

Synthesis of $[\text{Li}(\text{CH}_2\text{SiMe}_3)(\text{pmdeta})]$ and the Crystalline Monomeric Bulky Alkyl-lithium Complexes $[\text{LiR}(\text{tmeda})]$ and $[\text{LiR}(\text{pmdeta})]$ [$\text{R} = \text{CH}(\text{SiMe}_3)_2$]; X-Ray Crystal Structure of $[\text{Li}\{\text{CH}(\text{SiMe}_3)_2\}(\text{pmdeta})]$ $\{\text{tmeda} = \text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2, \text{pmdeta} = \text{Me}_2\text{N}[\text{CH}_2]_2\text{N}(\text{Me})[\text{CH}_2]_2\text{NMe}_2\}$ †

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Reaction of SiMe_4 or $\text{CH}_2(\text{SiMe}_3)_2$ in $n\text{-C}_6\text{H}_{14}$ with $\text{LiBu}^n(\text{pmdeta})$ affords in high yield $\text{Li}(\text{CH}_2\text{SiMe}_3)(\text{pmdeta})$ or $\text{Li}\{\text{CH}(\text{SiMe}_3)_2\}(\text{pmdeta})$, (**2**), respectively, the latter also being available from $\text{Li}\{\text{CH}(\text{SiMe}_3)_2\}(\text{tmeda})$, (**1**), and pmdeta ; crystalline compounds (**1**) and (**2**) are monomers (ebullioscopy, C_6H_{12}), and for (**2**) this is also shown by X-ray crystallography, with the short Li–C distance [2.13(5) Å] indicative of a covalent bond.

Organolithium adducts of nitrogen- or oxygen-containing donors usually possess oligomeric structures.¹ We draw attention to two monomeric lithium alkyls: (a) the formally electron-deficient (6e) $\text{LiR}(\text{tmeda})$, (**1**), and (b) the electron-precise (8e) $\text{LiR}(\text{pmdeta})$ [$\text{tmeda} = \text{tetramethylethylenetriamine}$, $\text{pmdeta} = \text{pentamethyldiethylenetriamine}$, and $\text{R} = \text{CH}(\text{SiMe}_3)_2$]. Noteworthy features include (i) simple essentially quantitative preparative procedures (reactions i and ii of Scheme 1) [direct metallation of the silylated hydrocarbon $\text{CH}_2(\text{SiMe}_3)_2$, (**3**), for (**1**) or (**2**); or of SiMe_4 for $\text{Li}(\text{CH}_2\text{SiMe}_3)(\text{pmdeta})$, (**4**)], (ii) the isolation of pure crystalline alkyl-lithium reagents (**1**) or (**2**), (iii) the exchange of co-ordinated tmeda by pmdeta (step iii of Scheme 1), and (iv) an X-ray structure analysis of $\text{LiR}(\text{pmdeta})$, (**2**), representing the first¹ structurally characterised monomeric lithium alkyl in which the alkyl moiety is void of electron-rich or aryl α -substituents.

Whereas lithiation of SiMe_4 with $\text{LiBu}^n(\text{tmeda})$ gave partial substitution of both SiMe_4 and tmeda substrates,² use of LiBu^n in the presence of tmeda resulted in only ca. 40% lithiation of SiMe_4 .³ In contrast, we now find that almost quantitative SiMe_4 metallation occurs when using $\text{LiBu}^n(\text{pmdeta})$, as determined by n.m.r. spectroscopy; the product $\text{Li}(\text{CH}_2\text{SiMe}_3)(\text{pmdeta})$, (**4**), is a viscous liquid and was derivatised (reaction iv in Scheme 1) as $\text{CH}_2(\text{SiMe}_3)_2$, (**3**). This is a further example of the increased reactivity and superior selectivity of pmdeta compared with tmeda in lithiations (*cf.*,⁴ reactions of α -trimethylsilyl-*o*-xylenes). Solutions containing $\text{LiCH}(\text{SiMe}_3)_2$

were previously accessible from either $\text{ClCH}(\text{SiMe}_3)_2$ (using Li metal)⁵ or $\text{CH}_2(\text{SiMe}_3)_2$ [using LiBu^n in tetrahydrofuran (thf) with $\text{P}(\text{O})(\text{NMe}_2)_3$ (hmpa) at -78°C].⁶ We now show that metallation of $\text{CH}_2(\text{SiMe}_3)_2$ does not require the highly reactive LiBu^n , but is effective with the readily accessible LiBu^n . Moreover, a feature of the use of tmeda or pmdeta is the ability to isolate crystalline $\text{LiR}(\text{base})$, (**1**) or (**2**), in excellent yield (ca. 80%).

