7)	106.4(2)	O(4)–Si(5)–C(49)	111.4(2)	Si(6)–O(5)–Ti	138.4(2)
O(2)–Na(2)–O(7)	67.0(2)	C(1)–Si(1)–C(7)	108.6(2)	O(9)–Si(5)–C(49)	106.6(2)	Si(6)–O(5)–Na(2)	122.2(2)
O(4)–Ti–O(3)	87.5(2)	O(2)–Si(2)–O(1)	109.1(2)	O(4)–Si(5)–C(55)	110.3(2)	Ti–O(5)–Na(2)	88.3(2)
O(4)–Ti–O(5)	89.7(2)	O(2)–Si(2)–C(13)	109.1(2)	O(9)–Si(5)–C(55)	107.6(3)	Si(4)–O(6)–Si(3)	129.9(3)
O(3)–Ti–O(5)	96.9(2)	O(1)–Si(2)–C(13)	107.9(3)	C(49)–Si(5)–C(55)	111.2(3)	Si(3)–O(7)–Ti	138.1(3)
O(4)–Ti–O(2)	176.4(2)	O(2)–Si(2)–C(19)	111.1(2)	O(5)–Si(6)–O(9)	111.1(2)	Si(3)–O(7)–Na(2)	116.6(2)
O(3)–Ti–O(2)	90.4(2)	O(1)–Si(2)–C(19)	109.2(2)	O(5)–Si(6)–C(61)	111.9(2)	Ti–O(7)–Na(2)	85.2(2)
O(5)–Ti–O(2)	87.6(2)	C(13)–Si(2)–C(19)	110.3(2)	O(9)–Si(6)–C(61)	107.4(2)	Si(4)–O(8)–Ti	138.4(3)
O(4)–Ti–O(7)	95.8(2)	O(7)–Si(3)–O(6)	110.5(2)	O(5)–Si(6)–C(67)	109.2(2)	Si(4)–O(8)–Na(1)	122.1(2)
O(3)–Ti–O(7)	174.5(2)	O(7)–Si(3)–C(31)	112.7(2)	O(9)–Si(6)–C(67)	107.6(2)	Ti–O(8)–Na(1)	86.6(2)
O(5)–Ti–O(7)	87.6(2)	O(6)–Si(3)–C(31)	107.8(3)	C(61)–Si(6)–C(67)	109.6(2)	Si(6)–O(9)–Si(5)	129.7(3)

Table 2 Selected bond lengths (Å) and angles (°) for compound **2**

Hf–O(4$^{\mathrm{I}}$)	1.961(5)	Si(2)–O(2)	1.611(6)
Hf–O(4)	1.961(5)	Si(2)–O(3)	1.631(6)
Hf–O(1)	2.014(6)	Si(2)–C(19)	1.864(5)
Hf–O(1$^{\mathrm{I}}$)	2.014(6)	Si(2)–C(13)	1.870(6)
Hf–N(1)	2.383(7)	Si(3)–O(4)	1.606(5)
Hf–N(1$^{\mathrm{I}}$)	2.383(7)	Si(3)–O(3)	1.606(6)
Si(1)–O(1)	1.601(6)	Si(3)–C(25)	1.866(5)
Si(1)–O(2)	1.628(6)	Si(3)–C(31)	1.883(5)
Si(1)–C(1)	1.862(5)	N(1)–C(41)	1.323(12)
Si(1)–C(7)	1.875(5)	N(1)–C(37)	1.328(12)
O(4$^{\mathrm{I}}$)–Hf–O(4)	103.3(3)	C(1)–Si(1)–C(7)	110.4(3)
O(4$^{\mathrm{I}}$)–Hf–O(1)	95.2(3)	O(2)–Si(2)–O(3)	111.1(3)
O(4)–Hf–O(1)	94.6(2)	O(2)–Si(2)–C(19)	107.3(3)
O(4$^{\mathrm{I}}$)–Hf–O(1$^{\mathrm{I}}$)	94.6(2)	O(3)–Si(2)–C(19)	109.6(3)
O(4)–Hf–O(1$^{\mathrm{I}}$)	95.2(3)	O(2)–Si(2)–C(13)	110.3(3)
O(1)–Hf–O(1$^{\mathrm{I}}$)	164.2(3)	O(3)–Si(2)–C(13)	108.7(3)
O(4$^{\mathrm{I}}$)–Hf–N(1)	168.8(2)	C(19)–Si(2)–C(13)	109.8(3)
O(4)–Hf–N(1)	87.9(2)	O(4)–Si(3)–O(3)	111.5(3)
O(1)–Hf–N(1)	84.5(3)	O(4)–Si(3)–C(25)	109.3(3)
O(1$^{\mathrm{I}}$)–Hf–N(1)	83.5(2)	O(3)–Si(3)–C(25)	109.6(3)
O(4$^{\mathrm{I}}$)–Hf–N(1$^{\mathrm{I}}$)	87.9(2)	O(4)–Si(3)–C(31)	109.2(3)
O(4)–Hf–N(1$^{\mathrm{I}}$)	168.8(2)	O(3)–Si(3)–C(31)	109.1(3)
O(1)–Hf–N(1$^{\mathrm{I}}$)	83.5(2)	C(25)–Si(3)–C(31)	108.1(3)
O(1$^{\mathrm{I}}$)–Hf–N(1$^{\mathrm{I}}$)	84.5(3)	C(41)–N(1)–C(37)	116.6(9)
N(1)–Hf–N(1$^{\mathrm{I}}$)	80.9(3)	C(41)–N(1)–Hf	123.3(6)
O(1)–Si(1)–O(2)	110.9(3)	C(37)–N(1)–Hf	120.1(7)
O(1)–Si(1)–C(1)	109.8(3)	Si(1)–O(1)–Hf	148.8(4)
O(2)–Si(1)–C(1)	107.6(3)	Si(2)–O(2)–Si(1)	149.6(4)
O(1)–Si(1)–C(7)	111.1(3)	Si(3)–O(3)–Si(2)	156.6(4)
O(2)–Si(1)–C(7)	106.9(3)	Si(3)–O(4)–Hf	158.9(4)

