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[Benzylbis(dimethylamino)methylsilyl-κ^2C,N](N,N,N′,N′-tetramethylethylenediamine-κ^2N,N)lithium(I)

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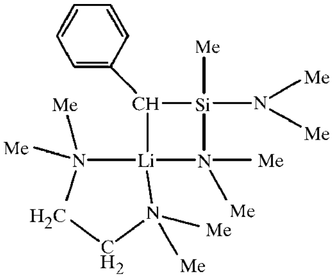
The title compound, $[Li(C_{12}H_{21}NSi)(C_6H_{16}N_2)]$, is an intermediate in the synthesis of the corresponding organometallic compounds. The molecule has an unusual C—Si—N—Li four-membered heterocycle which adopts a folded conformation, with the coordination around the Li, N, C and Si atoms being distorted tetrahedral. Its structure is strongly supported by ^{1}H NMR, ^{13}C NMR and ^{13}C–^{1}H correlation spectra. The compound has potential for application in the synthesis of other novel organometallic compounds.

Comment

Organolithium compounds, as versatile ligands in organometallic chemistry, have attracted intense research interest since the first such compound was discovered (Sapse & Schleyer, 1995). In this field, Lappert and co-workers have made a number of key investigations over the years. An attractive outcome of their investigations is that the interaction of a trimethylsilylmethyllithium reagent, Li[CHR_2] (where R is SiMe$_3$), with an α-hydrogen-free nitrile, R'CN, can yield α-L-azaallyl- (A), β-diketiminato- (B) and 1,3-diazaallyllithium (C) (Hitchcock *et al.*, 2000). Their work aroused our interest in seeking novel organolithium ligands by introducing one or two N atoms into the ligands. Our initial objectives were to discover new organolithium ligands and to investigate their structures. Further objectives are to use them as ligand-transfer reagents in order to gain access to a wider range of metal alkyls, and to use them as substrates for synthesis. Our initial target ligands were {PhCH[SiMe[N(CH$_3$)$_2$]$_2$]}Li(TMEDA) (TMEDA is *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) and {PhCH[SiMe$_2$N(CH$_3$)$_2$]}Li(TMEDA) (TMEDA is *N*,*N*,*N*′,*N*′-tetramethylethylenediamine). These compounds have a number of useful features; firstly, they are chiral; secondly, they have relative migratory potential in C—Si cleavage reactions; and thirdly, the chosen substituent –N(CH$_3$)$_2$ group is a potential coordination site. Thus, we have synthesized the title complex, (I), and its structure is reported here. Compound (I) has also been characterized by ^{1}H NMR, ^{13}C NMR and ^{13}C–^{1}H correlation spectra. Its structure shows several interesting features, which will now be discussed.



(I)

Selected geometric parameters of (I) are listed in Table 1 and the molecular structure is illustrated in Fig. 1. There is a central C1—Si1—N1—Li1 four-membered ring which adopts a folded conformation, with the dihedral angle between the C1—Li1—N1 and C1—Si1—N1 planes being 21.9 (1)° and with the coordination around the Li1, N1, C1 and Si1 atoms being distorted tetrahedral.

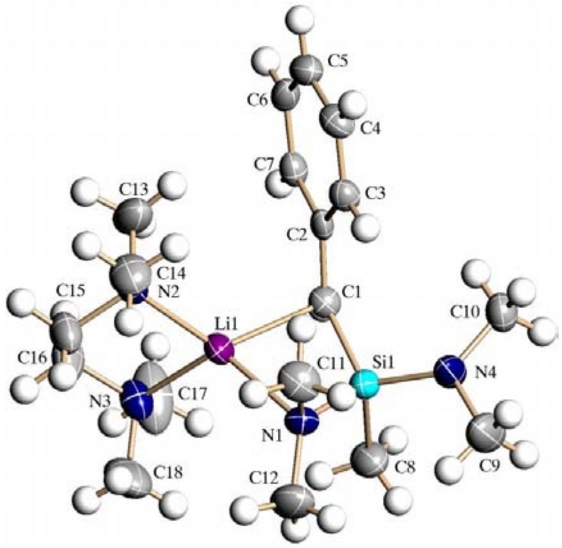


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by spheres of arbitrary radii.

The C1—Si1 bond length [1.787 (2) Å] is much shorter than common Si—Csp^3 bonds, which usually lie in the range 1.861–1.901 Å, and this can be attributed to delocalization of the negative charge, either by π–π bonding or, more likely, to negative hyperconjugation (Schleyer *et al.*, 1984; Brinkman *et al.*, 1994), leading to some double-bond character in the Si1—C1 bond. A similarly short bond length [1.793 (6) Å] is observed in the compound [(Me$_2$NMe$_2$Si)$_3$CLi] (Adam *et al.*, 1996).

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The Si1—N1 bond length [1.783 (2) Å] is longer than common Si—N bonds (1.710–1.721 Å) between three-coordinate N atoms and four-coordinate Si atoms in R_3SiNR_2 species (Lukevics *et al.*, 1985). A similarly long bond length [1.792 (4) Å] is observed in the compound [($Me_2NMe_2Si)_3CLi$] (Adam *et al.*, 1996). The long bond length is a consequence of the coordination of the N1 atom to atom Li1 and indicates a decrease in the strength of the interaction of atom Si1 with atom N1 in the molecule.

