The *N*-Lithiation of 2,4,6-Triphenylborazine[‡]

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Dedicated to Prof. Dr. Dr. h. c. mult. Rolf Huisgen on the occasion of his 85th birthday

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The reaction of the borazine $Ph_3B_3N_3H_3$, **1**, with a diethyl ether solution of LiMe/LiI/TMEDA yields $[(Ph_4B_3N_3H_3)Li(tmeda)LiI(tmeda)]$, **2**. However, when halide free LiMe is used in the presence of TMTA, then $(Ph_4B_3N_3H_3)Li(tmta)$, **3**, is formed which shows that a Me/Ph exchange occurs with the formation of LiPh which adds to **1** to form the borazinate **3**. A Bu/Ph exchange is also observed in the reaction of **1** with Li*t*Bu/tmta. The product isolated from THF is compound $[(Ph_4B_3N_3H_2Li–Li(thf)_3]$, **6c**, which results from deprotonation of and LiPh addition to **1**. A straightforward 1:1 LiPh addition reaction is observed on treatment of the borazine $Ph_3B_3N_3Me_3$, **4**, with LiPh in diethyl ether solution to give the borazinate $(Ph_4B_3N_3Me_3)Li(OEt_2)$, **5**. Reaction of **1** with LiPh (ratio 1:1) in diethylether produces $(Ph_4B_3N_3H_2Li)[Ph_3B_3N_3H_2Li(OEt_2)_2]$, **7**, while an excess of LiPh leads to triple deprotonation and LiPh addition to the N atoms of compound $(Ph_3B_3N_3Li_3)$ to give the adduct $[Ph_3B_3N_3Li_3(OEt_2)_3][LiPh(OEt_2)]$, **8**. All new compounds have been characterized by spectroscopic methods and X-ray structure determinations.

Introduction

Borazines of type $R_3B_3N_3H_3$ can be deprotonated at the NH groups by organyllithium compounds. The resulting *N*-lithioborazine derivatives have been used to synthesize new organylborazines by treating them with organyl halides.[2,3] So far, only *N*-monolithio-borazines, $R_3B_3N_3H_2Li$ (R = Me, *t*Bu, NMe_2) have been characterized structurally as complexes with ligands such as diethyl ether (OEt_2), tetrahydrofuran (THF), tetramethyl diethylene diamine (TMEDA) or 1,3,5-trimethyl-1,3,5-hexahydrotriazine (TMTA).[1] Deprotonation proceeds by an addition-elimination process as demonstrated for the reaction of $tBu_3B_3N_3H_3$ with *t*BuLi.[1] Solvates of *N*-lithioborazines $R_3B_3N_3H_2Li$ (R = Me, *t*Bu, Me_2N) are usually present in the solid state in the form of dimers. Monomers are obtained with bulky ligands such as TMTA and/or large substituents (*t*Bu) located at the boron atoms.[1]

In 2,4,6-triphenylborazine, **1**, the phenyl groups are twisted against the borazine plane by about 29°[4] leaving a cleft between the phenyl groups. Due to this geometry, it was expected that **1** might behave differently towards LiR compounds compared with 2,4,6-trimethylborazine. And this is indeed the case as we will show here.

Reaction of $Ph_3B_3N_3H_3$, 1, with MeLi and LiBu

Because of the fact that **1**[5] is much more soluble in diethyl ether or tetrahydrofuran than in hydrocarbons its behaviour towards organyllithium compounds was studied mostly in ether solvents. Scheme 1 gives an overview of the results.

LiMe was first used as a solution in diethyl ether which contained an equivalent amount of LiI. The 1:1 reaction in the presence of TMEDA led to the monodeprotonated triphenylborazine $Ph_3B_3N_3H_2Li(tmeda)$ cocrystallizing with LiI(tmeda) to give the product **2** (see Scheme 1). On the other hand, when halide free LiMe, prepared from Li metal and MeCl in diethyl ether, was activated by TMTA then the isolated compound **3** proved to be the Li complex of the 2,4,4,6-tetraphenylborazinate anion. This demonstrates that a LiMe/LiPh exchange has taken place, and that the generated LiPh has added to **1**. Compound **3** was isolated in 78% yield which fits well with Equations (1) and (2).

An organyl group exchange was also observed when **1** was treated with a solution of LiBu and TMTA in diethyl ether. The tmta complex **6b** could not be characterized, but crystallization of the reaction product from THF gave crystals of **6c** which proved to be a lithium (*N*-lithio-tetraphenylborazinate) isolated as its THF solvate $[(Ph_4B_3N_3H_2Li)Li(thf)_3]$. Its formation is shown in Equations (3) and (4). A different solvate of this lithium *N*-lithio-tetraphenylborazinate could be isolated from a 1:1 reaction of LiPh in

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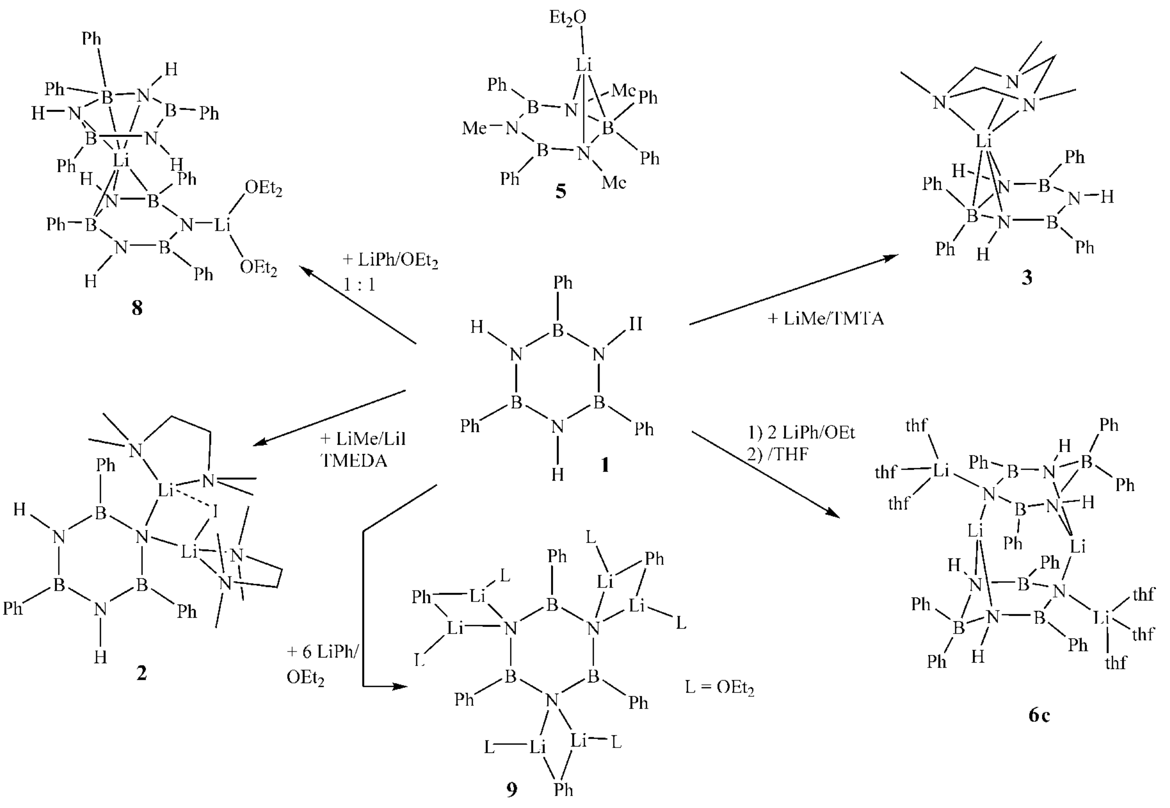


Scheme 1. Reactions of **1** with LiMe/LiI, LiMe and LiPh.

$$Ph_3B_3N_3H_3 + 3\ LiMe + 3\ TMTA \rightarrow Me_3B_3N_3H_3 + 3\ LiPh(tmta) \quad (1)$$

$$3\ \underset{\mathbf{1}}{Ph_3B_3N_3H_3} + 3\ LiPh(tmta) \rightarrow 3\ \underset{\mathbf{3}}{(Ph_4B_3N_3H_3)Li(tmta)} \quad (2)$$

diethyl ether with **1**. It was isolated as its bis(diethyl ether) adduct [$Ph_4B_3N_3H_2Li$]$Li(OEt_2)_2$, **6a**, which on treatment with THF converted to **6c**. These results suggest that **1** adds LiPh preferentially to give a stable tetraphenylborazinate. In order to test this assumption LiPh was allowed to react with $Ph_3B_3N_3Me_3$, **4**, where no deprotonation at the N atoms is expected. Indeed, LiPh adds readily to **4** producing a lithiumborazinate as shown in Equation (5) which was isolated as its mono diethyl ether adduct **5**.

$$5\ Ph_3B_3N_3H_3 + 6\ LiBu(tmta) \rightarrow 2\ Bu_3B_3N_3H_3 + 3\ \underset{\mathbf{6b}}{Ph_4B_3N_3H_2Li_2(tmta)_n} + 3\ PhH + 6 - n\ TMTA \quad (3)$$

$$Ph_4B_3N_3H_2Li_2(tmta)_n + 3\ THF \rightarrow \underset{\mathbf{6c}}{Ph_4B_3N_3H_2Li_2(thf)_3} + n\ TMTA \quad (4)$$

$$\underset{\mathbf{4}}{Ph_3B_3N_3Me_3} + LiPh + OEt_2 \rightarrow \underset{\mathbf{5}}{Ph_4B_3N_3Me_3Li(OEt_2)} \quad (5)$$

It was, therefore, of interest to test how LiPh in diethyl ether solution would react with **1**. As depicted in Scheme 1 and Equations (6) and (7), reactions indeed occur but are always accompanied by the deprotonation of **1**. In the case of the 1:1 reaction [Equation (6)] the isolated crystals proved to be composed of the components $Ph_3B_3N_3H_2Li$ and $Ph_4B_3N_3H_3Li(OEt_2)_2$, **7**, which are linked by Li–N and Li–B bonds as shown by its molecular structure determined by X-ray crystallography (see Figure 2a).

