Monomeric *N*-Lithioaryl- and *N*-Lithioborylstannylamines from Distannylamines☆

Thomas Seifert[+], **Wolfgang Storch***, **and Martina Vosteen**

Institute of Inorganic Chemistry, Ludwig-Maximilians-Universität München,
Meiserstraße 1–3, D-80333 Munich, Germany
E-mail: wst@anorg.chemie.uni-muenchen.de

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8-Aminoquinoline reacts with (dimethylamino)trimethylstannane in a 2:1 molar ratio, undergoing transamination to the distannylamine **1a**. The 9-[bis(trimethylstannyl)amino]-9-borabicyclo[3.3.1]nonane (**1b**) is obtained by the stannazane cleavage reaction of tris(trimethylstannyl)amine with 9-chloro-9-BBN. The cleavage of one Sn–N bond of the distannylamines **1a** and **1b** with MeLi yields the first two monomeric *N*-lithioaminostannanes, **2a** and **2b**, which can be stored at ambient temperature without decomposition. The molecular structures of **1a**, **1b**, **2a**, and **2b** have been determined by multinuclear magnetic resonance spectra in solution, as well as by X-ray structure analysis. Characteristic features are the intramolecular adduct formation of the quinoline ring nitrogen atom with one of the stannyl groups in **1a**, as well as with the lithium cation in **2a**, and the surprisingly short bonds between the central nitrogen atom and the adjacent elements [$d_{(NSn)}$: 2.02 Å, $d_{(NB)}$: 1.38 Å, $d_{(NC)}$: 1.34 Å, $d_{(NLi)}$: 1.95 Å] detected in the molecular structures of the lithium salts.

Introduction

Distannylamines have been shown to be useful precursors for the synthesis of novel main-group element nitrogen compounds[1]. Stannazane cleavage reactions, proceeding under mild conditions, may also serve for the preparation of doubly metallated alkali metal imides, RNM_2 (e.g. with M = Li, Na, K). Their molecular structures in solution as well as in the solid state are scarcely known, with the exception of the complex structure of dilithiated α-naphthylamine, which crystallizes as a cyclooligomeric aggregate containing ten molecular units with intermolecular Li–N bridging bonds[2]. Monometallated metal organostannylamides of the type $RN(SnMe_3)M$ (**2**) which, in contrast to some silylated homologues[3], have hitherto been unknown, should be accessible as intermediates en route to doubly metallated species.

Investigations of the stabilities, structures, and reactivities of the metal amides of primary amines, bearing one N–Li and one N–Sn bond instead of two N–H bonds, are of potential importance with regard to the synthesis of new main-group element nitrogen heterocycles, as well as of unsaturated Sn–N compounds under kinetically controlled conditions. Moreover, the influence of the electropositive lithium atom on the electron densities of the nitrogen atom and its adjacent bonds could be of particular interest.

We describe here the syntheses, structures, and spectroscopic properties of two distannylamines of the type $R{-}N(SnMe_3)_2$ (**1**) and of their *N*-lithiated derivatives **2**.

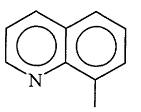
Results and Discussion

8-[Bis(trimethylstannyl)amino]quinoline (**1a**) was obtained by a well-established transamination reaction[4]. A 2:1 molar ratio of $Me_2N{-}SnMe_3$ and 8-aminoquinoline was heated at 80°C for 25 h, leading to reaction according to Eq. 1. No further purification was needed after removal of the volatile components in vacuo, since the reaction proceeded quantitatively. **1a** was recrystallized from hexane in good yield.

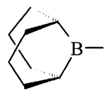
$$\text{Quin-NH}_2 \xrightarrow[-\,2\,\text{Me}_2\text{NH}]{+\,2\,\text{Me}_2\text{N-SnMe}_3} \underset{\mathbf{1a}}{\text{Quin-N(SnMe}_3)_2} \qquad (1)$$

$$\text{N(SnMe}_3)_3 \xrightarrow[-\,\text{Me}_3\text{SnCl}]{+\,9\text{-Chloro-9-BBN}} \underset{\mathbf{1b}}{9\text{-BBN-N(SnMe}_3)_2} \qquad (2)$$

Quin =



9-BBN =



9-[Bis(trimethylstannyl)amino]-9-borabicyclo[3.3.1]nonane (**1b**) was formed in quantitative yield by mixing CH_2Cl_2 solutions of 9-chloro-9-BBN and $N(SnMe_3)_3$ at −40°C, according to Eq. 2. The distannylaminoborane **1b**, purified by crystallization from hexane at −20°C, is the only such compound yet to be characterized in the solid state.

The spectroscopic data of compounds **1a** and **1b** are listed in Table 1, and confirm the proposed structures. At room temperature, the ^{119}Sn-NMR signal of **1a** at $\delta = 26.4$

[+] X-ray structure analysis.

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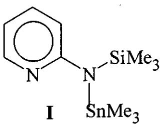
indicates a remarkably better shielding of the tin nuclei relative to all known distannylamines. However, at −80°C, the ^{119}Sn-NMR spectrum shows two different signals at δ = 61.6 and −18.4, the latter falling in the range of pentacoordinated tin atoms. This is possibly due to the interaction of one tin atom with the lone-pair electrons of the quinoline nitrogen atom. At −60°C, the two signals collapse and only one fairly broad signal is observed. Furthermore, two resonance signals are detected in the ^{15}N-NMR spectrum at ambient temperature; the signal at $\delta = -318$ can be assigned to the nitrogen atom of the exocyclic amino group, and that at $\delta = -89$ to the nitrogen nucleus of the quinoline ring.

Table 1. ^{7}Li-, ^{11}B-, $^{14/15}$N-, and ^{119}Sn-NMR data of the distannylamines **1**, the lithioaminostannanes **2**, and another compound for comparison

	1a	1b	2a	2b	$Me_2BN(SnMe_3)_2$
δ^7Li			3.12	2.86	
δ^{11}B		56.2		48.6	53.4
$\delta^{(14)15}$N	−318.0[a] −89.0[b]	−289.0	−214.2[a] −96.4[b]	−228.0	(−272)
δ^{119}Sn	26.4	48.6	5.39	0.08	47.5

[a] Exocyclic nitrogen nucleus. – [b] Endocyclic nitrogen nucleus.



