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Bis{μ-*N*-[(2-(dimethylamino)ethyl]-*N*′-(trimethylsilyl)benzamidinato}dilithium(I)

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Key indicators

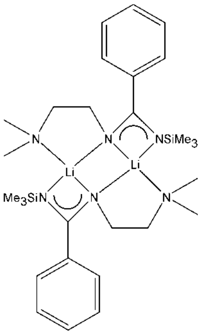
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.008 Å
R factor = 0.068
wR factor = 0.176
Data-to-parameter ratio = 16.2

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

The title compound, $[Li_2(C_{14}H_{24}N_3Si)_2]$, has been prepared in hexane and its structure has been determined. It crystallizes as a dimer with twofold rotation symmetry and the coordination geometry around the Li atoms is distorted tetrahedral, with each of the Li atoms bonding to two N atoms of an amidinate fragment in one ligand and to two N atoms of the other ligand in the dimer.

Comment

Amines and their derivatives have served as prospective ligands in the field of coordination chemistry (Li *et al.*, 2002). Their complexes with some later transition metals can be used as catalysts for the polymerization of α-olefins. In the case of unsymmetrical amines, it may be interesting to investigate the efficiency of the transition metal complexes in asymmetric synthesis. In our earlier publications, we have shown that the interaction of a trimethylsilylmethyllithium reagent Li[CHR_2] (R = SiMe$_3$) and an α-hydrogen-free nitrile can yield a 1-azaallyl- (Hitchcock *et al.*, 1994), a β-diketiminato- (Antolini *et al.*, 2000), or a 1,3-diazaallyllithium compound (Hitchcock *et al.*, 1999), as a result of 1,3-migration of an SiMe$_3$ group from carbon or nitrogen to nitrogen. These lithium complexes can be used as important ligands to combine with some transition metals to give novel complexes (Li *et al.*, 2003).



(I)

We chose unsymmetrical *N*,*N*-dimethylethylenediamine to form the title 1,3-diazaallyllithium, (I). This ligand has been used to synthesize a vanadium complex (Brandsma *et al.*, 1998). We used a similar method to synthesize the title lithium complex and obtained colourless crystals suitable for X-ray analysis. The molecular structure of (I) shows that the reaction involved a silicotropic rearrangement resulting in an N$\cdots$C$\cdots$N conjugated anion. This crystallographic study reveals some interesting features. The N$\cdots$C$\cdots$N fragments as η^3-anions have some degree of π-electron delocalization [Li$\cdots$C = 2.361 (9) Å, and Li—N = 1.992 (10) and

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2.120 (9) Å]. Both of the N atoms in the N⋯C⋯N conjugated anion are sp^2-hybridized; the sums of the angles around N2 and N3 are 352.8 and 359.7°, respectively. Two N atoms of the other ligand in the dimer are also coordinated to Li [Li—N = 2.050 (10) and 2.064 (10) Å]. The four-membered Li/N2/C5/N3 ring adopts a butterfly conformation. The angle between the Li/C5/N2 and Li/C5/N3 planes is 14.2 (5)°. Geometric parameters of the amidinate moiety of (I) are listed in Table 1 and the molecular structure is illustrated in Fig. 1.

Experimental

The title compound was prepared according to published methods (Brandsma *et al.*, 1998). A solution of *N,N*-dimethylethylenediamine (0.885 g, 0.01 mol) in 30 ml hexane was reacted with 7 ml *n*-butyllithium (1.44 *M* in hexane) at 273 K in hexane and stirred for a further 12 h. An equivalent of $SiMe_3Cl$ (1.5 ml, 0.01 mol) was then added by syringe to this solution at 195 K. The mixture was warmed slowly to room temperature and stirred for a further 12 h. The mixture was then filtered and 7 ml of *n*-butyl lithium (1.44 *M* in hexane) was added to the solution, again at 273 K, followed by dropwise addition of 1 ml benzonitrile (0.01 mol) to this solution at 273 K with stirring for 5 h. This solution was concentrated to yield the title crystalline product.

Crystal data

$[Li_2(C_{14}H_{24}N_3Si)_2]$
$M_r = 538.78$
Monoclinic, $C2/c$
$a = 21.104$ (2) Å
$b = 9.1302$ (10) Å
$c = 18.3734$ (19) Å
$\beta = 103.935$ (2)°
$V = 3436.1$ (6) Å^3
$Z = 4$

$D_x = 1.042$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9407 reflections
$\theta = 2.3$–27.6°
$\mu = 0.13$ mm^{-1}
$T = 293$ (2) K
Block, colourless
0.40 × 0.40 × 0.30 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.951$, $T_{\max} = 0.963$
6849 measured reflections

3016 independent reflections
2510 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.029$
$\theta_{\max} = 25.0°$
$h = -24 \rightarrow 16$
$k = -10 \rightarrow 10$
$l = -17 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.068$
$wR(F^2) = 0.177$
$S = 1.06$
3016 reflections
186 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0886P)^2 + 4.4198P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.42$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Li—N3	1.992 (10)	Li—N2^{i}	2.064 (10)
Li—N1^{i}	2.050 (10)	Li—N2	2.120 (9)
C5—N2—C4	120.0 (4)	C5—N3—Si1	131.4 (4)
C5—N2—Li	83.2 (4)	C5—N3—Li	88.5 (4)
C4—N2—Li	149.6 (4)	Si1—N3—Li	139.8 (3)

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

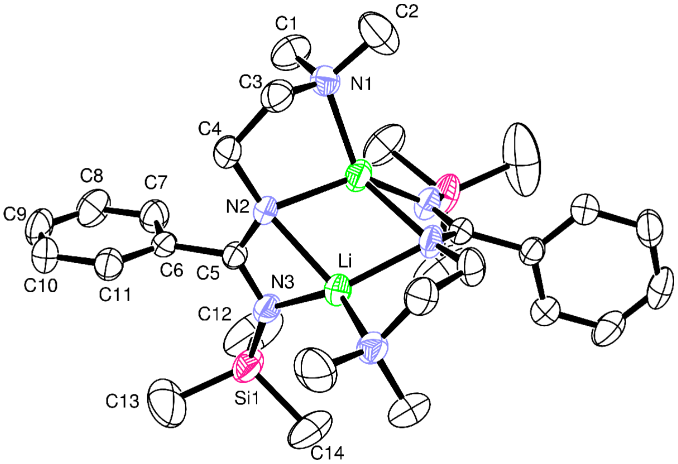

Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by small spheres of arbitrary radii.

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 $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C})$, but each group was allowed to rotate freely about its C—C 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 $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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