DALTON
FULL PAPER

Tris(triorganosilyl)methyl derivatives of potassium and lithium bearing dimethylamino or methoxy substituents at silicon. Crystal structures of $KC(SiMe_3)_2(SiMe_2NMe_2)$, $KC(SiMe_2NMe_2)_3$ and $[LiC(SiMe_3)(SiMe_2OMe)_2]_2$

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The compounds $HC(SiMe_3)(SiMe_2X)_2$, X = NMe_2 or OMe, have been synthesized in several steps from the phenyl derivative $HC(SiMe_3)(SiMe_2Ph)_2$ and metallated to give organometallic compounds of the type $MC(SiMe_3)(SiMe_2X)_2$, M = K or Li. The structures of the compounds $KC(SiMe_3)_2(SiMe_2NMe_2)$ and $KC(SiMe_2NMe_2)_3$ consist of infinite chains in which cations are co-ordinated to both nitrogen and carbon centres, whereas the lithium compound $[LiC(SiMe_3)(SiMe_2OMe)_2]_2$ crystallises in a lattice of dimeric cage molecules. Structural trends in the series $MC(SiMe_3)_n(SiMe_2X)_{3-n}$, n = 0–3, M = K or Li, X = NMe_2 or OMe, are discussed.

The tris(triorganosilyl)methyl derivatives of the metals of Groups 1, 2 and 3 show a remarkable range of structural types, which include monomeric and dimeric molecular species, ate complexes, and ionic compounds containing discrete carbanions with planar CSi_3 skeletons.[1] In these structures the cations interact with (a) negative charge localised on the bulky carbanion, (b) lone pairs on solvent molecules or on substituents within the organosilicon ligand, or (c) π systems, which may also be in ligand substituents or solvent species. The diversity of structures shows that the balance between these interactions is sometimes a subtle one. For example, although the compounds KR **1**[2] and RbR[3] [R = $C(SiMe_3)_3$] crystallise from solutions containing donors such as Et_2O or thf (tetrahydrofuran) without incorporation of solvent, compound **1** is obtained as an adduct $KC(SiMe_3)_3$·tmen from solutions containing *N,N,N′,N′*-tetramethylethane-1,2-diamine (tmen).[4]

In order to throw light on the relative affinities of alkali metal cations for carbanionic centres and lone pairs in more detail we have synthesized a number of compounds in which the ligands have bulk similar to that of the $C(SiMe_3)_3$ group but contain donor substituents at silicon. We have previously described organometallic compounds containing the ligands $C(SiMe_3)_2(SiMe_2NMe_2)$,[5] $C(SiMe_2NMe_2)_3$,[6–8] $C(SiMe_3)_2(SiMe_2OMe)$[9–14] and $C(SiMe_2OMe)_3$.[15] In this paper we report a synthetic route to derivatives of the ligands $C(SiMe_3)(SiMe_2NMe_2)_2$ and $C(SiMe_3)(SiMe_2OMe)_2$, and note the remarkably elegant pattern of structural changes as the Me groups are replaced by X in two series of derivatives, the potassium compounds **1**–**4** of the general type $KC(SiMe_3)_n(SiMe_2NMe_2)_{3-n}$ (n = 0–3) and the lithium compounds $LiC(SiMe_3)_n(SiMe_2OMe)_{3-n}$ **5**–**8**. The structure of the solvent-free compound **5** was described previously by Uhl and co-workers.[16] The isolation and some reactions of $LiC(SiMe_3)(SiMe_2NMe_2)_2$ are also described, but crystals suitable for an X-ray study have not yet been obtained.

Results and discussion

Ligand precursors

In previous work on the syntheses of mono-substituted compounds $LiC(SiMe_3)_2(SiMe_2X)$, with X = OMe **6** or NMe_2 **9**, we began from halide precursors $YC(SiMe_3)_2(SiMe_2X)$, Y = Cl, Br or I. The analogous disubstituted halides $YC(SiMe_3)(SiMe_2X)_2$ were not readily available so we explored the possibility of synthesizing organometallic compounds from the silicon-substituted methanes $HC(SiMe_3)(SiMe_2X)_2$ **III**, X = NMe_2, and **IV**, X = OMe. These ligand precursors were obtained from readily available starting materials by the reaction sequences in Scheme 1.

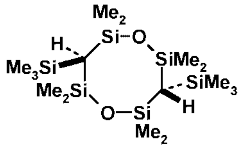
$$HCBr_3 \xrightarrow{(i)} HCBr(SiMe_2Ph)_2 \xrightarrow{(ii)} \underset{\mathbf{I}}{HC(SiMe_3)(SiMe_2Ph)_2} \xrightarrow{(iii)}$$

$$\underset{\mathbf{II}}{HC(SiMe_3)(SiMe_2Br)_2} \xrightarrow{(iv)} \underset{\mathbf{III},\ X = NMe_2,\ \mathbf{IV},\ X = OMe}{HC(SiMe_3)(SiMe_2X)_2}$$

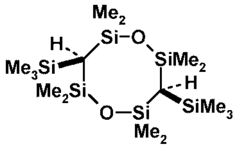
Scheme 1 (i) $2LiBu/2Me_2PhSiCl$ (Yield 80%), (ii) $LiBu/Me_3SiCl$ (95%), (iii) Br_2/Al, (iv) NMe_2H (X = NMe_2) or $MeOH/Et_3N$ (X = OMe) (85%).

Overall yields of 60–65% were readily obtained in the conversion of $HCBr_3$ into **III** or **IV**. Steps (i) and (ii) have been described previously.[4] Complete reaction in the conversion of **I** into **II** was achieved within 3 h when an excess of bromine (Br_2/**I** *ca.* 2.4) was used. Some of the excess reacted with the bromobenzene formed by cleavage of the Si–Ph bonds to give *p*-dibromobenzene, which could be removed by fractional sublimation after the conversion of the crude dibromide **II** into **III** or **IV**.

The dibromide **II** was isolated as a white, moisture-sensitive solid, melting just below room temperature. It was shown by GC-MS that slow hydrolysis in hydrocarbon solution gave two compounds, formed in the ratio 3 : 1, with almost identical mass spectra and judged to be *cis* and *trans* isomers **Va** and **Vb**.