I

These findings are in good agreement with investigations on compounds of type **I**[5], which have been proposed to form an intramolecular Sn–N adduct. The NMR data and the X-ray structure analysis of **1a** (see below) also confirm this hypothesis. The ^{119}Sn- and ^{15}N-NMR data of the borylated distannylamines **1b** are in good agreement with the data of known compounds[6]. However, the ring strain of the bicyclic boryl group causes a deshielding of the boron nucleus ($\Delta\delta$ = 5 ppm), as well as a modest upfield shift of the nitrogen signal ($\Delta\delta$ = 17 ppm) relative, for example, to $Me_2BN(SnMe_3)_2$ (see Table 1). However, the data still indicate multiple bonding between the boron and the nitrogen atoms, in accordance with previous data[7].

The reaction of aryldistannylamines with R = C_6H_5 (**1c**), 2,4,6-$Me_3C_6H_2$ = Mes (**1d**), and 2,6-$i$$Pr_2C_6H_3$ = Dipp (**1e**), in the presence of L = 1,4,7-pentamethyldiethylenetriamine (pmdta), with organolithium compounds in a 1:1 molar ratio led to a mixture of products according to Eq. 4[8]. The monolithium salts **2c** to **2e**, which form even at −50°C, decompose at ambient temperatures, probably under dismutation into the distannylamines **1c** to **1e** and the dilithioamines **3** according to Eq. 4. The species **1c** to **1e** and the byproduct $SnMe_4$ (see Eq. 3) can be detected by NMR, but there is no spectroscopic evidence for the dilithioimines, which are thought to be the main components of the insoluble residue obtained.

$$\underset{\mathbf{1}}{R{-}N(SnMe_3)_2} \xrightarrow[-\ SnMe_4]{+\ MeLi/\ L\ /\ tBuOMe} \underset{\mathbf{2}}{R{-}N(SnMe_3)Li \cdot L} \qquad (3)$$

The following combinations of R and L have been investigated:

	1a/2a	1b/2b	1c/2c	1d/2d	1e/2e
R	Quin	9-BBN	Ph	Mes	Dipp
L	tmeda	pmdta	pmdta	pmdta	pmdta

$$\underset{\mathbf{2}}{2\ ArN(SnMe_3)Li \cdot L} \longrightarrow \underset{\mathbf{1}}{ArN(SnMe_3)_2} + \underset{\mathbf{3}}{[ArNLi_2]} + 2\ L \qquad (4)$$

$$\underset{\mathbf{3}}{[ArNLi_2]} + 2\ Me_3SiCl \longrightarrow \underset{\mathbf{4}}{ArN(SiMe_3)_2} + 2\,LiCl \qquad (5)$$

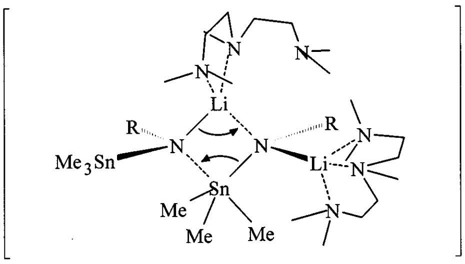
Treatment of this residue with Me_3SiCl according to Eq. 5 gave a mixture of products, which did not unambiguously confirm the presence of dilithioimides of type **3**. The disilazane derivatives **4** could only be detected in trace amounts, since silylstannylamines, Ar–N($SiMe_3$)$SnMe_3$, are also formed under the chosen reaction conditions. Details of these investigations will be discussed elsewhere[9].

In contrast, the treatment of **1a** with LiMe·L (L = tmeda) in *tert*-butyl methyl ether (diveron) solution gave the lithium aryl(trimethylstannyl)amide **2a** in good yield under mild conditions (−30°C). This product is stabilized by complexation of the lithium cation by one equivalent of the diamine tmeda. It is very soluble in diveron, and moderately soluble in petroleum ether, benzene, and hexane. **2a** can be recrystallized from a hexane/diveron mixture by storing the solution at −20°C for 2 days. It can be stored for weeks at ambient temperature under argon without decomposition.

The NMR spectra in diveron solution show a sharp resonance signal of the ^{7}Li nuclei at δ = 3.12 and a broad signal of the ^{119}Sn nuclei at δ = 5.39. The ^{15}N-NMR spectrum shows two signals, one due to the amido nitrogen atom at $\delta = -214.2$ and another due to the ring nitrogen atom at $\delta = -96.4$. Compared to the starting material **1a**, the substitution of the stannyl group for the lithium cation causes a large downfield shift of the amido nitrogen signal ($\Delta\delta$ = 100 ppm) and a significant upfield shift of the ring nitrogen signal ($\Delta\delta = -7$ ppm), due to the influence of the electropositive lithium atom on the paramagnetic term of the ^{15}N shielding[9]. In analogy to information obtained from a low-temperature ^{119}Sn-NMR study of the distannazane **1a** the ^{15}N-NMR data of **2a** clearly indicate a coordination of the lone-pair electrons of the quinoline nitrogen atom to the lithium cation, as well as high electron density concentrated at the amido nitrogen atom. Single-crystal structure determinations of the species **1a** and **2a** confirm the nature of the bonding, as deduced from the NMR data in solution. Clearly, the chelation of the lithium atom is responsible for the stability of the stannylated lithium amide **2a**.

The function of the amidoquinoline group as a chelate ligand presumably prevents the dismutation postulated for the derivatives **2c**, **2d**, and **2e** according to Eq. 4. The decomposition could probably proceed, with the formation of a dimer as an intermediate, under partial displacement of the chelate ligand pmdta by the amido nitrogen atom (Figure 1).

Figure 1. Postulated dimeric intermediate of RN(SnMe$_3$)Li·L (**2**)



After the dismutation of **2**, the products **1** and **3** (see Eq. 4) can be formed by simultaneous 1,2-migration of a lithium atom and a stannyl group.