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

615m, 554m, 526s, 507m, 490m, 445m, 400m, 345m, 310m, 227m and 215m cm^{-1}. NMR ($C_6D_5CD_3$): ^{23}Na, δ 9.32 (s) (300 K); ^{29}Si, δ −39.98 (s) (297 K).

[Hf{Ph$_2$Si(OSiPh$_2$O)$_2$}$_2$(py)$_2$]·2C$_6$H$_5$Me. A solution of [(Ph$_2$SiONa)$_2$O] (7.20 mmol) in thf (30 cm^3) was added to a slurry of $HfCl_4$ (0.77 g, 2.40 mmol) in thf (30 cm^3) at 0 °C. After stirring overnight, the volatiles were removed under vacuum and toluene (30 cm^3) was added to the white residue. The toluene-insoluble products were filtered off and the resulting clear, colourless solution was concentrated to around 15 cm^3. Pyridine (3 cm^3) was added until the solution became turbid. On heating the solution became clear and colourless crystals were deposited on cooling to room temperature (2.82 g, 71.2%), m.p. 125–129 °C (Found: C, 65.05; H, 4.90; N, 1.60. Calc. for $C_{96}H_{86}HfN_2O_8Si_6$: C, 66.15; H, 4.95; N, 1.60%). IR (Nujol): 1605m, 1590m, 1428s, 1307m, 1220m, 1157m, 1120s, 1055vs, 1026s, 1011s, 996s, 960vs, 802m, 741m, 716s, 697s, 677m, 632m, 537m, 525m, 500m, 488m, 425m, 401m, 385m, 315w, 283w and 221m cm^{-1}. ^{29}Si NMR ($C_6D_5CD_3$, 300 K): δ −26.8 (s), −45.7 (s), −49.4 (s), −50.0 (s) and −51.2 (s).

[Ti{O(SiPh$_2$O)$_2$}$_3$Li$_2$]·3py. A solution of LiI (0.24 g, 1.79 mmol) in thf (20 cm^3) was added dropwise at 0 °C to a solution of compound **1** (1.32 g, 0.89 mmol) in toluene (20 cm^3). After the solution was stirred overnight, all the volatiles were removed under vacuum and toluene (30 cm^3) was added to the white residue. The toluene-insoluble products were filtered off and the resultant pale yellow filtrate was concentrated to around 15 cm^3. Pyridine (2 cm^3) was added until the solution became turbid. This suspension was heated to give a clear solution and colourless crystals (0.68 g, 47.7%), m.p. 108 °C (decomp.), were deposited on cooling to room temperature (Found: C, 66.20; H, 4.85; N, 3.10. Calc. for $C_{87}H_{75}Li_2N_3O_9Si_6Ti$: C, 68.00; H, 4.90; N, 2.75%). IR (Nujol): 1593m, 1495m, 1214m, 1121s, 1068s, 1054s, 1036m, 999m, 927s, 743m, 716m, 699s, 625w, 555w, 532m, 506m, 491m, 464w, 444w, 399w, 345w, 311w and 227m cm^{-1}. NMR: ^{7}Li (CDCl$_3$), δ 3.08 (s) (297 K); ^{29}Si ($C_6D_5CD_3$), δ −42.0 (s) (300 K).