Va



Vb

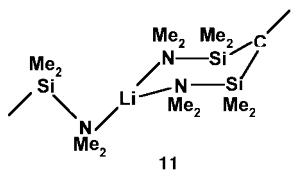
Treatment of the dibromide with methanol gave the desired product **IV** along with a mixture of the cyclic compounds **Va** and **Vb**, even when water was rigorously excluded. It seems that under the reaction conditions methanol reacts with the HBr liberated by methanolysis to give MeBr and water, and that the water then reacts with the dibromide to give the compounds **Va**, **Vb** and more HBr. In accord with this suggestion, when Et_3N was added to the solution of the dibromide before the slow addition of methanol the HBr was removed as triethylammonium bromide and the hydrolysis of **II** to give **V** was suppressed. Dimethylamino groups were introduced in the same way to give compound **III**; in this case the amine served both as a nucleophile and as a base to remove the HBr generated in the aminolysis.

Compounds **III** and **IV** were characterised by multinuclear NMR and mass spectroscopy. In keeping with Bent's rule, the replacement of a methyl substituent at Si by a more electronegative group increases the coupling constants $^1J_{CSi}$ at the remaining bonds to silicon. Replacement of Me by NMe_2 increases the coupling constants by *ca.* 5 Hz and replacement by OMe increases the coupling constants by *ca.* 10 Hz.

The reaction of the dibromide **II** in light petroleum containing triethylamine with water gave a colourless oil which appeared from its mass and NMR spectra to be one of the isomers **Va** or **Vb**, probably formed from the intermediate $HC(SiMe_3)(SiMe_2Br)(SiMe_2OH)$, but complete characterisation was not attempted.

The compound $LiC(SiMe_3)(SiMe_2NMe_2)_2$ 10

The reaction between butyllithium and compound **III** proceeded much faster than the corresponding reactions with $HC(SiMe_3)_2(SiMe_2X)$ or $HC(SiMe_3)(SiMe_2X)_2$ (X = Me or Ph,[4,17]) suggesting that it is facilitated by initial co-ordination of NMe_2 to lithium. A similar acceleration of metallation was noticed in the synthesis of $LiC(SiMe_2NMe_2)_3$ **11**.[6] The product $LiC(SiMe_3)(SiMe_2NMe_2)_2$ **10** separated from toluene as poorly formed crystals that were unsuitable for an X-ray study and did not dissolve in benzene itself but did so when thf was added. These observations suggest that the solid is polymeric, like that of the trisubstituted compound **11** and that intermolecular Li···N interactions are broken by addition of thf. The NMR spectroscopic data given in the Experimental section are thus those for the thf complex of **10**.



11

The use of compound **10** as a ligand transfer reagent was demonstrated by the reaction with $SnMe_3Cl$. Multinuclear NMR data suggested that the products were a mixture of the tin compound $Me_3SnC(SiMe_3)(SiMe_2NMe_2)_2$ **12** (80%) and the ligand precursor **III** (20%), but attempts to separate these compounds by fractional crystallisation or sublimation were not successful. Ligand transfer was observed also in reactions with $MgBr_2(thf)_2$ or $LiAlH_4$, but again the organomagnesium or -aluminium products could not be separated from **III**.

The compounds $MC(SiMe_3)(SiMe_2OMe)_2$, M = Li or K

The compound $HC(SiMe_3)(SiMe_2OMe)_2$ **IV** reacted with methyllithium at 0 °C to give a complex mixture that, after aqueous work-up, was found by GC-MS to contain $HC(SiMe_3)_2(SiMe_2OMe)$, indicating that the LiMe had attacked Si–OMe as well as C–H bonds, eqn. (1). This was not surprising

$$\underset{\mathbf{IV}}{HC(SiMe_3)(SiMe_2OMe)_2} + LiMe \longrightarrow LiOMe + \underset{\mathbf{VI}}{HC(SiMe_3)_2(SiMe_2OMe)} \quad (1)$$

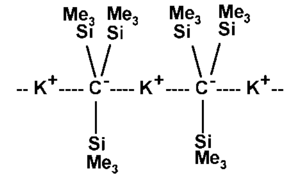
in view of our previous observation[13] that although in one experiment we obtained the chloride $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2Cl)$ by treatment of $HC(SiMe_3)_2(SiMe_2OMe)$ **VI**, with methyllithium followed by $SiMe_2Cl_2$ the result was not reproducible. Attempts to repeat the preparation gave $(Me_3Si)_3CSiMe_2Cl$ showing that the LiMe had attacked the Si–OMe bond. (We have exploited this type of reaction by using $SiMe_3OMe$ or $SiMe_3OEt$ to remove traces of LiMe from $LiC(SiMe_3)_3$, made by metallation of $HC(SiMe_3)_3$.[17]) We therefore turned to $LiNPr^i_2$ (LDA) as an alternative metallating agent.[18] The reaction between **IV** and LDA proceeded smoothly at −60 °C and the lithium compound $LiC(SiMe_3)(SiMe_2OMe)_2$ **7** was isolated in good yield. Its crystal stucture is discussed below. A full study of the potential of the reagent **7** as a ligand transfer reagent has not yet been made, but reactions with $SnCl_2$ and $LiAlH_4$ gave the compounds $SnCl\{C(SiMe_3)(SiMe_2OMe)_2\}$ and $LiAlH_3\{C(SiMe_3)(SiMe_2OMe)_2\}\cdot$thf, respectively. Crystals of these compounds suitable for X-ray diffraction studies have not so far been obtained but measurement of the $^6Li\text{-}\{^1H\}$ nuclear Overhauser effect[19] for the latter shows the presence in solution of Li···H–Al interactions like those observed in the related compound $Li(thf)AlH_3\{C(SiMe_3)_2(SiMe_2OMe)\}$.[20]

The compound **IV** was also metallated by methylpotassium. The reaction was rapid even at −40 °C, but it was not possible to isolate a pure sample of the extremely air- and moisture-sensitive organopotassium compound $KC(SiMe_3)(SiMe_2OMe)_2$. Its formation was however demonstrated by addition of $HgBr_2$ in Et_2O. A white precipitate of KBr was formed immediately and the mercury derivative $HgBr\{C(SiMe_3)(SiMe_2OMe)_2\}$ **13** was extracted into toluene and isolated as colourless crystals.

