Synthesis, Crystal Structure and Reactions of the Dimeric Organolithium Compound [{[(MeO)Me$_2$Si]$_3$CLi}$_2$]†

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Treatment of the compound $(Me_3Si)_3CCl$ with ICl followed by MeOH–Et_3N gave the methoxy-derivative $[(MeO)Me_2Si]_3CCl$. This reacted with LiBu^n at −78 °C to give $[(MeO)Me_2Si]_3CLi$ **3**, which was used to prepare the compounds $SiMe_2X\{C[SiMe_2(OMe)]_3\}$ (X = H, Cl, $OCOCF_3$ or NCO) and $SiPh_2H\{C[SiMe_2(OMe)]_3\}$. An X-ray diffraction study has shown that in the solid state the lithium compound **3** is dimeric, with the carbanionic fragments bound by two oxygen atoms to one lithium and by carbon and the third oxygen to the other. The Li–C bond [2.401(9) Å] is longer than usual and the C–$SiMe_2$(OMe) bonds [mean 1.805(4) Å] are short.

The organolithium reagents $(Me_3Si)_3CLi$ and $(PhMe_2Si)_3CLi$ have been used to synthesise a range of organometallic compounds having unusual structures and showing many novel reactions.[1] As part of a study of the effects of other substituents at silicon on the chemistry of compounds of this general type we have utilised the reagents $[(MeO)Me_2Si]_n(Me_3Si)_{3-n}CLi$ **1**–**3**. The compound with $n = 1$ has been discussed elsewhere;[2–4] here we describe the synthesis and reactions of the compound with $n = 3$ and give a full account of its structure which has so far been reported only briefly.[5] A few experiments on the compound with $n = 2$ are also described.

$[(MeO)Me_2Si](Me_3Si)_2CLi$ **1** $[(MeO)Me_2Si]_2(Me_3Si)CLi$ **2**

$[(MeO)Me_2Si]_3CLi$ **3**

Experimental

Schlenk-tube techniques were used for the manipulation of air- and moisture-sensitive compounds. Solvents were dried by standard procedures. The NMR spectra from samples in $CDCl_3$ were recorded at 90 or 360 MHz: chemical shifts are relative to $SiMe_4$ or $CFCl_3$. Mass spectra were obtained by electron impact at 70 eV (*ca.* 1×10^{-17} J): m/z values refer to ions with ^{28}Si and ^{35}Cl and relative intensities (in parentheses) to the strongest peak.

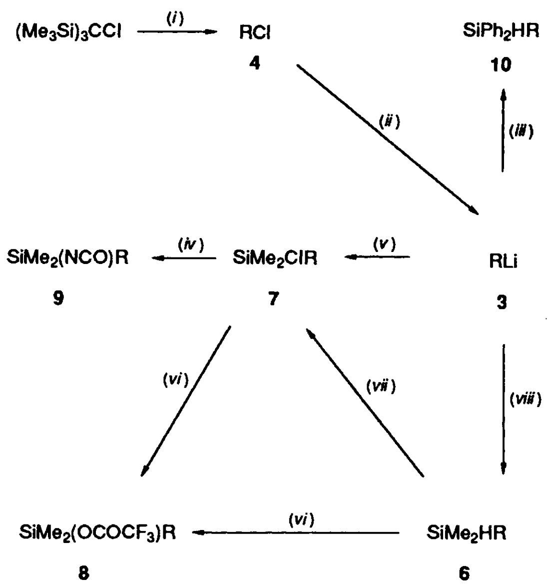
Chlorotris(methoxydimethylsilyl)methane **4** *and Chlorobis-(methoxydimethylsilyl)(trimethylsilyl)methane* **5**.—A large excess of ICl (54 g, 0.334 mol) in CCl_4 (20 cm^3) was added during 2 h to a solution of $(Me_3Si)_3CCl$[6,7] (10 g, 0.036 mol) in CCl_4 (48 cm^3) at 20 °C. The mixture was stirred for 2 h and a solution of Et_3N (14.8 cm^3, 0.108 mol) in MeOH (123 cm^3) was added. Stirring was continued for 72 h at 20 °C, then the solution was shaken with aqueous sodium metabisulfite and diethyl ether (70 cm^3) was added to the mixture. The organic layer was separated, washed thoroughly with water, and dried ($MgSO_4$). The solvent was removed under vacuum to leave a pale yellow oil, which was heated at 60 °C and 0.05 Torr to give a colourless crystalline sublimate, $[(MeO)Me_2Si]_3CCl$ (6.0 g, 65%), m.p. 72–74 °C (Found: C, 38.5; H, 8.6. $C_{10}H_{27}ClO_3Si_3$ requires C, 38.1; H, 8.6%); δ_H 0.28 (18 H, s, $SiMe_2$) and 3.47 (9 H, s, OMe); δ_C −1.4 (s, $SiMe_2$) and 50.9 (s, OMe); m/z 299 (10, $[M - Me]^+$), 194 (60, $[M - SiMe_4O_2]^+$), 179 (10, $[M - Me - SiMe_4O_2]^+$), 143 (10), 129 (10), 101 (20), 89 (70), 75 (25) and 59 (100%).

