Solvates of Lithium Tetrahydridoborates with Various Amines: From Molecular to Extended Structures of Lithium Tetrahydridoborate[‡]

Hans Herrmann Giese,[a] Tassilo Habereder,[a] Jörg Knizek,[a] Heinrich Nöth,*[a] and Marcus Warchhold[a]

Dedicated to Prof. Dr. Dr. h. c. Gerhard Fritz on the occasion of his 80th birthday

Keywords: Lithium / Borates / Coordination chemistry

Several solvates of $LiBH_4$ with amines have been prepared and characterized by X-ray structure determinations. $LiBH_4 \cdot 3H_2NPh$ (**1**) is monomeric with a triply bridging BH_4 group. $LiBH_4 \cdot 2en$ (**3**) is shown to be an ionic compound containing chains of cationic $[Li(en)_2)]^+$ units. In contrast, the BH_4 group of $LiBH_4 \cdot$triene (**4**) forms triple hydride bridges to the Li centers of a Li(triene) chain, making the Li atoms hexacoordinated by 3 × N and 3 × H atoms. Reaction of $LiBH_4$ with *tert*-butylamine generates the compound $3LiBH_4 \cdot 4H_2NtBu$ (**2**). The structure of **2** consists of an infinite chain of $LiBH_4$ units having three different kinds of Li centers, two of which have an environment of 2 × N and 4 × H atoms, whereas the third type is surrounded by five hydrogen atoms. Pyrrolidine reacts with $LiBH_4$ to give $LiBH_4 \cdot HNC_4H_8$ (**5**), the structure of which in the solid state shows an infinite chain with heptacoordinated Li centers (N and 6 × H). In contrast, dibenzylamine gives the compound $LiBH_4 \cdot 2HN(CH_2Ph)_2$ (**6**), which is dimeric with hexacoordinated Li centers (2 × N and 4 × H) in the crystal, and a similar structure was found for $LiBH_4 \cdot (iPrNCH_2)_3$ (**7**) but with heptacoordinated Li ions (3 × N and 4 × H). Addition of $(MeNCH_2)_3$ to $LiBH_4$ in toluene leads to $4LiBH_4 \cdot 2(MeNCH_2)_3$ (**8**), in which the two amine ligands bind to two Li ions, Li1 being hexacoordinated by (4 + 2) N atoms, Li2 by 2 × N atoms and 4 × H atoms from two different BH_4 groups. Li2 is part of a layer structure composed of $Li_3(BH_4)_4^-$ units. In contrast, a chain structure is evident in $3LiBH_4 \cdot 2(PhCH_2NCH_2)_3$ (**9**), as shown by the presence of separate $Li[(PhCH_2NCH_2)_3]_2$ cations and $Li_2(BH_4)_3$ anionic building blocks.

Introduction

Alkali metal tetrahydridoborates, particularly $NaBH_4$, are commercially produced.[2] Large quantities of $NaBH_4$ are used for the bleaching of pulp[3] and it is also useful for depositing heavy metals in waste water.[4] $LiBH_4$, on the other hand, is a very useful reducing agent of wide applicability.[5] Its reducing power is superior to that of $NaBH_4$ and its solubility is generally greater than that of $NaBH_4$. The solubility of $LiBH_4$ depends on the solvation of this compound by the solvent and a number of ether and amine solvates have been described in the literature.[4,6] However, in most cases, information about their structures in the crystal has not been available until recently.[6]

The structures of solvates of $LiBH_4 \cdot nL$ depend on the type and number (n) of ligand molecules (L). This results in a large variety of structures that range from mononuclear species through a preference for dinuclear molecules to extended chains and double chains to three-dimensional arrays. We report here new information on amine solvates of $LiBH_4$ that adds to the diversity of structures in the crystalline state but also shows that the BH_4 group is a particularly versatile ligand.[7]

Syntheses

It is well known that the alkali metal tetrahydridoborates, particularly $LiBH_4$ and $NaBH_4$, dissolve well in liquid ammonia or primary amines. Extraction of $NaBH_4$ from the solid mixture of NaOMe/$NaBH_4$ by isopropylamine is a known technical process.[8] An even better solvent is liquid ammonia, which dissolves 104 g of $NaBH_4$ in 100 mL,[9] while only 20 g of KBH_4 is soluble in the same amount of solvent.[10] Nevertheless, the composition of the solvates, particularly with primary amines, has yet to be well established in most cases.[11]

In the present work two routes have been used to obtain and isolate amine solvates of $LiBH_4$. The first method involves treatment of $LiBH_4$ with an excess of an amine in the presence of a nonpolar solvent such as toluene. In the second route, $LiBH_4$ is simply dissolved in the amine and the solvate isolated from the resulting solution. The ligand displacement reaction as depicted in Equation (2) was less successful. Reactions according to Equation (1) have been used to prepare compounds **1**−**9**.

$$LiBH_4 + nL \rightarrow LiBH_4 \cdot n\,L \qquad (1)$$

$$LiBH_4 \cdot OEt_2 + n\,L \rightarrow LiBH_4 \cdot n\,L + OEt_2 \qquad (2)$$

We report here only on those amine solvates that were obtained in the form of single crystals. Our attempts to pre-

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[‡] Metal Hydridoborates and (Hydridoborato)metalates, 27. − Part 26: Ref.[1]

[a] Department of Chemistry, University of Munich, Butenandtstraße 5−13, House D, 81377 Munich, Germany

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$LiBH_4 \cdot 3\,NH_2Ph$ **1**

$3\,LiBH_4 \cdot 4\,NH_2tBu$ **2**

$LiBH_4 \cdot 2$ en **3**

$LiBH_4 \cdot$ triene **4**

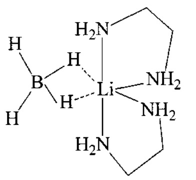
$LiBH_4 \cdot NHC_4H_8$ **5**

$LiBH_4 \cdot 2\,NH(CH_2Ph)_2$ **6**

$LiBH_4 \cdot (iPrNCH_2)_3$ **7**

$2\,LiBH_4 \cdot (MeNCH_2)_3$ **8**

$3\,LiBH_4 \cdot 2\,(PhCH_2NCH_2)_3$ **9**



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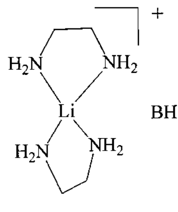

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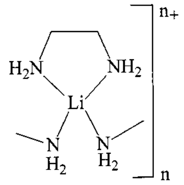

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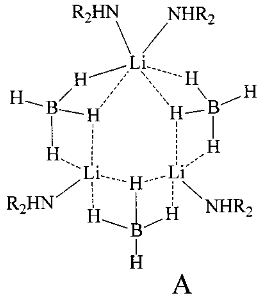

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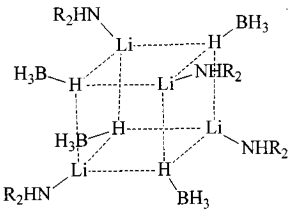


B

pare single crystals of isopropylamine and ethylamine have so far failed. Even the solid products that we isolated were difficult to analyze due to rapid loss of amine. Therefore, their composition could not be reliably determined.

It should be noted that, according to ^{11}B NMR spectroscopic data, the amine not only solvates $LiBH_4$ but also removes a BH_3 group to form amine−borane adducts $L{\cdot}BH_3$ that are readily identified by the typical 1:3:3:1 quadruplet in the ^{11}B NMR spectra.[12] This kind of behavior is more pronounced for toluene solutions than for hexane solutions. In the case of the formation of **8**, a substantial amount of $(MeNCH_2)_3{\cdot}BH_3$ was formed; the compound was isolated and subjected to a crystal structure determination.[13]

NMR and IR Spectra

Although the structures of the $LiBH_4$ solvates in the solid state are of special interest, their state in solution is at least of the same importance because reactions, for instance the reduction of functional groups of organic compounds, are performed in solvents. However, knowledge about the structure in the solid state may be helpful in the assignment of IR data.

Table 1 summarizes the ^{11}B and ^7Li NMR spectroscopic data. It should be noted that there is only one ^7Li signal for each of the compounds investigated. This is, at first glance, a rather surprising observation. If the solid and solution state for the dimeric molecules $[LiBH_4{\cdot}(MeNCH_2)_3]_2$[6b] and $[LiBH_4{\cdot}(iPrNCH_2)_3]_2$ (**7**) were the same, one would expect only a single signal. However, the shielding should be different because in the former compound only two of the three ring nitrogen atoms coordinate to Li (in the solid state) while all three nitrogen atoms of the $(iPrNCH_2)_3$ ligand bind to the Li center. Indeed, the ^7Li NMR signal for the latter compound is better shielded. On the other hand, if the solid-state structure of compound **9** was retained in solution then one would expect at least two signals, one of them being highly shielded due to the coordination of one of the three Li centers (vide infra) to six nitrogen atoms. However, only a single signal is observed. Therefore, the ^7Li NMR spectrum is not compatible with the structure found in the crystal indicating dynamic behaviour in solution.

