Synthesis and Molecular Structure of the Solvent-Free $[LiN(SiMe_3)(2,6\text{-}iPr_2C_6H_3)]_2$ Dimer

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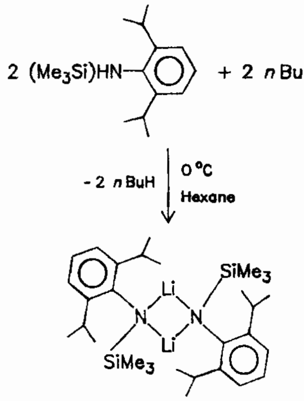
$[LiN(SiMe_3)Ar]_2$ (**1**, Ar = 2,6-$iPr_2C_6H_3$) is prepared by the reaction of $HN(SiMe_3)Ar$ with *n*BuLi in *n*-hexane. This compound with an unusual structure contains a four-membered $[LiN]_2$ heterocycle with two solvent-free two-coordinate Li centers. Its molecular structure represents the first solid-state X-ray analysis of an uncomplexed $[LiN]_2$ dimer.

Amidolithium compounds have been extensively used both as precursors of other metal amides and as strong Brønsted bases or nucleophiles in organic syntheses[1]. Only a very small number of the known lithium amide molecular structures contain no coordinating solvent bound to the lithium atom. For uncomplexed species either $[LiN]_4$ tetramers or $[LiN]_3$ trimers seem to be the preferred structural units, with relatively wide angles at Li[2]. For example, the NLiN angles in the $[Li\overline{NCMe_2(CH_2)_3C}Me_2]_4$ tetramer[3] and the $[LiN(SiMe_3)_2]_3$ trimer[4] are 168.5(4) and 147(3)°, respectively. Although a molecular model of the dimer $[LiN(SiMe_3)_2]_2$[5], as determined by gas-phase electron diffraction, has been reported with NLiN angles of 100(3)°, to our knowledge no such solvent-free $[LiN]_2$ dimer is known in the solid state. In this paper we report on the X-ray crystal structure of $[LiN(SiMe_3)Ar]_2$ (**1**, Ar = 2,6-$iPr_2C_6H_3$) as an unprecedented example of this unusual $[LiN]_2$ structure type.

$HN(SiMe_3)Ar$ was treated with *n*BuLi in *n*-hexane to obtain a quantitative yield of **1**. Upon brief exposure to air this white product decomposes to form a black product.



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Colorless plate-like crystals of **1** suitable for single-crystal X-ray analysis were obtained from an *n*-hexane solution. Details of the data collection, solution and refinement are given in the Experimental section and selected bond lengths as well as angles and complete atomic coordinates are given in Tables 1 and 2. The title compound contains two similar but independent monomers in the asymmetric unit. Application of the centers of symmetry at (1, 0.5, 0) and (0.5, 0, 0.5) yields the two $[LiN]_2$ dimers. One of these is shown in Figure 1. The $SiMe_3$ groups are *trans* to each other across the plane formed by the four-membered $[LiN]_2$ ring; likewise the aromatic groups also adopt a *trans* configuration. This allows these bulky groups to be well separated in space. The more sterically demanding trimer geometry, which $[LiN(SiMe_3)_2]_3$ adopts[4], is not favored in our compound, presumably due to the bulky aromatic groups. In the analogous $[LiC]_n$ system a bulky substituent like $C(SiMe_3)_3$ leads to a dimeric structure, as demonstrated by a recently reported solvent-free $[LiC(SiMe_3)_3]_2$ dimer, while Me/Et, $CH_2(SiMe_3)$, and $CH(SiMe_3)_2$ groups form LiC tetramers, hexamers, and polymers, respectively[6].

Table 1. Selected bond lengths [Å] and angles [°] for $[LiN(SiMe_3)Ar]_2$ (**1**, Ar = 2,6-$iPr_2C_6H_3$)

Li(1)-N(1)	1.961 (4)	Li(1)-N(1A)	1.962 (5)
N(1)-C(1)	1.419 (3)	N(1)-Si(1)	1.707 (2)
N(1)-Li(1A)	1.962 (5)	Li(2)-N(2)	1.958 (4)
Li(2)-N(2A)	1.949 (5)	N(2)-C(21)	1.422 (3)
N(2)-Si(2)	1.701 (2)	N(2)-Li(2A)	1.949 (5)
N(1)-Li(1)-N(1A)	106.3(2)	Li(1)-N(1)-C(1)	109.1(2)
Li(1)-N(1)-Si(1)	113.8(2)	C(1)-N(1)-Si(1)	124.9(1)
Li(1)-N(1)-Li(1A)	73.7(2)	C(1)-N(1)-Li(1A)	90.2(2)
Si(1)-N(1)-Li(1A)	133.7(2)	N(2)-Li(2)-N(2A)	106.3(2)
Li(2)-N(2)-C(21)	103.1(2)	Li(2)-N(2)-Si(2)	119.5(2)
C(21)-N(2)-Si(2)	126.4(1)	Li(2)-N(2)-Li(2A)	73.7(2)
C(21)-N(2)-Li(2A)	98.9(2)	Si(2)-N(2)-Li(2A)	122.1(2)

