

# [(1-*tert*-Butyl-2-phenylvinylamino)(dimethylamino)dimethylsilyl- $\kappa^2$ N,N'] (N,N,N',N'-tetramethylenediamine- $\kappa^2$ N,N')lithium(I)

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## Key indicators

Single-crystal X-ray study

$T = 178$  K

Mean  $\sigma(\text{C}-\text{C}) = 0.006$  Å

$R$  factor = 0.058

$wR$  factor = 0.066

Data-to-parameter ratio = 15.9

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

The crystal structure of the title compound,  $[\text{Li}(\text{C}_{16}\text{H}_{27}\text{N}_2\text{Si})\text{-(C}_6\text{H}_5\text{N}_2)]$ , contains the N—Si—N—Li four-membered heterocycle. The heterocycle contains a planar three-coordinated N-atom centre, a four-coordinated N-atom centre, a four-coordinate Li-atom centre and a four-coordinated Si-atom centre, and adopts a folded conformation. There are two molecules in the asymmetric unit.

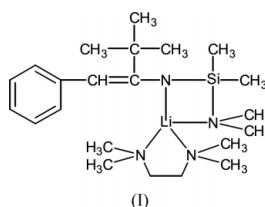
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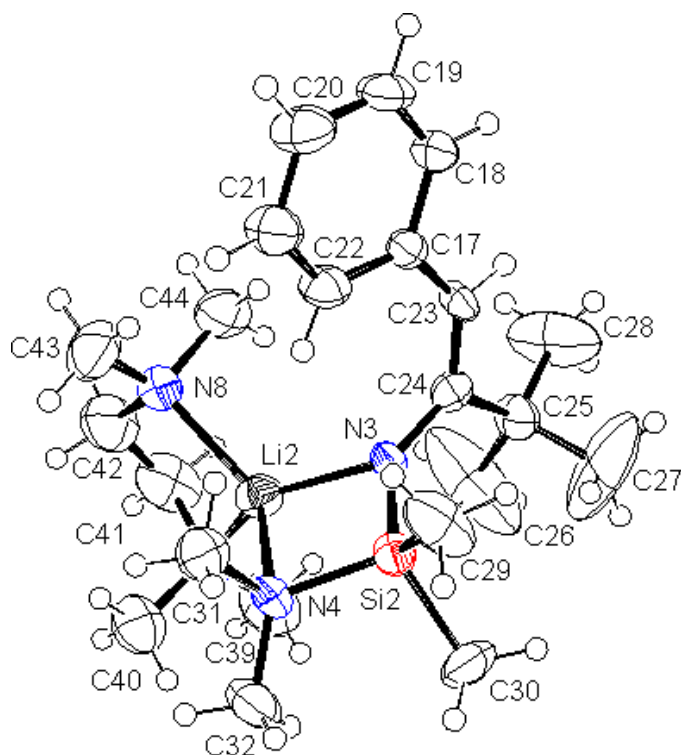
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## Comment

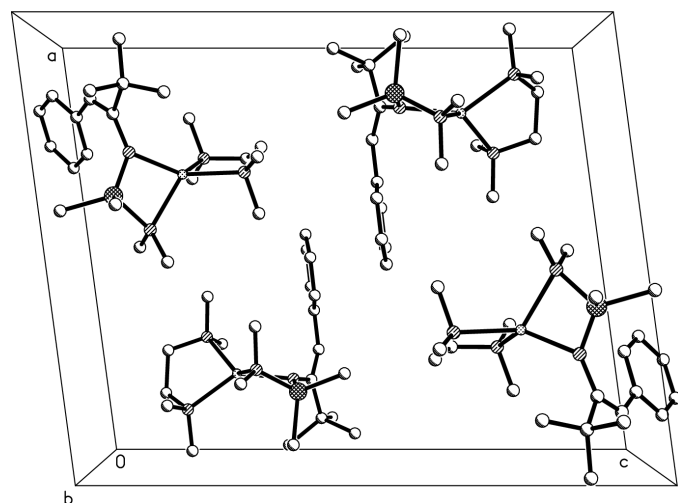
There is much current interest in the structures of organolithium compounds. We describe below an organolithium compound that has an unprecedented structure with several unusual features and possesses important potential for the synthesis of other novel organometallic compounds.



The novel title compound, (I), containing the N—Si—N—Li fragment, has been characterized by single-crystal X-ray diffraction analysis. There are two molecules in the asymmetric unit. Selected geometric parameters are listed in Table 1 and the molecular structure is illustrated in Fig. 1. This compound shows several interesting features. There is a four-membered ring in which two N atoms are bonded to Li; the ring contains a planar-coordinated N atom (N3, sum of angles  $359.9^\circ$ ), a four-coordinate Li center, and a four-coordinate N center. The four-membered ring adopts a folded conformation. The angle between the Li2/N3/Si2 and Li2/N4/Si2 planes is  $14.6(1)^\circ$ . The angle between the N3/Si2/N4 and N3/Li2/N4 planes is  $15.0(2)^\circ$ . As a consequence of the coordination of N4 to Li, the Si2—N4 bond length [ $1.766(3)$  Å] is longer than the N3—Si2 bond length [ $1.649(3)$  Å]; in the  $R_3\text{Si}-\text{NR}'_2$  species, the Si—N bond lengths fall in the range  $1.710\text{--}1.721$  Å (Lukevics *et al.*, 1985). The N3—C24 bond length [ $1.383(4)$  Å] is much shorter than the common N—C $_{sp^3}$  bond length, which usually lies in the range  $1.45\text{--}1.48$  Å, and this can be attributed to delocalization of the negative charge, either by  $\pi\text{--}\pi$  bonding or, more likely, by negative conjugation, leading to some double-bond character in the N3—C24 bond (Brinkman *et al.*, 1994). It is noteworthy that many novel species should be capable of formation by use of the title compound.