Table 1. δ^7Li and $\delta^{11}B$ data and coupling constants $^1J(^{11}B^1H)$ (1:4:6:4:1 quintuplets) for lithium tetrahydridoborate amine solvates

Compound	δ^7Li	$\delta^{11}B$	$^1J(^{11}B^1H)$ [Hz]	Solvent
1	0.1	−38.0	81	aniline
2	1.07	−38.3	81	C_6D_6
3	2.0	−38.3	81	pyridine
4	1.7	−38.1	81	pyridine
5	1.32	−41.1	87	C_6D_6
6	–	−38.2	81	MeC_6H_{11}
7	0.097	−38.5	81	toluene
8	0.74	−38.6	96	toluene
9	0.347	−39.4	unresolved	C_6D_6

A considerable degree of deshielding occurs for compounds with an $LiBH_4$/N ratio close to 1:1. However, it is unlikely that the chain structure of $3LiBH_4{\cdot}4H_2NtBu$ is retained in solution. The chains are expected to break down into smaller units, possibly into units such as those suggested in formulas **A** (for **2**) or **B** (for **5**). A tetrameric unit is not unfeasible because such a unit has been found for

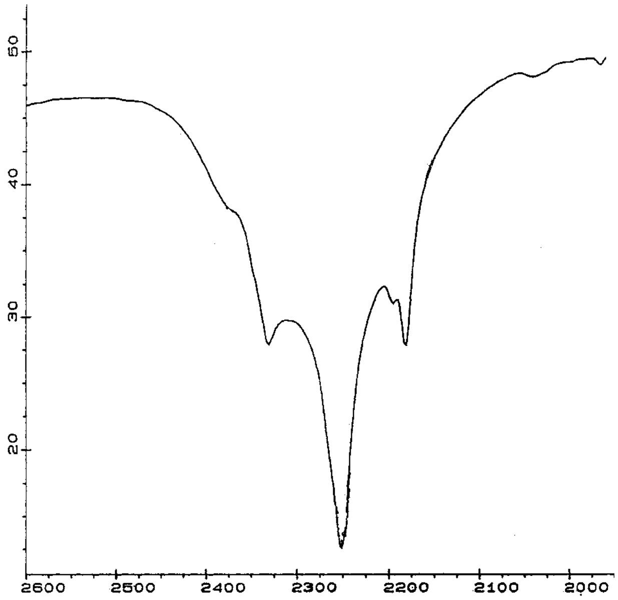


Figure 1. IR spectrum of $LiBH_4{\cdot}3H_2NPh$ (**1**) in Nujol; only the B−H stretching region is depicted

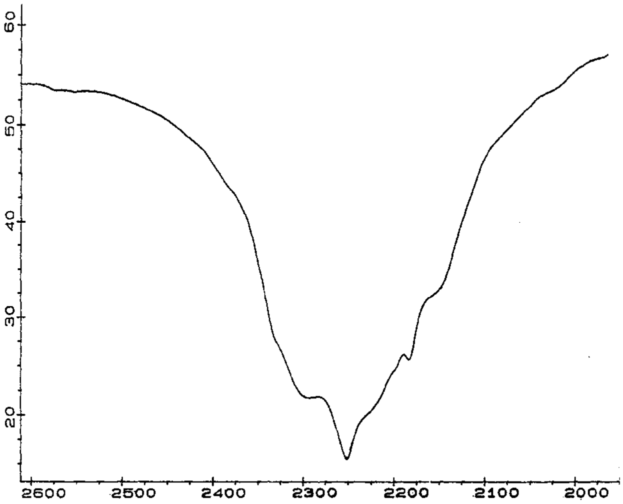


Figure 2. IR spectrum of $LiBH_4{\cdot}2en$ (**3**) in Nujol; only the B−H stretching region is shown

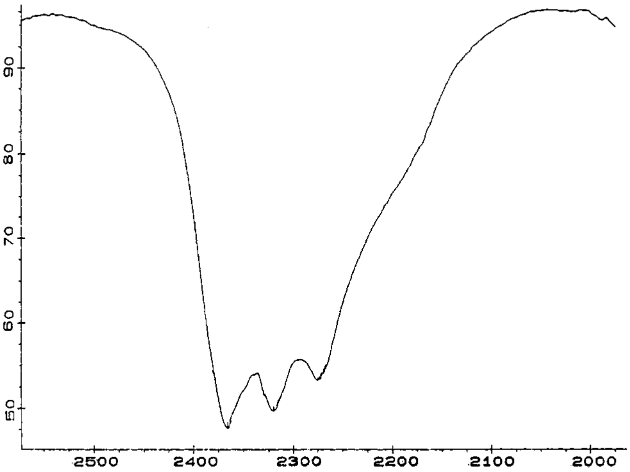


Figure 3. IR spectrum of $3LiBH_4{\cdot}4tBuNH_2$ (**2**) in Nujol showing the B−H stretching region

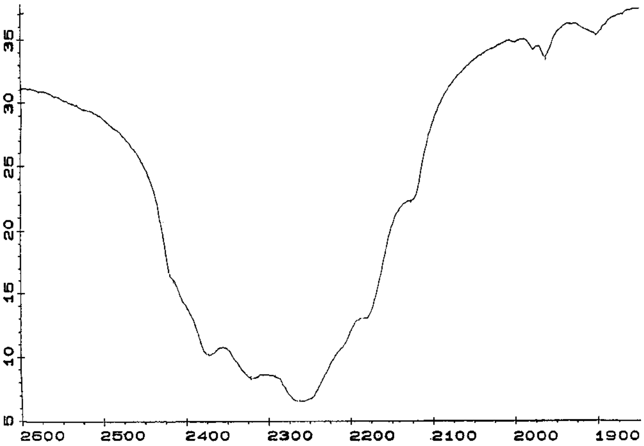


Figure 4. IR spectrum of $\{Li[(PhCH_2NCH_2)_3]_2\}Li_2(BH_4)_3$ (**9**) in Nujol showing the B−H stretching region

$[NaBH_4{\cdot}L]_4$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane).[6b]

All compounds show only one 1:4:6:4:1 quintuplet for the BH_4 anion in the proton-coupled ^{11}B NMR spectrum except for compound **9**, which gave rise to a broad signal without fine structure due to B,H coupling. The $\delta^{11}B$ values span a narrow range from $\delta = -38.3$ to -41.1. Therefore, irrespective of the composition of the compounds, all BH_4 groups are chemically equivalent in solution, as are their H atoms. In addition, $^1J(BH)$ does not allow a structural distinction of the various Li···H−B interactions observed in the crystal structures.

Figure 1 (compound **1**), Figure 2 (**3**), Figure 3 (**2**), and Figure 4 (**9**) show some IR spectra measured from Nujol mulls and the values of the B−H stretching bands observed for compounds **1**−**9** are given in the Exp. Sect.

One might expect that the B−H stretching bands for $[LiBH_4(MeNCH_2)_3]_2$[6b] and **7** should be rather similar because both show the same type of bonding for the BH_4 group (vide infra). Nevertheless, noticeable differences do exist. Even if we neglect the shoulder at 2154 cm^{-1} for $[LiBH_4(MeNCH_2)_3]_2$, the wave numbers are sufficiently different for the two species, as exemplified by the strong bands at 2272 and 2366 cm^{-1} for the former and 2185 and 2378 cm^{-1} for the latter compound. The IR spectrum of compound **9**, with its $Li_2(BH_4)_3$ chain, shows four strong B−H stretching bands with two shoulders, all of which are rather broad. This spectrum is indicative of the presence of different BH_4 groups, and its features are similar to those of the IR spectrum in the B−H stretching region of compound **8** with its sheet-like arrangement of the $Li_3(BH_4)_4$ anionic lattice. In any case, the IR spectra of compounds

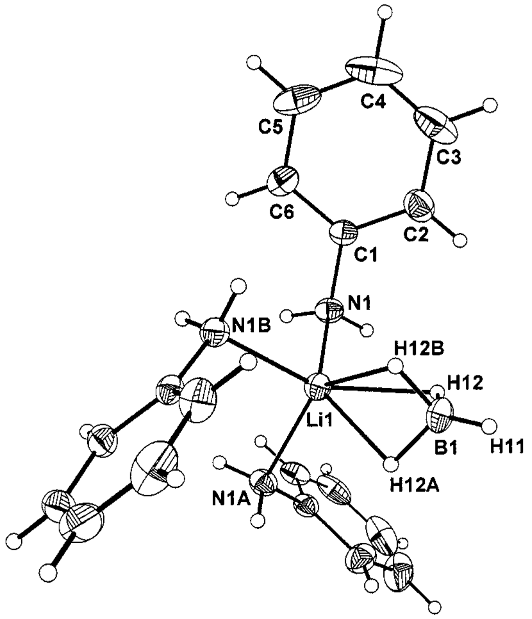


Figure 5. Molecular structure of $LiBH_4{\cdot}3NH_2Ph$ (**1**); only one of the two independent molecules is depicted; thermal ellipsoids represent a 25% probability; selected atom distances (in Å): molecule 1: Li1−N1 2.135(2), Li1···B1 2.279(6), N1−C1 1.416(2), B1−H11(term.) 0.86(5), B1−H12(bridge) 1.10(4); molecule 2: Li2−N2 2.137(2), Li2···B2 2.363(6), N2−C7 1.418(2), B2−H21(bridge) 0.89(5), B2−H22(term.) 0.94(4); selected bond angles (in °): molecule 1; N1−Li1−B1 116.1(1), C1−N1−Li1 113.6(1), N1−Li1−N1A 102.1(1), B1−H12−Li1 92(2), H11−B1−H12 120.9(2); molecule 2: N2−Li2−B2 112.5(1), C7−N2−Li2 113.3 (1), N7−Li2−N(7A) 106.3 (1), B2−H21−Li2 106(2), H21−B2−H22 126(3)

1−9 do not allow unequivocal assignment to a specific bonding pattern of the BH_4 groups to the Li centers.

Structures of the Amine Solvates of $LiBH_4$

The most simple structure amongst the solvates of primary amines with $LiBH_4$ is the aniline solvate $LiBH_4{\cdot}3H_2NPh$, (**1**, see Figure 5). Compound **1** crystallizes trigonally in the space group *R*3 with $Z = 6$, i.e. there are two independent molecules in the unit cell. Both molecules have C_3 symmetry, with the threefold axis running through the Li and B atoms and the terminal hydrogen atom of a μ_3^1-BH_4 group. The Li−B distances in the two molecules are significantly different [Li1−B1 2.279(6), Li2−B2 2.363(6) Å]. This is due to different N−Li−B bond angles. At atom Li1 the angle is larger [116.1(1)°] than at atom Li2 [112.5(1)°]. However, the bond angles Li−N−C are identical for both molecules.

