

Triaminoboranes and Their Metallation to *N*-Lithiotriaminoboranes<sup>[‡]</sup>Ulrike Braun,<sup>[a][‡‡]</sup> Tassilo Habereeder,<sup>[a]</sup> Heinrich Nöth,<sup>\*[a]</sup> Hans Piotrowski,<sup>[a]</sup> and Marcus Warchhold<sup>[a]</sup>**Keywords:** Boranes / Deprotonation / Lithium / Nitrogen / X-ray diffraction

In order to study the competition between deprotonation, borate formation, and B–N bond cleavage, six triaminoboranes bearing 1–3 NH functions were treated with butyllithium. The 2-anilino-1,3,2-diazaborolidine **1** was cleanly deprotonated, but the resulting *N*-lithio compound could not be crystallized. However, as a result of slow hydrolysis, the lithium 2-oxido derivative **7** was isolated in low yield as a dimeric ether solvate. Double deprotonation of 2-(dimethylamino)-1,3,2-benzodiazaborolidine (**9**) was accompanied by B–N bond cleavage. The dilithio derivative reacted with Me<sub>3</sub>SiCl to produce 2-dimethylamino-1,3-bis(trimethylsilyl)-1,3,2-benzodiazaborolidine (**11**). Similarly, dianilino(diphenylamino)borane (**2**) was readily deprotonated to the insoluble dilithium compound. B–N bond cleavage also occurred, however, and the solvates Ph<sub>2</sub>NLi·dme (**13**) and Ph<sub>2</sub>NLi·2py (**14**) were isolated. These are dimeric, the former with a planar Li<sub>2</sub>N<sub>2</sub> ring, the latter possessing an N–Li–N–Li chain structure. Triply metallated trianilino-borane (**15**) crystallized as dimeric B(NLiPh)<sub>3</sub>·LiCl·(OEt<sub>2</sub>)<sub>3</sub> (**15A**). Treatment of trianilino-

borane (**3**) with LiBu in 1:1 and 1:2 ratios showed that the deprotonation was accompanied by the formation of anilino-(butyl)borates. Treatment of the dilithio derivative of **3** with Me<sub>3</sub>SnCl afforded B[N(SnMe<sub>3</sub>)Ph]<sub>3</sub> (**23**), a result of substituent exchange. Tris(2-pyridylamino)borane (**4**), with a planar skeleton, reacted with BuLi both by deprotonation and by B–N bond cleavage. The metallated triaminoborane crystallized as dimeric Li<sub>4</sub>B(NR\*)<sub>3</sub>NHR\*(THF)<sub>3</sub> (**18**; R\* = 2-pyridyl). Tris(8-quinolylamino)borane (**5**) can also be triply lithiated according to <sup>11</sup>B and <sup>7</sup>Li NMR spectroscopic data. X-ray determination of the structures of compounds **1**–**3** showed the absence of N–H···N hydrogen bonding, which seems to be responsible for the planar structures of compounds **4** and **5**. The planarity of the BN<sub>3</sub> units in **3** and **4** was retained in the trilithiated compounds **15A** and **18**, as ascertained by X-ray structure determination.

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## Introduction

The metallation of aminoboranes R<sub>3–n</sub>B(NHR')<sub>n</sub> by organolithium reagents LiR to give (lithioamino)boranes acts in competition with the formation of aminoborates Li[R<sub>4–n</sub>B(NHR')<sub>n</sub>] and/or B–N bond cleavage. This was demonstrated by us in 1980,<sup>[2]</sup> after the first successful lithiation of a cyclic aminoborane.<sup>[3]</sup> As expected, (lithioamino)boranes are useful reagents for the syntheses not only of other metallated aminoboranes<sup>[2,4,5–7]</sup> by transmetallation reactions, but also for syntheses of diborylamines<sup>[8–10]</sup> and BN heterocycles.<sup>[5,6,11]</sup> So far, only a few structures of (lithioamino)boranes have been determined: the ionic [Li(OEt<sub>2</sub>)<sub>3</sub>][mes<sub>2</sub>B=N=Bmes<sub>2</sub>],<sup>[12]</sup> the dimeric Li(OEt<sub>2</sub>)<sub>2</sub>·Nmes–Bmes<sub>2</sub>,<sup>[7]</sup> and the solvent-free trimeric (lithioamino)-9-borabicyclonane.<sup>[13]</sup> In the presence of chelating ligands, monomeric molecular (lithioamino)boranes, such as *t*Bu<sub>2</sub>B(*t*BuN)Li·tmen or (Me<sub>3</sub>Sn)N–BC<sub>8</sub>H<sub>14</sub>Li·pmdeta

(pmdeta = pentamethyldiethylenetriamine),<sup>[14,15]</sup> were obtained and their structures determined. In comparison with lithium organylamides<sup>[16,17]</sup> the tendency of the lithium (diorganylboryl)amides to associate through Li–N bridges did not seem to be significantly altered. Dimetallation of bis-(*tert*-butylamino)organylboranes was reported by Meller et al.,<sup>[6]</sup> whilst it is only recently that a threefold lithiation of the borazine (PhB–NH)<sub>3</sub> was successfully achieved, resulting in the compound (PhBNLi)<sub>3</sub>·(LiPh)<sub>3</sub>·(THF)<sub>3</sub>, characterized by X-ray diffraction analyses.<sup>[18]</sup>

*N*-Lithiation of triaminoboranes offers a unique chance to study the influence of electronic and steric effects. One might expect that the metallation of triaminoboranes of type (R<sub>2</sub>N)<sub>2</sub>B–(NHR) would proceed more readily than that of R<sub>2</sub>BNHR,<sup>[5]</sup> as the amino groups make the boron atom less prone to attack by a nucleophile, thereby promoting the deprotonation of the NH group. On the other hand, double and triple deprotonation of aminoboranes B(NHR)<sub>3</sub> would probably become more difficult as the number of deprotonation steps increased, because introduction of an increasing number of lithium atoms would be expected to result in highly associated molecular aggregates through Li–N coordination. For this reason we synthesized

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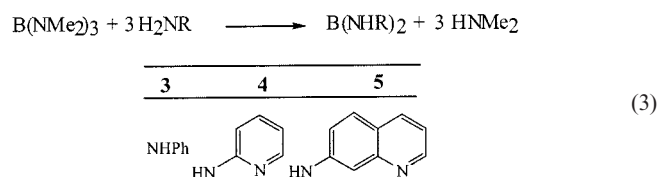
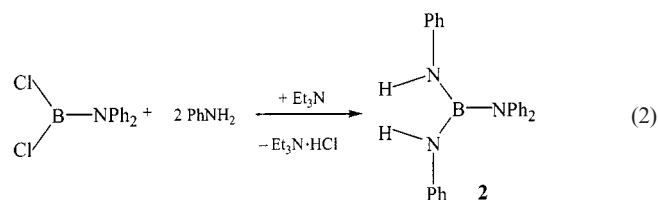
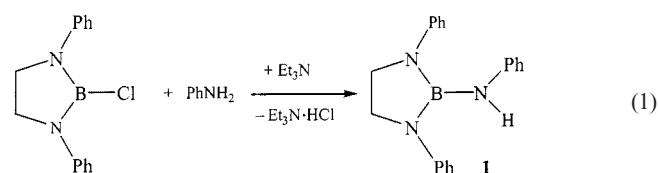
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a number of new triaminoboranes possessing NHR groups, studied their metallation with BuLi, and characterized their *N*-lithio derivatives.

## New Triaminoboranes

### Synthesis

In order to study the competition between *N*-metallation, B–N bond cleavage, and borate formation, we first chose an aminoborane of type (R<sub>2</sub>N)<sub>2</sub>BNHR, with only one N–H bond. The molecule of choice was 2-anilino-1,3-diphenyl-1,3,2-diazaborolidine (**1**), obtained by treatment of 2-chloro-1,3-diphenyl-1,3,2-diazaborolidine with aniline in the presence of triethylamine as shown in Equation (1).



The preparation of dianilino(diphenylamino)borane (**2**) by aminolysis of B(NMe<sub>2</sub>)<sub>3</sub> with diphenylamine (1:1 ratio), followed by aminolysis with aniline, was unsuccessful; we observed no reaction at reflux temperature between the tris(dimethylamino)borane and diphenylamine, although several successful syntheses of unsymmetrically substituted triaminoboranes by transamination reactions have been reported.<sup>[19,20]</sup> The low basicity of diphenylamine (p*K*<sub>A</sub> = 0.9)<sup>[21,22]</sup> and steric effects may be responsible for the failure of this reaction, in spite of the fact that the resulting dimethylamine can readily be removed to drive the process towards the side of the transamination products. More surprising was the observation that LiNPh<sub>2</sub> did not react with Cl–B(NMe<sub>2</sub>)<sub>2</sub> to produce Ph<sub>2</sub>N–B(NMe<sub>2</sub>)<sub>2</sub>, either in THF or in toluene. However, dichloro(diphenylamino)borane reacted with aniline in the presence of triethylamine according to Equation (2) to give Ph<sub>2</sub>NB(NHPh)<sub>2</sub> (**2**) in 71% yield.

Trianilinoborane (**3**) was readily obtained from aniline and B(NMe<sub>2</sub>)<sub>2</sub>,<sup>[19]</sup> whilst tris(2-pyridylamino)borane (**4**)<sup>[23]</sup>

and tris(8-aminoquinolyl)borane (**5**) were prepared by the same procedure as shown in Equation (3).

### Spectra

The NMR spectra (<sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C, and <sup>14</sup>N) of compounds **1–5** were fully compatible with the suggested structures (e.g., chemically and magnetically equivalent anilino and amino heterocyclic groups). As was to be expected for triaminoboranes, the <sup>11</sup>B chemical shifts varied very little and were in the range typical of this class of compounds. The line widths, however, varied significantly. The sharpest signal was found for tris(2-pyridylamino)borane (**4**; *h*<sub>1/2</sub> = 220 Hz) and the broadest for the quinoline derivative **5** (450 Hz). Only a single broad <sup>14</sup>N resonance, at δ = –323, was found for compound **2**, and one at δ = –292 for compound **3**. On the other hand, the two types of N atoms in compounds **4** and **5** were readily recognizable. The resonances were at δ = –106 and –79, respectively, for the heterocyclic N atoms, while those of the amino groups were observed at δ = –310 and –327. This was consistent with <sup>15</sup>N NMR spectroscopic data of aminoboranes<sup>[24]</sup> and N-heterocycles.<sup>[25]</sup>

Interestingly, the <sup>1</sup>H resonances for the NH protons of the anilino groups were found as signals at δ = 4.65 ± 0.14, while those for **4** and **5** were observed at δ = 9.85 and 8.15, respectively. We attribute this to intramolecular N–H⋯N interactions in the latter two compounds, and this was supported by the NH stretching vibrations found for these two aminoboranes at 3293 and 3340 cm<sup>–1</sup>. In **1** to **3**, these vibrations were observed at higher wavenumbers (3384, 3387, and 3384 cm<sup>–1</sup>). Obviously, the intramolecular N–H⋯N interaction was weaker in **5** than in **4**. This is consistent with the molecular structures of these compounds as determined by X-ray structure analysis.

### Molecular Structures

The triaminoboranes **1–5** were characterized by X-ray structure analysis. Compound **1** crystallizes in the monoclinic system, space group *I*2/*a* and *Z* = 8. Figure 1 shows its molecular structure. The three B–N bonds are of equal lengths. Their common value (1.435 Å) corresponds very well with B–N bond lengths observed for other triaminoboranes.<sup>[26]</sup> All the N atoms and the B atom reside in planar environments, but because of the incorporation of the boron atom into a five-membered ring system a sharp N–B–N bond angle of 107.4(1)° results; this fits nicely for a five-membered ring system. Consequently, the other two N–B–N bond angles are wider than 120°. Typical for the structure of **1** is the propeller-like arrangement of the phenyl groups, with interplanar angles to the BN<sub>3</sub> plane of 31.6, 41.7, and 52.1°, the last being that made by the anilino group, which is more twisted than the other two phenyl groups. In the crystal there are neither intra- nor intermolecular N–H⋯N hydrogen bonds.