In one experiment carried out under seemingly identical conditions but on a smaller scale the main product was $[(MeO)Me_2Si]_2(Me_3Si)CCl$ **5**. A solution of ICl (13.6 g) in CCl_4 (5 cm^3) was added during 30 min to $(Me_3Si)_3CCl$ (2.5 g) in CCl_4 (12 cm^3). After 2 h Et_3N (0.025 mol) in MeOH (30 cm^3) was added and the mixture was worked up as above. The product was shown by gas chromatography–mass spectrometry to consist of a 1:9 mixture (1.2 g, 45%) of compound **4** and compound **5** which was identified spectroscopically. δ_H 0.20 (9 H, s, Me_3Si), 0.28 (12 H, s, $SiMe_2$OMe) and 3.47 (6 H, s, OMe); m/z 298 (5, $[M]^+$), 283 (15, $[M - Me]^+$), 194 (35, $[M - SiMe_3OMe]^+$), 179 (10, $[M - Me - Me_3SiOMe]^+$), 89 (90, $[SiMe_2OMe]^+$) and 59 (100%).

Dimethyl[tris(methoxydimethylsilyl)methyl]silane **6**.—A solution of LiBu^n (7.95 mmol) in hexane (3.2 cm^3) was added to one of $[(MeO)Me_2Si]_3CCl$ **4** (2.00 g, 6.36 mmol) in tetrahydrofuran (thf) (20 cm^3) at −78 °C. The solution was stirred at −78 °C for 10 min, then $SiMe_2ClH$ (0.75 g, 7.95 mmol) was added, and the mixture was allowed to warm to −25 °C during 2 h. Solvents and volatile materials were removed under vacuum and pentane was added to the residue. The mixture was filtered and solvent was evaporated from the filtrate to leave a white solid, which was sublimed (100 °C, 0.05 Torr) to give $SiMe_2H\{C[SiMe_2(OMe)]_3\}$ **6** 1.9 g (89%), m.p. 193 °C (Found: C, 43.0; H, 10.0. $C_{12}H_{34}O_3Si_4$ requires C, 42.6; H, 10.0%); δ_H 0.22 (18 H, s, $SiMe_2$OMe), 0.23 (6 H, s, $SiMe_2$H), 3.34 (9 H, s, OMe), and 4.11 (1 H, m, Si*H*); δ_C 0.44 ($SiMe_2$H), 1.56 ($SiMe_2$OMe), 9.16 (CSi_3) and 49.6 (OMe); δ_{Si} −17.8 [d, $^1J(^{29}Si–H)$ 186 Hz, $SiMe_2$H) and 14.0 (s, $SiMe_2$OMe); m/z 337 (10, $[M - H]^+$), 323 (40, $[M - Me]^+$), 233 (65), 217 (55), 203 (60), 173 (20), 129 (15), 89 (50), 73 (35) and 59 (100%).

Chlorodimethyl[tris(methoxydimethylsilyl)methyl]silane **7**.—(*a*) A solution of $[(MeO)Me_2Si]_3CCl$ **4** (3.0 g, 9.55 mmol) in thf (30 cm^3) was treated with LiBu^n (12 mmol) in hexane (4.8 cm^3) at −78 °C as described above. After 10 min $SiMe_2Cl_2$ (1.45 cm^3, 12 mmol) was added and the mixture allowed to warm to 20 °C during 2 h, then filtered. Solvent was removed from the filtrate and the residue sublimed (60 °C, 0.05 Torr) to give colourless

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.
Non-SI unit employed: Torr ≈ 133 Pa.