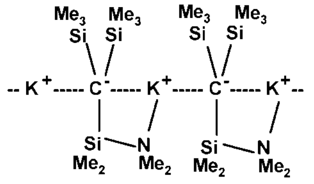
The ^1H and ^{13}C NMR spectra of the precursors **III** and **IV** and the organometallic compounds of tin, *e.g.* **12**, mercury, *e.g.* **13**, and aluminium, *e.g.* $LiAlH_3\{C(SiMe_3)(SiMe_2OMe)_2\}\cdot$thf, show separate resonances for two diastereotopical positions in the $SiMe_2$ fragments. In contrast, the alkyllithium compounds **7** and **10** show only one sharp peak indicating that the methyl groups exchange positions rapidly on the NMR timescale. We previously attributed the similar exchange in the compounds $MC(SiMe_3)(SiMe_2Ph)_2$, M = Li, Na or K, to inversion at the carbon centre; transfer of charge from the alkali metal makes it more planar relative to halide or hydride precursor, and lowers the inversion energy barrier.[4]

Structures of $KC(SiMe_3)_n(SiMe_2NMe_2)_{3-n}$, n = 0–3

The structures of compounds **2** and **4** are shown in Figs. 1 and 2. The three compounds **1**,[2] **2**, and **4** form chains of alternate cations and anions with planar CSi_3 skeletons (sum of angles 360.0, 360.0, 359.3°, respectively).



1



2

The C1···K···C1′ angles are 178.5(3)° in **1** and 175.67(4)° in **2**, and the corresponding K···C1···K′ angles are 179.2(3) and 174.26(4)°. In both cases therefore the CKCK axis is almost linear. The chains in **4** are more puckered, with C1···K···C1′ 166° and K···C1···K′ 134°. In all cases the chains are

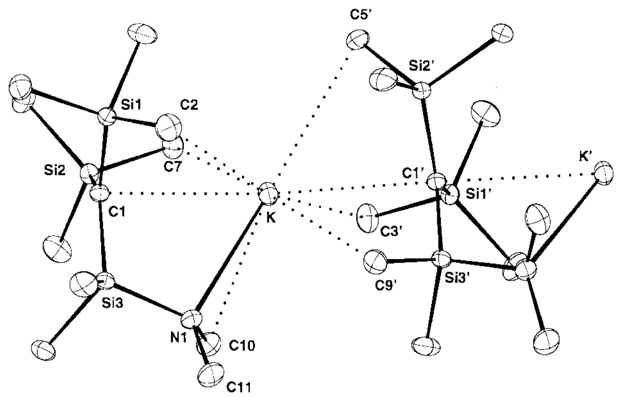


Fig. 1 The structure of $KC(SiMe_3)_2(SiMe_2NMe_2)$ **2**.

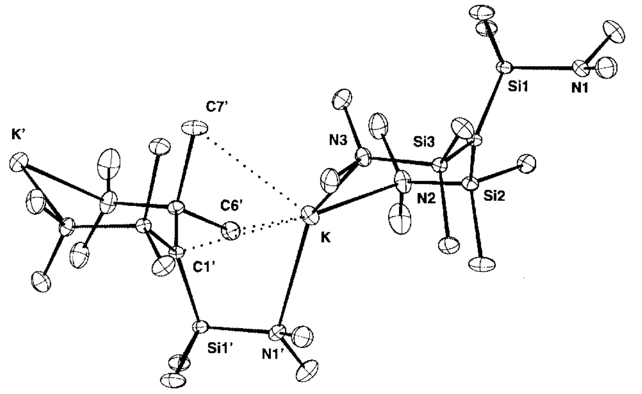


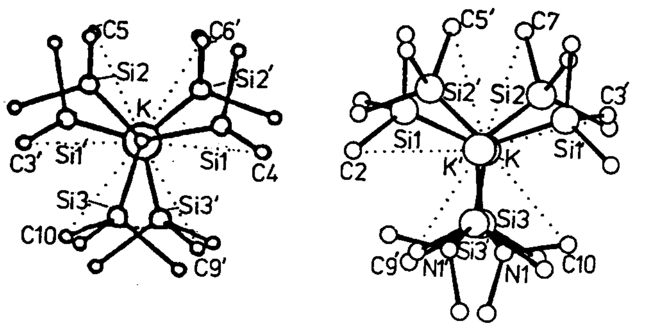
Fig. 2 The structure of $KC(SiMe_2NMe_2)_3$ **4**.

arranged so that the potassium ions in one chain lie alongside carbanion centres in the neighbouring chains. This arrangement provides interchain electrostatic attraction which is balanced by repulsions between methyl groups at the anion periphery.

In all three compounds the inner C–Si bonds are exceptionally short, indicating that the carbanionic charge is delocalised over the CSi_3 core. In contrast, the outer Si–Me bond lengths are only slightly longer than that, 1.875 Å, found in $SiMe_4$.[21] The potassium cations interact with the $[CSi_3]^-$ core but K···Me are only a little longer than K···C1 distances.

As Me groups on the periphery of the anions are successively replaced by NMe_2 groups the interaction between the potassium and the two neighbouring carbanionic centres weakens and becomes more unsymmetrical [K···C1 and K···C1′ distances 3.090(11) and 3.104(11) Å in **1**, 3.1870(10) and 3.2041(13) Å in **2**, 3.222(6) and 4.25 Å in **4**] and the K–N interactions become stronger [2.8484(12) in **2**, 2.812(5), 2.821(6) and 2.823(5) Å in **4**]. The K–N bond lengths are similar to those in related compounds.[22,23] The number of short (<3.5 Å) K···Me contacts decreases from six in **1** and **2** to two in **4**.

One of the short K···Me contacts in compound **2** is between the K atom and C10 of the NMe_2 group; indeed the K···C10 distance (3.1126(17) Å) is 0.7 Å shorter than the K···C1 distance (3.1870(10) Å). The short K···Me contact results in a K–N–C10 angle of 86.14(8)° and makes the K–N–C11 angle 128.00(10)°. A search of the Cambridge Crystallographic Data Base suggests that K···Me distances in, for example, *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (pmdta) complexes are usually 3.6–3.8 Å, with the methyl groups attached to nitrogen pointing away from potassium. One exception which shows some similarity to **2** is $[K(pmdta)(CPh_3)]$, in which there are K···C contacts of 3.276(3), 3.220(3) and 3.128(3) Å to Me_2N groups, and corresponding K–N–C angles of 92, 87 and 88°.[24] In this case and in **2** the K atom appears (from bond distances) to interact in quasi-η^2 fashion with nitrogen and methyl within the same NMe_2 group.



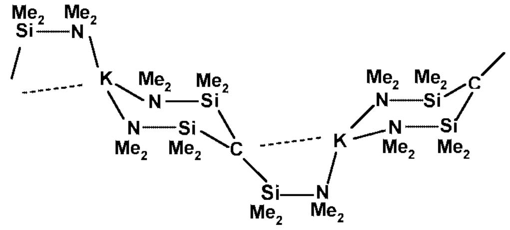
1 **2**

Fig. 3 Views across and along the chains in the structures of compounds **1**[2] and **2**.

