The Structural Chemistry of *N*-Monolithium Borazines[‡]

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Dedicated to Prof. Dr. H. Schmidbaur on the occasion of his 70th birthday

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Trimethylborazine ($Me_3B_3N_3H_3$, **1**) reacts with RLi (R = *n*Bu, *t*Bu) in hexane solution by alkyl group exchange to give a mixture of borazines $Me_{3-n}R_nB_3N_3H_3$. In contrast, deprotonation of **1** to $Me_3B_3N_3H_2Li$ (**2**) occurs upon treatment with MeLi in diethyl ether solution or RLi (R = *n*Bu, *t*Bu) complexed with tetramethylethylenediamine (TMEDA), pentamethyldiethylentriamine (PMDTA), or trimethylhexahydrotriazine (TMTA) in hexane solution, to give solvates of **2**. $[(Me_3B_3N_3H_2)Li(OEt_2)]$ (**2a**), $[(Me_3B_3N_3H_2)Li(tmta)]$ (**2c**), and $[(Me_3B_3N_3H_2Li)_4(tmeda)_3]$ (**2b**) contain dimeric units of **2**. In the case of **2b** two of these dimers are bridged by one tmeda molecule, while the other two are coordinated to a lithium atom of one of its dimeric units, respectively. This molecule therefore contains tri- and tetracoordinated Li atoms. In contrast, $[(Me_3B_3N_3H_2)Li(pmdta)]$ (**2c**) is monomeric. The *N*-lithiation leads to a distortion of the planar B_3N_3 ring system: the B–N bonds at the metallated N atoms are short, the next opposite B–N pair is the longest, followed by a shorter B–N bond involving the B atom in the *para* position. However, all B–N bonds are longer than in the parent compound **1**. Reaction of $tBu_3B_3N_3H_3$ (**3**) with *t*BuLi in the presence of triisopropylhexahydrotriazine (TIPTA) in hexane leads to the salt $[(tipta)_2Li][tBu_4B_3N_3H_3]$ (**4**), while deprotonation occurs with *t*BuLi(tmta) to give monomeric $[(tBu_3B_3N_3H_2)Li(tmta)]$ (**5**) after refluxing the reaction mixture. Similarly, $(Me_2N)_3B_3N_3H_3$ (**6**) can be deprotonated with RLi in the presence of TMTA to give monomeric $[\{(Me_2N)_3B_3N_3H_2\}Li(tmta)]$ (**7b**). The *N*-lithiation has almost no influence on the shielding of the boron nucleus of the borazine nuecleus. Attempts to obtain di- and trilithiated **1** as pure compounds failed: alkyl group exchange and borate formation as well as destruction of the borazine ring were detected by NMR spectroscopy. However, treatment of these reaction mixtures with MeBr gave $Me_3B_3N_3NH_{3-n}Me_n$ (n = 0–3).

Introduction

Borazines are isoelectronic with benzene and its derivatives.[2] The term "inorganic benzene" has been coined for borazine ($B_3N_3H_6$) because many of its physical properties are similar to those of benzene. However, it is quite clear that the B–N bond polarity is responsible for the inherent chemical differences between the two compounds. For instance, the structure of $[(\eta^6\text{-}C_6Me_6)Cr(CO)_3]$[3] is different to that of $[(\eta^3\text{-}B_3N_3Et_6)Cr(CO)_3]$:[4] while the former shows a planar benzene ring with its MCO bonds pointing to the middle of the C=C bonds of benzene,[3] the borazine complex possesses a puckered six-membered ring where the MCO bond points towards the nitrogen atoms.[4] More recently, DFT calculations by Jemmis et al. have shown that borazine, in spite of its 6π-electron character, is not an aromatic system but is rather antiaromatic,[5] in spite of the fact that the borazine ring and most of its derivatives are planar and possess equal B–N bond lengths. As expected, $B_3N_3H_6$ exhibits two ^1H NMR signals at δ = 5.4 ppm ($^1J_{^{15}N,^1H}$ = 52 Hz) and δ = 4.65 ppm ($^1J_{^{11}B,^1H}$ = 134 Hz).[6] These protons are deshielded relative to those of benzene.

Due to the polarity of the B–N bond, the NH protons of borazines of type $(RB{=}NH)_3$ are acidic. Therefore, it should be easy to deprotonate the NH groups of these borazines. The first deprotonation reactions of borazines were reported by Wagner and Bradford.[7] The resulting *N*-lithioborazines were used to prepare *N*,*B*-borazinylborazines. These *N*-lithioborazines have a synthetic potential similar to aryllithium compounds[8] but, to the best of our knowledge, *N*-lithioborazines have never been isolated, and no structural information is available on these compounds to date. Here we report on the synthesis, characterization and structure determination of several *N*-lithioborazines of type $(R_3B_3N_3H_2)Li$ (R = Me, *t*Bu, Me_2N).

Results

N-Monolithiation of Borazines $(RBNH)_3$

Reactions in Non-Polar Solvents

2,4,6-Trimethylborazine (**1**)[9] is stable up to 450 °C and against photolysis.[10,11] It dissolves in many polar and non-

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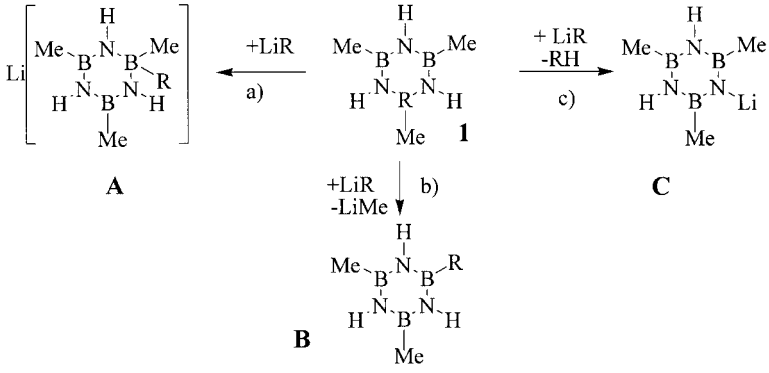


Scheme 1.

polar solvents. Three types of reactions can be expected with RLi compounds: a) addition of RLi across a B–N bond of the borazine derivative, b) exchange of the methyl groups by R of the organometallic compound, c) deprotonation of an NH group (see Scheme 1).

Compounds of type **A** may be precursors for compounds of type **B**, while compound of type **C** are the desired *N*-metallated borazines **2.** In addition, one may also expect ring-opening reactions which may finally lead to *N*-lithioaminoboranes of type R(Me)B–NHLi[12] in the presence of an excess of RLi. Although reactions of 2,4,6-triorganylborazines with *n*BuLi have been described,[8] the formation of *N*-lithioborazines has only been deduced from reaction products obtained with alkyl halides and *B*-haloborazines.[8]

Reaction of **1** with *n*BuLi or *t*BuLi in a 1:1 ration in hexane solution led to products containing tetracoordinate ($\delta_{^{11}B}$ ranging from –2.0 to –4.1 ppm) and tricoordinate boron atoms. Chemical shifts of 38.1 and 36.2 ppm are typical for borazines. A precipitate that formed in these reactions proved to be MeLi (qualitatively checked by gas evolution on hydrolysis). Mass spectrometry of the oily residue obtained from the hexane solutions showed a mixture of all possible *n*-butylmethylborazines $Bu_nMe_{3-n}B_3N_3H_3$ (n = 1, 2, 3). Surprisingly, the 1:1 reaction of *t*BuLi in hexane with **1** also leads to all members of the series $(t\text{Bu})_nMe_{3-n}B_3N_3H_3$ (n = 0, 1,2, 3) with $t\text{BuMe}_2B_3N_3H_3$ the main product ($\delta_{^{11}B}$ = 38.2, 36.0 ppm; ratio 1:2). We were, however, not able to reliably observe B–N cleavage reactions or the *N*-lithiation of **1** in non-polar solvents.

Reactions in the Presence of Auxiliary Bases

It is well known that the reactivity of organolithium compounds is strongly enhanced by polar solvents such as ethers or in non-polar solvents in the presence of donor molecules such as TMEDA because this changes the degree of association of the RLi molecules. Therefore, we studied the reaction of **1** with RLi compounds in diethyl ether solution. In our case both MeLi and *n*BuLi in diethyl ether reacted smoothly with deprotonation of **1** according to Equation (1). The resulting *N*-lithioborazine was isolated as the diethyl ether solvate **2a**. These reactions were quantitative after keeping the reaction mixture under reflux, and yields of up to 85% were obtained.

$$\underset{\mathbf{1}}{2\,Me_3B_3N_3H_3} + 2\,LiR + 2\,OEt_2 \rightarrow \underset{\mathbf{2a}}{Me_3B_3N_3H_2Li{\cdot}OEt_2} + 2\,RH \quad (1)$$

$$4\,Me_3B_3N_3H_3 + 4\,LiBu + 3\,TMEDA \rightarrow \underset{\mathbf{2b}}{(Me_3B_3N_3H_2Li)_4(tmeda)_3} + 4\,BuH \quad (2)$$

$$\underset{\mathbf{2c}}{(Me_3B_3N_3H_2Li)(tmta)} \qquad \underset{\mathbf{2d}}{(Me_3B_3N_3H_2Li)(pmdeta)}$$

$$\underset{\mathbf{3}}{t\text{Bu}_3B_3N_3H_3} + t\text{BuLi} + 2\,TIPTA \rightarrow \underset{\mathbf{4}}{[t\text{Bu}_4B_3N_3H_3]Li(tipta)_2} \quad (3)$$

$$t\text{Bu}_3B_3N_3H_3 + Lit\text{Bu} + TMTA \rightarrow \underset{\mathbf{5}}{t\text{Bu}_3B_3N_3H_2Li(tmta)} + t\text{BuH} \quad (4)$$

N-Lithiation of **1** can also be achieved in hexane upon treatment with *n*BuLi or *t*BuLi in the presence of TMEDA at –78 °C and refluxing the resulting suspension for several days. The precipitate proved to be compound **2b**, as shown in Equation (2). Single crystals of **2b** were obtained from the filtrate. This somewhat unusual stoichiometry is also observed when an excess of TMEDA was employed. When reaction (2) was followed by ^{11}B NMR spectroscopy a signal appeared at δ = 3.6 ppm along with those of the borazine, which indicates that the first step in the reaction is the addition of BuLi to **1** with formation of the borazinate $[(Me_3BuB_3N_3H_3)Li]$ (see Scheme 1). The solvates **2c** and **2d** were obtained from **1** in the presence of trimethylhexahydrotrazine (TMTA) or pentamethyldiethylenetriamine (PMDTA), respectively. All compounds of type **2** are moisture sensitive.