Scheme 1 R = $[(MeO)Me_2Si]_3C$. (*i*) ICl, then MeOH–Et_3N; (*ii*) $LiBu^n$, -78 °C; (*iii*) $SiPh_2ClH$; (*iv*) AgNCO; (*v*) $SiMe_2Cl_2$; (*vi*) $AgOCOCF_3$; (*vii*) PCl_5; (*viii*) $SiMe_2ClH$

crystals of $SiMe_2Cl\{C[SiMe_2(OMe)]_3\}$ **7** (1.7 g, 44%), m.p. 198 °C (Found: C, 38.6; H, 8.95. $C_{12}H_{33}ClO_3Si_4$ requires C, 38.7; H, 8.9%); δ_H 0.33 (18 H, s, Si*Me*$_2$OMe), 0.54 (6 H, s, $SiMe_2Cl$) and 3.40 (9 H, s, OMe); *m/z* 357 (60, $[M - Me]^+$), 342 (5) and 237 (100%).

(*b*) A solution of $SiMe_2H\{C[SiMe_2(OMe)]_3\}$ **6** (0.10 g, 0.27 mmol) in CCl_4 (5 cm^3) was stirred with PCl_5 (0.11 g, 0.54 mmol) for 30 min at 20 °C. The solvent was removed under vacuum and the residue was extracted with pentane. The extract was filtered and solvent was evaporated from the filtrate to leave a white solid, which was sublimed and shown to be $SiMe_2Cl\{C[SiMe_2(OMe)]_3\}$ (0.09 g, 90%), with properties identical with those given above.

Dimethyl(trifluoroacetoxy)[tris(methoxydimethylsilyl)methyl]silane **8**.—A solution of $SiMe_2H\{C[SiMe_2(OMe)]_3\}$ **5** (0.10 g, 0.30 mmol) in CH_2Cl_2 (10 cm^3) was stirred with $AgOCOCF_3$ (0.073 g, 0.33 mmol) at 20 °C for 30 min. The mixture was filtered and solvent was removed from the filtrate under vacuum. The residue was sublimed (75 °C, 0.05 Torr) to give white crystals of $SiMe_2(OCOCF_3)\{C[SiMe_2(OMe)]_3\}$ (0.10 g, 80%), m.p. 63–65 °C (Found: C, 37.7; H, 7.4. $C_{14}H_{33}F_3O_5Si_4$ requires C, 37.3; H, 7.3%); δ_H 0.27 (18 H, s, Si*Me*$_2$OMe), 0.55 (6 H, s, $SiMe_2OCOCF_3$), and 3.34 (9 H, s, OMe); δ_F -76.4; *m/z* 435 (100, $[M - Me]^+$) and 421 (30). Compound **4** was also made in 74% yield from the reaction between $SiMe_2Cl\{C(SiMe_2(OMe)]_3\}$ and $AgOCOCF_3$ in CH_2Cl_2 at 20 °C.

Isocyanatodimethyl[tris(methoxydimethylsilyl)methyl]silane **9**.—A solution of $SiMe_2Cl\{C[SiMe_2(OMe)]_3\}$ (10.1 g, 0.27 mmol) in anhydrous MeCN (10 cm^3) was stirred with freshly prepared dry AgOCN for 2 h at 20 °C. The mixture was filtered and solvent evaporated from the filtrate to leave a solid which was sublimed to give white crystals of $SiMe_2(NCO)\{C[SiMe_2(OMe)]_3\}$ (0.08 g, 85%), m.p. 169 °C (Found: C, 41.6; H, 8.9; N, 3.4. $C_{13}H_{33}NO_4Si_4$ requires C, 41.2; H, 8.7, N, 3.7%); ν(NCO) at 2280 cm^{-1}; δ_H 0.27 (18 H, s, Si*Me*$_2$OMe), 0.37 (6 H, s, $SiMe_2NCO$) and 3.39 (9 H, s, OMe). In one experiment in which the MeCN contained traces of water the product was the silanol $SiMe_2(OH)\{C[SiMe_2(OMe)]_3\}$ identified by mass spectroscopy: *m/z* 339 (100, $[M - Me]^+$), 234 (5, $[M - SiMe_4O_2]^+$) and 219 (10%, $[M - Me - SiMe_4O_2]^+$).

