Journal of Organometallic Chemistry, 303 (1986) 321–327
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PREPARATION AND CRYSTAL STRUCTURE OF DIMETHYLTRIS(TRIMETHYLSILYL)METHYLSILANATOLITHIUM TETRAHYDROFURANATE

PETER B. HITCHCOCK, NABEEL H. BUTTRUS and ALICE C. SULLIVAN*

School of Chemistry and Molecular Science, University of Sussex, Brighton BN1 9QJ (Great Britain)

(Received October 15th, 1985)

Summary

A single crystal X-ray diffraction study has shown that the solid isolated after treatment of $(Me_3Si)_3CSiMe_2OH$ with MeLi in THF is the dimeric species $[(Me_3Si)_3CSiMe_2OLi \cdot thf]_2$. Cryoscopy shows the product to be a tetramer in benzene.

There is much current interest in metal alkoxide compounds, particularly those having bulky alkoxide ligands [1]. Although many related silanolate compounds are known [2], structures have been determined in only a few cases. We now report the first example of a dimeric lithium silanolate, $[(Me_3Si)_3CSiMe_2OLi \cdot thf]_2$ (thf = tetrahydrofuran).

Experimental

Preparation of dimethyltris(trimethylsilyl)methylsilanatolithium tetrahydrofuranate $[(Me_3Si)_3CSiMe_2OLi \cdot thf]_2$ *(1)*

Methyllithium (6 cm^3 of a 1.63 mol dm^{-3} solution in Et_2O; 9.78 mmol), was added dropwise under argon to a stirred solution of dimethyltris(trimethylsilyl)methylsilanol [3] (3.0 g, 9.78 mmol) in tetrahydrofuran (20 cm^3) at room temperature. The mixture was stirred for 1 h and the solvent then removed under vacuum. The residual white powder was extracted with toluene and the filtered extract evaporated to dryness to leave compound **1** as a white powder (3.75 g, 95%). Crystals were obtained when a solution of the product in 9/1 toluene/tetrahydrofuran was kept at −10°C for several days, as air- and moisture-sensitive colourless prisms, m.p. 142°C, δ(H) (toluene-d_8) 0.24 (6H, s, $SiMe_2$), 0.33 (27H, s, $C(SiMe_3)$), 1.39 (4H, m, THF), 3.51 (4H, m, THF); $\delta(^7Li)$ (toluene-d_8 rel. to ext. $LiNO_3$ in D_2O) −0.028 (s); molecular weight in freezing benzene 1413 (dimer 735).