There is a rather distorted tetrahedral arrangement around the Li atom in (I), with bond angles ranging from 81.60 (15) to 127.43 (19)°. The dihedral angle between the N4—Si1—C1 and C1—Si1—N1 planes is 59.4 (1)°, which indicates that the terminal N4 group is bent substantially out of the central ring system. The N4—Si1—N1—Li1 torsion angle of 142.46 (13)° indicates a *trans* configuration of the molecule about the Si1—N1 bond. The C8—Si1—C1 and Si1—C1—Li1 planes are almost perpendicular [dihedral angle = 96.76 (15)°].

All of these features, *i.e.* the longer bond length of Si1—N1, the shorter bond length of Si1—C1, the rather distorted tetrahedral arrangement around the Li atom, the *trans* configuration of the molecule about the Si1—N1 bond and the folded conformation of the C1—Si1—N1—Li1 four-membered ring, are required to minimize intramolecular steric strain.

It is noteworthy that, in the solid, {PhCH[SiMe[N($CH_3)_2]_2$]}Li(TMEDA) exists as a monomer in which one –NMe_2 group is engaged in coordination to the Li atom. Much novel chemistry has emerged through applying the very bulky {PhCH[SiMe[N($CH_3)_2]_2$]}$^-$ ligand to a wide range of metals and metalloids. Even more unusual species might be expected to be formed by the use of (I) as a source of novel organometallic compounds, in which the amino group is available to coordinate to the metal atom to which the central C atom is attached or to another metal centre or to both. Studies of these possibilities are under way.

Experimental

n-Butyllithium was added dropwise to a solution of toluene and TMEDA (molar ratio 1:1:1) in hexane at 273 K and the temperature was allowed to rise to room temperature. The mixture was stirred for more than 24 h, and then an equimolar amount of bis(dimethylamino)methylchlorosilane was added at 273 K and the temperature was again allowed to rise to room temperature. The mixture was stirred for a further 15 h, yielding a white precipitate (LiCl) which was removed by filtration. The compound benzylbis(dimethylamino)methylsilane was isolated as a colourless liquid by vacuum distillation of the filtrate. A solution of *n*-butyllithium in hexane was added slowly to benzylbis(dimethylamino)methylsilane and TMEDA in pentane (molar ratio 1:1:1) at ambient temperature and the mixture was stirred for 18 h. The solution was then concentrated carefully under vacuum, yielding yellow crystals of (I). Crystals suitable for single-crystal X-ray diffraction were grown from a concentrated hexane solution at 253 K. All reactions were performed under argon using standard Schlenk techniques. The hexane was dried by distilling with a sodium–potassium alloy; the pentane was distilled from a drying agent with sodium. Spectroscopic analysis, ^{1}H NMR (C_6D_6, δ): 6.99–7.23 (*m*, 5H), 2.75 (*m*, 12H), 2.45 (*s*, 1H), 1.58–2.21 (*m*, 16H), 0.34 (*s*, 3H); ^{13}C NMR (C_6D_6, δ): 156.1, 119.8, 109.4, 56.2, 45.2, 39.5, 38.6, 37.5, 24.2, −3.0.

Crystal data

$[Li(C_{12}H_{21}NSi)(C_6H_{16}N_2)]$
$M_r = 344.55$
Monoclinic, $P2_1/c$
$a = 13.946$ (4) Å
$b = 9.805$ (2) Å
$c = 17.236$ (4) Å
$\beta = 112.523$ (3)°
$V = 2177.0$ (9) Å^3
$Z = 4$
$D_x = 1.051$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1985 reflections
$\theta = 2.4$–22.5°
$\mu = 0.11$ mm^{-1}
$T = 183$ (2) K
Block, yellow
0.40 × 0.30 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.956$, $T_{\max} = 0.978$
8766 measured reflections
3841 independent reflections
2779 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.040$
$\theta_{\max} = 25.0$°
$h = -16 \rightarrow 16$
$k = -11 \rightarrow 11$
$l = -14 \rightarrow 20$
Intensity decay: 3.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.060$
$wR(F^2) = 0.134$
$S = 1.00$
3841 reflections
226 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.061P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Li1—N2	2.085 (5)	Si1—N4	1.720 (2)
Li1—N3	2.104 (4)	Si1—N1	1.783 (2)
Li1—N1	2.203 (4)	Si1—C1	1.787 (2)
Li1—C1	2.261 (5)	Si1—C8	1.869 (3)
N2—Li1—N3	87.48 (17)	C1—Si1—C8	108.69 (12)
N2—Li1—N1	126.2 (2)	C11—N1—C12	108.9 (2)
N3—Li1—N1	118.18 (19)	C11—N1—Si1	116.35 (16)
N2—Li1—C1	127.43 (19)	C12—N1—Si1	122.83 (17)
N3—Li1—C1	120.2 (2)	C11—N1—Li1	96.01 (17)
N1—Li1—C1	81.60 (15)	C12—N1—Li1	125.01 (19)
N4—Si1—N1	106.83 (11)	Si1—N1—Li1	83.49 (13)
N4—Si1—C1	115.45 (10)	C2—C1—Si1	134.22 (18)
N1—Si1—C1	109.59 (10)	C2—C1—Li1	102.57 (18)
N4—Si1—C8	111.60 (12)	Si1—C1—Li1	81.69 (13)
N1—Si1—C8	104.05 (11)		

All H atoms were initially located in a difference Fourier map. H atoms on Csp^3 atoms were then constrained to an ideal geometry, with C—H distances of 0.96–0.98 Å and with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C). H atoms on Csp^2 atoms were allowed to ride on their parent atoms, with C—H distances of 0.93 Å and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1140). Services for accessing these data are described at the back of the journal.

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