Diphenyl[tris(methoxydimethylsilyl)methyl]silane **10**.—A solution of $LiBu^n$ (5 mmol) in hexane (2 cm^3) was added to $[(MeO)Me_2Si]_3CCl$ (1.5 g, 4.8 mmol) in thf (15 cm^3) at -78 °C. The solution was stirred at -78 °C for 10 min, then $SiPh_2ClH$ (1.0 g, 5.0 mmol) was added. The mixture was allowed to warm to 20 °C overnight. Volatile materials were then removed under vacuum and the white residue was extracted with pentane. The extract was filtered, and solvent was evaporated under vacuum to leave a white solid, which was recrystallised from pentane to give $SiPh_2H\{C[SiMe_2(OMe)]_3\}$ **10** (1.4 g, 65%), m.p. 132–134 °C (Found: C, 57.0; H, 8.3. $C_{22}H_{38}O_3Si_4$ requires C, 57.1; H, 8.3%); δ_H 0.07 (18 H, s, Si*Me*$_2$OMe), 3.39 (9 H, s, OMe) and 7.1–8.1 (10 H, m, Si*Ph*$_2$H). The crystal structure of this compound has been described elsewhere.[8]

[Bis(methoxydimethylsilyl)(trimethylsilyl)methyl]chlorodimethylsilane **11**.—A mixture of $[(MeO)Me_2Si]_2(Me_3Si)CCl$ (90%) and $[(MeO)Me_2Si]_3CCl$ (10%) (1.0 g) in thf (30 cm^3), made as described above, was treated with $LiBu^n$ (5 mmol) in hexane (2.0 cm^3) at -78 °C. The solution was stirred for 10 min at -78 °C, then $SiMe_2Cl_2$ (0.60 cm^3, 5 mmol) was added and the mixture allowed to warm to 20 °C during 2 h and filtered. Solvent was evaporated from the filtrate to give a white solid, which was sublimed (60 °C, 0.05 Torr) and shown by ^{1}H NMR and mass spectroscopy to be $SiMe_2Cl\{C(SiMe_3)[SiMe_2(OMe)]_2\}$ **11**; {δ_H 0.28 (9 H, s, $SiMe_3$), 0.36 (12 H, s, Si*Me*$_2$OMe), 0.62 (6 H, s, $SiMe_2Cl$) and 3.47 (6 H, s, OMe); *m/z* 356 (40, $[M]^+$), 341 (38, $[M - Me]^+$), 325 (20, $[M - OMe]^+$), 237 (100, $[M - Me - SiMe_4O]^+$), 221 (67, $[M - Me - SiMe_4O_2]^+$), 89 (30, $[SiMe_2OMe]^+$) and 59 (63%)} containing 5% of compound **7**.

The Lithium Reagent $[(MeO)Me_2Si]_3CLi$ **3**.—The isolation of compound **3** has been described:[5] $\delta_C(C_6D_5CD_3)$ 3.7 (Me_2Si) and 49.8 (OMe); δ_{Si} 13.9.

Crystallography.—Crystal data. $C_{20}H_{54}Li_2O_6Si_6$ **3**, M = 573.1, orthorhombic, space group *Cmca*, a = 15.588(2), b = 12.852(1), c = 17.503(3) Å, U = 3506.5 Å^3, Z = 4, D_c = 1.09 g cm^{-3}, $F(000)$ = 1248, monochromated Mo-Kα radiation, λ = 0.710 69 Å, μ = 2.6 cm^{-1}.

Structure determination. Data were measured on an Enraf-Nonius CAD4 diffractometer with a crystal of size 0.3 × 0.25 × 0.2 mm. Intensities for $+h +k +l$ reflections with $2 < \theta < 25°$ were measured by a θ–2θ scan with width $\Delta\theta = (0.8 + 0.35 \tan\theta)°$. Two standard reflections showed no significant variation. Data were corrected for Lorentz and polarisation effects but not for absorption: 1599 reflections with $|F^2| > \sigma(F)^2$ were used in the structure analysis.