The NLiN bond angle [106.3(2)°] of the dimer **1** is significantly smaller than in LiN trimers or tetramers (144 – 168°), but is comparable to $[LiN]_2$ dimers that contain complexing solvent molecules. For example, similar LiNLi angles are seen in $[LiN(SiMe_3)_2 \cdot Et_2O]_2$ [104.9(3)°][7], $[LiN(SiMe_3)_2 \cdot THF]_2$ [106.3(3)°][8], $[LiN(CH_2Ph)_2 \cdot Et_2O]_2$ [104.0(4)°][9], and $[LiN(CH_2Ph)_2 \cdot hmpa]_2$ [102.7(4)°][9].

As expected, the average LiN distance in **1** (1.958 Å) is significantly shorther than in the aforementioned $[LiN]_2$ di-

Chem. Ber. **124** (1991) 2223 – 2225 © VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1991 0009 – 2940/91/1010 – 2223 $ 3.50+.25/0

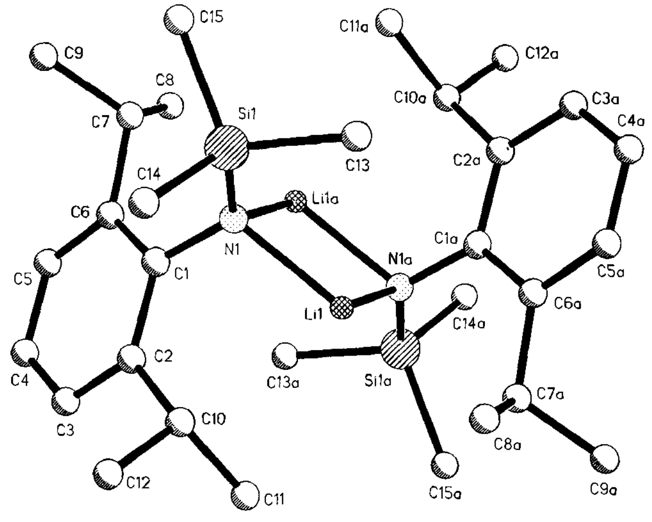

Figure 1. Perspective view of one of the two similar but independent $[LiN(SiMe_3)Ar]_2$ dimers in the asymmetric unit of **1**. The hydrogen atoms have been omitted for clarity

mers [1.992–2.055(8) Å] which all possess a coordinating solvent at the lithium center. In addition, several close Li···H and Li···C contacts (Figure 2) have been observed in **1**, suggesting interactions between Li and some atoms of the aromatic groups. It is interesting to note that there are two LiH interactions of less than 2.33 Å around each lithium center. In one molecule this stems from two hydrogen atoms on separate isopropyl groups and in the second molecule from two hydrogen atoms on the same isopropyl group (Figure 2). However, the importance of such interactions in stabilizing the lithium atom in this compound is difficult to determine solely from the Li···H distances. First, the hydrogen atom positions cannot be determined to high accuracy in X-ray diffraction studies. In addition, in a PRDDO molecular orbital calculation study of the electronic structure of alkyllithium clusters Dixon and coworkers[10] note that Li···HC overlap populations (a reflection of LiH interaction) may differ significantly even though Li···CHC distances remain quite similar.