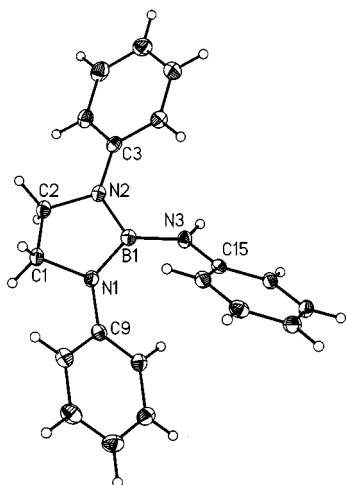


Figure 1. Molecular structure of **1** in ORTEP presentation; selected bond lengths and bond angles: B1–N1 1.436(2), B1–N2 1.437(2), B1–N3 1.433(2), N1–C9 1.409(2), N2–C3 1.402(2), N3–C15 1.400(2), N1–C1 1.473(2), N2–C2 1.471(2), C1–C2 1.523(2) Å; C1–N1–B1 109.0(1), C3–N2–B1 131.2(1), B1–N2–C2 108.9(1), C3–N2–C2 119.5(1), B1–N3–C15 127.5(1), N3–B1–N2 125.1(1), N1–B1–N2 107.4(1)°; torsion angle: N1–C1–C2–N2 –26.8°

Crystals of dianilino(diphenylamino)borane (**2**) are triclinic, space group  $P\bar{1}$  with  $Z = 2$ . Figure 2 shows its molecular structure. In contrast to those in **1**, its B–N bond lengths differ significantly. The B–N bond of the diphenylamino group [1.470(3) Å] is longer than the B–N bonds to the anilino groups (average 1.425 Å). Since the angle between the  $\text{BN}_3$  plane and the  $\text{C1N1C2}$  unit of the diphenylamino group is at 26.6° only slightly larger than the interplanar angles to the anilino groups (24.5 and 23.5°), this longer B–N bond must be the result of the low basicity of the diphenylamine. Because of the steric requirement of the diphenylamino group, the phenyl groups of the anilino groups are pointing away from the  $\text{Ph}_2\text{N}$  substituent. This results in a *cisoidal* arrangement for the N–H units. The C–N–B bond angles of the anilino substituents are quite open (132.8° and 130.9°). This is not imposed by steric requirements of the diphenylamino group, as the same feature is also observed in compound **3**.

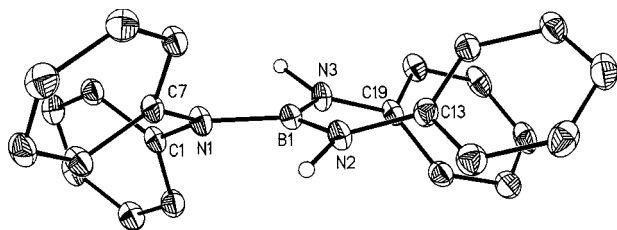


Figure 2. The molecular structure of **2** in the crystal; selected bond lengths and bond angles: B1–N1 1.470(3), B1–N2 1.422(3), B1–N3 1.427(3), N1–C1 1.330(3), N1–C7 1.423(3), N2–C13 1.415(3), N3–C19 1.414(3) Å; B1–N1–C1 120.7(2), B1–N1–C7 123.1(2), C1–N1–C7 116.2(2), B1–N2–C13 132.8(2), H2–N2–C13 113(1), H2–N2–B1 114(1), B1–N3–C19 130.9(2), H3–N3–C19 116(1), H3–N3–B1 113(1), N1–B1–N3 117.5(2), N2–B1–N3 125.9(2), N1–B1–N2 116.6(1)°

Trianilinoborane (**3**) crystallizes in the monoclinic system, space group  $P2_1/c$ ,  $Z = 4$ . Its molecular structure is shown in Figure 3. Although one might expect that the three B–N bonds would be of equal lengths, one finds that this holds only for two of them (B1–N1 and B1–N2, average 1.430 Å), while the B1–N3 bond is slightly but significantly longer [1.442(2) Å]. As might be expected, the boron atom is  $\text{sp}^2$ -hybridized; the sum of its bond angles is 360°. As was also the case for the triaminoborane **2**, we observe B–N–C bond angles wider than the expected 120°. The three phenyl groups of **3** are arranged in a propeller-like fashion, and this has the effect that the N–H groups are *transoid* to each other. There are, however, no intermolecular N–H⋯N interactions.

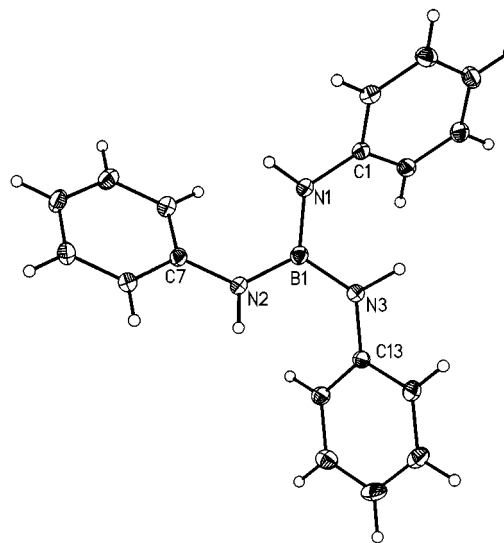


Figure 3. Structure representation of compound **3** in ORTEP description; selected bond lengths and bond angles: B1–N1 1.428(2), B1–N2 1.431(2), B1–N3 1.442(2), N1–C1 1.409(2), N2–C7 1.414(2), N3–C13 1.402(2) Å; N1–B1–N3 119.1(2), N2–B1–N3 119.5(2), N1–B1–N2 121.3(1), B1–N1–C1 127.8(1), B1–N2–C7 128.2(1), B1–N3–C13 129.0(1)°; angles between the planes of the phenyl groups: C1–C6/C7–C12 74.4, C1–C6/C13–C18 107.1, C7–C12/C13–C18 110.2°

The main difference between tris(2-pyridylamino)borane (**4**) and trianilinoborane (**3**) is that all atoms of the molecule of **4** lie in or close to a common plane (see Figure 4), the interplanar angles of the aminopyridine substituents to the  $\text{BN}_3$  plane being less than 5.7°. All B–N bonds are of equal lengths (1.432 Å), and are typical of triaminoboranes.<sup>[26]</sup> Intramolecular N–H⋯N bridges are the most likely reason for the coplanarity of the molecule. On the other hand, the B–N–C bond angles lie between 130.5 and 132.0°. This certainly makes hydrogen bonds weaker, because a 120° B–N–C bond angle would allow a closer intramolecular N⋯N distance, which is actually 2.809 Å. The “hydrogen bond” bond angles range from 134 to 137°. This geometry therefore seems to be in better accord with a dipolar interaction  $\text{N–H}(\delta^+) \cdots \text{N}(\delta^-)$ . A similar structure has been observed for the hydrazinoborane  $\text{B}(\text{NH–NMe}_2)_3$ , which has a planar  $\text{BN}_6\text{H}_3$  skeleton with the  $\text{NC}_2$  group perpendicular

to the  $\text{BN}_6$  plane. The  $\text{N}\cdots\text{N}$  distance is  $2.41(3)$  Å,<sup>[27]</sup> much shorter than in compound **4**.

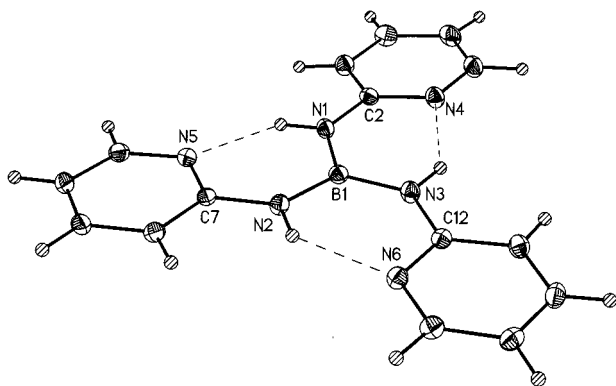


Figure 4. The molecular structure of **4** in the crystal; selected atom distances and bond angles: B1–N1 1.434(2), B1–N2 1.432(2), B1–N3 1.431(2), N1–C2 1.385(2), N2–C7 1.379(2), N3–C12 1.378(2), N5⋯H1 2.08, N4⋯H3 2.07, N6⋯H2 2.12 Å; B1–N1–C1 130.5(1), B1–N1–H1 114(1), B1–N2–C7 131.3(1), B1–N2–H2 115(1), H2–N2–C7 114(1), B1–N3–C12 132.0(1), B1–N3–H3 112(1), C12–N3–H3 116(1), N1–B1–N2 120.0(1), N1–B1–N3 119.9(1), N2–B1–N3 120.2(1)°

Tris(8-quinolylamino)borane (**5**) crystallizes in the triclinic system, space group  $P\bar{1}$ ,  $Z = 2$  (Figure 5). The molecular planes of the aminoquinoline substituents are not uniformly twisted relative to the  $\text{BN}_3$  plane, but by  $18.7^\circ$  (N1),  $33.9^\circ$  (N3), and  $24.4^\circ$  (N5). Interactions between their N–H protons and the N atom of the heterocycle occur not between adjacent heterocycles as in compound **4**, but within its own heterocyclic system. The  $\text{N}\cdots\text{N}$  distance is, at  $2.720$  Å, somewhat shorter than in **4**. As is to be expected for a five-membered “ring” (including a hydrogen bond), the angles at the bridging H atoms are sharp at ca.  $100^\circ$ .

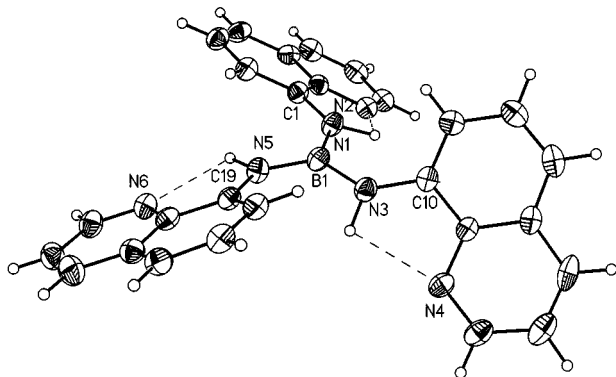


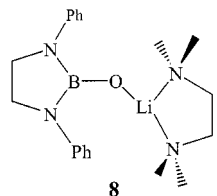
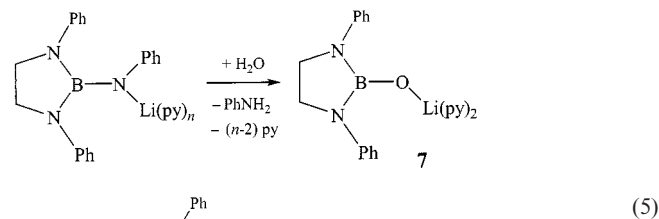
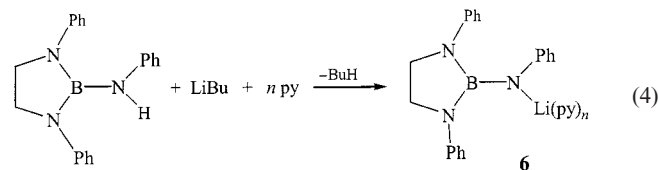
Figure 5. The molecular structure of **5** in the crystal; selected atom distances and bond angles: B1–N1 1.429(4), B1–N3 1.448(4), B1–N5 1.427(4), N1–C1 1.409(4), N3–C10 1.389(4), N5–C19 1.401(4), N2⋯H1–N 2.25, N4⋯H3–N 2.35, N6⋯H5–N 2.25 Å; B1–N1–C1 130.5(3), B1–N3–C10 131.2(3), B1–N5–C19 131.6(3), N1–B1–N3 119.3(3), N1–B1–N5 120.8(3), N3–B1–N5 119.6(3)°; torsion angle: C1–N1–C2–N2:  $-26.8^\circ$

All B–N–C bond angles are wider than  $130^\circ$ , as found for all  $\text{B}(\text{NHR})$  units in compounds **1–5**. However, it was surprising to find that one of the three B–N bonds of **5** is  $0.02$  Å longer than the other two. This indicates a somewhat weaker B–N bond with less  $\pi$ -bonding, and this longer bond is indeed associated with the substituent that shows the strongest twisting.

