Crystal Structure of $[Li(tmen)_2][Li\{C(SiMe_3)_3\}_2]$. A Multinuclear Magnetic Resonance Study of Tris(trimethylsilyl)methyllithium–Tetrahydrofuran(1/2) and –*N,N,N′,N′*-Tetramethylethylenediamine (1/1) (tmen)†

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A single-crystal X-ray study of $(Me_3Si)_3CLi{\cdot}tmen$ (tmen = *N,N,N′,N′*-tetramethylethylenediamine) shows that it crystallises with the ionic structure $[Li(tmen)_2][Li\{C(SiMe_3)_3\}_2]$ but that the anions pack with different orientations from those in crystalline $[Li(thf)_4][Li\{C(SiMe_3)_3\}_2]$ (thf = tetrahydrofuran). The ^1H, ^7Li, ^{13}C and ^{29}Si NMR spectra of $(Me_3Si)_3CLi{\cdot}2thf$ and $(Me_3Si)_3CLi{\cdot}tmen$ in thf and toluene, and ^7Li, ^{13}C and ^{29}Si NMR spectra of the solids are described. Spectra obtained from solutions below *ca.* 25 °C show the presence of ion pairs $[Li(thf)_4][Li\{C(SiMe_3)_3\}_2]$ or $[Li(tmen)_2][Li\{C(SiMe_3)_3\}_2]$, together with further species which appear to be different in thf and toluene. Spectra from solutions at higher temperatures show inter-species exchange on the NMR timescale.

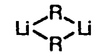
Tris(trimethylsilyl)methyllithium, RLi **1** [R = $(Me_3Si)_3C$], is usually obtained by metallation of tris(trimethylsilyl)methane, RH, with methyllithium in thf–diethyl ether [1,2] or butyllithium–tmen in hexane.[3] The compounds that crystallise out are the dialkyllithiates **2** or **3** in which donor species are incorporated into the cations.[4,5] More recently, the reaction between RHgBr and 2 equivalents of butyllithium in hexane has been shown to give solvent-free RLi which is dimeric (**4**) in the solid, with two-co-ordinate lithium interacting with the central carbon atom on the group R and more weakly with the C and H atoms of the Me_3Si groups attached to it.[6]

$[Li(thf)_4][LiR_2]$

2

$[Li(tmen)_2][LiR_2]$

3



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The reagent **1** has been used to synthesise compounds in which the bulky group R is attached to a wide range of elements but the actual organolithium species in solution have not been firmly established. For some years it has been our practice to monitor the progress of the reaction between methyllithium and $(Me_3Si)_3CH$ by NMR spectroscopy at 60 or 90 MHz, the sharp peak due to RH being progressively replaced by a much broader peak at lower frequency. The broadness of the signal from the lithium reagent suggested that in solution there might be several species that were exchanging on the NMR timescale. This was confirmed by spectra obtained at 250–500 MHz and the lineshapes were found to depend on solvent, concentration and temperature. The solid-state NMR spectra were recorded in order to determine whether the ionic species observed in the crystal were present in solution also.

We discuss the results below together with the crystal structures of compounds **2** and **3**, which have previously been described only briefly.[4,5]

Experimental

Organolithium compounds were protected from air and moisture by use of Schlenk-tube techniques. Solid samples for NMR measurements were prepared in a glove-box.

NMR Measurements.—The ^1H and ^{13}C NMR spectra of samples in $[^2H_8]$toluene or $[^2H_8]$thf were recorded on Bruker WM 360, AC 300, AC-P 250 or AMX 500 instruments with solvent peaks as internal standards and ^{29}Si NMR spectra [refocused INEPT (insensitive nuclei enhanced by polarisation transfer) with or without ^1H decoupling] on the AC 300 and AC-P 250 spectrometers. Chemical shifts (ppm) are relative to $SiMe_4$. The ^7Li NMR spectra were recorded on the AC-P 250 with 1 mol dm^{-3} LiCl in D_2O as external reference. Cross-polarisation magic-angle-spinning (CP MAS) NMR spectra were recorded on the Bruker AC-P 250 instrument with a spinning rate of *ca.* 4 kHz.

Tris(trimethylsilyl)methane.—A cold (−78 °C) solution of LiBu (0.75 mol) in hexane (300 cm^3) was added dropwise to a mixture of $CHBr_3$ (0.25 mol, 22 cm^3), $SiMe_3Cl$ (0.9 mol, 115 cm^3) and thf (300 cm^3) cooled to −78 °C. After addition was complete the stirred mixture was allowed to warm to room temperature. It was then filtered and solvent was removed from the filtrate under reduced pressure to give $(Me_3Si)_3CH$ (39 g, 65%), b.p. 98–102 °C at 21 Torr (lit.[2] 104 °C at 20 Torr), $\delta_H(CCl_4–CH_2Cl_2)$ −0.80 (1 H, s, CH) and 0.10 (27 H, s, $SiMe_3$). The NMR data in ref. 2 are incorrect.

Tris(trimethylsilyl)methyllithium–thf(1/2).—Solid samples were made as described previously.[4]

Tris(trimethylsilyl)methyllithium–tmen(1/1).—An excess of tmen (7.0 g, 0.06 mol) was added to a solution of compound **2** (4.8 g) in toluene (80 cm^3) and the mixture was stirred for 10 min. Solvent was removed in vacuum and the residue washed several times with light petroleum (b.p. 60–80 °C) and pumped dry.