**Figure 1**  
One molecule of the asymmetric unit 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 compound, viewed along the *b* axis. For clarity, all H atoms have been omitted.

## Experimental

*n*-Butyllithium was added dropwise to a solution of toluene and TMEDA (*N,N,N',N'*-tetramethylethylenediamine) (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 dimethyl(dimethylamino)chlorosilane (molar ratio 1:1) was then added at 273 K and the temperature was allowed to rise to room temperature. The mixture was stirred for a further 15 h, yielding a white precipitate (LiCl). The mixture was filtered and benzyl(dimethyl)(dimethylami-

no)silane was isolated, as a colorless liquid, by vacuum distillation of the filtrate. A solution of Li<sup>*n*</sup>Bu in hexane was slowly added to benzyl(dimethyl)(dimethylamino)silane and TMEDA in pentane (molar ratio 1:1:1) at ambient temperature. The mixture was stirred for 18 h, Bu<sup>*n*</sup>CN (molar ratio 1:1) was added and stirring was continued for a further 4 h. The solution was concentrated and yielded colorless crystals of the title compound under vacuum. Crystals suitable for a single-crystal X-ray diffraction study were grown from a concentrated hexane solution at 253 K. All reactions were performed under argon, using standard Schlenk techniques. Hexane was dried by distilling from a sodium–potassium alloy, and pentane was distilled from a drying agent from sodium.

## Crystal data

[Li(C<sub>16</sub>H<sub>27</sub>N<sub>2</sub>Si)(C<sub>6</sub>H<sub>16</sub>N<sub>2</sub>)]  
*M<sub>r</sub>* = 398.63  
 Monoclinic, *P*<sub>2</sub><sub>1</sub>  
*a* = 14.819 (3) Å  
*b* = 9.4142 (16) Å  
*c* = 18.635 (3) Å  
 $\beta$  = 97.674 (3)°  
*V* = 2576.4 (8) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.028 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 1711 reflections  
 $\theta$  = 2.4–18.0°  
 $\mu$  = 0.10 mm<sup>-1</sup>  
*T* = 178 (2) K  
 Block, colorless  
 0.40 × 0.30 × 0.30 mm

## Data collection

Bruker CCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
*T<sub>min</sub>* = 0.960, *T<sub>max</sub>* = 0.969  
 10 666 measured reflections

8386 independent reflections  
 4772 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.043  
 $\theta_{max}$  = 25.0°  
*h* = −17 → 16  
*k* = −11 → 11  
*l* = −18 → 22

## Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.058  
*wR* (*F*<sup>2</sup>) = 0.066  
*S* = 0.83  
 8386 reflections  
 527 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0005P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.34 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{min} = -0.25 \text{ e } \text{Å}^{-3}$   
 Absolute structure: Flack (1983),  
 3546 Friedel pairs  
 Flack parameter = 0.05 (11)

**Table 1**

Selected geometric parameters (Å, °).

Li2–N3	2.013 (7)	Si2–C29	1.876 (3)
Li2–N7	2.143 (7)	Si2–C30	1.876 (4)
Li2–N8	2.137 (7)	N3–C24	1.383 (4)
Li2–N4	2.220 (7)	N4–C31	1.467 (4)
Si2–N3	1.649 (3)	N4–C32	1.480 (4)
Si2–N4	1.766 (3)		
N3–Li2–N7	136.9 (4)	C24–N3–Li2	131.4 (3)
N3–Li2–N8	120.4 (4)	Si2–N3–Li2	94.3 (2)
N7–Li2–N8	84.9 (3)	C31–N4–C32	108.6 (3)
N3–Li2–N4	77.5 (2)	C31–N4–Si2	116.0 (2)
N7–Li2–N4	114.2 (3)	C32–N4–Si2	118.4 (3)
N8–Li2–N4	130.1 (3)	C31–N4–Li2	103.2 (3)
N3–Si2–N4	101.99 (15)	C32–N4–Li2	124.3 (3)
N3–Si2–C29	114.94 (16)	Si2–N4–Li2	84.3 (2)
N4–Si2–C29	111.60 (17)	C24–C23–C17	132.1 (4)
N3–Si2–C30	119.26 (17)	C23–C24–N3	125.8 (4)
N4–Si2–C30	104.52 (18)	C23–C24–C25	117.6 (4)
C29–Si2–C30	104.14 (19)	N3–C24–C25	116.5 (3)
C24–N3–Si2	134.2 (3)		

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*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(C). 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  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The methyl groups (C26, C27 and C28) seem to be disordered the disorder but could not be resolved. Several higher symmetry space groups ( $P2_1/c$ ,  $P2_1/m$ ,  $P2_1/n$  and  $P2_12_12_1$ ) were examined, but none fitted the diffraction data.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE* (Bruker, 1998); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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