If the course of the dismutation reaction of compounds of type **2** is dependent on the basicity of the central nitrogen atom, then Lewis acidic substituents R that reduce the basicity of the nitrogen atom should be as significant as sterically hindering or chelating groups in controlling the reaction. Therefore, the introduction of dialkylboryl groups can be expected to reduce the bridging tendency of the nitrogen lone-pair electrons through π-bonding with boron.

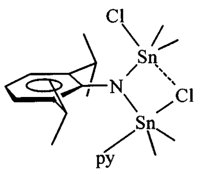
In fact, the synthesis of the monomeric *N*-lithiostannylaminoborane **2b** from distannylaminoborane **1b** proceeds under mild conditions in the presence of pmdta, which stabilizes the Li cation by complexation according to Eq. 3. Product **2b** can be stored indefinitely at ambient temperatures and can even be warmed to 50°C in diveron solution without decomposition.

In all probability, effective (pp) π interaction of the lone-pair electrons at the nitrogen atom with the vacant p orbital of the B atom reduces the donor ability of the nitrogen atom, thereby preventing dimerization and subsequent decomposition of the lithium amide **2b**.

The metallation of the nitrogen atom leads to a large upfield shift of the boron signal of about $\Delta\delta = 8$ ppm compared to that in the distannylamine **1b**. One common explanation would be a strengthening of the B−N π bond[10], due to the high electron density concentrated at the nitrogen atom as a consequence of the polar Li−N bond. An alternative explanation might be the decreased polarity and increased s electron density of the B−N σ bond. However, the unexpectedly large downfield shift of the ^{15}N-NMR signal ($\delta = -228$, recorded at −50°C to depress quadrupolar relaxation with the boron nucleus) is supportive of the first explanation. Surprisingly though, the ^{119}Sn-NMR signal, like the boron NMR signal, is shifted upfield by $\Delta\delta \approx 50$ ppm ($\delta = 0.08$). This can only be due to a significant change in electron density in the Sn−N σ bond, since ab initio calculations rule out any significant Sn−N π interaction[11]. The increase of s electron density in the Sn−N single bond is also indicated by the small but negative $^{1}J(^{119}Sn^{15}N)$ coupling[1c]. Further conclusions can be drawn from the molecular structures in the solid state (see below).

Molecular Structures

The structures of the distannylamines and of the *N*-lithiostannylamines were determined by X-ray crystallography. Figures 2, 3, 4, and 5 show ORTEP plots of the molecules **1a**, **1b**, **2a**, and **2b**, respectively. Selected bonding parameters are listed in the caption of each figure. Contrary to the structural information implied by the NMR data in solution at ambient temperatures, the characteristic features of the molecular structure of **1a** (Figure 2) in the solid state are determined by an intramolecular donor−acceptor interaction between the quinoline nitrogen atom and the tin atom of one of the trimethylstannyl groups. Compared to the adduct Me$_3$SnCl·py (d_{SnN}: 2.26 Å)[12] and the distannylamine pyridine adduct **5** (d_{SnN}: 2.426 Å)[13], the Sn2−N2 bond of 2.531 Å is remarkably long, owing to the ring strain arising from the formation of the intramolecular adduct.



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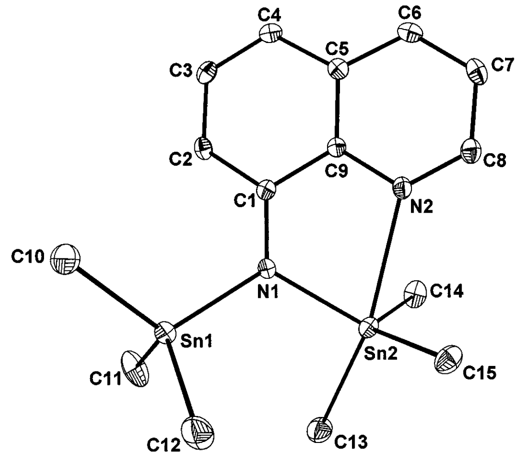
As a consequence of the relatively weak N2−Sn2 interaction, the trigonal-bipyramidal environment of the Sn2 center is considerably distorted, as shown by the 12° deviation of the angle N2−Sn2−C13 from 180°. Moreover, the sum of the angles of the trigonally coordinated ligands at the tin center is only 348° rather than 360°.

Figure 2. Molecular structure of QuinN[Sn(CH$_3$)$_3$]$_2$ (**1a**) with an ORTEP-type description; thermal ellipsoids represent a 25% probability; hydrogen atoms are omitted for the sake of clarity[a]



[a] Selected bond lengths [Å] and bond angles [°] (estimated standard deviations are given in parentheses as units in the last digit): Sn1−N1 2.064(3), Sn2−N1 2.099(3), Sn2−N2 2.531(3), N1−C1 1.381(4), Sn1−C10 2.144(4), Sn1−C12 2.142(4), Sn2−C13 2.177(4), Sn2−C14 2.146(4); Sn1−N1−Sn2 118.3(1), Sn1−N1−C1 121.8(2), Sn2−N1−C1 119.8(2), N1−Sn2−N2 71.3(1), N2−Sn2−C13 167.9(2), N1−Sn2−C13 98.2(1), C14−Sn2−C15 117.1(2), C14−Sn2−N1 116.6(1), C15−Sn2−N1 114.7.

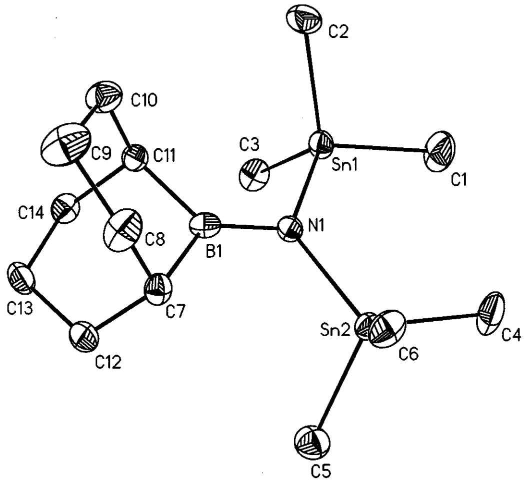


Figure 3. Molecular structure of 9-BBN−N[Sn(CH$_3$)$_3$]$_2$ (**1b**) with an ORTEP-type description; thermal ellipsoids represent a 25% probability; hydrogen atoms are omitted for the sake of clarity[a]

[a] Selected bond lengths [Å] and bond angles [°] (estimated standard deviations are given in parentheses as units in the last digit): Sn1−N1 2.071(6), Sn2−N1 2.059(6), N1−B1 1.42(1), C7−B1 1.58(1), C11−B1 1.66(1), Sn1−C1 2.13(1), Sn1−C2 2.15(1), Sn1−C3 2.13(1), Sn2−C4 2.150(9), Sn2−C5 2.145(10), Sn2−C6 2.14(1); Sn1−N1−Sn2 126.1(3), Sn1−N1−B1 117.0(5), Sn2−N1−B1 116.9(5), C7−B1−C11 107.8(7), N1−Sn1−C1 114.2(4), N1−Sn2−C4 111.0(3), N1−B1−C7 126.9(8), N1−B1−C11 125.3(8).