The crystals that separated from a toluene solution of $LiBH_4$ after addition of tBuNH$_2$ had the (unexpected) composition $3LiBH_4{\cdot}4t$BuNH$_2$ (**2**). This compound crystallizes monoclinically in the space group *C*2/*c*. Figure 6 represents the contents of the asymmetric unit.

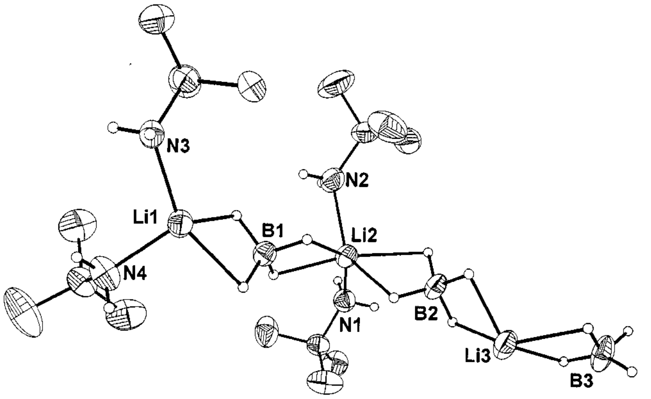


Figure 6. Molecular structure of $3LiBH_4{\cdot}4NH_2t$Bu (**2**) in the asymmetric unit; thermal ellipsoids are presented on a 25% probability scale; selected bond lengths (in Å): Li1−N4 2.076(5), Li1−N3 2.089(5), Li1···B1 2.476(5), B1···Li2 2.609(5), Li2−N1 2.086(5), Li2−N2 2.092(5), Li2···B2 2.500 (5), B2···Li3 2.404(6), Li3···B3 2.382(6); selected bond angles (in °): N3−Li1−N4 108.5(2), N4−Li1−3.1 112.6(2), N3−Li1−B1 127.8(2), B1−Li2−N1 121.9(2), B1−Li2−N2 90.2(2), B2−Li2−B1 116.1(2), N2−Li2−B2 122.1(2), B2−Li3−B3 125.2(2)

It should be noted that there are *three* different Li centers, and it is clear that only atom Li2 is coordinatively saturated (e.g. hexacoordinated) while atoms Li1 and Li3 are not. Only two of the three Li centers bind to two amine molecules each, while atom Li3 does not bear an amine ligand. The N−Li−N bond angles at Li1 and Li2 are close to tetrahedral [N3−Li1−N4, N1−Li2−N2 110.4(2)°]. If we consider the BH_4 group to be a pseudohalide − considering the boron atom as the center of a pseudofluoride − then we can assume that atom Li2 sits in a distorted tetrahedral environment, with bond angles Li−B−Li ranging from 98.1(2) to 122.1(2)°. However, the bridging hydrogen atoms are, of course, closer to the Li center than the boron atoms and are normally taken as the coordination partner. In this case it is clear that the H−Li−H bond angles must be rather sharp as a consequence of the tetrahedral BH_4 group. The typical feature of compound **2** is that, as far as the *asymmetric* unit is concerned, each BH_4 group acts as a $2\mu_2^1$ group. This is shown by the fact that we note two LiH_2B bridges from each BH_4 group to two *different* Li centers (see Figure 6). Inspection of the structure of **2** in the lattice shows that the molecular part of the asymmetric unit is the subunit of an extended chain (see Figure 7). We see that atom Li3 is surrounded by three BH_4 groups that supply, in total, five hydrogen atoms for coordination. For this $Li(BH_4)_3$ unit, two BH_4 groups retain one B−H bond in a terminal position and the other three H atoms form a double hydride bridge and a single bridge to atoms Li3 and Li3A, respectively. The third BH_4 group (B2) interacts with atom Li3 through two hydride bridges. Atom Li1 is hexacoordinated: There are two hydrogen atoms each from two different BH_4 groups (Figure 7). However, the group $B(1)H_4$ is exceptional because all four H atoms coordinate to Li centers (Li1, Li2). The bonding mode in this case is $2\mu_1^2,2\mu_1^1$.[6b] Li2 is also hexacoordinated, but in a different way to Li1 because the two adjacent BH_4 groups supply double hydride bridges. In summary, two Li atoms of **2** are hexacoordinated and one is pentacoordinated.

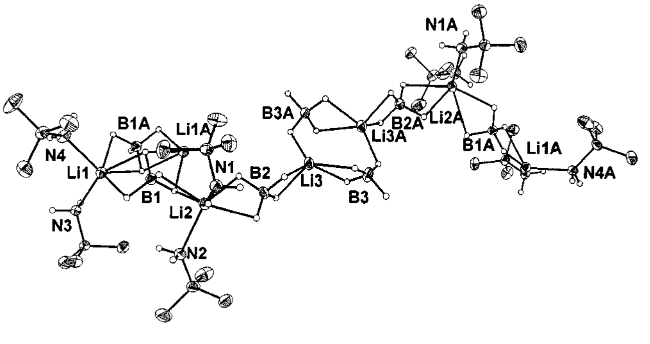
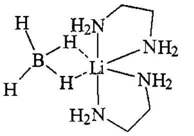


Figure 7. Chain arrangement of $3LiBH_4{\cdot}4NH_2t$Bu (**2**) in the lattice; note the pentacoordination at atom Li3

Ethylenediamine (en) is the simplest primary diamine. It forms the solvate $LiBH_4{\cdot}2en$ (**3**) which by X-ray structure determination is shown to be the ionic compound $[Li(en)_2]BH_4$ in the solid state. The cationic part does *not* have the simple structure, as shown by formula **3b**. Rather the $Li(en)_2$ unit forms an extended chain (Figure 8) because every Li center is part of only one LiN_2C_2 five-membered ring. The second en molecule bridges the Li atoms as indicated in formula **3c**. The BH_4 groups do not coordinate with Li atoms. Figure 9 shows a view of the contents of **3** in the unit cell down the *b* axis.



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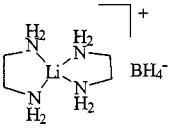

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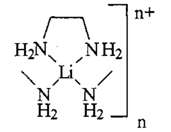

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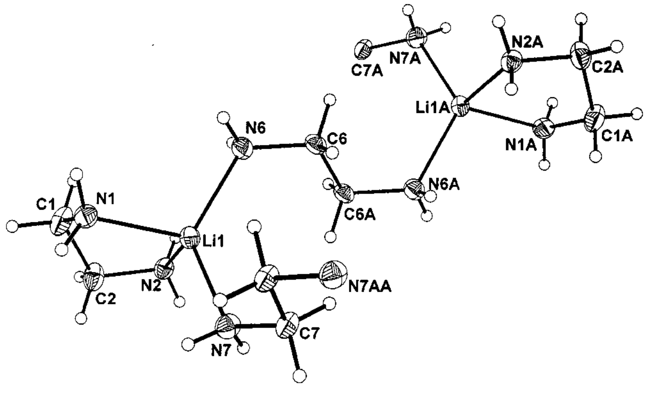


Figure 8. The Li(en)$_2$ chain in the lattice of LiBH$_4$·2en (**3**); only part of one of the two independent chains is presented but data are given for both cations; selected bond lengths (in Å): cation of molecule 1: N1−C1 1.468(3), N2−C2 1.466(2), N1−Li1 2.059(3), N2−Li1 2.052(3), N6−Li1 2.059(4), N7−Li1 2.071(4), B1−H 1.09(6)−1.16(3); cation of molecule 2: N3−C4 1.465(3), N4−Li3 1.464(3), N3−Li2 2.061(3), N4−Li2 2.059(4), N5−Li2 2.060(4), N8−Li2 2.065(4), B2−H 1.05(3)−1.16(3); selected bond angles (in °): C1−N1−Li1 102.5(2), C2−N2−Li1 102.8(1), N7−Li1−N6 123.7(2), N1−Li1−N6 108.8(2), N2−Li1−N7 100.6(2), N1−Li1−N7 113.6(2), N2−Li1−N6 111.0(2), N2−Li1−N1 88.3(1); for molecule 2: N4−Li2−N5 110.2(2), N5−Li2−N3 109.0(2), N5−Li2−N8 124.0(2), N4−Li2−N3 88.2(1), N4−Li3−N8 106.0(2), N3−Li2−N8 113.5(2)

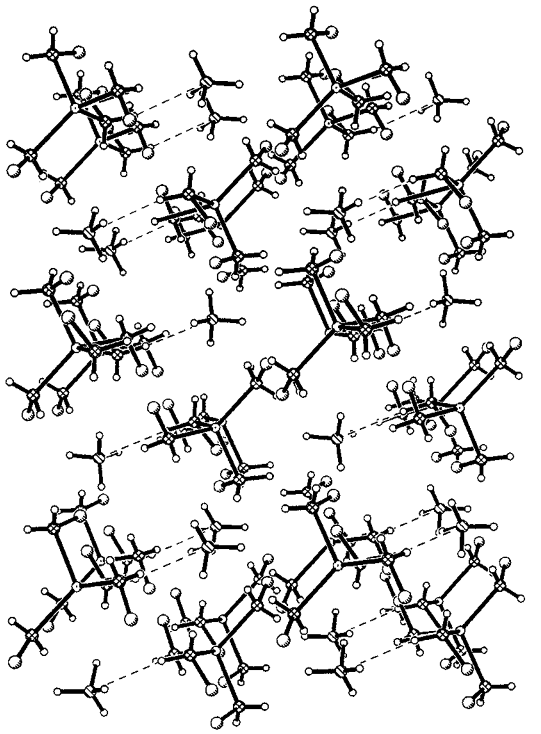


Figure 9. Plot of the structure of compound **3** in the crystal in a view down the *b* axis