The bis(trimethylsilyl)methyl-lithium base adducts (**1**) and (**2**) have been characterised by microanalysis and n.m.r. spectroscopy,[†] derivatisation to give $\text{CH}(\text{SiMe}_3)_3$ (see iv in

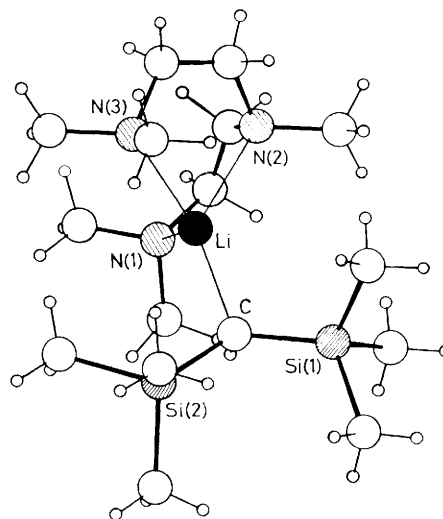
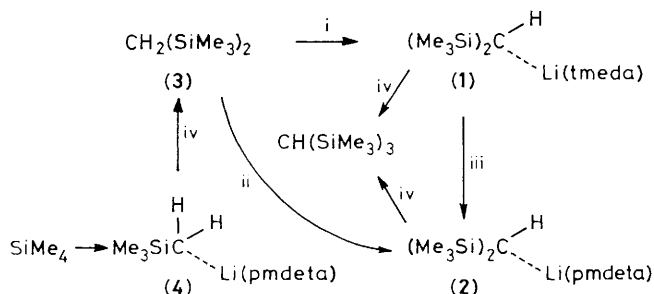


Figure 1. Molecular structure of $\text{Li}\{\text{CH}(\text{SiMe}_3)_2\}(\text{pmdeta})$, (**2**). Selected bond lengths (Å) and angles ($^\circ$): Li–C 2.13(5), Li–N(2) 2.30(4), Li–N(1) 2.27(5), Li–N(3) 2.20(4), Si(1)–C 1.78(3), Si(2)–C 1.79(3), $\langle \text{Si}-\text{CH}_3 \rangle$ 1.8 $^\circ$, $\langle \text{N}(2)-\text{CH}_3 \rangle$ 1.4 $^\circ$, $\langle \text{N}(2)-\text{CH}_2 \rangle$ 1.4 $^\circ$; C–Li–N(2) 134(2), C–Li–N(1) 113(2), C–Li–N(3) 129(2), N(2)–Li–N(1) 79(2), N(2)–Li–N(3) 80(2), N(1)–Li–N(3) 111(2), Si(1)–C–Si(2) 124(2), Li–C–Si(1) 117(2), Li–C–Si(2) 112(2).



Scheme 1. Reagents and conditions: i, LiBu^n in C_6H_{14} (1 mol) + tmeda (1 mol), 12 h, 25°C , colourless crystals of (**1**) (m.p. $49\text{--}50^\circ\text{C}$) from C_6H_{12} at -78°C ; ii, LiBu^n in C_6H_{14} (1 mol) + pmdeta (1 mol), $\frac{1}{2}$ h, 20°C , colourless crystals of (**2**) (m.p. $230\text{--}232^\circ\text{C}$) from C_6H_{12} at -30°C ; iii, (**1**) in C_6H_6 , pmdeta (1 mol), $\frac{1}{2}$ h, 0°C ; iv, SiClMe_3 in C_6H_{14} .

† No reprints available.

[†] ^1H N.m.r. (C_6D_6) τ : (**1**) 8.19 (s, $\text{H}_3\text{C}-\text{N}$), 8.38 (s, CH_2), 9.68 (s, $\text{H}_3\text{C}-\text{Si}$), and 11.76 (s, HC); (**2**) 8.1 (amine H unresolved), 9.75 (s, $\text{H}_3\text{C}-\text{Si}$), and 12.1 (s, HC); (**4**) 8.1 (amine H unresolved), 9.64 ($\text{H}_3\text{C}-\text{Si}$), and 11.67 (s, $\text{H}_2\text{C}-\text{Li}$). ^{13}C (^1H) n.m.r. (C_6D_6 , SiMe_4) (**1**) 56.0 (s, $\text{H}_3\text{C}-\text{N}$), 45.2 (s, CH_2), 6.8 (s, CH_3-Si), and 2.1 p.p.m. (s, CH); (**2**) 58.4, 56.4 (s, CH_2-N), 46.5 [s, $\text{N}(\text{CH}_3)_2$], 44.2 (s, $\text{N}-\text{CH}_2$), 7.6 (s, CH_3-Si), and 1.9 p.p.m. (s, CH–Li); (**4**) 57.4, 54.5 (s, CH_2-N), 46.0 [s, $\text{N}(\text{CH}_3)_2$], 44.7 (s, $\text{N}-\text{CH}_3$), 6.8 (s, CH_3-Si), and -4.9 p.p.m. (s, CH_2-Li).