TABLE 1

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	*x*	*y*	*z*
Si(1)	3823(4)	6288(4)	1913(2)
Si(2)	2346(12)	7149(12)	1497(4)
Si(3)	2758(10)	5574(9)	1239(3)
Si(4)	1814(8)	5878(11)	2016(4)
Si(5)	7269(5)	6178(5)	1062(2)
Si(6)	8558(13)	6574(8)	333(5)
Si(7)	6696(17)	7249(13)	485(5)
Si(8)	6754(20)	5572(11)	277(6)
O(1)	6290(8)	6246(8)	1213(4)
O(2)	4616(8)	6261(8)	1590(4)
O(3)	5707(9)	4572(8)	1568(4)
O(4)	5661(10)	7895(8)	1643(4)
C(1)	2694(12)	6277(12)	1674(5)
C(2)	7391(13)	6344(11)	545(4)
C(3)	3959(16)	7071(13)	2245(6)
C(4)	4003(15)	5448(12)	2268(6)
C(5)	1487(17)	7176(16)	1098(8)
C(6)	1865(16)	7727(11)	1994(8)
C(7)	3388(16)	7700(13)	1278(7)
C(8)	3329(14)	6122(16)	817(6)
C(9)	3407(14)	4699(11)	1346(6)
C(10)	1567(17)	5185(14)	1098(8)
C(11)	1952(15)	6186(13)	2516(6)
C(12)	589(13)	6209(16)	1856(8)
C(13)	1878(17)	4712(12)	2013(7)
C(14)	8125(20)	6778(24)	1363(7)
C(15)	7656(17)	5131(17)	1118(9)
C(16)	9403(17)	5815(18)	623(11)
C(17)	9008(20)	7535(17)	505(9)
C(18)	8726(17)	6302(14)	−151(6)
C(19)	6485(16)	5884(14)	−269(5)
C(20)	7906(30)	4878(17)	172(8)
C(21)	5782(17)	5171(14)	486(7)
C(22)	7101(28)	7718(12)	−44(7)
C(23)	5436(18)	7035(21)	465(10)
C(24)	6868(27)	8034(17)	872(8)
C(25)	6084(15)	4509(11)	1963(7)
C(26)	5895(18)	3813(15)	2043(9)
C(27)	5499(20)	3386(12)	1725(11)
C(28)	5601(20)	3878(11)	1389(7)
C(29)	6318(20)	7834(15)	1944(7)
C(30)	6231(22)	8769(19)	2065(10)
C(31)	5756(17)	9116(13)	1812(7)
C(32)	5346(17)	8639(12)	1552(7)
Li(1)	5527(34)	5705(24)	1442(16)
Li(2)	5520(29)	6904(22)	1436(12)
Si(2)′	2687(11)	6746(10)	1223(4)
Si(3)′	2409(8)	5236(7)	1562(3)
Si(4)′	1674(13)	6594(7)	2010(5)
Si(6)′	8418(9)	5911(10)	310(5)
Si(7)′	7522(15)	7406(9)	425(5)
Si(8)′	6437(11)	6116(11)	270(5)

TABLE 2

SELECTED BOND LENGTHS (Å) AND ANGLES (°)

Li(1)-O(1)	1.72(5)	Li(1)-O(2)	1.79(5)
Li(2)-O(1)	1.85(4)	Li(2)-O(2)	1.88(4)
Li(1)-O(3)	2.14(5)	Li(2)-O(4)	1.97(4)
O(1)-Si(5)	1.579(14)	O(2)-Si(1)	1.656(14)
mean Si(O)-C	1.93(6)	mean Si-C(Me)	2.02(8)
Me-Si-Me	99(1)-119(2)		
Si-C-Si	101(1)-120(1)		
Li(1)-O(1)-Li(2)			76(2)
Li(1)-O(2)-Li(2)			73(2)

Crystal data for 1. $C_{32}H_{82}Li_2O_4Si_8$, $M = 735.4$, orthorhombic, space group *Pbca*, a 15.121(6), b 18.335(1), c 35.297(1) Å, U 9785.6 Å^3, $Z = 8$, D_c 0.99 g cm^{-3}. Cu-K_α radiation (Ni filter), λ 1.5418 Å, μ 23.1 cm^{-1}.

A crystal ca. 0.5 × 0.5 × 0.5 mm, sealed in a capillary under argon was mounted on an Enraf–Nonius CAD4 diffractometer. Intensities for unique data with $2 < \theta < 55°$ were measured by an ω–2θ scan with a maximum scan time of 60 s. No correction was made for absorption. 1962 reflections with $|F^2| > \sigma(F^2)$ were used in the refinement where $\sigma(F^2) = [\sigma^2(I) + (0.02I)^2]^{1/2}/\text{Lp}$.

The structure was solved by direct methods using MULTAN, and refinement was by full matrix least-squares. The silicon atoms in the $(Me_3Si)_3C$ groups were found to be disordered equally between two sets of sites. No attempt was made to include H atoms. Refinement with all atoms anisotropic converged at $R = 0.15$, $R' = 0.14$ with a weighting scheme of $w = (\sigma^2(F))^{-1}$. A final difference map had peaks of up to 0.44 eÅ^{-3}. All calculations were carried out on a PDP11/34A computer using the Enraf–Nonius SDP-Plus program package.

Atomic coordinates are given in Table 1, bond lengths and angles in Tables 2 and 3.

