Preparation and Crystal Structure of the Novel Internally Solvated Dimeric Organolithium Compound [{$LiC(SiMe_2OMe)_3\}_2$]

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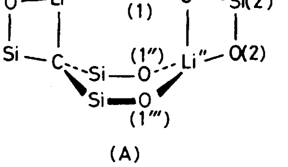
The organolithium reagent derived from $(MeOMe_2Si)_3CCl$ has been shown to crystallize as the dimeric species [{$LiC(SiMe_2OMe)_3\}_2$], in which the Li–C bonds are exceptionally long and the C–$SiMe_2OMe$ bonds unusually short.

There is much current interest in both theoretical and experimental aspects of the structures of organolithium compounds.[1] Among the most interesting (*cf.* ref. 2) of the structures determined recently are those of the compounds derived from the bulky carbon acids $(Me_3Si)_3CH$ and $(PhMe_2Si)_3CH$; the first of these has the formula [Li(thf)$_4$][Li{$C(SiMe_3)_3\}_2$] (thf = tetrahydrofuran), and is the first example of an 'ate' derivative of lithium,[3] and the second is a monomeric species [$LiC(SiMe_2Ph)_3 \cdot$ thf] containing 2-co-ordinate lithium and an additional weak Li–Ph interaction.[4] We have now found that the lithium derivative of the related carbon acid $(MeOMe_2Si)_3CH$ has a very different structure, crystallizing as a dimer (**1**), free from external ligands. The immediate precursor of (**1**) was the chloride $(MeOMe_2Si)_3CCl$, which was made from $(Me_3Si)_3CCl$[5] by reaction with ICl to give $(ClMe_2Si)_3CCl$ followed by treatment of the latter with MeOH in the presence of Et_3N. A solution of Bu^{n}Li (11.3 mmol) in 1:1 thf–hexane (10 cm^3) was added dropwise to a solution of $(MeOMe_2Si)_3CCl$ (11.3 mmol) in thf (10 cm^3) at −78 °C. The mixture was stirred for 2 h at −78 °C then allowed to warm to 0 °C and the volatile material was pumped off. The residue was washed with heptane, dried, and extracted with warm toluene. When the extract was kept at room temperature, crystals of (**1**) separated; δ_H (in [$^2H_8$]toluene) 0.26 (18H, s, $SiMe_2$) and 3.13 (9H, s, OMe); δ_{Li} (in [$^2H_8$]toluene relative to external $LiNO_3$ in D_2O) −0.54 p.p.m. Some of the crystals were suitable for *X*-ray diffraction study.†

The structure of (**1**), with details of the atom numbering, is shown in Figure 1, and the essential skeleton is depicted more clearly in (A). It will be seen that two molecules of $LiC(SiMe_2OMe)_3$ associate to give a cage dimer. Each of the component molecules in the dimer has one of its own OMe groups internally co-ordinated to its own Li atom (to give a planar 4-membered ring), and its two remaining OMe groups are co-ordinated to the Li atom of the other component molecule to give two 6-membered rings in boat conformations. The dimer has point group symmetry C_{2h} with the mirror plane through the two 4-membered rings and the two-fold rotation axis perpendicular to it passing through the inversion centre midway between Li and Li″. The angles in the 4-membered rings range from 76.6(3) to 103.9(2)° and there is considerable distortion from the tetrahedral in the co-ordination around the lithium atoms.

[{$LiC(SiMe_2OMe)_3\}_2$]

(**1**)



(A)

An important feature of the structure is the C–Li bond length, 2.401(9) Å, which is markedly larger than that normally found for compounds with single carbon–lithium contacts {*e.g.* the corresponding bond length is 2.13(5) in $(Me_3Si)_2CHLi(Me_2NCH_2CH_2NMeCH_2CH_2NMe_2)$[6] and 2.12(2) Å in [$(PhMe_2Si)_3CLi(thf)$] in which the weak Li–Ph interaction involves a Li–C distance of 2.40 Å[4]} and larger than those commonly found even for carbon bridging between lithiums.[1a] This long C–Li distance in (**1**) implies considerable ionic character, and the dimer can be regarded as consisting of essentially two ion pairs held rigidly together by the intra- and inter-molecular co-ordination. The substantial carbanionic character at the central carbon atom is reflected in the large central Si–C–Si bond angles, mean 117.1(1)°, consistent with a high degree of sp^2 character in the C–Si bonds. Probably as a result of negative hyperconjugation, and possibly also of some $(p\rightarrow d)_\pi$ interaction between the carbon and silicon atoms,[7]