Crystal Structure of Compound 3.—*Crystal data.* $C_{32}H_{86}Li_2N_4Si_6$, *M* = 709.5, orthorhombic, space group *Iba*2, *a* =

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: Torr ≈ 133 Pa.

Dedicated to Professor H. Nöth on his 65th birthday.

19.252(2), b = 14.006(2), c = 18.169(2) Å, U = 4899.2 Å^3, Z = 4, D_c = 0.96 g cm^{-3}, $F(000)$ = 1584, monochromated Mo-Kα radiation, λ = 0.710 69 Å, μ = 1.9 cm^{-1}.

Structure determination. Data were measured on an Enraf–Nonius CAD4 diffractometer at 20 °C with a crystal of size 0.5 × 0.5 × 0.5 mm sealed in a thin-walled capillary. Intensities for $+h$ $+k$ $+l$ reflections with $2 < \theta < 25°$ were measured by a θ–2θ scan with width $\Delta\theta = (1.0 + 0.35 \tan\theta)$. Two standard reflections monitored every hour showed no significant variation. Data were corrected for Lorentz and polarisation effects but not for absorption: 1263 reflections with $|F^2| > \sigma(F^2)$ were used in the structure analysis (226 parameters).

The structure was initially assumed to be in the space group $Iba2$ since with Z = 4 the space group $Ibam$ would imply that both ions were disordered. A partial structure was found by direct methods using MULTAN[7] and the remaining atoms were located from electron-density maps. Both cation and anion lie across crystallographic two-fold axes: the anion has alternative Si sites with equal occupancy so the anion symmetry is approximately $2/m$, compatible with $Ibam$. There is no disorder in the cation so the space group must be $Iba2$. Refinement of non-hydrogen atoms with anisotropic thermal parameters was by full-matrix least squares and the z coordinate of Li(1) was fixed in order to define the origin. Refinement converged at R = 0.093, R' = 0.111 with $w = 1/\sigma^2(F)$. Hydrogen atoms were not included. The shift/error in the final cycle was 0.3 and the residual electron density everywhere was < 0.3 e Å^{-3}.

Table 1 Fractional atomic coordinates (× 10^4) for compound **3** with estimated standard deviations (e.s.d.s) in parentheses

	x	y	z
Si(1)	3888(3)	1451(4)	611(4)
Si(2)	3394(3)	−589(5)	339(4)
Si(3)	3724(4)	703(5)	−993(4)
Si(4)	6260(3)	−723(6)	887(4)
Si(5)	6605(3)	580(4)	−396(3)
Si(6)	6054(3)	−1445(5)	−715(5)
Li(1)	5000(1)	0(0)	29(0)
C(1)	3895(4)	425(6)	−36(9)
C(2)	2996(7)	1644(9)	956(7)
C(3)	4482(8)	1258(10)	1371(8)
C(4)	4277(6)	2620(8)	−228(16)
C(5)	3704(6)	−1793(7)	−49(13)
C(6)	2418(5)	−535(7)	−96(12)
C(7)	3396(8)	−557(12)	1371(7)
C(8)	3029(6)	1819(11)	−1204(9)
C(9)	4531(6)	1287(11)	−1517(8)
C(10)	3479(9)	−546(12)	−1603(8)
Li(2)	5000(0)	5000(0)	2536(15)
N(1)	4188(5)	5726(11)	1793(7)
N(2)	4167(5)	4294(6)	2994(5)
C(11)	3562(7)	4797(12)	2845(7)
C(12)	3568(6)	5079(14)	2050(10)
C(13)	4220(8)	5583(12)	1000(7)
C(14)	4218(9)	6791(11)	2156(13)
C(15)	4040(7)	3317(9)	2822(8)
C(16)	4232(12)	4101(14)	3836(10)

Table 2 Selected intramolecular distances (Å) and angles (°) for compound **3** with e.s.d.s in parentheses

Li(1)–C(1)	2.213(5)	Si(4)–C(1′)	1.755(12)
Si(1)–C(1)	1.857(9)	Si(5)–C(1′)	1.826(8)
Si(2)–C(1)	1.846(8)	Si(6)–C(1′)	1.890(11)
Si(3)–C(1)	1.811(12)		
C(1)–Li(1)–C(1′)	174(2)	N(1)–Li(2)–N(2″)	85.4(2)
N(1)–Li(2)–N(1″)	108(1)	N(2)–Li(2)–N(2″)	132(1)
N(1)–Li(2)–N(2)	123.6(3)		

Single and double primes indicate symmetry-related positions at $1 - x$, $\bar{y}$, z and $1 - x$, $1 - y$, z respectively.

A PDP 11/34 computer and the Enraf–Nonius structure package were used in the structure solution and refinement. Scattering factors were taken from ref. 8. Final atom coordinates are given in Table 1 and selected bond lengths and angles in Table 2. The anion and cation are shown in Fig. 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Results and Discussion

Preparation of $(Me_3Si)_3CH$.—The route to this compound described here gives about the same yield as that used previously.[1,2] The reagents are more expensive but the method appears to be more reliable and the product cleaner.

