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Key indicators

Single-crystal X-ray study
T = 190 K
Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
R factor = 0.054
wR factor = 0.065
Data-to-parameter ratio = 17.0

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

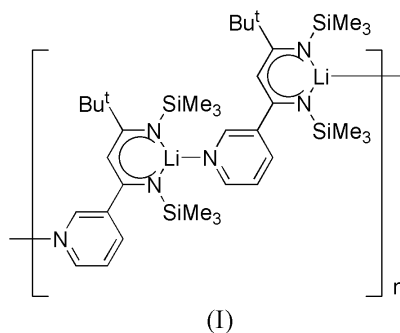
catena-Poly[lithium(I)- μ -1-tert-butyl-3-(3-pyridyl)-N,N'-bis(trimethylsilyl)propane-1,3-diiminato]

The title compound, $[\text{Li}(\text{C}_{18}\text{H}_{32}\text{N}_3\text{Si}_2)]_n$, is a convenient ligand-transfer reagent for the synthesis of metal complexes of this β -diketiminato ligand. Lithium is coordinated by three N atoms: two are in the delocalized NCCCN fragment and one is from the pyridyl in an adjacent molecule. Owing to the coordination of lithium by the pyridyl N atom, the crystal structure displays a one-dimensional polymeric structure.

Received 3 February 2005
Accepted 16 February 2005
Online 26 February 2005

Comment

β -Iminoamine compounds have been used as precursors for monoanionic bidentate ligands as early as 1968 (Parks & Holm, 1968), with research on this unique ligand system increasing significantly over the past decade (Hitchcock *et al.*, 1994a; Laurence *et al.*, 2002). This class of ligand combines a number of advantages, among which are ease of synthesis, easy variation of substituents, extreme steric bulk, and strong donor properties. The synthesis, structures and reactions of alkali metal (in particular lithium) 1,3-bis(trimethylsilyl)-1-azaallyls and β -diketiminates, including their role as precursors for preparing unusual transition metal and main group element complexes, have been reported (Chen *et al.*, 2002; Laurence *et al.*, 2002). In order to study the steric and electronic effects of the ligand and its metal complexes, a pyridyl group was introduced into the β -diketiminato ligand. We report here the synthesis and structure of a novel ligand-transfer reagent, the title lithium β -diketiminato compound, (I).



The molecular structure of (I) is shown in Fig. 1 and selected geometric parameters are listed in Table 1. The N1—C7, C7—C6, C6—C1 and C1—N2 bond lengths are 1.317 (4), 1.399 (4), 1.405 (4) and 1.317 (3) Å, respectively. These bond lengths are longer than the normal C=N and C=C double-bond lengths of 1.290 (2) and 1.359 (3) Å, respectively, and shorter than the normal single-bond lengths of 1.364 (3) and 1.455 (3) Å, respectively (Chen *et al.*, 2004). This fact suggests delocalization of electrons within the π -system of the β -

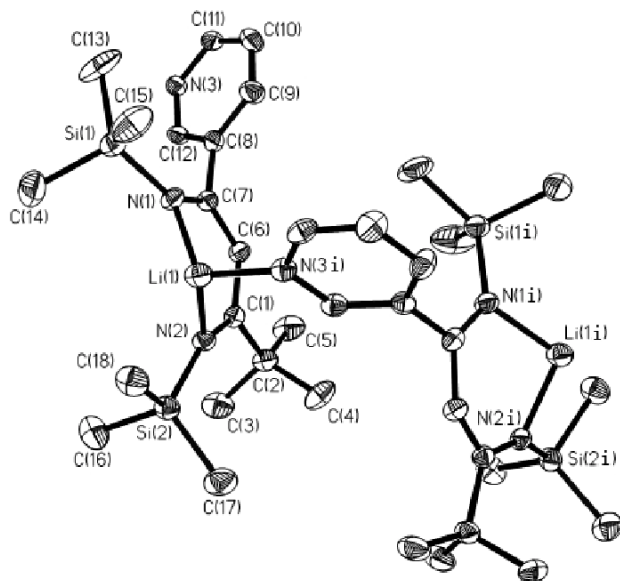


Figure 1
Two repeat units of the polymeric structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity. [Symmetry code as in Table 1.]

diketiminate ligand; this does not extend fully to the pyridyl ring (*cf.* the dihedral angle of 102.5°). The distances between Li1 and atoms C1, C6 and C7 are quite long, suggesting a negligible η^5 - π -bond contribution to β -diketiminate–Li bonding in (I).

Mononuclear β -diketiminate lithium complexes having a tetrahedral coordination and binuclear complexes having both chelating and bridging ligands and a four-membered Li_2N_2 ring have been reported previously (Hitchcock *et al.*, 1994*b*). In compound (I), however, the Li atom is coordinated by atoms N1 and N2 of the β -diketiminate ligand and pyridyl atom N3ⁱ from a neighbouring molecule [symmetry code: (i) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$] to form a polymeric structure (Fig. 2). The Li atom adopts a distorted trigonal planar LiN_3 coordination geometry. The distance from the Li atom to the N1–N2–N3ⁱ plane is 0.57 (2) Å. The five atoms N1/C7/C6/C1/N2 of the ligand deviate slightly from perfect coplanarity (mean deviation = 0.0312 Å), with the Li atom located 0.86 (2) Å from the plane.

