The novel linear-polymeric organolithium compound $\{(Me_2NMe_2Si)_3CLi\}_\infty$

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The compound $(Me_2NMe_2Si)_3CH$ is readily metallated by MeLi in THF to give the linear-polymeric $\{(Me_2NMe_2Si)_3CLi\}_\infty$, in which two of the N atoms in each planar carbanionic unit $(Me_2NMe_2Si)_3C^-$ are attached to one lithium atom and the remaining N atom to another Li atom; each Li shows planar three-coordination.

There is much current interest in the structures of organic derivatives of alkali-metal compounds,[1] and especially of organolithium compounds.[2] We describe below an organolithium compound that has an unprecedented structure, with several unusual features, and possesses important potential for synthesis of other novel organometallic compounds.

The new species, **1**, was made by metallation of $(Me_2NMe_2Si)_3CH$ [prepared from the previously described[3] $(BrMe_2Si)_3CH$] with MeLi in Et_2O or THF (tetrahydrofuran).† The metallation was complete within 3 h at room temperature, in contrast with that of the related substrate $(Me_3Si)_3CH$, which required 4–6 h in refluxing THF.[4] The formation of **1** is probably facilitated by coordination of the amino group to the metal.

The product was recrystallized from toluene and an X-ray diffraction study showed the crystal to consist of a parallel array of linear polymers based on the unit depicted in Fig. 1.‡ This unit shows several interesting features, as follows.

(*a*) There is a central six-membered ring that can be regarded as a chair form of cyclohexane with two carbon atoms replaced by silicon atoms, two by nitrogen atoms, and one by a lithium atom. This last atom is then bonded to the nitrogen atom of an Me_2NSi group in the next molecule. (For an account of interesting compounds in which there is intra- or intermolecular coordination of N centres to Li, see ref. 5.)

(*b*) The ring contains a planar carbanion centre (sum of angles 359.6°), a planar three-coordinate Li centre (sum of angles 359.5°), and two four-coordinate N centres. There is a considerable distance within the chain between the negative carbanion centre and the region of positive charge around the Li centre (with the positive charge formally dispersed over three N atoms). We are aware of no other polymeric organoalkali-metal compound in which there are such 'free' carbanionic centres; there are some, of the type $\cdots R^-M^+R^-M^+\cdots$ [*e.g.* R = $(Me_3Si)_3C$, M = K,[6] Rb;[7] R = $(PhMe_2Si)_3C$, M = Na,[8] K,[6] Cs;[9] R = $(Me_3Si)_2CH$, M = Li,[10a] Na[10b]] in which there are planar or near-planar carbanionic centres, but in each case there is interaction between such centres and alkali-metal ions on either side of them in the chain. In the crystals of **1** the parallel chains line up with the Li atoms in one chain almost alongside the carbanionic centre in the adjacent chain but at much too long a distance (*ca.* 7 Å) for significant interaction.

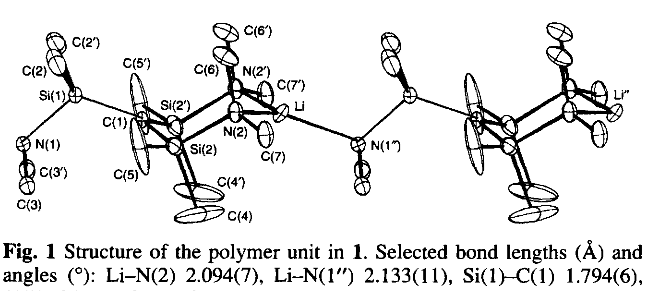

Fig. 1 Structure of the polymer unit in **1**. Selected bond lengths (Å) and angles (°): Li–N(2) 2.094(7), Li–N(1'') 2.133(11), Si(1)–C(1) 1.794(6), Si(2)–C(1) 1.791(3), Si(1)–N(1) 1.827(5), Si(2)–N(2) 1.792(4), N(2)–Li–N(2') 109.7(5), N(2)–Li–N(1'') 124.9(3), C(1)–Si(1)–N(1) 115.3(3), Si(1)–C(2)–Si(2) 121.5(2), Si(2')–C(1)–Si(2) 116.6(3), C(1)–Si(2)–N(2) 114.4(2), Si(2)–N(2)–Li 107.5(3) (Symmetry transformations used to generate equivalent atoms: ' $x, -y + \frac{1}{2}, z$; '' $x, y, z - 1$).

(*c*) The $C{-}SiMe_2NMe_2$ bonds, mean 1.793(6) Å, are much shorter than common Si–C(sp^3) bonds, which usually lie in the range 1.86–1.90 Å;[11] similarly short bonds, mean 1.80 Å, were observed in the carbanion of the salt $[Li(12\text{-crown-}4)_2][C(FMe_2Si)(Me_3Si)_2]$,[12] and can be attributed to delocalization of the negative charge either by $d_\pi{-}p_\pi$ bonding or, more likely, to negative hyperconjugation,[13] leading to some double-bond character in the Si–C bonds.

