Molecular Structures of Bis(trimethylsilyl)methyl-lithium [$(LiR)_n$, R = $CH(SiMe_3)_2$] in the Vapour (Gas-phase Electron Diffraction: a Monomer, n = 1) and the Crystal (*X*-Ray: a Polymer, n = ∞)†

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Gaseous bis(trimethylsilyl)methyl-lithium (LiR) at *ca.* 413 K is a monomer with Li–C 2.03(6) Å and the $SiMe_3$ groups only slightly distorted from an eclipsed conformation with respect to each other; crystalline LiR is a polymer, having three 'molecules' of monomer in the asymmetric unit, the Li–C distances range from 2.14(3) to 2.27(2) Å and average 2.19(5) Å, <CLiC angles are 147(1), 151(1), and 152(1)°, and <LiCLi angles are 152(1)—153(1)°.

The structures of alkyl-lithium compounds are a topic of current experimental[1—8] and theoretical[9] interest. We now present diffraction results on bis(trimethylsilyl)methyl-lithium LiR [R = $CH(SiMe_3)_2$], both in the gas-phase (at 413 K) and the crystal, each of which is without precedent. For gaseous LiR, the gas-phase electron diffraction (g.e.d.) data (Figure 1) represent not only the first for a gaseous alkali-metal (M) alkyl compound, but a unique (other than for high temperature MX species) demonstration of a mono-co-ordinate environment at M. Crystalline LiR, Figure 2, is shown to be a linear polymer, an arrangement not previously found for any other alkali-metal complex.

Some key structural parameters for alkyl-lithium compounds, other than those in which the ligand is polyhapto (such as benzyl-lithium[7]), are shown in Table 1. There now exist four possible monomeric skeletal arrangements, shown schematically in (**1**) (this work), (**2**),[3] (**3**),[4a] and (**4**).[4b] The alternatives are dimers, tetramers, or hexamers. The most recent study of the (complicated) molecular structure of an alkyl-lithium compound in a hydrocarbon solvent is that of ref. 8; $LiBu^s$ is believed to be a mixture of dimer, tetramer, and hexamer, and there are fast exchange processes at equilibrium.

Calculations for methyl-lithium give Li–C (sp^3) as 2.00 (3-21G/3-21G *ab initio*) or 1.82 Å (MNDO) for the unsaturated monomer, 2.15 or 2.04 Å for the corresponding dimer, and 2.19 or 2.20 Å for the tetramer, with slightly higher values for solvated species (*e.g.*, 2.24 Å for monosolvated tetramer).[9]

We now find that g.e.d. results (for experimental details, see ref. 10) on bis(trimethylsilyl)methyl-lithium (LiR) vapour, at nozzle temperature of *ca.* 413 K are consistent with a model consisting only of monomers, although small percentages of dimers or higher oligomers cannot be excluded. Assuming C_2 symmetry of the $C(SiMe_3)_2$ moiety affords the structure illustrated in Figure 1, with Li–C 2.03(6) Å. The $SiMe_3$ groups are twisted 9(3)° away from their eclipsed conformation, when viewed along the Si · · · Si axis, and with one Si–C bond of each $SiMe_3$ group being approximately *anti* to the further central Si–C bond. The methyl groups are twisted 14(5)° (mean value) away from their reference staggered positions. The least-squares fit was not significantly improved by introducing a non-zero tilt angle of the $SiMe_3$ groups. Owing to the low scattering power of the lithium atom and the Li–C bond length not being very different from the Si–C distances, the position of the Li atom could not be determined with high accuracy.

The <SiCSi angle, 119.0(1.5), is smaller than in $CH_2(SiMe_3)_2$, 123.2(9)°,[11] or LiR(pmdeta), 124(2)°,[3] but

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† No reprints available.

Table 1. Some structural parameters for prototypal monohapto alkyl-lithium compounds {R^1 = $CH(SiMe_3)_2$, R^2= $C(SiMe_3)_3$, R^3 = $C(SiMe_2Ph)_3$, tmeda = $Me_2N[CH_2]_2NMe_2$, pmdeta = $MeN(CH_2CH_2NMe_2)_2$, thf = tetrahydrofuran}.