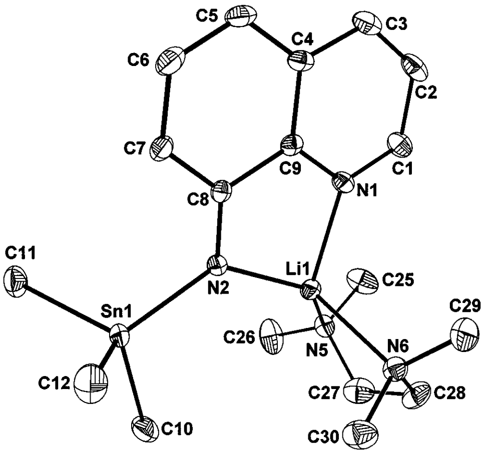


Figure 4. Molecular structure of QuinN(Li)Sn(CH$_3$)$_3$ (**2a**) with an ORTEP-type description; thermal ellipsoids represent a 25% probability; hydrogen atoms are omitted shown for the sake of clarity[a]

[a] Selected bond lengths [Å] and bond angles [°] (estimated standard deviations are given in parentheses as units in the last digit): Sn1−N2 2.031(3), C8−N2 1.351(5), Li1−N2 1.968(7), Li1−N1 2.035(8), Li1−N5 2.116(8), Li1−N6 2.115(8), Sn1−C10 2.149(5), Sn1−C11 2.154(5), Sn1−C12 2.147(5); Sn1−N2−Li1 130.0(3), Sn1−N2−C8 119.5(3), C8−N2−Li1 110.1(3), N1−Li1−N2 85.9(3), N2−Li1−N5 133.7(4), N1−Li1−N5 119.1(3), N1−Li1−N6 110.0(3), N5−Li1−N6 86.7(3), C10−Sn1−C11 108.4(2), C10−Sn1−N2 105.0(2), C11−Sn1−N2 114.3(2); second molecule: Sn2−N4 2.028(3), C20−N4 1.339(5), Li2−N4 1.957(7), Li2−N3 2.088(7), Li2−N7 2.160(7), Li2−N8 2.147(8), Sn2−C22 2.143(5), Sn2−C23 2.165(5), Sn2−C24 2.147(5); Sn2−N4−Li2 122.8(2), Sn2−N4−C20 123.1(3), C20−N4−Li2 112.7(3), N4−L1−N3 84.0(3), N4−Li2−N7 135.5(4), N4−Li2−N8 124.1(4), N7−Li2−N8 86.0(3), C22−Sn2−C23 109.4(2), C22−Sn2−C24 111.4(3), C22−Sn2−N4 99.9(2) C24−Sn2−N4 111.4(2).

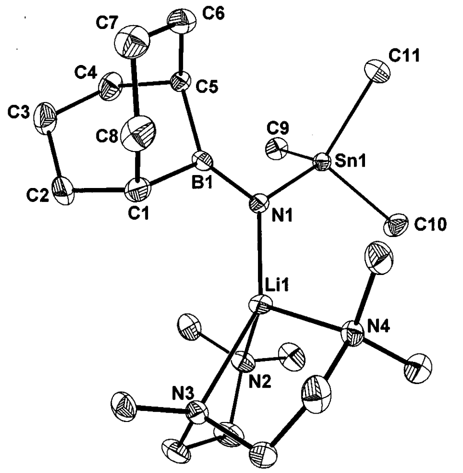


Figure 5. Molecular structure of 9-BBN−N(Li)Sn(CH$_3$)$_3$ (**2b**) with an ORTEP-type description; thermal ellipsoids represent a 25% probability; hydrogen atoms are omitted for the sake of clarity[a]

[a] Selected bond lengths [Å] and bond angles [°] (estimated standard deviations are given in parentheses as units in the last digit): Sn1−N1 2.020(3), B1−N1 1.381(6), Li1−N1 1.945(8), Li1−N2 2.144(8), Li1−N3 2.337(8), Li1−N4 2.149(8), B1−C1 1.623(6), B1−C5 1.608(6), Sn1−C9 2.159(5), Sn1−C10 2.161(5), Sn1−C11 2.154(5); Sn1−N1−Li1 126.7(3), Sn1−N1−B1 117.7(3), B1−N1−L1 115.6(3), N1−Li1−N2 111.4(4), N1−Li1−N3 147.7(4), N1−Li1−N4 112.1(4), C9−Sn1−C10 105.6(2), C9−Sn1−N1 113.1(2), C11−Sn1−N1 112.8(2).

Surprisingly, the Sn−C bond lengths are rather insensitive to the different coordination numbers of Sn1 and Sn2. The ring strain may also be responsible for the large N1−Sn2 distance of 2.099(3) Å, which represents the largest nitrogen−tin distance yet found in distannylamines[14]. The N1−Sn1 bond length of 2.064(3) Å is, however, in good accord with those found for other Sn−N−Sn units. The sum of the angles at the amino nitrogen atom of 360° confirms this to be a planar unit, as is usually the case. The fairly short N1−C1 distance of 1.381(4) Å can be explained by the strong σ-N−C bond, due to the large overlap of the sp^2-sp^2 bond orbitals of each atom.