Reaction of $t\text{Bu}_3B_3N_3H_3$ (**3**)[13] with *t*BuLi in hexane at low temperature in the presence of tri(isopropyl)hexahydrotriazine (TIPTA) leads to the salt $[(t\text{Bu}_4B_3N_3H_3)Li(tipta)_2]$ (**4**), as depicted in Equation (3). However, the same reaction in the presence of TMTA yields compound **5** after

keeping the mixture at reflux. Compound **5** was obtained as single crystals from the solution.

In analogy to the reaction of **1** with *n*BuLi in hexane, we observed an Me_2N/nBu exchange with tris(dimethylamino) borazine (**6**),[14,15] which we prepared from the trichloroborazine $Cl_3B_3N_3H_3$ and Me_3SiNMe_2. However, deprotonation of **6** to **7a** occurred with RLi (R = Me, *n*Bu) in the presence of PMDTA, which on crystallization from CH_2Cl_2 gave compound **8**.[16] Single crystals of **7a** were obtained on crystallizing the precipitate from diethyl ether [see Equation (5) with R = Me]. Compounds **7b** and **7c** were obtained in a similar manner.

$$\underset{\mathbf{6}}{(Me_2N)_3B_3N_3H_3} + LiR + PMDTA \rightarrow \underset{\mathbf{7a}}{(Me_2N)_3B_3N_3H_2Li(pmdta)} + RH \quad (5)$$

$\underset{\mathbf{7b}}{(Me_2N)_3B_3N_3H_2Li(tmta)}$ $\underset{\mathbf{7c}}{(Me_2N)_3B_3N_3H_2Li(tmeda)}$

The *N*-lithiation of the triphenylborazine $Ph_3B_3N_3H_3$ is more complicated than those of the three borazines described in this study. We will report on this shortly.

Multilithiation of 2,4,6-Trimethylborazine

In principle it should be possible to deprotonate **1** not only once but also twice or even three times with RLi compounds. The reaction with MeLi (ratio 1:1) in diethyl ether proceeds quantitatively to give $[(Me_3B_3N_3H_2)Li]$, but all our attempts to isolate pure TMEDA, PMDTA or TMTA complexes of $[(Me_3B_3N_3H)Li_2]$ and $[(Me_3B_3N)Li_3]$ failed. In each case the formation of the tetramethylborate anion was detected in solution by ^{11}B NMR spectroscopy. This indicates that the borazine ring was cleaved to a degree of about 5%.

In order to demonstrate that multilithiation has indeed occurred we treated the solid reaction products with MeBr. After refluxing the mixture and removal of insoluble material (impure LiBr) the filtrate was distilled. A fraction with a boiling point of 85–104 °C (350–500 torr) was obtained for the 1:2 reaction and a fraction with a boiling point of 71–120 °C (300–400 torr) for the 1:3 reaction. NMR spectroscopy and particularly mass spectra showed that the product obtained by distillation contained 2,4,6-$Me_3B_3N_3H_3$, 1,2,4,6-$Me_3B_3N_3H_2Me$, 1,2,3,4,6-$Me_3B_3N_3HMe_2$ and $Me_3B_3N_3Me_3$. This reveals that mono-, di- and tri-lithiation has occurred.

Molecular Structures

Relevant structural parameters of the *N*-monolithioborazine solvates **2a** (Figure 1), **2b** (Figure 2), **2c** (Figure 3), **2d** (Figure 4), **5** (Figure 6), and **7a** (Figure 7) as well as the borazinate **4** (Figure 5) are summarized in Table 1 and Table 2.

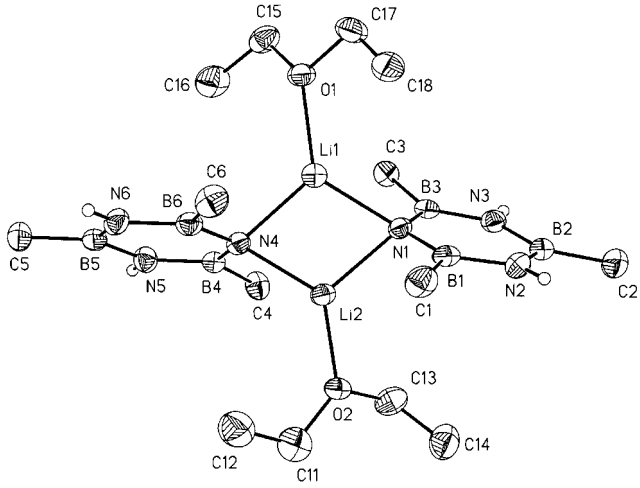


Figure 1. Molecular structure of **2a**. Thermal ellipsoids are shown with 25% probability. Selected atom distances [Å] and bond angles [°] (see also Table 1): Li1–O1 1.985(7), Li2–O2 1.914(7), B1–C1 1.601(6), B2–C2 1.578(6), B3–C3 1.585(6), B4–C4 1.588(5), B5–C5 1.579(6), B6–C6 1.585(6); O1–Li1–N1 128.8(3), O1–Li1–N4 124.3(3), N1–Li1–N4 106.9(3), O2–Li2–N1 121.0(3), O2–Li2–N4 129.4(3)], Li1–N4–Li2 72.4(3), B1–N1–B3 117.4(3), N1–B1–N2 120.2(4), B1–N2–B2 124.2(4), N2–B2–N3 113.4(4), B2–N3–B3 124.2(4), N3–B3–N1 120.4(4), B4–N4–B6 117.9(3), N4–B4–N5 119.0(3), B4–N5–B5 123.8.4(3), N5–B5–N6 114.4(4), B5–N6–B6 124.1(3), N6–B6–N4 119.8(4), N1–B1–C1 122.2(4), C1–B1–N2 117.6(4), C2–B2–N2 123.5(5), C2–B2–N3 123.1(4), C3–B3–N3 117.1(4), C3–B3–N1 125.2(5), Li1–O1–C15 124.9(3), Li1–O1–C17 119.8(3), C15–O1–C17 111.0(4), Li2–O2–C11 129.9(4), Li2–O2–C13 114.2(3), C11–O2–C13 113.4(4). Interplanar angles [°]: Li1N1Li2/B1N1B3 67.7, Li1N1Li2/Li1N4Li2 7.0, Li1N4Li2/B4N4B6 70.6, N4Li1N1/O1C15C17 46.3, C11O2C13/N4Li2N1 55.4. Maximum deviation from the borazine rings: 0.0278 Å for N1 and 0.0183 Å for N4.

All *N*-monolithiated borazines show a significant but systematic distortion of the borazine ring. Most rings remain planar but some of them show slight deviations from planarity. The greatest deviation is found for compound **2d**, where interplanar angles for B1B3N2N3e/-N1B1N3 of 4.5° and B1B3N2N3/N2B2N3 of 2.8° are observed, although these distortions are not highly significant. However, the changes in BN bond lengths for all *N*-monolithioborazines are significant as the BN bonds are no longer equal as found for the borazines **1**[17] and **4**,[18] and, most likely, the BN bonds of $tBu_3B_3N_3H_3$ are also of equal lengths. This change is due to the fact that the N1 ring atom becomes tetra-coordinated due to the dimerization of the $Me_3B_3N_3H_2Li$ units. In general, one can see that the BN bond lengths to the tetracoordinated N atoms are shorter than all other BN ring bonds (see Table 1). In addition, the BN bonds next to the BN bonds at N1, i.e. the pair B1–N2 and B3–N3, are longest while the BN bonds at atom B2 are closer to those of **1** (1.39 Å). However, even these are definitely longer than in the parent borazines, for example **1** with 1.39 Å.[17,18] This bond-length asymmetry also affects, of course, the bond angles, which are 121.0° for N–B–N

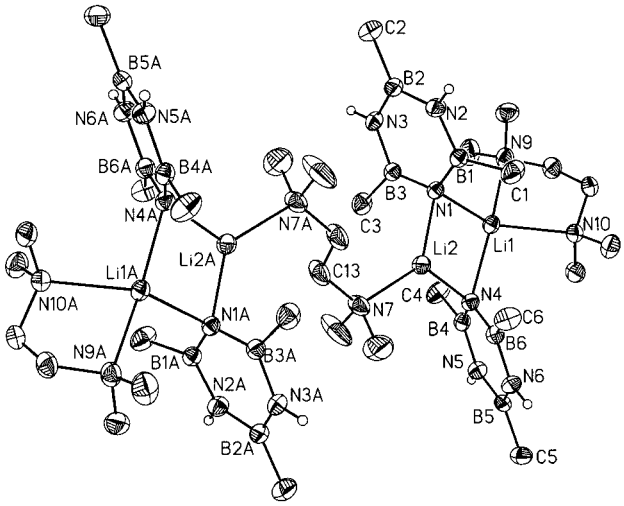


Figure 2. Molecular structure of **2b**. Thermal ellipsoids are shown with 25% probability. Selected atom distances [Å] and bond angles [°] (see also Table 1): Li1–N9 2.366(4), Li1–N10 2.301(4) Li2–N7 2.121(4), Li2–N4 1.990(4), Li2–N1 1.991(5), B1–C1 1.587(4), B2–C2 1.574(4), B3–C3 1.593(4), B4–C4 1.587(4), B5–C5 1.577(4), B6–C6 1.592(4), Li1···Li2 2.487(5); B3–N1–Li2 102.0(2), B3–N1–Li1 118.2(2), Li2–N1–B1 128.7(2), B2–N2–B1 123.5(2), B2–N3–B3 123.3(2), B2–N3B3 123.3(2), N3–B3–N1 120.5(2), N1–Li1–N4 100.5(2), N1–Li1–N9 98.1(2), N1–Li1–N10 146.2(2), N4–Li1–N9 146.8(2), N4–Li1–N10 99.6(2), N4–Li2–C7 140.2(2), N1–Li1–N7 128.5(2).