Empirical formula	Degree of molecular aggregation in crystal (vapour)	Co-ordination number of Li	Co-ordination number of C_α of alkyl group	Li–C/Å	Ref.
LiR^1	(Monomer), (**1**)	1	4	2.03(6)	This work
$LiR^1(pmdeta)^a$	Monomer, (**2**)	4	4	2.13(5)	3
$[LiR^2{}_2]^-$	Monomer, (**3**)	2	4	2.16(1), 2.20(1)	4a
$LiR^3(thf)$	Monomer, (**4**)	2/3[f]	4	2.12(1)	4b
$Li(CH_2PMe_2)$ (tmeda)[b]	Dimer	4	4	2.150(8), 2.141(6)	6b
$Li(CH_2SMe)$ (tmeda)[c]	Dimer	4	5	2.256(6), 2.227(7)	2c
$Li[C(SiMe_3)_2\text{-}2\text{-}(C_5H_4N)]$	Dimer	2	4	2.213(7)	6a
$LiMe(tmeda)_{\frac{1}{2}}$[d]	Tetramer	4	6	2.234(6), 2.74(6), 2.279(6)	1b
LiEt[e]	Tetramer	3	6	2.2052(6), 2.2455(5), 2.4082(6)[g]	1c
LiC_6H_{11}	Hexamer	3	6	2.184(3), 2.300(4)	1a
LiR^1	Polymer	2	5	2.19(5) (average)	This work

[a] A similar structure is that of $Li\{C(Ph)S[CH_2]_3S\}(tmeda)(thf)$ (ref. 2b). [b] A similar structure is that of $[Li(CH_2SPh)(tmeda)]_2$ (ref. 2c) and $[Li\{C(Me)S[CH_2]_3S\}(tmeda)]_2$ (ref. 2b). [c] A similar structure is that of $[Li\{CCH_2(CH)CH_2\}(tmeda)]_2$ (ref. 7) and $\{Li(CHCH_2CH_2)\}_2(LiBr)_2(OEt_2)_4$ (ref. 1d). [d] A similar structure is that of $[Li\{CH(Me)[CH_2]_2OMe\}]_4$ (ref. 5). [e] A similar structure is that of $(LiMe)_4$ (ref. 7). [f] The Li atom is bonded to C_α of R^3 and O of thf, but there is also a close contact [2.40(2) Å] to the *ipso*-carbon atom of one of the phenyl groups, see (**4**). [g] These represent distances from a particular C_α to its three nearest Li neighbours at 113 K; another C_α has distances 2.2007(6), 2.2352(5), and 2.3919(6) Å.

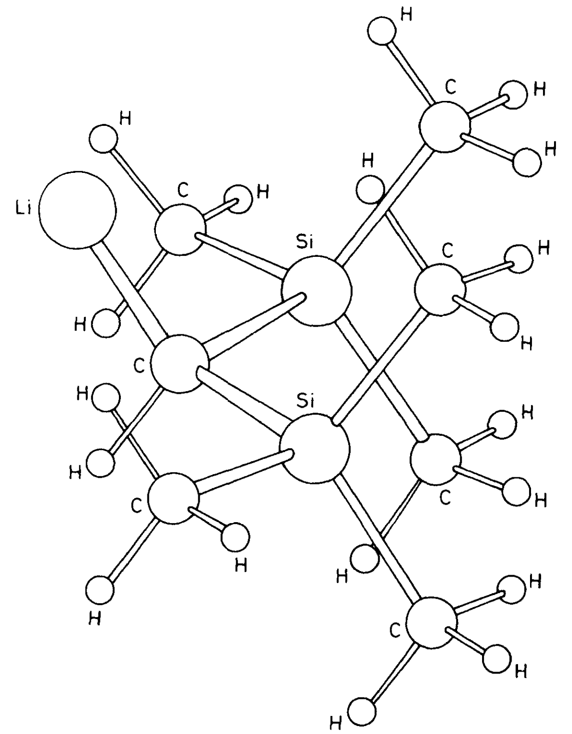


Figure 1. Molecular model of $Li[CH(SiMe_3)_2]$, as determined by gas-phase electron diffraction. Selected bond lengths (Å) and angles (°): Li–C 2.03(6), C–$SiMe_3$ 1.892(2), Si–CH_3 1.877(2), C–H 1.108(6); Si–C–Si 119.0(1.5), C–Si–CH_3 111.0(1.2), Si–C–H(CH_3) 112.3(1.4), Si–C–Li 115(2).

there is a significant deformation from a tetrahedral value, as there is for <LiCSi, 115(2)° [*cf.*,[3] 112(2) and 117(2)° in LiR(pmdeta)]. The observed conformation with regard to the $SiMe_3$ groups is similar to that found in $CH_2(SiMe_3)_2$,[11] suggesting that 1,2- are more important than 1,3-interactions.