$$2\ Ph_3B_3N_3H_3 + 2\ LiPh + 2\ OEt_2 \rightarrow \underset{\mathbf{7}}{[(Ph_4B_3N_3H_3Li(OEt_2)_2][Ph_3B_3N_3H_2Li]} + 2\ PhH \quad (6)$$

$$Ph_3B_3N_3H_3 + 2\ LiPh + 2\ OEt_2 \rightarrow \underset{\mathbf{6a}}{Ph_4B_3N_3H_2Li_2(OEt_2)_2} + PhH \quad (7)$$

When **1** was allowed to react with LiPh in a 1:2 ratio in diethyl ether, both addition and deprotonation of **1** occurred within a single molecule of **1** to give [$Ph_4B_3N_3H_2Li$]-Li. The compound was isolated as its bis(diethyl ether) solvate, $Ph_4B_3N_3H_2Li_2(OEt_2)_2$, **6a**, which readily looses most of its diethyl ether in vacuo. This compound can be transferred like **6b** into its tris(THF) complex **6c**, but single crystals of good quality were obtained only by its preparation according to Equations (3) and (4). This compound is also formed when the ratio of **1**/LiPh was increased up to 1:4 (as shown by ^1H and ^{11}B NMR spectroscopy). However, when this ratio was increased to 1:6 then a new compound **8** (see Scheme 1) could be isolated. This compound proved to be the triply deprotonated borazine **1**, $Ph_3B_3N_3(Li{\cdot}OEt_2)_3$, stabilized by 3 equiv. of $LiPh(OEt_2)$ [Equation (8)].

$$Ph_3B_3N_3H_3 + 6\ LiPh + 6\ OEt_2 \rightarrow \underset{\textbf{8}}{Ph_3B_3N_3Li_3(OEt_2)_3{\cdot}(LiPh{\cdot}OEt_2)_3} \qquad (8)$$

The conclusion that we can draw is that a detailed study of the behaviour of borazines $R_3B_3N_3H_3$ with active organylmetal compounds offers an interesting new area of research akin to metal aryls.

Molecular Structures

Although single crystals were obtained of the new compounds [with the exception of **6a** and **6b** most of them showed only weak diffracting power even at low temperature (–80 °C)]. The molecular structures of compounds **2** to **8** are depicted in Figures 1–6, and relevant bonding parameters of B_3N_3 rings are presented in Tables 1 and 2. Two types of B_3N_3 rings can be compared: (a) *N*-lithioborazines in compounds **2** and **7**, with **6c** as a special case; and (b) lithioborazinates containing a tetracoordinated boron atom as found in compounds **3**, **5**, **6c** and **7**. For all cases the numbering in the figures starts with N1 (or the analogous atom N4 in combined borazines/borazinates or if two independent molecules are present in the unit cell) carrying one or two Li atoms. Atoms B2 (and/or B5) stand in *para* position to N1 (N4). In the case of the borazinates, B2 (and/or B5) are tetracoordinate B atoms. For centrosymmetric dimers only the asymmetric unit will be discussed in addition to the bonds from the Li atom that bridges the two rings. However, when there are two independent molecules in the unit cell, then the data of only one of them will be described provided that there are no strong deviations in the bonding parameters. This is, for instance, the case for **6c**. A selection of additional parameters is listed in the captions to the figures. While most of the observed Li–N distances were found in the range of 2.0 to 2.3 Å there are also short Li–B distances (2.2–2.4 Å) that we take as Li–B bonds. Li–B distances that are larger than 2.5 Å were considered to be nonbonded distances.

Compound **2** (see Figure 1) is a molecular complex of LiI with the *N*-lithioborazine $Ph_3B_3N_3H_2Li$. Each of the Li atoms is coordinated to one molecule of TMEDA, respectively. The LiN_2 planes of the tmeda ligands at Li1 and Li2 stand almost perpendicular to one another. The four N–Li–N bond angles at atom Li2 range from 84.2(2) to 116.3(2) indicating a distorted tetrahedral array. The Li2–I1 distance is 2.769(5) Å, similar to that found for $LiI(thf)_3$ [2.741(7) Å] [6] or LiI(pmdta) [2.75(3), 2.67(3) Å][7] while compound $[(tmeda)_2Li]I$ has an ionic structure.[8] Atom Li1 of **2** is

Table 1. Bond lengths [Å] and bond angles [°] of compounds **2** and **7** containing a $Ph_3B_3N_3H_2Li$ unit. Values for **7a/7b** refer to the two independent molecules in the unit cell. Numbering scheme for **7b** refers to the equivalent atoms in **7a**.

	N1–B1	B1–N2	N2–B2	B2–N3	N3–B3	B3–N1	N1–Li1
2	1.421(3)	1.449(5)	1.419(4)	1.423(4)	1.445(3)	1.425(3)	1.999(5)
7a*	1.423(5)	1.440(5)	1.419(5)	1.415(5)	1.443(5)	1.435(5)	1.991(7)
7b*	1.432(6)	1.431(5)	1.423(6)	1.419(5)	1.434(5)	1.442(6)	2.000(7)
	B1–N1–B3	N1–B1–N2	B1–N2–B2	N2–B2–N3	B2–N3–B3	N3–B3–N1	Li1–N1–Li2
2	117.4(2)	120.4(2)	122.9(2)	115.4(2)	122.9(9)	120.3(2)	104.9(2)
7a*	117.3 (3)	120.7(3)	122.6(3)	115.4(3)	122.8(3)	120.7(3)	130.2(3)
7b*	117.0(4)	121.5(3)	122.4(4)	115.3(4)	123.6(3)	119.8(4)	126.3(3)

Table 2. Bond lengths [Å] and bond angles [°] of compounds containing a lithium tetraphenylborazinate unit. Values for **5a/5b** and **7a/7b** refer to the independent molecules in the unit cell.

	N1–B1	B1–N2	N2–B2	B2–N3	N3–B3	B3–N1
3	1.444(5)	1.407(5)	1.559(5)	1.574(5)	1.421(5)	1.439(5)
5a*	1.458(3)	1.407(3)	1.566(3)	1.587(4)	1.419(3)	1.442(3)
6c	1.442(4)	1.425(4)	1.555(4)	1.549(4)	1.430(4)	1.434(4)
	N4–B4	B4–N5	N5–B5	B5–N6	N6–B6	B6–N4
5b*	1.455(3)	1.411(3)	1.602(3)	1.599(4)	1.396(3)	1.459(3)
7a**	1.423(5)	1.414(5)	1.560(5)	1.564(5)	1.425(5)	1.433(5)
7b**	1.429(6)	1.410(6)	1.569(5)	1.563(5)	1.411(5)	1.442(5)
	B1–N1–B3	N1–B1–N2	B1–N2–B2	N2–B2–N3	B2–N3–B3	N3–B3–N1
3	121.4(3)	117.1(4)	125.3(3)	104.0(3)	122.5(3)	118.4 (3)
5a*	119.0(2)	118.4(2)	125.9(2)	106.6(2)	125.9(2)	118.1(2)
6c	115.9(2)	121.4(3)	123.8(2)	102.3(2)	124.3(2)	121.8(3)
	B4–N4–B6	N4–B4–N5	B4–N5–B5	N5–B5–N6	B5–N6–B6	N6–B6–N4
5b*	120.2(2)	117.1(2)	124.5(2)	106.9(2)	127.2(2)	118.2(2)
7a**	122.8(4)	116.6(4)	123.6(3)	102.2(3)	124.4(3)	116.8(3)
7b**	122.6(3)	116.9(′3)	124.4(4)	102.2(3)	123.7(3)	116.7(3)

tricoordinate and is located in a planar environment of three N atoms (sum of bond angles = 359.8°). Quite unusual is the very open N1–Li1–N4 bond angle of 166.5(3)°. This arrangement seems to be due to a weak dipolar interaction of Li1 with I1. The Li1···I1 distance is 3.78 Å. A comparatively sharp bond angle is observed for Li1–N1–Li2 with 104.9(2)°.

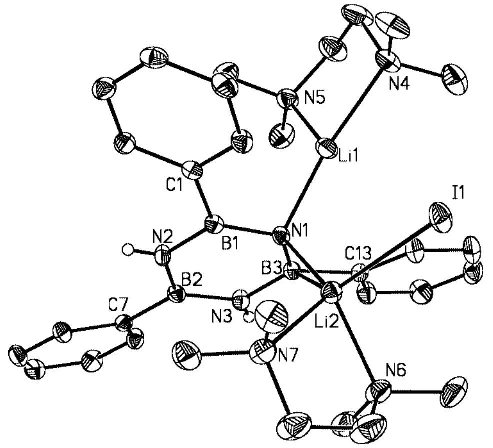


Figure 1. ORTEP plot of the molecular structure of **2**. Thermal ellipsoids are represented at a 25% probability scale. Selected bond lengths [Å] and angles [°]: B1–C1 1.595(4), B3–C13 1.598(4), B2–C7 1.582 (4), Li1–N1 1.999(5), Li1–N4 2.148(5), Li1–N5 2.140(6), Li2–N1 2.094(5), Li2–N6 2.152 (5), Li2–N7 2.223(5), Li2–I1 2.769(5), Li1···Li2 3.245(7). Li1–N1–Li2 104.9(2), B1–N1–Li1 107.3(2), B3–N1–Li1 111.6(2), B1–N1–Li2 109.5(2), B3–N1–Li2 105.3(2), N5–Li1–N4 85.3(2), N1–Li1–N5 108.2(2), N1–Li1–N4 166.5(3), N1–Li2–N6 126.2(2), N1–Li2–N7 116.3(2), N6–Li2–N7 84.2(2), B1–C1–C2 120.9(2), B2–C7–C8 121.7(2), C8–C7–C12 116.4(2), B3–C13–C14 122.6(2), C18–C13–C14 115.9(2). Torsion angles [°]: B2–N2–B1–C1 173.4, B2–N3–B3–C13 171.2, C8–C7–B2–N2 –20.7.

The geometry of the $Ph_3B_3N_3H_2Li$ unit is close to that found for $Me_3B_3N_3H_2Li$.[1] The borazine ring is not planar as shown by an interplanar angle of 7.4° for B1N1B3/B1N2N3B3. Angles B1–N1–B3 and N2–B2–N3 are smaller than 120° with 117.4(2)° and 115.4(2)° while all other endocyclic bond angles are 120° or a few degrees larger (see Table 1). Thus, the borazine unit is elongated along the N1···B2 vector. Typical are the B1–N2 and N3–B3 bonds which are elongated with respect to all the other B–N bonds. The phenyl groups are arranged in a propeller-like fashion and form torsion angles with the borazine ring of 14.7, 18.3, and 19.3° at atoms B3, B1 and B2 respectively, i.e. they are less twisted than in the parent compound **1**.

