

[Benzylidimethyl(dimethylamino)silyl- κ^2C,N]- (N,N,N,N -tetramethylethylenediamine- κ^2N,N)- lithium(I)

He-Ping Shi, Dian-Sheng Liu and
Shu-Ping Huang*

School of Chemistry and Chemical Engineering,
The Shanxi University, Taiyuan, People's
Republic of China

Correspondence e-mail: szf@sxu.edu.cn

Key indicators

Single-crystal X-ray study

$T = 183\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.008\text{ \AA}$

R factor = 0.076

wR factor = 0.104

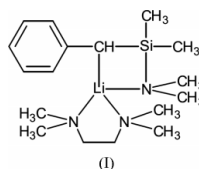
Data-to-parameter ratio = 16.7

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The molecule of the title compound, $[\text{Li}(\text{C}_{11}\text{H}_{18}\text{NSi})\text{-(C}_6\text{H}_5\text{N}_2)]$ contains a four-membered heterocycle with a folded conformation. The coordination around the Li, N, C and Si atoms in this ring is distorted tetrahedral.

Comment

Organolithium compounds are intriguing from a number of points of view, *viz.* structural, bond theoretical and practical. The N atom is found in a large number of saturated and unsaturated organolithium compounds, in segments such as $\text{N}-\text{Li}-\text{C}$, $\text{N}-\text{Li}-\text{N}$, $\text{Si}-\text{N}-\text{C}$, $\text{Si}-\text{N}-\text{Li}$, *etc.* Recently, we have synthesized the title compound, (I), containing a $\text{C}-\text{Si}-\text{N}-\text{Li}$ ring. The title compound has unusual features and is potentially useful for the synthesis of other novel organo-metallic compounds. This compound has been characterized by single-crystal X-ray diffraction analysis. Selected geometric parameters of (I) are listed in Table 1 and the molecular structure is illustrated in Fig. 1.



The four-membered heterocyclic ring adopts a folded conformation. The angle between the $\text{C1}-\text{Li1}-\text{N1}$ and $\text{C1}-\text{Si1}-\text{N1}$ planes is $20.8(3)^\circ$. The N atom is bonded to the Li atom and the ring contains a four-coordinate Li centre. As a consequence of the coordination of the N atom to the Li atom, the $\text{Si1}-\text{N1}$ bond [$1.787(4)\text{ \AA}$] is longer than an average $\text{N}-\text{Si}$ bond [$1.75(2)\text{ \AA}$] between three-coordinate N and four-coordinate Si (Allen *et al.*, 1987), as nitrogen is four-coordinate in (I). Coordination of each of the atoms in the heterocyclic ring, C1, Li1, N1 and Si1, is distorted tetrahedral. The $\text{Li1}-\text{N2}$ and $\text{Li1}-\text{N3}$ bond distances of the five-membered chelate ring (see Table 1 and Fig. 1) are not significantly different, and are a little shorter than the $\text{Li1}-\text{N1}$ bond of the four-membered ring. The $\text{Si1}-\text{N1}$ and $\text{Si1}-\text{C1}$ bond lengths are essentially equal and a little shorter than the two exocyclic bonds $\text{Si1}-\text{C8}$ and $\text{Si1}-\text{C9}$.

Experimental

n-Butyllithium was added dropwise to an equimolar solution of toluene and TMEDA (*N,N,N',N'*-tetramethylethylenediamine) 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

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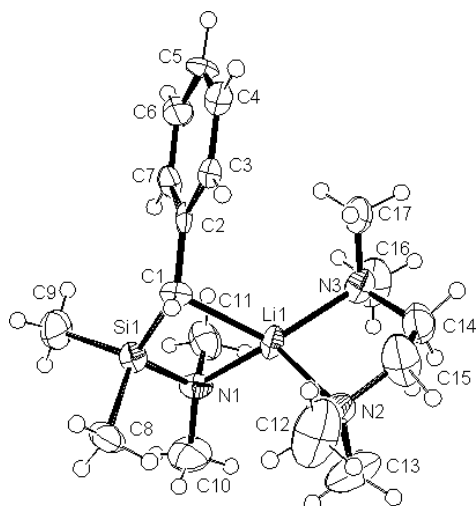


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by small spheres of arbitrary radii.