## *N*-Lithiotriaminoboranes

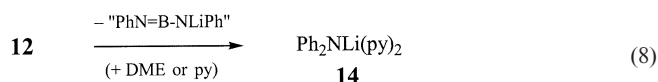
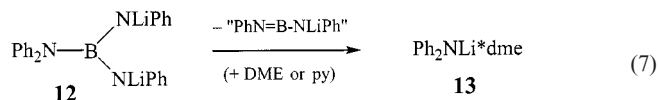
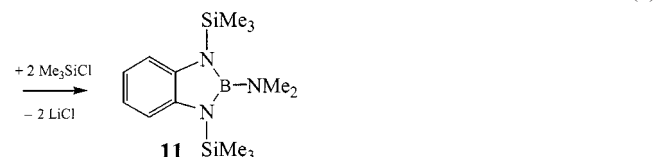
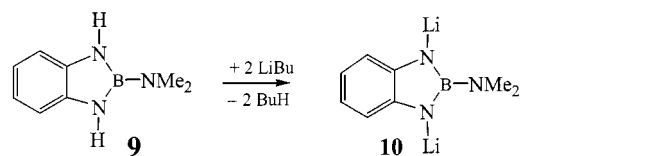
### Synthesis

The triaminoboranes mentioned above were metallated with *n*-butyllithium under various conditions. In the case of **1**, the metallation proceeded smoothly, according to Equation (4). Monitoring of the deprotonation by  $^{11}\text{B}$  NMR was not advisable, because the shielding of the boron nucleus did not change significantly (from  $\delta^{11}\text{B} = 23.8$  to  $23.0$  in this case). On the other hand, the  $^{11}\text{B}$  NMR spectrum ruled out both the formation of a borate and B–N bond cleavage. In the first of these two cases, a highfield shift should be observed, in the second case a shift to lower field should be expected.<sup>[28]</sup> Attempts to crystallize compound **6** from toluene failed. Crystals were obtained after addition of pyridine, but these proved to be the hydrolysis product **7** [see Equation (5)]. Tetramethylethylenediamine seemed to be a better ligand than pyridine for crystal formation. However, the “crystals” of **8** proved to be amorphous.<sup>[29]</sup>



Double metallation of the benzodiazaborolidine **9** by 2 equiv. of  $\text{LiBu}$  at  $-78^\circ\text{C}$  occurred readily, only a single  $^{11}\text{B}$  NMR signal being present after metallation ( $\delta^{11}\text{B} = 29.3$ ). At  $-60^\circ\text{C}$ , however, a white solid separated from the gray-green suspension, and no  $^{11}\text{B}$  NMR signals could any longer be observed in the solution. Obviously, the product **10** had become insoluble. For this reason it was impossible to grow single crystals, nor was it possible to obtain crystals from the solid dissolved in pyridine. On the other hand, the

elemental analysis of the precipitate was almost consistent with dimetallated **10** as far as the C/N ratio was concerned. In order to show that **10** had indeed been formed in the reaction described by Equation (6), the precipitate was treated with Me<sub>3</sub>SiCl. As expected, the bis(trimethylsilyl) derivative **11** was obtained and characterized by NMR spectroscopy.



The lithiation of dianilino(diphenylamino)borane (**2**) by BuLi in the presence of dimethoxyethane (DME) produced a yellow orange solution, the <sup>11</sup>B NMR spectrum of which showed two signals at δ = 28.9 and –10 in an intensity ratio of 85:15, provided that the spectrum was measured as rapidly as possible. We assigned the lowfield signal to the metallated product **12** and the highfield signal to a product containing tetracoordinated boron atoms. The orange solution turned brown within a few hours, with the formation of a white precipitate. No <sup>11</sup>B NMR signals could then be detected in the supernatant solution. Nevertheless, crystals separated slowly from the solution, and these were identified as Ph<sub>2</sub>NLi·dme (**13**). Equation (7) describes a formal decomposition process for **12**.

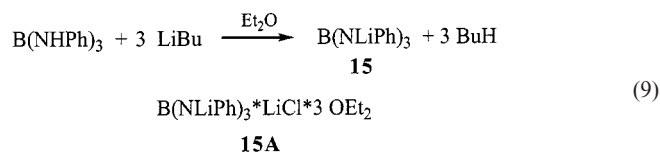
When pyridine was used to stabilize **12**, a clear yellow solution resulted. Its <sup>11</sup>B NMR spectrum, with signals at δ = –17.6, –15.4, 0.2, 1.9, 3.0, and 43.2, demonstrated a much more complex reaction than that observed in the presence of DME. Obviously, aminoborates such as Li[(PhLiN)<sub>2</sub>B(NPh<sub>2</sub>)Bu] or aminoborane–pyridine adducts such as (PhHN)<sub>2</sub>(Ph<sub>2</sub>N)B·py may form besides BuB(NPh<sub>2</sub>)(NLiPh). Crystals separated from the solution, and these proved to be LiNPh<sub>2</sub>·(py)<sub>2</sub> [**14**; see Equation (8)]. The lithium diphenylamides **13** and **14** were dimeric in the solid state (vide infra) but had different structures.

So far, the stoichiometry of the reaction has not been determined, as LiNPh<sub>2</sub> was almost certainly not the main product. We assume that B–N bond cleavage of **2** occurred, most probably at a stage after dimetallation of **2**.

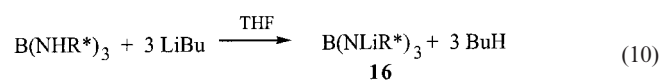
It followed from the previous observations that multimetallation required a polar solvent, in order to prevent the rapid formation of insoluble products. The triple lithiation of B(NHPh)<sub>3</sub> was therefore studied in the presence of ether. The reaction, as in Equation (9), proceeded readily at low temperature. Two <sup>11</sup>B NMR signals were found at δ = 35.4 and –3.5, the latter representing a minor component. The signal at δ = 35.4 was assigned to compound **15**. However, the formation of a precipitate could not be prevented. The solid, on dissolution in THF, showed the same signals as the ether solution. Moreover, the <sup>1</sup>H NMR spectrum showed the absence of NH protons, a good indication of successful triple metallation. The minor component was, most probably, due to the formation of LiBuB(NHPh)<sub>3</sub> or LiB(NHPh)<sub>4</sub>.<sup>[30]</sup> From the solution, compound **15** was isolated as B(NLiPh)<sub>3</sub>·LiCl·3OEt<sub>2</sub> (**15A**) in 86% yield.<sup>[31]</sup>

The triple metallation of **4** was performed in THF as a solvent, as the solubility of the aminoborane in ether was rather low. The solution obtained after metallation showed a single but rather broad <sup>11</sup>B NMR signal at δ ≈ 40. This lowfield shift (δ = 15.8) indicated a reaction according to Equation (10), since there was also a lowfield shift of δ = 11.2 found for the triple lithiation of compound **4**. However, the product proved to be not **16**, but rather its adduct with LiNHR. Therefore, B–N cleavage as in Equation (11) must also have occurred, to produce Li<sub>4</sub>B(NR\*)<sub>3</sub>(NHR\*)·(THF)<sub>3</sub> (**18**; R\* = 2-pyridyl). Equations (10) to (13) summarize the results. The formation of borate **19** was indicated by an <sup>11</sup>B NMR signal at δ<sup>11</sup>B = –9.<sup>[5,28]</sup>

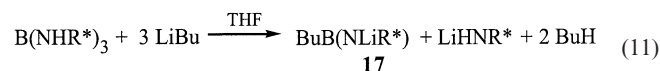
Although the composition of **18** might suggest the formation of a tetraaminoborate, this was not the case, as verified by the <sup>11</sup>B NMR spectrum and the determination of its molecular structure (vide infra).



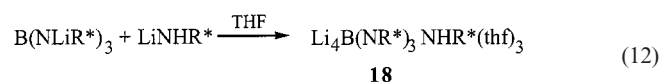
(9)



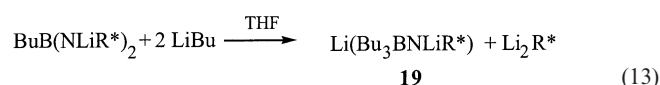
(10)



(11)



(12)



(13)

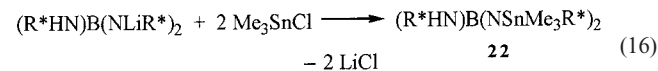
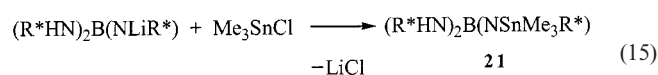
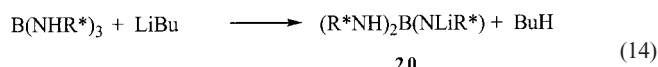
R\*NH = 2-pyridylamino group

In order to provide more insight into the metallation of **4**, reactions in a 1:1 and a 1:2 ratio were studied in addition to the 1:3 ratio. The observed  $^{11}\text{B}$  NMR signals are summarized in Table 1. In all cases, two main products were formed. The signal at  $\delta^{11}\text{B} = 23.3$  indicated that the environment about the tris(2-pyridylamino)borane was not greatly changed by the *N*-metallation. It may well be that the signals represented a mono- and a dilithiated **4**. On trimetallation, however, a noticeable deshielding indicated significant changes in triply metallated **4**. Since  $^{11}\text{B}$  NMR signals at  $\delta = -9.5$  were absent in the 1:1 and 1:2 reactions but one was observed in the 1:3 reaction, it appeared that this signal resulted from the anion  $[\text{Bu}_3\text{BNHR}^*]^-$ , as there was a sufficient supply of  $\text{Bu}^-$  anions under these conditions, and the observed chemical shift observed was similar to the value for  $\text{Na}(\text{Et}_3\text{BNH}_2)$  ( $\delta^{11}\text{B} = -9.8$ ).<sup>[28]</sup> The boron resonances at  $\delta = -1.5$  and  $-3.3$  (see Table 1) were consistent with the formation of  $\text{Li}[\text{BuB}(\text{NHR}^*)_3]$  or/and  $\text{Li}[\text{BuB}(\text{NHR}^*)_2(\text{NLiR}^*)]$ .<sup>[28]</sup>

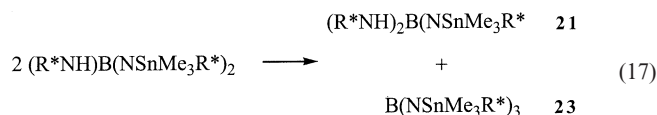
Table 1.  $^{11}\text{B}$  NMR signals observed in reactions of tris(2-pyridyl-amino)borane with various ratios of BuLi; the resonances in *italics* represent the main species

| Reagent ratio |              |      |      |                            | Solvent       |
|---------------|--------------|------|------|----------------------------|---------------|
| 1:1           | -3.3         | -0.9 | -1.5 | 1.4 23.3                   | THF           |
| 1:2           | -3.3         | -0.9 | 1.2  | 1.4 23.5                   | THF           |
| 1:3           | -9.5         |      |      | 1.3 39.6                   | THF           |
| 1.3           | -9.3         | 0    | 0.6  | 1.5 36, br. <sup>[a]</sup> | diethyl ether |
|               | -24.6, -28.6 |      |      |                            |               |

<sup>[a]</sup> The only signal obtained on dissolving the precipitate in THF.



To provide experimental evidence for the existence of monolithio compound **20**, stannylation by  $\text{Me}_3\text{SnCl}$  as in Equation (14) was attempted. The mono(trimethylstannyl) compound **21** was obtained, but could be characterized only by  $^{119}\text{Sn}$  NMR spectroscopy.<sup>[32]</sup> However, the reaction of  $\text{R}^*\text{NH}-\text{B}(\text{NLiR}^*)_2$  as shown in Equation (15) did not generate compound **22**. The solution showed  $^{119}\text{Sn}$  and  $^{11}\text{B}$  NMR signals, as observed in the stannylation of **20**, but there were additional signals in both NMR spectra. Amongst these were  $^{119}\text{Sn}$  ( $\delta = 9.2$ ) and  $^{11}\text{B}$  resonances ( $\delta = 30.2$ ) that we assigned to tris[2-pyridyl(trimethylstannyl)amino]borane (**23**), a compound that could be isolated and structurally characterized by X-ray crystallography. Obviously, the distannylated molecule **22** had exchanged  $\text{Me}_3\text{Sn}$  groups to give **23** and **21** as represented in Equation (17).



In contrast to the triple metallation of **4**, attempts to achieve the triple metallation of tris(8-quinolylamino)borane (**5**) in THF were futile. No single crystals separated from the violet-red solution, although a single broad  $^{11}\text{B}$  NMR signal at  $\delta = 32.9$  might have been indicative of the triple metallation. This assumption was supported by a single  $^7\text{Li}$  resonance. However, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were inconclusive.