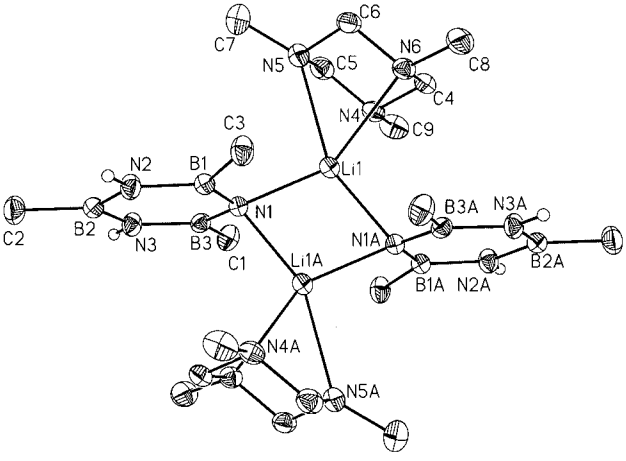


Figure 3. Molecular structure of **2c**. Thermal ellipsoids are shown with 25% probability. Selected atom distances [Å] and bond angles [°] (see also Table 1): Li1–N1 2.049(3), Li1–N1A 2.114(4), Li1–N4 2.199(4), Li1–N5 2.415(4), Li1–N6 2.557(3), Li1···Li1A 2.480(6), B1–C3 1.589(3), B2–C2 1.585(3), B3–C1 1.586(3), C6–N5 1.443(3), N5–C5 1.443(3), C6–N6 1.451(3), N5–C6 1.443(3), N4–C9 1.456(3), N5–C7 1.457(3), N6–C68 1.458(3); N1–Li1–N1A 107.0(1), N1–Li1–N4 128.2(2), N1–Li1–N5 97.5(1), N1–Li1–MN6 147.5(2), Li1–N1–Li1A 73.0(1), Li1–N1–B1 131.5(2), N1–B1–N2 119.8(2), B1–N2–B2 124.1(2), N2–B2–N3 114.8(2), B2–N3–B3 122.7(2), N3–B3–N1 121.1(2), N1–B1–C1 124.2(2), C1–B1–N2 119.8(2), N2–B2–C2 122.5(2), N3–B2–C2 122.8(2), N3–B3–C3 115.3(2), N1–B3–C3 123.6(2), N4–C4–CN5 197.8(2), C4–N5–C5 109.8(2), N5–C5–N6 107.6(2), C5–N6–C4 110.0(2), N6–C6–N4 109.0(2). Interplanar angles [°]: B3–N1–B1/N2–B2–N3 6.0.

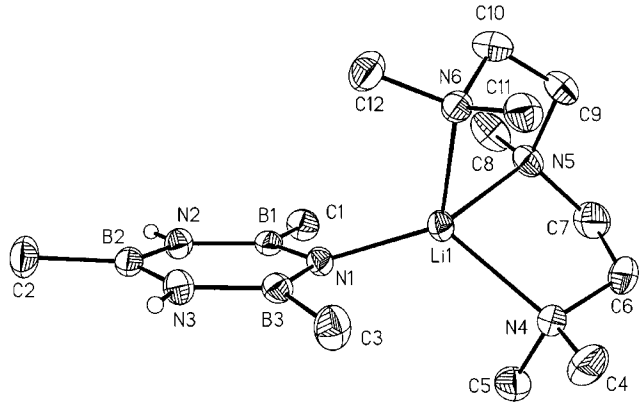


Figure 4. Molecular structure of **2d**. Thermal ellipsoids are depicted with 25% probability. Selected atom distances [Å] and bond angles [°] (see also Table 1): B1–C1 1.602(3), B2–C2 1.589(4), B3–C3 1.589(4), Li1–N1 1.975(4), Li1–N4 2.222(4), Li1–N5 2.203(4), Li1–N6 2.176(4); N1–B1–N2 120.1(2), B1–N2–B2 123.7(2), B2–N3–B3 122.5(2), N3–B3–N1 121.4(2), N1–B1–C1 124.0(2), N2–B1–C1 115.9(2), N3–B2–C2 122.1(2), N2–B2–C2 123.1(2), N3–B3–C3 115.8(2), N1–B3–C3 122.8(2), N1–Li1–N4 123.3(2), N1–Li1–N5 133.0(2), N1–Li1–N6 112.6(2), N4–Li1–N5 82.0(1), N4–Li1–N6 113.4(2), N5–Li1–N6 85.1(1). B2–N1–Li1 157.8. Interplanar angles [°]: Li1N1Li2/B1N1B2N2B3N3 76.7. Max. deviation from borazine plane: –0.0351 Å for N1.

and 119.8° for B–N–B in **1**. For all *N*-monolithioborazines we find a small bond angle at the *para* position B2, centered around 114°, while the B1–N1–B3 bond angles are close to 117°. All other endocyclic bond angles are 120° or up to 4° larger. This distortion leads to a lengthening of the B2–N1 distance across the six-membered ring. Relevant data are given in Table 2. The longest N1···B2 distance is found for the *t*Bu derivative **4** (3.005 Å).

The Li–N1(4) bond lengths are found to cover only a small range, but this bond is particularly short for the monomeric species **2d**, where the N1 atom remains tri-coordinated.

In general, the borazine units in the dimeric species are not orthogonal to the Li_2N_2 rings but neither are they parallel to one another. For instance, the borazine rings in **2a** are twisted against each other by 278.9°, and they form interplanar angles with the Li_2N_2 mean plane of 68.8° and 70.8°, respectively.

Compound **2b** is exceptional insofar as the dimeric *N*-lithioborazine rings contain a tri- and a tetracoordinated Li atom. This is due to the fact that one of the three TMEDA molecules forms a bridge between the two dimeric borazine units, while the other two bind to the remaining Li atoms in a bidentate manner. Consequently, the Li–N bond lengths to these ligands are different, being shorter for the tri-coordinated Li atoms.

Compound **2c** is centrosymmetric. It exhibits longer Li–N bonds both to N1 and the TMTA ligand as the Li atoms are pentacoordinate. Moreover, the TMTA molecule binds asymmetrically to the Li atoms. The borazine ring forms an interplanar angle with the Li_2N_2 plane of 84.8°.

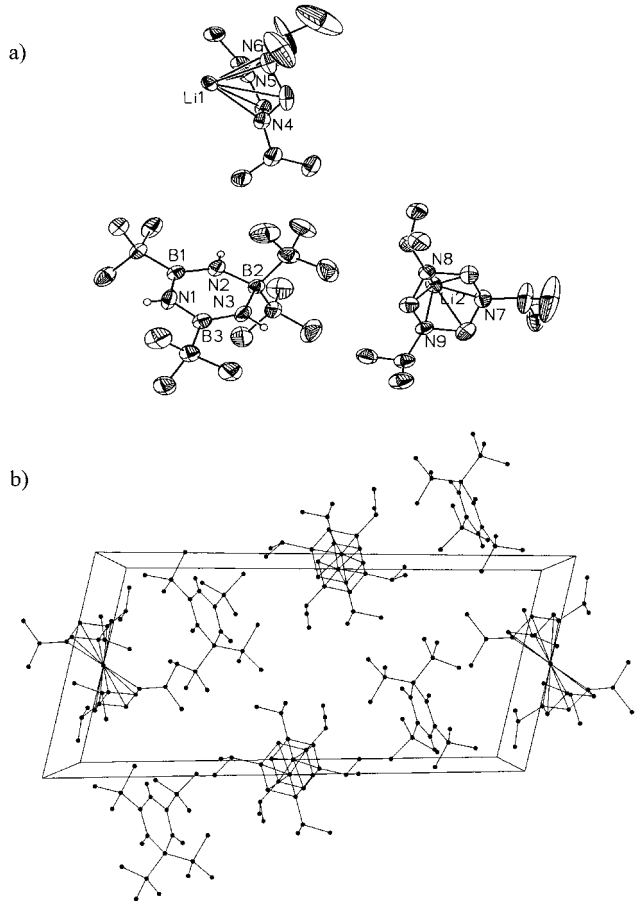


Figure 5. a) The contents of the asymmetric unit and the molecular structure of $[t\mathrm{Bu}_4\mathrm{B}_3\mathrm{N}_3\mathrm{H}_3][\mathrm{Li}(\mathrm{tipta})]$ (**4**). Thermal ellipsoids are shown with 25% probability. Selected atom distances [Å] (see Table 1) and bond angles [°]: N1–B1–N2 115.6(4), B1–N2–B2 129.7(4), N2–N3–B3 128.6(4), N3–B3–N1 116.3(4), N1–B1–C1 119.8(4), N2–B2–C2 107.7(3), N2–B2–C4 109.0(4), N1–B3–C3 119.4(4), C2–B2–C4 117.3(3). b) View of the unit cell down the *a* axis.