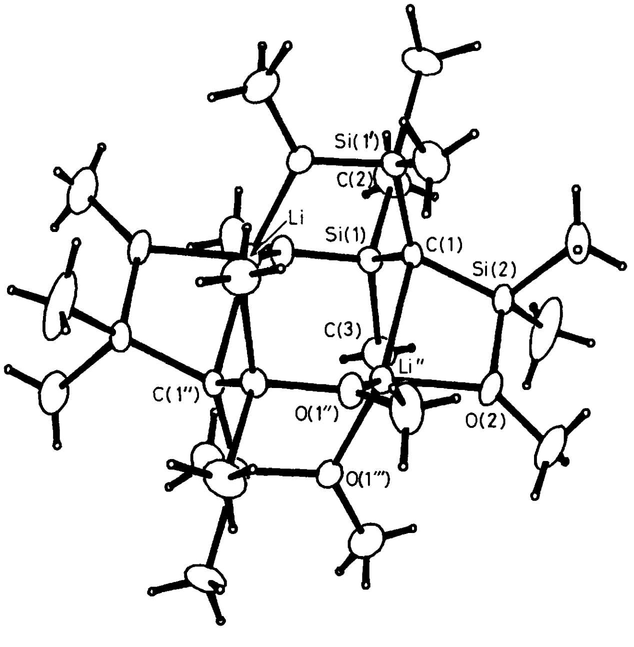


Figure 1. Crystal structure of (**1**), showing the atom numbering. Selected dimensions: Si(1)–C(1) 1.799(2), Si(2)–C(1) 1.816(4), Si(1)–C(3) 1.865(4), Si(1)–C(2) 1.887(4), O(1″)–Li″ 1.925(6), O(2)–Li″ 1.983(9), C(1)–Li″ 2.401(9) Å; O(2)–Si(2)–C(1) 103.9, Si(2)–O(2)–Li″ 98.7(3), O(2)–Li″–C(1) 76.6(3), Si(2)–C(1)–Li″ 80.8(2), Si(1)–C(1)–Si(1′) 117.2(2), Si(1)–C(1)–Si(2) 117.1(1), O(1′)–Li″–O(1″) 98.5(4), O(1″) –Li″–O(2) 112.7(3), O(1″) –Li″–C(1) 127.0(2)°.

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† *Crystal data:* $C_{20}H_{54}O_6Li_2Si_6$; M_r = 573.1, orthorhombic, space group *Cmca*, $a = 15.588(2)$, $b = 12.852(1)$, $c = 17.503(3)$ Å, $Z = 4$, $D_c = 1.09$ g cm^{-3}, monochromated Mo-K_α radiation, $\mu = 2.6$ cm^{-1}. R = 0.048, R' = 0.055 for 1599 unique reflections with $|F^2| > \sigma(F^2)$ measured on an Enraf-Nonius CAD-4 diffractometer in the range $2 < \theta < 25°$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

these bonds are abnormally short, *viz.* 1.799(2) and 1.816(4) Å, whereas in compounds containing $(Me_3Si)_3C$ and $(PhMe_2Si)_3C$ ligands the central C–Si bonds are usually markedly longer than the peripheral Si–C bonds; *e.g.*, the respective relevant mean bond lengths in $(Me_3Si)_3CBPh_2$ are 1.934(3) and 1.873(6),[8] those in $(Me_3Si)_3CSiMe_2Ph$ are 1.915(9) and 1.876(15),[9] and those in the less crowded $(PhMe_2Si)_3CH$ are 1.895(1) and 1.862(13) Å.[10] (However, the central Si–C bonds in the anion $[Li\{C(SiMe_3)_3\}_2]^-$ appear to be shorter than the peripheral Si–Me bonds, and this has been attributed to substantial carbanionic character at the central carbon atom.[11])

We cannot yet say whether (**1**) retains its structure in solution in the presence of a co-ordinating solvent such as thf. That the reagent formed under such conditions can be used in synthesis was demonstrated by treating $(MeOMe_2Si)_3CCl$ in thf at −78 °C with Bu^nLi in hexane, then adding $SiMe_2HCl$ and allowing the mixture to warm up. Work-up gave $(MeOMe_2Si)_3CSiMe_2H$ (89%), m.p. 172—174 °C; δ_H ($CDCl_3$) 0.22 (18H, s, Si*Me*$_2$OMe), 0.23 (6H, d, Si*Me*$_2$H), 3.34 (9H, s, OMe), and 4.08 (1H, m, SiH); δ_{Si} ($CDCl_3$) 14.0 (s, $SiMe_2OMe$) and −17.8 (d, $SiMe_2H$); *m/z* 337 ($[M - H]^+$) and 323 ($[M - Me]^+$).

The bulky $(Me_3Si)_3C$ ligand has been attached to over 30 elements, to give compounds all of which have unusual (and some of them highly abnormal) properties.[12] The availability of the reagent described here for introduction of the $(MeOMe_2Si)_3C$ ligand, which is of comparable bulk but also has its own sub-ligands available for co-ordination to metal centres, should lead to preparation of a further range of highly novel species.

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