Results and discussion

The dimer **1** shown in Fig. 1 has a non-planar 4-atom Li_2O_2 central core. The bulky silanolate group prevents the lithium atom from attaining a coordination number of more than three, the third site being occupied by a molecule of tetrahydrofuran. There is a dihedral angle of 29.3° between the planes described by O(1), O(2), Li(1), O(3), and O(1), O(2), Li(2), O(4). This contrasts with the geometry of the related alkoxide $[(Me_3C)_3COLi \cdot thf]_2$ [1f] and phenoxide $[Li(OC_6H_4Me\text{-}4\text{-}Bu^t{}_2\text{-}2,6\text{-}) \cdot Et_2O]_2$ [1g], which have planar Li_2O_2 central cores. The wide variations in the bond lengths and angles and the deviation from planarity in the Li_2O_2 core indicate that there is considerable strain in molecule **1**. The bulky $(Me_3Si)_3CSiMe_2$ groups and the coordinated THF molecules lie on opposite sides of this core.

The nature of the disorder in the $(Me_3Si)_3C$- ('trisyl') groups is shown in Fig. 2. There is disorder between two alternative orientations of the group represented by the filled bonds and the unfilled bonds. In both cases the methyl C atoms are at nearly the same position, and a single site is refined for each. However, because the

TABLE 3

INTRAMOLECULAR DISTANCES (Å) AND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Si(1)–O(2)	1.656(14)	Si(1)–C(1)	1.91(2)
Si(1)–C(3)	1.86(2)	Si(1)–C(4)	2.01(2)
Si(2)–C(1)	1.80(3)	Si(2)–C(5)	1.92(3)
Si(2)–C(6)	2.18(3)	Si(2)–C(7)	2.02(3)
Si(3)–C(1)	2.01(2)	Si(3)–C(8)	1.99(3)
Si(3)–C(9)	1.92(3)	Si(3)–C(10)	2.00(3)
Si(4)–C(1)	1.94(2)	Si(4)–C(11)	1.87(2)
Si(4)–C(12)	2.03(2)	Si(4)–C(13)	2.14(3)
Si(5)–O(1)	1.579(14)	Si(5)–C(2)	1.86(2)
Si(5)–C(14)	2.00(3)	Si(5)–C(15)	2.02(3)
Si(6)–C(2)	1.96(3)	Si(6)–C(16)	2.15(4)
Si(6)–C(17)	1.98(3)	Si(6)–C(18)	1.80(3)
Si(7)–C(2)	1.98(3)	Si(7)–C(22)	2.14(3)
Si(7)–C(23)	1.95(4)	Si(7)–C(24)	2.00(4)
Si(8)–C(2)	1.96(3)	Si(8)–C(19)	2.05(3)
Si(8)–C(20)	2.19(5)	Si(8)–C(21)	1.80(4)
O(1)–Li(1)	1.72(5)	O(1)–Li(2)	1.85(4)
O(2)–Li(1)	1.79(5)	O(2)–Li(2)	1.88(4)
O(3)–C(25)	1.51(3)	O(3)–C(28)	1.43(3)
O(3)–Li(1)	2.14(5)	O(4)–C(29)	1.46(3)
O(4)–C(32)	1.48(3)	O(4)–Li(2)	1.97(4)
C(25)–C(26)	1.34(3)	C(26)–C(27)	1.49(5)
C(27)–C(28)	1.50(4)	C(29)–C(30)	1.77(4)
C(30)–C(31)	1.31(4)	C(31)–C(32)	1.41(4)
Si(2)′–C(1)	1.81(2)	Si(3)′–C(1)	2.00(2)
Si(4)′–C(1)	2.03(3)	Si(6)′–C(2)	1.93(3)
Si(7)′–C(2)	2.00(3)	Si(8)′–C(2)	1.79(3)