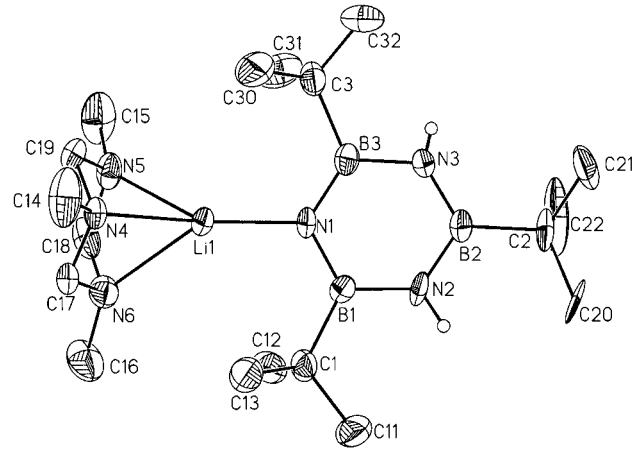


Figure 6. Molecular structure of **5** as found in the asymmetric unit. Thermal ellipsoids are depicted on a 25% probability scale. Selected atom distances [Å] and bond angles [°] (see also Table 1): B1–C1 1.610(7), B2–C3 1.603(8), B3–C3 1.640 (8). Li1–N4 2.224(7), Li1–N5 2.318(8), Li1–N6 2.395(9); N1–B1–N2 118.5(4). B1–N2–B2 124.3(3), B2–N3–B3 124.1(6), N3–B3–N1 120.2(5), N1–Li1–N4 143.1(4), N1–Li1–N5 136.1(4), N1–Li1–N6 143.3(4), N4–Li1–N5 62.4(2), N4–Li1–N6 60.0(2), N5–Li1–N6 61.2(2), N1–B1–C1 124.2(6), N3–B2–C2 124.2(6), N1–B3–C3 123.7(5).

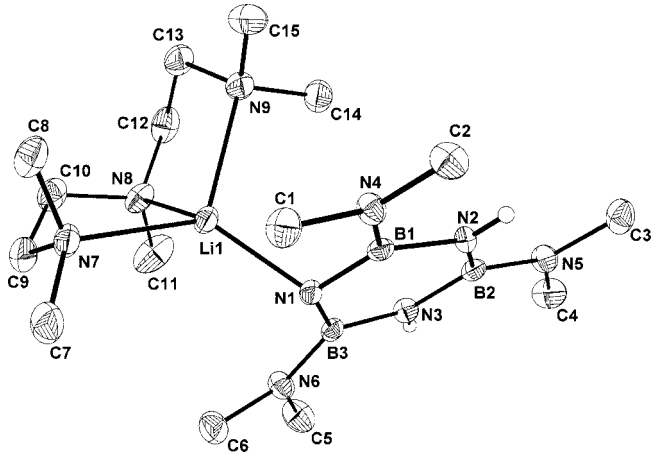


Figure 7. Molecular structure of **7a**. Thermal ellipsoids are depicted on a 25% probability scale. Selected atom distances [Å] and bond angles [°] (see also Table 1): Li1–N1 2.002(4), Li1–N7 2.261(5), Li1–N8 2.217(6), Li1–N9 2.231(6); B1–N1–B3 117.1(3), N1–B1–N2 121.3(2), B1–N2–B2 122.9(3), N2–B2–N3 115.2(3), B2–N3–B3 121.8(3), N3–B3–N1 120.7(3), Li1–N1–B1 112.5(3), Li1–N1–B3 112.5(2), N1–B1–N4 122.2(3), N2–B1–N4 116.7(3), N2–B2–N5 122.2(3), N3–B2–N5 122.4(3), N3–B3–N6 117.3(3), N1–B3–N6 120.0(4), N7–Li1–N8 83.0(2), N7–Li1–N9 113.7(2), N8–Li1–N9 81.2(2). Li1–N1–B2 130.1(3).

In contrast to **2c**, the *t*Bu derivative **5** is a monomer. We attribute this to a steric effect both of the *t*Bu groups and the bulky TIPTA ligand.

The strongest distortion of the borazine ring was observed in **7a**. Atoms B1 and B3 are found below the mean ring-plane. We regard this ring distortion as a consequence of a steric interaction of the Me_2N groups with the PMDTA ligands. The sum of the bond angles at atom N1 in this molecule is 342.5°. This is due to the fact that the Li atom is considerably bent out of the borazine mean-plane as shown by a B2–N1–Li1 angle of 124.4°. It is also worth noting that the exocyclic BN bonds next to atom N1 are longer [1.451 and 1.455(4) Å] than the exocyclic BN bond at atom B2 [1.436(4) Å].

The lithium borazinate **4** differs, of course, in its structure from the *N*-lithioborazines due to the presence of a tetracoordinated boron atom in the ring. The B–N bonds to this boron atom are longer than the other ring BN bonds as the B1–N2 and the N3–B3 bonds are the shortest, but the N2–B2–N3 bond angle is small (105.9°), while the B1–N1–B3 bond angle is wide. Therefore, the charge distribution is strongly influenced whether deprotonation has occurred or carbanion addition.

Table 1. Selected B_3N_3 ring parameters (bond lengths in angstroms and bond angles in degrees).

	2a	2b	2b	2c	2d	4	5	7a
B1–N1	1.417(6)	1.415(3)	1.421(2)	1.414(3)	1.439(7)	1.419(3)	1.422(6)	1.411(4)
B3–N1	1.415(5)	1.415(3)	1.4204(3)	1.420(3)	1.437(7)	1.408(3)	1.411(7)	1.413(4)
B1–N2	1.438(6)	1.448(3)	1.449(3)	1.459(3)	1.396(6)	1.466(3)	1.449(7)	1.465(4)
B3–N3	1.440(6)	1.448(3)	1.446(3)	1.455(3)	1.394(6)	1.460(3)	1.449(8)	1.469(4)
B2–N2	1.425(6)	1.419(3)	1.421(3)	1.414(3)	1.543(6)	1.410(3)	1.426(8)	1.430(4)
B2–N3	1.415(6)	1.414(3)	1.414(3)	1.412(2)	1.560(6)	1.418(2)	1.376(9)	1.430(4)
B1–N1–B3	117.4(3)	117.5(2)	117.0(2)	117.2(2)	124.7(4)	117.1(2)	118.3(4)	117.1(2)
N2–B2–N3	113.4(4)	114.3(2)	115.3(2)	114.8(2)	105.1(4)	114.8(2)	114.9(5)	115.3(3)

Table 2. Atom distances across the borazine rings and selected bond lengths and angles at Li atoms.

	2a	2b	2c	2d	4	5	7a
Li···Li	2.365	2.487	2.480	–	–	–	–
N1–B2	2.952	2.949	2.954	2.955	3.005	2.931	2.957
N4–B5	2.944	2.960					
Li1–N1	2.009	2.121	2.049	1.975	2.049	1.960	2.002
Li1–N4	2.057	2.162					
Li2–N1	2.026	1.991					
Li2–N4	1.970	1.990					
Li1–N1–B2	156.5	140.5	156.2	157.8	–	175.8	130.1
Li2–N1–B2	136.8	144.1					
Li1–N4–B5	131.1	143.9					
Li2–N4–B5	150.0	141.6					
Li1–N1–Li2	73.7	74.3	73.0	–	–	–	–
Li1–N1–Li2	72.4	73.5	73.0				
N1–Li1–N4	106.9	100.5	107.0				
N1–Li2–N4	108.4	111.7	167.0	–	–	–	–

NMR Spectroscopy

Table 3 contains relevant NMR spectroscopic data of the *N*-monolithioborazines. For all compounds of type **2** the proton resonances of the BMe groups are deshielded relative to **1**, with the exception of **2d**. The protons of the *ortho*-BMe groups are usually more deshielded than those at the *para*-BMe group. The exception for **2d** is due to the fact that this compound is monomeric while **2a**–**c** are dimeric. This also has the consequence that the proton resonances for the NH units are more deshielded in **2d** than in the other solvates of type **2**. Moreover, the shielding of the BMe protons at the *ortho* positions is 0.33 to 0.40 ppm larger than at the *para* position. In the case of mononuclear **2d** the reverse situation is true, i.e. the protons of the *ortho*-BMe groups are more deshielded than those in the *para* position. This suggests that the charge distribution in mononuclear *N*-lithioborazines differs from that of dimeric *N*-lithioborazines.

The ^{13}C resonances of the boron-bonded C atoms could only be observed as broad signals for **2b**–**d**, but not for **2a** and **2e.** It is well known that the large quadrupole moment of boron has a great influence on the relaxation time of the ^{13}C resonance, leading to broad signals, and this may also prevent the observation of the expected ^{13}C NMR signal.

It is somewhat surprising that *N*-lithiation has only a marginal effect on the shielding of the boron nuclei, and there is also no drastic effect on the linewidths of these signals. On the other hand, the ^{7}Li resonances depend in a first approximation on the coordination number of the Li

Table 3. NMR spectroscopic data of *N*-lithioborazines in C_6D_6 solution.

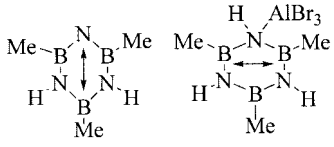
	δ^1H *p*-BMe	δ^1H *o*-BMe	δ^1H NH	$\delta^{13}C$ BMe	$\delta^{11}B$ ($h_{1/2}$; Hz)	$\delta^{7}Li$ ($h_{1/2}$; Hz)
1	0.23		4.37	1.65	36.0	–
2a	0.47 (3 H)	0.59 (6 H)	4.66 (2 H)	n. obs.	35.4 (180)	1.41 (8)
2b	0.46 (3 H)	0.56 (6 H)	4.60 (2H)	2.17	36.2(160)	1.99 (2.35)
2c	0.49 (3 H)	0.63 (6 H)	4.56 (2 H)	1.79	36.2 (190)	2.57 (5)
2d	0.64 (3 H)	0.52 (6 H)	4.79 (2 H)	1.79	36.0 (260)	2.09 (9)
	o-NMe_2	*p*-NMe_2	NH	NMe_2		
6	2.43	2.34	3.07	36.9	26.2 (200)	–
7a	2.98	2.76	3.44	37.0	26.2 (200	1.46 (10)
7b	2.47	2.34	2.95	36.8	26.2 (190)	2.68 (10)
7c	2.44	2.46	2.94	36.4, 36.8	26.1 (170)	1.38 (10)

atoms. Those which are tricoordinate are at lower frequencies, the tetracoordinate ones are found at around δ = 2 to 2.4 ppm and the pentacoordinate Li atom of **2d** is even more strongly deshielded.