The Solid-state Structures of Compounds **2** *and* **3**.—The crystal structure of compound **2** was briefly described in 1983.[4] Although the main features were clear the residual R of 0.18 was so high that it was not considered worth reporting further details. The structure determination of the tmen derivative **3** was better but disorder in the anions, of a kind commonly found in compounds containing the $(Me_3Si)_3C$ group,[9] kept the standard deviations in the molecular parameters high. The compound, however, clearly has the ionic structure $[Li(tmen)_2][LiR_2]$ [R = $C(SiMe_3)_3$], with the ions shown in Fig. 1.

In the $[LiR_2]^-$ anions steric strain is relieved by rotation of the $SiMe_3$ groups by *ca.* 40° from staggered positions about the Si–C

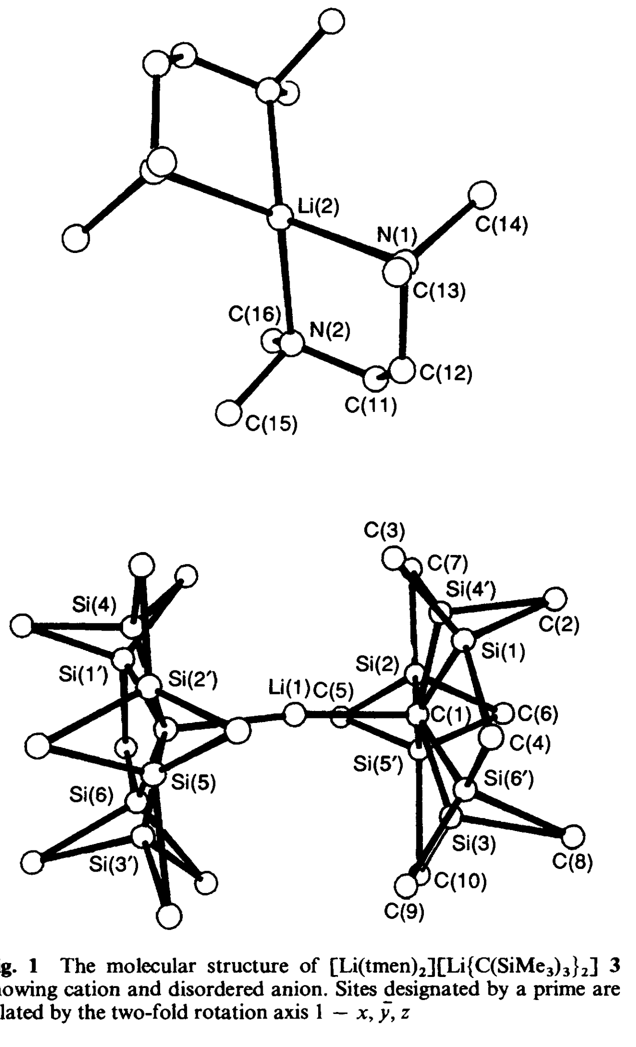


Fig. 1 The molecular structure of $[Li(tmen)_2][Li\{C(SiMe_3)_3\}_2]$ **3** showing cation and disordered anion. Sites designated by a prime are related by the two-fold rotation axis $1 - x$, $\bar{y}$, z

bonds. The $SiMe_3$ groups attached to a particular central carbon all rotate in the same direction, so that the group R as a whole is chiral. The anions are thus diastereoscopic; *meso* combinations LD or DL are centrosymmetrical and combinations LL or DD have two-fold axes (Fig. 2). The results obtained using X-ray crystallography depend on how the diastereoisomers pack. If all (or nearly all) are *meso* and the orientations in the lattice form a regular pattern good quality X-ray data are obtained as in R_2M (M = Mg[10] or Hg[11]) and it is possible to locate the hydrogen atoms. If centrosymmetric diastereoisomers pack with random orientations in the lattice, or if the lattice contains both *meso* LD and chiral LL and DD forms, the effect is to give an electron-density map with non-crystallographically determined $2/m$ symmetry, as in the anion of compound **3**. There are alternative locations for each Si atom but by chance the positions of the C atoms in the D and L forms almost coincide. The anion in the salt **2**, required to be centrosymmetric by the space group $P\bar{1}$, appears to be reasonably well ordered in the solid state but considerable disorder in the $[Li(thf)_4]^+$ cations lowers the quality of the X-ray data.

Restricted Rotation in the Solid Structures.—The ^{13}C CP MAS NMR spectrum of compound **2** showed peaks at δ_C 25.7 and 69.3 associated with thf, a weak quaternary signal at δ_C 3.7, and two peaks at δ_C 7.9 and 8.5 with relative intensities 2 : 1. The splitting of the Me_3Si peak presumably indicates that rotation about the Si–C bonds is restricted in the solid. This rotation involves two energy barriers.[12] The lower barrier, associated with the staggered position [Fig. 3(*a*)], results mainly from 1,3-interactions between methyl groups in the Me–Si–C–Si–Me system. If the barrier is surmounted Me_B and Me_C become equivalent but both are different from Me_A. The three Si atoms are equivalent. The higher barrier corresponds to movement through the eclipsed position [Fig. 3(*b*)]; this makes all three methyl groups as well as all three Si atoms equivalent. The NMR data for the $[Li(thf)_4]^+$ salt **2** suggest that at room temperature rotation about the C–Si bonds through the lower barrier is allowed but that through the higher barrier is restricted. For the $[Li(tmen)_2]^+$ salt; however, only one peak is obtained in both the ^{13}C and ^{29}Si NMR spectra, indicating that the $SiMe_3$ groups are free to rotate through both staggered and eclipsed positions.