(Attention has recently been drawn to the similar η^2 interaction between the metal and the ethyl group in $TiEtCl_3$.[25]) The short K···C(10) contact in **2** is associated with a large Si2–C–Si3 angle; a similar distortion of the CSi_3 system giving unequal Si–C–Si angles was observed in $RbC(SiMe_3)_3$.[3] However, our X-ray data are insufficiently precise to reveal distortions within methyl groups due to agostic interactions between the metal and hydrogen atoms or C–H bonds, so it is not clear whether the short K···C distances in compounds **1**, **2** and **4** indicate weak K···Me attraction or simply reflect the compromise between $K^+\cdots CSi_3^-$ attraction and Me···Me repulsion. Short K···Me distances have also been noted in a number of similar compounds,[1c] for example tris(trimethylsilyl)silyl,[26a] diisopropyl-[26b] and bis(trimethylsilyl)-amido[26c] derivatives and the nature of analogous Li···Me interactions in organometallic compounds and amides has been studied in considerable detail by several research groups.[27]

The effect of Me···Me repulsion shows also in the configuration of $SiMe_3$ or $SiMe_2X$ groups (X = NMe_2 or Ph) about the central CMC axis. These are staggered in isolated sodate[28a] or potassate[28b] ions but almost eclipsed in compound **1** (Fig. 3), in which the presence of a potassium ion on either side of the CSi_3 system results in rotation of $SiMe_3$ groups so that methyl groups interlock; *e.g.* C5 lies between C3′ and C6′. Similar considerations apply in **2**, in which the NMe_2-bearing silyl groups are also eclipsed.

The co-ordination on the right side of the potassium in compound **2** (see Fig. 1) resembles that in **1**; on the left side however there is a chelate ring but with a much longer M–C bond than those found in the compounds $\overline{ML_nC(SiMe_3)_2(SiMe_2N}Me_2)$, $ML_n = Li(thf)_2$, $AlCl_2$, $AlPh_2$ or $GaCl_2$.[5] A similar ring appears in **4** (compare the co-ordination on the left side of Figs. 1 and 2) but the two additional NMe_2 groups co-ordinate to potassium to give a six-membered ring in a chair conformation like that in the structure of $LiC(SiMe_2NMe_2)_3$ **11**.[6] In the latter the co-ordination round the lithium is planar and the configuration at the bridging $SiMe_2$ group is such that there are no close contacts between the lithium and either the central carbon or methyl groups at the anion periphery.



4

In the potassium analogue **4** the metal is larger and more polarisable, so that there is room for additional contacts both with the central carbon and with methyl groups attached to the

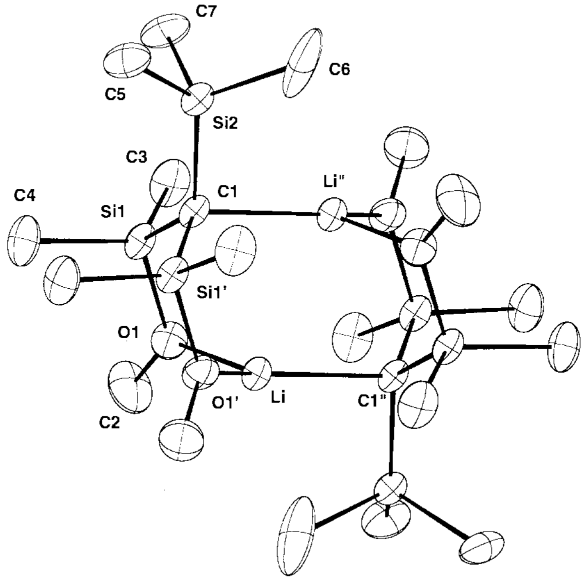
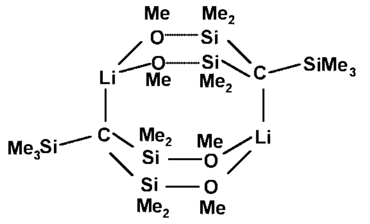


Fig. 4 The structure of $LiC(SiMe_3)(SiMe_2OMe)_2$ **7**.

Table 1 Bond lengths (Å) and angles (°) in $KC(SiMe_3)_2(SiMe_2NMe_2)$ **2**, $KC(SiMe_2NMe_2)_3$ **4**, and $LiC(SiMe_3)(SiMe_2OMe)_2$ **7**

2			
K–N	2.8484(12)	Si–C1	1.8181(12)[a]
Si3–N1	1.7982(12)	Si–Me	1.8920(14)[a]
K···C1	3.1870(12)	K···C7	3.2932(14)
K···C2	3.49	K···C9′	3.4036(16)
K···C3′	3.44	K···C10	3.1126(17)
K···C5′	3.43	K···C1′	3.2041(13)
Si1–C1–Si2	116.52(5)	C1–Si3–N1	112.85(5)
Si1–C1–Si3	117.80(6)	Si3–N–K	98.63(4)
Si2–C1–Si3	125.66(7)	Me–Si–Me	103.33(8)[a]
C10–N1–C11	109.18(13)		
4			
K–N1′	2.821(6)	K–N2	2.823(5)
K–N3	2.812(5)	Si–N	1.784(5)[a]
Si1–C1	1.823(5)	Si2–C1	1.815(5)
Si3–C1	1.805(6)	Si–Me	1.895(7)[a]
K···C6′	3.34	K···C1	4.25
K···C1′	3.222(6)	K···C7′	3.54
N1′–K–N2	116.5(2)	C1–Si1–N1	111.7(2)
N1′–K–N3	127.3(2)	C1–Si2–N2	115.7(3)
N3–K–N2	89.3(2)	C1–Si3–N3	112.8(2)
Si1–C1–Si2	117.0(3)	Si1′–N1′–K	101.7(2)
Si1–C1–Si3	122.9(3)	Si2–N2–K	112.2(2)
Si2–C1–Si3	119.4(3)	Si3–N3–K	114.4(2)
7			
Li–O	1.912(6)	L1–C1″	2.256(9)
Si1–O1	1.683(3)	Si1–C1	1.808(3)
Si1–C3	1.863(4)	Si1–C4	1.877(4)
Si2–C1	1.832(5)	Si2–Me	1.869(10)[a]
O1–C2	1.413(5)		
O1′–Li–O1	101.2(4)	O1–Li–C1″	128.3(2)
Li–O1–Si1	110.6(3)	Li–C1–Si1	109.0(2)
Si1–C1–Si1′	115.6(3)	C1–Si–O1	105.4(2)
O1–Si1–C3	104.2(2)	Si1–O1–Li	110.6(3)
Si1–C1–Si2	114.5(2)	Si2–C1–Li	91.1(3)
O1–Si1–C4	106.7(2)	C–Si2–C[a]	104.2(6)
C3–Si1–C4	106.5(2)	C1–Si2–C[a]	114.3(5)
C1–Si1–C3	115.7(2)	C2–O1–Si1	120.6(3)
C1–Si1–C4	117.4(2)	C2–O1–Li	128.8(3)

[a] Mean value with e.s.d.s of individual measurements in parentheses.