The protons of the Me_2N groups in compound **4a** are deshielded with respect to the parent borazine **4**. Those in compounds **7b** and **7c** are less influenced than those of the monomer **7a**. This suggests that compounds **7b** and **7c** are most likely dimeric with Li_2N_2 bridges. The protons of the NH groups of these latter compounds are slightly shielded compared with the parent molecule, while those of **7a** are deshielded. Compounds **7a** and **7c** show ^{7}Li resonances for tetracoordination at Li, and a higher coordination number is suggested by the stronger deshielding of the Li nucleus in compound **7b**. This could be achieved if the Li atom coordinate in a different way with the borazine N-atoms.

Discussion

The reaction of lithium organyls RLi (R = Me, Bu, *t*Bu) with 2,4,6-trimethylborazine in hexane leads to an exchange of the alkyl groups but not to deprotonation of an NH group of the borazine. This has also been observed for 2,4,6-tris(dimethylamino)borazine, where an Me_2N/R exchange occurs in hexane. However, **1** can be deprotonated at the NH groups in the presence of diethyl ether or an auxiliary nitrogen base such as TMEDA, PMDTA or TMTA. These reactions produce complexes of *N*-monolithioborazines. The characteristic features of these compounds are the small endocyclic ring angles at N1 and B2 while those at N2 and N3 span the range 120–124°. Even more pronounced are the long BN bonds between the *ortho* and *meta* positions of the ring (B1–N2 and N3–B3) while those at B2 and at N1 can be considered to be essentially equal. This shows that the negative charge at the atom N1 obviously weakens the B1–N2 and N3–B3 bonds inductively. Thus, we observe a distortion of the borazine rings, as shown in Scheme 2. In contrast, the $AlBr_3$ adduct of **1** shows the opposite effect, i.e. a widening of the endocyclic bond angles at N1 and B2 and a shortening of the B1–N2 and N3–B3 bonds due to electron withdrawal from the ammonium-type N atom by $AlBr_3$.[19] The small ring angles at atom N1 of the *N*-lithio derivatives of **2**, **5** and **7** can be explained by the VSERP theory of bonding, as the lone pairs of electrons at N1 occupy a larger space. Of course, one has to take the highly polar Li–N interactions into account. Although we have studied the *N*-lithiation of borazines by ab initio methods, we will report on theoretical studies at higher levels of theory in due course.[20]



Scheme 2.

It is quite clear that the Li compounds described here can be looked at as formal analogues of aryllithium compounds. For instance. $[LiPh(tmeda)]_2$[21] is structurally akin to compound **2b**, while $[Li(mes)(THF)_2]_2$[22] can be compared with **2a** although the latter has only tricoordinate Li atoms in contrast to the tetracoordinate Li atoms in the mesityl derivative. In this compound the longest C–C bonds are at the carbon atom bonded to Li [C1–C2 = 1.431(2) and C1–C6 = 1.424(2) Å]. Those adjacent to these [C2–C3 = 1.397(2) and C5–C6 = 1.399(2) Å] are shorter, followed by C4–C4 and C4–C5 with 1.393(2) and 1.394(2) Å, respectively. This suggest a different electron distribution in $[Li(mes)(THF)_2]_2$ compared to **2a**. These effects have been addressed H. Bock et al.[23]

However, the bond angles C6–C1–C2 and C3–C4–C5 in $[Li(mes)(THF)_2]_2$ are acute [113.1(1)° and 116.9(1)°] as is also the case for $[LiPh(tmeda)]_2$[24] A similar situation is also observed for tetrameric $[LiPh(OEt_2)]$.[25] There is also a shortening of the C–C bonds on going from the *ipso*-C atom to the *para*-C atom. So, similar to the *N*-lithioborazines described here, a lengthening of the C–C bonds from the *ipso*-C to the *ortho*-C carbon atom seems to be common for aryllithiums, in contrast to the alternating change in the B–N bond lengths in the *N*-lithioborazines.

So far there is no organometallic analogue of $[\{(Me_2NB)_3N_3H_2\}Li(pmdta)]$. We had expected that the Me_2N group may also coordinate to the Li atom, but this is not the case, most likely for two reasons. First, the Me_2N groups form BN π-bonds. This reduces their basicity and, therefore, also their tendency to act as a Lewis base. Secondly, for steric reasons these groups are not able to form chelates as observed in aryllithiums where the phenyl groups carries R_2NCH_2 substituents.[26–28]

The *N*-lithioborazines have proved to be useful reagents for the preparation of a large variety of borazine derivatives which are either not accessible or difficult to prepare by other routes. We will report on these results shortly.

Experimental Section

All experiments were performed by Schlenk techniques employing dry dinitrogen gas or argon as a protective gas. Glassware was heated to 400 °C, filled with dinitrogen gas and allowed to cool. Solvents were dried by conventional methods. NMR: Bruker ACP 200 (^{1}H, ^{7}Li, ^{11}B, ^{13}C), Jeol GSX 270 (^{1}H, ^{7}Li, ^{11}B, ^{29}Si) or Jeol EX 400 (^{1}H, ^{11}B,^{13}C). Standards: C_6D_6, $SiMe_4$, external 1 M aqueous LiCl, $BF_3{\cdot}OEt_2$. IR: Nicolet 520 FT-IR, Nujol hostaflon mulls. Raman: Perkin–Elmer PE 2000, 9324 cm^{-1}, 300 mW. X-ray: Siemens P4 diffractometer equipped with a CCD detector and a LT2 low temperature device. Mo-K_α radiation, graphite monochromator. Commercial chemicals: $BF_3{\cdot}OEt_2$ (BASF), BCl_3 (Elektroschmelzwerk Kempten), Me_3SiCl, $(Me_3Si)_2NH$ (Wacker Chemie), TMEDA, PMDTA, 1,3,5-trimethyl (or isopropyl)hexahydrotriazine (Fluka). Li compounds (Chemetall GmbH).

2,4,6-Trimethylborazine (1):[13] Freshly distilled $(Me_3Si)_2NH$ (250 mL, 1.2 mol, b.p. 134–127 °C) dissolved in CH_2Cl_2 (250 mL) was placed in a one-litre, three-necked flask fitted with a dry ice and an H_2O reflux condenser, a magnetic stirring bar and a pressure equalizer. After cooling to –78 °C $MeBCl_2$ (120.9 g, 1.25 mol) was condensed into the stirred solution within a period of 2 h. During this process a pressure equalizer was placed on top of the dry

ice reflux condenser, and the water-cooled condenser was closed with a stopcock. Some smoke formation was observed at the beginning of the $MeBCl_2$ addition. The solid that formed was later isolated and characterized as NH_4Cl (3–5% based on $MeBCl_2$). The ^{11}B NMR signals found after that time were at δ = 2.8 ppm [$MeBCl_2$·$HN(SiMe_3)_2$], 36 ppm ($Me_3B_3N_3H_3$), 37.6 ppm [$MeClBN(SiMe_3)_2$], 43.3 $(MeBNH)_2$, 48.9 ppm [$MeB(NHBMe)_n$-$NHSiMe_3$] and 63.0 ppm ($MeBCl_2$) in a ratio of 1:12:4:3:2:1). The solution was then heated to reflux (water-cooled condenser) for 4 to 10 d until the ^{11}B NMR spectrum showed only the signal of **1** at δ = 36 ppm. The ^1H NMR spectrum demonstrated the presence of **1** (δ = 0.23 and 4.37 ppm) and Me_3SiCl (δ = 0.63 ppm, $^2J_{^{29}Si,^1H}$ = 7 Hz) with some minor impurities. The insoluble material was removed from the turbid solution by filtration through a G3 glass frit. Solvent and Me_3SiCl were stripped off in vacuo. The residue solidified within a few hours. Crystallization from hexane provided **1** in 95% yield (46.5 g, 379 mmol), m.p. 36 °C. ***Caution:*** *$MeBCl_2$ ignites in contact with air, therefore precautions have to be taken to avoid contact of the rather volatile boron halide with air. $MeBCl_2$ should be stored in a Schlenk tube equipped with a grease-free stopcock and stored at a temperature below –30 °C.* ^1H NMR (400 MHz, C_6D_6): δ = 0.23 (s, 9 H, C*H3*), 4.37 (br. s, 3 H, NH) ppm. ^{13}C NMR (100 MHz): δ = 1.34 ppm (CH_3). ^{11}B NMR (64 MHz): δ = 36.0 ppm.

Reaction of 1 with *n*BuLi in Hexane (1:1): The borazine **1** (1.15 g, 9.3 mmol) was dissolved in hexane (3.5 mL) and the solution cooled to –30 °C. A solution of *n*BuLi (6.1 mL, 1.6 M in hexane, 9.7 mmol) was slowly added while stirring. A white precipitate formed quickly. No gas evolution was noted. After allowing the suspension to attain ambient temperature it was heated to reflux for 2 h. The solid was then removed by filtration (G3 frit, MeLi, Li_2CH_2). All volatile material was removed in an oil-pump vacuum at 20 °C from 5 mL of the reaction solution and the residue dissolved in 1 mL of C_6D_6. This solution showed ^{11}B NMR signals at δ = 38.1 and 36.2 ppm. The residue obtained from the hexane solution exhibited the following prominent signals in the mass spectrum (correct isotopic pattern) at 70 eV: *m*/*z* (%) = 248 (61) (2,4,6-$Bu_3B_3N_3H_3$), 207 (66) (2,4,6-$Bu_2MeB_3N_3H_3$), 165 (31) (2,4,6-$BuMe_2B_3N_3H_3$), 123 (100) ($Me_3B_3N_3H_3$).