O(2)–Si(1)–C(1)	110(8)	O(2)–Si(1)–C(3)	112(1)
O(2)–Si(1)–C(4)	108(1)	C(1)–Si(1)–C(3)	113(1)
C(1)–Si(1)–C(4)	113(1)	C(3)–Si(1)–C(4)	101(1)
C(1)–Si(2)–C(5)	118(2)	C(1)–Si(2)–C(6)	105(1)
C(1)–Si(2)–C(7)	110(1)	C(5)–Si(2)–C(6)	111(1)
C(5)–Si(2)–C(7)	104(1)	C(6)–Si(2)–C(7)	109(1)
C(1)–Si(3)–C(8)	106(1)	C(1)–Si(3)–C(9)	114(1)
C(1)–Si(3)–C(10)	112(1)	C(8)–Si(3)–C(9)	110(1)
C(8)–Si(3)–C(10)	112(1)	C(9)–Si(3)–C(10)	102(1)
C(1)–Si(4)–C(11)	114(1)	C(1)–Si(4)–C(12)	110(1)
C(1)–Si(4)–C(13)	110(1)	C(11)–Si(4)–C(12)	106(1)
C(11)–Si(4)–C(13)	108(1)	C(12)–Si(4)–C(13)	110(1)
O(1)–Si(5)–C(2)	114(1)	O(1)–Si(5)–C(14)	113(1)
O(1)–Si(5)–C(15)	108(1)	C(2)–Si(5)–C(14)	111(1)
C(2)–Si(5)–C(15)	103(1)	C(14)–Si(5)–C(15)	107(1)
C(2)–Si(6)–C(16)	102(1)	C(2)–Si(6)–C(17)	112(1)
C(2)–Si(6)–C(18)	115(1)	C(16)–Si(6)–C(17)	103(1)
C(16)–Si(6)–C(18)	101(1)	C(17)–Si(6)–C(18)	119(2)
C(2)–Si(7)–C(22)	106(1)	C(2)–Si(7)–C(23)	111(2)
C(2)–Si(7)–C(24)	118(2)	C(22)–Si(7)–C(23)	109(2)
C(22)–Si(7)–C(24)	106(2)	C(23)–Si(7)–C(24)	107(2)
C(2)–Si(8)–C(19)	111(1)	C(2)–Si(8)–C(20)	96(2)
C(2)–Si(8)–C(21)	120(1)	C(19)–Si(8)–C(20)	99(1)
C(19)–Si(8)–C(21)	110(2)	C(20)–Si(8)–C(21)	119(2)
Si(5)–O(1)–Li(1)	138(2)	Si(5)–O(1)–Li(2)	142(2)

TABLE 3 (continued)

Li(1)-O(1)-Li(2)	76(2)	Si(1)-O(2)-Li(1)	141(2)
Si(1)-O(2)-Li(2)	135(2)	Li(1)-O(2)-Li(2)	73(2)
C(25)-O(3)-C(28)	113(2)	C(25)-O(3)-Li(1)	108(2)
C(28)-O(3)-Li(1)	139(2)	C(29)-O(4)-C(32)	117(2)
C(29)-O(4)-Li(2)	106(2)	C(32)-O(4)-Li(2)	137(2)
Si(1)-C(1)-Si(2)	114(1)	Si(1)-C(1)-Si(3)	108(1)
Si(1)-C(1)-Si(4)	110(9)	Si(2)-C(1)-Si(3)	109(1)
Si(2)-C(1)-Si(4)	111(1)	Si(3)-C(1)-Si(4)	105(1)
Si(5)-C(2)-Si(6)	120(1)	Si(5)-C(2)-Si(7)	101(1)
Si(5)-C(2)-Si(8)	108(1)	Si(6)-C(2)-Si(7)	105(1)
Si(6)-C(2)-Si(8)	114(1)	Si(7)-C(2)-Si(8)	107(1)
O(3)-C(25)-C(26)	101(2)	C(25)-C(26)-C(27)	115(3)
C(26)-C(27)-C(28)	104(2)	O(3)-C(28)-C(27)	101(2)
O(4)-C(29)-C(30)	93(2)	C(29)-C(30)-C(31)	110(3)
C(30)-C(31)-C(32)	112(2)	O(4)-C(32)-C(31)	107(2)
O(1)-Li(1)-O(2)	109(3)	O(1)-Li(1)-O(3)	125(3)
O(2)-Li(1)-O(3)	126(3)	O(2)-Li(2)-O(4)	123(2)
O(1)-Li(2)-O(2)	100(2)	O(1)-Li(2)-O(4)	134(3)
Si(2)'-C(1)-Si(3)'	106(1)	Si(2)'-C(1)-Si(4)'	112(1)
Si(3)'-C(1)-Si(4)'	103(1)	Si(6)'-C(2)-Si(7)'	103(1)
Si(6)'-C(2)-Si(8)'	109(1)	Si(7)'-C(2)-Si(8)'	101(1)

