A New Lithium Amide with Bulky Substituents – Molecular Structure of N-Lithio-N-trimethylsilyl-9-amino-9-borabicyclo[3.3.1]nonane; Competition between N-Li and BN(pp)π Interactions

Bernd Wrackmeyer*, Bernd Schwarze, Jürgen Weidinger, Wolfgang Milius

Laboratorium für Anorganische Chemie, Universität Bayreuth, D-95440 Bayreuth, Germany

Dedicated to Prof. Dr. Hans Bürger on the occasion of his 60th birthday

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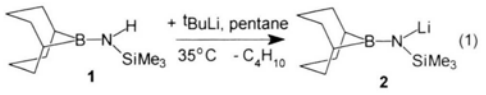
N-Lithio-N-trimethylsilyl-9-amino-9-borabicyclo[3.3.1]nonane (**2**) was prepared from the reaction of N-trimethylsilyl-9-amino-9-borabicyclo-[3.3.1]nonane (**1**) with *tert*-butyl lithium; **2** crystallizes as a trimer with a planar N_3Li_3 ring. The nitrogen atoms are tetrahedrally coordinated, but should be treated as sp^2 hybridised, because the BN double bond, typical of aminoboranes, is retained.

Lithium amides Li-NR^1R^2 (R^1,R^2 = alkyl, aryl or silyl) are of great importance in organic and organometallic synthesis, and therefore considerable efforts have been made to characterize these compounds in the solid state [1,2] and in solution [3]. In the case of unsolvated lithium amides, aggregation to dimers, trimers, stagged hexamers or ladder-type structures is observed [1,2]. The surroundings of the nitrogen atoms resemble a distorted tetrahedron corresponding approximately to sp^3 hybridisation. This view may be too simple, as has been shown recently for the structures of thf-solvated lithium anilides [4] in which phenyl-N-(pp)π interactions play a role. Substituents such as silyl and/or boryl groups at the nitrogen atom, in lithium amides may also well compete with the positively charged lithium atoms for an interaction with nitrogen electron density.

N-Lithioaminoboranes are useful reagents [5–7], but their molecular structure in the solid state has not been determined so far. N-Lithioaminosilanes have also proved very useful in synthesis, and the molecular structure of N-lithio-bis(trimethylsilyl)amine has been determined and shown to be a trimer [8,9]. Dimers are present in its complex with two equivalents of $MeP(O)Ph_2$ [10]. We have now prepared the new lithium amide **2** in which the nitrogen atom bears a trimethylsilyl and a 9-borabicyclo[3.3.1]nonyl group. Compound **2** is obtained in 95% yield as a colourless solid by treatment of the aminoborane **1** [11] with tert-butyl lithium [eq. (1)]. It is moderately soluble in hexane, benzene or toluene, and can be stored for prolonged time without decomposition at ambient temperature under inert atmosphere of N_2 or Ar.



Single crystals of **2**, suitable for X-ray structural analysis, were obtained from hexane solution by recrystallization in a soxhlet apparatus, which allowed for the first time to determine the molecular structure of an N-lithioaminoborane. As shown in Fig. 1, compound **2** crystallizes as a trimer with a planar (mean deviation 3.5 pm) N_3Li_3 ring [average values N-Li 197.8(4) pm, N-Li-N 151.4(4)°, and Li-N-Li 88.3(4)°]. All boryl groups in the trimer are in *cis*-positions with respect to the ring plane. There appears to be slight disorder in each 9-borabicyclo[3.3.1]nonyl fragment with respect to chair or boat conformation of one of the six-membered rings. Intermolecular contacts between the trimers seem to be weak or negligible. In the unit cell, the trimers are arranged in such a way that the boryl groups are distant and the silyl groups are close to each other. Within the trimer, there are numerous short Li-H, Li-C and Li-Si contacts compensating for the low coordination number of the lithium atoms.

The N_3Li_3 ring and the perpendicular arrangement of the substituents in **2** remind very much of the molecular structure of $[(Me_3Si)_2NLi]_3$ [average values [9] N-Li 200(2)pm, N-Li-N 147(3)° and Li-N-Li 92(2)°], in which "onium"-type configuration has been assigned to the nitrogen atoms. However, in the case of **2**, the lengths of the BN bonds [average value B-N 140.1(6) pm] clearly indicate BN double bonds [12] (typically, the lengths of BN single bonds with trigonal boron and nitrogen atoms fall in the range between 147–149 pm [12]), and therefore the nitrogen atoms cannot be

* Reprint requests to Prof. Dr. B. Wrackmeyer.