The solvate of lithium tetrahydridoborate with diethylenetriamine has the composition LiBH$_4$·(H$_2$N−CH$_2$−CH$_2$)$_2$NH (**4**). Figure 10 describes the structure of two formula units of **4** in the crystal which form part of an extended chain. Each Li atom is hexacoordinated by three nitrogen and three hydrogen atoms. Each BH$_4$ group supplies three hydrogen atoms through three Li···H−B bridges (μ_3^1-mode). Consequently, the Li···B atom distance is fairly short at 2.336(4) Å. The Li···N distances range from 2.085(3) to 2.161(3) Å, the longest bond being formed with the secondary nitrogen atom of the triamine. It is interesting that the amine does not act as a tridentate ligand in forming complex **4a**. Rather a chain structure results with a *syn* orientation of the BH$_4$ groups. Li···H distances span a small range, the shortest distance being 2.13 Å and the longest 2.29 Å, while the B···H distances to the terminal hydrogen atom H [1.17(3) Å] seem to be longer than the three bridge B−H bonds [1.03(3), 1.10(3), and 1.15(3) Å]. Inspection of the geometry of the BH$_4$ group reveals the presence of a distorted *tetrahedron* whose H−B−H bond angles can be quite narrow (103°) or quite open (122°). As expected, the N2−Li1−N3 bond angle of the LiN$_2$C$_2$ five-membered ring is small [85.8(1)°] while the bond angle N(1B)−Li1−N2 is tetrahedral [109.8(1)°]. Astonishingly, the N−C−C bond angles also vary significantly, the smallest one being 109.2(2)° and the largest 116.0(2)°.

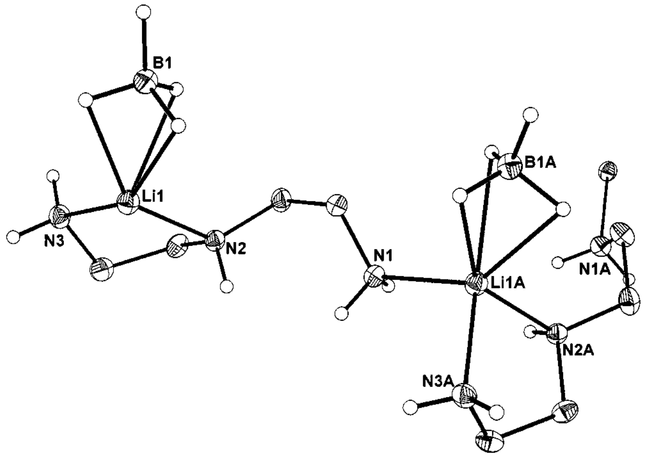
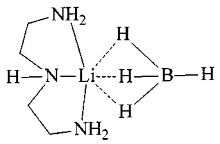


Figure 10. Structure of LiBH$_4$·triene (**4**); two molecular units that are part of a chain are depicted; thermal ellipsoids are drawn on a 25% probability scale; selected atom distances (in Å): Li1−N2 2.161(3), Li1−N3 2.085(3), Li1···B1 2.336(4), N1−Li1A 2.698(3), B−H (term.) 1.17, B−H (bridge) 1.03−1.15; selected bond angles (in °): Li1−N3−C4 101.5(1), Li1−N2−C3 102.8(1), Li1A−N1−C1 117.3(1), H13−B1−Li1 164.2(2), N3−Li1−N2 85.8(1), N1B−Li1−B1 113.3(1), N3−Li1−H13(term.) 151.4(2), N3−Li1−N1B 100.0(1), N2−Li1−N18 109.8(1), N3−Li1−B1 124.4(1), N2−Li1−B1 119.5(1); note that N1B binds to Li1



4a

Lithium tetrahydridoborate−pyrrolidine, LiBH$_4$·HNC$_4$H$_8$ (**5**), was not expected to have a simple structure because there is only one amine ligand available for coordination to the Li center. Moreover, the crystal contains toluene, its composition being 2LiBH$_4$·2NHC$_4$H$_8$·C$_6$H$_5$CH$_3$.

Figure 11 represents the contents of the asymmetric unit of **5** in the triclinic cell. This arrangement is reminiscent of the structure of [LiBH$_4$·tmen][14] because the two BH$_4$ groups are of the $2\mu_1^1,\mu_1^2$ type, i.e. there are two single Li−H−B bridges to two different Li centers while a third hydrogen atom bridges two Li atoms. In addition, another BH_4 group supplies two H atoms through LiH_2B bridges. This situation means that the Li centers are heptacoordinated.

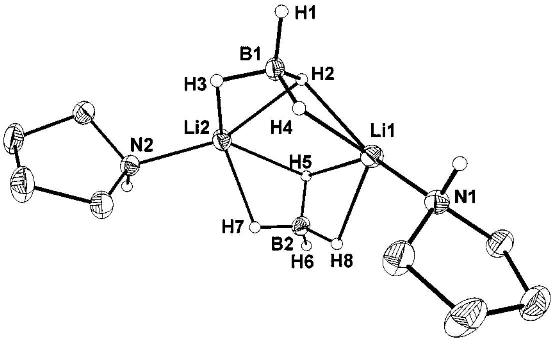


Figure 11. Structure of $LiBH_4\cdot HNC_4H_8$ (**5**) in the crystal; the contents of the asymmetric unit are depicted; the C atoms of the disordered toluene molecule are not included; thermal ellipsoids are drawn on a 25% probability scale; selected atom distances (in Å): N1−Li1 2.022(6), N2−Li2 2.205(5), Li1−B1 2.561(6), Li1−B2 2.530(6), Li2−B1 2.527(6), Li2−B2 2.569(6), Li1−H 2.08−2.23, Li2−H 2.03−2.09, B1−H 1.08(3)−1.15(3), B2−H 1.05(4)−1.14(4); selected bond angles (in °): N1−Li1−B1 116.5(2), N1−Li1−B2 118.6(2), N2−Li2−B1 118.0(2), N2−Li2−B2 116.7(2), N1−Li1−H8 95(1), N1−Li1−H5 145.0(9), N1−Li1−H2 141.0(9), N1−Li1−H4 93(1), N2−Li2−H7 94(1), N2 − Li2−H5 140.9(9), N2−Li2−H3 92.4(9)

The structure of **5** shows short Li−N bonds [2.024(6) Å] and rather uniform Li···H distances [2.09(3) Å], and this is also true for the B−H bond lengths [1.10(4)−1.15(4) Å]. The H−B−H bond angles are close to tetrahedral, meaning that the asymmetry induced at the BH_4 groups by the different interactions of its hydrogen atoms with the Li centers is not reflected in different bond angles.

Figure 12 shows how the smallest unit forms an infinite chain in the lattice by the action of inversion center. For the sake of clarity several pyrrolidine units are not depicted. The result of this symmetry operation is also depicted in Figure 13, which shows a view down the *b* axis. In the chain each Li center is not only coordinated to an N atom but also to three different BH_4 groups, all of which are of the $2\mu_1^1,\mu_1^2$ type.

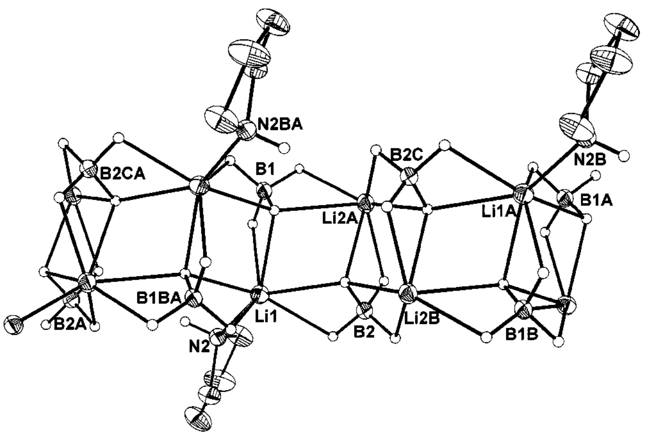


Figure 12. View of the chain of compound **5** in the lattice; only part of the pyrrolidine ligands is depicted in the interest of clarity

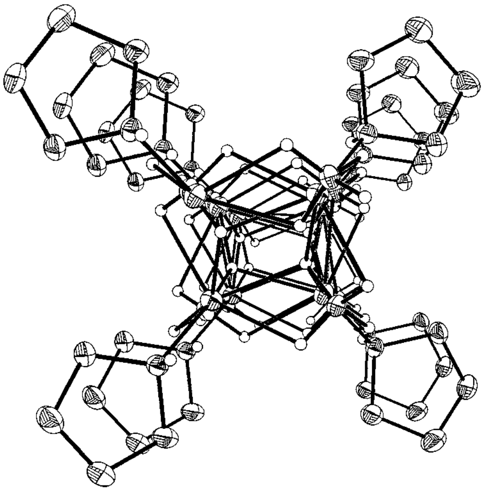


Figure 13. View of the chain down the *b* axis

It is amazing that $LiBH_4$ adds only one pyrrolidine molecule but two dibenzylamines in spite of the fact that the dibenzylamine is sterically more demanding. Compound **6**, $LiBH_4\cdot 2HN(CH_2Ph)_2$, crystallizes in the monoclinic system and the unit cell contains dimeric units. Figure 14 depicts the molecular structure of this system, which has a center of symmetry.

