

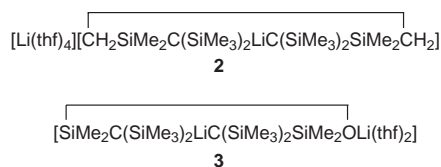
A novel molecular species incorporating a cyclic organolithate anion and a disiloxane-solvated lithium cation

Colin Eaborn,*† Salima M. El-Hamruni, Peter B. Hitchcock and J. David Smith*†

School of Chemistry, Physics and Environmental Sciences, University of Sussex, Brighton, UK BN1 9QJ

The disiloxane $O\{SiMe_2CH(SiMe_3)_2\}_2$ is readily metallated by $LiMe$ in thf ($thf = tetrahydrofuran$) to give the compound $SiMe_2C(SiMe_3)_3LiC(SiMe_3)_2SiMe_2OLi(thf)_2$, the crystal structure of which is reported.

In 1983 we reported the first diorganolithate, $[Li(thf)_4][Li\{C(SiMe_3)_3\}_2]$ **1** ($thf = tetrahydrofuran$)¹ and more recently we described the related cyclic species **2**.² We have now obtained and structurally characterized the somewhat more distantly related cyclic lithate **3**, which has unprecedented features.



We have found that the disiloxane $O\{SiMe_2CH(SiMe_3)_2\}_2$ ³ is metallated by $LiMe$ in thf at room temperature, that is much more readily than $(Me_3Si)_3CH$,⁴ probably because of initial interaction of the siloxane oxygen atom with the Li of the $LiMe$.[‡] Recrystallization of the product, **3**, from heptane gave crystals suitable for an X-ray diffraction study, which yielded the structure shown in Fig. 1.§

The main novel features of **3** are as follows.

(a) In contrast to **1** and **2**, in each of which the lithate anion and the solvated lithium cation are well separated, compound **3** is a molecular dipolar species, the $Li(2)^+$ centre being attached to the lithate ion *via* the oxygen of the siloxane linkage. Both the $O(1)$ and $Li(2)$ atoms have essentially planar geometries [sum of angles $358.6(5)$ and $360.0(6)^\circ$, respectively]. The $Si-O-Si$ angle is $138.5(3)^\circ$, a fairly normal value for a siloxane linkage.⁵ The angle between the bonds to the thf molecules, $O(3)-Li(2)-O(2)$ $101.2(6)^\circ$, is narrow, presumably to minimize steric interactions.

(b) As far as we can ascertain compound **3** is the first example of a structurally characterized disiloxane-metal complex in which the ligand is attached to the metal only through its oxygen atom. In all other examples of coordination of disiloxane oxygen to a metal this bonding is supported by bonding through another atom of the ligand; examples include systems of the types $Me_3SiO-Pd-Si$,⁶ $Me_3SiO-Zr-CH_2SiMe_2$,⁷ and $Me_3SiO-Li-N-Si$.⁸ (A polysiloxane analogue of a crown ether complex, $[K(OSiMe_2)_7]^+$,⁹ and siloxane-solvation of Na and K centres within complex polysiloxane frameworks¹⁰ were recently reported.) Remarkably, since siloxanes are normally thought to be much weaker donors than organic ethers,^{6,7,11} the $Li-O$ bond to the siloxane oxygen in **3**, $1.917(12)$ Å, is not significantly longer than those to the thf molecules, mean $1.912(12)$ Å. [See also (d) below. In contrast, the $O-M$ bonds in the Pd and Zr compounds mentioned above are rather long, and this was attributed to the poor donor ability of siloxanes.^{6,7}] The interaction of the oxygen lone pair with Li leads to a large increase in the $Si-O$ bond length to a mean of $1.704(5)$ Å from the $1.63-1.64$ Å usually found in disiloxanes.⁵

(c) The mean $Li-C$ bond length in **3**, $2.12(2)$ Å, is not significantly different from that in **1**, $2.18(1)$ Å, or **2**, $2.156(4)$ Å. To accommodate the demands of the six-membered ring the $C-Li-C$ angle is lowered to $144.2(7)^\circ$, compared with 180° in **1** and $171.4(7)^\circ$ in **2**. The closest contacts between the Li atom and the methyl groups are to $C(6)$ and $C(18)$ [$Li-C(6)$ 3.12 , $Li-C(18)$ 3.00 Å], there are corresponding contacts (3.04 Å) in **2**.