The data, collected with the unit cell a = 17.503(3), b = 12.852(1), c = 15.588(3) Å, were consistent with space group *Aba*2 or *Abam*. The structure was solved in space group *Aba*2 by direct methods using MULTAN[9] but it was found to have a mirror plane, the space group was thus assumed to be *Abam* and transformed to the standard setting *Cmca* for full-matrix least-squares refinement using anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were found in a difference map and included with isotropic thermal parameters. Refinement converged at R = 0.048, R' = 0.055 with $w = 1/\sigma^2(F)$.

A PDP 11/34 computer and the Enraf-Nonius structure determination package were used in the structure solution and refinement. Scattering factors were taken from ref. 10. Final atom coordinates are given in Table 1, and bond lengths and angles in Table 2. The molecule is shown in Fig. 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters. Structure factor tables are available from P.B.H.

Results and Discussion

The synthesis and reactions of the organolithium compound **3**

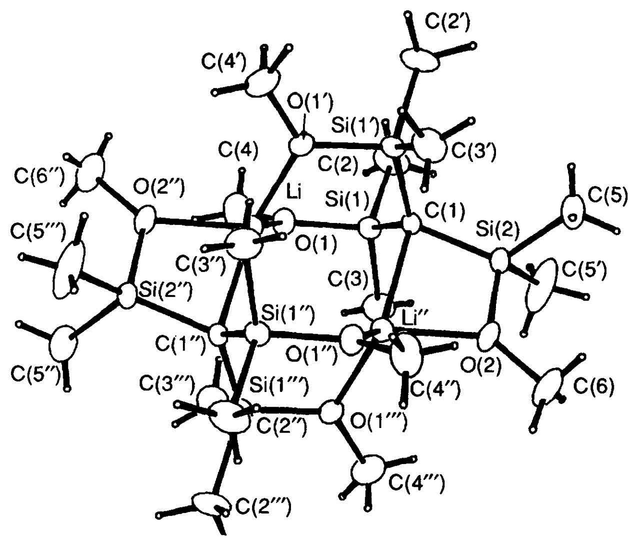


Fig. 1 Structure of the dimer $[\{[(MeO)Me_2Si]_3CLi\}_2]$ **12**

Table 1 Fractional atomic coordinates ($\times 10^4$) for compound **3** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Si(1)	985(1)	635(1)	1279(1)
Si(2)	0	2560(1)	700(1)
O(1)	936(1)	−646(2)	1091(1)
O(2)	0	2594(3)	−246(2)
C(1)	0	1180(3)	923(2)
C(2)	1176(3)	749(4)	2340(2)
C(3)	1997(2)	1076(4)	812(3)
C(4)	1527(3)	−1373(3)	1409(3)
C(5)	929(4)	3355(3)	999(4)
C(6)	0	3549(5)	−686(4)
Li	0	−1075(6)	446(4)

Table 2 Intramolecular distances (Å) and angles (°) for compound **3** with e.s.d.s in parentheses

Si(1)–O(1)	1.680(2)	Si(1)–C(1)	1.799(2)
Si(1)–C(3)	1.865(4)	Si(1)–C(2)	1.887(4)
Si(2)–O(2)	1.655(4)	Si(2)–C(1)	1.816(4)
Si(2)–C(5)	1.848(5)	O(1)–C(4)	1.426(5)
O(2)–Li″	1.983(9)	O(1)–Li	1.925(6)
C(1)–Li″	2.401(9)	O(2)–C(6)	1.449(7)
O(1)–Si(1)–C(1)	106.0(2)	O(1)–Si(1)–C(2)	106.0(2)
O(1)–Si(1)–C(3)	104.5(2)	C(1)–Si(1)–C(2)	116.4(2)
C(1)–Si(1)–C(3)	116.9(2)	C(2)–Si(1)–C(3)	105.9(2)
O(2)–Si(2)–C(1)	103.9(2)	O(2)–Si(2)–C(5)	105.6(2)
C(1)–Si(2)–C(5)	118.6(2)	C(5)–Si(2)–C(5′)	103.2(2)
Si(1)–O(1)–C(4)	122.5(2)	Si(1)–O(1)–Li	115.5(3)
C(4)–O(1)–Li	122.0(3)	Si(2)–O(2)–C(6)	123.6(4)
Si(2)–O(2)–Li″	98.7(3)	C(6)–O(2)–Li″	137.7(4)
Si(1)–C(1)–Si(1′)	117.2(2)	Si(1)–C(1)–Si(2)	117.1(1)
Si(1)–C(1)–Li″	108.9(2)	Si(2)–C(1)–Li″	80.8(2)
O(1)–Li–O(1′)	98.5(4)	O(1)–Li–O(2″)	112.7(3)
O(1)–Li–C(1″)	127.0(2)	O(2)–Li″–C(1)	76.6(3)