An *N*-lithioborazine unit is also present in compound **7** which is a borazine borazinate (see Figure 2a). Its two B_3N_3 rings are joined by atom Li2 coordinated to three N and two B atoms of the two rings while the second lithium atom (Li1) is coordinated to the N1 atom and two diethyl ether molecules.[9] The *N*-lithioborazine part (N1 to B3, N1A to B3A) is planar and stands almost parallel to the N4B4N5N6 plane of the borazinate unit (interplanar angle = 5.2°). Quite open are the Li1–N1–Li2 and N1–Li2–N6 bond angles with 126.2(3)° and 136.4(3)°, respectively. As shown in Table 1, the molecular parameters of the borazine ring are similar to those of compound **2**. The bonding, however, is drastically different in the borazinate unit due to the presence of the tetracoordinate B5 atom. This has the consequence that the B_3N_3 ring deviates strongly from planarity and adopts a tub shape with the B5 and N4 atoms pushed outside of the ring plane B4N5N6B6. Interplanar angles are N6B5N5/N6B6N5B4 = 31.3° and B6N4B4/B6N6B4N5 = 6.1°. This distortion of the borazine ring into a tub shape is obviously not only the consequence of the presence of the tetracoordinate B5 atom but also a consequence of the fact that the Li2 atom coordinates to N5 and N6 of the borazinate ring and to N1 of the borazine unit with Li2–N5, Li2–N6 and Li2–N1 distances of 2.157(7), 2.187(7) and 2.250 (6) Å, respectively. The sum of the bond angles at atom Li1 is 353.6° while it is 334.7° for atom Li2 (to atoms N1, N5, and N6) which joins the two B_3N_3 rings. There are two independent molecules in the unit cell. Figure 2b) depicts the core structures of the two independent molecules of **7** which are rather similar. There are no Li–Li bonding interactions.

Compound **3** crystallizes in two isomeric forms as a lithium tetraphenylborazinate (see Figure 3a,b). Its essential bonding parameters are listed in Table 2. As found for the borazinate part in compound **7** the Li atom coordinates with N atoms of the ring adjacent to the tetracoordinate B atom. In this case the atom Li1 is pentacoordinate by five N atoms, e.g. there are three Li–N bonds to the tmta molecule which range from 2.170 to 2.202(6) Å, while those to the borazinate atoms N2 and N3 are 2.222(6) and 2.184(7) Å, respectively. In addition Li1 coordinates also to atom C7. Figure 3b shows the core structure of compound **3** demonstrating that its Li atom is in an interesting coordinative situation as four N atoms and the Li atom form a plane while atoms N5 and C7 lie outside of this plane. This results in a strongly distorted octahedral coordination of the Li1 atom [bond angles: B2–Li1–C13 178.3(4), N3–Li1–N6 174.9(3), C7–Li1–N5 169.8(3), N2–Li1–N4 172.5(3), C7–Li1–N4 107.3(3), C7–Li1–N6 106.6(3)].

The sum of bond angles at atoms B1 and B3 is 360°. Nevertheless, the B_3N_3 ring in **3** is no longer planar and adopts like the corresponding ring in **5** a tub conformation with interplanar angles B2B3N3/N2B2B1N3 of 27.1°, and B1N1N2/N2B2B1N3 of 11.9°. All endocyclic bond angles at the B atoms are smaller than 120° while those at the N atoms are larger. B–N and B–C bonds to the tetracoordinate atom B2 are longer than those to the tricoordinate atoms. A new feature is that the B–N bonds next to the B2–N bonds are shorter than those to atom N1. This distinguishes the borazinates from the *N*-lithioborazines, and this has also been observed for the borazinates **3**, **5**, and **6c**, although the latter is a special case.

The borazinate **5** shows almost the same features as compound **3**. Once again there are two independent molecules in the unit cell which differ by the coordination of the Li atoms. These two molecules are shown in Figure 4a,b. In molecule **5a** the Li1 atom coordinates to the O atom of

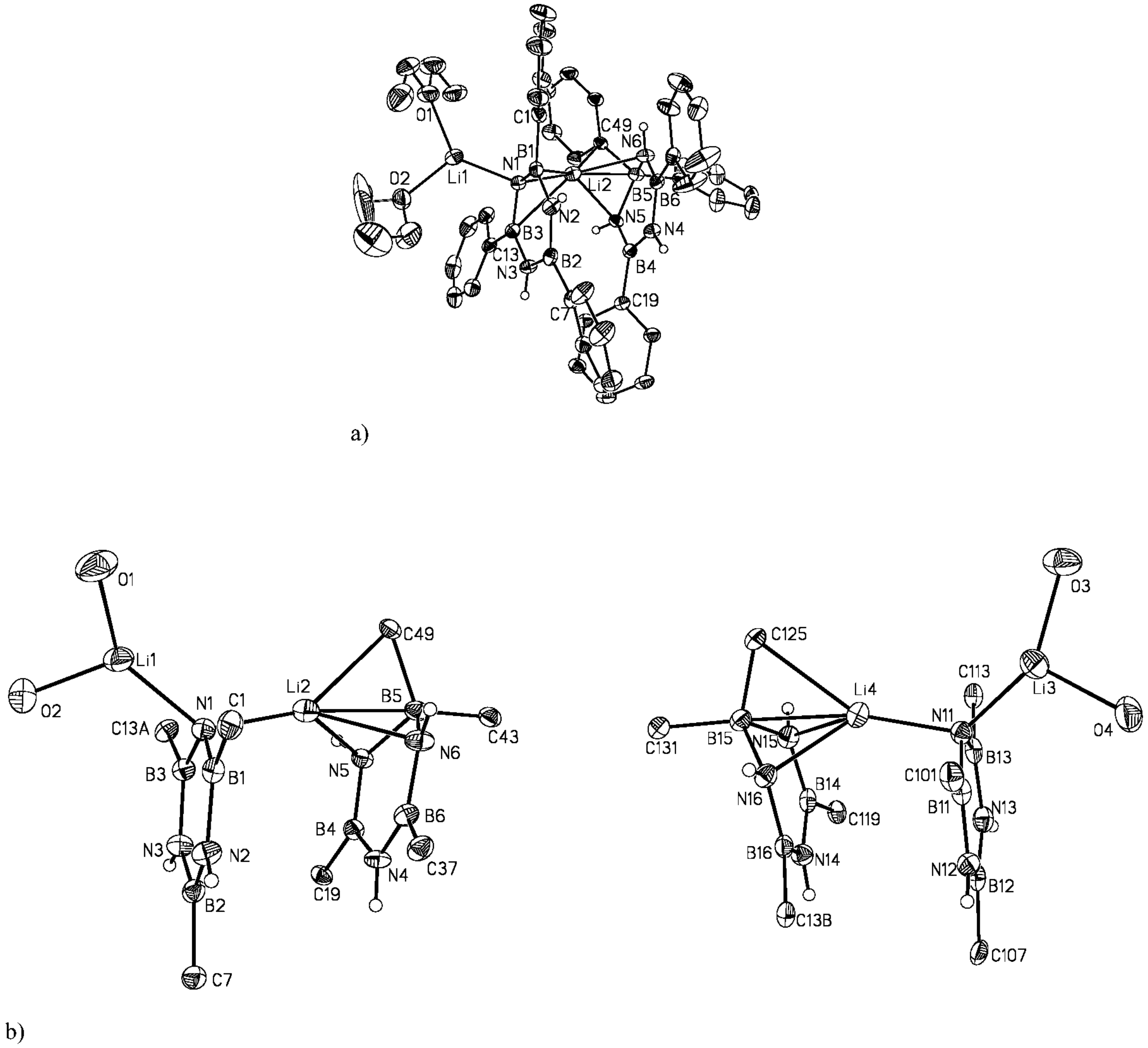


Figure 2. (a) Molecular structure of compound **7**. Thermal ellipsoids are represented at a 25% probability scale. Selected bond lengths [Å] and angles [°]: O1–Li1 1.961(7), O2–Li1 1.968(9), N1–Li1 1.991(8), N1–Li2 2.025(8), N5–Li2 2.178(7), N6–Li2 2.213(8), B5–Li2 2.298(8), C49–Li2 2.416(7), O3–Li3 1.941(9), O4–Li3 1.950(9), N11–Li3 2.000(8), N11–Li4 2.012(7), N15–Li4 2.180(7), Li–N16 2.158(7), B1–C1 1.653(6), B1–C7 1.636(5), B2–C13 1.576(6), B3–C19 1.595(5), B4–C25 1.584(6), B5–C31 1.602(5), B6–C37 1.581(6), B7–C43 1.644(6), B7–C49 1.648(5), B8–C55 1.589(5), B9–C61 1.573(5), B10–C67 1.598(5), B11–C73 1.574(5), B12–C79 1.583(5), B1–C1 1.602(5), B2–C7 1.584(6), B3–C13 1.581(6), N4–C19 1.576(6), B5–C25 1.653(6), B5–C37 1.595(5), B5–C31 1.636(5), B6–C37 1.5895(5). O1–Li1–O2 104.6(4), O1–Li1–N1 111.9(4), O2–Li1–N1 137.1(4), N1–Li2–N5 131.3(4), N5–Li2–N6 67.3(2), N1–Li2–N6 136.1(3), Li1–N1–Li2 126(3), B1–N1–Li1 100.3(3), B1–N1–Li2 95.4(3), B3–N1–Li1 116.5(3), B1–N1–B3 117.0(3). Interplanar angles [°]: B1N2B3N3/B1N1B3 4.5, B1N2B3N3/N2B2N3 5.2, B1N2B3N3/C18C13C14 19.3, B1N2B3N3/C7C8C12 19.9, B1N2B3N3/C C16C 26.3; B4N5N6B6/B4N4B6 33.2, B4N5N6B6/N5B5N6 26,7, B4N5N6B6/C20C19C24 69.5, B4N5N6B6/ C38C37C42 16.7, N5B5N6/C44C43C48 90.5, N5B5N6/ C50C49C54 52.5. Second molecule: B11N12N13B13/B1111B13 2.7, B11N12N13B13/N12B23N13 4.7, B11N12N13B13/C102C101C106 150.2, B11N12N13B13/C108C107C112 14.8, B11N12N13B13/C114C113C118 6.9. (b) The core structure of the two independent molecules of **7**.

the diethyl ether molecule and to two N atoms next to the tetracoordinate B atom of the borazinate ring. In addition there is a weak Li–C interaction. While the Li2 atom of the second isomer shows less symmetry because the Li–N bonds involve not only one N atom next to the tetracoordinate atom B5 but also one to atom N4.