## Structures

The pyridine adduct of lithium 1,3-diphenyl-2-oxido-1,3,2-diazaborolidine (**7**) crystallizes in the triclinic space group  $P\bar{1}$  with two independent dimeric molecules (Figure 6 depicts only one of the two molecules). Each molecule has a crystallographic center of inversion, generating four-membered planar  $\text{Li}_2\text{O}_2$  rings. The Li–O bonds of the rings are significantly different, with bond lengths of 1.926(4) and 1.894(3) Å in molecule 1 and 1.912(4) and 1.966(3) Å in molecule 2. Moreover, the O–Li–O and Li–O–Li bond angles are different for the two molecules (97.8° and 82.2°, and 118.8° and 84.0°, respectively). Two pyridine molecules per Li ion complete the coordination shell around the Li centers, with N–Li–N bond angles of 96.0° (molecule 1) and 93.9° (molecule 2). Surprisingly, these angles are more acute than the O–Li–O bond angles, in spite of the fact

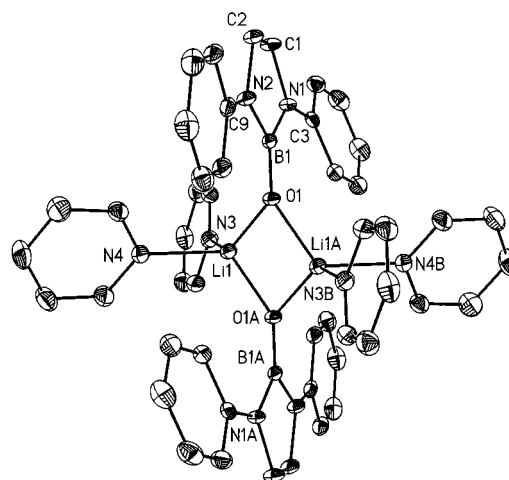


Figure 6. One of the two dimeric molecules of **7**; hydrogen atoms are omitted for clarity; selected bond lengths and bond angles: B1–O1 1.320(2), Li1–O1 1.926(4), Li1A–O1 1.894(3), B1–N2 1.467(3), B1–N1 1.478(3), N1–C3 1.391(3), N1–C1 1.466(2), C2–N2 1.455(2), N2–C9 1.386(3), Li1–N3 2.152(4), Li1–N4 2.128(4) Å; B1–O1–Li1 127.9(2), B1–O1–Li1A 146.4(2), Li1–O1–Li1A 82.2(2), O1–Li1–O1A 97.8(2), O1–Li1–N4 126.4(2), O1–Li1–N3 108.3(2), O1A–Li1–N3 117.1(2), N3–Li1–N4 95.0(2), O1–B1–O1A 128.0(2), O1–B1–N2 127.6(2), N1–B1–N2 104.4(2), C1–N1–C3 118.0(2), B1–N1–C3 129.9(2), B1–N1–C1 111.1(2), C2–N2–C9 118.5(2), B1–N2–C9 129.9(2), B1–N1–C2 111.4(2)°

that the N atoms are not part of a ring system. Consequently, the O–Li–N bond angles are more open, giving rise to Li ions with a rather distorted “tetrahedral” environment.

B–N bonds longer than those in compound **1** are found in **7**. The lengthening by ca. 0.04 Å is due to the negative charge at the oxygen atom. On the other hand, the B–O distance [1.320(3) Å] is shorter than those in B(OMe)<sub>3</sub>, (MeBO)<sub>3</sub>,<sup>[33]</sup> or B<sub>2</sub>(OMe)<sub>4</sub>,<sup>[34]</sup> and similar to the B–O distances of 1.317(6) Å found in [thf·LiOB(mes)<sub>2</sub>]<sub>2</sub> (mes = 2,4,6-trimethylphenyl)<sup>[35]</sup> and 1.345 Å in [LiOB[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>].<sup>[36]</sup> The B–O bond order in **7** is therefore higher than that in methylborates or trimethylboroxine, and this is also responsible for the longer B–N bonds.

The molecular structure of dimeric Ph<sub>2</sub>NLi·dme (**13**) is shown in Figure 7. The centrosymmetric molecule has a four-membered, rhombic Li<sub>2</sub>N<sub>2</sub> ring. Each Li ion is coordinated by two oxygen and two nitrogen atoms, with different Li–O and Li–N bond lengths, a sharp Li–N–Li bond angle (80(1)°), and a more open N–Li–N bond angle of 99(1)°.

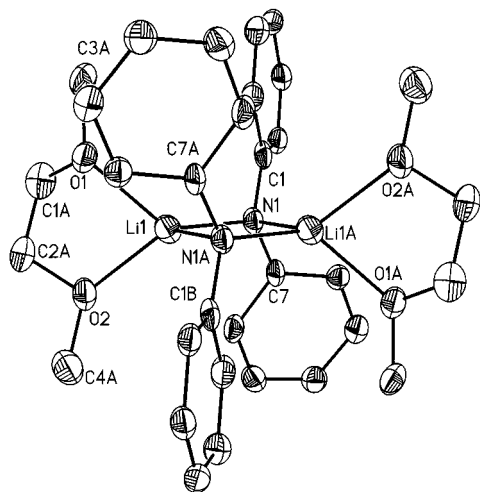


Figure 7. Molecular structure of the dimeric **13**; selected bond lengths and bond angles: Li1–N1 2.07(2), Li1A–N1 2.14(3), Li1–O1 2.07(2), Li1–O2 2.12(2), N1–C1 1.41(1), N1–C7 1.425(8) Å; Li1–N1–Li1A 80(1), N1–Li1–N1A 99(1), O1–Li1O2 79.7(7), O1–Li1–N1 125(1), Li1–N1–C7 124.2(5), C1–N1–C7 115.8(9)°

While the structure of **13** resembles the structures of dimeric (smes)HNLi·OEt<sub>2</sub><sup>[37]</sup> [smes = 2,4,6-tris(*tert*-butyl)phenyl] or (Me<sub>3</sub>Si)[(Me<sub>3</sub>Si)<sub>3</sub>Si]NLi<sup>[38]</sup> as far as the association through Li–N bonds is concerned, lithium amides with tetracoordinated Li centers are more common.<sup>[16]</sup> However, a much more interesting structure was found for dimeric Ph<sub>2</sub>NLi·(py)<sub>2</sub> (**14**), the molecular structure of which is shown in Figure 8. There are two kinds of Li ions. Li1 is surrounded by a plane of three nitrogen atoms in which the N1–Li1–N2 bond angle is quite open, at 139.8°. The longest Li–N bond is that formed with the pyridine nitrogen atom, followed by those with the nitrogen atom of the tetracoordinated Ph<sub>2</sub>N group (2.042 Å), while the bond to the

tricoordinated N2 atom is, as might be expected, even shorter (1.950 Å). While the Li1–N1–Li2 bond angle is almost tetrahedral, the C14–N1–C2 bond angle is more open, at 119.0(3)°. The tetracoordinated Li2 atom bears three pyridine molecules, with an average Li–N bond length of 2.111 Å. The phenyl rings at N2 form interplanar angles with the N<sub>3</sub>Li plane of 17.6–0.7°, and the interplanar angle between N2C<sub>2</sub> and Li1N<sub>3</sub> at 95.6° shows an almost orthogonal orientation. This allows the pyridine ring N3 to adopt a staggered conformation not only with the phenyl groups at N2, but also with the plane around atom N1.

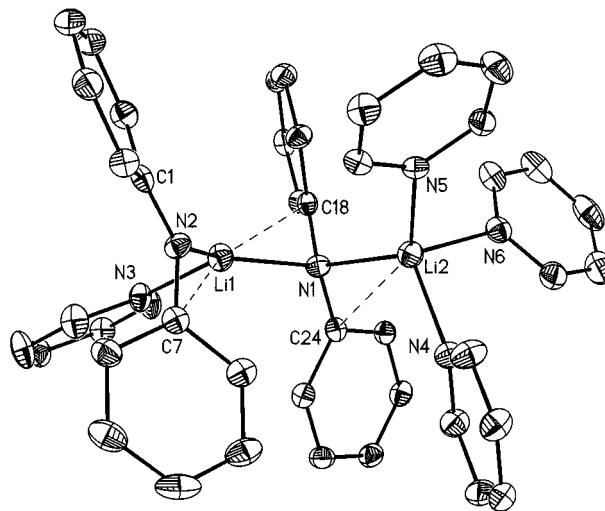


Figure 8. Molecular structure of dimeric **14**; selected bond lengths and bond angles: Li1–N1 2.042(6), Li1–N2 1.950(7), Li1–N3 2.054(7), Li2–N1 2.132(7), Li2–N4 2.137(7), Li2–N5 2.077(7), Li2–N6 2.119(6), C1–N2 1.368(4), C7–N2 1.393(4), C18–N1 1.405(4), C24–N1 1.410(4) Å; Li1–N1–Li2 108.1(3), Li1–N1–C18 95.3(3), Li1–N1–C24 121.0(3), Li2–N1–C18 111.7(3), Li2–N1–C24 101.8(2), C1–N2–C7 119.4(3), C1–N2–Li1 128.9(3), Li1–N2–C7 111.3(3), N1–Li1–N2 139.8(3), N1–Li1–N3 108.8(3), N2–Li1–N3 109.1(3), N5–Li2–N6 105.2(3), N1–Li2–N5 122.0(3), N1–Li2–N6 105.3(3), N4–Li2–N5 100.3(3), N4–Li2–N6 104.3(3), N1–Li2–N4 118.0(3)°

The triply lithiated trianilinoborane **15**, which crystallized as B(NLiPh)<sub>3</sub>·LiCl·3OEt<sub>2</sub> (**15A**), once again proved to be dimeric in the solid state, its core structure containing eight Li atoms. Figure 9 shows the molecular structure. The dimeric molecule is centrosymmetric. Four Li atoms (Li1, Li1A, Li3, Li3A) are three-coordinated by one O, N, and Cl atom each, while the other four Li centers are tetracoordinated, atoms Li2 and Li2A by two N atoms, one O atom, and one Cl atom, and atoms Li4 and Li4A by three N atoms and one Cl atom. In order to describe the structure of **15A** it is best to start from the B(NLiPh)<sub>3</sub> unit. The core atoms of this molecule are shown in Figure 10.

The most important feature of compound **15A** is the planar BN<sub>3</sub> unit, which shows different B–N bond lengths of 1.429(9), 1.459(9), and 1.509(9) Å to atoms N1, N3, and N2, respectively. While B1–N1 is practically of the same length as in the parent compound **3**, the other two B–N

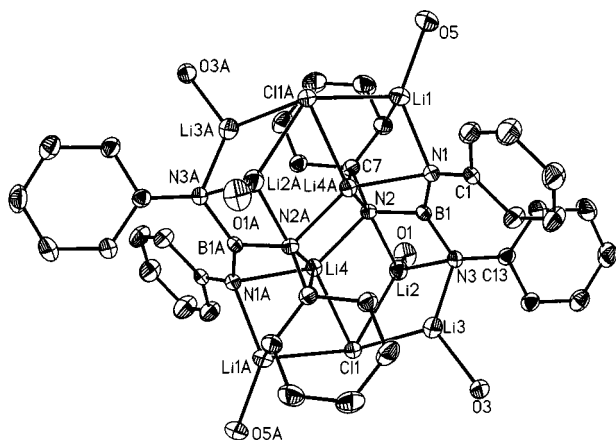


Figure 9. Molecular structure of compound dimeric **15A**; hydrogen atoms and C atoms of the ether molecules omitted for clarity

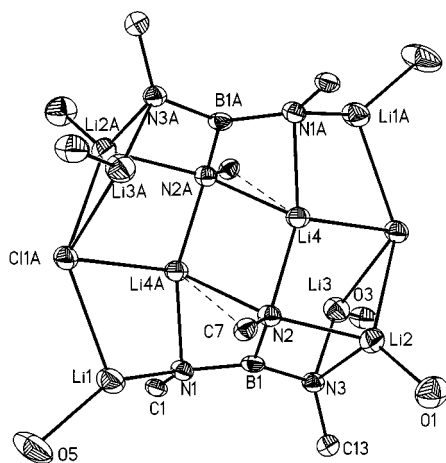


Figure 10. The core structure of  $[B(NLiPh)_3 \cdot LiCl \cdot 3 OEt_2]_2$  (**15A**)<sub>2</sub>; only the *ipso*-C atoms of the phenyl rings are shown; the Et groups of the ether molecules have also been removed; selected bond lengths and bond angles: B1–N1 1.429(4), B1–N2 1.509(4), B1–N3 1.459(4), Li1–N1 2.021(6), N1–Li4A 2.029(5), Li3–N3 1.083(7), Li2–N3 1.983(7), Li4–N2 2.006(5), Li4A–N2 2.154(5), N1–C1 1.400(3), N2–C7 1.364(4), N3–C13 1.373(3), C11–Li2 2.564(5), C11–Li3 2.377(5), C11–Li4 2.362(5), C11A–Li1 2.451(5), Li1–O1 1.901(6), Li2–O2 1.910(6), Li3–O3 1.925(6) Å; N1–B1–N3 132.9(3), N1–B1–N2 113.9(2), N3–B1–N2 112.1(2), Li1A–C11–Li3 121.1(2), Li1A–C11–Li2 130.2(2), Li4–C11–Li1A 64.7(2), Li4–C11–Li2 67.5(2), Li4–C11–Li3 88.7(2), Li2–C11–Li3 69.8(2)°

bonds are significantly elongated. Actually, the long B1–N2 bond corresponds to a single bond between  $sp^2$ -type B and N atoms. The reasons for these differences are the different N–B–N–C torsion angles and the number of coordinated Li atoms at the N atoms. Thus, the B1N1N2N3/B1N1C1 interplanar angle is 21.5°, which still allows for BN- $\pi$ -bonding. While atom Li1 is part of the planar environment around atom N1 (sum of bond angles 357.8°), one may note that the atom Li4A has an N1–Li4A distance of 2.209(5) Å and lies 1.934 Å above the

B1N1C1Li1 plane. However, the N1–Li1 distance is 2.961(6) Å, the same distance as found for N1–Li4A. The situation at atom N3 is similar to that at N1, but there is greater torsion, as demonstrated by the angle of 50.8° between the B1N1N3 and B1N3C13 planes. This has the consequence of weaker BN- $\pi$ -bonding, as revealed by the longer B1–N3 bond. The distance from N3 to Li3 [1.983(7) Å] is shorter than that to Li2 [2.005(5) Å], but the B1N3C13Li3 atom system lies almost in a plane (B1 being –0.192 Å distant). Finally, the interplanar angle B1N1N2N3/B1N2C7 is 57.6°, and this seems to be a reason for the long B1–N2 bond to which the pentacoordinated atom N2 contributes. The coordination of Li2 and Li4A by two N atoms of the trianilidoborane unit is what most probably gives rise to an N1–B1–N3 bond angle as wide as 132.9(3)°.