The distannylamine **1b** (Figure 3), with a cyclic dialkylboryl group attached to the nitrogen atom, also shows planar coordination at the central nitrogen atom. It represents the first example of this class of compounds for which the molecular structure has been determined in the solid state. Characteristic features are the large Sn−N−Sn angle of 126.1°, as also found in aryldistannylamines[15], and the fairly small C−B−C angle of 107.8(7)° in the boryl group, probably due to the ring strain of the bicyclic substituent. Compared to the quinoline group in **1a**, the 9-borabicyclo[3.3.1]nonyl group is sterically less demanding. This might account for the larger Sn−N−Sn angle in **1b** (difference ca. 8°) compared to that in **1a**. Moreover, the stannylaminoborane **1b** shows a significant elongation of the Sn−N bonds [$d_{(\mathrm{SnN})}$ = 2.07 Å] compared to those in other distannazanes with bulkier groups R attached to the nitrogen atom [$d_{(\mathrm{SnN})}$ = 2.05 Å][15]. This is presumably due to the electron-withdrawing properties of the boryl group on the pair of electrons at the central nitrogen atom. Therefore, the ^2J(Sn/Sn) coupling transmission, which has been thought to be dependent on the Sn−N−Sn angle[16] and on the Sn−N bond lengths[1c], seems to be particularly predominated by the position of the lone-pair electrons at the nitrogen atom (see NMR discussion).

The effective (pp) π interaction of the lone-pair electrons of the nitrogen atom with the vacant p orbital of the boron atom is indicated by the short B−N bond of 1.42(1) Å. The small torsion angle Sn1−N1−B1−C11 of about 2° additionally underlines the double bond character of this bond.

Instead of the associated structures usually found for R_2NLi compounds[17], the *N*-lithiostannylamines **2a** and **2b**, derivatives of the distannylamines **1a** and **1b**, crystallize as monomeric molecular units (shown in Figures 4 and 5). The unit cell in the crystal of compound **2a** contains two independent molecules, which show slightly different bond lengths and angles. Significant differences in bond lengths are only detectable in case of the N−Li distances (ca. 0.04 Å). The characteristic features of both lithioamines are the surprisingly short Sn−N bonds of 2.028(3) for **2a** and 2.020(3) Å for **2b**, respectively. The sum of the covalent radii of the elements is 2.033 Å[18]. Moreover, the N2−C8 distance of 1.339(5) Å in **2a** is considerably shorter than that in **1a** (see above), indicating a significant enhancement of the N−C double bond character. These findings can be explained in terms of the transfer of the high electron density, primarily located at the nitrogen atom of the amino group (as a consequence of the polar and indeed essentially ionic character of the Li−N bond[17]), into the adjacent bonds. Support for this explanation comes from the NMR studies, which indicate a remarkable high-field shift of the ^{119}Sn signals of **2a** and **2b** relative to those of the distannylamines **1a** and **1b**. The sum of the angles at the amine nitrogen atom, as well as at the quinoline nitrogen atom, is 360°, confirming the sp^2 hybridization of these centers. Therefore, two different Li−N bond lengths have been found, taking the lithium cation to be the center of a spirocyclic ring fragment. Short distances are present due to the typical sp^2-hybridized nitrogen atoms of the chelating aminoquinoline group acting as a donor ligand [$d_{(\mathrm{LiN})}$: ca. 1.97/2.03 Å]. Two long Li−N bonds are formed with the sp^3-hybridized nitrogen atoms [$d_{(\mathrm{LiN})}$: ca. 2.11 Å] of the chelating diamine tmeda. The tetrahedral symmetry around the metal cation is slightly distorted. There is no simple explanation for the deviation of the coordination of the lithium center from tetrahedral symmetry other than packing effects.

The structure of the *N*-lithiated stannylaminoborane **2b** is the third example of a monomeric *N*-lithioaminoborane[10][19], but it is the first one with essentially planar cores of $C_2BN(Li)Sn$ atoms with only small dihedral angles between the boron and nitrogen planes. The structure indicates the influence that the electropositive metal cation attached to the nitrogen atom exerts on the adjacent B−N and Sn−N bonds. Compared to the distannylborylamine **1b**, the B−N bond of **2b** [$d_{(\mathrm{BN})}$: 1.381(6) Å] is shortened by about 0.04 Å, and represents one of the shortest B−N double bonds yet found[10].

Short B−N bonds in aminoboranes are usually explained in terms of an enhancement of B−N π bonding. However, short B−N bonds are also present in lithioaminoboranes, such as $t\mathrm{Bu}_2\mathrm{B{-}N(Li)}t\mathrm{Bu}\cdot\mathrm{OEt}_2$, although here there is a fairly large dihedral angle of 30.4° between the boron and nitrogen planes[19]. Moreover, the B−N bond length of 1.40 Å in the *N*-silylated lithioaminoborane 9-BBN−NLi−SiMe$_3$, which crystallizes as a trimer with pseudo-tetracoordinated nitrogen atoms, is indicative of B−N double bonds[1a]. Therefore, the short bonds are more likely to be attributable to the positive inductive effect of the lithium atom, which strengthens the σ bonds. This is also the case for the adjacent Sn−N bond, which is extremely short compared to that in the starting material **1b**. Taking into account that, on the basis of ab initio calculations, any π-bonding in Sn−N bonds is negligible, the electron-donating property of the lithium atom, as discussed above, is solely responsible for the strengthening of the σ bonds.