Experimental

All manipulations were carried out under argon using standard Schlenk techniques. Solvents (hexane and diethyl ether) were distilled from drying agents and degassed with argon prior to use. The NMR spectra were recorded on a Bruker DKX300 instrument and solvent resonances were used as the internal references for ^1H and ^{13}C spectra. For the preparation of (I), a solution of bis(trimethylsilyl)methyl lithium (0.54 g, 3.25 mmol) in Et_2O (20 ml) was cooled to 273 K. To this solution, trimethylacetone nitrile (0.34 ml, 3.25 mmol) was added slowly *via* a syringe. The mixture was stirred at 273 K for 30 min and then warmed slowly to room temperature and allowed to react for 2 h. After recooling the mixture to 273 K, *m*-cyanopyridine (0.321 g, 3.09 mmol) in diethyl ether was added and the temperature was allowed to rise to room temperature; the mixture was stirred for a further 8 h, yielding a brown precipitate. The mixture was filtered and

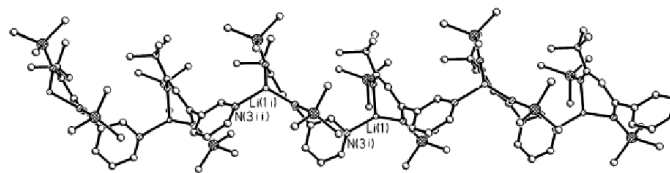


Figure 2
Part of the crystal structure of (I), showing the formation of a one-dimensional polymeric structure along [100]. For clarity, H atoms have been omitted.

the filtrate was concentrated to *ca* 10 ml and then cooled at 243 K for 2 d to give yellow crystals (0.82 g, 75%) of the title compound, (I). ^1H NMR (C_6D_6 , 298 K, 300 MHz): δ 8.99 (*s*, 1H, *m*-pyridyl), 8.60 (*d*, 2H, *m*-pyridyl), 7.09 (*s*, 1H, *m*-pyridyl), 5.52 (*s*, 1H, CH), 1.16 (*s*, 9H, CMe_3), 0.49 (*s*, 9H, SiMe_3), 0.01 (*s*, 9H, SiMe_3). ^{13}C NMR (C_6D_6 , 298 K, 75 MHz): δ 181.14 (1C of diketimine), 161.55 (1C of diketimine), 149.69 (2C of *m*-pyridine ring), 122.84 (2C of *m*-pyridine ring), 98.63 (1C of diketimine), 99.77 (1C of diketimine), 29.41 (3C of *tert*-butyl), 3.85 (3C of SiMe_3), 1.71 (3C of SiMe_3).

Crystal data

$[\text{Li}(\text{C}_{18}\text{H}_{32}\text{N}_3\text{Si}_2)]$
 $M_r = 353.59$
Monoclinic, $P2_1/n$
 $a = 11.398$ (4) Å
 $b = 18.283$ (6) Å
 $c = 11.659$ (4) Å
 $\beta = 115.690$ (5) $^\circ$
 $V = 2189.3$ (13) Å³
 $Z = 4$

$D_x = 1.073$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 1413 reflections
 $\theta = 2.4$ – 27.4°
 $\mu = 0.17$ mm⁻¹
 $T = 190$ (2) K
Block, yellow
0.30 × 0.20 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2000)
 $T_{\text{min}} = 0.952$, $T_{\text{max}} = 0.968$
8928 measured reflections

3845 independent reflections
1749 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.068$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -11 \rightarrow 13$
 $k = -20 \rightarrow 21$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.065$
 $S = 0.84$
3845 reflections
226 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0002P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.25$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.25$ e Å⁻³

Table 1

Selected geometric parameters (Å, $^\circ$).

Li1–N1	1.924 (5)	N2–C1	1.317 (3)
Li1–N2	1.946 (5)	N2–Si2	1.697 (3)
Li1–N3 ⁱ	2.033 (6)	C1–C6	1.405 (4)
N1–C7	1.317 (4)	C6–C7	1.399 (4)
N1–Si1	1.716 (2)		
N1–Li1–N2	102.1 (3)	C1–N2–Si2	146.7 (2)
N1–Li1–N3 ⁱ	119.0 (3)	C1–N2–Li1	110.6 (3)
N2–Li1–N3 ⁱ	114.4 (3)	Si2–N2–Li1	102.6 (2)
C7–N1–Si1	134.1 (2)	N2–C1–C6	122.1 (3)
C7–N1–Li1	106.5 (3)	C7–C6–C1	129.1 (3)
Si1–N1–Li1	119.4 (2)	N1–C7–C6	128.6 (3)

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

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 $U_{iso}(H) = 1.5U_{eq}(C)$. H atoms on Csp^2 atoms were allowed to ride on their parent atoms, with C–H distances of 0.93 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL/PC*.

We thank the Natural Science Foundation of China (No. 20171030 to DSL) the Natural Science Foundation of Shanxi province (No. 20011008 to DSL) and the Youth Science Foundation of Shanxi Province (No. 20001004 to XC).

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