As shown in Figure 10, the Cl anion is coordinated to the Li atoms of the  $B(NLiPh)_3$  unit, with distances of 2.564, 2.377, and 2.362 Å to atoms Li2, Li3, and Li4, respectively. The presence of the chloride results in the formation of a distorted cubane unit in which one corner of the cube is missing. The Cl ion is surrounded by four Li ions. An unusually open coordination at Cl results, and this is best described as a strongly distorted trigonal bipyramid with a coordination partner missing in the equatorial plane. Atoms Li1, Li1A, Li3, and Li3A coordinate with three ligand atoms (O, N, Cl) in a nonplanar fashion.

The triply lithiated **4** crystallizes with one molecule of  $LiHNR^*$  as  $[Li_4B(NR^*)_3HNR^*(THF)_3]_2$  (**18**)<sub>2</sub>. Its molecular structure is shown in Figure 11 and the monomeric unit is displayed in Figure 12. As may be noted, the metallation of compound **5** leaves the boron atom in a planar environment, the extra  $LiHNR^*$  group not being bonded to atom B1 to generate a tetraamidoborate. One B–N bond of the  $B(NLiR^*)_3$  unit is short, at 1.440(3) Å (B1–N1), while the other two are of almost equal lengths [1.476(3) for N2 and 1.467(3) Å for N3]. Thus, all B–N bonds are longer than those in the parent compound **4**. Each N atom of the  $BN_3$  unit is coordinated to two Li atoms, but there is only one Li atom (Li3) that bridges two N atoms of the  $BN_3$  unit. This gives rise to a small N1–B1–N3 bond angle of 111.8(2)°. The twisting of the CNB planes relative to the  $BN_3$  plane is 24.4, 50.7, and 88.2° (at N1, N3, N2), respectively.

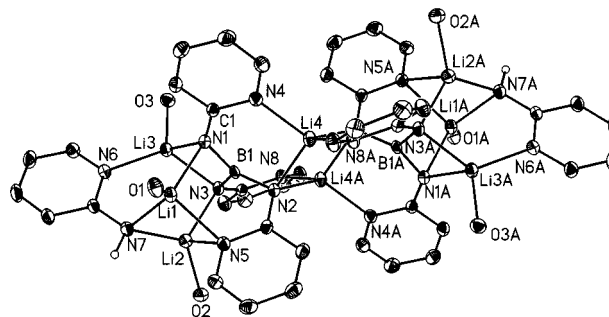


Figure 11. The molecular structure of  $[B(NLiR^*)_3 \cdot LiHNR^*(THF)_3]_2$  (**18**)<sub>2</sub>; hydrogen atoms removed, as well as the C atoms of the coordinated THF molecules

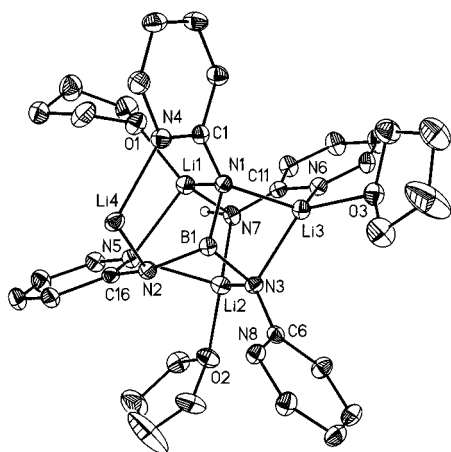


Figure 12. The asymmetric (monomeric) unit of **18**; bond lengths and bond angles: B1–N1 1.440(3), B1–N2 1.476(3), B1–N3 1.467(3), N1–C1 1.353(3), N2–C16 1.332(3), N3–C6 1.338(3), Li1–N1 2.114(5), Li3–N1 2.046(4), Li4–N2 2.065(4), Li2–N3 2.067(4) Å; N1–B1–N2 125.1(2), N1–B1–N3 111.8(2), N2–B1–N3 122.4(2), C1–N1–B1 123.9(2), C1–N1–Li3 138.3(2), C1–N1–Li1 106.8(2), B1–N2–C16 113.8(2), B1–N2–Li4 108.6(2), B1–N2–Li4A 104.7(2), Li4–N2–Li4A 78.4(2), Li4–N2–C16 117.7(2), Li4A–N2–C16 128.5(2), B1–N3–C6 122.9(2), B1–N3–Li2 96.5(2), B1–N3–Li3 87.6(2), C6–N3–Li2 123.3(2), C6–N3–Li3 125.4(2), Li2–N3–Li3 91.8(2)°

The Li–N atom distances in (**18**)<sub>2</sub> span a range from 2.036(5) to 2.114(5) Å for the amino nitrogen atoms, and 2.038(4) to 2.155(4) Å for the pyridine nitrogen atoms, with the exception of the Li2–N5 distance of 2.286(4) Å. The reason for the long distance is most probably the specific situation at atom N5, since this atom is the only pyridine nitrogen atom that coordinates to two Li centers.

The (stannylamino)borane **23** crystallizes in the monoclinic system, its molecular structure being shown in Figure 13. The B–N bond lengths range from 1.435(6) to 1.457(6) Å. These are slightly longer than those in the parent compound **5**. All Sn–N bonds to the amino nitrogen atoms are of equal length. The pyridine nitrogen atoms are oriented towards the tin atoms of each Me<sub>3</sub>SnNR\* unit. This may indicate the presence of Sn–N interactions. If there are any, then these must be quite weak, as the C–Sn–C bond angles deviate only slightly from the tetrahedral angle.

All amino nitrogen atoms reside in a planar environment, but the SnNC planes at N1, N2, and N3 are twisted relative to the BN<sub>3</sub> plane by 40.6, 38.1, and 46.1°, respectively. These torsion angles explain the lengths of the B–N bonds. The twisting results from the steric requirement of the trimethylstannyl groups and is the most striking difference on comparison of this structure with the parent compound **4**. As would be expected, the Sn–C bond lengths are in the typical range (2.12–2.15 Å).<sup>[39,40]</sup>

## Discussion

The deprotonation of aminoboranes bearing RHN groups by butyllithium depends on the steric and electronic

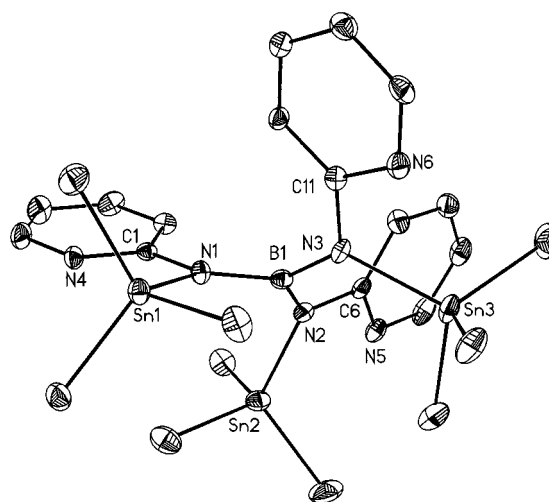


Figure 13. ORTEP plot of compound **23**; H atoms have been omitted for clarity; selected bond lengths and bond angles: B1–N1 1.443(7), B1–N2 1.435(6), B1–N3 1.457(6), N1–Sn1 2.109(4), N2–Sn2 2.119(4), N3–Sn3 2.110(3), Sn1...N4 2.717, Sn2...N5 2.703, Sn3...N6 2.672, N1–C1 1.396(5), N2–C6 1.383(6), N3–C11 1.385(5) Å; N1–B1–N2 121.2(4), N1–B1–N3 118.5(4), N2–B1–N3 120.3(4), B1–N1–C1 123.6(4), C1–N1–Sn1 108.2(3), B1–N1–Sn1 128.2(3), B1–N2–C6 123.7(4), C6–N2–Sn2 107.9(3), B1–N2–Sn2 128.4(3), B1–N3–C11 124.0(4), C11–N3–Sn3 107.8(3), B1–N3–Sn3 128.1(3), N1–Sn1–C16 104.6(2), N1–Sn1–C17 111.5(2), N1–Sn1–C18 113.0(2)°

shielding of the boron atom, the structure of the aminoborane, and the solvent used. In almost all so far known cases, including the results presented here, there is competition between deprotonation and borate formation, as well as B–N bond cleavage. The last can be impeded if the boron atoms are part of a ring system, as shown for the triazaboradecalin system<sup>[3]</sup> or for borazines (RB=NH)<sub>3</sub>.<sup>[18]</sup> However, an exocyclic B–N bond is comparatively easily cleaved, as demonstrated by compound **2**, while borate formation can be fully or at least partly suppressed by the use of *t*BuLi.<sup>[41]</sup> In the case of the double deprotonation of the aminoborane **2**, one observed the formation of a borate, most probably Li[BuB(NPh<sub>2</sub>)(NLiPh)<sub>2</sub>], in solution besides Ph<sub>2</sub>NB–(NLiPh)<sub>2</sub>. Both compounds might be the source of LiNPh<sub>2</sub>, which was formed slowly. Isolated Ph<sub>2</sub>NLi solvates form dimers, as is well known for various lithium diorganylamides. However, chain-like dimers of lithium diorganylamides are rare.<sup>[16,17]</sup>

Neither borate formation nor B–N bond cleavage was observed in the triple lithiation of trianilinoborane (**3**) in the presence of ether, unlike in the case of tris(2-pyridylamino)borane, in which B–N cleavage to give LiNHR\* occurred. This amide cocrystallized with B(NLiR\*)<sub>3</sub> in a 1:1 ratio to give (**18**)<sub>2</sub>, a cluster with an Li<sub>8</sub>N<sub>8</sub> core. In addition, (2-aminopyridyl)butylborates were also formed. Nevertheless, deprotonation was the dominant reaction both for **3** and for **4**.

However, as we have seen for compound **18**, the metallated triaminoboranes did not add amide ions to form tetraaminoborates. These latter are scarce anyhow, and form readily only when the amido group is derived from a

heterocyclic system, such as the anions of pyrrole,<sup>[42]</sup> indole,<sup>[43]</sup> pyrazole,<sup>[44,45]</sup> or dihydropyridine.<sup>[46]</sup> In these cases, the parent triaminoborane is comparatively Lewis-acidic. This is obviously not the case for the tris(lithioamino)boranes; the negative charge at the nitrogen atoms reduces the Lewis acidity of the boron center. Therefore, an amide does not attack at the boron center, but rather forms coordinative Li–N bonds. The lithium atoms adopt coordination numbers ranging from 3 to 5. Therefore, in comparison with lithium amides,<sup>[16,17]</sup> the borylated lithium amides offer a much more versatile structural chemistry similar to that of lithiated silylamides<sup>[16]</sup> and aminophosphanes.<sup>[47]</sup> In addition, they are very useful reagents. This has been shown previously,<sup>[5–10,48]</sup> and we will report on this point in a forthcoming paper describing the synthesis and reactions of (*t*BuLi)B(R)tmp (tmp = 2,2,6,6-tetramethylpiperidino) (see ref.<sup>[44]</sup>).

## Experimental Section

**General:** All experiments required anhydrous conditions. Schlenk techniques were employed, with dinitrogen as a protecting gas. The amines are commercially available; the liquids were dried with either KOH or CaH<sub>2</sub> and distilled, and the solids were recrystallized before use. BuLi was obtained from Chemetall GmbH. NMR: Bruker ACP 200 (<sup>7</sup>Li, <sup>11</sup>B, <sup>119</sup>Sn), JEOL GSX 270, and JEOL EX 400 (<sup>1</sup>H, <sup>13</sup>C, <sup>119</sup>Sn) with Me<sub>4</sub>Si, C<sub>6</sub>D<sub>6</sub>, BF<sub>3</sub>·OEt<sub>2</sub>, and SnMe<sub>4</sub> as standards. Elemental analyses were performed in the microanalytical laboratory of this department. X-ray: Siemens P4 diffractometer equipped with a CCD area detector, graphite monochromator, and Mo-*K*<sub>α</sub> source or a STOE IPS diffractometer (compounds **7** and **23**). Data sets were collected at –80 °C (Siemens LT2 device).