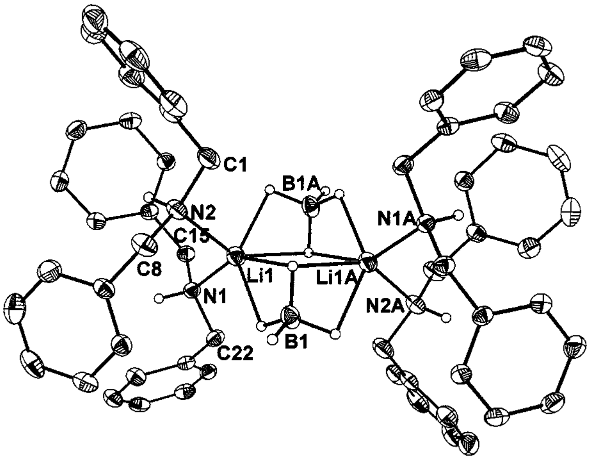


Figure 14. Molecular structure of dimeric $LiBH_4\cdot 2NH(CH_2Ph)_2$ (**6**); thermal ellipsoids are drawn on a 25% probability scale; selected atom distances (in Å): Li1−N1 2.126(3), Li1−N2 2.131(4), Li1···B1 2.516(4), Li−H 1.9−2.2, B−H 1.1−1.2; selected bond angles (in °): N1−Li1−N2 107.5(1), N1−Li1−B1 122.0(1), N2−Li1−B1 101.9(2), Li1−B1−Li1A 80.3(1), B1−Li1−B1A 99.7(1)

The structure of **6** is analogous to the structure of $(LiBH_4\cdot tmen)_2$.[14] As expected the N1−Li1−N2 bond angle is wider (107.5°) than for $[LiBH_4\cdot tmen]_2$ (74.6°) because the nitrogen atoms are not constrained in a five-membered ring. A second consequence is that the Li−N bond lengths are shorter.

We have already reported that $[LiBH_4(MeNCH_2)_3]_2$[6b] has a structure closely related to the structure of $[LiBH_4\cdot tmen]_2$,[14] because only *two* of the *three* nitrogen atoms of $(MeNCH_2)_3$ coordinate to a Li center.[6b] A structure related but different to $[LiBH_4(MeNCH_2)_3]_2$ is displayed by dimeric $LiBH_4(i\text{Pr}NCH_2)_3$ (**7**). As Figure 15 reveals, all three nitrogen atoms of the amine ligand are now bonded to the Li ion, and two monomeric units are joined through two $\mu_1^2,2\mu_1^1$-BH$_4$ units. Nevertheless, the triazacyclohexane ligand is not symmetrically bonded to the Li center; Li−N bond lengths are 2.10(1), 2.20(1), and 2.38(1) Å; Li−H distances range from 1.93 to 2.17 Å.

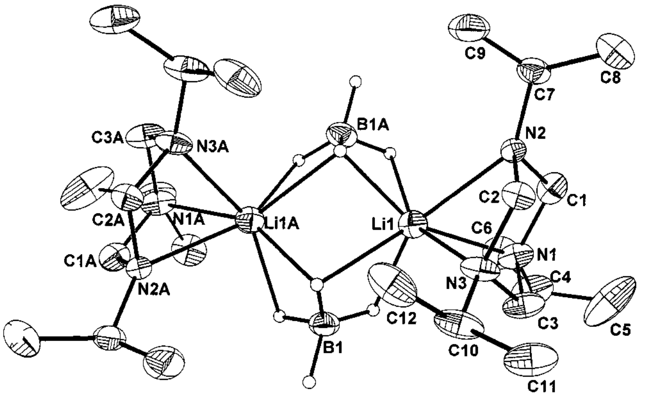


Figure 15. ORTEP plot of dimeric LiBH$_4$·(*i*PrNCH$_2$)$_3$ (**7**); hydrogen atoms bonded to carbon atoms are omitted; thermal ellipsoids represent a 25% probability; selected atom distances (in Å): Li1−N1 2.10(1), Li1−N2 2.38(1), Li1−N3 2.20(1), Li1···B1 2.53(1), Li1−H2 (Li1A) 1.93(6), Li1−H1 2.00(1), B−H (term.) 1.14(6), B−H (bridges) 1.12−1.14(5); selected bond angles (in °): N1−Li1−N3 65.5(4), N1−Li1−N2 62.9(4), N3−Li1−N2 60.8(4), B1−H1−Li1 (μ_1^1) 103.8(9), B1−H2−Li1 (μ_1^2) 100.7(6), B1−H2−Li1A (μ_1^2) 94.4(6), Li1A−H3−B1 (μ_1^1) 94.4(1), Li1−H2−Li1A 97.8(1)

If the reaction of LiBH$_4$ with (MeNCH$_2$)$_3$ is performed in toluene instead of in boiling xylene,[6b] then the product formed does not have a 1:1 composition but is 2LiBH$_4$·(MeNCH$_2$)$_3$ (**8**). The crystals of this compound are orthorhombic with space group *Pcca* but the structure could also be solved in the monoclinic space group *P*2$_1$/*c*. Figure 16 shows the contents of the asymmetric unit, which formally consists of a dimeric unit of **8**.

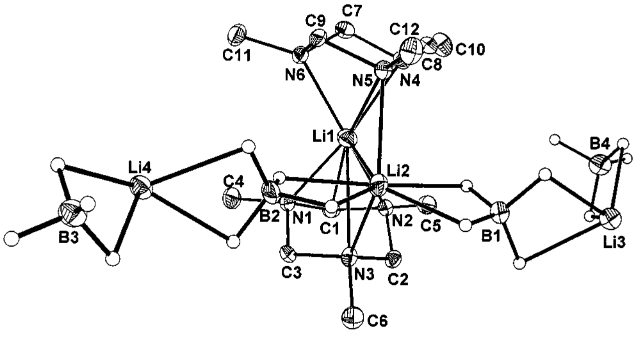


Figure 16. ORTEP plot for the contents in the asymmetric unit of 4LiBH$_4$·2(MeNCH$_2$)$_3$ (**8**); CH hydrogen atoms are omitted; thermal ellipsoids are depicted on a 25% probability scale; selected atom distances (in Å): Li1−N1 2.674(3), Li1−N2 2.141(1), Li1−N3 2.115(2), Li1···Li2 2.770(5), Li2−N1 2.297(2), Li2−B1 2.429(2), Li3···B1 2.376(3), Li3···B2 2.349(3), B3···Li3 2.319(3); selected bond angles (in °): N3−Li1−N1 58.48(6), N2−Li1−N1 57.83(6), N2−Li1−N3 66.28(5), N1−Li−N1A 99.75(1), N2−Li1−N2A 166.8(2), N3−Li1−N3A 157.4(2), N1−Li2−N1A 125.8(2), Li2−B1−Li3 161.2(2), B1−Li3−B2 126.2(1), Li3−B2−Li3B 167.8(2), B3−Li3−B1 126.2(1), B2−Li3−B3 125.4(1)

At first glance the unusual structural feature of compound **8** is that one Li center is "centrally" coordinated to two (MeNCH$_2$)$_3$ molecules while a second Li ion coordinates to two N atoms of the "sandwiched" Li1 atom. A closer look reveals that Li1 is asymmetrically coordinated to the N donor atoms and resides on a crystallographic twofold axis. There are four short Li1−N distances [2.115(2) to 2.142(1) Å] and two long ones [2.674(3) Å]. These latter distances are longer than the Li−C distances of Li1 to atoms C1 and C1A [2.467(2) Å]. The orientation of the two rings with respect to one another represents an "eclipsed" position. Atom Li2 coordinates with atoms N1 and N1A and the Li2−N bond lengths are 2.297(2) Å. One of the reasons for this asymmetry in coordination is the rather short Li1···Li2 distance of 2.770(5) Å.

The second feature is the presence of a layer structure of composition [Li$_3$(BH$_4$)$_4$]$^-$. Each Li center in this layer is hexacoordinated by six hydrogen atoms stemming from three BH$_4$ groups, each one corresponding to two Li(H$_2$)B units. This kind of 2μ_2^1 coordination finally leads to the two-dimensional array of LiBH$_4$ units as depicted in Figure 17. Thus, compound **8** can be given the formula [Li{(MeNCH$_2$)$_3$}$_2$][Li$_3$(BH$_4$)$_4$] where the chain atom Li2 "shares" the nitrogen atoms N1 and N1A with Li1.

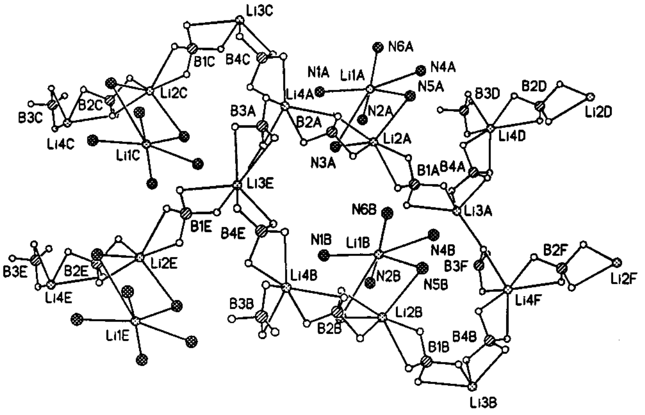


Figure 17. Part of the layer structure of compound **8** in the crystal; extension to the layer is through the B3- and Li3-type atoms; C and H atoms of the amine ligand have been removed for the sake of clarity; here, the structure is shown for the refinement in space group *P*2$_1$/*c*; in this space group the atoms on B3 and Li3 could be located and refined. However, it is more likely that the orthorhombic space group *Pcca* is correct; in this case atom B3 resides on a mirror plane and only three hydrogen atoms could be located but not the fourth; the action of the mirror plane leads, of course, to disorder of the H atoms of this BH$_4$ group

However, when 1,3,5-tribenzyl-1,3,5-triazacyclohexane is employed as a ligand for LiBH$_4$ then compound **9** is formed and this, by X-ray structure determination, can best be described as {Li[(PhCH$_2$NCH$_2$)$_3$]$_2$]}[Li$_2$(BH$_4$)$_3$]. The high steric demand of the ligand (PhCH$_2$NCH$_2$)$_3$ leads to a separation of one Li cation, out of three LiBH$_4$ units, from its anion with formation of the cation Li[(PhCH$_2$NCH$_2$)$_3$]$_2$$^+$, as shown in Figure 18. The Li center occupies a special position.