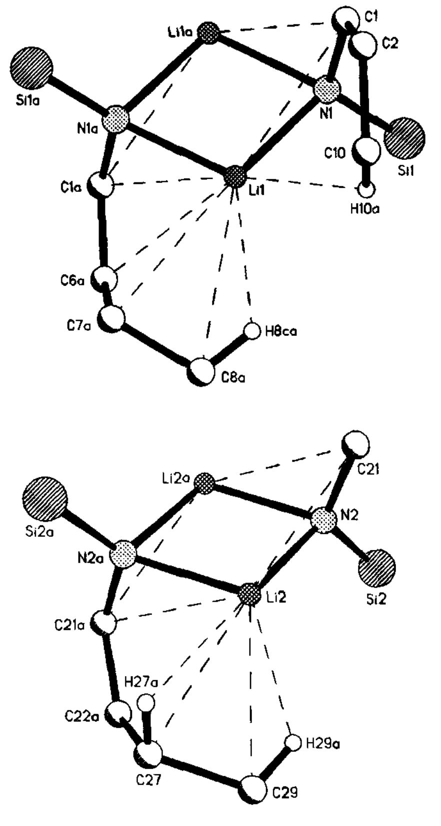

Figure 2. Li environments showing shortest Li···C (<2.82 Å) and Li···H (<2.33 Å) contacts for the two independent $[LiN(SiMe_3)Ar]_2$ molecules in the asymmetric unit of **1** (distances in Å). Li1···H8ca [2.275(5)], Li1···H10a [2.302(5)], Li1···C7a [2.746(5)], Li1···C6a [2.698(5)], Li1···C1a [2.424(5)], Li1···C1 [2.771(4)], Li2···H27a [2.272(5)], Li2···H29a [2.246(5)], Li2···C21a [2.585(5)], Li2···C27 [2.693(5)], Li2···C29 [2.790(5)], Li2···C21 [2.668(5)]

The ^{7}Li-NMR spectrum of **1**, which shows one signal at $\delta = 0.88$, seems to indicate that only one lithium species exists in solution. The ^{1}H-NMR spectrum of **1** is similar to that of its precursor, $HN(SiMe_3)Ar$, with some important exceptions. As expected, there is no NH proton signal at $\delta = 2.00$. In addition, the $SiMe_3$ methyl signals have moved downfield from $\delta = 0.01$ in $HN(SiMe_3)Ar$ to $\delta = 0.12$ in **1**. Finally, the appearance of two separate $HCMe_2$ methyl signals ($\delta = 0.89$ and 1.19) is consistent with the crystal structure of **1** if the rotation of the aromatic groups about the N–C bond is restricted. This hindered rotation might indicate that a larger aggregate than a LiN monomer exists in solution.

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Experimental

$HN(SiMe_3)(2,6\text{-}iPr_2C_6H_3)$ was prepared according to published methods[11]. *n*BuLi (1.6 M in *n*-hexane) was obtained from Janssen and used without further purification. *n*-Hexane was dried and distilled before use. – NMR: Bruker AM-250, solutions in C_6D_6, TMS and LiCl as external references for ^{1}H and ^{7}Li NMR, respectively. – MS: Finnigan MAT-8230 spectrometer, 70 eV. – All manipulations were carried out either on a vacuum line or in a MB-150B dry box from Braun under oxygen-free nitrogen. – Melting point: Sealed melting point capillary.

Lithium 2,6-Diisopropyl-N-(trimethylsilyl)anilide Dimer (**1**): A 1.6 M solution of *n*BuLi (3.5 ml, 5.6 mmol) was added slowly to an *n*-hexane solution of $HN(SiMe_3)(2,6\text{-}iPr_2C_6H_3)$ (1.35 g, 5.42 mmol) at 0°C. The cloudy white solution that formed was stirred at room temp. for 3 h to ensure complete reaction. The solvent was removed in vacuo leaving a white solid, m.p. 166–169°C (dec.). – MS (EI): *m/z* (%) = 510 (4) [M], 262 (39) $[Li_2N(SiMe_3)Ar]$, 249 (100) $[N(SiMe_3)Ar]$, 234 (96) $[N(SiMe_2)Ar]$, 176 (21) [NAr], 160 (11) [Ar], 73 (99) $[SiMe_3]$. – ^{1}H NMR (C_6D_6): $\delta = 6.98-7.16$ (m, 6H, aromatic H), 3.48 (sept, 4H, $HCMe_2$, $^3J_{HH} = 6.9$ Hz), 1.19 (d, 12H, $HCMe_2$), 0.89 (d, 12H, $HCMe_2$), 0.10 (s, 18H, $SiMe_3$). – ^{7}Li NMR (C_6D_6): $\delta = 0.88$ (s).

