Crystal Structure of the Tetrahydrofuran Adduct of Tris(trimethylsilyl)methyl-lithium, $[Li(thf)_4][Li\{C(SiMe_3)_3\}_2]$, an Ate Derivative of Lithium

Colin Eaborn,* Peter B. Hitchcock, J. David Smith,* and Alice C. Sullivan
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, U.K.

A crystal structure determination on the tetrahydrofuran adduct of tris(trimethylsilyl)methyl-lithium has shown it to be an ate complex, $[Li(thf)_4][Li\{C(SiMe_3)_3\}_2]$.

Tris(trimethylsilyl)methyl-lithium, which was first prepared in 1970 by metallation of tris(trimethylsilyl)methane with methyl-lithium in ether–tetrahydrofuran (thf),[1] has been widely used in recent years to attach the very bulky tris(trimethylsilyl)methyl group to a metal or metalloid centre, to give compounds of very unusual properties.[2–4] We have now isolated the thf adduct of this organolithium compound and determined its structure by *X*-ray diffraction. The results show that once again the presence of the tris(trimethylsilyl)methyl group induces novel characteristics.

A solution of tris(trimethylsilyl)methane (12.9 mmol) in thf (50 cm^3) was added to powdered methyl-lithium (12.9 mmol) and the resulting solution was kept at the reflux temperature for 6 h then stirred for a further 12 h at room temperature. The thf was removed *in vacuo* and the residue was thoroughly washed with pentane. The residual powder was dissolved in toluene, and the solution was kept at −10 °C for several hours, to give colourless transparent needles of $[Li(thf)_4][Li\{C(SiMe_3)_3\}_2]$ (6.4 g, 65%), which did not melt or collapse below 300 °C; ^1H n.m.r. (C_6D_6), δ 0.45 (s), 1.24 (t), and 3.32 (t) in the expected integration ratio. (The preparation and all manipulations were carried out under argon; both the crystals and the hydrocarbon solutions immediately turn orange-pink on exposure to traces of air.)

Crystal data: $[C_{16}H_{32}LiO_4][C_{20}H_{54}LiSi_6]$, $M = 765.5$, triclinic, space group $P\bar{1}$, $a = 9.411(3)$, $b = 12.045(3)$, $c = 23.354(7)$ Å, $\alpha = 94.47(2)$, $\beta = 90.09(3)$, $\gamma = 93.86(2)°$, $Z = 2$, $D_c = 0.97$ g cm^{-3}. Intensities for unique reflections with $\theta < 18°$ were measured on a CAD 4 diffractometer using monochromated Mo-K_α radiation and a crystal sealed in a capillary. Of 3863 reflections measured only 1526 had $I > \sigma(I)$. Using this limited data set the structure was solved by heavy-atom methods and refined by least squares with isotropic temperature factors to a residual R of 0.18. All the atoms, but particularly the carbon atoms of the thf groups, have high temperature factors, and a difference map shows many peaks of up to 0.7 e Å^{-3} which may represent alternative low occupancy sites for most atoms. In view of the limited data set it was not considered worthwhile to attempt further refinement.†

The unit cell contains two $[Li(thf)_4]$ cations related by an inversion centre and two crystallographically independent $[Li\{C(SiMe_3)_3\}_2]$ anions, each of which lies across an inversion centre. The anions are therefore linear, and the $C(SiMe_3)_3$ groups are staggered about the C–Li–C direction (see Figure 1). The two anions have essentially similar geometries. The Li–C bond lengths, 2.16(1) and 2.20(1) Å, respectively, in the two anions, are similar to that, 2.13(5) Å, in, for example, $[Li\{CH(SiMe_3)_2\}(pmdeta)]$ {pmdeta = $Me_2N[CH_2]_2N(Me)[CH_2]_2NMe_2$}.[5] In contrast to the data for all other known structures of tris(trimethylsilyl)methyl derivatives,[3,7] the mean Me_3Si–C distances, 1.82 Å (averaged over both anions), appear to be shorter than the mean Me–Si distances, of 1.95 Å, but this may be a reflection of the wide error limits in the present case. In the most closely analogous structure, that of the mercurial $[Hg\{C(SiMe_3)_3\}_2]$, the mean Me_3Si–C bond length is 1.887(4) Å and the mean Me–Si bond length is 1.871(3) Å.[3] As usual the Me_3Si–C–$SiMe_3$ angles, mean 114.5°, are larger, and the Me–Si–Me angles (mean 104.3°) smaller than tetrahedral; in $[Hg\{C(SiMe_3)_3\}_2]$ the corresponding angles are 112.6(2) and 106.0(1)°.