(d) In contrast to **2**, in which the exocyclic $C-SiMe_3$ bonds and endocyclic $C-SiMe_2CH_2$ bonds are all essentially of equal length, mean $1.829(4)^\circ$, in **3** the $C-SiMe_3$ bonds have a mean length of $1.835(4)^\circ$, effectively identical with those in **2**, but the endocyclic $C-SiMe_2O$ bonds have a mean length of only $1.806(6)^\circ$. This can be attributed to more effective delocalization of carbanionic charge by negative hyperconjugation¹² directed towards oxygen rather than towards carbon.⁷ Such enhancement of the negative charge on the oxygen atom could strengthen the $O(1)-Li(2)$ interaction. (Or, from an alternative viewpoint, this interaction could enhance the hyperconjugation.)

(e) The mean of the $Si-C-Si$ angles in **3** is 117.3° , compared with 115.9° in **2**, but, the separate values, and those of the $Li-C-Si$ angles, range more widely than in **2**. The $Me_3Si-C-SiMe_3$ angles, mean $114.0(2)^\circ$, are markedly smaller than the $Me_3Si-C-SiMe_2O$ angles, mean 119.6° , these latter angles varying

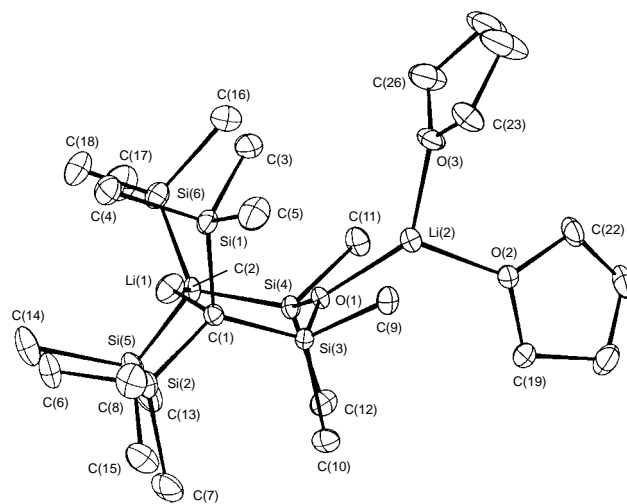


Fig. 1 Selected bond lengths (Å) and angles ($^\circ$) for **3**: $C(1)-Si(1)$ $1.843(7)$, $C(1)-Si(2)$ $1.829(7)$, $C(1)-Si(3)$ $1.809(6)$, $C(2)-Si(4)$ $1.804(6)$, $C(2)-Si(5)$ $1.834(7)$, $C(2)-Si(6)$ $1.836(7)$, $C(1)-Li(1)$ $2.105(14)$, $C(2)-Li(1)$ $2.13(2)$, $O(1)-Si(3)$ $1.706(5)$, $O(1)-Si(4)$ $1.702(5)$, $O(1)-Li(2)$ $1.917(12)$, $O(2)-Li(2)$ $1.909(12)$, $O(3)-Li(2)$ $1.914(13)$, $Si-Me$ (mean) $1.886(6)$; $Si(1)-C(1)-Si(2)$ $113.5(3)$, $Si(1)-C(1)-Si(3)$ $115.5(3)$, $Si(2)-C(1)-Si(3)$ $124.4(4)$, $Si(4)-C(2)-Si(5)$ $117.8(4)$, $Si(4)-C(2)-Si(6)$ $120.8(4)$, $Si(5)-C(2)-Si(6)$ $114.6(3)$, $C(1)-Li(1)-C(2)$ $144.2(7)$, $Li(1)-C(1)-Si(3)$ $93.2(4)$, $Li(1)-C(2)-Si(4)$ $94.8(4)$, $Li(1)-C(1)-Si(1)$ $99.6(5)$, $Li(1)-C(2)-Si(5)$ $104.5(5)$, $Li(1)-C(2)-Si(6)$ $97.2(5)$, $Si(3)-O(1)-Li(2)$ $109.1(5)$, $Si(4)-O(1)-Li(2)$ $111.0(5)$, $O(1)-Li(2)-O(2)$ $125.6(7)$, $O(1)-Li(2)-O(3)$ $133.2(7)$, $O(2)-Li(2)-O(3)$ $101.2(6)$, $Si(3)-O(1)-Si(4)$ $138.5(3)$, $O(1)-Si(3)-C(9)$ $100.3(3)$, $O(1)-Si(3)-C(10)$ $104.3(3)$, $O(1)-Si(4)-C(1)$ $99.4(3)$, $O(1)-Si(4)-C(12)$ $106.1(3)$, $Me-Si-Me$ (mean) $103.9(4)$.