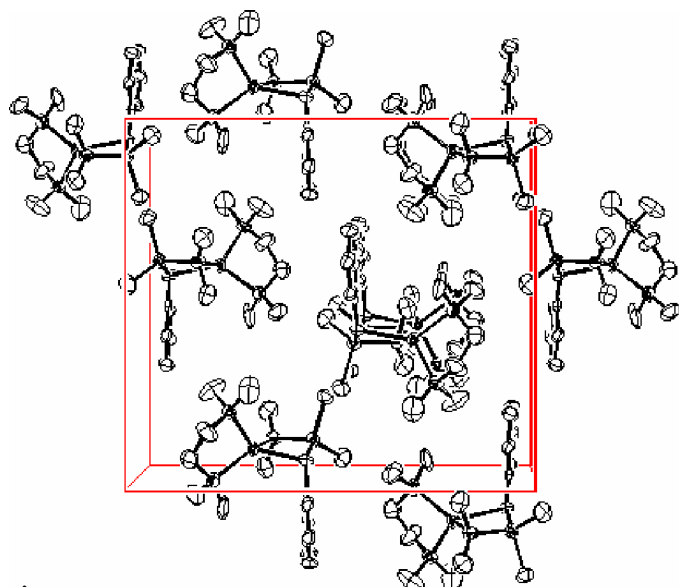


Figure 2
A packing diagram of the title molecule, viewed along the *a* axis. For clarity, all H atoms have been omitted.

dimethyl(dimethylamino)chlorosilane (molar ratio 1:1) was added at 273 K and the temperature was allowed to rise to room temperature. The mixture was stirred for a further 15 h, to yield a white precipitate (LiCl). The mixture was filtered and benzyl(dimethyl)(dimethylamino)silane was isolated by vacuum distillation as a colourless liquid. A solution of Li^tBu in hexane was slowly added to benzyl(dimethyl)(dimethylamino)silane and TMEDA in pentane (molar ratio 1:1) at ambient temperature. The mixture was stirred for 18 h. The title compound was obtained as a precipitate, which was dissolved in Et_2O . The solution was concentrated under vacuum, yielding yellow crystals of the title compound. Crystals suitable for a single-crystal X-ray diffraction study were grown from a concentrated Et_2O solution at 253 K. All reactions were performed under argon, using standard Schlenk techniques. The hexane was dried by distillation over a sodium–potassium alloy, and ether was distilled from sodium.

Crystal data

$[\text{Li}(\text{C}_{11}\text{H}_{18}\text{NSi})(\text{C}_6\text{H}_{16}\text{N}_2)]$
 $M_r = 315.50$
 Orthorhombic, $P2_12_12_1$
 $a = 8.533$ (4) Å
 $b = 14.753$ (6) Å
 $c = 16.241$ (7) Å
 $V = 2044.6$ (15) Å³
 $Z = 4$
 $D_x = 1.025$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 436 reflections
 $\theta = 2.7$ – 13.6°
 $\mu = 0.12$ mm⁻¹
 $T = 183$ (2) K
 Block, yellow
 $0.2 \times 0.2 \times 0.2$ mm

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.977$, $T_{\max} = 0.977$
 8455 measured reflections

3588 independent reflections
 1645 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.122$
 $\theta_{\max} = 25.0^\circ$
 $h = -8 \rightarrow 10$
 $k = -17 \rightarrow 15$
 $l = -19 \rightarrow 15$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.077$
 $wR(F^2) = 0.104$
 $S = 0.83$
 3588 reflections
 215 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2)]$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.24$ e Å⁻³
 $\Delta\rho_{\min} = -0.24$ e Å⁻³
 Absolute structure: (Flack, 1983),
 1527 Friedel pairs
 Flack parameter = -0.3 (3)

Table 1

Selected geometric parameters (Å, °).

Li1–N2	2.083 (9)	Si1–C1	1.785 (4)
Li1–N3	2.108 (10)	Si1–C8	1.865 (5)
Li1–N1	2.155 (9)	Si1–C9	1.879 (5)
Li1–C1	2.235 (10)	C1–C2	1.428 (6)
N1–Si1	1.787 (4)		
N2–Li1–N3	88.4 (4)	Si1–N1–Li1	85.6 (3)
N2–Li1–N1	119.9 (5)	C1–Si1–N1	106.5 (2)
N3–Li1–N1	128.1 (5)	C1–Si1–C8	109.3 (2)
N2–Li1–C1	119.3 (4)	N1–Si1–C8	105.7 (2)
N3–Li1–C1	123.9 (5)	C1–Si1–C9	118.8 (2)
N1–Li1–C1	81.4 (3)	N1–Si1–C9	108.5 (2)
C10–N1–C11	107.9 (4)	C8–Si1–C9	107.4 (3)
C10–N1–Si1	118.5 (4)	C2–C1–Si1	133.4 (4)
C11–N1–Si1	114.0 (4)	C2–C1–Li1	107.7 (4)
C10–N1–Li1	130.1 (4)	Si1–C1–Li1	83.2 (3)
C11–N1–Li1	98.5 (4)		

All H atoms were initially located in a difference Fourier map. The methyl H atoms were then constrained to an ideal geometry, with C–H distances of 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$, but each group was allowed to rotate freely about the C–N bond. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H distances in the range 0.95–1.00 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

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