**2-Anilino-1,3-diphenyl-1,3,2-diazaborolidine (1):** Aniline (0.87 mL, 9.5 mmol) and triethylamine (1.32 mL) were added to a stirred solution of 2-chloro-1,3-diphenyl-1,3,2-diazaborolidine<sup>[48]</sup> (2.43 g, 9.50 mmol) in toluene (80 mL). A precipitate formed. The mixture was heated under reflux overnight, the solid was removed by filtration (glass frit), and the orange-yellow solution was concentrated to approximately 50 mL in vacuo. Needles of **1** separated from the solution. Yield: 2.7 g, 71%; m.p. 153 °C. NMR (in C<sub>6</sub>D<sub>6</sub>): δ<sup>1</sup>H = 3.20 (s, 4 H, NCH<sub>2</sub>), 4.49 (s br., 1 H, NH), 6.47 (d, <sup>3</sup>J<sub>H,H</sub> = 7.3 Hz, 2 H, *o*-CH aniline), 6.66 (t, <sup>3</sup>J<sub>H,H</sub> = 7.6 Hz, 1 H, *p*-CH aniline), 6.80 (t, <sup>3</sup>J<sub>H,H</sub> = 7.2 Hz, 2 H, *p*-H Ph), 6.90 (t, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, 2 H, *m*-CH aniline), 6.93 (d, <sup>3</sup>J<sub>H,H</sub> = 7.6 Hz, 4 H, *o*-CH, Ph), 7.07 (t, <sup>3</sup>J<sub>H,H</sub> = 8.8 Hz, 4 H, *m*-CH, Ph); δ<sup>13</sup>C = 48.04 (CH<sub>2</sub>), 119.5 (*o*-C, Ph), 119.6 (*o*-C, aniline), 120.2 (*p*-C, aniline), 120.9 (*p*-C, Ph), 128.8 (*m*-C, aniline), 129.0 (*m*-C, Ph), 143.1 (*i*-C, aniline), 146.6 (*i*-C, Ph); δ<sup>11</sup>B = 23.0 (*h*<sub>1/2</sub> = 300 Hz). C<sub>20</sub>H<sub>20</sub>BN<sub>3</sub> (313.20): calcd. C 76.62, H 6.38, N 13.41; found C 76.31, H 6.67, N 13.31.

**Dianilino(diphenylamino)borane (2):** A solution of diphenylamine (4.23 g, 25.0 mmol) in toluene (150 mL) was cooled to –78 °C. A solution of BuLi in hexane (1.56 M, 16 mL) was added with stirring. A voluminous, white precipitate formed immediately, with some gas evolution. The suspension was allowed to attain ambient temperature. Stirring was continued for additional 3 h. After the mixture had again been cooled to –78 °C, a solution of BCl<sub>3</sub> in toluene (1.1 M, 22.7 mL, 25.0 mmol) was slowly added. Stirring was continued at ambient temperature overnight. The <sup>11</sup>B NMR spectrum taken after that time showed a signal at δ = 32.1 (**2**) and a tiny

signal at δ = 41.1, corresponding to 2-butyl-1,3-diphenyl-1,3,2-diazaborolidine (ratio approximately 97:3). The solid was removed from the suspension by filtration. A mixture of aniline (4.6 mL, 50 mmol) and triethylamine (7.0 mL) was added at –78 °C to the slightly yellow filtrate. After the reaction mixture had been heated at reflux overnight and after removal of the solid, the filtrate was concentrated in volume to approximately 50 mL. Crystals separated from the solution within a few days. Crystallization from toluene yielded **2** (6.44 g, 71.0%), m.p. 185 °C. C<sub>24</sub>H<sub>22</sub>BN<sub>3</sub> (362.81): calcd. C 79.83, H 6.06, N 11.58; found C 78.09, H 6.21, N 11.08.

**Trianilinoborane (3):**<sup>[49]</sup> Aniline (5.5 mL, 60 mmol) was added to a solution of B(NMe<sub>2</sub>)<sub>3</sub> (3.45 mL, 20 mmol) in toluene (70 mL). Gas evolution started, and became rapid on heating of the solution at reflux for 5 h. A single <sup>11</sup>B NMR signal at δ = 23.7 indicated a quantitative reaction. Crystals separated within a few hours. Half of the solvent was removed from the suspension in vacuo, and 6.6 g of **3** was isolated. Yield: 87%; m.p. 174 °C. NMR in C<sub>6</sub>D<sub>6</sub>: δ<sup>1</sup>H = 4.83 (br. s, 3 H, NH), 6.75 (dd, <sup>3</sup>J<sub>H,H</sub> = 8.5, <sup>4</sup>J<sub>H,H</sub> = 1.1 Hz, 6 H, *o*-H), 6.80 (tt, <sup>3</sup>J<sub>H,H</sub> = 7.6, <sup>4</sup>J<sub>H,H</sub> = 1.2 Hz, 3 H, *p*-H), 7.06 (t, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, 6 H, *m*-H); δ<sup>13</sup>C = 119.9 (*o*-C), 120.8 (*p*-C), 129.4 (*m*-C), 145.4 (*i*-C); δ<sup>11</sup>B = 23.7 (*h*<sub>1/2</sub> = 214 Hz); δ<sup>14</sup>N = –292.3.

**Tris(2-pyridylamino)borane (4):** 2-Aminopyridine (5.65 g, 59.4 mmol) and B(NMe<sub>2</sub>)<sub>3</sub> (20.0 mmol) were heated under reflux in toluene (150 mL). Gas evolution (dimethylamine) rapidly started, and the amine was trapped at –78 °C. On cooling of the solution to ambient temperature, a white precipitate of **4** formed. After filtration, the filtrate was cooled to 0 °C. Colorless needles separated; these were suitable for X-ray structure determination. Yield: 5.2 g (90%), m.p. 121 °C. NMR in C<sub>6</sub>D<sub>6</sub>: δ<sup>1</sup>H = 6.36 (ddd, <sup>3</sup>J<sub>H,H</sub> = 8.5, <sup>3</sup>J<sub>H,H</sub> = 5.4, <sup>4</sup>J<sub>H,H</sub> = 0.8 Hz, 3 H, C5-H), 6.46 (dt, <sup>3</sup>J<sub>H,H</sub> = 8.3, <sup>4</sup>J<sub>H,H</sub> = 0.7 Hz, 3 H, C3-H), 6.99 (ddd, <sup>3</sup>J<sub>H,H</sub> = 7.3, <sup>3</sup>J<sub>H,H</sub> = 7.4, <sup>4</sup>J<sub>H,H</sub> = 1.6 Hz, 3 H, C4r-H), 8.14 (ddm, <sup>3</sup>J<sub>H,H</sub> = 5.3, <sup>4</sup>J<sub>H,H</sub> = 1.8 Hz, 3 H, C6-H), 9.85 (s, 3 H, NH); δ<sup>13</sup>C = 113.6 (C3), 114.6 (C5), 137.4 (C4), 147.2 (C6), 159.6 (C2); δ<sup>11</sup>B = 24.2 (*h*<sub>1/2</sub> = 218 Hz); δ<sup>14</sup>N = –105.7 (pyN), –310.0 (NH). IR (Hostaflohn, cm<sup>–1</sup>): ν̃ = 3293 (NH<sub>2</sub>), 3090, 3059, 3043, 3022 (CH). C<sub>16</sub>H<sub>15</sub>BN<sub>5</sub> (290.13): calcd. C 57.14, H 5.71, N 26.62; found C 58.19, H 5.25, N 27.11.

**Tris(8-quinolylamino)borane (5):** Tris(dimethylamino)borane (1.8 mL, 19 mmol) was added to a suspension of 8-aminoquinoline (4.32 g, 30.0 mmol) in toluene (150 mL). The mixture was heated under reflux for 30 h. The red solution showed a broad <sup>11</sup>B NMR signal at δ = 24.7. After cooling of the solution to 0 °C, red needles separated within a few days. Yield: 3.75 g (85.3%), m.p. > 200 °C. NMR in C<sub>6</sub>D<sub>6</sub>: δ<sup>1</sup>H = 6.74 (dd, <sup>3</sup>J<sub>H,H</sub> = 3.7 Hz, 3 H, C3-H), 6.97 (d, br., <sup>3</sup>J<sub>H,H</sub> = 7.8 Hz, 3 H, C5-H), 7.21 (dd, <sup>3</sup>J<sub>H,H</sub> = 7.9, <sup>3</sup>J<sub>H,H</sub> = 7.9 Hz, 3 H, C6-H), 7.54 (dd, <sup>3</sup>J<sub>H,H</sub> = 8.4, <sup>4</sup>J<sub>H,H</sub> = 1.8 Hz, 3 H, C4-H), 7.72 (d, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, 3 H, C7-H), 8.15 (s 3 H, NH), 8.48 (dd, <sup>3</sup>J<sub>H,H</sub> = 4.0, <sup>4</sup>J<sub>H,H</sub> = 1.5 Hz, 3 H, C2-H); δ<sup>13</sup>C = 112.7 (C7), 116.6 (C5), 121.4 (C3), 129.2 (C10), 135.7 (C9), 136.1, C6), 140.2 (C4), 143.4 (C8), 146.9 (C2); δ<sup>11</sup>B (in toluene) = 24.7 (*h*<sub>1/2</sub> = 450 Hz); δ<sup>14</sup>N = –74.8 (ring N), –326.9 (NH). IR (Nujol, cm<sup>–1</sup>): ν̃ = 3340 (vNH). C<sub>27</sub>H<sub>21</sub>BN<sub>6</sub> (439.81): calcd. C 73.58, H 4.77, N 19.07; found C 73.33, H 4.82, N 18.61.

**2-[Lithio(phenyl)amino]-1,3-diphenyl-1,3,2-diazaborolidine (6) and Formation of Lithium 2-Oxido-1,3-diphenyl-1,3,2-diazaborolidine (7):** A solution of compound **1** (0.490 g, 1.56 mmol) in toluene (40 mL) was diluted with ether (10 mL), and the mixture was cooled to –78 °C. A solution of BuLi in hexane (1.0 mL, 1.56 mmol) was added by syringe, with stirring. The solution turned orange. At room temperature the solution showed only a single <sup>11</sup>B NMR sig-

nal at  $\delta = 23.8$  (**6**). The solid that was left on concentration of the solution also showed an  $^{11}\text{B}$  NMR signal at  $\delta = 23.8$  in deutero-benzene, which was assigned to **6**. Attempts to grow crystals from this solution failed. However, after addition of pyridine (3 mL) a few large crystals grew slowly at 0 °C over two weeks. These proved to be compound **7**, as also characterized by X-ray crystallography. **7**: NMR in  $\text{C}_6\text{D}_6$ :  $\delta^1\text{H} = 3.47$  (s, 4 H,  $\text{NCH}_2$ ), 6.82 (d,  $^3J_{\text{H,H}} = 8.5$  Hz, 2 H,  $p\text{-CH}$ ), 6.98 (t,  $^3J_{\text{H,H}} = 7.6$  Hz, 4 H,  $o\text{-CH}$ ), 7.28 (t,  $^3J_{\text{H,H}} = 7.8$  Hz, 4 H,  $m\text{-CH}$ ), 7.42 (t,  $^3J_{\text{H,H}} = 8.6$  Hz, 4 H,  $p\text{-CH}$ , py), 7.68 (t,  $^3J_{\text{H,H}} = 7.6$  Hz, 2 H,  $p\text{-CH}$ , py), 8.63 (d,  $^3J_{\text{H,H}} = 4.5$  Hz, 4 H,  $o\text{-H}$ , py);  $\delta^{13}\text{C} = 43.0$  ( $\text{CH}_2$ ), 113.0 ( $o\text{-C}$ ), 117.8 ( $p\text{-C}$ ), 123.5 ( $m\text{-C}$ , py), 129.3 ( $p\text{-C}$ , py), 148.1 (ipso-C), 149.6 ( $o\text{-C}$ , py);  $\delta^{11}\text{B} = 22.7$  ( $h_{1/2} = 350$  Hz);  $\delta^7\text{Li} = 1.59$ .  $\text{C}_{24}\text{H}_{24}\text{BLiN}_4\text{O}$  (402.2): calcd. C 71.66, H 6.01, N 13.93; found C 68.37, H 6.35, N 12.07.