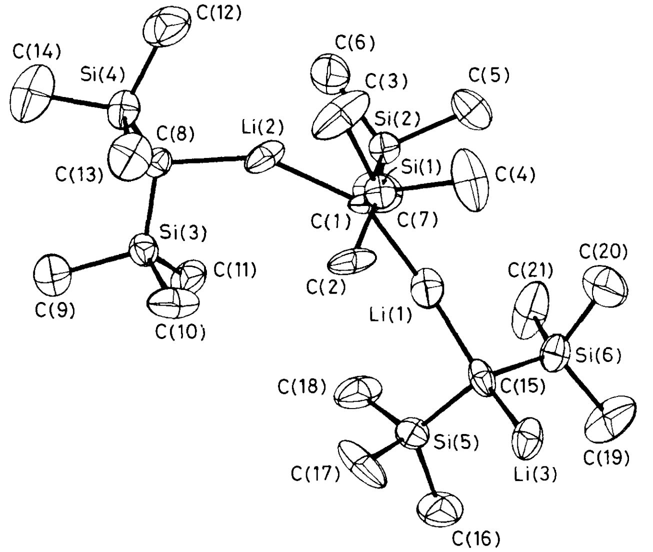
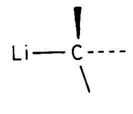


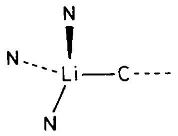
Figure 2. *X*-Ray crystal structure of $[LiCH(SiMe_3)_2]_\infty$, showing the trimeric unit cell and atom numbering scheme. Selected bond lengths (Å) and angles (°): Li(1)–C(1) 2.14(3), Li(1)–C(15) 2.21(3), C(1)–Li(2) 2.22(3), Li(2)–C(8) 2.18(3), Li(3)–C(8′) 2.27(2), Li(3)–C(15) 2.13(3); C(1)–Li(1)–C(15) 152(1), C(1)–Li(2)–C(8) 147(1), C(8′)–Li(3)–C(15) 151(1).

Suitable (colourless, pyrophoric) crystals for *X*-ray diffraction of $Li[CH(SiMe_3)_2]$ were obtained by recrystallisation from n-C_5H_{12} at −30 °C. *Crystal data:* $C_7H_{19}LiSi_2$, M = 166.4, triclinic, space group $P\bar{1}$, a = 9.496(4), b = 11.561(5), c = 17.032(19) Å, α = 76.45(4), β = 86.29(4), γ = 79.34(4)°, U = 1786.0 Å^3, Z = 6 (monomeric units), D_c = 0.93 g cm^{-3}.

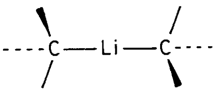
The structure of crystalline LiR was refined using 1280 observed reflections, measured on an Enraf-Nonius CAD-4 diffractometer with Mo-K_α radiation, μ = 2.4 cm^{-1}, to R = 0.053. Hydrogen atoms were included with fixed contribu-



(1)



(2)



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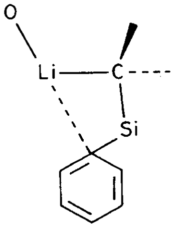

(4)

tions, and all non-hydrogen atoms were refined with anisotropic thermal parameters.‡

It is evident from Figure 2 that crystalline LiR is a linear polymer with a $-(\mathrm{LiC}_\alpha)-_\infty$ backbone. The average bond angles $<\mathrm{C}_\alpha\mathrm{LiC}'_\alpha$ are 150° and $<\mathrm{LiC}_\alpha\mathrm{Li}'$ range from 152(1) to 153(1)°. Electron-deficient alkyl compounds of lithium having a single alkyl bridge between two lithium atoms are, of course, unprecedented; however, there are a few examples of single alkyl bridges between successive transition metals,[12] as, for example, in $[\{\mathrm{Cu}(\mu\text{-}\mathrm{CH_2SiMe_3})\}_4]$[13] or $[\{\mathrm{ReMe_2}(\mu\text{-}\mathrm{Me})(\mathrm{PEt_2Ph})\}_3]$.[14]

It is interesting that LiR should be a monomer in the vapour and a polymer in the crystal, whereas the isoelectronic (but slightly less bulky) $\mathrm{Li[N(SiMe_3)_2]}$ is a cyclic dimer in the gas phase and a cyclic trimer in the solid;[15] aggregation in the amide does not require electron-deficient bonding, as in $(\mathrm{LiR})_\infty$, and thus the Li–N–Li bonds are significantly stronger than the corresponding Li–C–Li bonds.

We thank S.E.R.C. and Dow Corning PLC for a C.A.S.E. Award to A. J. T. and for other support, Siv. ing. Ragnhild Seip for recording the g.e.d. data, Mrs. Snefrid Gunderson for measuring the g.e.d. intensities, and N.S.F. for partial support for J. L. A.

Received, 21st May 1984; Com. 709

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.