X-Ray crystallography

Data were recorded on crystals sealed in glass capillaries under nitrogen, with a CAD4 diffractometer operating in the ω–2θ scan mode. The structures were solved by standard heavy-atom

Table 3 Atomic coordinates (× 10^4) for compound **1**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Na(1)	4 042(2)	7 017(1)	181(1)	C(37)	4 083(3)	6 193(2)	1 386(2)
Na(2)	1 156(2)	8 428(1)	1 297(1)	C(38)	4 759(4)	6 617(2)	1 429(2)
Ti	2 582(1)	7 705(1)	729(1)	C(39)	5 699(4)	6 474(3)	1 512(2)
Si(1)	2 006(1)	7 438(1)	−570(1)	C(40)	5 963(3)	5 909(3)	1 552(2)
Si(2)	414(1)	7 599(1)	194(1)	C(41)	5 287(4)	5 485(2)	1 508(2)
Si(3)	2 198(1)	7 324(1)	2 028(1)	C(42)	4 347(4)	5 627(2)	1 425(2)
Si(4)	2 827(1)	6 417(1)	1 271(1)	C(43)	2 106(3)	5 775(2)	1 070(2)
Si(5)	4 720(1)	8 289(1)	774(1)	C(44)	1 664(4)	5 453(2)	1 471(2)
Si(6)	3 099(1)	9 081(1)	713(1)	C(45)	1 148(4)	4 976(2)	1 321(3)
O(1)	905(3)	7 469(2)	−394(2)	C(46)	1 075(4)	4 820(2)	769(3)
O(2)	1 221(3)	7 652(2)	664(2)	C(47)	1 517(4)	5 142(3)	368(2)
O(3)	2 700(3)	7 593(2)	−60(2)	C(48)	2 033(4)	5 619(2)	518(2)
O(4)	3 940(3)	7 796(2)	760(2)	C(49)	5 503(3)	8 228(2)	1 399(2)
O(5)	2 438(3)	8 524(2)	709(2)	C(50)	6 466(4)	8 328(2)	1 389(2)
O(6)	2 412(3)	6 668(2)	1 847(2)	C(51)	6 995(3)	8 297(3)	1 873(3)
O(7)	2 398(3)	7 749(2)	1 524(2)	C(52)	6 560(5)	8 165(3)	2 367(2)
O(8)	2 797(3)	6 891(2)	796(2)	C(53)	5 597(5)	8 065(2)	2 377(2)
O(9)	4 198(3)	8 913(2)	813(2)	C(54)	5 069(3)	8 096(2)	1 893(2)
C(1)	2 171(4)	7 932(2)	−1 159(2)	C(55)	5 424(4)	8 279(2)	122(2)
C(2)	1 441(3)	7 980(2)	−1 542(2)	C(56)	6 168(4)	7 903(2)	63(2)
C(3)	1 527(4)	8 345(3)	−1 988(2)	C(57)	6 669(3)	7 890(3)	−426(3)
C(4)	2 343(5)	8 661(2)	−2 052(2)	C(58)	6 426(4)	8 253(3)	−855(2)
C(5)	3 074(4)	8 612(2)	−1 670(3)	C(59)	5 682(5)	8 629(3)	−796(2)
C(6)	2 987(3)	8 248(2)	−1 223(2)	C(60)	5 181(4)	8 642(2)	−307(3)
C(7)	2 218(4)	6 692(2)	−816(2)	C(61)	3 021(3)	9 476(2)	49(2)
C(8)	3 128(3)	6 528(2)	−945(2)	C(62)	2 341(3)	9 318(2)	−337(2)
C(9)	3 303(4)	5 977(3)	−1 120(2)	C(63)	2 297(4)	9 588(3)	−846(2)
C(10)	2 568(5)	5 591(2)	−1 167(2)	C(64)	2 934(5)	10 015(3)	−969(2)
C(11)	1 658(4)	5 756(2)	−1 038(2)	C(65)	3 614(4)	10 173(2)	−583(3)
C(12)	1 483(3)	6 306(2)	−863(2)	C(66)	3 658(3)	9 904(2)	−74(2)
C(13)	−222(3)	8 289(2)	134(2)	C(67)	2 741(3)	9 557(2)	1 293(2)
C(14)	−820(4)	8 468(2)	548(2)	C(68)	2 713(4)	9 332(2)	1 822(2)
C(15)	−1 251(4)	8 996(3)	512(3)	C(69)	2 426(4)	9 667(3)	2 260(2)
C(16)	−1 084(4)	9 344(2)	62(3)	C(70)	2 167(4)	10 227(3)	2 169(2)
C(17)	−486(5)	9 165(2)	−353(2)	C(71)	2 195(4)	10 453(2)	1 640(3)
C(18)	−55(4)	8 637(3)	−317(2)	C(72)	2 482(4)	10 117(2)	1 202(2)
C(19)	−430(3)	7 014(2)	357(2)	N(1)	5 235(5)	6 448(3)	−237(3)
C(20)	−74(3)	6 498(2)	538(2)	C(73)	5 441(7)	5 963(4)	0(5)
C(21)	−683(5)	6 058(2)	667(2)	C(74)	6 084(10)	5 582(6)	−242(8)
C(22)	−1 650(4)	6 135(2)	615(2)	C(75)	6 467(9)	5 721(7)	−734(7)
C(23)	−2 006(3)	6 652(3)	434(3)	C(76)	6 264(8)	6 222(7)	−978(6)
C(24)	−1 396(4)	7 091(2)	305(2)	C(77)	5 649(8)	6 570(6)	−709(5)
C(25)	918(2)	7 367(2)	2 235(2)	N(2)	167(5)	9 060(3)	1 790(3)
C(26)	661(3)	7 462(2)	2 778(2)	C(78)	−395(8)	8 874(5)	2 159(4)
C(27)	−284(4)	7 475(2)	2 919(2)	C(79)	−1 066(13)	9 220(8)	2 414(7)
C(28)	−972(2)	7 395(2)	2 515(3)	C(80)	−1 120(11)	9 739(11)	2 249(8)
C(29)	−716(3)	7 300(2)	1 972(2)	C(81)	−535(13)	9 970(7)	1 919(8)
C(30)	229(3)	7 287(2)	1 832(2)	C(82)	115(8)	9 599(5)	1 647(5)
C(31)	2 939(3)	7 485(2)	2 654(2)	N(3)	−180(9)	4 763(9)	7 095(5)
C(32)	3 384(4)	7 042(2)	2 929(3)	C(83)	12(11)	4 289(7)	7 451(8)
C(33)	3 864(4)	7 143(3)	3 421(2)	C(84)	726(12)	4 296(6)	7 819(6)
C(34)	3 899(4)	7 688(4)	3 638(2)	C(85)	1 246(11)	4 754(8)	7 859(7)
C(35)	3 454(4)	8 131(3)	3 363(3)	C(86)	1 122(12)	5 207(7)	7 584(8)
C(36)	2 974(4)	8 030(2)	2 871(2)	C(87)	414(14)	5 226(7)	7 218(8)