Reaction of 1 with *t*BuLi: Compound **1** (0.97 g, 7. 8 mmol) was dissolved in hexane (35 mL) and the solution cooled to –78 °C. While stirring, a solution of *t*BuLi in hexane (5.0 mL, 1.6 M, 8.0 mmol) diluted with hexane (20 mL) was added *slowly*. After addition of a few drops of the *t*BuLi solution a precipitate formed with no gas evolution. After addition was complete the suspension was allowed to attain room temperature and was then kept for 2 h under reflux. The solid was removed by filtration. The ^{11}B NMR spectrum of the filtrate showed that a Me/*t*Bu exchange had taken place ($\delta_{^{11}B}$ = 38.2, 36.0 ppm in a ratio of 1:2). The mass spectrum of the liquid that remained after evaporation of the solvent proved the presence of $tBu_3B_3N_3H_3$ (*m*/*z* = 248, 11%), $tBu_2MeB_3N_3H_3$ (*m*/*z* = 207, 32%), $tBuMe_2B_3N_3H_3$ (*m*/*z* = 165, 59%), and **1** (*m*/*z* = 123, 100%).

1-Lithio-2,4,6-trimethylborazine Diethyl Ether Adduct (2a): Trimethylborazine (**1**; 0.38 g, 3.1 mmol) was dissolved in diethyl ether (30 mL) and the solution cooled to –78 °C. With stirring, 1.95 mL of an *n*BuLi solution in hexane was added dropwise. This resulted in the formation of a white precipitate. After the suspension had attained room temperature it was heated to reflux until a slightly turbid solution had formed. Then, the very small amount of solid was removed by filtration and all volatile materials removed in vacuo. The oily residue, which was insoluble in pentane, solidified on cooling. It was dissolved in a minimum amount of diethyl ether from which single crystals of **2a** separated on cooling. Yield: 0.55 g (85%), m.p. 105 °C (dec.). ^1H NMR (C_6D_6; see also Table 2): δ = 0.98 (CH_2CH_3, 6 H), 3.17 (OCH_2, 4 H) ppm. ^{13}C NMR: δ = 14.7 (CH_2CH_3), 65.7 (OCH_2) ppm. IR (Nujol): $\tilde{\nu}$ = 3447 w, 3419 m, 2959 m, 1600 w, 1471 st, 1443 st, 1414 st, 1332 st, 1319 st, 1285 st, 1204 m, 1197 m, 1163 m, 1111 m, 1097 m, 1023 w, 886 st, 846 m, 785 m, 776 m, 758 st, 715 m, 587 st, 618 m, 392 m, 324 m. Raman: $\tilde{\nu}$ = 3430 w, 2970 st, 2934 vst, 2900 vst, 2844 m, 1459 m, 1440 m, 1071 w, 852 w, 519 st, 455 w, 340 w, 219 w, 120 m. $C_7H_{19}B_3LiON_3$ (202.63): calcd. C 41.49, H 10.44, N 20.73; found C 42.79, H 10.29, N 19.43.

1-Lithio-2,4,6-trimethylborazine Tetramethylethylenediamine (4/3) Adduct (2b): a) A solution of *n*BuLi in hexane (4.5 mL, 1.6 M, 7.2 mmol) was cooled to –78 °C and TMEDA (1.1 mL, 0.85 g, 7.3 mmol) dissolved in hexane (5 mL) was added with stirring. The precipitate that formed dissolved on warming the suspension to room temperature. This solution was placed into a cooled dropping funnel (–50 °C) and added with stirring to a solution of **1** (0.82 g, 6.7 mmol) in hexane (20 mL) kept at –78 °C. A slight gas evolution was noted and the formation of a suspension. This suspension was then kept at reflux for 4 d until no more gas evolution was observed. Solid material was then removed by filtration and dried in a stream of dinitrogen. Colorless crystals of **2b** separated from the filtrate on cooling to –25 °C. After crystallization from hexane the yield was 1.31 g (91%), m.p. 103–105 °C. ^1H NMR (C_6D_6; see also Table 2): δ = 1.95 (12 H, NMe), 1.97 (4 H, NCH_2) ppm. ^{13}C NMR: δ = 46.2 (NCH_3), 57.4 (NCH_2) ppm. IR (Nujol, Hostaflon): $\tilde{\nu}$ = 3447 w, 3430 m, 2993 m, 2957 st, 2885 m, 2877 m, 2825 st, 2775 st, 2726 w, 2704 w, 1475 vst, 1442 vst, 1414 st, 1370 w, 1358 w, 1331 w, 1286 st, 1249 w, 1217 m, 1179 w, 1158 m, 1130 w, 1110 w, 1100 m, 1074 m, 1034 m, 1024 m, 1008 m, 946 m, 880 st, 848 w, 838 w, 791 m, 715 st, 704 st, 684 w, 583 m, 524 m, 505 m, 458 w, 440 w, 346 m, 299 w, 286 w. Raman: $\tilde{\nu}$ = 3428 m, 2996 st, 2967 vst, 2903 vst, 2829 vst, 2778 st, 1474 st, 1448 m, 1435 m, 1409 w, 1312 w, 1290 w, 1220 w, 1159 w, 1073 w, 1026 w, 938 w, 870 w, 847 w, 793 w, 783 w, 521 st, 461 m, 449 m, 366 w, 121 m. $C_{30}H_{92}B_{12}Li_4N_{18}$ (862.70): calcd. C 41.77, H 10.74, N 29.33; found C 41.43, H 10.80, N 28.34.

b) A hexane solution of *n*BuLi (11.0 mL, 1.6 M, 17.6 mmol) was cooled to –30 °C and a hexane solution of TMEDA (10 mL, 4.2 g, 38 mmol) was added while stirring. The yellow solution was transferred into a dropping funnel and added to a stirred solution of **1** (1.98 g, 16.1 mmol) in hexane (40 mL). The resulting suspension was kept at reflux for 1 d. The solid was removed by filtration and dried (0.7 g of **2b**). It dissolved readily in diethyl ether. Crystals of **2b** were obtained from the diethyl ether solution as well as from the hexane solution on crystallization at –25 °C. Total yield: 3.1 g (90%). These crystals showed the same cell dimensions as those obtained by procedure a).

1-Lithio-2,4,6-trimethylborazine 1,3,5-Trimethylhexahydrotriazine Adduct (2c): Prepared in analogy to procedure a) for **2b**. A solution of *n*BuLi/tmta was prepared from *n*BuLi in hexane (4.90 mmol in 13 mL) and a solution of TMTA (0.63 g, 4.90 mmol) in hexane (5 mL). It was cooled to –50 °C and added to a solution of **1** (580 mg, 4.7 mmol) in hexane (30 mL) kept at –78 °C. The resulting mixture was kept at reflux for 2 d. After filtration crystals of dimeric **2c** separated from the filtrate on storing the solution at –5 °C. Yield: 0.43 g (89%); m.p. 116–119 °C. ^1H NMR (C_6D_6; see also Table 2): δ = 2.06 (9 H, NCH_3), 2.98 (br., 6 H, NCH_2) ppm. ^{13}C NMR: δ = 39.8 (NCH_3), 77.2 (NCH_2) ppm. IR (Nujol): $\tilde{\nu}$ = 3444 w, 3420 m, 2980 m, 1592 w, 1472 st, 1448 vst, 1434 vst, 1386

st, 1335 m 1282 st, 1276 vst, 1233 w, 1224 m, 1178 w, 1157 st, 1120 vst, 1099 w, 1087 m, 1070 w, 1049 w, 1016 m, 1004 w, 980 w, 940 st, 915 w, 888 m, 786 w, 770 w, 727 m, 716 m, 692 w, 622 w, 580 m, 558 m, 521 w, 477 m, 459 m, 394 w, 336 w, 270 m. Raman: $\tilde{\nu}$ = 2947 vst, 2903 vst, 2798 m, 2580 w, 2144 w, 1470 m, 1451 m, 931 w, 839 w, 471 w. $C_9H_{26}B_3LiN_6$ (215.70): calcd. C 41.94, H 10.17, N 32.61; found C 41.53, H 9.95, N 32.68.

1-Lithio-2,4,6-trimethylborazine Pentamethyldiethylenetriamine Adduct (2d): A solution of MeLi in diethyl ether (6.6 mmol, 1.6 M, 4.5 mL) was cooled to –78 °C. Then, a solution of PMDTA in hexane (2.52 g, 19.6 mmol, 5 mL) was added while stirring. After the mixture had attained room temperature the clear solution was added to a solution of **1** in hexane (0.58 g, 4.7 mmol, 30 mL) at –78 °C. Gas evolution started immediately by adding the MeLi/PMDTA solution with formation of a white solid. The suspension was then kept at reflux for four days. The resulting turbid solution showed a single ^{11}B NMR signal at δ = 36.0 ppm. From the suspension 1.3 g of a solid was isolated which dissolved readily in diethyl ether. Colorless prisms of **2d** separated from this diethyl ether solution on storing at –25 °C. Yield: 1.24 g (62%); m. p. 161 °C (dec.). ^{1}H NMR (C_6D_6; see also Table 2): δ = 2.12 (12 H, NCH_3), 2.19 (3 H, NCH_3), 2.39 (4 H, NCH_2), 2.50 (4 H, NCH_2) ppm. ^{13}C NMR: δ = 42.9 (NCH$_3$), 45.8 [N(CH$_3$)$_2$], 56.6 (CH$_2$); 58.1 (CH$_2$) ppm. IR (Nujol): $\tilde{\nu}$ = 3442 w, 3423 w, 2987 m, 1473 st, 1459 st, 1431 st, 1365 m, 1356 m, 1312 st, 1303 st, 1291 st, 1278 st, 1251 st, 1236 m, 1178 w, 1164 m, 1152 m, 1130 m, 1110 m, 1099 w, 1088 st, 1064 m, 1036 m, 1021 m, 998 w, 985 m, 944 w, 935 m, 899 m, 889 m, 879 m, 839 w, 790 w, 778 m, 763 st, 748 w, 711 st, 675 w, 604 w, 574 m, 521 w, 504 m, 488 w, 460 2 w, 448 w, 431 w, 404 w. Raman: $\tilde{\nu}$ = 2985 st, 2961 vst, 2923 st, 2895 vst, 2836 vst, 2784 st, 1475 m, 1442 m, 1290 w, 1149 w, 1024 w, 945 w, 792 w, 518 w, 465 w. $C_{12}H_{24}B_3LiN_6$ (301.82): calcd. C 47.75, H 11.35, N 27.85; found C 46.68, H 11.11, N 27.52.