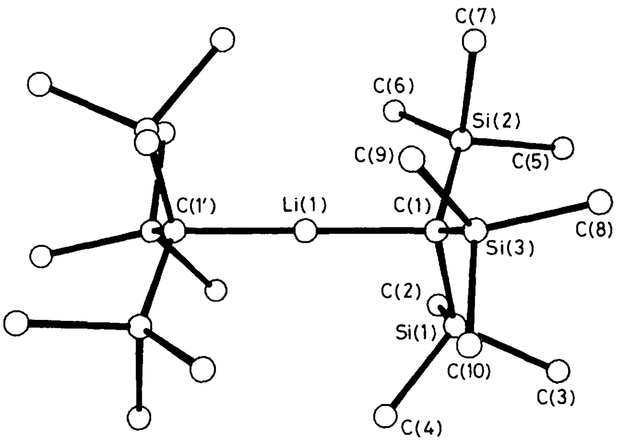

Figure 1. The structure of one of the anions of $[Li(thf)_4][Li\{C(SiMe_3)_3\}_2]$.

The cation has lithium tetrahedrally co-ordinated by four oxygen atoms, as in $[Li(thf)_4][Lu(2,6\text{-dimethylphenyl})_4]$.[6] The average Li–O bond length is 1.96(8) Å.

The results provide, we believe, the first structural characterization of a lithium ate species, although the existence of such compounds has been suspected for a long time.[8] Thus solutions of phenyl-lithium have been postulated to contain $Li[LiPh_2]$ ion pairs,[9] and those of 1 : 1 PhM–PhLi adducts to contain $M[LiPh_2]$ ion pairs (M = Na, K, Cs),[10] and a crystalline complex thought[8a] to be $[Na{\cdot}OEt_2]^+[LiPh_2]^-$ is known.[10] Calculations by Schleyer and his colleagues before our results were available had indicated that the anion $[Li(Me)OH]^-$ should be thermodynamically accessible,[11] and similar calculations have now indicated that this is also the case for $[LiMe_2]^-$.[12] It is possible that the geometry of the bulky tris(trimethylsilyl)methyl group disfavours alternative structures which are normally preferred for alkyl-lithium compounds, such as those with the alkyl group bridging between

---

† The atomic co-ordinates are available on request from the Cambridge Crystallographic Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW; any request should be accompanied by the full literature citation for this communication. Tables of temperature factors, and calculated and observed structure amplitudes are available as Supplementary Publication No. SUP 23702 from the British Library. For details see Instructions for Authors, *J. Chem. Soc., Perkin Trans.* 1 and 2, Issue 1, p. xvii.

lithium atoms, thus making possible isolation of the ate complex.‡

We thank the S.E.R.C. for support and thank Professor P. v. R. Schleyer for helpful comments and for communicating unpublished results.

Received, 28th April 1983; Com. 532

References

1 M. A. Cook, C. Eaborn, A. E. Jukes, and D. R. M. Walton, *J. Organomet. Chem.*, 1970, **24**, 529.

2 For leading references see C. Eaborn, *J. Organomet. Chem.*, 1982, **239**, 93.

3 F. Glockling, N. S. Hosmane, V. B. Mahale, J. J. Swindall, L. Magos, and T. J. King, *J. Chem. Res.*, 1977, (*S*), 116; (*M*), 1201.

4 H. J. Breunig, W. Kanig, and A. Soltani-Neshan, *Polyhedron*, 1983, **2**, 291.

5 M. F. Lappert, L. M. Engelhardt, C. L. Raston, and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1982, 1323.

6 S. A. Cotton, F. A. Hart, M. B. Hursthouse, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1972, 1225.

7 B. Beagley, R. G. Pritchard, C. Eaborn, and S. S. Washburne, *J. Chem. Soc., Chem. Commun.*, 1981, 710; B. Beagley and R. G. Pritchard, *J. Mol. Struct.*, 1982, **84**, 129; C. Eaborn, P. B. Hitchcock, and P. D. Lickiss, *J. Organomet. Chem.*, 1981, **221**, 13; C. Eaborn, P. B. Hitchcock, and K. D. Safa, *ibid.*, 1981, **222**, 187; C. Eaborn, N. Retta, J. D. Smith, and P. B. Hitchcock, *ibid.*, 1982, **235**, 265.

8 (a) G. Wittig, *Angew. Chem.*, 1958, **70**, 65; *Quart. Rev.*, 1966, **20**, 191; (b) W. Tochtermann, *Angew. Chem.*, 1966, **78**, 351.

9 G. Wittig, F. J. Meyer, and G. Lange, *Liebigs Ann. Chem.*, 1951, **571**, 167.

10 G. Wittig, R. Ludwig, and R. Polster, *Chem. Ber.*, 1955, **88**, 294; G. Wittig and F. Bickelhaupt, *ibid.*, 1958, **91**, 865.

11 T. Clark, E. Kaufmann, and P. v. R. Schleyer, personal communication.

12 E. Kaufmann and P. v. R. Schleyer, personal communication.

---

‡ The calculations on $[LiMe_2]^-$ indicate that the negative charge is shared by the two carbon atoms,[12] and Professor P. v. R. Schleyer suggests that stabilization of these negative charges on carbon by the adjacent silicon atoms contributes to the stability of the anion we have observed.