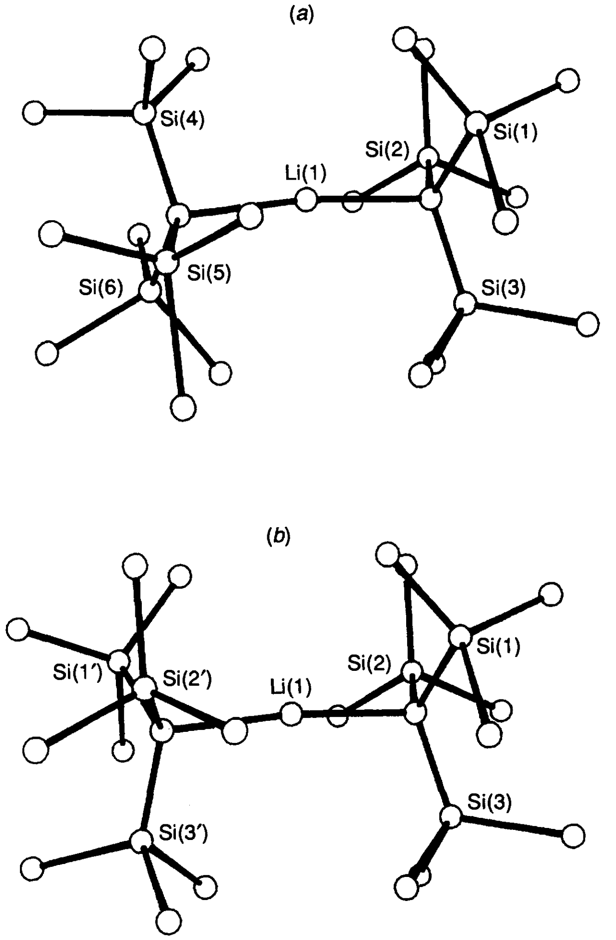


Fig. 2 The meso (DL) (*a*) and chiral (DD) (*b*) forms of the dialkyllithiate anion