techniques and refined by least-squares (on F^2) using SHELXL 93,[14] with phenyl groups treated as rigid hexagons [C–C 1.395 Å, C–C–C 120°, with inclusion of hydrogen atoms at fixed positions (C–H 0.96 Å)]. Data were corrected for absorption using an empirical method (ψ-scans), with $T_{min} = 89.41$, $T_{max} = 99.66$ for **1** and $T_{min} = 92.54$, $T_{max} = 99.84$ for **2**.

Crystal data for compound 1. $C_{87}H_{75}N_3Na_2O_9Si_6Ti$, $M = 1568.92$, monoclinic, $a = 14.2190(10)$, $b = 23.6010(10)$, $c = 24.2690(10)$ Å, $\beta = 90.610(10)°$, $U = 8143.8(7)$ Å^3, $Z = 4$, space group $P2_1/n$, $D_c = 1.280$ Mg m^{-3}, crystal size = 0.22 × 0.25 × 0.26 mm, λ(Mo-Kα) = 0.710 69 Å, $\mu = 0.263$ mm^{-1}, $F(000) = 3272$.

A total of 15335 reflections were measured of which 14291 were independent. Final $R1 = 0.0800$, $wR2 = 0.1603$ [$I > 2\sigma(I)$] and $R1 = 0.2524$, $wR2 = 0.2160$ (all data) for 901 parameters $\{w = 1/[\sigma^2(F_o^2) + (0.1347P)^2$, $P = (F_o^2 + 2F_c^2)/3\}$.