from 115.5(3) to 124.4(4)°. As in **2** the two CSi₃ systems on either side of the molecule are distorted and tilted (with respect to the Li–C bonds) differently; presumably this is predominantly to maximize Me...Me distances, but it also accommodates the observed Me...Li interactions. In consequence the molecule as a whole has no symmetry.

Compound **3** can be expected to serve as a source of the dicarbanionic ligand (Me₃Si)₂CSiMe₂OSiMe₂C(SiMe₃)₂. This ligand should give novel cyclic and linear-polymeric derivatives of a range of metals, and may be especially effective in the case of cyclic derivatives of elements for which the dialkylmetals prefer a bent C–M–C framework, e.g. Ca,¹³ Yb^{14,15} and Eu.¹⁵

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Notes and References

† E-mail: c.eaborn@sussex.ac.uk; j.d.smith@sussex.ac.uk

‡ Water (0.3 cm³) was added to a solution of (Me₃Si)₂(CIME₂Si)CH¹⁶ (4.74 g) in 1,4-dioxane (40 cm³) and the mixture was stirred at room temperature overnight. The solvent was removed to leave (Me₃Si)₂(HOME₂Si)CH³ which was distilled under vacuum then left exposed to the air for 3 days to give O{SiMe₂CH(SiMe₃)₂}₂, with ¹H NMR data identical with those previously reported.³ A solution of LiMe (1.20 mmol) in hexane (0.90 cm³) was added dropwise at room temperature to a stirred solution of the O{SiMe₂CH(SiMe₃)₂}₂ (0.27 g, 0.60 mmol) in thf (10 cm³). The mixture was stirred overnight at room temperature and the solvent then removed under vacuum to leave a sticky solid, which was crystallized from heptane at room temperature. ¹H NMR (C₆D₆): δ_H 0.43 (coincident s, 48 H, SiMe₃ and SiMe₂), 1.30 (s, 8 H, thf) and 3.30 (s, 8 H, thf). δ_C 7.7 (SiMe₃), 8.7 (SiMe₂), 25.1 (thf) and 68.8 (thf). δ_{Si} –10.8 (SiMe₃) and 2.2 (SiMe₂). δ_{Li} 0.63 and 0.78, overlapping. The yield of **3** as estimated from the ¹H NMR spectrum of the initial product solution was >90%.

§ *Crystal data* for **3**: *M* = 607.2; monoclinic, space group *P*2₁/*n* (non-standard no. 14), *a* = 9.416(2), *b* = 16.959(2), *c* = 23.900(4) Å, β = 93.51(10), *U* = 3809(1) Å³, *D*_c = 1.06 Mg m^{–3}, *Z* = 4, *F*(000) = 1336, Mo–Kα radiation, λ = 0.710 73 Å, crystal size 0.2 × 0.2 × 0.1 mm, μ(Mo–Kα) = 0.24 mm^{–1}, *T* = 173(2) K. CAD4 diffractometer, θ–2θ scan mode, 2 < θ < 25°, 6677 independent reflections. Structure solution by direct

methods (SHELXS-86) and full matrix least-squares refinement on *F*² (SHELX-93) with all non-hydrogen atoms anisotropic and H atoms in riding mode with *U*_{iso} = 1.5*U*_{eq}(C). Final *R*₁ = 0.089 for 4429 reflections with *I* > 2σ(*I*), *wR*₂ 0.253 (all data). CCDC 182/870.

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