It should be noted that the six Li−N distances of the cations Li1 and Li4 are rather similar, spanning the range from 2.223(2) to 2.293(3) Å. Atoms Li1 and Li4 are located on a crystallographic inversion center and, consequently, three N−Li−N bond angles within each cation are 180°.

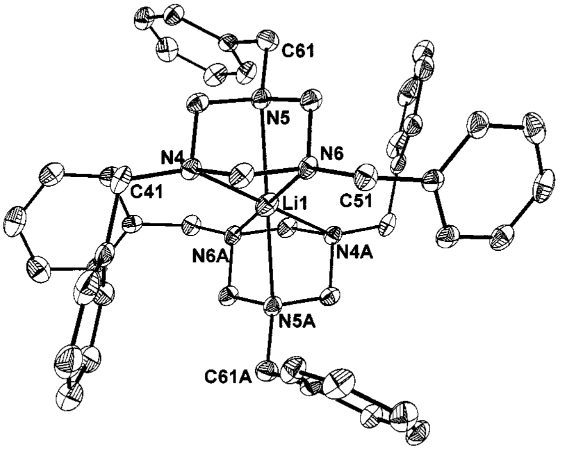


Figure 18. One of the two independent centrosymmetric [Li$(PhCH_2NCH_2)_3$] cations of compound **9**; hydrogen atoms omitted; selected atom distances (in Å): Li1−N4 2.339(3), Li1−N5 2.285(3), Li1−N6 2.315(3); selected bond angles (in °): N4−Li1−N5 60.9(1), N4−Li1−N6 60.9(1), N5−Li1−N6 61.3(1); N4−Li1−N4A 180

For each heterocycle all N−Li−N bond angles are close to 63°.

The plot shown in Figure 19 demonstrates that the cations Li$[(PhCH_2NCH_2)_3]_2^+$ separate the chain structure of the anionic part of **9**. There are two different kinds of BH_4 units. The BH_4 groups of atoms B1 and B3 are typical $2\mu_1^1,\mu_1^2$ ligands, each having one terminal B−H bond. However, the BH_4 group of atom B3 uses all of its four hydrogen atoms for bridging to three Li atoms in a $3\mu_1^1,\mu_1^2$ function. However, there were non-negligible residuals around atom B2, and particularly at the adjacent Li3 atom. Moreover, the thermal motion of atom B2 was suspect and the tricoordinated H atom shows a somewhat longer Li−H distance [2.17(5) Å] than the dicoordinated H atoms. Indeed, refinement of the H atom positions of this exceptional BH_4 group was best for a disorder involving two sites, one with one Li−H bond (2.1 Å) and an almost planar BH_3 group, and a second site with a distorted BH_4 group. This disorder refined well with SOF = 0.5 (see Figure 20). Indeed, the thermal ellipsoid for B3 is compatible with this kind of disorder. It seems, therefore, that a BH_3 group is stabilized by the lattice. We have noticed this kind of structure in two out of three crystal structure determinations of compound **9**. Consequently, we found an electron density for a hydrogen atom bonded to Li3 (2.1 Å). The plot in Figure 19 demonstrates the packing of the cations and anion in the lattice.

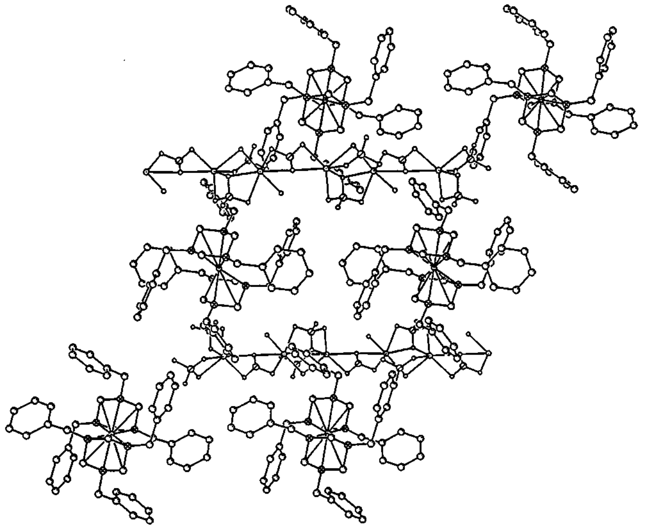


Figure 19. Arrangements of atoms in compound **9** in the crystal separated into Li$[(PhCH_2NCH_2)_3]_2$ cations and anionic $[Li_2(BH_4)_3]$ chains; these are depicted for the BH_3/LiH disorder in the chain

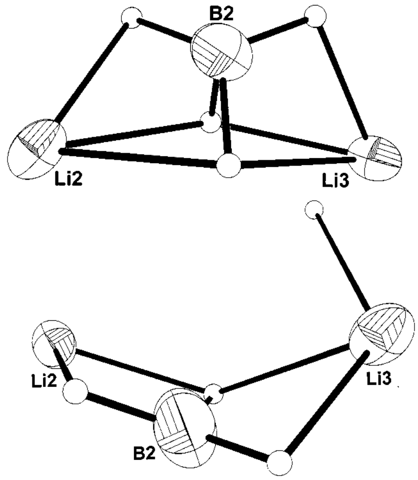


Figure 20. Disordered arrangement of the B2(H)$_4$ group between atoms Li2 and Li3; the tetrahedral BH_4 group (top) and the BH_3 (LiH) group (bottom)

Discussion

It has previously been noted that the bonding mode of the BH_4 group in mononuclear $LiBH_4\cdot nL$ species depends on the number of ligands L and their steric demand. For $n = 3$ and L = pyridine[6b] or aniline the anion BH_4^- uses three of its hydrogen atoms to form Li−H−B bridges. However, if the ligand is sterically more demanding, e.g. collidine with $n = 2$, only a bidentate μ_2^1-BH_4 group is present.[6b]

On the other hand, if the ratio Li/N is 1:2, as found for $LiBH_4\cdot 2HN(CH_2Ph)_2$ (**6**), dimers are formed. The structure and bonding of **6** correspond with the prototype of this pattern, $[LiBH_4\cdot tmen]_2$,[14] where the BH_4 group functions as a $2\mu_1^1,\mu_1^2$-ligand, i.e. one hydrogen atom binds to two Li centers with the other two forming single Li−H−B bridges. This structural feature is also realized in $[LiBH_4\cdot(MeNCH_2)_3]_2$ even if the Li/N ratio is 1:3. However, the effective Li/N ratio is 1:2 because only two out of the three nitrogen atoms of the ligand coordinate strongly to the Li center.[6b] In compound **2**, $3LiBH_4\cdot 4H_2NtBu$, the Li/N ratio is only 1:1.33. Thus, the Li ions cannot all be coordinated by two nitrogen atoms. The possible structures $(LiBH_4\cdot 2H_2NtBu)\cdot 2(LiBH_4\cdot H_2NtBu)$ or $[Li(H_2NtBu)_4]$-$[Li_2(BH_4)_3]$ are not formed but rather

$2(LiBH_4{\cdot}2H_2NtBu){\cdot}(LiBH_4)$. The "$LiBH_4$" part is, of course, coordinatively unsaturated and shares BH_4 groups with the amine carrying $LiBH_4{\cdot}2H_2NtBu$ units, as depicted in Figure 7.

This feature becomes even more apparent for $LiBH_4{\cdot}HNC_4H_8$ (**5**) with a ratio Li/N = 1:1. Formation of a chain structure through BH_4 sharing leads to hexacoordinated, coordinatively saturated Li centers. In this case, the BH_4 group joins two Li ions through $2\mu_2^1$ bridges and all four hydrogen atoms are used for coordination through double hydrogen bonds $Li(H)_2B$.

Unexpectedly, $LiBH_4{\cdot}(iPrNCH_2)_3$ (**7**) also forms dimers like $LiBH_4{\cdot}$tmen, and $LiBH_4{\cdot}(MeNCH_2)_3$, in spite of the fact that in **7** all three N atoms of the heterocycle coordinate to Li while in the other two compounds the Li centers carry only two N atoms. However, the coordination in **7** is asymmetric: There are two short Li−N distances (2.10, 2.20 Å) and a significantly longer one (2.38 Å). This situation is in contrast to that in $LiBH_4{\cdot}$PMDTA,[6b] which is mononuclear in spite of the fact that the three nitrogen atoms of the pentamethyldiethylenetriamine ligand are also asymmetrically bonded. Clearly, PMDTA is sterically more demanding than $(iPrNCH_2)_3$, and this may be the reason why **7** is dimeric in the crystal.

An Li/N ratio of 1:1.5 is present in the compound $2LiBH_4{\cdot}(MeNCH_2)_3$ (**8**) and a 1:2 ratio in $3LiBH_4{\cdot}2(PhCH_2NCH_2)_3$ (**9**). In both cases, extended structures are formed but there are significant differences between the two compounds. Due to the large steric effect of the ligand tribenzyl-1,3,5-triazacyclohexane, one Li center is "sandwiched" between two amine ligands, which surround the cation centrosymmetrically. Thus, compound **9** contains tris(tetrahydridoborato)dilithiate anionic units, which form a chain structure in the crystal. In the case of compound **8** the nitrogen ligand also sandwiches a Li center by four short and two longer Li−N bonds, but two of the six nitrogen atoms bind a second Li atom, which is additionally coordinated to two BH_4 groups. The resulting unit, which finally leads to a layer structure, therefore has the composition $Li_3(BH_4)_4^-$, where one of the three Li centers coordinates with the amine ligand.