methyl C positions represent an average of two close but not identical positions, any bond lengths and angles involving the methyl groups are unreliable.

We believe that this is the first observation of a dimeric structure for an alkali

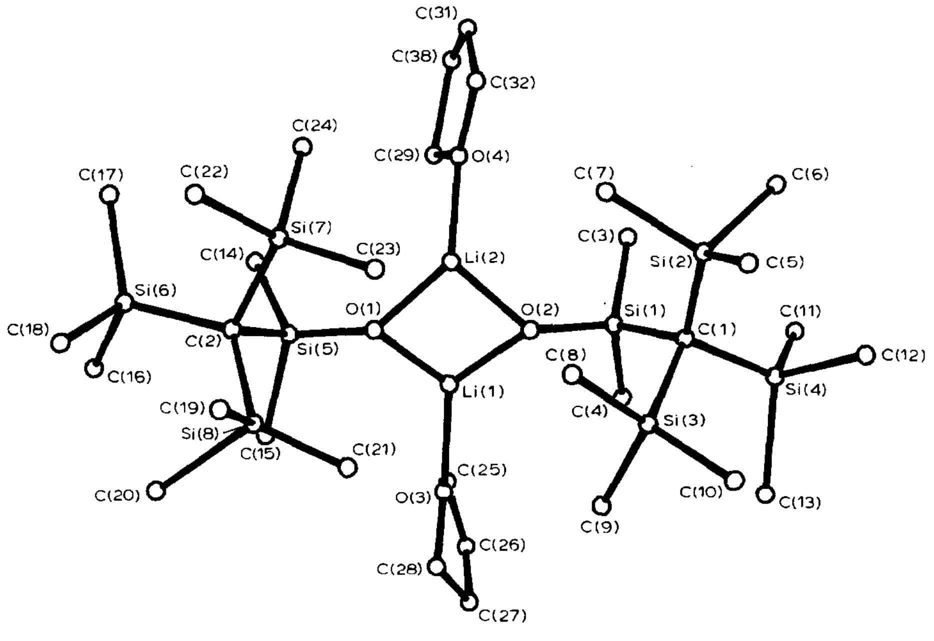

Fig. 1. The molecular structure and atom numbering scheme for $[(Me_3Si)_3CSiMe_2OLi \cdot thf]_2$.