**Double Metallation of 2-(Dimethylamino)-1,3,2-benzodiazaborolidine (9)**: The diazaborolidine **9**<sup>[50]</sup> (0.26 g, 1.6 mmol) was added to a solution of tetramethylethylenediamine (0.46 mL, 3.2 mmol) in tetrahydrofuran (80 mL). After this had been cooled to  $-78$  °C, a hexane solution of BuLi (2.1 mL, 1.56 M) was added to the vigorously stirred solution. The color of the solution turned from yellow to gray-green. An  $^{11}\text{B}$  NMR spectrum at  $-78$  °C showed only one signal at  $\delta = 29.3$ . On warming, a precipitate formed at about  $-60$  °C, and no  $^{11}\text{B}$  NMR signal was then observed in the supernatant solution at room temperature. When the solution was kept at  $-78$  °C and the solvent was removed stepwise in vacuo, no crystals separated. The solid that was formed at  $-60$  °C was dried in vacuo.

Elemental analysis: C 48.12, H 5.88, N 17.92, corresponding to  $\text{C}_8\text{H}_{11.6}\text{N}_{2.54}$  instead of  $\text{C}_8\text{H}_{10}\text{N}_3(\text{BLi}_2)$  for **10**.

**2-(Dimethylamino)-1,3-bis(trimethylsilyl)-1,3,2-benzodiazaborolidine (11)**:  $\text{Me}_3\text{SiCl}$  (0.34 mL) was added at  $-78$  °C to **10** (1.35 mmol) in THF (80 mL). The stirred suspension was allowed to attain ambient temperature. All volatiles were removed from the gray-green solution in vacuo, and hexane (30 mL) was added to the oily residue. This resulted in a brown solution and a white insoluble product (LiCl). The solid was separated by filtration. From the filtrate all volatile material was removed. The liquid residue was dissolved in  $\text{CDCl}_3$  and characterized as **11** by NMR spectroscopy. NMR:  $\delta^1\text{H} = 0.55$  (s, 18 H, SiMe), 2.67, (s, 6 H, NMe), 6.91 (m, 2 H, C3 H, C6-H), 7.25 (m, C4-H, C5-H);  $\delta^{13}\text{C} = 1.9$  SiMe, 41.4 (CMe=, 114.3, C3, C6), 118.9 (C4, C5), 142.0 (C1,C2);  $\delta^{11}\text{B} = 32.0$  ( $h_{1/2} = 227$  Hz);  $\delta^{27}\text{Si} = 4.7$ .

**Double Metallation of Dianilino(diphenylamino)borane and Formation of  $\text{LiNPh}_2$** : Dimethoxyethane (0.41 g, 4.5 mmol) was added to compound **2** (1.63 g, 4.50 mmol) in toluene (80 mL). The solution was cooled to  $-78$  °C. A hexane solution of LiBu (5.7 mL, 9.0 mmol) was added dropwise with stirring. After the yellow/orange solution had been allowed to attain ambient temperature, it showed two  $^{11}\text{B}$  NMR signals at  $\delta = 28.9$  (**12**) and  $-10.0$ , in an intensity ratio of 85:15. Solvent was removed in vacuo, to leave 10 mL of a solution. At 0 °C, colorless crystals separated within several days and proved to be  $\text{LiNPh}_2\cdot\text{dme}$  (**13**). The supernatant liquid showed  $^{11}\text{B}$  NMR signals at  $\delta = -0.3$  (weak), 30.8 (main signal), and 42.0

Table 2. Crystallographic parameters, information about data collection, and structure solution of compounds **1–5**

| Compound                             | 1                                                                   | 2                                                                    | 3                                                                   | 4                                                                  | 5                                                                  |
|--------------------------------------|---------------------------------------------------------------------|----------------------------------------------------------------------|---------------------------------------------------------------------|--------------------------------------------------------------------|--------------------------------------------------------------------|
| Empirical formula                    | $\text{C}_{20}\text{H}_{20}\text{BN}_3$                             | $\text{C}_{24}\text{H}_{22}\text{BN}_3$                              | $\text{C}_{18}\text{H}_{18}\text{BN}_3$                             | $\text{C}_{27}\text{H}_{21}\text{BN}_6$                            | $\text{C}_{15}\text{H}_{15}\text{BN}_6$                            |
| Formula mass                         | 313.20                                                              | 363.26                                                               | 287.16                                                              | 440.31                                                             | 290.14                                                             |
| Crystal size [mm]                    | $0.10 \times 0.20 \times 0.20$                                      | $0.10 \times 0.10 \times 0.30$                                       | $0.20 \times 0.30 \times 0.30$                                      | $0.10 \times 0.10 \times 0.20$                                     | $0.1 \times 0.2 \times 0.7$                                        |
| Crystal system                       | monoclinic                                                          | triclinic                                                            | monoclinic                                                          | triclinic                                                          | monoclinic                                                         |
| Space group                          | $I2/a$                                                              | $P\bar{1}$                                                           | $P2_1/c$                                                            | $P\bar{1}$                                                         | $P2_1/c$                                                           |
| $a$ [Å]                              | 19.015(1)                                                           | 9.413(1)                                                             | 10.0512(8)                                                          | 7.2478(8)                                                          | 16.249(1)                                                          |
| $b$ [Å]                              | 7.5388(5)                                                           | 9.776(1)                                                             | 19.902(2)                                                           | 11.622(1)                                                          | 5.4326(4)                                                          |
| $c$ [Å]                              | 23.557(2)                                                           | 11.435(1)                                                            | 8.3524(7)                                                           | 13.531(2)                                                          | 16.331(1)                                                          |
| $\alpha$ [°]                         | 90                                                                  | 93.178(2)                                                            | 90                                                                  | 89.536(2)                                                          | 90                                                                 |
| $\beta$ [°]                          | 90.446(1)                                                           | 107.399(2)                                                           | 113.114(1)                                                          | 78.233(2)                                                          | 96.031(9)                                                          |
| $\gamma$ [°]                         | 90                                                                  | 93.886(2)                                                            | 90                                                                  | 86.265(2)                                                          | 90                                                                 |
| $V$ [Å <sup>3</sup> ]                | 3376.8(4)                                                           | 998.5(2)                                                             | 1536.6(2)                                                           | 1113.4(2)                                                          | 1433.6(2)                                                          |
| $Z$                                  | 8                                                                   | 2                                                                    | 4                                                                   | 2                                                                  | 4                                                                  |
| $\rho$ (calcd.) [Mg/m <sup>3</sup> ] | 1.232                                                               | 1.208                                                                | 1.241                                                               | 1.313                                                              | 1.344                                                              |
| $\mu$ [mm <sup>-1</sup> ]            | 0.073                                                               | 0.071                                                                | 0.074                                                               | 0.080                                                              | 0.085                                                              |
| $F(000)$                             | 1328                                                                | 384                                                                  | 608                                                                 | 460                                                                | 608                                                                |
| Index range                          | $-24 \leq h \leq 24$<br>$-10 \leq k \leq 8$<br>$-29 \leq l \leq 29$ | $-11 \leq h \leq 11$<br>$-12 \leq k \leq 12$<br>$-14 \leq l \leq 14$ | $-13 \leq h \leq 6$<br>$-24 \leq k \leq 24$<br>$-10 \leq l \leq 10$ | $-9 \leq h \leq 9$<br>$-14 \leq k \leq 15$<br>$-17 \leq l \leq 17$ | $-19 \leq h \leq 19$<br>$-6 \leq k \leq 6$<br>$-19 \leq l \leq 19$ |
| $2\theta$ [°]                        | 57.74                                                               | 57.88                                                                | 58.30                                                               | 58.00                                                              | 51.70                                                              |
| Temp. [K]                            | 188(2)                                                              | 191(2)                                                               | 193(2)                                                              | 193(2)                                                             | 200(2)                                                             |
| Refl. collected                      | 9133                                                                | 5816                                                                 | 9024                                                                | 6528                                                               | 7902                                                               |
| Refl. unique                         | 3221                                                                | 3045                                                                 | 2546                                                                | 3420                                                               | 2740                                                               |
| Refl. observed (4 $\sigma$ )         | 2630                                                                | 2049                                                                 | 2060                                                                | 1593                                                               | 1873                                                               |
| $R$ (int.)                           | 0.0206                                                              | 0.0288                                                               | 0.0252                                                              | 0.0301                                                             | 0.0393                                                             |
| No. of variables                     | 221                                                                 | 256                                                                  | 202                                                                 | 311                                                                | 259                                                                |
| Weighting scheme <sup>[a]</sup>      | 0.6340/1.2204                                                       | 0.1100/0.0000                                                        | 0.0640/0.3750                                                       | 0.0480/0.000                                                       | 0.1496/0.000                                                       |
| $x/y$                                |                                                                     |                                                                      |                                                                     |                                                                    |                                                                    |
| GOOF                                 | 1.032                                                               | 0.980                                                                | 1.026                                                               | 0.843                                                              | 0.684                                                              |
| Final $R$ (4 $\sigma$ )              | 0.0410                                                              | 0.0564                                                               | 0.0420                                                              | 0.0659                                                             | 0.0355                                                             |
| Final $wR2$                          | 0.1021                                                              | 0.1456                                                               | 0.1067                                                              | 0.1751                                                             | 0.0928                                                             |
| Larg. res. peak [e/Å <sup>3</sup> ]  | 0.143                                                               | 0.219                                                                | 0.147                                                               | 0.291                                                              | 0.157                                                              |

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

(weak, Bu<sub>2</sub>BNPh<sub>2</sub>). In a similar experiment, pyridine was added as an auxiliary base to the metallated solution of **2**. A yellow solution resulted. At 0 °C crystals separated, and proved on X-ray crystallography to be LiNPh<sub>2</sub>·2 py (**14**). The supernatant solution showed <sup>11</sup>B NMR signals at δ = −17.6, −16.4, 0.2, 1.9, 3.0, and 43.2. The last signal is most probably due to Bu<sub>2</sub>BNPh<sub>2</sub> (compounds of type Bu<sub>2</sub>B–NR<sub>2</sub> show resonances in the range of δ = 51–45).<sup>[18]</sup>

**Triple Metallation of Trianilinoborane:** Compound **3** (0.97 g, the compound contained chloride!) was dissolved in ether (80 mL) and cooled to −78 °C, and BuLi in hexane (1.56 M, 10.2 mmol, 6.5 mL) was added with stirring. After the solution had attained ambient temperature, a white precipitate appeared. The yellow solution showed an <sup>11</sup>B NMR signal at δ = 35.4 (*h*<sub>1/2</sub> = 640 Hz). Solvent was removed until 30 mL of a solution remained, from which crystals separated within a few hours at 0°. The crystals readily lost coordinated ether in vacuo; if drying was carried out carefully, however, the composition of the crystals was B(NLiPh)<sub>3</sub>·LiCl·3OEt<sub>2</sub> (**15A**). The <sup>11</sup>B NMR spectrum of the solid, dissolved in THF, was the same as that of the solution. The NMR spectroscopic data were consistent with the formation of B(NLiPh)<sub>3</sub>·*n*OEt<sub>2</sub>. NMR in C<sub>6</sub>D<sub>6</sub>: δ<sup>1</sup>H = 0.92 (t, <sup>3</sup>*J*<sub>H,H</sub> = 7.0 Hz, 18 H, Me), 3.14 (q, <sup>3</sup>*J*<sub>H,H</sub> = 6.9 Hz, 12 H, OCH<sub>2</sub>), 6.85 (t, <sup>3</sup>*J*<sub>H,H</sub> = 7.0 Hz, 3 H, *p*-H), 6.96 (d, <sup>3</sup>*J*<sub>H,H</sub> = 7.5 Hz, 6 H, *o*-H), 7.23 (t, <sup>3</sup>*J*<sub>H,H</sub> = 7.0 Hz, 6 H, *m*-H); δ<sup>13</sup>C = 14.6 (Me), 64.9 (OCH<sub>2</sub>), 117.7 (*p*-C), 125.8 (*o*-C), 128.8 (*m*-C), 160.0 (CNLi); δ<sup>11</sup>B = 35.4 (*h*<sub>1/2</sub> = 640 Hz); δ<sup>7</sup>Li = 1.24. C<sub>30</sub>H<sub>45</sub>BCLi<sub>4</sub>N<sub>3</sub>O<sub>3</sub> (569.71): calcd. C 63.19, H 7.90, N 7.37; found C 62.09, H 7.78, N 7.89.