The crystal lattices of **2** and **3** (Fig. 4) are similar to that of

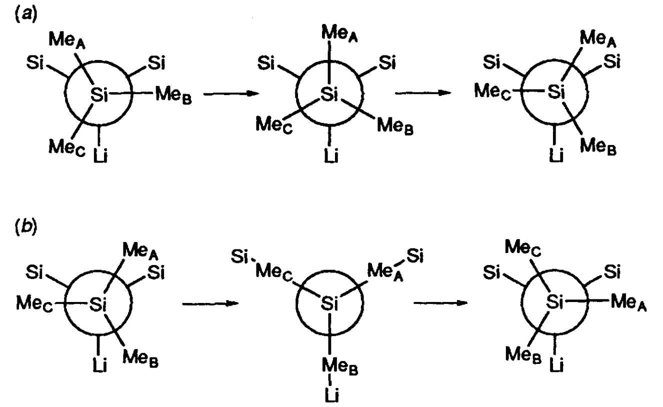


Fig. 3 Newman projections along the Si–C bonds in compound **2**

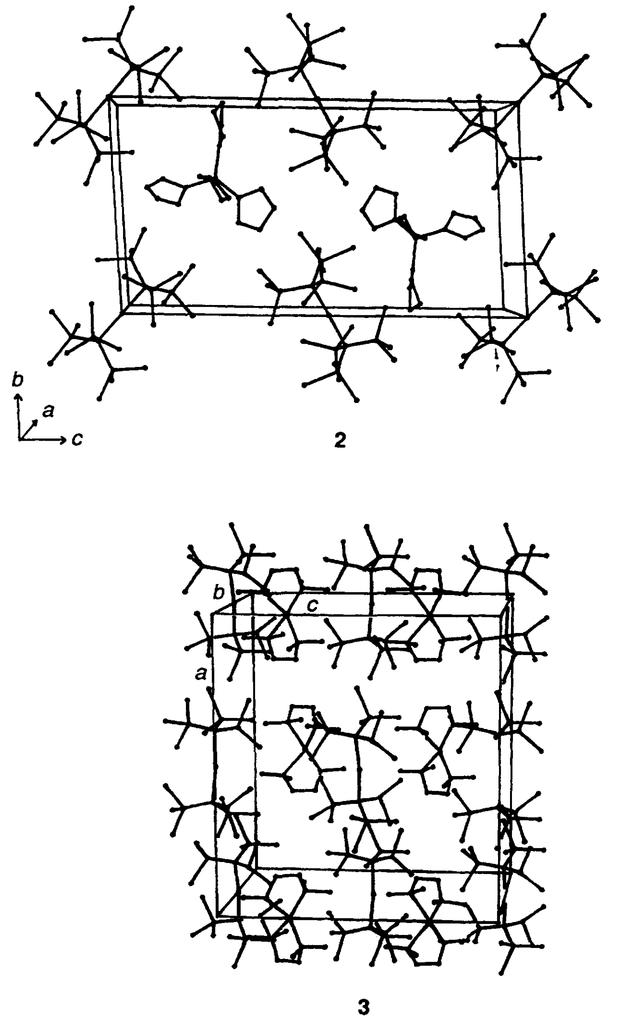


Fig. 4 Packing diagrams for compounds **2** and **3**

caesium chloride. Each cation has eight anion neighbours at the corners of a distorted cube and each anion has eight cation neighbours. The anions are distorted from spheres into short fat cylinders. In compound **2** these pack in the commonly observed herring-bone pattern with the almost spherical cations in the interstices. In compound **3**, however, the anion axes are parallel. It seems that the latter arrangement allows greater rotational freedom about the Si–C bonds, as shown in the NMR spectra, and also greater disorder, as detected by X-ray diffraction. It is possible that the rotational freedom is determined by the number of tight interionic contacts but attempts to test this hypothesis were frustrated by the poor quality of the X-ray data. There are no significant differences in bond lengths and angles in the anions of **2** and **3**, and no significant differences between interionic contacts in the two compounds.

Proton, ^{13}C and ^{29}Si NMR Spectra of $(Me_3Si)_3CLi{\cdot}2thf$ *in thf and Toluene.*—The 250 MHz ^{1}H NMR spectrum of a 1.37 mol dm^{-3} solution of **1** in [$^2H_8$]thf at 318 K showed a broad signal at *ca.* δ_H 0 on which was superimposed a weak but very sharp signal at δ_H 0.10 ascribed to $(Me_3Si)_3CH$, inevitably present because of slight hydrolysis of the sample. On cooling the broad resonance split into two sharp peaks (Fig. 5 and Table 3), indicating that now two species, designated **A** and **B**, were exchanging slowly on the NMR timescale. The ^{13}C and ^{29}Si NMR spectra showed similar features. From the relative intensities (**A**:**B** = *ca.* 2:1 at 288 K and *ca.* 1:1 at 248 K) and selective decoupling experiments it is clear that the high frequency resonances in the ^{1}H and ^{29}Si NMR spectra and the low frequency resonance in the ^{13}C NMR spectrum are associated with the same species (**A**), and that this predominates at (*a*) higher temperatures [Fig. 5(*a*)–(*c*)] and (*b*) at higher concentrations [Fig. 5(*a*)].

The ^{13}C resonances of the quaternary carbon atoms are difficult to detect. By using the refocused INEPT pulse sequence[13] based on long-range coupling constants $^3J(^{13}C\text{-}SiC^1H) \approx 2.0$ Hz[14] with ^{1}H decoupling, broad signals for **A** (δ_C 4.0) and **B** (δ_C 1.5) were found at 273 K. After adding tmen to this solution the appearance of the $^{13}C(CSi_3)$ resonances changed whereas all other resonances [^{1}H, $^{13}C(CH_3)$, ^{29}Si] were unaffected. At 253 K a 1:1:1 triplet appeared at δ_C 3.0 [$^1J(^{13}C^7Li)$ 9.8 Hz] and the ^{13}C resonance at δ_C 1.5 was sharper, showing ^{29}Si satellites with correct relative intensities for the CSi_3 fragment corresponding to $^1J(^{29}Si^{13}C)$ 60.3 Hz.