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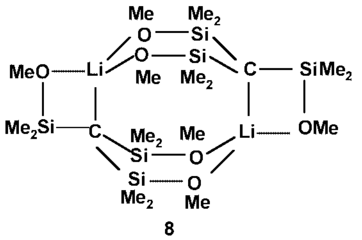

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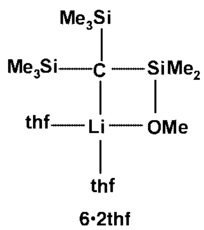

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neighbouring silicon atoms. The K–N bonds lie on one side of the potassium and the configuration at the bridging $SiMe_2$ group, in contrast to that in **11**, brings the adjacent CSi_3^- centre near to the potassium to give close contacts to C1′, C6′ and C7′ (Fig. 2). The structural data for compounds **1**, **2** and **4** show that although potassium bonds preferentially to nitrogen rather than to carbon (*cf.* $KCPh_3$ and $KCPh_2C_5H_4N$[21]), supplementary K···Me contacts are important in determining the detailed geometry.

The structure of $LiC(SiMe_3)(SiMe_2OMe)_2$ 7

The structure of compound **7** is shown in Fig. 4 and bond lengths and angles are given in Table 1. Two $LiC(SiMe_3)(SiMe_2OMe)_2$ units are joined into a cage with a core having 2/*m* symmetry, like that in **8**. The $Si(2)Me_3$ groups are disordered across the mirror plane so that the Si–Me bond lengths have higher estimated standard deviations (e.s.ds) than those in the rest of the molecule. Nevertheless the mean Si–Me distance (1.869 Å) in the $SiMe_3$ groups is not significantly different from that in the molecule as a whole or from that in **8** (1.867 Å). The Li–O bond length, 1.912(6) Å, is at the lower end of the range found in organometallic compounds.[29] In contrast the Li–C″ bonds, 2.256(9) Å, are long; *cf.* 2.291(6) Å in the electron deficient dimer $[LiC(SiMe_3)_3]_2$[16] and 2.12(2) in $LiC(SiMe_2Ph)_3$·thf.[30] The dimers can thus be regarded as comprising two $LiC(SiMe_3)(SiMe_2OMe)_2$ units held by strong co-ordination between two methoxy groups of one monomer and the lithium of the other.

In the series of compounds **6**–**8** direct comparison of bond lengths and angles can be made only between **7** and **8**, which have similar structures. Co-ordination of an extra OMe group in **8** results in a shorter mean Si–C1 distance (1.805 Å *cf.* 1.816 Å in **7**), a more planar configuration at C1 (mean Si–C–Si 117.1°, *cf.* 115.2 in **7**) and a significantly longer Li–C1 bond (2.401(9) Å, *cf.* 2.256(9) Å in **7**). All these changes suggest that increased co-ordination of lithium by oxygen leads to increased transfer of electronic charge to the carbon centre. Compound **6** has been isolated only as an adduct in which the lithium is made more basic by co-ordination with thf: this makes the mean Si–C1 bond [1.806 Å in **6**·2thf] shorter than that in **7**, and the mean Si–C–Si angle larger. The longer Li–C1 bonds in **6** and **8** compared with those in **7** may be attributed, at least in part, to the higher co-ordination number of lithium. A comparison of the chelate rings in **6**·2thf with those in **8** shows that the shorter Li–C bond in **6**·2thf [2.304(11) Å *cf.* 2.401(9) in **8**] is associated with a longer Si–O bond length [1.684(4) Å, *cf.* 1.655(4) in **8**] and shorter C–Si [1.792(6) Å *cf.* 1.816(4) in **8**] and Li–O bond lengths [1.933(11) Å, *cf.* 1.983(9) in **8**]. In all three compounds **6**·2thf, **7** and **8** the Si–Me bonds are shorter than the Si–Me_2OMe bonds, as found in previous work.[31] There is little variation in the Si–O bond lengths: apart from the short bond length in **8** all others fall in the narrow range 1.680(2) to 1.684(4) Å. As in **6**·2thf and **8**, the configuration at oxygen in

7 is planar (sum of angles 360°). The LiO_2C configuration at lithium is nearly planar (sum of angles 357.8°): the sum of the corresponding angles in **8** is lowered to 352.5° as a consequence of the formation of an extra Li–O interaction. The $Li \cdots Me$ distances in **7** are longer ($Li \cdots C6$ 2.69(1) Å) than those in the dimer of **5** [$Li \cdots Me$ 2.466(6), 2.541(7) Å].[16] Only those $Li \cdots Me$ distances that are less than *ca.* 2.7 Å are considered to indicate significant agostic interactions.[27]

The high solubility of the oligomeric bis(methoxy) compound **7** contrasts sharply with the low solubility of the polymeric bis(dimethylamino) compound **10**. If **10** were to crystallise with a dimeric structure like that of **7** there would be unfavourable steric interactions between N-methyl and Si-methyl substituents, which would be eclipsed about the Si–N bond.

The new organoalkali metal compounds **2**–**4** and **6**–**8** are potential reagents for the synthesis of a range of new organometallic compounds. Some of these have been described elsewhere.[5,15]

Experimental

Air and moisture were excluded as far as possible from all reactions by use of Schlenk techniques and Ar as a blanket gas. All glassware was flame-dried under vacuum. Solvents were dried by normal procedures and distilled immediately before use. The NMR spectra were recorded on samples dissolved in C_6D_6 at 300.13 (^1H), 75.43 (^{13}C), 116.59 (^7Li), 50.7 (^{15}N), and 99.4 (^{29}Si) MHz. Chemical shifts are relative to $SiMe_4$ for H, C and Si, aqueous LiCl for Li and $MeNO_2$ for N. The C, H analyses were by Medac Ltd or SACS, University of North London, but because of the extreme sensitivity of the compounds towards oxidation and hydrolysis satisfactory values could not be obtained in some cases.