Reaction of 1 with MeLi (1:2): Trimethylborazine (**1**; 642 mg, 5.2 mmol) dissolved in diethyl ether (30 mL) was cooled to –78 °C and treated while stirring with a MeLi solution (10.3 mmol in 6.4 mL of diethyl ether). A precipitate formed, and the supernatant solution showed ^{11}B NMR signals at δ = –19.9 (BMe_4^-) and 37.3 ppm in an intensity ratio of 1:6. The suspension was cooled again to –78 °C and treated with a solution of MeBr (1.14 g, 12 mmol) in diethyl ether (5 mL). This mixture was kept at reflux for 2 d. The ether was then removed by distillation. An oily residue remained which was treated with hexane (50 mL) to give a suspension. From this suspension LiBr (0.9 g, 10.4 mmol) was isolated by filtration. The filtrate was distilled. A liquid fraction was obtained using a 30 cm Vigreux column to give 0.52 g of a fraction with a boiling range of 85–104 °C at 350–500 torr. MS (70 eV): *m*/*z* (%) = 165 (61) ($Me_3B_3N_3Me_3$), 151 (95) ($Me_3B_3N_3HMe_2$), 137 (100) ($Me_3B_3N_3H_2Me$), 123 (75) ($Me_3B_3N_3H_3$), 95 (33) ($Me_2B_2N_2HMe$), 81 (35) ($Me_2B_2N_2H_2$), 66 (41) (MeB_2N_2H), 55 (26) (MeBNMe), 41 (38) (MeBNH).

Reaction of 1 with MeLi (1:3): In analogy with the previous experiment a solution of **1** (1.06 g, 8.6 mmol) in diethyl ether (30 mL) was treated with MeLi (26.1 mmol, 16.3 mL of a 1.6 M diethyl ether solution) at –78 °C. The mixture was kept at reflux for 20 h showing ^{11}B NMR signals at δ = –19.9 and 37.3 ppm in a 1:7 ratio. Treatment of the suspension with MeBr (2.56 g, 27 mmol) and work up after refluxing for 2 d gave an oily fraction with a boiling range of 71–102 °C/300–400 torr. MS (70 eV): *m*/*z* (%) = 165 (65) ($Me_3B_3N_3Me_3$), 151 (100) ($Me_3B_3N_3HMe_2$), 137 (93) ($Me_3B_3N_3H_2Me$), 123 (62) ($Me_3B_3N_3H_3$), 95 (37) ($Me_2B_2N_2HMe$), 81 (26) ($Me_2B_2N_2H_2$), 66 (43) MeB_2N_2 H), 55 (57) (MeBNMe), 41 (14) (MeBNH).

Lithium Bis(1,3,5-triisopropylhexahydrotriazine)tetra(*tert*-butyl)borazinate (4): (tBu)$_3$B$_3$N$_3$H$_3$[13] (**3**; 1.45 g, 5.83 mmol) was dissolved in hexane (30 mL), and the solution cooled to –78 °C. Then, a solution of (iPr$_3$NCH$_2$)$_3$ (2.56 g, 12 mmol) and tBuLi (8.5 mL, 1.45 M, 12.3 mmol) in hexane (25 mL) was added slowly dropwise while stirring. Stirring was continued at ambient temperature for 2 h. The slightly turbid solution was filtered, and the filtrate reduced in volume by 1/3. Storing the solution at –25 °C produced a crop of single crystals (yield 1.5 g, 20%); X-ray structure analysis showed them to be compound **4**.

1-Lithio-2,4,6-tri(*tert*-butyl)borazine-1,3,5-trimethylhexahydrotriazine (5): A solution of tBu$_3$B$_3$N$_3$H$_3$ (1.70 g, 6.83 mmol) was dissolved in diethyl ether (20 mL). A solution prepared from a hexane solution of tBuLi (1.45 M, 4.8 mL, 6.96 mmol) diluted with 20 mL of hexane was then added at –30 °C. The mixture was heated to reflux for 24 h to give a turbid solution. After filtration the filtrate was kept at –25 °C. The crystals that formed within a few days were isolated. Yield: 1.65 g (66.6%). These proved to be compound **5** by X-ray structure analysis.

2,4,6-Tris(dimethylamino)borazine (6):[14] A solution of Me_2NSiMe_3 (11.73 g, 100 mmol) in CH_2Cl_2 (50 mL) was slowly added at –78 °C to a solution of $Cl_3B_3N_3H_3$ (6.1 g, 33 mmol) in dichloromethane (300 mL). After the solution had attained room temperature the ^{11}B NMR spectrum showed a quantitative conversion of the chloroborazine to **6**. All volatile material was removed under an oil pump vacuum and the solid residue crystallized twice from CH_2Cl_2 (80 mL each): Yield: 6.9 g (99%); m.p. 112–115 °C.

Reaction of 2,4,6-Tris(dimethylamino)borazine with *tert*-Butyllithium: The borazine **6** (923 mg, 4.4 mmol) was dissolved in hexane (25 mL) and cooled to –78 °C. Then a solution tBuLi in hexane (4.6 mmol, 16.9 mL) was added. The resulting suspension was kept at reflux for 2 d. 5 mL of the supernatant solution was taken as a probe. The solvent was removed in vacuo and the residue dissolved in C_6D_6 for NMR investigation. ^{1}H NMR (C_6D_6): δ = 0.92 (s, $BCMe_3$), 1.03 (s, $BCMe_3$), 1.08 (s, $BCMe_3$), 2.19 (s, NMe_2), 2.43 (s, NMe_2), 2.47 (s, NMe_2), 3.09 (br., NH), 3.22 (br., NH) ppm. ^{13}C NMR: δ = 30.1 (NMe_2), 32.1 (NMe_2), 36.5 (NMe_2), 36.7 (NMe_2), 36.9 (NMe_2), 37.9 ppm (br., BCMe$_3$). ^{11}B NMR: δ = 25.9, 37.9 ppm (2:1). ^{7}Li NMR: δ = 1.29 ppm.

1-Lithio-2,4,6-tris(dimethylamino)borazine Pentamethyldiethylenetriamine Adduct (7a): Compound **6** (1.25 g, 5.9 mmol) was dissolved in hexane (25 mL) and cooled to –78 °C. While stirring, a solution of nBuLi (3.9 mL, 1.6 M, 6.2 mmol) and PMDTA (4.0 mL, 3.32 g, 19.1 mmol) in hexane (24 mL) was added dropwise. The suspension that formed was kept at reflux for 12 h. The solid was separated by filtration. A small amount of **6** crystallized from the filtrate on reduction of the volume of the solution in vacuo. The solid was treated with diethyl ether (2 × 30 mL). Only about 25% dissolved. Crystals of **7a** separated from the diethyl ether solution on concentration and cooling to –25 °C; m.p. 119–121 °C. ^{1}H NMR (C_6D_6; see also Table 2): δ = 2.12 (s, 12 H, 2 NMe_2), 2.19 (s, 3 H, NMe), 2.31 (s, 4 H, NCH_2), 2.39 (s, 4 H, NCH_2) ppm. ^{13}C NMR: δ = 42.9 (NMe), 45.9 (NMe_2), 56.6 (NCH_2), 58.0 (NCH_2) ppm. IR (Nujol, Hostaflon): $\tilde{\nu}$ = 3481 st, 3463 st, 2957 m, 2969 m, 2862 st, 2821 m, 2801 m, 2773 m, 1520 vst, 1474 st, 1431 vst, 1416 m, 1402 m, 1370 st,1352 m, 1328 w, 1303 m, 1263 m, 1198 w, 1152 w, 1100 st, 1043 m, 1032 st, 978 m, 943 w, 897 w, 860 w, 793 m, 717 w, 701 w, 695 st, 662 w, 586 st, 491 w, 464 w, 408 w, 333 w, 311 w. $C_{15}H_{43}B_3LiN_9$ (388.9): calcd. C 46.32, H 11.14, N 32.41; found C 43.41, H 10.29, N 31.98.

1-Lithio-2,4,6-tris(dimethylamino)borazine Tetramethylethylendiamine Adduct (7b): Prepared in analogy to **5**, from a solution of **6**

(1.22 g, 5.8 mmol) in diethyl ether (25 mL), MeLi (commercial grade containing iodide; 3.8 mL, 1.6 M, 6.1 mmol) and TMEDA (3.0 mL, 20 mmol) diluted with diethyl ether (25 mL). The mixture was stirred for 4 d at room temperature. Half of the diethyl ether was then removed from the solution. Colorless prisms crystallized (105 mg, 2.87 mmol) at –25 °C which proved to be LiI(tmeda)$_2$.[30] After stirring the solution for 4 d and fractional crystallization (by removing solvent) **7b** separated as a microcrystalline powder. Yield: 731 mg (38%). Single crystals formed from the filtrate on standing for several days at –25 °C, m.p. 191–194 °C (dec.). ^{1}H NMR (C_6D_6): δ = 2.09 (s, 12 H, $CNMe_2$), 2.23 (s, 4 H, NCH_2) ppm. ^{13}C NMR: δ = 46.1 ($CNMe_2$), 58.2 (NCH_2) ppm. IR (Nujol, Hostaflon): $\tilde{\nu}$ = 3848 w, 3440 w, 2874 m, 2831 m, 2805 m, 2785 m, 1518 vst, 1492 st, 1431 st, 1415 vst, 1390 vst, 1371 st, 1342 st, 1325 st, 1306 m, 1295 m, 1274 m, 1213 w, 1197 w, 1165 m, 1150 w, 1115, 1099 st, 1063 m, 1055 m, 1044 w, 981 m, 955 st, 871 w, 844 m, 799 m, 727 w, 695 m, 680 w, 636 m, 587 w, 565 w, 520 m, 495 w. $C_{12}H_{36}B_3LiN_8$ (331.85): calcd. C 43.43, H 10.93, N 33.77; found C 41.24, H 10.88, N 32.91.