(*d*) As a consequence of the coordination of the N atoms to Li, the Si–N bonds are exceptionally long, especially those within the ring [Si(1)–N 1.827(5), Si(2')–N 1.792(4) Å]; those in $R_3Si{-}NR'_2$ species fall in the range 1.71–1.72 Å.[14]

It is noteworthy that in the solid the analogous species $(MeOSiMe_2Si)_3Li$ exists as dimers in which all three OMe groups are likewise engaged in coordination to Li, two within a six-membered ring, though in this case constrained into a boat conformation (see the skeleton depicted in Fig. 2) but with the third intramolecularly coordinated within its component molecule, and the carbanionic centre definitely bonded to a Li centre, though at an unusually long distance of 2.401(9) Å.[15] It can be seen that breaking of the weak C–Li bonds in the dimer would give a unit closely analogous to that in **1** with the potential to form a similar linear polymer. Conversely **1** could conceivably break down under appropriate conditions to give dimers like those in Fig. 2.

Much novel chemistry has emerged from use of the reagent $(Me_3Si)_3CLi$ to attach the very bulky ligand $(Me_3Si)_3C^-$ to a wide range of metals and metalloids. [For the nature of the reagent in the solid and in solution see ref. 4(*b*)]. Even more unusual species should be formed by analogous use of **1** as a source of the equally bulky ligand $(Me_2NMe_2Si)_3C^-$, in which the amino groups are available to coordinated either to the metal atoms to which the central carbon is attached or to another metal centre, or to both. We have shown that **1** can be used in this way by treating it with $SiMe_2HCl$, $SnMe_3Cl$, and $HgBr_2$ to give $Si\{C(SiMe_2NMe_2)_3\}Me_2H$, $Sn\{C(SiMe_2NMe_2)_3\}Me_3$ and $Hg\{C(SiMe_2NMe_2)_3\}_2$, respectively.

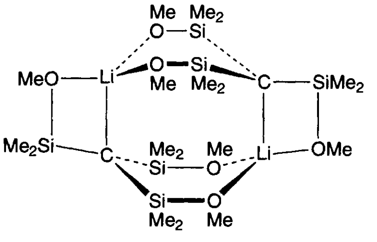

Fig. 2 The skeleton of the dimer formed by $(MeOSiMe_2Si)_3CLi$

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Footnotes

† Anhydrous Me_2NH (36 g, 0.80 mol) was condensed into a stirred solution of $(BrMe_2Si)_3CH$ (34 g, 0.80 mol) in Et_2O (300 cm^3) held at −78 °C under argon. The stirred mixture was allowed to warm to room temp. and stirring was continued for a further 4 h. The solution was filtered, the solvent removed under vacuum, and the residue distilled at 110 °C (*ca.* 0.04 mmHg) to give $(Me_2NMe_2Si)_3CH$ (23.3 g, 91%); NMR (C_6D_6) δ_H 0.05 (s, CH), 0.22 (s, MeSi) and 2.39 (s, MeN); δ_C 1.1 (MeSi), 6.1 (CH), 38.4 (MeN); *m/z* 304 (5%, M − Me), 274 (80, M − Me_2NH), 28 (100).

A solution of MeLi (8.22 mmol) in THF (25 cm^3) was added to a solution of $(Me_2NMe_2Si)_3CH$ (2.63 g) in THF under argon. The mixture was stirred for 3 h, the solvent then removed under vacuum, and the residue was washed with cold light petroleum (bp 40–60 °C) then recrystallized from toluene to give crystals of **1** (2.1 g; 78%), mp 198.5–199.5 °C (after turning brown at 185 °C) (Found: C, 47.5; H, 10.6; N, 12.5. $C_{13}H_{36}LiN_3Si_3$ requires: C, 47.9: H 11.4; N 12.9%); NMR (THF) δ_H 0.12 (18H, s, SiMe) and 2.41 (18H, s, NMe); δ_{Si} 10.2 and 6.5 (in 1 : 2 ratio).

‡ *Crystal data*: $C_{13}H_{36}LiN_3Si_3$, M = 325.7, orthorhombic, space group *Pnma* (no. 62), a = 14.660(2), b = 15.649(3), c = 8.485(3) Å, U = 1946.6(8) Å^3, Z = 4, D_o = 1.11 g cm^{-3}, $F(000)$ = 720, λ = 0.71073 Å, μ = 2.4 cm^{-1}. Intensities were measured on an Enraf-Nonius CAD4 diffractometer for 1775 unique reflections with $2 < \theta < 25°$. The structure was solved by direct methods (SHELXS-86) and refined by full-matrix least squares on F^2 (SHELXL-93) using all data. Non-hydrogen atoms were anisotropic and H atoms were included in riding mode. Final residuals were $R1$ = 0.070, $wR2$ = 0.160 [for 1070 reflections with $I > 2\sigma(I)$] and $R1$ = 0.126, $wR2$ = 0.194 (for all data). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/4.

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