Preparations

Bis(bromodimethylsilyl)(trimethylsilyl)methane II. Aluminium powder (0.05 g) was added to a solution of the phenyl derivative **I**[4] (17.6 g, 49 mmol) in light petroleum (bp 40–60 °C, 50 cm^3) at 0 °C. Bromine (18.7 g, 120 mmol) was then added dropwise, the mixture was stirred at room temperature for 2 h, and volatile material removed in vacuum to leave a black oil, which could be used directly for the syntheses of compounds **III** and **IV** (see below) or distilled at 50 °C/10^{-3} Torr to give **II** as a colourless viscous oil, which crystallised slowly at 0 °C (Found: C, 25.6; H, 4.9. $C_8H_{22}Br_2Si_3$ requires C, 26.5; H, 6.1%). δ_H 0.37 (9 H, s, $SiMe_3$), 0.07, 0.08 (6 H, s, $SiMe_2$) and 0.14 (1 H, s, CH). δ_C 12.0 ($SiMe_3$), 2.8, 6.4 ($SiMe_2$) and 14.0 (CH). δ_{Si} −0.7 ($SiMe_3$) and 27.1 (SiBr). The C, H analyses suggested that the compound was not obtained pure but its identity was confirmed by the conversion into **III** and **IV**.

Bis(dimethylaminodimethylsilyl)(trimethylsilyl)methane III. The dark oil described in the previous section was dissolved in light petroleum (30 cm^3) and the solution added during 1 h to a vigorously stirred solution of Me_2NH (9.5 g, 211 mmol) in light petroleum (20 cm^3) at −60 °C. The mixture was allowed to warm to room temperature and stirred overnight, the supernatant solution separated, the precipitate of Me_2NH_2Br washed with light petroleum (4 × 10 cm^3) and the washings combined with the main solution. The solvent was pumped away, *p*-dibromobenzene sublimed out at 40 °C/10^{-3} Torr, and the residue distilled at 76 °C/10^{-3} Torr to give compound **III** as a colourless, viscous liquid (11.8 g, 84% from **I**) (Found: C, 49.6; H, 11.6; N, 9.7. $C_{12}H_{34}N_2Si_3$ requires C, 49.6; H, 11.7; N, 9.7%). δ_H −0.24 (1 H, s, CH), 0.17 (6 H, s, $SiMe_2$), 0.175 (9 H, s, $SiMe_3$), 0.18 (6 H, s, $SiMe_2$) and 2.36 (12 H, s, NMe_2). δ_C 1.32, 1.45 ($^1J_{CSi}$ = 57, $SiMe_2$), 3.12 ($^1J_{CSi}$ = 52, $SiMe_3$), 5.9 ($^1J_{CSiN}$ = 42, $^1J_{CSiMe}$ = 37 Hz, CH) and 38.4 (NMe_2). δ_N −380.1. δ_{Si} −2.15 ($SiMe_3$) and 4.7 (SiN). *m*/*z* 275 (5, *M* − Me), 246 (100, *M* − NMe_2), 230 (70, *M* − NMe_2 − CH_4), 203 (50, $Me_3SiC(SiMe_2H)_2$), 129 (40, $HC(SiMe_2)_2$) and 73 (40%, $SiMe_3$).

Dimethylaminodimethylsilylbis(trimethylsilyl)methylpotassium 2. Neat $(Me_3Si)_2(Me_2NMe_2Si)CH$[5] (1.18 g, 4.51 mmol) was added to a suspension of MeK (4.60 mmol) in cold (−10 °C) diethyl ether (30 cm^3) and the mixture was allowed to attain room temperature then stirred overnight. Dry tmen (0.1 cm^3, 0.66 mmol) was added and stirring continued for 15 min. The solvent was removed under vacuum and the residue washed with light petroleum (bp 40–60 °C, 20 cm^3) then crystallised from hot benzene to give air- and moisture-sensitive colourless needles of compound **2** (0.88 g, 65%). Satisfactory C, H, N analyses could not be obtained. δ_H (C_6D_6) 0.34 (s, 6 H, $SiMe_2$), 0.38 (s, 18 H, $SiMe_3$) and 2.33 (s, 6 H, NMe_2). δ_C 4.1 ($SiMe_2$), 8.7 ($SiMe_3$) and 39.8 (NMe_2).

Tris(dimethylaminodimethylsilyl)methylpotassium 4. A suspension of $KOBu^t$ (0.24 g, 2.14 mmol) in heptane (30 cm^3) was added to a suspension of $LiC(SiMe_2NMe_2)_3$[6] (0.71 g, 2.18 mmol) in heptane (25 cm^3) at room temperature and the mixture stirred for 48 h. The solid was allowed to settle, the supernatant solution siphoned off, and the residue washed with heptane (3 × 40 cm^3) then recrystallised from hot benzene–thf (10 : 1) to give colourless air- and moisture-sensitive crystals of **4** (0.66 g, 85%) (Found: C, 41.2; H, 10.0; N, 11.6. $C_{13}H_{36}KN_3Si_3$ requires C, 43.6; H, 10.1; N, 11.7%). δ_H (thf-d_8) −0.09 (s, 10 H, $SiMe_2$) and 2.46 (s, 18 H, NMe_2). δ_C 2.7 ($^1J_{CSi}$ = 73.4, CSi_3), 3.9 ($^1J_{CSi}$ = 52.3 Hz, $SiMe_2$) and 40.0 (NMe_2). δ_N −371.3. δ_{Si} −2.0. *m*/*z* 274 (90, $R_2C{=}SiMe_2$, R = $SiMe_2NMe_2$), 259 (50, $R_2C{=}SiMe_2$ − Me), 232 (90, $R(HMe_2Si)CHSiMe_2$), 216 (70, R_2C), 115 (40, RCH), 102(45, R), 73 (40, $SiMe_3$) and 59 (100%, $SiMe_2H$).

Bis(methoxydimethylsilyl)(trimethylsilyl)methane IV. Compound **I** (7.80 g, 22 mmol) was converted into the bromide **II** by the procedure described above and the product dissolved in light petroleum (30 cm^3). To this solution was added Et_3N (1.20 g), then, dropwise, MeOH (10 cm^3). The white precipitate of Et_3NHBr was filtered off and extracted with light petroleum (4 × 10 cm^3). The filtrate and extracts were combined, the solvent was removed and the residue distilled at 50 °C/10^{-3} Torr. The distillate contained a small amount of *p*-dibromobenzene but this was easily removed by sublimation at 40 °C/10^{-3} Torr into an air condenser. Yield 4.82 g (83%) (Found: C, 44.9; H, 10.7. $C_{10}H_{28}O_2Si_3$ requires C, 45.3; H, 10.6%). δ_H −0.23 (1 H, s, CH), 0.22, 0.23 (6 H, s, $SiMe_2$), 0.26 (9 H, s, $SiMe_3$) and 3.21 (6 H., s, OMe). δ_C 1.02, 1.15 ($SiMe_2$), 2.80 ($SiMe_3$), 8.71 ($^1J_{CSiO}$ = 46.5, $^1J_{CSiMe}$ = 36.5 Hz, CH) and 49.6 (OMe). δ_{Si} −1.8 ($SiMe_3$) and 15.8 (SiO). *m*/*z* 249 (100, *M* − Me), 219 (*M* − Me − CH_2O), 145 (10, $Me_2SiCH{=}SiMeOMe$), 129 (20, $Me_2SiCH{=}SiMe_2$), 89 (15, $SiMe_2OMe$), 73 (10, $SiMe_3$) and 59 (10%, $SiMe_2H$).