Compound **6c** (see Figure 5) is a special case because it combines both a borazinate and a deprotonated N atom within a single borazine ring. It crystallizes from THF as $Ph_4B_3N_3H_2Li_2(thf)_3$. This molecule is present in the solid state as a dimer where the Li atom of the two borazinate units binds the two rings together each forming three Li–N bonds. Therefore, all ring nitrogen atoms are involved in bonding. Both independent Li atoms (Li1 and Li2) show tetracoordination. The Li atom of the *N*-lithioborazine part is coordinated to the N1 atom of its ring and three O atoms of the THF molecules. Figure 5a shows the dimeric molecule (for clarity two phenyl groups are depicted only by their *ipso*-C atoms) while Figure 5b depicts the disorder of two of the three THF molecules.

In all compounds with a borazinate unit there are Li···B interactions. In **5** the shortest Li–B contact is Li1–B2 with

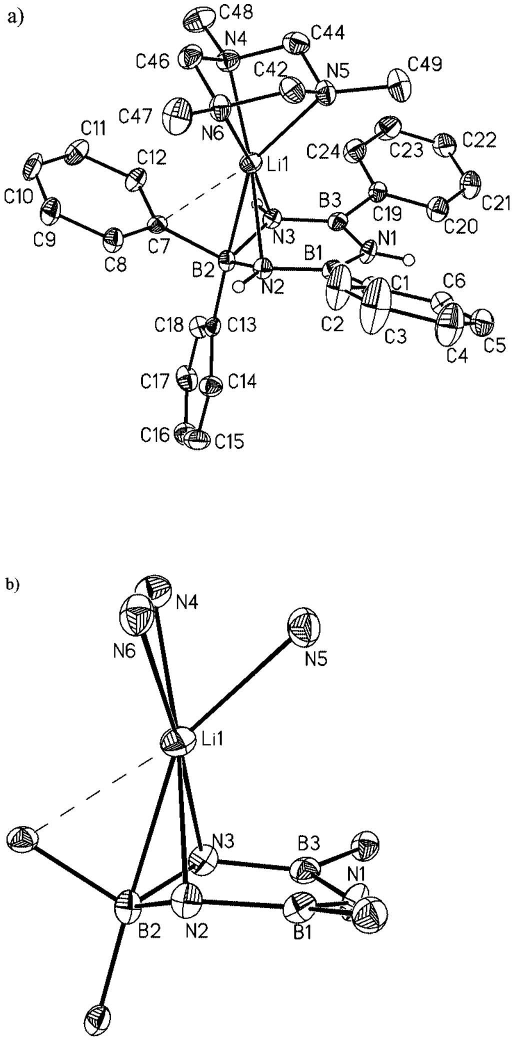


Figure 3. (a) ORTEP plot of the molecular structure of **3**. Thermal ellipsoids are represented at a 25% probability scale. Selected bond lengths [Å] and angles [°]: Li1–N2 2.186(7), Li1–N3 2.235(7), Li1–N4 2.165(7), Li1–N5 2.188(7), Li1–N6 2.196(7), Li1–C7 2.453(7), B1–C1 1.580(5), B2–C7 1.650(5), B2–C13 1.630(6), B3–C19 1.585(6). N2–Li1–N4 172.5(3), N2–Li1–N5 118.3(3), N2–Li1–N6 109.5(3), N3–Li1–N4 117.1(3), N3–Li1–N4 117.0(3), N3–Li1–N5 120.6(3), N3–Li1–N6 174.9(4), N4–Li1–N5 65.1(2), N4–Li1–N6 65.1(2), N5–Li1–N6 64.5(2), N1–B1–C13 119.8(3), N2–B1–C1 122.9(3), N2–B2–C7 109.6(3), N2–B2–C13 112.0(3), C7–B2–C13 107.2(3), N3–B3–C19 121.8(3), B1–N2–Li1 98.1(3), B2–N3–Li1 72.5(2), B2–N2–Li1 74.2(3), B3–N3–Li1 99.6(3). Torsion angles [°]: N1–B1–N2–B2 11.2, B1–N2–B2–N3 –32.4, N2–B2–N3–B3 35.2, B2–N3–B3–N1 –17.7, N3–B3–N1–B1 –10.6, B3–N1–B1–N2 13.8. Interplanar angles [°]: B1N2B3N3/B1N1B3 10.9, B1N2B3N3/N2B2N3 27.4, B1N2B3N3/C6C1C2 22.1, B1N2B3N3/C8C7C12 68.8, B1N2B3N3/C14C13C18 77.1, B1N2B3N3/C20C19C24 23.6. (b) Core structure of compound **3** showing the geometry around the Li1 atom.

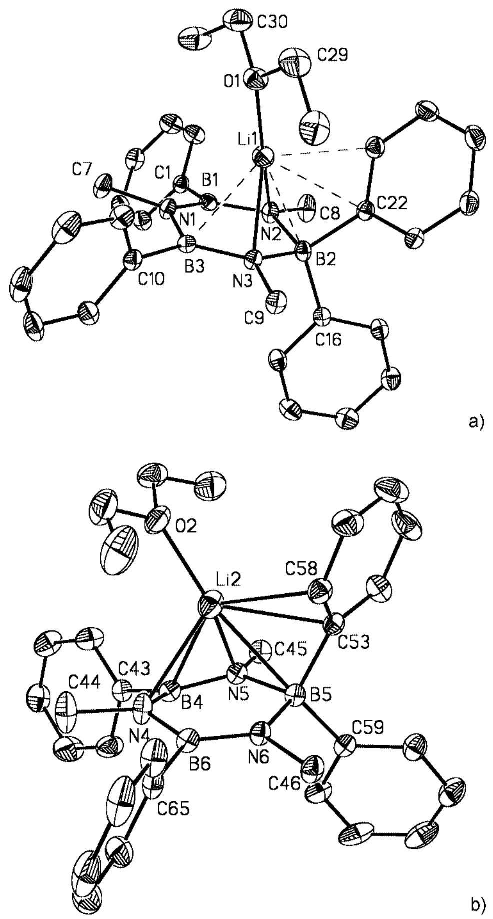


Figure 4. (a) ORTEP plot of one of the two isomeric molecules of compound **5a**. Thermal ellipsoids are represented at a 25% probability scale. Selected bond lengths [Å] and angles [°]: Li1–O1 1.928(4), Li1–N1 2.167(5), Li1–N2 2.349(4), Li1–N3 2.518(5), Li1–B2 2.652(5), Li1–B3 2.420(5), Li1–C4 2.454(5), Li1–O1 1.928(5), B1–C1 1.587(4), B2–C16 1.632(4), B2–C22 1.665(3), B3–C10 1.584(3). O1–Li1–N1 120.5(2), O1–Li1–N2 157.4(3), O1–Li1–N3 134.2(3), N1–Li1–N2 60.6(1), N1–Li1–N3 62.8(1), N2–Li1–N3 67.9(1). Interplanar angles [°]: B1N2N3B3/B1N1B3 14.0, B1N2N3B3/N2B2N3 10.8. B1N23N3B3/C1C2C6 120.0, B1N2N3B3/C10C11C15 107.4, B1N23N3B3/C16C17C21 91.5, B1N2N3B3/C22C23C27 117.4. (b) The structure of the second isomer of compound **5b**. Selected bond lengths [Å] and angles [°]: Li2–N4 2.143(6), Li2–N5 2.426(3), Li2–B4 2.485(6), Li2–B5 2.400(5), Li2–C53 2.414(6), Li2–C58 2.399(6), B4–C43 1.587(4), B5–C53 1.662(4), B5–C59 1.628(4), B6–C65 1.569(4). O2–Li2–N4 114.6(2), O2–Li2–N5 136.5(3), N4–Li2–N5 64.4(2), N4–B4–Li2 73.4(2), N5–B4–Li2 62.2(2), B4–N4–Li2 71.5(2), B4–N5–Li2 82.2(2). Interplanar angles [°]: B4N4N6B6/B4N4B6 10.7, B4N5N6B6/N5B5N6 2.8.

2.314(8) Å, in **6c** the Li–B distances are 2.342(8) Å for Li1–B2, 2.213(3) for Li1–B3, 2.400(5) for Li2–B4, and 2.485(6) Å for Li2–B5, while the distance Li2–B3a is 2.701(6) Å. Moreover, in compound **3** the shortest Li–B distances are Li2–B5 with 2.298(8) and Li4–B15 2.277(8) Å; all other Li–B distances are larger ranging from 2.583 to 2.694(4) Å. Taking these distances into account there are obviously η-(BN)Li interactions in these compounds similar to the Li–C interactions of aryllithium compounds.[10] However, in contrast to (Et$_3$B$_3$N$_3$Me$_3$)Cr(CO)$_6$[11] with its puckered borazine ring, the B_3N_3 rings deviate either only slightly from planarity or adopt a tub or a twist conformation for borazinates. Thus, the *N*-lithioborazines and borazinates are structurally quite different compared to aryllithium compounds.