Scheme 1), as well as molecular weight determinations in cyclohexane (Singer method). Both are monomeric, which is particularly surprising for the open shell compound (1), and contrasts with the dimeric structures found in [$\{\text{LiPh}(\text{tmeda})\}_2\]^7$ and [$\{\text{Li}(\text{bicyclo}[1.1.0]\text{butyl})(\text{tmeda})\}_2\]^8$. As the ligand $\overline{\text{C}}\text{H}(\text{SiMe}_3)_2$ readily stabilises compounds of unusually low co-ordination number,⁹ a monomeric structure of (1) presumably has a steric origin.

As $\text{CH}(\text{SiMe}_3)_3$ can be further lithiated at the tertiary carbon using LiMe in OEt_2 but not $\text{LiBu}^{\text{M}}(\text{tmeda})$,¹⁰ we conclude that kinetic acidity increases in the sequence $\text{SiMe}_4 < \text{CH}_2(\text{SiMe}_3)_2 < \text{CH}(\text{SiMe}_3)_3$.

The asymmetric unit of the structure of $\text{Li}\{\text{CH}(\text{SiMe}_3)_2\}(\text{pmdeta})$ comprises a single molecule of (2), there being no significant intermolecular contacts. Environments about the Li and $\text{C}(\alpha)$ atoms are best described as distorted tetrahedra (Figure 1) with the *pmdeta* configuration and bonding similar to that found in [$\{\text{Li}(\text{pmdeta})\}_2(\text{PhCH}=\text{CHPh})$].¹¹ Of particular interest in the alkyl group is the $\text{Si}-\text{C}(\alpha)-\text{Si}$ angle, $124(2)^\circ$, which is splayed well above sp^3 hybridised values, a distortion possibly resulting from SiMe_3 repulsions.[§] The $\text{Si}-\text{C}(\alpha)-\text{Li}$ angles are also enlarged, but to a lesser extent. The terminal $\text{Si}-\text{C}$ distances are unexceptional at 1.8_6 \AA with $\text{C}(\alpha)-\text{Si}$ distances somewhat low, $1.79(3) \text{ \AA}$, perhaps reflecting back-bonding from $\text{C}(\alpha)$ to Si d-orbitals. Although the accuracy of the structure is low and caution needs to be exercised in comparing it with other structures, the $\text{Li}-\text{C}(\alpha)$ bond, $2.13(5) \text{ \AA}$, is not dissimilar to that found in $\{(2\text{-lithio-2-methyl-2,3-dithian})(\text{tmeda})\}_2$, 2.19 \AA ,¹⁴ in which the very short $\text{Li}-\text{C}$ distance, coupled with electron density analyses, was taken as evidence for a covalent, or, at most, polarised, $\text{Li}-\text{C}$ bond.

Crystal data: $\text{C}_{16}\text{H}_{42}\text{LiN}_3\text{Si}_2$, $M = 339.5$, monoclinic, space group $P2_1/n$, $a = 16.93(2)$, $b = 15.173(5)$, $c = 9.635(9) \text{ \AA}$, $\beta = 102.42(8)^\circ$, $U = 2417(4) \text{ \AA}^3$, $Z = 4$, $D_c = 0.93 \text{ g cm}^{-3}$. The structure was solved from 963 'observed' (out of the 2272

independent) diffractometer reflections measured to $2\theta = 40^\circ$, R is 0.16.¶

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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. Because of the low precision of the determination, a consequence of limited data and high thermal motion, the structure determination will not be reported elsewhere; the structure factor table is available as Supplementary Publication, No. SUP 23488, (7 pp.). For details of how to obtain this material see Notice to Authors, No. 7, *J. Chem. Soc., Dalton or Perkin Trans.*, 1980, Index Issues.

§ It compares with $\text{Si}-\text{C}-\text{Si}$ $123.2(9)^\circ$ in $\text{CH}_2(\text{SiMe}_3)_2$ (ref. 12) and $117.2(4)^\circ$ for $\text{CH}(\text{SiMe}_3)_3$, (ref. 13) as determined by electron diffraction.