**Triple Metallation of Tris(2-pyridylamino)borane and Formation of **18**:** Compound **4** (0.490 g, 1.69 mmol) was dissolved in THF (40

mL). The solution was cooled to −78 °C, stirred, and allowed to react with a hexane solution of BuLi (1.56 M, 3.3 mL). After the solution had attained ambient temperature, the slightly turbid, yellow solution showed <sup>11</sup>B NMR signals at δ = 1.3 and −9.5. Solvents were evaporated from the clear filtrate in vacuo to leave 30 mL of a solution, which was layered with hexane (20 mL) and kept at −20 °C. Within 1 d colorless crystals had separated. These rapidly became turbid on standing at ambient temperature, and did so more rapidly in vacuo; no elemental analysis was therefore performed. The identity of **18** was ascertained by X-ray structure determination. The same reaction was performed in ether instead of THF. In this case, more solid material separated. The solid, dissolved in THF, showed only a single <sup>11</sup>B NMR signal at δ = 35.0 (*h*<sub>1/2</sub> = 1330) corresponding to **18** was observed. The filtrate gave <sup>11</sup>B resonances at δ = 1.5, 0.6, −24.6, and −28.6.

**Triple Metallation of Tris(8-quinolylamino)borane:** In analogy to the lithiation of compound **4**, compound **5** (0.97 g, 2.2 mmol), dissolved in THF (90 mL), was metallated at −78 °C with BuLi in hexane (1.56 M, 4.2 mL). An intensively violet solution formed. At ambient temperature, one <sup>11</sup>B NMR signal at δ = 32.8 (*h*<sub>1/2</sub> = 1240 Hz) and a single <sup>7</sup>Li signal at δ = 2.46 were found. All attempts to induce crystallization by cooling or dissolving the residue (after removal of THF and hexane) in ether, toluene, ether/pyridine, or pyridine failed, only violet oils being observed. A solution of the oil in [D<sub>8</sub>]THF revealed more <sup>1</sup>H NMR signals than expected.

**Double Metallation of **4** and Formation of Tris(trimethylstannyl-2-pyridylamino)borane (**23**):** A solution of **4** (0.40 g, 1.4 mmol) in THF (80 mL) was metallated at −78 °C with a hexane solution of LiBu (1.77 mL, 2.80 mmol). The solution at ambient temperature

Table 3. Crystallographic parameters, information about data collection, and structure solution of compounds **7**, **13**, **14**, **15A**, **18**, and **23**

|                                            | <b>7</b>                                                                                     | <b>13</b>                                                                     | <b>14</b>                                                         | <b>15A</b>                                                                      | <b>18</b>                                                                      | <b>23</b>                                                         |
|--------------------------------------------|----------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------|-------------------------------------------------------------------|---------------------------------------------------------------------------------|--------------------------------------------------------------------------------|-------------------------------------------------------------------|
| Empirical formula                          | C <sub>48</sub> H <sub>48</sub> B <sub>2</sub> Li <sub>2</sub> N <sub>8</sub> O <sub>2</sub> | C <sub>32</sub> H <sub>40</sub> Li <sub>2</sub> N <sub>2</sub> O <sub>4</sub> | C <sub>44</sub> H <sub>40</sub> Li <sub>2</sub> N <sub>6</sub>    | C <sub>30</sub> H <sub>45</sub> BCLi <sub>4</sub> N <sub>3</sub> O <sub>3</sub> | C <sub>36</sub> H <sub>49</sub> BLi <sub>4</sub> N <sub>8</sub> O <sub>4</sub> | C <sub>24</sub> H <sub>39</sub> BN <sub>6</sub> Sn <sub>3</sub>   |
| Formula mass                               | 804.451                                                                                      | 530.54                                                                        | 666.70                                                            | 569.71                                                                          | 696.40                                                                         | 778.548                                                           |
| Crystal size [mm]                          | 0.50 × 0.50 × 0.65                                                                           | 0.02 × 0.20 × 0.30                                                            | 0.10 × 0.30 × 0.30                                                | 0.10 × 0.20 × 0.20                                                              | 0.3 × 0.3 × 0.4                                                                | 0.05 × 0.08 × 0.20                                                |
| Crystal system                             | triclinic                                                                                    | triclinic                                                                     | monoclinic                                                        | monoclinic                                                                      | triclinic                                                                      | monoclinic                                                        |
| Space group                                | <i>P</i> $\bar{1}$                                                                           | <i>P</i> $\bar{1}$                                                            | <i>P</i> 2 <sub>1</sub> / <i>c</i>                                | <i>C</i> 2/ <i>c</i>                                                            | <i>P</i> $\bar{1}$                                                             | <i>P</i> 2 <sub>1</sub> / <i>n</i>                                |
| <i>a</i> [Å]                               | 13.354(2)                                                                                    | 10.122(4)                                                                     | 20.986(2)                                                         | 13.487(1)                                                                       | 11.9799(9)                                                                     | 12.692(1)                                                         |
| <i>b</i> [Å]                               | 13.719(2)                                                                                    | 10.876(4)                                                                     | 9.259(1)                                                          | 20.448(2)                                                                       | 12.954(1)                                                                      | 15.230(1)                                                         |
| <i>c</i> [Å]                               | 13.812(2)                                                                                    | 14.756(5)                                                                     | 20.893(3)                                                         | 24.929(2)                                                                       | 14.859(1)                                                                      | 15.878(2)                                                         |
| $\alpha$ [°]                               | 88.87(2)                                                                                     | 82.67(1)                                                                      | 90                                                                | 90                                                                              | 80.759(1)                                                                      | 90                                                                |
| $\beta$ [°]                                | 79.41(2)                                                                                     | 74.055(7)                                                                     | 113.670(2)                                                        | 100.162(1)                                                                      | 67.421(1)                                                                      | 93.987(12)                                                        |
| $\gamma$ [°]                               | 60.43(2)                                                                                     | 89.148(8)                                                                     | 90                                                                | 90                                                                              | 66.129(1)                                                                      | 90                                                                |
| <i>V</i> [Å <sup>3</sup> ]                 | 2155.6(5)                                                                                    | 1548.8(9)                                                                     | 3718.3(7)                                                         | 6767.0(9)                                                                       | 1947.0(3)                                                                      | 3061.8(5)                                                         |
| <i>Z</i>                                   | 2                                                                                            | 2                                                                             | 4                                                                 | 8                                                                               | 2                                                                              | 4                                                                 |
| $\rho$ (calcd.) [Mg/m <sup>3</sup> ]       | 1.2394(3)                                                                                    | 1.138                                                                         | 1.191                                                             | 1.118                                                                           | 1.188                                                                          | 1.6890(3)                                                         |
| $\mu$ [mm <sup>−1</sup> ]                  | 0.076                                                                                        | 0.073                                                                         | 0.070                                                             | 0.145                                                                           | 0.077                                                                          | 2.450                                                             |
| <i>F</i> (000)                             | 848                                                                                          | 568                                                                           | 1408                                                              | 2432                                                                            | 740                                                                            | 1520                                                              |
| Index range                                | −17 ≤ <i>h</i> ≤ 17<br>−18 ≤ <i>k</i> ≤ 17<br>−18 ≤ <i>l</i> ≤ 15                            | −12 ≤ <i>h</i> ≤ 7<br>−7 ≤ <i>k</i> ≤ 11<br>−10 ≤ <i>l</i> ≤ 18               | −26 ≤ <i>h</i> ≤ 23<br>−11 ≤ <i>k</i> ≤ 11<br>−26 ≤ <i>l</i> ≤ 25 | −18 ≤ <i>h</i> ≤ 13<br>−26 ≤ <i>k</i> ≤ 26<br>−30 ≤ <i>l</i> ≤ 30               | −14 ≤ <i>h</i> ≤ 14<br>−16 ≤ <i>k</i> ≤ 16<br>−20 ≤ <i>l</i> ≤ 13              | −15 ≤ <i>h</i> ≤ 13<br>−18 ≤ <i>k</i> ≤ 18<br>−19 ≤ <i>l</i> ≤ 19 |
| 2 $\theta$ [°]                             | 56.08                                                                                        | 57.92                                                                         | 58.26                                                             | 58.56                                                                           | 57.34                                                                          | 51.84                                                             |
| Temp. [K]                                  | 200(3)                                                                                       | 193(2)                                                                        | 193(2)                                                            | 193(2)                                                                          | 193                                                                            | 200(3)                                                            |
| Refl. collected                            | 15632                                                                                        | 1792                                                                          | 20944                                                             | 19239                                                                           | 11340                                                                          | 17655                                                             |
| Refl. unique                               | 9511                                                                                         | 1738                                                                          | 6024                                                              | 6222                                                                            | 5919                                                                           | 5898                                                              |
| Refl. observed (4 $\sigma$ )               | 4756                                                                                         | 554                                                                           | 2782                                                              | 3164                                                                            | 4242                                                                           | 3695                                                              |
| <i>R</i> (int.)                            | 0.0712                                                                                       | 0.0087                                                                        | 0.1314                                                            | 0.0692                                                                          | 0.0237                                                                         | 0.0705                                                            |
| No. of variables                           | 554                                                                                          | 361                                                                           | 469                                                               | 405                                                                             | 479                                                                            | 316                                                               |
| Weighting scheme <sup>[a]</sup> <i>x/y</i> | 0.0510/0                                                                                     | 0.0472/0                                                                      | 0.05580/0                                                         | 0.07440/0.8627                                                                  | 0.1022/0.3850                                                                  | 0.01320/0                                                         |
| GOOF                                       | 0.827                                                                                        | 0.769                                                                         | 0.970                                                             | 1.011                                                                           | 1.061                                                                          | 0.785                                                             |
| Final <i>R</i> (4 $\sigma$ )               | 0.0506                                                                                       | 0.0566                                                                        | 0.0711                                                            | 0.0613                                                                          | 0.0559                                                                         | 0.0309                                                            |
| Final <i>wR</i> <sub>2</sub>               | 0.1060                                                                                       | 0.1296                                                                        | 0.1189                                                            | 0.1338                                                                          | 0.1586                                                                         | 0.0498                                                            |
| Larg. res. peak [e/Å <sup>3</sup> ]        |                                                                                              | 0.118                                                                         | 0.206                                                             | 0.287                                                                           | 0.340                                                                          |                                                                   |

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

showed  $^{11}\text{B}$  NMR signals at  $\delta = 1.4, 1.2, -0.9$ , and  $-3.3$ , in addition to a dominant signal at  $\delta = 23.5$ . While stirring, a solution of  $\text{Me}_3\text{SnCl}$  (0.28 g, 1.4 mmol) in THF was added. A  $^{119}\text{Sn}$  NMR spectrum taken after 2 h showed signals at  $\delta = 30.8, 26.2$ , and  $9.2$ , the last signal resulting from **23**. The resonance at  $\delta = 26.2$  most probably corresponds to the monostannylation product **21**. Two signals were observed in the  $^{11}\text{B}$  NMR spectrum, at  $\delta = 30.9$  and  $22.9$ . THF was removed in vacuo. A waxy material was left behind, and was treated with toluene (20 mL). Crystals of **23** separated on cooling of the solution to  $-20^\circ\text{C}$ . Yield: 0.33 g (31%), m.p.  $87^\circ\text{C}$ . NMR in  $\text{C}_6\text{D}_6$ :  $\delta^1\text{H} = 0.39$  (br., 27 H, Me), 6.18 [br., 3 H, C(5)H], 6.24 [m, 3 H, C(3)H], 7.84 [br., 3 H, C(6)H];  $\delta^{13}\text{C} = -0.87$  (Me), 113.3 (C3), 137.3 (C4), 146.5 (C6);  $\delta^{11}\text{B} = 30.9$  ( $h_{1/2} = 370\text{ Hz}$ );  $\delta^{119}\text{Sn} = 9.2$ .  $\text{C}_{24}\text{H}_{39}\text{BN}_6\text{Sn}_3$  (777.88): calcd. C 37.02, H 5.01, N 10.80; found C 37.16, H 5.16, B 10.62.

**X-ray Structure Determinations:** Crystals were covered with perfluoroether oil – those that readily lost coordinated solvent in pre-cooled oil (approximately  $-40^\circ\text{C}$ ). The selected crystal was placed on a glass fiber and mounted on the goniometer head. The reflections on five sets of frames were used for a preliminary determination of the unit cell, by use of the program implemented in SMART.<sup>[51]</sup> Data were collected in the hemisphere mode, and reduced with the SAINT program.<sup>[51]</sup> For absorption correction the SADABS<sup>[51]</sup> program was employed. The structures were solved by direct methods implemented in the SHELX97 program package.<sup>[52]</sup> Non-hydrogen atoms were refined in an isotropic description. Hydrogen atoms were placed in calculated positions and included in the final cycles of refinement by application of a riding model. One disordered ether molecule was found in the structure of compound **15A**, while compound **18** contains one uncoordinated THF molecule for each molecule of **18**. Tables 2 and 3 summarize data relevant to crystallography, data collection and refinement. CCDC-168322 to -168332 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/contents/retrieving.html](http://www.ccdc.cam.ac.uk/contents/retrieving.html) or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

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