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Experimental Section

General: All operations were performed under dry argon. Glassware was dried prior to use by heating in vacuo. − NMR spectra were recorded with Bruker AC P 200 (^{11}B), Jeol GSX 270 (^{15}N, ^{119}Sn), and Jeol EX 400 (^{1}H, ^{7}Li, ^{13}C) instruments; standards: TMS (internal, ^{1}H, ^{13}C), ext. 1 M LiCl solution (^{7}Li), ext. $BF_3\cdot Et_2O$ (^{11}B), ext. CH_3NO_2 (^{15}N), tetramethyltin (external ^{119}Sn). ^{15}N-NMR spectra were recorded by polarization transfer techniques: refocused INEPT pulse sequence based on the $^2J(^{15}N^1H)$ and the $^3J(^{15}N^1H)$ coupling constants of ca.12 Hz and ca.1.5−2 Hz, respectively, (assumed values). The notation $^nJ(^{119/117}Sn^mX)$ represents the coupling of both isotopomers with X if the coupling cannot be observed separately. Chemical shifts, δ, are given in ppm, coupling constants, *J*, in Hz. − Mass spectra: Varian CH7 instrument with electron impact ionization at 70 eV. The masses found refer to the isotopes ^{1}H, ^{7}Li, ^{12}C, ^{11}B, ^{14}N, ^{120}Sn. − Elemental analyses: Microchemical Laboratory of the Institute. − X-ray: Siemens P4 diffractometer, CCD area detector with Siemens LT 2 device; Mo-K_α radiation, λ = 0.71063 Å, graphite monochromator; single crystals, coated with perfluoro ether oil, were mounted on a glass fibre. Crystal data were determined and intensity data recorded at 173−193 K (see Table 2); data reduction was performed with the program SAINT, structure solution by Patterson method and refinement using the SHELXTL system[20]; final refinement was performed using the SHELX-97 programs[21]. All atoms except the hydrogen atoms were described with anisotropic temperature factors; all hydrogen positions were geometrically placed [d(CH) = 0.96 Å] and refined by using the riding model and fixed U_i. Details of the crystal structure determinations are available on request from Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk] on quoting the depository numbers CSD-101616 (**1a**), -101617 (**1b**), -101618 (**2a**), -101619 (**2b**), the names of the authors, and the full journal citation.

Starting Materials: $N(SnMe_3)_3$[22] was prepared according to a modified literature procedure[23] from $NaNH_2/NH_3/OEt_2/$

Me_3SnCl; 9-chloro-BBN[24] and Me_2NSnMe_3[25] were prepared according to literature procedures. The MeLi solution (ca. 1.6 M in Et_2O) was supplied by Chemetall, Frankfurt.

8-[Bis(trimethylstannyl)amino]quinoline (**1a**): A mixture of 8-aminoquinoline (5.0 g, 35 mmol) and Me_2NSnMe_3 (20.8 g, 92 mmol) was stirred at room temp. A slighty exothermic reaction occurred, with evolution of Me_2NH. After heating the reaction mixture at 80°C for 25 h, so as to complete the elimination of Me_2NH, the excess Me_2NSnMe_3 was condensed at 10^{-3} Torr into a cold trap at −60°C. The residual orange, viscous liquid was dissolved in 40 ml of hexane and kept at 4°C for 4 d, yielding 14.1 g (86%) of **1a** as orange crystals suitable for X-ray analysis; m.p. ca. 12−15°C. − ^1H NMR (C_6D_6): $\delta = 0.38$ [s, $^2J(^{119/117}Sn^1H) = 53.7$ Hz, 18 H, $SnMe_3$], 6.74 (dd, 1 H, 7-H), 6.82 (m, 2 H, 5-H/6-H), 7.24 (dd, 1 H, 3-H), 7.61 (dd, 1 H, 4-H), 8.87 (dd, 1 H, 2-H). − ^{13}C NMR: $\delta = -0.75$ [$^1J(^{119/117}Sn^{13}C) = 389.1$ Hz, $SnMe_3$], 117.5 [$^3J(^{119/117}Sn^{13}C) = 35.1$ Hz, C-7], 120.7 (C-5), 129.5 (C-3), 136.2 (C-10), 136.5 (C-6), 138.3 (C-9), 142.7 (C-4), 149.2 (C-8), 154.9 (C-2). − ^{15}N NMR: $\delta = -318.0$ [$^1J(^{117/119}Sn^{15}N) = 28.8$ Hz, Sn*N*Sn], −89.0 [$^1J(^{117/119}Sn^{15}N) = 35.0$ Hz, C*N*C]. − ^{119}Sn NMR: $\delta = 26.2$ [$^2J(^{119}Sn^{117}Sn) = 46.7$ Hz]. − $C_{15}H_{24}N_2Sn_2$ (469.8): calcd. C 38.35, H 5.16, N 5.96; found C 40.10, H 5.15, N 6.74. − Mol. mass: 470 (MS).

9-[Bis(trimethylstannyl)amino]-9-borabicyclo[3.3.1]nonane (**1b**): $N(SnMe_3)_3$ (12.1 g, 24 mmol) was dissolved in 20 ml of CH_2Cl_2. At −40°C, this solution was added dropwise with stirring to a solution of 9-chloro-9-borabicyclo[3.3.1]nonane (3.7 g, 24 mmol) in 10 ml of CH_2Cl_2. After allowing the reaction mixture to slowly warm to ambient temp. (15 h), all volatile components were removed in vacuo (25−80°C/10^{-3} Torr). From a solution of the colourless non-volatile residue in 50 ml of hexane, 9.1 g (82%) of **1b** crystallized after storing the mixture at −20°C for 10 d; m.p. 60−62°C. The crystals were found to be suitable for X-ray analysis. − ^1H NMR (C_6D_6): $\delta = 0.24$ [s, $^2J(^{119/117}Sn^1H) = 53.9$ Hz, 18 H, $SnMe_3$], 1.21 (m, 4 H, BCCCH), 1.42−1.46 (m, 2 H, BCH), 1.78−1.86 (m, 8 H, BCCH). − ^{13}C NMR $\delta = -2.07$ [$^1J(^{119/117}Sn^{13}C) = 363.5$ Hz, $SnMe_3$], 23.7 (BCC*C*H), 31.4 (BCH), 34.2 (BC*C*H). − ^{11}B NMR: $\delta = 56.2$. − ^{15}N NMR: $\delta = -289.0$ [$^1J(^{117/119}Sn^{15}N) = 31.9$ Hz, Sn*N*Sn]. − ^{119}Sn NMR: $\delta = 48.6$. − $C_{14}H_{32}BNSn_2$ (462.6): calcd. C 36.35, H 6.97, N 3.03; found C 36.24, H 6.73, N 2.96. − Mol. mass: 463 (MS).