Crystal data for compound 2. $C_{96}H_{86}HfN_2O_8Si_6$, $M = 1742.70$, monoclinic, $a = 27.334(2)$, $b = 17.278(2)$, $c = 19.451(2)$ Å, $\beta = 107.47(5)°$, $U = 8763(2)$ Å^3, $Z = 4$, space group $A2/n$ (no. 15), $D_c = 1.321$ Mg m^{-3}, crystal size = 0.18 × 0.15 × 0.22 mm, λ(Mo-Kα) = 0.710 69 Å, $\mu = 0.1329$ mm^{-1}, $F(000) = 3584$.

A total of 6421 reflections were measured of which 6081 were independent. Final $R1 = 0.0638$, $wR2 = 0.1696$ [$I > 2\sigma(I)$] and $R1 = 0.1094$, $wR2 = 0.1928$ (all data) for 431 parameters. $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{\frac{1}{2}}$ $\{w = 1/[\sigma^2(F_o)^2 + (0.0772P)^2]\}$.

Table 4 Atomic coordinates ($\times 10^4$) for compound **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Hf	2500	6183(1)	2500	C(21)	1330(3)	4604(5)	−961(4)
Si(1)	1167(1)	6198(2)	2056(1)	C(22)	1010(4)	4000(4)	−897(4)
Si(2)	1051(1)	6261(2)	408(1)	C(23)	711(3)	4071(4)	−435(4)
Si(3)	2099(1)	7191(1)	861(1)	C(24)	732(3)	4745(4)	−37(4)
N(1)	2356(3)	5134(4)	1668(4)	C(25)	1978(3)	8253(3)	875(4)
O(1)	1760(2)	6022(3)	2449(3)	C(26)	1547(3)	8591(4)	400(4)
O(2)	1021(2)	6024(4)	1195(3)	C(27)	1472(4)	9385(5)	418(5)
O(3)	1572(2)	6751(3)	466(3)	C(28)	1829(4)	9842(3)	911(6)
O(4)	2345(2)	6887(3)	1672(3)	C(29)	2260(4)	9504(4)	1387(5)
C(1)	760(2)	5562(4)	2430(3)	C(30)	2335(3)	8710(4)	1369(4)
C(2)	356(3)	5132(5)	1992(3)	C(31)	2569(2)	7025(3)	338(3)
C(3)	71(3)	4651(5)	2299(5)	C(32)	3091(2)	7053(4)	698(3)
C(4)	190(3)	4600(5)	3045(5)	C(33)	3443(2)	7003(4)	312(4)
C(5)	594(3)	5030(6)	3483(3)	C(34)	3273(3)	6924(4)	−433(4)
C(6)	879(3)	5511(5)	3176(3)	C(35)	2751(3)	6896(4)	−793(3)
C(7)	1013(2)	7242(3)	2155(4)	C(36)	2398(2)	6946(4)	−407(3)
C(8)	503(2)	7453(4)	2038(4)	C(37)	2636(5)	5068(6)	1219(5)
C(9)	370(2)	8231(5)	2018(5)	C(38)	2558(6)	4511(7)	708(6)
C(10)	746(3)	8798(3)	2116(5)	C(39)	2198(5)	3969(6)	666(6)
C(11)	1255(3)	8586(3)	2233(4)	C(40)	1897(5)	3998(6)	1112(6)
C(12)	1389(2)	7809(4)	2253(4)	C(41)	1995(4)	4606(5)	1611(5)
C(13)	484(2)	6865(4)	−74(3)	C(42)	1698(5)	7157(15)	−2514(6)
C(14)	141(3)	6601(4)	−713(4)	C(43)	1717(6)	7929(13)	−2307(8)
C(15)	−274(3)	7057(6)	−1079(4)	C(44)	1389(7)	8199(9)	−1936(9)
C(16)	−347(3)	7776(6)	−806(5)	C(45)	1042(5)	7698(12)	−1773(7)
C(17)	−4(4)	8040(4)	−167(5)	C(46)	1023(5)	6926(11)	−1981(7)
C(18)	411(3)	7585(4)	199(4)	C(47)	1351(6)	6656(10)	−2351(7)
C(19)	1051(2)	5348(3)	−102(3)	C(48)	1404(21)	6071(29)	−2461(28)
C(20)	1351(3)	5278(4)	−564(4)				

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Acknowledgements

We thank the EPSRC for an ear-marked studentship (to M. L.), EPSRC and SHELL Research Ltd. for a Quota/CASE award (to S. A. A. S.) and Mr. Peter Haycock of the University of London Intercollegeate Research Service for ^{29}Si, ^{23}Na and ^{7}Li NMR spectra.

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Received 23*rd October* 1995; *Paper* 5/06958K