$C_{30}H_{52}Li_2N_2Si_2$ (510.8)	Calcd.	C 70.54	H 10.26	N 5.48
	Found	C 69.63	H 10.20	N 5.48

Crystal Structure of **1**: Slow solvent reduction of an *n*-hexane solution of **1** results in colorless plate-like crystals. Using an inert

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for $[LiN(SiMe_3)Ar]_2$ (**1**). Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
Li(1)	10908(5)	4173(4)	295(3)	44(2)
N(1)	10171(2)	5941(2)	721(1)	21(1)
C(1)	8927(2)	6025(2)	1240(1)	21(1)
C(2)	8891(2)	5071(2)	1860(1)	23(1)
C(3)	7618(2)	5084(2)	2289(2)	29(1)
C(4)	6349(3)	6009(2)	2131(2)	32(1)
C(5)	6369(2)	6941(2)	1537(1)	30(1)
C(6)	7626(2)	6990(2)	1098(1)	25(1)
C(7)	7556(3)	8075(2)	474(2)	38(1)
C(8)	6595(3)	8051(3)	-269(2)	67(1)
C(9)	7066(4)	9390(3)	920(2)	63(1)
C(10)	10212(2)	3984(2)	2045(1)	27(1)
C(11)	10067(3)	2697(2)	1702(2)	37(1)
C(12)	10539(3)	3863(3)	2986(2)	39(1)
Si(1)	11477(1)	6674(1)	937(1)	29(1)
C(13)	13039(3)	5903(4)	232(2)	83(2)
C(14)	12030(3)	6509(3)	2061(2)	50(1)
C(15)	11046(4)	8439(3)	728(2)	75(2)
Li(2)	5915(4)	-110(5)	4480(3)	52(2)
N(2)	3851(2)	529(2)	4319(1)	19(1)
C(21)	3601(2)	1888(2)	4376(1)	20(1)
C(22)	2597(2)	2616(2)	4991(1)	22(1)
C(23)	2501(2)	3914(2)	5113(2)	29(1)
C(24)	3336(3)	4537(2)	4648(2)	34(1)
C(25)	4294(3)	3846(2)	4040(2)	31(1)
C(26)	4439(2)	2552(2)	3893(1)	24(1)
C(27)	8371(2)	-2014(2)	4466(1)	23(1)
C(28)	9955(2)	-2742(2)	4538(2)	33(1)
C(29)	7968(3)	-1922(2)	3526(1)	33(1)
C(30)	5533(2)	1863(2)	3214(1)	27(1)
C(31)	7075(3)	1729(3)	3481(2)	39(1)
C(32)	5279(3)	2533(3)	2351(2)	40(1)
Si(2)	3032(1)	-278(1)	3661(1)	19(1)
C(33)	3489(3)	-139(2)	2506(1)	33(1)
C(34)	3665(3)	-2019(2)	3955(2)	29(1)
C(35)	1024(2)	237(2)	3737(2)	30(1)

mounting oil, we were able to rapidly isolate and mount suitable crystals[12]. These were transferred immediately to the low-temperature gas stream of the diffractometer, where the crystals were stable. Data were collected at −120°C on a Siemens-Stoe AED four-circle diffractometer by using graphite-monochromated Mo-K_α radiation. 2θ-ω scans with online profile fitting[13] and variable scan speeds were employed. The structure was solved by Direct Methods (SHELXS-86)[14] and refined by full-matrix least squares techniques (SHELX-76, modified by the author) (Table 2).

Crystallographic data for **1**: $C_{30}H_{52}Li_2N_2Si_2$, $M_r = 510.8$, colorless, crystal dimensions $0.4 \times 0.4 \times 0.7$ mm³, triclinic, $a = 9.699(2)$, $b = 10.787(2)$, $c = 15.750(3)$ Å, $\alpha = 89.74(2)$, $\beta = 88.24(2)$, $\gamma = 74.36(2)°$, $V = 1586.0(5)$ Å³, space group $P\bar{1}$, $Z = 2$, $F(000) = 560$, $d_{calc} = 1.07$ gcm^{-3}, $\mu = 0.13$ mm^{-1}, 5401 reflections collected ($8 < 2\Theta < 48°$), 4943 unique and 4503 observed reflections with $F > 4.0\sigma(F)$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted at calculated positions, except for those on the isopropyl methyl groups which were located from difference Fourier maps and subsequently moved along the C−H vector to an idealized length of 0.96 Å. The full-matrix refinement of 329 parameters converged with $R = 0.045$, $R_w = 0.067$, $w^{-1} = \sigma^2(F) + 0.0001 F^2$ and maximum/minimum rest electron density $+0.4/-0.4$ eÅ^{-3}.

Further details of the crystal structure investigation are available on request from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-55317, the names of the authors, and the journal citation.

CAS Registry Numbers

1: 134286-02-5 / **1** (Salz): 134208-71-2 / *n*BuLi: 109-72-8 / HN-$(SiMe_3)(2,6\text{-}iPr_2C_6H_3)$: 78923-65-6

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