(8-Aminoquinolyl)(lithio)(trimethylstannyl)amine·tmeda (**2a**): To 5 ml of an MeLi solution (1.6 M in diethyl ether) at 25°C, tmeda (0.97 g, 8.33 mmol) was added dropwise, and then the solvent was removed in vacuo at 25°C/10^{-1} Torr. The colourless solid residue was dissolved in 30 ml of *tert*-butyl methyl ether, and to this solution 14.9 ml (8.33 mmol) of a solution of **1a** (0.56 M in *tert*-butyl methyl ether) was added dropwise at −30°C, resulting in a deep-red colouration. After stirring for 2.5 h, the reaction mixture was allowed to warm to ambient temp. Filtration of the slightly cloudy solution (G4), concentration of the filtrate to a volume of ca. 25 ml under reduced pressure, and storing the concentrate at −20°C for 20 d gave **2a** as dark-red crystals, suitable for X-ray analysis: yield 2.43 g (68%); m.p. 134−136°C. − ^1H NMR (C_6D_6): $\delta = -0.69$ [s, $^2J(^{119/117}Sn^1H) = 53.9$ Hz, 9 H, $SnMe_3$], 2.70 (s, 12 H, NCH_3), 2.89 (s, 4 H, NCH_2-), 6.70 (m, 2 H, 5-H, 6-H), 7.41 (t, 1 H, 3-H), 7.52 (dd, 1 H, 7-H), 8.28 (dd, 1 H, 4-H), 8.61 (dd, 1 H, 2-H). − ^{13}C NMR: $\delta = -1.32$ ($SnMe_3$), 46.2 (N*C*H_3), 58.2 (N*C*H_2-), 114.2 [$^3J(^{119/117}Sn^{13}C) = 77.6$ Hz, C-7], 120.0 (C-5), 130.2 (C-3), 136.8 (C-10), 137.2 (C-6), 141.4 (C-4), 155.2 (C-9), 163.6 (C-8),

Table 2. X-ray structure analysis data of **1a**, **1b**, **2a**, and **2b**

Compound	**1a**	**1b**	**2a**	**2b**
Chem. formula	$C_{15}H_{24}N_2Sn_2$	$C_{28}H_{64}B_2N_2Sn_4$	$C_{18}H_{31}LiN_4Sn$	$C_{20}H_{46}LiN_4Sn$
Formula weight	469.74	925.19	429.10	479.05
Cryst. size [mm]	0.2 × 0.3 × 0.4	0.1 × 0.2 × 0.3	0.3 × 0.3 × 0.4	0.2 × 0.2 × 0.3
Cryst. system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2(1)/c$	$P\bar{1}$	$P2(1)/c$	$P2(1)/c$
a [Å]	14.528(4)	9.70820(10)	13.89870(10)	13.29350(10)
b [Å]	10.028(3)	14.92160(10)	11.07780(10)	10.2085(2)
c [Å]	12.350(4)	15.4379(2)	27.8251(2)	18.87590(10)
α [°]	90.00	66.548(1)	90.00	90.00
β [°]	96.783(7)	73.685(1)	95.980(1)	91.025(1)
γ [°]	90.00	71.99	90.00	90.00
V [Å^3]	1786.8(9)	1918.94(3)	4260.83(6)	2561.18(6)
Z	4	2	8	4
ρ(calcd.) [Mg/m^3]	1.746	1.601	1.338	1.242
μ [mm^{-1}]	2.786	2.590	1.205	1.008
$F(000)$	912	912	1760	1008
Index range	$-15 \le h \le 18$	$-10 \le h \le 10$	$-17 \le h \le 18$	$-15 \le h \le 13$
	$-12 \le k \le 12$	$-16 \le k \le 16$	$-14 \le k \le 14$	$-12 \le k \le 12$
	$-15 \le l \le 15$	$-16 \le l \le 14$	$-37 \le l \le 34$	$-22 \le l \le 22$
2θ [°]	57.58	46.50	58.62	49.42
Temp. [K]	183	183	193	173(2)
Refl. collected	9913	8234	23832	12138
Refl. unique	3208	4328	8435	3644
Refl. observed (4σ)	2955	3963	5239	3435
R (int.)	0.0402	0.0195	0.0390	0.0278
No. of variables	202	338	447	252
Weighting scheme x/y[a]	0.0151/1.9239	0.0204/17.3145	0.0000/12.3307	0.0000/7.8454
GooF	1.197	1.135	1.129	1.234
Final R (4σ)	0.0227	0.0414	0.0339	0.0361
Final $wR2$	0.0540	0.0963	0.0746	0.0847
Larg. res. peak [e/Å^3]	0.553	0.873	2.173	0.905

[a] $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$.

166.4 (C-2). − ^{7}Li NMR: δ = 3.12. − ^{15}N NMR: δ = −214.2, −96.4. − ^{119}Sn NMR: δ = 5.18 (br.). − $C_{18}H_{31}LiN_4Sn$ (479.1): calcd. C 50.21, H 7.26, N 13.02; found C 48.60, H 6.73, N 11.86.

(9-Borabicyclo[3.3.1]nonyl)}(lithio)(trimethylstannyl)amine·pmdta (**2b**): To 2.4 ml of an MeLi solution (1.6 M in diethyl ether) at 25°C, pmdta (0.69 g, 4.0 mmol) was added dropwise, and then the solvent was removed in vacuo at 25°C/10^{-1} Torr. The colourless, oily residue was diluted with 20 ml of *tert*-butyl methyl ether. To this solution, a solution of **1b** (1.85 g, 4.00 mmol) in 15 ml of *tert*-butyl methyl ether was added dropwise at −50°C. After allowing the mixture to slowly warm to ambient temp. over a period of 15 h, and then storing the colourless solution at −20°C for 28 d, **2b** (1.19 g, 62%) crystallized as colourless prisms; m.p. 124−127°C. The crystals were found to be suitable for X-ray analysis. − ^{1}H NMR (C_6D_6): δ = 0.38 [s, $^{2}J(^{119/117}\mathrm{Sn}^{1}\mathrm{H})$ = 48.4 Hz, 18 H, SnMe$_3$], 1.24 (m, 4 H, BCCCH), 1.44−1.50 (m, 2 H, BCH), 1.89−1.96 (m, 8 H, BCCH), 2.11 [s, 12 H, MeN(C$_2$H$_4$N*Me*$_2$)$_2$], 2.18 [s, 3 H, *Me*N(C$_2$H$_4$NMe$_2$)$_2$], 2.40−2.52 [m, 8 H, MeN(*C*$_2$H$_4$NMe$_2$)$_2$]. − ^{13}C NMR: δ = −3.06 [$^{1}J(^{119/117}\mathrm{Sn}^{13}\mathrm{C})$ = 291.7 Hz, SnMe$_3$], 24.9 (BCC*C*H), 32.2 (BCH), 35.1 (BC*C*H), 45.7 [MeN(C$_2$H$_4$N*Me*$_2$)$_2$], 53.4 [*Me*N(C$_2$H$_4$NMe$_2$)$_2$], 56.7 + 57.8 [MeN(*C*$_2$H$_4$NMe$_2$)$_2$]. − ^{7}Li NMR: δ = 2.86. − ^{11}B NMR: δ = 48.5. − ^{15}N NMR: δ = −228.0 [$^{1}J(^{117/119}\mathrm{Sn}^{15}\ \mathrm{N})$ = 10.4 Hz, Li*N*Sn]. − ^{119}Sn NMR: δ = 0.08 (br.). − $C_{20}H_{46}BLiN_4Sn$ (473.1): calcd. C 50.14, H 9.68, N 11.70; found C 53.30, H 10.18, N 12.54.