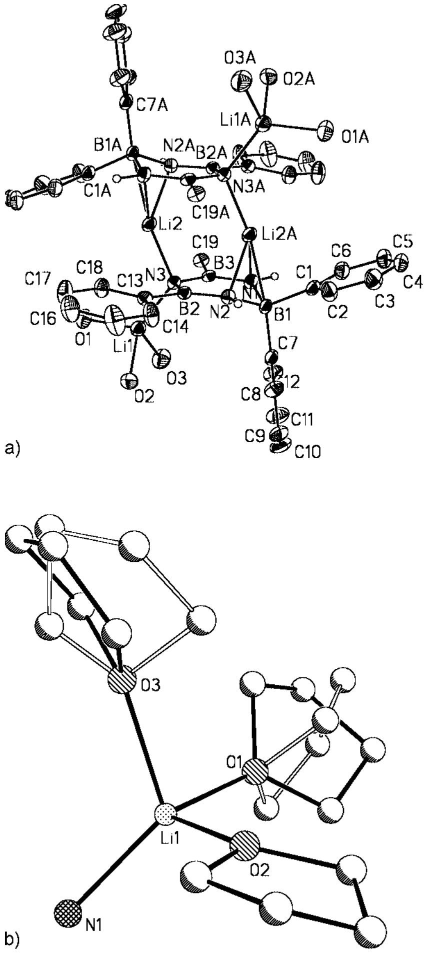


Figure 5. (a) Molecular structure of compound **6c**. Thermal ellipsoids are depicted on a 25% probability scale. Only the *ipso*-C atoms of the phenyl groups are shown for clarity. Selected bond lengths [Å] and angles [°]: Li1–O1 1.977(6), Li1–O2 2.024(6), Li1–O3 2.084(6), Li1–N1 2.073(6), Li2–N1 2.003(6), Li2–N2A 2.137(6), Li2–N3A 2.169(6), Li2···Li2A 3.29(1), Li2A–B1 2.641(6), Li2–B1A 2.311(6), B1–C1 1.601(4), B2–C7 1.635(5), B2–C13 1.652(5), B3–C19 1.603(4). O1–Li1–O2 103.9(3), O1–Li1–O3 95.9(2), O2–Li1–O3 95.3(3), N1–Li1–O1 124.1(3), N1–Li1–O2 113.1(3), N1–Li1–O3 119.7(3), N1–Li2–N2A 132.5(3), N1–Li2–N3A 135.0(3), N2A–Li2–N3A 68.3(2), Li1–N1–Li2 118.3(2), B1–N1–Li1 111.2(2), B3–N 1–Li1 107.0(2), B1–N1–Li2 101.5(2), B3–N1–Li2 103.0(2). Interplanar angles [°]: B1N1N3B3/B1N1B3 2.6, B1N1N3B3/N2B2N3 27.8, B1N1N3B3/C19C20C24 12.9, B1N1N3B3/C2C1C6 7.6, N2B2N3/C14C13C18 50.5, N2B2N3/C8C7C12 125, C13C14C18/C8C7C12 75.5. (b) Plot of the disordered THF molecules in compound **6c**.

Finally, Figure 6 represents the molecular structure of compound **8**. Several crystals were subjected to data collection, but all of them diffracted very weakly even when fairly large crystals were used. Therefore, we will not discuss any bonding parameters, but use the result of the "best" crystal structure solution (R_1 = 16.2%) to show its rather unusual structure which can be looked at as a triply *N*-lithiated 2,4,6-triphenylborazine stabilized by three molecules of phenyllithium. Each Li atom binds to one diethyl ether molecule.

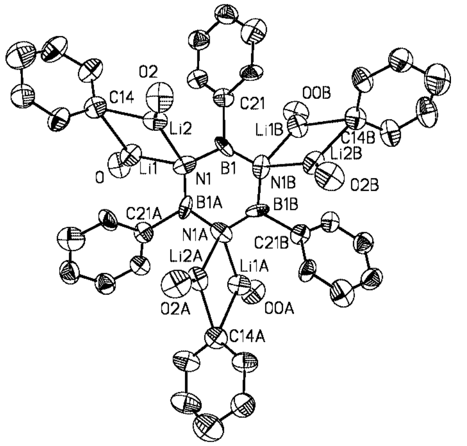


Figure 6. ORTEP plot of the molecular structure of compound **8**. Thermal ellipsoids represent a 25% probability. Selected bond lengths [Å] and angles [°]: Li1–O1 1.96(2), Li1–N1 2.03(2), Li1–C14 2.15(2), Li1···Li2 2.35(2), Li2–O2 1.92(2), Li2–N1 2.02(9), Li2–C14 2.22(2), Li2···B1 2.71(2), B1–N1 1.43(1), B1–N1B 1.46(1), B1–C14 1.63(2), B1···Li1B 2.60(2), N1–B1A 1.46(1). O1–Li1–N1 132(1), O1–Li1–C14 110.8(9), N1–Li1–C14 113.4(9), O2–Li2–N1 127.4(9), O2–Li2–C14 117(1), N1–Li2–C14 110.7(8), N1–B1–N1B 126(1), N1B–B1–C21 117.(1), B1–N1–B1A 114(1), B1–N1–Li2 103(1), B1–N1–Li1 137.0(8), Li1–N1–Li2 71.0(7), B1A–N1–Li2 136.5(9), B1A–N1–Li1 95.2(9), Li1–C14–Li2 64.9(7). Interplanar angles [°]: B_3N_3/C1C2C6 39.9, B3N3/N1Li1Li2 53.8, N1Li1Li2/C14C15C19 90.0, C7Li1Li2/C14C15C19 90.0.

NMR and IR Spectra

^{11}B NMR spectroscopic data allow a clear distinction between *N*-lithioborazines and lithium borazinates (see Tables 3 and 4). For the former, the ^{11}B resonance is practically the same as for **1** with somewhat broader line widths. For **2** a slightly better shielded ^{11}B nucleus is observed although two kinds of tricoordinate B atoms might have been detected. This suggests that either this molecule is fluxional in solution or that the shift difference between the boron atoms B1 and B3 that are adjacent to the deprotonated nitrogen atom N1 and to the boron atom B2 is marginal. We prefer this latter alternative as two kinds of phenyl groups are observed both in the ^{13}C and ^{1}H NMR spectra. The borazinates, however, show two ^{11}B NMR signals in a 1:2 ratio for the tetracoordinate B2 atoms and the tricoordinate B1 and B3 atoms. The latter are in general slightly better shielded – by about 1 ppm – than those of the parent compound **1**. As expected, the ^{11}B NMR signal of the tetracoordinate B2 atoms are observed at lower frequencies with δ^{11}B at about –5 ppm. They also show much sharper signals compared to the tricoordinate B atoms (Table 3 and Table 4).

The ^{7}Li resonances indicate that the structures found for the solid state are retained in solution as compounds **2**, **6**, and **7** show two different ^{7}Li NMR signals. We assign the signals in the higher field (in the range of 0.9 to –0.39 ppm) to the "terminal" Li atoms while those in the range from 1.58 to 2.4 ppm are assigned to those of the borazinates where the Li atom binds to the borazinate nitrogen atoms.

There are two sets of signals for the C atoms of the phenyl groups bound to B1/B3 and B2 atoms in compounds

Table 3. Chemical shifts for ^{1}H, ^{7}Li, and ^{11}B NMR of compounds **1**–**7** (in C_6D_6; ppm) and line widths in brackets [Hz].

	δ^{1}H(NH)	B–Ph			δ^{11}B	δ^{7}Li
		ortho	*meta*	*para*		
1	5.89	7.53	7.28	7.29	34.8	
2	5.70	7.74 (B-2)	7.26 (B-2)	7.34 (B-2)	34.1	2.4 [50]
		7.91 (B-1,3)	7.31 (B-1,3)	7.38 (B-1,3)	350	
3	4.77 (N-2,3-H)	7.95 (B-2)	6.80 (B-2)	7.58 (B-2′)	–5.2 [150]	2.1 [40]
	5.81 (N-1-H)	8.03 (B-2)	6.95 (B-2′)	7.65 (B-2)	33.1 [400]	
		8.11 (B-1,3)	7.15 (B-1,3)	7.86 (B-1,3)		
4	2.72 (NMe)		7.2–7.9			
5	2.49 (N-2,3-Me)	7.35 (B-1,3)	7.13 (B-1,3′)	7,25 (B-2′)	1.9 [130]	2.1 [40]
	2.71 (N-1-Me)	7.59 (B-2,2)	7.17 (B-2)	7.26 (B-2)		
			7.19 (B-2)	7.30 (B-1,3)		
7	4.64 (2′,3′-H)		6.94–7.58		–4.6 [170]	0.9 [80]
	5.57 (N-2,3-H)				33.5 [360]	2.4 [120]
	5.74 (N-1′-H)					
6a	5.78 (br.)	7.51 (B-2)	6.93 (B-2)	7.21 (B-2)	–5.9 [130]	–0.39 [150]
		7.71 (B-2′)	6.99 (B-2′)	7.27 (B-2′)	36.8 [800]	3.0 [150]
		8.02 (B-1,3)	7.10 (B-1,3)	7.42 (B-1,3)		
6c	5.78 (br.)	7.55 (B-2)	6.95 (B-2)	7.29 (B-2)	–3.5 [170]	–0.39 [40])
		7.71 (B-2′)	7.19 (B-2′)	7.33 (B-2′)	34.2 [400]	1.58 [10]
		7.73 (B-1,3)	7.25 (B-2,4)	7.49 (B-1,3)		
8	–	7.70 (B)	6.87 (PhB)	7.35 (BPh)	39.6 [800]	2.9 [190]
		8.01 (PhLi)	7.15 (PhLi)	7.21 (PhLi)		
PhLi		8.01	6.96	7.01		

Table 4. ^{13}C chemical shifts of the phenyl groups attached to the boron atoms of compounds **2**–**7** (in C_6D_6); $B^{13}C$ carbon signals have not been observed.

	δ^{13}C(PhB)	
1	128.4, 130.1, 132.4	
2	B-2	B-1,3
	127.9, 128.5, 132.3	128.0, 128.8, 132.6
3	B-2	B-1,3
	127.6,127.8,129.0	128.1 130.0, 132.1
	129.8, 131.7, 131.9	
4	B-2	B-1,3
	127.6, 127.9, 128.4	128.3, 128.6, 133.4
	128.5, 131.0, 131.4	
5	B-2,5	B-1,3,4,6
	127.3, 127.4, 129.2,	128.1, 128.3, 129.0,
	128.2, 128.5, 129.3,	130.2, 131.8, 132.1
	131.6, 132.4, 132.5	
6a	B-2	B-1,3
	127.4, 127.5, 128.9,	128.5, 129.9, 132.5
	129.0, 131.9, 132.0	
6c	B-2	B-1,3
	127.3, 127.6, 129.0,	128.4, 129.8, 132.4
	129.1, 131.8, 132.2	
7a,**b**	B-5	B-2
	127.3, 127.4, 129.2	128.2, 128.5, 132.5
	129.3, 131.6, 132.4	B-1,3
	B-4,6	128.3, 129.0, 132.1s
	128.1, 130.2, 131.8	
8	B-Ph	Li-Ph
	127.4, 128.5, 129.0	121.8, 133.5, 143.6, 145.4
PhLi	121.7, 126.7, 127.7	
	143.8	

having an *N*-lithioborazine skeleton while for the borazinates the two phenyl groups at the tetracoordinate boron atom B2 are chemically and magnetically different (see data in Table 3). ^{13}C NMR signals for the boron bonded *ipso*-C atoms could not be observed. This is a well-known phenomenon. The ^{1}H NMR signals of the phenyl groups show the expected ^{3}J(H,H) coupling with a value of 7 Hz. All NH proton signals are slightly deshielded compared with those of **1**. In the case of the borazinates two broad signals are observed in contrast to a single resonance for the *N*-lithioborazines.