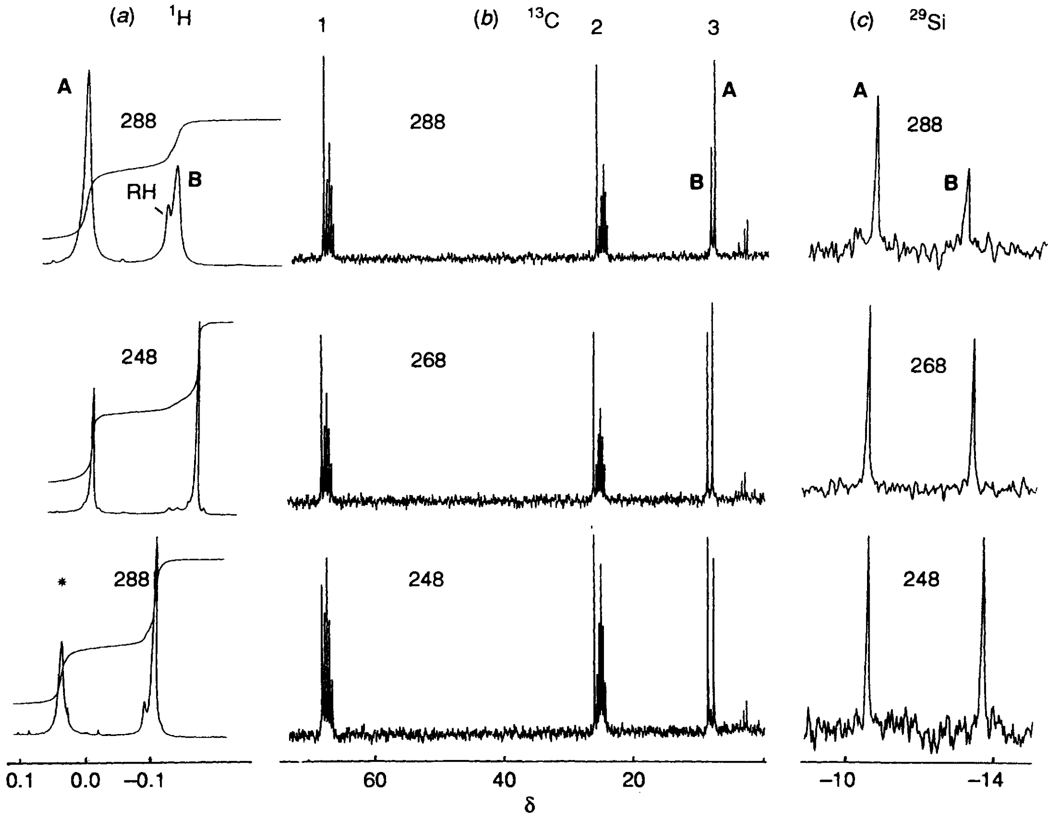


Fig. 5 (*a*) ^{1}H, (*b*) ^{13}C and (*c*) ^{29}Si NMR spectra of compound **2** in [$^2H_8$]thf. All samples were 1.37 mol dm^{-3} except for that marked * (0.50 mol dm^{-3})

Table 3 NMR parameters (ppm)[a]

	^{1}H(SiMe$_3$)	^{13}C(Me)	^{13}C(CSi$_3$)	^{29}Si	^{7}Li
[Li(thf)$_4$][LiR$_2$] (solid)	*b*	8.0, 8.5	3.7	−10.0	1.7,[c] 2.8[d]
A (thf, 295 K)	0.02	7.9	4.0	−10.6[e]	1.4,[c] 3.2[f]
B (thf, 295 K)	−0.11	8.6	1.5[g]	−13.2	1.3[f]
C (toluene, 273 K)	0.31	7.9	*b*	−10.2	−1.93
D (toluene, 273 K)	0.57	8.3	*b*	*b*	*b*
[Li(tmen)$_2$][LiR$_2$] (solid)	*b*	—	3.85	−9.9	1.5, 2.3
[Li(tmen)$_2$][LiR$_2$][h]	0.31, 0.22	—	—	−10.3	0.5,[c] 0.1

[a] See text for reference peaks. [b] Not observed. [c] Sharp, assigned to cation. [d] Very broad, assigned to anion. [e] $^1J(^{29}Si\text{–}^{13}CH_3)$, 47, $^1J(^{29}Si\text{–}CSi_3)$ 42.2, $^3J(^{29}Si\text{–}^1H)$ 7 Hz. [f] Assignment uncertain (see text). [g] $^1J(^{29}Si\text{–}^{13}C)$ 60.3 Hz, measured at 253 K in thf–tmen (see text). [h] In toluene at 288 K.

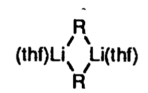
On cooling, both triplet and singlet became broader and at 213 K neither could be detected. The absence of splitting due to $^1J(^{13}C^7Li)$ for the signal at δ_C 1.5 can be explained by postulating fast exchange at the C–Li bond (see below). At lower temperature this process becomes slower and the ^{13}C resonance is broadened. The broadening of the ^{13}C resonance at δ_C 3.0 can be ascribed to increasingly efficient ^7Li quadrupolar relaxation at lower temperature. All these processes lead to shorter $T_2(^{13}C)$ values, hence the application of polarization-transfer techniques for detection of these ^{13}C resonances is no longer straightforward.

The spectra of samples dissolved in toluene were also recorded but because of the lower solubility compared with that in thf the range of concentrations which could be examined was more limited: see Fig. 6 in which the peaks corresponding to 1–3 in Fig. 5(*b*) are shown at various temperatures. All three peaks showed that there was more than one species in solution below room temperature with fast exchange on the NMR timescale at higher temperatures. The low frequency signals in the ^1H and ^{13}C NMR spectra and the high frequency ^{29}Si signals were associated with the species **C** which predominated at (*a*) high temperature and (*b*) lower concentrations.

Identification of Species **A** *and* **C**.—It is commonly found that organolithium compounds dissolve in organic solvents to form oligomers.[15] Many of these have been isolated in the solid state and their structures determined by X-ray crystallography.[16] Others have been identified by NMR spectroscopy, especially by measurements of $^6Li-^{13}C$ coupling constants. In general, in strong donor solvents such as thf the higher oligomers predominate at higher temperatures and higher concentrations; the degradation to lower oligomers on cooling is attributed to the stronger co-ordination of solvent at low temperatures.[17,18] In non-polar solvents such as toluene higher oligomers predominate at higher concentrations and lower temperatures.[19]

Ionic structures such as those adopted by **2** and **3** are rare. It is therefore of interest to ask whether any of the species **A**–**D** detected by NMR can be identified with the structures found in the solid. The ^{29}Si CP MAS NMR spectrum of solid **2** showed one sharp peak at δ_{Si} −10.0, which is assigned to the silicon atoms of the anion. Since the signals from species **A** observed in thf and species **C** in toluene show the same chemical shift (Table 3), it is likely that the ionic form persists in solution though the possibility that the ^{29}Si signals of **A** and **C** are from different species which accidentally have the same chemical shift cannot be ruled out. Once the ^{29}Si signal is identified the associated ^{13}C and ^1H peaks can be found from the relative intensities of peaks in spectra recorded on the same sample for different nuclei. The marked concentration-dependence of the equilibria between **A** and **B** and between **C** and **D** makes deductions based on spectra for different nuclei recorded on different samples extremely unreliable.