1-Lithio-2,4,6-tris(dimethylamino)borazine 1,3,5-Trimethylhexahydrotriazine Adduct (7c): A solution of MeLi in diethyl ether (2.8 mL, 4.5 mmol) and 2.8 mL of TMTA (19.8 mmol) was slowly added at –78 °C to a stirred solution of **6** (776 mg, 3.70 mmol) in diethyl ether (25 mL). A precipitate formed and a gas was produced. The suspension was kept for 17 h at reflux. Then the solid (1.05 g) was isolated by filtration. It dissolved completely in diethyl ether (50 mL). After removal of about 1/3 of the solvent the solution was kept at –25 °C where a crystal powder separated. The yield was not determined. Single crystals suitable for X-ray structure determination separated from the filtrate on further standing. ^{1}H NMR (C_6D_6): δ = 2.50 (s, 9 H, CH_2NCH_3), 2.62 (6 H, NCH_2) ppm. ^{13}C NMR: δ = 40.1 (CH_2NCH_3), 77.3 (CH_2N) ppm. IR (Nujol, Hostaflon): $\tilde{\nu}$ = 3480 m, 3405 m, 2970 w, 2926 m, 2865 st, 1520 vst, 1465 st, 1431 vst, 1416 vst, 1494 st, 1367 st, 1363 st, 1314 m, 1302 m, 1275 m, 1263 m, 1247 m, 1196 w, 1157 w, 1100 st, 978 st, 943 w, 915 w, 883 w, 861 w, 825 w, 768 w, 738 w, 716 m, 694 st, 587 br, 491 w, 453 w. $C_{12}H_{35}B_3LiN_9$ (345.85): calcd. C 41.76, H 10.49, N 36.45; found C 39.10, H 10.48, N 36.53.

X-ray Structure Determination: Relevant crystallographic data and information on data collection and structure solution are summarized in Table 4 and Table 5. Single crystals were placed in a poly(fluoro ether) oil (stock point –40 °C) and a suitable specimen selected and mounted on the tip of a glass fiber. An N_2 gas stream was cooled to –80 °C and the crystal, fixed on a goniometer head, was placed in the gas stream. Reflections of 5 sets of 15 frames were used to determine the unit cell with the program SMART.[31] Data collection was performed in the hemisphere mode, and the data reduced by applying the program SAINT.[32] No absorption correction was applied, except for **8**. The structures were solved with either SHELXTL or SHELX 90[33] Non-hydrogen atoms were refined with anisotropic thermal parameters. Most hydrogen atom positions were found from difference Fourier calculation, but in most cases their positions were calculated, and a riding model applied in the refinement with $U_i = 1.2U_{ij}$ of the corresponding C atom. The H position on the N atoms was taken from the difference Fourier map and refined isotropically. Compound **6a** showed

Table 4. Crystallographic data.

	2a	**2b**	**2c**	**2d**
Empirical formula	$C_{14}H_{42}B_6Li_2N_6O_2$	$C_{15}H_{46}B_6Li_2N_9$	$C_9H_{26}B_3LiN_6$	$C_{12}H_{34}B_3LiN_6$
Formula mass	405.28	431.35	257.73	301.82
Crystal size [mm]	0.3×0.3×0.4	0.25×0.3×0.3	0.4×0.5×0.5	0.20×0.32×0.35
Crystal system	triclinic	monoclinic	monoclinic	orthorhombic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P2_12_12_1$
a [Å]	8.719(4)	12.806(4)	8.486(2)	8.945(2)
b [Å]	11.946(7)	10.106(3)	13.140(4)	14.397(4)
c [Å]	14.214(7)	22.238(7)	14.662(5)	15.372(3)
α [°]	82.77(1)	90	90	90
β [°]	73.99(2)	96.01(1)	99.53(1)	90
γ [°]	73.90(2)	90	90	90
V [Å^3]	1365(1)	2862(2)	1612.3(9)	1979.6(8)
Z	2	4	4	4
ρ(calcd.) [Mg m^{-3}]	0.986	1.001	1.062	1.013
μ [mm^{-1}]	0.061	0.059	0.064	0.060
F(000)	440	940	560	664
Index range	$-8 \le h \le 10$	$-14 \le h \le 14$	$-8 \le h \le 8$	$-11 \le h \le 11$
	$-14 \le k \le 14$	$-11 \le k \le 8$	$-14 \le k \le 14$	$-17 \le k \le 17$
	$-16 \le l \le 16$	$-24 \le l \le 24$	$-16 \le l \le 16$	$-17 \le l \le 17$
2θ [°]	49.42	46.50	46.50	57.46
Temperature [K]	183	193(2)	183(3)	193
Reflections collected	6579	11756	6659	11550
Reflections unique	3494	3667	2137	3977
Reflections observed (4σ)	2599	2940	1888	3368
R(int.)	0.0503	0.0334	0.0352	0.0341
No. variables	297	301	186	335
Weighting scheme[a] x/y	0.0942/1.1942	0.0566/1.5741	0.0340/0.7760	0.0929/0.4822
GOOF	1.092	1.078	1.111	1.118
Final R (4σ)	0.0820	0.0587	0.0501	0.0518
Final $wR2$	0.2062	0.1363	0.1111	0.1133
Largest residual peak [e Å^{-3}]	0.284	0.258	0.188	0.144

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

Table 5. Crystallographic data.

	4	**5**	**7a**	**8**[16]
Empirical formula	$C_{40}H_{92}B_3LiN_9$	$C_{18}H_{44}B_3LiN_6$	$C_{15}H_{43}B_3LiN_9$	$C_{24}H_{67}B_3Cl_2Li_2N_{12}$
Formula mass	738.60	383.96	388.95	641.11
Crystal size [mm]	0.20×0.20×0.30	0.40×0.60×0.60	0.1×0.3×0.4	0.2×0.2×0.3
Crystal system	triclinic	orthorhombic	monoclinic	monoclinic
Space group	$P\bar{1}$	$Pna2_1$	$P2_1/c$	$P2_1/n$
a [Å]	10.151(1)	11.724(1)	15.233(5)	9.9919(1)
b [Å]	10.878(1)	13.9201(1)	9.815(3)	26.2337(4)
c [Å]	23.331(2)	15.982(2)	16.370(6)	15.4240(2)
α [°]	103.323(2)	90	90	90
β [°]	97.802(2)	90	97.49(1)	99.533(1)
γ [°]	90.360(2)	90	90	90
V [Å^3]	2481.7(4)	2608.3(5)	2426.6(14)	3987.18(9)
Z	2	4	4	4
ρ(calcd.) [Mg m^{-3}]	0.988	0.978	1.065	1.068
μ [mm^{-1}]	0.058	0.057	0.066	0.194
F(000)	826	848	856	1400
Index range	$-12 \le h \le 12$	$-12 \le h \le 12$	$-18 \le h \le 18$	$-11 \le h \le 11$
	$-13 \le k \le 13$	$-13 \le k \le 14$	$-13 \le k \le 8$	$-29 \le k \le 29$
	$-24 \le l \le 29$	$-16 \le l \le 16$	$-21 \le l \le 20$	$-18 \le l \le 18$
2θ [°]	52.74	43.92	58.48	49.42
Temperature [K]	193	193	193	193
Reflections collected	13987	9287	13427	19014
Reflections unique	7268	3049	4621	6425
Reflections observed (4σ)	3405	2628	2544	5053
R(int.)	0.0862	0.0211	0.0591	0.0352
No. variables	505	305	272	463
Weighting scheme[a] x/y	0.1136/0.1876	0.1522/1.0943	0.0621/0.7677	0.0433/3.4600
GOOF	1.044	1.067	1.058	1.079
Final R (4σ)	0.0847	0.0780	0.0714	0.0581
Final $wR2$	0.2009	0.2154	0.1406	0.1276
Largest residual peak [e Å^{-3}]	0.381	0.342	0.203	0.625

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

a site-disordered pmdta ligand. Free refinement converged at a SOF value close to 0.5. In the final cycles of refinement the SOF was fixed to 0.5. Figure 7 shows only one orientation. Also, the *t*Bu group of compound **4** is site disordered and gave a good fit with SOF = 0.5. Only one orientation is depicted in Figure 6.
CCDC-253312 to -253319 (for **2a**–**d**, **4**, **5**, **7a** and **8**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[16] A solution of PMDTA (3.11 g, 17.9 mmol) in hexane (5 mL) was added at –78 °C to a stirred solution of *n*LiBu (11.2 mL, 1.6 M, 17.9 mmol). At room temperature the clear solution was placed into a dropping funnel cooled to –50 °C. It was then added to a solution of **6** (3.71 g, 1.7 mmol) in hexane (30 mL). A precipitate formed with some gas evolution. After addition the mixture was kept at reflux for 1 d. The solid was isolated by filtration and CH_2Cl_2 (40 mL) was added to achieve crystallization. At –5 °C crystals, mostly single crystals, separated which proved to be **8**. Yield: 8.8 g (76.7%); m. p. 112–115 °C. ^{1}H NMR (C_6D_6): δ = 2.18 (s, 12 H, 2 NMe_2), 2.29 (s, 3 H, NMe), 2.31 (s, 4 H, NCH_2), 2.43 (s, 18 H, $BNMe_2$), 2.48 (s, 4 H, NCH_2), 3.07 (br., 3 H, NH) ppm. ^{13}C NMR: δ = 36.9 ($BNMe_2$), 44.2 (NMe), 46.0 (NMe_2), 55.3 (CH_2), 57.2 ppm (CH_2). ^{11}B NMR: δ = 26.2 ppm ($h_{1/2}$ = 200 Hz). ^{7}Li NMR: δ = 1.95 ppm. $C_{24}H_{67}B_3Cl_2Li_2N_{12}$ (641.10): calcd. C

44.96, H 10.53, Cl 11.06, N 26.22; found C 43.94, H 10.40, Cl 11.21, N 25.96. Crystallographic data are listed in Table 5.
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