B–N stretching bands of the BN ring modes are found in a range from 1475 to 1370 cm^{-1}. In most cases the band at 1472 cm^{-1} of **1** is shifted to smaller wave numbers indicating a weakening of the B–N bonding.

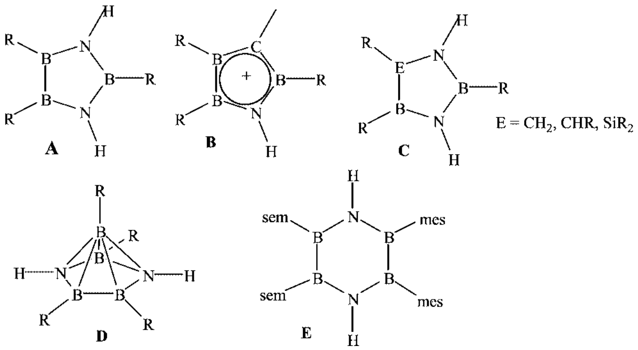
Discussion and Conclusion

The question of bonding in borazines in comparison to benzene is still not definitely settled[12] and whether borazines are supposed to be antiaromatic or aromatic depends on whether one discusses magnetic properties or bond energies. However, there is consent that borazines are much more reactive than benzene and its derivatives due to the B–N bond polarity. This not only relates to the ready addition of electrophiles to its N atoms but also of nucleophiles to the B atoms, and borazinate formation is a typical example of the latter. In addition, borazines of type $R_3B_3N_3H_3$ are also weak protic acids as was first shown by Wagner and Bradford[2,3] and delineated also in this and the previous study.[1] In the resulting *N*-lithioborazines and lithium borazinates the Li atoms coordinate in most cases to two N atoms of a B_3N_3 ring, but also all three atoms may be used for this purpose (**6c**). The resulting lithium tetraphenylborazinates add LiI or $Ph_3B_3N_3H_2Li$ in a 1:1 ratio (compounds **2** and **7**) or the borazinates may even dimerize (compounds **6** and **7**). Quite unusual is the 1:1 deprotonation and borazinate formation at a single borazine ring as found for the 1:2 reaction of LiPh with **1** to give compound **7**. And in the case of the 1:6 ratio of **1** with LiPh even a triple deprotonation was observed, the compound $Ph_3B_3N_3Li_3$, being stabilized by the addition of three molecules of LiPh, **8**. These are reactions unprecedented compared with the behaviour of benzene derivatives.

The ring planarity of the B_3N_3 ring is lost by the formation of the borazinate anion which adopts a tub shape conformation or contains twisted B_3N_3 rings. In these cases, the Li cation coordinates to two or even three ring N atoms. In the latter case, one observes dimerization via two Li bridges between two B_3N_3 rings (**6c** and **7**). Borazinate formation is accompanied with a strengthening of the two B–N bonds adjacent to the tetracoordinate boron atoms, while these bonds are weaker (longer) in the *N*-lithioborazines. This indicates that the electron distribution in these two ring systems is different. Although the monolithioborazines may be looked at as isoelectronic counterparts to aryllithium compounds[9,10] this statement may be far too short-fetched. Observed Li–N and Li–B interactions are not necessarily an indication of η-(NB)Li bonding. In the case of $(Et_3B_3N_3Et_3)Cr(CO)_3$, this type of interaction has been disputed because the borazine ring is puckered and the CO bonds are close to linearity with the Cr–C bonds.[13] However, a more recent theoretical treatment of the bonding in borazine tricarbonylchromium compounds is in favour of π-bonding.[14] One argument given is that the puckering of the ring is only weak and not comparable with a hexahydrotriazine.

The *N*-lithioborazines are also structurally not close to the $Cr(CO)_3$ complexes of borazines.[11] None of the compounds contain a Li atom that sits symmetrically above the B_3N_3 ring plane. An approximation is, however, found in one of the two isomers of **5** but two of its three Li–B distances are >2.5 Å. Thus, the structural chemistry of *N*-lithioborazine and lithium borazinates is unique which is, of course, due to the B–N bond polarity of the borazine ring system. One may try, however, to find similarities between the structures of *N*-lithioborazines and lithium carboranates.[15,16] In the latter class of compounds the solvated Li cation may be coordinated to a B–B, B–C or a C–C bond or to an open face of the carborane as found for *closo-exo*-5,6-[μ-$H_2Li(thf)_2$][1-$Li(thf)_2$-2-(Me_3Si)-3-(R)-2,4-(Me_3Si)-2,4-$C_2B_4H_4$] (R = $SiMe_3$, Me).[17] In this complex, one Li cation sits on top of an open C_2B_3 face while the second is bonded sidewise to a B–B bond. This lithium carboranate on reaction with YCl_3 produces the complex [$Li(thf)_4$]{(1-Cl-1-H_6)-2,2′,3,3′(Me_3Si)$_4$-4,4′,5,5′-Li(thf)[1,1′-*commo*-Y(2,3-$C_2B_4H_4$)$_2$]}[18] where the Li cation of the yttriate coordinates to four B atoms (2 each per carborane unit) with Li–B distances of 2.31(4), 2.27(4), and 2.49(4) Å. In the starting material the Li–B distances are Li1–B3 2.291(9), Li1–B4 2.371(9), and Li1–B5 2.237(10) Å.[17] A totally different situation results for the lithium salt of the triboracyclobutane dianion {[$Me_3Si(CH_2SiMe_3)B$][B(duryl)]$_2$}$^{2-}$ where both THF-solvated Li cations coordinate to two boron atoms of the BBB triangle with Li–B distances of 2.309(5), 2.325(5) for the Li(thf) group and 2.323(5) and 2.529(5) Å for the $Li(thf)_2$ unit. The Li atom lies almost in the B_3 plane.[19] Reduction of the six-membered [MeB(CHMe)]$_3$ by Li metal in diethyl ether or THF occurs in several steps leading finally to an *arachno*-borane structure for [MeBCH(Me)-Li]$_3$.[20] In this molecule the Li atoms bridge to basal adjacent C atoms but binds also to B atoms with distances ranging from 2.239(6) and 3.251(6) Å. Li–C bond lengths are somewhat longer at 2.247–2.456(6) Å.

Obviously, there are no close similarities between *N*-lithioborazines and lithium carboranates, the closest ones are those in which a Li atom coordinates to two borazine rings or to two open faces of two carborane anions. η^6-Coordination of an *N*-lithioborazine results in one of the isomers of compound **5**, but only when relatively long Li–N and Li–B distances are included. Carborane anions usually offer a pentagonal face as the most basic site for Li coordination while in *N*-lithioborazines Li–N coordination prevails. This situation may change for the following five-membered rings (Scheme 2) which on deprotonation may behave more like the carboranes.



Scheme 2.

Moreover, the deprotonation of the *arachno*-diazahexaborane and/or its classical isomer, 1,4-diazatetraborinane should provide interesting examples for studying the relationships between carboranes offering a B_3C_2 open face and its isoelectronic BN analogue.

Experimental Section

General Remarks: All experiments were carried out using standard Schlenk techniques under argon. Organyllithium compounds were obtained as diethyl ether or hexane solutions from Chemetall AG. Solvents were dried and distilled under nitrogen. NMR spectra were recorded with a Jeol EX00 for ^1H, ^7Li, ^{11}B, ^{13}C NMR (399.782, 157.48, 128.262, 100.531 MHz, respectively) spectra using $SiMe_4$ and C_6D_6 as internal standards with a 1 M aqueous LiCl solution, or $BF_3·OEt_2$ as the external standard. A Siemens P4 diffractometer equipped with the low-temperature device LT2 was used for intensity data collection with Mo-$K_α$ radiation and a CCD area detector. Data were recorded at –80 °C.

2,4,6-Triphenylborazine (1):[4,13] Freshly distilled $(Me_3Si)_2NH$ (93.8 mL, 72.6 g, 450 mmol) was dissolved in dichloromethane (250 mL) and the solution cooled to –78 °C. Then $PhBCl_2$ (75.0 g, 472 mmol) was added with stirring. The mixture was then kept at 55 °C for 10 d. Within this period the ^{11}B NMR signal for the

PhB(Cl)NHSiMee$_3$ (δ^{11} B = 37.6 ppm) vanished and only the signal for **1** was observed (δ^{11}B = 34.8 ppm). All volatiles (CH$_2$Cl$_2$, Me$_3$SiCl) were then removed in vacuo and the residue crystallized from diethyl ether. Yield: 45.4 g, 98%. M.p. 180–185 °C. ^{13}C NMR (C$_6$D$_6$): δ = 128.4, 130.1, 132.4 ppm. ^{11}B NMR: δ = 34.8 ppm.

(Tetramethylethylenediamine)lithium–2,4,6-triphenylborazine–(tetramethylethylenediamine)lithium Iodide (2): **1** (1.03 g, 3.34 mmol) was dissolved in diethyl ether (60 mL) at 0 °C. With stirring, a solution of commercial LiMe (containing LiI) in diethyl ether (2.20 mL, 3.52 mmol) and TMEDA (1.0 mL) was added drop wise to the borazine solution. After warming to ambient temperature, the clear solution was stirred for 2 d and then reduced in volume to about 20 mL. At –5 °C colorless prisms separated from the slightly brown solution. Yield: 2.10 g, 92%. M.p. 173–175 °C. ^{1}H NMR (C$_6$D$_6$): δ = 2.00 (s, 24 H, NCH_3), 2.14 (s, 8 H, NCH_2) ppm. ^{13}C NMR: δ = 46.0, 58.2 ppm. ^{11}B NMR: δ = 34.1 ($h_{1/2}$ = 350 Hz) ppm. C$_{30}$H$_{49}$B$_3$IN$_7$Li$_2$ (680.98): calcd. C 52.91, H 7.25, I 18.63, N 14.40; found C 52.86, H 7.13, I 18.51, N 14.22.