The nature of the species **B** and **D** is less obvious: for **B**, two possibilities seem to be **5** and **6**. Unfortunately the ^{13}C resonances of **A** and **B** are insufficiently resolved to allow determination of the R:thf mole ratio. Structure **5**, a bis(thf) adduct of **4**, would be very crowded. The C ··· C distance in **4** is



5

RLi·*n*thf

6

3.946(5) Å,[6] *i.e.* about the same as those in the zinc alkyls [Zn{C(SiMe$_3$)$_2$(SiMe$_2$X)}$_2$], *viz.* 3.964(4) (X = Me), 3.936(4) (X = OH) or 3.948 Å (X = OCOCF$_3$)[20] in which the alkyl groups interlock sufficiently to prevent attack on the Zn–C bond by many electrophilic or nucleophilic reagents. Co-ordination of **4** by thf is thus unlikely without considerable expansion of the four-membered ring. Structure **6** with $n = 1$ is found in solid (Me$_2$PhSi)$_3$CLi·thf,[21] and since the (Me$_3$Si)$_3$C is slightly more compact than the (Me$_2$PhSi)$_3$C group it is possible that a second thf molecule could be weakly co-ordinated. Structure **6** would be favoured by low temperatures, when co-ordination of thf would be strongest, and low concentration, as found for **B**.

A possible mechanism for the exchange on the NMR timescale above about 25 °C could involve separation and return of solvent.

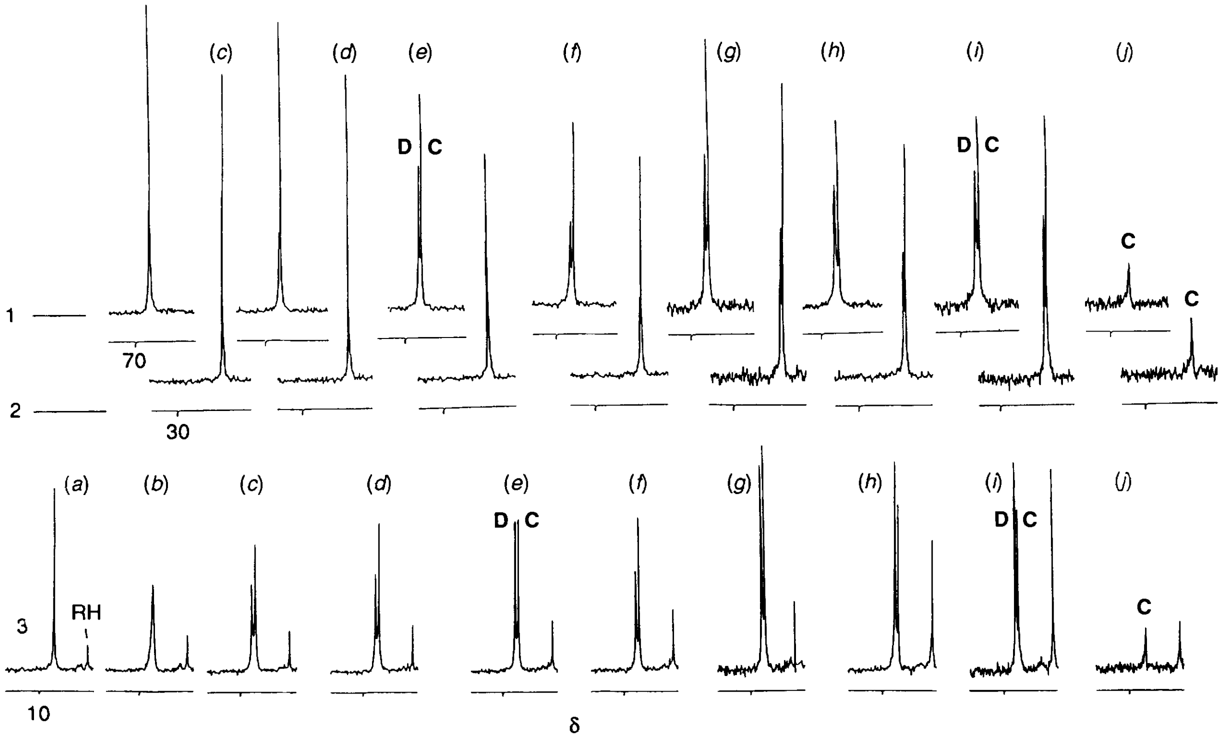
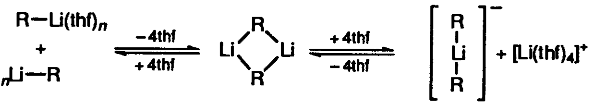


Fig. 6 Carbon-13 spectra of compound **2** (0.5 mol dm^{-3}) in [$^2H_8$]toluene at (*a*) 333, (*b*) 313, (*c*) 303, (*d*) 298, (*e*) 293, (*f*) 288, (*g*) 283, (*h*) 273, (*i*) 263 and (*j*) 233 K. At 233 K the ionic form separates out. The peaks labelled 1–3 correspond to those shown for the [$^2H_8$]thf solution in Fig. 5(*b*)