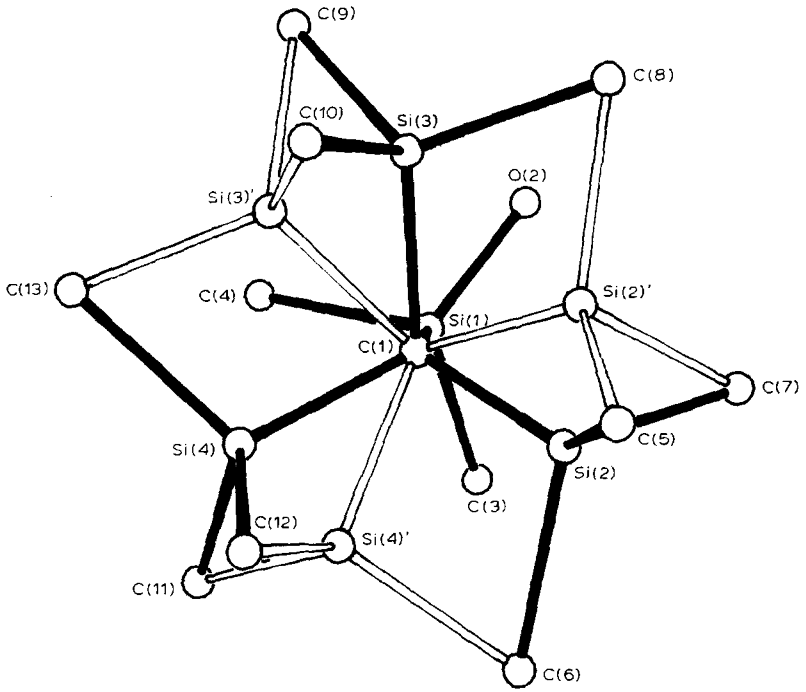

Fig. 2. One of the $(Me_3Si)_3C$ groups showing disordered Si positions. The other $(Me_3Si)_3C$ group is similarly disordered.

metal silanolate; all the other known structures are of the 'cubane' type [4–6]. The Si–O distances and the Si(O)–C distances are similar to those found in related systems. The Si–O distances also agree well with those in sodium orthosilicate Na_4SiO_4 [7].

Although compound **1** is dimeric as solid, like many other alkali metal silanolates it was found to be tetrameric in freezing benzene solution, and the usual cubane structure in which lithium has a coordination number of four is probably adopted. The ^7Li NMR spectrum showed only one peak, which did not change on raising or lowering the temperature, suggesting that only one species is present in solution. In view of the tetrameric nature of **1** in solution, it is possible that compounds such as $[M(OSiMe_3)(OPMe_3)]$ [6] with M = Li, Na or K, which are tetrameric in solution may also be dimeric in the solid.

It is noteworthy that Damrauer suggested [8] that the silanol $(Me_3Si)_3CSiMe_2OH$ cannot be metallated by n-butyllithium. Previous work by Eaborn et al., [3] as well as the present work show that it can be readily metallated with MeLi in THF.

Acknowledgement

We thank the S.E.R.C. for financial support via Professor C. Eaborn.

References

1 (a) M.L. Listemann and R.R. Schrock, Organometallics, 4 (1985) 74; (b) M.H. Chisholm and D.M. Hoffmann, J. Am. Chem. Soc., 104 (1984) 6815; (c) F.A. Cotton, W. Schwotzer and E.S. Shamshoum,

Organometallics, 2 (1983) 1167; (d) T.V. Lubben, P.T. Wolczanski and G.D. Van Duyne, Organometallics, 4 (1984) 977; (e) B.D. Murray and P.P. Power, J. Am. Chem. Soc., 106 (1984) 7011; (f) J. Hvoslef, H. Hope, B.D. Murray and P.P. Power, J. Chem. Soc., Chem. Commun., (1983) 1438; (g) B. Cetinkaya, I. Gumrukai and M.F. Lappert, J. Am. Chem. Soc., 102 (1980) 2086.

2 (a) H. Schmidbaur, Angew. Chem. Int. Ed. Engl., 4 (1965) 201; (b) F. Schindler and H. Schmidbaur, Angew. Chem. Int. Ed. Engl., 6 (1967) 683.

3 C. Eaborn and K.D. Safa, J. Organomet. Chem., 234 (1982) 7.

4 H.F. Grutzmacher, K. Hoffmann and E. Weiss, Chem. Ber., 103 (1970) 1190.

5 O. Graalmann, U. Klingebiel, W. Clegg, M. Haase and G.M. Sheldrick, Angew. Chem. Int. Ed. Engl., 23 (1984) 891.

6 J. Aldkofer and H. Schmidbaur, Chem. Ber., 105 (1972) 1956.

7 M.G. Barker and P.G. Gadd, J. Chem. Res. (S), (1981) 274.

8 R. Damrauer, J. Organomet. Chem., 216 (1981) C1.