(1,3,5-Trimethylhexahydrotriazine)lithium 2,4,4,6-Tetraphenylborazinate (3): **1** (1.17 g, 3.79 mmol) was placed into a flask containing diethyl ether (60 mL). The suspension was cooled to 0 °C. To a solution of LiMe (prepared from Li grains and MeCl in diethyl ether, 4.0 mmol, 2 5 mL, 1.6 M) diluted with diethyl ether (10 mL) was added trimethylhexahydrotriazine (1.1 mL, 7.8 mmol). This LiMe reagent was slowly added dropwise into the diethyl ether solution of **1** at 0 °C. A clear solution resulted which was stirred for 2 d and then reduced in volume in vacuo. On keeping the solution at –5 °C, colorless prisms of **3** separated (1.90 g, 3.63 mmol, 95%). M.p. 91–95 °C. ^{1}H NMR (C$_6$D$_6$): δ = 1.95 (s, 9 H, NCH$_3$), 3.01 (s, 6 H, NCH$_2$) ppm. ^{13}C NMR: δ = 38.4, 76.6 ppm (azin). ^{11}B NMR: δ = –5.2 ($h_{1/2}$ = 150 Hz), 33.1 ($h_{1/2}$ = 400 Hz) ppm (ratio 1:2). ^{7}Li NMR: δ = 2.1 ($h_{1/2}$ = 40 Hz) ppm. IR (Nujol/Hostaflon; only medium to strong signals): $\tilde{\nu}$ = 3411 m, 3077 m, 3053 m, 3030 m, 3013 m, 2992 m, 2050 m, 2870 m, 2795 m, 2734 m, 2720 m, 2711 m, 1600 m, 1502 st, 1474 st, 1441 vst, 1422 vst, 1408 vst, 1347 m, 1314 m, 1272 st, 1502 st, 1474 st, 1441 vst, 1408 vst, 1347 m, 1314 m, 1272 st, 1195 m, 1157 m, 1118 vst, 1029 m, 1016 st, 939 st, 930 m, 866 m, 762 m, 756 m, 732 st, 704 vst, 671 st, 6521 m, 581 m, 557 m cm^{-1}. C$_{30}$H$_{38}$B$_3$LiN$_6$ (522.06): calcd. C 69.02, H 7.34, N 16.10; found C 68.08, H 7.42, N 15.71.

(Diethyl ether)lithium 1,3,5-Trimethyl-2,4,6,6-tetraphenylborazinate (5): To a stirred solution of (PhBNMe)$_3$, **4**,[13] in diethyl ether (0.304 g, 0.86 mmol, 40 mL) was added at 0 °C a solution of LiPh (0.45 mL, 0.9 mmol) in diethyl ether/cyclohexane (1:1). The resulting clear yellow solution was stirred for 2 d at ambient temperature and then reduced to a volume of ca. 20 mL in vacuo. On storing the solution at –5 °C crystals separated within a few days. Yield: 0.42 g of **5**, 95%. M.p. 165 °C (dec.). ^{1}H NMR (C$_6$D$_6$): δ = 0.68 (t, 6 H, CH$_2$CH_3), 2.49 (s, 6 H, 1,5-NCH$_3$), 2.71 (s, 3 H, 3-NCH$_3$), 2.90 (q, 4 H, OCH$_2$), 7.13 (t, 4 H, *m*-PhB-2,6, $^3J_{\rm H,H}$ = 7.0 Hz), 7.17 (t, 2 H, *m*-PhB-4, $^3J_{\rm H,H}$ = 7.0 Hz), 7.19 (t, 2 H, *m*-PhB, $^3J_{\rm H,H}$ = 7.0 Hz), 7.25 (t, 1 H, *p*-PhB-4, $^3J_{\rm H,H}$ = 7.0 Hz), 7.26 (t, 1 H, *p*-PhB-4′, $^3J_{\rm H,H}$ = 7.0 Hz), 7.30 (t, 2 H, *m*-PhB-2,6, $^3J_{\rm H,H}$ = 7.0 Hz), 7.35 (dd, 4 H, *o*-PhB-2,6, $^3J_{\rm H,H}$ = 7.0, $^4J_{\rm H,H}$ = 1.0 Hz), 7.59 (d, 4 H, *o*-PhB-2,2′, $^3J_{\rm H,H}$ 7.0 Hz) ppm. ^{13}C NMR (C$_6$D$_6$): δ = 14.9 (CH$_2$CH$_3$), 36.6 (NCH$_3$), 37.2 (NCH$_3$), 64.6 (OCH$_2$) ppm. ^{11}B NMR: δ = 1.9 ($h_{1/2}$ = 130 Hz), 37.2 ($h_{1/2}$ = 400 Hz) ppm. ^{7}Li NMR: δ = 2.1 ($h_{1/2}$ = 40 Hz) ppm. IR (Nujol/Hostaflon; only medium to very strong signals): $\tilde{\nu}$ = 3067 st, 3044 st, 3006 st, 2997 st, 2982 st, 2945 st, 2894 st, 2852 m, 2819 m, 1595 st, 1567 m, 1497 st, 1481 st, 1466 st, 1431 st, 1397 vst, 1368 st, 1355 vst, 1298 vst, 1265 st, 1258 st, 1194 m, 1160 m, 1146 st, 1111 m, 1064 st, 1044 m, 1019 st, 999 m, 912 m, 900 m, 854 m, 845 m, 756 wt, 721 st, 716 st, 704 vst, 621 m, 617 m, 486 m cm^{-1}. C$_{31}$H$_{39}$ B$_3$LiN$_3$O (509.05): calcd. C 73.15, H 7.72, N 8.25; found C 71.88, H 7.73, N 8.16.

Bis(diethyl ether)lithium 2,4,6,6-Tetraphenylborazinate–lithium–2,4,6-triphenylborazine (7): To a stirred solution of **1** (0.858 g, 2.7 mmol) in diethyl ether (50 mL) was slowly added a 2 M solution of LiPh (1.39 mL, 2.78 mmol) in diethyl ether/cyclohexane. The brownish solution was then stirred for 5 d at ambient temperature followed by reduction of its volume to 20 mL in vacuo. The solution was kept at –5 °C. Colorless crystals separated from the slightly brown solution. Yield: 1.05 g of **7**, 91%. M.p. 130–132 °C (dec.). ^{1}H NMR (C$_6$D$_6$): δ = 1.07 (t, 12 H, CH$_2$CH_3, $^3J_{\rm H,H}$ = 7 Hz), 3.20 (q, 8 H, OCH$_2$, $^3J_{\rm H,H}$ = 7 Hz), 4.64 (br. s, 2 H, N-1′,5′-H), 5.57 (br. s, 2 H, N-3,5-H) 6.94–7.58 (m, 35 H, PhB) ppm. ^{13}C NMR: δ = 15.2 (CH$_2$CH$_3$), 65.8 (OCH$_2$) ppm. ^{11}B NMR: δ = –4.6 ($h_{1/2}$ = 170 Hz), 33.5 ($h_{1/2}$ = 360 Hz) ppm. ^{7}Li NMR: δ = 0.9 ($h_{1/2}$ = 80 Hz), 2.4 ($h_{1/2}$ = 120 Hz) ppm. IR (Nujol, Hostaflon; only medium to very strong bands quoted): $\tilde{\nu}$ = 3446 m, 3430 m, 3074 m, 3049 st, 3009 st, 2997 st, 2977 st, 2931 st, 2898 m, 2862 m, 1599 vst, 1571 m, 1501 vst, 1479 st, 1424 vst, 1399 vst, 1359 m, 1339 m, 1312 st, 1300 m, 1264 m, 874 m, 752 st, 743 m, 705 vst, 663 m, 652 m, 682 m, 515 m cm^{-1}. C$_{50}$H$_{60}$ B$_6$Li$_2$N$_6$O$_2$ (855.82): calcd. C 70.17, H 7.07, N 9.82; found C 70.95, H 7.89, N 9.43.

Bis(diethyl ether)lithium *N*-Lithio-tetraphenylborazinate (6a): To a stirred solution of **1** (0.640 g, 2.07 mmol) in diethyl ether (60 mL) a solution of LiPh in diethyl ether/cyclohexane (2 M, 2.15 mL, 4.3 mmol) was added dropwise at 0 °C. The mixture was stirred 4 d at ambient temperature. Then its volume was reduced to about 20 mL in vacuo. The brown solution was stored at –5 °C. After a few days, colorless crystals were isolated. Yield: 0.962 g of **6a**, 85%. The same compound was also obtained by treating **1** with 3 or 4 equiv. of LiPh (only tested by ^{11}B NMR). When compound **6a** was kept in vacuo, 1.5 equiv. of diethyl ether was lost. M.p. 140–142 °C. ^{1}H NMR: δ = 1.07 (t, CH$_2$CH_3, $^3J_{\rm H,H}$ = 7 Hz), 3.20 (q, $^3J_{\rm H,H}$ = 7 Hz, 8 H, OCH_2), 5.78 (br. s, 4 H, HN-1,1′,5,5′) ppm. ^{13}C NMR: δ = 15.3 (CH$_2$CH$_3$), 65.7 (OCH$_2$) ppm. ^{11}B NMR: δ = –5.9 ($h_{1/2}$ = 130 Hz), 36.8 ($h_{1/2}$ = 800 Hz) ppm. ^{7}Li NMR: δ = –0.39 ($h_{1/2}$ = 150 Hz), 3.0 ($h_{1/2}$ = 150 Hz) ppm. IR (Nujol, Hostaflon; only medium to very strong bands quoted): $\tilde{\nu}$ = 3096 m, 3047 m, 2926 m, 1596 m, 1499 m. 1483 m, 1434 st, 1343 vst, br, 1278 st, 1245 m, 1188 m, 1070 m, 1027 m, 851 st, 805 m, 755 m, 737 st, 703 vst, 683 st, 585 m, 491 m cm^{-1}. C$_{52}$H$_{54}$B$_6$Li$_4$N$_6$O (891.67) [dimeric mono(diethyl ether) adduct]: calcd. C 71.65, H 6.24, N 9.64; found C 71.39, H 6.27, N 9.03.