Bis(dimethylaminodimethylsilyl)(trimethylsilyl)methyllithium 10. Butyllithium (2.5 M in hexanes, 2.0 cm^3) was added dropwise to a solution of compound **III** (1.07 g, 3.7 mmol) in light petroleum (40 cm^3) at −78 °C. The stirred mixture was allowed to warm to room temperature overnight and the solvent removed to leave a yellow solid, which was recrystallised from warm (50 °C) toluene to give small ill formed crystals of **10**. Yield: 53% (Found: C, 47.5; H, 10.6; N, 9.2. $C_{12}H_{33}LiN_2Si_3$ requires C, 48.6; H, 11.2; N, 9.4%). The compound was insufficiently soluble in C_6D_6 for satisfactory NMR measurements, so data were recorded from a solution containing the minimum amount of thf to give a clear solution: δ_H 0.45 (12 H, s, $SiMe_2$), 0.49 (9 H, s, $SiMe_3$), 1.3 (thf), 2.29 (12 H, s, NMe_2), and 3.5 (thf). δ_C 4.4 ($SiMe_3$), 5.8 ($^1J_{CSi}$ = 60 Hz, CSi_3), 8.9 ($SiMe_2$), 39.7 (NMe_2), 25.5 and 68.1 (thf). δ_{Si} −10.2 ($SiMe_3$) and 5.7 (SiN).

Table 2 Summary of crystallographic data for compounds **2**, **4** and **7**

	2	**4**	**7**
	$KC(SiMe_3)_2(SiMe_2NMe_2)$	$KC(SiMe_2NMe_2)_3$	$LiC(SiMe_3)(SiMe_2OMe)_2$
Empirical formula	$C_{11}H_{30}KNSi_3$	$C_{13}H_{36}KN_3Si_3$	$C_{10}H_{27}LiO_2Si_3$
Formula weight	299.73	357.8	270.5
T/K	160(2)	173(2)	173(2)
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$ (no. 14)	Cc (no. 5)	$Cmca$ (no. 64)
a/Å	9.4021(9)	16.219(5)	15.569(3)
b/Å	14.6824(14)	9.486(2)	12.603(2)
c/Å	12.7646(12)	13.656(4)	16.848(2)
β/°	92.586(2)	99.67(2)	—
U/Å^3	1760.3(3)	2071.2(10)	3305.8(9)
Z	4	4	8
μ/mm^{-1}	0.487	0.43	0.27
Reflections collected	13832	1881	2954
Unique reflections	4042 (R_{int} = 0.0149)	1881	1513 (R_{int} = 0.0206)
Reflections with $I > 2\sigma(I)$	3740	1818	1184
$R1$, $wR2$ ($I > 2\sigma(I)$)	0.026, 0.073	0.040, 0.118	0.058, 0.153
(all data)	0.029, 0.075	0.043, 0.132	0.076, 0.167

δ_{Li} 0.15. δ_N −372.0. Crystals were obtained from toluene, benzene, or heptane–thf, but none was suitable for an X-ray study.

{Bis(dimethylaminodimethylsilyl)(trimethylsilyl)methyl}trimethyltin 12. When an excess of Me_3SnCl (0.76 g, 3.82 mmol) in light petroleum (10cm^3) was added dropwise to a solution of compound **10** (1.11 g, 3.76 mmol) in toluene (10 cm^3) at 0 °C a white solid separated immediately. The mixture was stirred overnight then filtered. The presence of **12** in the filtrate was indicated by NMR spectroscopy but a sample free from **III** could not be isolated. δ_H 0.28 (9 H, s, $SiMe_3$), 0.30, 0.31 (6 H, s, $SiMe_2$), 0.34 (9 H, s, $^2J_{SnH}$ = 49 Hz, $SnMe_3$) and 2.42 (12 H, s, NMe_2). δ_C −0.65 ($^1J_{CSn}$ 327), 4.48, 4.52 ($^3J_{CSn}$ = 47, $SiMe_2$), 5.9 ($^3J_{CSn}$ = 50 Hz, $SiMe_3$), 14.6 (CSi_3Sn) and 40.3 (NMe_2). δ_{Si} −3.1 ($^2J_{SiSn}$ = 33, $SiMe_3$) and 3.0 ($^2J_{SiSn}$ = 42 Hz, $SiMe_2$). δ_{Sn} −13.1.

Bis(methoxydimethylsilyl)(trimethylsilyl)methyllithium 7. A solution of $LiNPr^i{}_2$, made from $NPr^i{}_2H$ (0.5 cm^3) in thf (10 cm^3) and LiBu (1.6 cm^3 2.5 M solution in hexanes), was cooled to −78 °C and neat compound **IV** (1.0 g) added slowly. The mixture was stirred for 1 h at −78 °C, then the solvent was pumped away to leave a sticky residue, which was recrystallised from light petroleum at 5 °C. Yield 90%. Found: C, 43.8; H, 9.9. Calc. for $C_{10}H_{27}LiO_2Si_3$: C, 44.4; H, 10.1%. δ_H 0.30 (12 H, s, $SiMe_2$), 0.33 (9 H, s, $SiMe_3$) and 3.09 (6 H, s, OMe); δ_C 2.8 ($SiMe_2$), 3.6 ($SiMe_3$), 9.3 (CSi_3) and 49.8 (OMe). δ_{Li} 0.83. δ_{Si} −2.0 (SiO) and −10.7 ($SiMe_3$).