Since the BH_4 group can be regarded as a "pseudofluoride" one may expect that amine complexes of lithium halides form similar structures. However, structural analogs of the amine complexes of $LiBH_4$ have not been reported to date. The only compound having an extended chain is LiCl−15-crown-5.[15] All others are either dimeric, trimeric, or tetrameric.[16] In these cases pyridines, tmen, or PMDTA were used as ligands and comparisons are limited. Thus, at the present time, the anion BH_4^- proves to be a most versatile ligand. In addition, it is demonstrated for the first time that certain amine solvates of $LiBH_4$ form polymeric anionic units $[Li_n(BH_4)_{n+1}]^-$. However, the solid-state structures do not seem to be retained in solution because only one type of BH_4 ion is detected by ^{11}B NMR spectroscopy as well as single ^7Li resonances, irrespective of the various kinds of structures found for the solid state.

Experimental Section

All experiments were performed under dry nitrogen with strict exclusion of moisture. Consequently, all solvents were dried and stored under nitrogen. $LiBH_4$ was of commercial grade (Chemetall GmbH), as were the amines, which were dried by treatment with CaH_2 followed by distillation, in the case of liquids, or by recrystallization of the vacuum-dried solids. − NMR: Bruker AC 200 (^{11}B), Jeol 270 (^1H, ^{13}C), Jeol EX400 (^7Li); Standards: $BF_3{\cdot}OEt_2$ external; 1 M aq. LiCl solution, external; C_6D_6 and $SiMe_4$ internal. − IR: Nicolet-FT spectrophotometer. − Elemental analyses: Microanalytical Laboratory of the Department of Chemistry, University of Munich.

Lithium Tetrahydridoborate−Aniline(1:3) (1): $LiBH_4$ (231 mg, 10.6 mmol) was suspended in aniline (20 mL). After stirring for 20 min, the turbid solution was filtered and the filtrate stored at 8 °C. Clear needles of **1** suitable for X-ray structure analysis separated within a few days. Yield: 257 mg of **1** (8%), m.p. 58−62 °C (dec.). On removing aniline from the filtrate a larger amount of **1** was isolated (yield not determined). − NMR (in aniline): ^7Li NMR: δ = 0.1(3). − ^{11}B NMR: δ = −38.0 [quint, $^1J(^{11}B^1H)$ = 81 Hz]. − IR (Nujol, B−H stretching region): $\tilde{\nu}$ = 2377 cm^{-1} w, 2331 m, 2252 vst, 2196 m, 2183 m. − $C_{18}H_{25}BLiN_3$ (301.23): calcd. C 71.79, H 8.37, N 13.95; found C 69.77, H 8.52, N 13.53.

Lithium Tetrahydridoborate−*tert*-Butylamine(3:4) (2): $LiBH_4$ powder (250 mg, 11 mmol) was suspended in toluene (10 mL) with stirring and *tert*-butylamine (1.2 mL, 11.3 mmol) was added. The suspension was heated at reflux for 30 min. The insoluble material was removed by filtration (G3 frit) and the solution cooled to −20 °C in a refrigerator. Clear needles separated from the solution within one week. Yield: 190 mg (18%), m.p. ca. 10 °C. A further quantity of compound **2** was isolated from the concentrated filtrate. − NMR (C_6D_6 + TMS): ^7Li NMR: δ = 1.07. − ^{11}B NMR: δ = −38.3 [quint, $^1J(^{11}B^1H)$ = 81 Hz]. − IR (B−H stretching region): $\tilde{\nu}$ = 2366 cm^{-1} st, 2320 st, 2275 st. − $C_{16}H_{56}B_3Li_3N_4$ (357.90): calcd. C 53.69, H 15.77, B 9.06, Li 5.82, N 15.65; found C 51.96, H 15.92, B 8.9, Li 5.9, N 16.62.

Lithium Tetrahydridoborate−Ethylenediamine(1:2) (3): $LiBH_4$ (58.5 mg, 2.69 mmol) was suspended in a mixture of ethylenediamine (171 mg, 2.85 mmol) and pyridine (5 mL). After addition of methylcyclohexane (1 mL) the slightly turbid solution was subjected to filtration and the filtrate kept at 8 °C. Crystals of **3** separated in a few hours. These crystals deteriorated quickly in a stream of nitrogen. Yield: 35 mg of **3** (9%), m.p. 91 °C. From the filtrate a further quantity of **3** could be obtained by reducing the volume of the solution. − NMR (pyridine): ^7Li NMR: δ = 2.0. − ^{11}B NMR: δ = −38.3 [quint, $^1J(^{11}B^1H)$ = 81 Hz]. − IR (Nujol, B−H stretching region): $\tilde{\nu}$ = 2300 cm^{-1} sh, 2252 st, 2220 sh, 2183 m, 2147 m. − A satisfactory elemental analysis could not be obtained.

Lithium Tetrahydridoborate−Diethylenetriamine (4): $LiBH_4$ (190 mg, 8.71 mmol) was dissolved in a mixture of diethylenetriamine (895 mg, 8.67 mmol) and pyridine (10 mL). After stirring for 15 min, toluene (1 mL) was added and insoluble material was removed by filtration. After keeping the solution at 8 °C, colorless prisms separated. Yield: 121 mg (11%), m.p. 110−118 °C (dec.). − NMR (pyridine): ^7Li NMR: δ = 1.7 (s). − ^{11}B NMR: δ = −38.1 [quint, $^1J(^{11}B^1H)$ = 81 Hz]. − IR (Nujol, B−H stretching region): $\tilde{\nu}$ = 2326 cm^{-1} sh, 2251 st br, 2219 sh, 2182 sh. − $C_4H_{17}BLiN_3$ (125.17): calcd. C 38.45, H 13.71, N 33.63; found C 38.68, H 13.39, N 32.14.

Lithium Tetrahydridoborate−Pyrrolidine (5): A suspension of $LiBH_4$ (410 mg, 19 mmol) in toluene (45 mL) and pyrrolidine (1.56 mL, 18.9 mmol) was heated to reflux for 10 min. Most of the solid dissolved and the insoluble material was removed from the hot solution. The filtrate was cooled to −20 °C. Colorless needles separated within 12 h. The needles were isolated by filtration using a cooled frit. Single crystals for X-ray determination were removed directly from the suspension. Yield: 106 mg (54%), m.p. ca. 0 °C. − NMR (C_6D_6 + TMS): ^{7}Li NMR: δ = 1.32. − ^{11}B NMR: δ = −41.1 [quint, $^1J(^{11}B^1H)$ = 87 Hz]. − IR (B−H stretching region): ṽ = 2252 cm^{-1} st, 2279 st, 2355 sh. − $C_4H_{13}BLiN$ (92.90): calcd. C 48.05, H 14.87, B 11.64, Li 7.47, N 15.08; found C 48.79, H 14.00, B 11.0, Li 7.4, N 15.47.

Lithium Tetrahydridoborate−Dibenzylamine(1:2) (6): Dibenzylamine (50 mL) was saturated with $LiBH_4$ and excess $LiBH_4$ was removed by filtration. The clear solution was layered with cyclohexane (20 mL). A precipitate formed and was filtered off. ^{11}B NMR of the solution showed the presence of a BH_4 unit and a BH_3 group in a 3:7 ratio. The filtrate was cooled to 8 °C. Crystals of **6** separated as colorless prisms, m.p. 81−83 °C (dec.). − ^{11}B NMR: δ = −38.2 [quint, $^1J(^{11}B^1H)$ = 81 Hz], −14.0 (broad). − ^{1}H NMR (C_6D_6): δ = 0.6 [1:1:1:1 q, $^1J(^{11}B^1H)$ = 81 Hz]. − IR (B−H stretching region): ṽ = 2370 cm^{-1} st, 2332 st, 2305 st, 2272 st, 2238 st. − $C_{28}H_{34}BLiN_2$ (416.30): calcd. C 80.78, H 8.23, N 6.73, B 2.60, Li 1.67; found C 76.91, H 7.91, N 6.42, B 2.95, Li 1.97.

Lithium Tetrahydridoborate−1,3,5-Triisopropyl-1,3,5-triazacyclohexane (7): To a stirred suspension of $LiBH_4$ (440 mg, 20 mmol) in toluene (36 mL) was added the ligand (4.84 mL, 20.2 mmol). Most of the $LiBH_4$ dissolved on heating the suspension at reflux for 30 min. Insoluble material had to be rapidly removed from the suspension because crystals settled quite quickly from the solution on cooling to room temperature. Yield: 1.9 g (40%), m.p. 98−102 °C (dec.). − ^{7}Li NMR (toluene): δ = 0.097. − ^{11}B NMR (C_6D_6 + TMS): δ = −15.9 [q, $^1J(^{11}B^1H)$ = 60 Hz], −38.5 [quint, $^1J(^{11}B^1H)$ = 81 Hz], ratio ca. 1:8. − IR (B−H stretching region): ṽ = 2185 cm^{-1} st, 2250 m, 2283 m, 2316 w, 2334, w, 2378 st. − $C_{12}H_{31}BLiN_3$ (235.14): calcd. C 61.29, H 13.29, B 4.60, N 17.87; found C 59.92, H 12.96, B 4.30, N 18.52.