6 **4** **2**

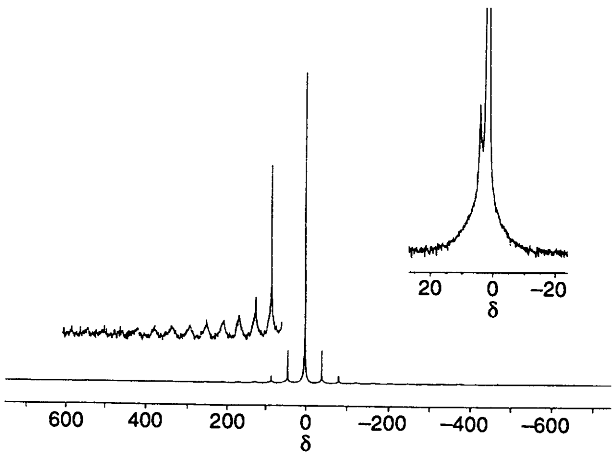


Fig. 7 Lithium-7 CP MAS NMR spectrum of compound **2**

We observed many years ago[22] that when tris(trimethylsilyl)methyllithium **1** is heated at 70 °C (0.01 Torr) a white sublimate is obtained in low (< 50%) yield. The NMR spectra of this show that it consists mainly of unchanged **1**, but the formation of large amounts of RH as a decomposition product frustrated attempts to record the mass spectrum of the subliming lithium species. The volatility of **1** could be readily explained by the formation of a covalent species such as **6**.

The situation in toluene is different from that in thf. The ionic form **2** (species **C**) predominates at high temperatures but at high concentrations it is converted into species **D**. By analogy with other organolithium compounds[16] this is probably some kind of aggregate, *e.g.* a double ion pair $[Li(thf)_4]_2[LiR_2]_2$ or an unsolvated trimer $[(LiR)_3]$ or tetramer $[(LiR)_4]$.

Proton, ^{13}C *and* ^{29}Si *NMR Spectra of* $(Me_3Si)_3CLi \cdot tmen$ *in Toluene*.—Our work on the tmen complex is less complete than that on the thf adduct described above but the main features of the NMR spectra are similar. The predominant species is identified as the ate complex **3** by comparison of the ^{29}Si chemical shifts in the solid state and in solution.

Lithium-7 NMR Spectra of $(Me_3Si)_3CLi$.—The ^7Li NMR spectra from samples in both toluene and thf were recorded over a range of temperatures. They all showed a strong peak ($w_{\frac{1}{2}}$ 15 Hz) at δ_{Li} 1.3, a very broad peak at δ_{Li} 3.1 and a broad peak at δ_{Li} 4.2. In the sample associated with Fig. 1, which is known from measurements on ^1H, ^{13}C and ^{29}Si NMR spectra to contain roughly equal amounts of species **A** and **B**, each of the two broad peaks in the ^7Li NMR spectra appeared to be only 10% of the intensity of the sharp peak. The ^7Li CP MAS NMR spectrum of the solid (Fig. 7) showed a sharp resonance at δ_{Li} 1.7, a small peak at δ_{Li} 4.1 (*ca.* 3%) and a very broad resonance centred at δ_{Li} 2.8, with intensity spread over many side bands. The sharp peak is associated with the Li atoms of the cation $[Li(thf)_4]^+$, which relax slowly in the symmetrical environment and the broad peak with the anion $[LiR_2]^-$, in which the electric-field gradient at lithium is non-zero. The small peak may indicate the presence of an impurity such as $[Li(thf)_4]OH$ formed from accidental admission of moisture during sample preparation. The solid-state results suggest that the peak at δ_{Li} 4.2 in the solution spectra should be assigned to a hydrolysis product, the broad peak at δ_{Li} 3.1 to $[LiR_2]^-$ and the sharper peak at δ_{Li} 1.3 (which may have a shoulder at slightly higher frequency) to the cation $[Li(thf)_4]^+$ and species **B** and **D**. Since the signals from **A** and **B** are incompletely resolved and it is difficult to make accurate integrations over very broad peaks, the ^7Li NMR solution spectra could not be used to confirm the conclusions from ^1H, ^{13}C and ^{29}Si NMR spectra described above.

The ^7Li NMR spectra of $[Li(tmen)_2][LiR_2]$ show similar features. Chemical shifts are given in Table 3.

Conclusion

The solid-state structures of compounds **2** and **3** both contain dialkyllithiate anions. For each compound the ionic form predominates both in thf and in toluene. At low temperatures and low concentrations in thf, the ionic form **2** is partly converted into a second form which is tentatively assigned as $RLi(thf)_n$ with $n = 1$ or 2. At higher temperatures the two forms interchange rapidly on the NMR timescale. A second form is also observed in toluene, but as this predominates at high concentrations it is probably some kind of aggregate. The ate species can be identified in solution from ^{29}Si NMR spectra. The changes in chemical shifts in the ^1H, ^7Li and ^{13}C NMR spectra from one species to another are insufficient at the instrument frequencies currently available to make unambiguous assignments possible.

Acknowledgements

The authors thank the SERC and the Royal Society for financial support.

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Received 4*th May* 1993; *Paper* 3/02516K