{Bis(methoxydimethylsilyl)(trimethylsilyl)methyl}chlorotin 14. A sample of compound **7** (3.80 mmol) in thf (10 cm^3), prepared as described in the preceding section, was added slowly to a solution of $SnCl_2$ (0.80 g, 4.22 mmol) in thf (10 cm^3) at 0 °C and the mixture stirred at room temperature for 2 h. All volatile components were removed in vacuum and the dark residue was extracted with toluene (3 × 10 cm^3). The pale yellow extract was cooled to 5 °C to give **14** as an off-white powder (1.1 g, 65%). Found: C, 27.9; H, 6.5. $C_{10}H_{28}ClO_2Si_3Sn$ requires C, 28.7; H, 6.5%. δ_H 0.09 (6 H, s, $SiMe_2$), 0.30 (9 H, s, $SiMe_3$), 0.48 (6 H, s, $SiMe_2$) and 3.06 (6 H, s, OMe). δ_C 4.14, 4.19 ($SiMe_2$), 4.45 ($SiMe_3$), 28.4 ($^1J_{CSn}$ = 304, $^1J_{CSiMe}$ = 35.8, $^1J_{CSiO}$ = 54.8, CSi_3) and 50.9 Hz (OMe)]. δ_{Si} −4.0 ($^2J_{SnSi}$ = 60, SiMe) and 23.3 ($^2J_{SnSi}$ = 34 Hz, SiO).

(Tetrahydrofuran)lithium{bis(methoxydimethylsilyl)(trimethylsilyl)methyl}trihydroaluminate 15. A solution of compound **7** (4.55 mmol) in thf (10 cm^3) was added dropwise to one of freshly recrystallised $LiAlH_4$ (0.23 g, 6.0 mmol) in thf (5 cm^3) and the mixture then stirred overnight. The solvent was pumped away, the residue extracted with light petroleum (3 × 10 cm^3) and the extract reduced to 5 cm^3, then stored at −20 °C. A small amount of crystalline material separated during several weeks but most of the product remained in solution. A satisfactory C, H analysis was not obtained but the composition of the product was confirmed by NMR measurements. δ_H 0.00, 0.58 (12 H, s, $SiMe_2$), 0.50 (9 H, s, $SiMe_3$), 1.38 (4 H, s, thf), 3.27 (6 H, s, OMe) and 3.59 (4 H, s, thf). δ_C 1.0 ($SiMe_3$), 2.7, 3.7 ($SiMe_2$), 28.2 (thf), 50.6 (OMe), and 65.5 (thf). δ_{Li} 0.27, $\Delta\nu_{\frac{1}{2}}$ 10 Hz. δ_{Al} 115, $\Delta\nu_{\frac{1}{2}}$ 1.1 kHz. δ_{Si} 22.7 (SiO) and −8.2 ($SiMe_3$). The identity of each resonance was confirmed by a ^{29}Si–^{1}H correlation experiment and a study of the heteronuclear Overhauser effect, in which the ^{6}Li signal was observed during irradiation of narrow regions of the ^{1}H spectrum,[19] showed the presence of Al–H signals in the range δ 3–5.

Bis(methoxydimethylsilyl)(trimethylsilyl)methylmercury bromide 13. Liquid $HC(SiMe_3)(SiMe_2OMe)_2$ **IV** (0.63 g, 2.4 mmol) was added to a suspension of KMe (5.4 mmol) in Et_2O (5 cm^3) at −10 °C and the mixture stirred at this temperature for 2 h. An NMR spectrum of a sample filtered from the turbid suspension showed that compound **IV** had been cleanly converted into a single product, assumed to be the potassium derivative $KC(SiMe_3)(SiMe_2OMe)_2$, δ_H 0.38 (9 H, s, $SiMe_3$), 0.45 (12 H, s, $SiMe_2$) and 3.14 (6 H, s, OMe), but it was not possible to obtain a pure sample of the exceedingly air- and moisture-sensitive solid that remained when the solvent was pumped away. In another experiment **IV** (2.5 mmol) in Et_2O (10 cm^3) was treated with KMe as described above, then $HgBr_2$ (1.10 g, 3.0 mmol) in Et_2O was added. The stirred mixture was allowed to warm to room temperature overnight, the ether was pumped off, and the residue was extracted with toluene (30 cm^3). The extract was reduced to 3 cm^3 to yield an oily precipitate, which gave colourless crystals of **13** (0.43 g, 31%), mp 79–81 °C, on storage at −20 °C (Found: C, 20.9; H, 5.1. $C_{10}H_{27}BrHgO_2Si_3$ requires C, 22.0; H, 5.0%); δ_H −0.06 (9 H, s, $SiMe_3$), 0.20 (12 H, s, br, $SiMe_2$) and 3.27 (3 H, s, OMe). δ_C 0.7, 1.2 ($SiMe_2$), 2.7 ($SiMe_3$), 9.3 (CSi_3) and 50.9 (OMe). δ_{Si} −3.2 ($SiMe_3$) and 20.4 (SiO). m/z 529 (1, M − Me), 454 (3), 406 (30) and 362 (100).

Reaction of compound II with water. The diphenyl compound **I** (2.68 g, 7.53 mmol) was converted into the dibromide **II** which was then dissolved in light petroleum (10 cm^3). To this Et_3N (1.20 g, 11.9 mmol) was added, then water (2 cm^3) and the mixture stirred for 1 h. The precipitated Et_3NHBr was filtered off and washed with light petroleum (4 × 10 cm^3) and the filtrate and extracts were combined. The solvent was evaporated under vacuum and p-dibromobenzene removed by sublimation to leave a colourless oil (1.3 g, 3.0 mmol, 80%), which was judged from NMR spectroscopy to be an isomer of **V**, but a full characterisation was not attempted. δ_H −0.23 (1 H, s, CH), 0.08 (9 H, s, $SiMe_3$), 0.24 and 0.29 (4 H, s, $SiMe_2$). δ_C 2.5 ($SiMe_3$), 3.5, 4.6 ($SiMe_2$) and 11.3 (CH). δ_{Si} 4.3 ($SiMe_3$) and 14.7 (SiO).

Crystallography

Data for compound **2** were collected at the University of Newcastle on a SMART CCD area detector diffractometer and the structure solved by heavy atom methods. Data for **4** and **7** were collected at the University of Sussex on an Enraf-Nonius CAD4 diffractometer. The structures were solved by direct methods (SHELXS 86) and refined by full-matrix least squares (SHELXL 93).[32] Details are given in Table 2. In the structure of **7** the dimeric molecules lie on sites of crystallographic symmetry with the C atoms of the $Si(2)Me_3$ group disordered across the mirror plane. In all structures non-H atoms were anisotropic and H atoms were included in riding mode with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for Me groups.

CCDC reference number 186/1581.

See http://www.rsc.org/suppdata/dt/1999/3267/ for crystallographic files in .cif format.

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