Lithium Tetrahydridoborate−(1,3,5-Trimethyl-1,3,5-triazacyclohexane)(4:2) (8): Lithium tetrahydridoborate (1.03 g, 47.4 mmol) was suspended in toluene (40 mL). The amine (6.65 mL, 47.4 mmol) was added to the stirred suspension and stirring was continued for 2 h. The suspension was quickly heated to reflux and kept at this temperature for 10 min. Insoluble materials were removed from the hot solution and the filtrate cooled to −20 °C. Prismatic crystals separated within 12 h. Yield: 2.97 g (73.4%), m.p. 78 °C. − ^{7}Li NMR (toluene): δ = 0.74. − ^{11}B NMR (toluene): δ = −38.6 [quint, $^1J(^{11}B^1H)$ = 86 Hz]. − IR (B−H stretching region): ṽ = 2184 cm^{-1} sh, 2253 st, 2319 m, 2328 m, 2373 st. − $C_{12}H_{42}B_4Li_4N_6$ (341.48): calcd. C 42.20, H 12.40, B 12.66, N 24.61; found C 42.10, H 12.05, B 12.10, N 24.62.

Lithium Tetrahydridoborate−(1,3,5-Tribenzyl-1,3,5-triazacyclohexane)(3:2) (9): To a stirred suspension of $LiBH_4$ (220 mg, 10 mmol) in toluene (20 mL) was added the amine ligand (3.57 g, 10.1 mmol). After keeping the mixture at reflux for 1 h, the hot suspension was filtered. Crystals separated within 4 h from the filtrate, which was kept at −20 °C. Yield: 720 mg (28%), m.p. 134−136 °C. A second crop was isolated on reducing the volume of the filtrate under vacuum. The yield of the second crop was not determined. − ^{7}Li NMR (C_6D_6 + TMS): δ = 0.347. − ^{11}B NMR ([D$_8$]toluene): δ =

Table 2. Crystallographic data and data referring to structure solution and refinement

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Empirical formula	$C_{36}H_{50}B_2Li_2N_6$	$C_{16}H_{56}B_3Li_3N_4$	$C_8H_{40}B_2Li_2N_8$	$C_4H_{17}BLiN_3$	$C_{10.5}H_{28}BLi_2N_2$	$C_{28}H_{34}BLiN_2$	$C_{12}H_{31}BLiN_3$	$C_6H_2B_2Li_2N_3$	$C_{48}H_{66}B_3Li_3N_6$
Mol. mass	602.32	357.90	283.98	124.96	217.85	416.32	235.15	170.76	780.32
Cryst. size [mm]	0.2×0.2×0.4	0.1×0.2×0.3	0.4×0.4×0.4	0.3×0.4×0.4	0.1×0.1×0.4	0.10×0.1×0.2	0.2×0.2×0.2	0.1×0.2×0.3	0.2×0.2×0.3
Cryst. system	hexagonal	monoclinic	triclinic	orthorhombic	triclinic	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	*R*3	*C*2/*c*	$P\bar{1}$	*Pbcn*	$P\bar{1}$	*C*2/*c*	*C*2/*c*	*Pcca*	*P*2(1)/*c*
a [Å]	16.089(1)	25.309(1)	8.3580(7)	17.323(2)	7.2034(3)	21.2514(3)	15.818(7)	17.393(1)	20.01(2)
b [Å]	16.089(1)	12.0228(7)	7.8086(7)	10.4162(9)	11.0569(2)	10.4618(2)	17.80(1)	8.1514(6)	18.67(2)
c [Å]	12.659(1)	20.049(1)	15.224(1)	9.7331(8)	11.1010(3)	26.1103(1)	14.51(1)	17.332(1)	13.031(8)
α [°]	90	90	90.021(1)	90	89.052(1)	90	90	90	90
β [°]	90	97.820(1)	94.237(2)	90	80.062(2)	113.72	108.79(2)	90	90.37(2)
γ [°]	120	90	90.005(2)	90	78.593(2)	90	90	90	90
V [Å^3]	2837.7(4)	6044.0(6)	990.9(2)	1756.2(3)	853.55(5)	5314.73(1)	3911(4)	2457.3(3)	4867(6)
Z	3	8	2	8	2	8	8	8	4
ρ(calcd.) [Mg/m^3]	1.057	0.787	0.952	0.945	0.848	1.041	0.799	0.923	1.065
μ [mm^{-1}]	0.061	0.043	0.059	0.057	0.046	0.059	0.046	0.052	0.061
F(000)	972	1632	320	560	242	1792	1056	752	1680
Index range	$-18 \leq h \leq 20$	$-28 \leq h \leq 28$	$-11 \leq h \leq 8$	$-21 \leq h \leq 21$	$-8 \leq h \leq 4$	$-26 \leq h \leq 26$	$-15 \leq h \leq 14$	$-23 \leq h \leq 21$	$-25 \leq h \leq 24$
	$19 \leq k \leq 19$	$-13 \leq k \leq 13$	$-9 \leq k \leq 9$	$-13 \leq k \leq 13$	$-12 \leq k \leq 12$	$-13 \leq k \leq 9$	$-22 \leq k \leq 22$	$-10 \leq k \leq 10$	$-21 \leq k \leq 22$
	$15 \leq l \leq 15$	$-21 \leq l \leq 21$	$-19 \leq l \leq 19$	$-13 \leq l \leq 8$	$-13 \leq l \leq 13$	$-32 \leq l \leq 32$	$-17 \leq l \leq 17$	$-21 \leq l \leq 21$	$-14 \leq l \leq 15$
2 θ [°]	56.60	47.64	57.84	58.22	49.42	52.74	54.88	58.74	55.18
Temp. [K]	193(2)	163(2)	183(2)	183(2)	163(5)	193(2)	153(2)	187(2)	173(2)
Refl. collected	5510	13237	5760	9257	4064	13893	10260	13752	17190
Refl. unique	2639	4205	3007	1761	2152	4582	3184	2716	7002
Refl. obs. (4σ)	1971	2975	2505	1334	1612	3229	1664	1563	3773
R (int.)	0.0250	0.0691	0.0512	0.1045	0.0287	0.0395	0.0474	0.0437	0.0678
No. variables	157	322	229	92	212	313	176	142	601
Weighting	0.0718/	0..0249/	0.1179/	0.0938/	0.1100/	0.0340/	0.2845/	0.1546/	0.0137/
scheme[a] *x*/*y*	0.000	8.0550	0.3734	0.4630	05769	2.9179	21.2104	0.000	3.3565
GOOF	0.966	1.170	1.040	1.080	1.095	1.084	1.103	1.006	1.180
Final *R* (4σ)	0.0421	0.0808	0.0705	0.0602	0.0794	0.0521	0.1529	0.0645	0.0595
Final *wR*2	0.1023	0.1433	0.1966	0.1524	0.2106	0.1020	0.4378	0.2086	0.1031
Larg. resid. peak [e/Å^3]	0.111	0.228	0.238	0.254	0.304	0.191	0.881	0.466	0.134

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

−11.9 (br), −39.4 (br), ratio ca. 1:10. − IR (B−H stretching region): $\tilde{\nu}$ = 2415 cm^{-1}, 2372, 2330, 2253, 2189, 2125. − $C_{48}H_{66}B_3Li_3N_6$ (780.32): calcd. C 71.87, H 8.78, N 10.48; found C 71.72, H 7.98, N 10.54.

X-ray Structure Determinations: X-ray structure determinations were performed with a Siemens P4 diffractometer, using Mo-K_α radiation and a graphite monochromator. Data were collected with a CCD area counter at 193 K (Siemens LT2 device). Several drops of a suspension containing the single crystals were transferred to precooled perfluoro polyether oil and kept at −40 °C. The selected single crystal was mounted on a glass fiber. The dimensions of the unit cell were calculated from the reflections of a total of 75 frames recorded for five different settings of the crystal using the program SMART.[17] Data collection was performed in the hemisphere mode by recording 1200 frames with $\Delta = 0.3°$ at two different χ settings. The program SAINT[18] was used for data reduction. Structure solution and refinement was carried out with the programs SHELX93[19] by applying direct methods. Non-hydrogen atoms were refined with anisotropic thermal parameters. Positions of hydrogen atoms attached to boron atoms were taken from the difference Fourier map. Their positions and isotropic thermal parameters were refined. All other H atoms were placed in calculated positions and included in the refinement with a riding model. − Compound **5** was obtained from toluene solution. There were five peaks that we assigned to C atoms of a disordered toluene but the C−C distances were rather irregular. One of these C atoms could not be refined anisotropically. − The structure of compound **8** was solved and refined in two space groups, monoclinic $P2_1/c$ and orthorhombic *Pcca*. The β angle was very close to 90° and, in the first runs, a solution was only obtained for the $P2_1/c$. In this solution all four H atoms could be located at B3. Refinement in *Pcca* led to more favorable *R* values, although the H atoms at B3 refined to give a disordered arrangement at B3 due to its position on a mirror plane. − A disorder was also found for the $B(3)H_4$ group in compound **9**, which indicates a disordered tetrahedral BH_4 group and a BH_3 and LiH group. These were included in the refinement with SOF = 0.5, a value indicated by a previous refinement without constraints. − A summary of crystallographic data and information referring to data collection and refinement is given in Table 2. Additional material (without structure factor tables) are deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-143680 (**1**), -143681 (**2**), -143682 (**3**), -143683 (**4**), -143684 (**5**), -143685 (**6**), -143686 (**7**), -143687 (**8**), -143688 (**9**). Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.uk].

Acknowledgments

This work was supported by Fonds der Chemischen Industrie and particularly by Chemetall GmbH. IR spectra were recorded by Mrs. E. Kiesewetter and NMR spectra by P. Meyer and M. Vosteen. We are grateful for this support.

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Received April 14, 2000
[I00144]