Single, double and triple primes here and in Fig. 1 indicate symmetry-related positions at $\bar{x},y,z$; $\bar{x},\bar{y},\bar{z}$; and $x,\bar{y},\bar{z}$ respectively.

are summarised in Scheme 1. Compound **4** was made in fair yield from $(Me_3Si)_3CCl$ [6,7] by treatment first with a large excess of ICl and then with MeOH–Et_3N. The intermediate $(ClMe_2Si)_3CCl$ was not isolated, though it was clear from experiments in NMR tubes that it was formed *via* a series of partially chlorinated compounds. In most cases the final product was solely $(ClMe_2Si)_3CCl$ but on one occasion, for unknown reasons, the main product was $[(MeO)Me_2Si]_2(Me_3Si)CCl$ **5**. Attempts to isolate pure **5** were unsuccessful.

Compound **4** was metallated with butyllithium in the usual way [11] to give the reagent **3**, which was used *in situ* at −78 °C to make the organosilanes **6**, **7** and **10**. The hydride **6** was converted into the chloride **7** almost quantitatively by treatment with a two-fold excess of phosphorus(V) chloride. The trifluoroethanoate **8** was obtained in high yield from both the chloride **7** and the hydride **6**. These substitutions are facilitated by powerful anchimeric assistance from γ-OMe groups, and the effect is so great that even hydride may be readily displaced from silicon by treatment with silver salts, as found earlier for reactions of $SiMe_2H\{C(SiMe_3)_2[SiMe_2(OMe)]\}$.[3] The reaction between **7** and silver cyanate in MeCN gave the isocyanate **9**. It is likely that the initial product was the isomeric cyanate which rearranged to the thermodynamically more stable isocyanate,[12] but an attempt to detect the cyanate by monitoring the reaction at 0 °C by NMR spectroscopy was unsuccessful. When the MeCN contained traces of water the product was the silanol $SiMe_2(OH)\{C[SiMe_2(OMe)]_3\}$. It was shown previously that cyanate is an exceedingly good leaving group from silicon and that silanols can be conveniently made by treatment of halides with AgOCN in incompletely dried solvents.[13]

The chloride **5**, containing 10% of **4**, was metallated with butyllithium in the same way as **4** and the products used *in situ* to make the chlorosilane **11** contaminated with **7** (Scheme 2).

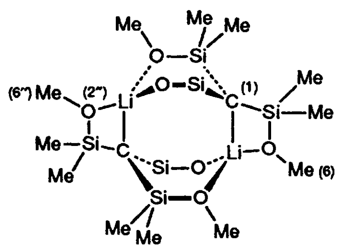
$$\underset{\mathbf{5}}{[(MeO)Me_2Si]_2(Me_3Si)CCl} \xrightarrow{(i)} \underset{\mathbf{2}}{[(MeO)Me_2Si]_2(Me_3Si)CLi} \xrightarrow{(ii)} \underset{\mathbf{11}}{SiMe_2Cl\{C(SiMe_3)[SiMe_2(OMe)]_2\}}$$

Scheme 2 (*i*) LiBu; (*ii*) $SiMe_2Cl_2$

The lithium reagent **3** was normally used as prepared in hexane–thf. The species in solution are not known, but when the solvent was evaporated a colourless, air-sensitive solid was isolated and recrystallised from toluene. This solid was free from donor solvents and from toluene and contained the dimeric species, shown in Fig. 1. Each $[(MeO)Me_2Si]_3C$ group is bound to one lithium through carbon C(1) and an oxygen O(2) of a β-OMe group and to the other lithium through the oxygen atoms of the two other β-OMe groups. The resulting dimer **12** has point symmetry C_{2h} with the two four-membered rings C(1)Si(2)O(2)Li″ and C(1″)Si(2″)O(2″)Li and their exocyclic carbon atoms C(6) and C(6″) coplanar and the perpendicular two-fold axis passing through the centre of inversion midway between Li and Li″. The cage structure **12** is, as far as we are aware, unprecedented in organolithium chemistry, though four-membered chelate rings obtained by co-ordination through a β-OMe group are found in the tetramers **13**,[14] **14**,[15] and **15**[16] and in the dimers **16**,[17,18] which are linked by further Li–C interactions to tetramers both in the crystal and in solution.