☆ Dedicated to Professor *Heinrich Nöth* on the occasion of his 70th birthday.

[1] [1a] W. Storch, H. Nöth, *Angew. Chem.* **1976**, *88*, 231; *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 235. − [1b] S. Diemer, H. Nöth, W. Storch, *Functionally Substituted Diborylamines*, in preparation. − [1c] A. Appel, C. Kober, C. Neumann, H. Nöth, M. Schmidt, W. Storch, *Chem. Ber.* **1996**, *129*, 175−189 and refs. quoted therein.

[2] D. R. Armstrong, D. Barr, R. Snaith, *Angew. Chem.* **1991**, *103*, 1702−1704; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1707−1709.

[3] [3a] B. Wrackmeyer, B. Schwarze, J. Weidinger, M. Milius, *Z. Naturforsch.* **1997**, *52b*, 431−433. − [3b] M. Westerhausen, W. Schwarz, *Z. Anorg. Allg. Chem.* **1993**, *619*, 1053−1063. − [3c] T. Fjeldberg, P. B. Hitchcock, M. F. Lappert, A. J. Thorne, *J. Chem. Soc., Chem. Commun.* **1984**, 822−826. − [3d] R. Köster, G. Seidel, *Angew. Chem.* **1981**, *93*, 1009−1010; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 972−973.

[4] [4a] K. Jones, M. F. Lappert, *Proc. Chem. Soc.* **1962**, 358− 359. − [4b] K. Jones, M. F. Lappert, *J. Chem. Soc.* **1965**, 1944−1951.

[5] B. Wrackmeyer, G. Kehr, H. Zhuo, S. Ali, *Magn. Res. Chem.* **1996**, *34*, 921−928.

[6] W. Storch, H. Nöth, *Chem. Ber.* **1977**, *110*, 1636−1642.

[7] G. Schmid, R. Boese, D. Bläser, *Z. Naturforsch.* **1982**, *B37*, 1230−1236; H. Nöth, H. Prigge, A.-R. Rotsch, *Chem. Ber.* **1977**, *119*, 1361−1367.

[8] S. Lustig, Diplomarbeit, Universität München, **1994**.

[9] B. Wrackmeyer, W. Storch, M. Vosteen, *NMR Studies on Lithiostannylamines and -imines*, in preparation.

[10] H. Chen, R. A. Bartlett, M. M. Olmstead, P. P. Power, S. C. Shoner, *J. Am. Chem. Soc.* **1990**, *112*, 1048−1055.

[11] C. Kober, J. Kroner, W. Storch, *Angew. Chem.* **1993**, *105*, 1693−1695; *Angew. Chem. Int. Ed. Engl.* **1993**, *31*, 1608−1610.

[12] R. Hulme, *J. Chem. Soc.* **1963**, 1524−1527; V. G. Kumar Das, L. K. Mun, W. Chen, *Organometallics*, **1987**, *6*, 10−14.

[13] C. Kober, H. Nöth, W. Storch, *Chem. Ber.* **1997**, *130*, 765−769.

[14] C. Kober, H. Nöth, W. Storch, *Structure Investigations of Distannazanes*, in preparation.

[15] S. Diemer, H. Nöth, K. Polborn, W. Storch, *Chem. Ber.* **1992**, *125*, 389−400.

[16] W. Biffar, T. Gasparis-Ebeling, H. Nöth, W. Storch, B. Wrackmeyer, *J. Magn. Res.* **1981**, *44*, 54−61.

[17] K. Gregory, P. V. R. Schleyer, R. Snaith, *Adv. Inorg. Chem.* **1991**, *37*, 47−49; R. E. Mulvey, *Chem. Soc. Rev.* **1991**, *20*, 167−172.

[18] Calculated from the sum of the covalent radii by applying the Schomaker−Stevenson correction: A. F. Wells, *Structural Inorganic Chemistry*, 4th ed., Clarendon, Oxford University Press, **1979**, p. 236.

[19] [19a] P. Paetzold, C. Pelzer, R. Boese, *Chem. Ber.* **1988**, *121*, 51−59. − [19b] R. A. Bartlett, X. Feng, M. M. Olmstead, P. R. Power, K. J. Weese, *J. Am. Chem. Soc.* **1988**, *109*, 4851−4854.

[20] *SHELXTL-Plus*, *PC version*, Siemens Analytical X-ray Instruments, Inc., Madison, WI, **1980**.

[21] G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structures*, University of Göttingen, **1997**.

[22] K. Sisido, S. Kozima, *J. Org. Chem.* **1964**, *29*, 907−909.

[23] P. Otto, Ph. D. Thesis, University of Munich, **1986**.

[24] H. C. Brown, S. U. Kularni, *J. Organomet. Chem.* **1979**, *168*, 281−286.

[25] C. M. Wright, E. L. Muetterties, *Inorg. Synth.* **1976**, *10*, 137−139.

[98133]