Tris(tetrahydrofuran)lithium *N*-Lithio-2,2,4,6-tetraphenylborazinate (6c): *N*,*N*′,*N*′′-trimethylhexahydrotriazine (1.83 g, 14.2 mol) was added to a hexane solution of *n*BuLi (5.0 mL. 1.6 M, 8.0 mmol). This slightly yellow solution was then added to a stirred solution of **1** (2.34 g, 7.76 mmol) in hexane (40 mL). Gas evolution was noted after a few drops had been added. After addition, the mixture was kept at reflux for 14 h. The solid (1.65 g, most likely **6b**) was isolated by filtration and was then dissolved in THF (25 mL). After removal of the solvent, a brown oil remained. Most of the oil solidified on storing for several days. The resulting colorless crystals were isolated and washed with a small amount of pentane. Yield: 1.62 g of **6c**, 56%. M.p. 148–151 °C. Several of the crystals had single-crystal quality. By dissolving **6a** in THF the same compound separated from a concentrated solution kept at –25 °C. ^{1}H NMR: δ = 1.37 (t, $^3J_{\rm H,H}$ = 7 Hz, 24 H, OCH$_2$CH), 3.54 (q, $^3J_{\rm H,H}$ = 7 Hz, 24 H, OCH$_2$), 5.78 (br. s, 4 H, N-1,1′,5,5′) ppm. ^{13}C NMR: δ = 26.2 (OCH$_2$CH$_2$), 68.3 (OCH$_2$) ppm. ^{11}B NMR: δ = –3.5, 34.2 ppm. ^{7}Li NMR: δ = –0.39 ($h_{1/2}$ = 40 Hz), 1.58 ($h_{1/2}$ = 10 Hz) ppm.

IR (Nujol, Hostaflon; only medium to very strong bands quoted): $\tilde{\nu}$ = 3011 m, 2982 m, 1950 m, 2799 m, 1599 m, 1502 st, 1449 st, 1425 st, 1399 st, 1339 cm^{-1}. $C_{36}H_{46}B_3Li_2N_3O_3$ (615.13): calcd. C 70.30, H 7.54, N 6.83; found C 69.41, H 7.34, N 6.67.

1,3,5-Tris[(diethyl ether)lithio]-2,4,6-triphenylborazine–Tris(phenyllithium–diethyl ether) (8): To a stirred solution of **1** (450 mg, 1.47 mmol) in diethyl ether (40 mL), a solution of PhLi in diethyl ether/cyclohexane (1:1, 4.5 mL, 9.0 mmol) was slowly added at 0 °C. The brown solution was stirred for 3 d. Then its volume was reduced to ca. 20 mL. Moisture-sensitive crystals separated from the solution within a few days at –5 °C. Some of them had single-crystal quality but showed low diffracting power. Yield: 1.37 g of **8**, 1.34 mmol, 92%. M.p. 166–168 °C. ^{1}H NMR (C_6D_6): δ = 0.75 (t, $^3J_{H,H}$ = 6 Hz, 36 H, CH_2CH_3), 2.90 (q, $^3J_{H,H}$ = 6 Hz, 24 H, OCH_2), 6.87 (t, $^3J_{H,H}$ = 7 Hz, 6 H, *m*-PhB), 7.15 (t, $^3J_{H,H}$ = 7 Hz, 6 H, *m*-PhLi), 7.21 (t, $^3J_{H,H}$ = 7 Hz, 3 H, *p*-PhLi), 7.35 (t, $^3J_{H,H}$ = 7 Hz, 3 H, *p*-PhB), 7.70 (d, $^3J_{H,H}$ = 7 Hz, 6 H, *o*-PhB), 8.01 (d, $^3J_{H,H}$ = 7 Hz, 6 H, *o*-PhLi) ppm. ^{13}C NMR: δ = 14.6 (CH_2CH_3), 65.1 (OCH_2), 121.8 (*i*-PhLi), 127.4 (*p*-PhLi), 128.5 (*m*-PhLi), 129.0 (*p*-PhB), 133.5 (*m*-PhB), 143.6 (*o*-PhB), 145.4 (*o*-PhB) ppm. ^{11}B NMR: δ = 39.6 ($h_{1/2}$ = 800 Hz). ^{7}Li NMR: δ = 2.9 ($h_{1/2}$ = 190 Hz). IR (Nujol, Hostaflon; only medium to very strong bands quoted): $\tilde{\nu}$ = 3063 m,3048 m, 2979 m, 2936 m, 2889 m, 1594 m, 1483 m, 1467 m, 1457 m, 1447 m, 1430 st, 1408 m, 1387 m, 1330 vst, 1316 vst, 1261 st, 1210 m, 1189 st, 1153 m, 1095 m, 1064 st, 1044 m, 1023 m, 1005 m, 978 m, 836 m, 789 m, 764 m, 740 st, 726 st, 675 m, 622 m, 616 st, 593 m, 445 m, 434 st cm^{-1}. $C_{60}H_{90}B_3Li_6N_3O_6$ (1023.47): calcd. C 70.41, H 8.86, N 4.11; found C 68.78, H 8.49, N 4.79.

X-ray Crystal Structure Analyses: Crystals were placed under a blanket of a cold stream of N_2 in perfluoroether oil (stock point –40 °C). The selected single crystal was mounted on the tip of a glass fiber and placed on a supporting copper rod which was transferred onto the goniometer head cooled to –80 °C with a Bruker LT2 device. After centering the crystal, data on 5 different sets of 15 frames each were recorded using a Siemens P4 diffractometer equipped with a CCD detector. These data were used to determine the unit cell with the program SMART.[21] Data collection was performed using the hemisphere mode of the program SMART. Data on 1200 frames were collected which were reduced with the program SAINT.[22] The normalized data set was then used to obtain a model structure.[23] As most data sets showed only weak reflection beyond 2θ > 30°, several cycles of isotropic refinements of found non-hydrogen positions were necessary to complete the non-hydrogen framework. After refinement with anisotropic thermal parameters, most hydrogen positions were observed after several cycles. Only the found positions for NH hydrogen atoms were isotropically refined. The CH hydrogen atoms were placed in calculated positions and refined with a riding model in the final cycles of refinement (not so for compound **5** where several hydrogen positions at the phenyl groups were freely refined but in the final cycles with fixed U_i values). The U_{ij} values of the carbon atoms of the diethyl ether molecule showed too long C–O bonds and too short C–C distances, suggesting site disorder. However, a split-model calculation did not significantly improve the *R* value. Therefore, the data of the unsplit situation is quoted. On the other hand, two of the three THF molecules of **6c** were site-disordered. The refinement showed about equal occupancy of the two positions. Therefore, in the final cycles SOF was fixed to 0.5. In case of compound **8** data

Table 5. Crystallographic data for compounds **2**–**8**.

	2	**3**	**4**	**5**	**6c**	**8**
Empirical formula	$C_{30}H_{49}B_3ILi_2N_7$	$C_{30}H_{37}B_3LiN_6$	$C_{31}H_{39}B_3LiN_3O$	$C_{100}H_{121}B_{12}Li_4N_{12}O_4$	$C_{72}H_{92}B_6Li_4N_6O_6$	$C_{60}H_{84}B_3Li_6N_3O_6$
Formula mass	680.97	521.03	509.02	1712.57	1230.14	1017.37
Crystal size [mm]	0.40×0.40×0.60	0.2×0.27×0.5	0.20×0.30×0.30	0.20×0.20×0.30	0.2×0.2×0.3	0.4×0.49×0.55
Crystal system	monoclinic	orthorhombic	triclinic	monoclinic	monoclinic	hexagonal
Space group	*P*21/*c*	*Pbca*	*P*1	*P*21/*c*	*P*21/*n*	*R*3
a [Å]	13.6330(4)	15.2568(2)	11.5296(8)	23.4276(3)	12.9042(8)	22.005(3)
b [Å]	14.6656(5)	16.7596(3)	16.147(1)	20.7481(3)	20.106(1)	22.005(3)
c [Å]	18.9577(7)	23.8982(1)	17.208(1)	23.5936(1)	14.2005(8)	23.604(5)
α [°]	90.00	90.00	103.238(1)	90.00	90.00	90.00
β [°]	106.025(1)	90.00	103.286(1)	119.16 (1)	105.574(1)	90.00
γ [°]	90.00	90.00	92.420(2)	90.00	90.00	120.00
V [Å^3]	3643.0(2)	6110.7(1)	3005.5(4)	10014.9(2)	3549.1(4)	9898(3)
Z	4	8	4	4	2	6
ρ(calcd.) [Mg/m^3]	1.242	1.133	1.125	1.136	1.151	1.024
μ [mm^{-1}]	0.908	0.066	0.066	0.067	0.070	0.062
F(000)	1408	2216	1088	3636	1312	3276
Index range	$-17 \le h \le 17$	$-16 \le h \le 16$	$-12 \le h \le 12$	$-30 \le h \le 29$	$-15 \le h \le 13$	$-22 \le h \le 22$
	$-17 \le k \le 17$	$-18 \le k \le 18$	$-16 \le k \le 716$	$-25 \le k \le 25$	$-23 \le k \le 23$	$-21 \le k \le 21$
	$-23 \le l \le 3$	$-26 \le l \le 26$	$-19 \le l \le 9$	$-30 \le l \le 29$	$-16 \le l \le 16$	$-23 \le l \le 23$
2θ [°]	57.98	46.52	46.52	51.5	49.42	41.62
T [K]	193(2)	193	193	183	193	193
Reflections collected	20309	25177	13520	54348	17491	11121
Reflections unique	7184	4372	7007	16329	5692	2297
Reflections observed (4σ)	5948	2627	5469	12140	3479	1359
R(int.)	0.0183	0.1064	0.0174	0.0359	0.0404	0.1279
No. of variables	404	361	712	1298	498	235
Weighting scheme[a] *x*/*y*	0.0452/3.5395	0.0422/5.6631	0.0683/1.4601	0.0553/17.9596	0.0810/2.5368	0.1321/105.16
GOOF	1.053	1.105	1.021	1.153	1.024	1.101
Final *R* (4σ)	0.0356	0.0751	0.0471	0.0900	0.0697	0.1607
Final wR_2	0.0904	0.1320	0.1289	0.1960	0.1660	0.3715
Largest residual peak [e/Å^3]	0.899	0.438	0.381	0.811	0.369	0.283

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

for several crystals were measured. But even the "best" set of data gave no R_2 value better than 37%. Selected crystallographic data are found in Table 5. Additional data related to the X-ray structures are deposited with the Cambridge Crystallographic Data Centre. CCDC-260218 to -260223 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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