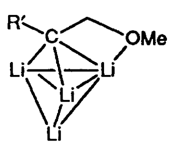
Strain in the chelate rings is shown by the small angles at lithium [76.3(3)], carbon [80.8(2)] and at the planar oxygen [98.7(3)°], and by the Li–O(2″) distance [1.983(9) Å] which is significantly longer than the Li–O(1) and Li–O(1′) separations between monomer units [1.925(6) Å]. The Li–O(2″) distance in **12** is longer than the corresponding distances in the chelate rings of compounds **13**–**16**. The Li–O(1) bond length is at the lower end of the range (1.91–2.01 Å) normally found in organolithium reagents,[19] though it is significantly longer than that [1.85(2) Å] in $(PhMe_2Si)_3CLi(thf)$ **17**, in which the lithium is essentially two-co-ordinate.

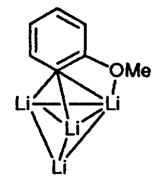
In contrast, the Li–C bond in compound **12** [2.401(9) Å] is at the upper end of the observed range:[19] *cf.* 2.12(2) Å in **17**, 2.291(6) Å in solvent-free $[\{(Me_3Si)_3CLi\}_2]$ **18**,[20] and 2.18–2.36 Å in **13**–**16** in which each lithium interacts with three carbon neighbours. Indeed, the Li–C distance in **12** is similar to that between lithium and the *ipso*-C of a phenyl group in **17** [2.40(2) Å], and to that between lithium and the γ-carbon in **18** [2.466(6) Å].[20] The fact that the Li–C bond is much longer than usual suggests that the carbon atom may have substantial carbanionic

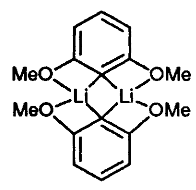


Some methyl groups omitted

12





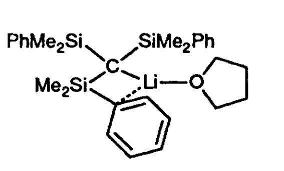


13 R′ = H
14 R′ = Me

15

16

In 13 – 15 only one alkyl group of the tetramer is shown



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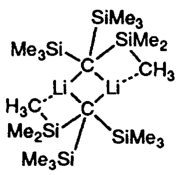

18

character and is consistent with the conclusion from *ab initio* calculations that carbanions are strongly stabilised by adjacent SiH_3 groups.[21,22]

In compounds in which the $(Me_3Si)_3C$ group is attached to Si, B or P, C–$SiMe_3$ bond lengths of 1.90–1.95 Å are observed but in compounds in which the $(Me_3Si)_3C$ group is attached to a metal the C–$SiMe_3$ bonds are somewhat shorter [*cf.* mean 1.855(3) Å in **18**]. There is commonly also a shortening of Si–C bonds when silicon is attached to oxygen. Thus C–$SiMe_2$(OMe) bonds are typically 1.85–1.88 Å.[8,23] In **12**, in which C is attached to a metal and Si to oxygen, both effects are apparent. Even so the C–$SiMe_2$(OMe) bonds in **12** [mean 1.805(4) Å] seem exceptionally short. To the extent that the C(1) atom has carbanionic character there may be shortening of the bonds as a consequence of negative hyperconjugation and $(p \rightarrow d)_\pi$ interaction, with the former probably the more important. Calculations predict an Si–C bond length of 1.814 Å for $[H_3Si–CH_2]^-$ compared with 1.855 Å for the bond in $H_3Si–CH_2Li$.[21]

The ^1H and ^{13}C NMR spectra of compound **3** in toluene at 25 °C each show only two signals, from the methyl groups attached to silicon and oxygen, instead of the four expected from the crystal structure. The ^{29}Si NMR spectrum shows only one signal. Either the dimers dissociate in solution or there is rapid exchange between inter- and intra-molecularly bridging (MeO)-$SiMe_2$ groups on the NMR time-scale for all three nuclei. We have not made a full variable-temperature study or molecular-weight measurements.

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