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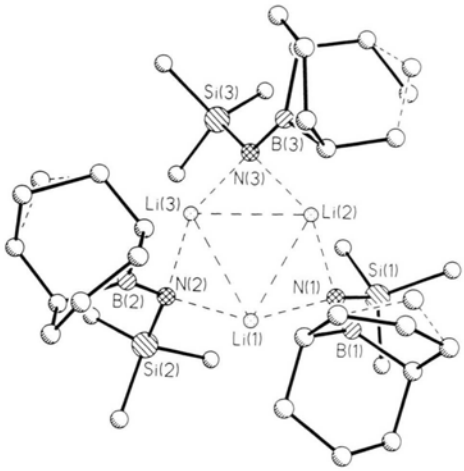

Fig. 1. Molecular structure (without hydrogen atoms) of trimeric N-lithio-N-trimethylsilyl-9-amino-9-borabicyclo[3.3.1]nonane (**2**). Selected bond lengths [pm] and angles [°]: N(2)-Li(1) 198.6(7), N(2)-Li(3) 197.8(8), N(2)-B(2) 139.8(5), N(2)-Si(2) 172.8(3); Li(1)-N(2)-Li(3) 90.0(3), N(2)-Li(1)-N(1) 147.8(5), N(2)-Li(3)-N(3) 150.3(4), B(2)-N(2)-Si(2) 121.6(3).

assigned an "onium" configuration. The presence of a BN double bond is also evident from the small Si-N-B-C torsion angles (all < 3°). Thus, the nitrogen atoms are sp^2 hybridised, in spite of their tetrahedral environment. The orientation of the lone pair of electrons, not involved in BN(pp)π bonding, at each nitrogen atom points into the space between pairs of lithium atoms. In accordance with the mainly ionic character of the N-Li interactions [1], difference electron density maps, based on the experimental X-ray diffraction data, of the planar N_3Li_3 ring show that essentially all electron density is located at the nitrogen atoms, slightly shifted towards the centre of an imaginary line connecting each pair of lithium atoms. The rather small structural differences between **2** and other known trimers [1,8,9] suggests that the concept of an sp^3 hybridised, ammonium-type nitrogen atom should be reconsidered, at least in the case of $[(Me_3Si)_2NLi]_3$.

The synthetic potential of **2** [13] is similar to that of the widely used reagent N-lithio-bis(trimethylsilyl)amine [14–16], with the additional advantage of the presence of the boryl group. The structural features of the products of the reactions of **2** with element halides will be of considerable interest.

Experimental

All compounds were handled under an atmosphere of dry argon or nitrogen, using carefully dried solvents. Reagents such as *tert*-butyl lithium were used as commercially obtained, and **1** was prepared as reported [11]. NMR measurements were carried out using a Bruker ARX 250 spectrometer, equipped with a multinuclear unit. Chemical shifts are given with respect to Me_4Si [$\delta^1H(C_6D_5H)$ = 7.15; $\delta^{13}C(C_6D_6)$ = 128.0; $\Xi(^{29}Si)$ = 19.867184 MHz] and external Et_2O-BF_3 [$\Xi(^{11}B)$ = 32.083971 MHz].

N-Lithio-N-trimethylsilyl-9-amino-9-borabicyclo[3.3.1]nonane (**2**)

A solution (50 ml) of ^{t}BuLi in hexane (1.6 M) was heated at reflux and 16.65 g (80 mmol) of N-trimethylsilyl-9-amino-9-borabicyclo[3.3.1]nonane (**1**) dissolved in 50 ml of hexane were slowly added within 30 min. Evolution of gas finished after 30 min, and all volatile material was removed in vacuo. A colourless solid was left which was taken up in 100 ml of hexane and transferred into a soxhlet apparatus. After 4 h of extraction the hexane solvent was removed *in vacuo*. 16.2 g (95%) of **2** were obtained as a crystalline solid [m.p. > 170°C (decomp.)]. ^{1}H NMR (C_6D_6): δ = 1.90–1.77 (m, BCCH), 1.40–1.38 (m, BCCCH), 1.27 [broad] (BCH), 0.24 (s, $SiMe_3$); ^{11}B NMR (C_6D_6): δ = 54.8; ^{13}C NMR (C_6D_6): δ = 33.9 (BC**C**), 29.3 [broad] (BC), 23.5 (BCC**C**), 4.5 ($SiMe_3$); ^{29}Si NMR (C_6D_6): δ = −4.3.

X-ray analysis and crystal data for 2: The colorless crystal of **2** was grown from a hexane solution by using a soxhlet apparatus and put into a Lindemann capillary (0.3 mm diameter). $C_{33}H_{69}B_3Li_3N_3Si_3$; M = 645.4; crystal system orthorhombic, space group Pbca, a = 11.789(3), b = 21.161(6), c = 33.760(1) Å; U = 8423.1 Å^3; Z = 8; F (000) = 2832; D_c = 1.018 Mgm^{-3}; absorption coefficient μ = 0.14 mm^{-1}; crystal shape irregular; size 0.30 x 0.25 x 0.20 mm^3. Data collection and processing: Siemens CCD System, distance crystal-detector 5.94 cm, axis ω (graphite-monochromated MoK_α radiation), T = 296 K; 2Θ range $2 \leq 2\Theta \leq 50°$, step size 0.2°, number of frames 600, exposure time per frame 62s; 15613 intensities measured, 6604 independent (R_{int} = 4.0%); 4996 observed [$F_0 > 4.0\ \sigma(F_0)$]. Structure solution and refinement: direct methods (SHELXTL PLUS program package); full-matrix least squares on $w(F_o\text{-}F_c)^2$; no isotropic extinction correction; hydrogen atoms refined isotropically with fixed thermal parameters (riding model), all other atoms anisotropic except C13, C23 and C33; 404 parameters refined against F; R/wR ($w^{-1} = \sigma^2(F) + 0.000005\ F^2$) 8.7% /

9.0%; max., min. residual electron density 0.40, -0.34 $e\text{Å}^{-3}$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for this material should quote the full literature citation.

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