Metal Tetrahydridoborates and Tetrahydridometallates, 22[◇]

Structural Chemistry of Lithium Tetrahydroborate Ether Solvates☆

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$LiBH_4 \cdot OEt_2$ (**1**) and $LiBH_4 \cdot O(Me)CMe_3$ (**2**) form double-stranded chains in the solid state. While 3 hydrides of the BH_4 group in **1** bind to three different Li atoms through Li···H–B interactions, the fourth H atom interacts with three adjacent Li centers. In contrast, in compound **2** there are two single Li···H–B bonds and two doubly bridging hydrogen atoms, the latter again interacting with three lithium centers. Moreover, the arrangements of the ether molecules in **1** and **2** are different. $LiBH_4 \cdot 2$ DME (**3**) (DME = dimethoxyethane) forms a molecular lattice, in which the BH_4^- anions are present in $Li\cdots H_2BH_2$ bridges. The same structural feature is present in $LiBH_4 \cdot$ TG (**4**) (TG = triglyme = triethylene glycol dimethyl ether), but the TG molecule coordinates to two Li centers through two of its four oxygen atoms in such a manner that a chain structure results. The compound $LiBH_4 \cdot 3$ THF (**5**) exists as discrete molecules in the lattice. Its BH_4^- anion is triply bridging to the Li center. In contrast, $LiBH_4 \cdot C_3H_6O_2$ (**6**) (1,3-dioxolane) is polymeric. Due to the presence of two μ^2_2-BH_4 groups, a chain of the type $\cdots Li(H_2BH_2)Li(H_2BH_2)\cdots$ is formed, and the 1,3-dioxolane molecules connect the chains through Li–O coordination to form a three-dimensional array. In spite of the variations in the bonding of the BH_4 group to Li centers, the Li atoms are hexacoordinated in **3** to **6** but are heptacoordinated in **1** and **2**.

Introduction

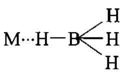
Lithium tetrahydridoborate is a commercially available reagent which surpasses $NaBH_4$ in terms of its reactivity[2]. It is widely used, and most reactions are performed in diethyl ether (OEt_2) or tetrahydrofuran (THF) as $LiBH_4$ is more rapidly hydrolyzed than $NaBH_4$[3]. Several ether solvates of $LiBH_4$ are known, but the only one to have been structurally characterized is 2 $LiBH_4 \cdot$18-crown-6[4] and more recently $LiBH_4 \cdot OEt_2$[17]. Most of the other ether solvates of $LiBH_4$ were first described in the period from 1950 to 1974[5], and only a few have subsequently been investigated in detail by vibrational and/or NMR spectroscopy[6]. To date, the following solvates have been characterized: $LiBH_4 \cdot n OEt_2$ (n = 0.5, 1, 2)[7][8], $LiBH_4 \cdot n$THF (n = 1, 2)[2c][8], $LiBH_4 \cdot O\mathit{i}Pr_2$[2c], and $LiBH_4 \cdot$1,4-dioxane[2c][9].

Meanwhile, several modes of bonding or interaction of the BH_4^- ion with metal centers have been established[5]. In mononuclear species $M(BH_4)_n$ or $L_mM(BH_4)_n$, μ_1-, μ_2-, or μ_3-BH_4 groups may be present, as shown in formulae **A**−**C**, which have local C_{3v}, C_{2v}, and C_{3v} point-group symmetry, respectively. BH_4 groups acting as bridges between two metal centers (type **D**) are found in solid $Be(BH_4)_2$[10], $Zr_3(BH_4)_6H_6 \cdot 4\ PMe_3$[11], and $Cr_2(BH_4)_4 \cdot dipy_2 \cdot Cr(BH_4)_2 \cdot dipy \cdot TMEDA$[12]. Although the double μ_2-bridging mode **B** prevails, other bonding modes are possible as depicted in **E**−**I**. Type **G** has been observed in dimeric $LiBH_4 \cdot$TMEDA[13]. We use the notation shown in **A** to **I** to describe the hydride bridges. The subscripts indicate the number of hydrogen atoms of the BH_4 group that interact with *one* metal atom, while the superscripts denote the number of hydrogen atomss that interact with different metal centers. Thus, for example, $\mu_1{}^3$ would indicate a hydrogen atom of the BH_4^- anion that forms bridges to three metal atoms. The examples given demonstrate that the BH_4^- anion is a very versatile ligand[14].

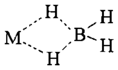
Synthesis

The synthesis of ether solvates of $LiBH_4$ can be achieved in various ways. One method is to dissolve $LiBH_4$ in the respective ether, and to crystallize the solvates either by cooling of the saturated solution or by removal of the solvent. A second method is to replace the solvate molecule with a more strongly coordinating ether. Thirdly, the ether can be added to a suspension of $LiBH_4$ in hexane or toluene. Using these methods, the following solvates have been obtained as single crystals (see Experimental Section for the method used): $LiBH_4 \cdot OEt_2$ (**1**), $LiBH_4 \cdot$DIV (**2**), $LiBH_4 \cdot 2$ DME (**3**), $LiBH_4 \cdot$TG (**4**), $LiBH_4 \cdot 3$ THF (**5**), $LiBH_4 \cdot$ DIOXL (**6**) [DIV = $MeOCMe_3$, DME = $MeOCH_2CH_2OMe$, TG = $MeO(CH_2CH_2O)_3Me$, DIOXL = $C_3H_6O_2$, 1,3-dioxolane]. No single crystals could be obtained in the case of $LiBH_4 \cdot$1,4-dioxane[9] due to its very low solubility.

[◇] Part 21: Ref.[1].



A μ_1^1-BH$_4$



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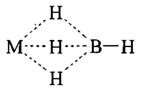
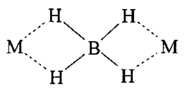
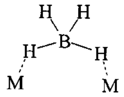


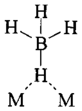
C μ_3^1-BH$_4$



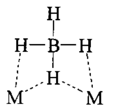
D $2\mu_2^1$-BH$_4$



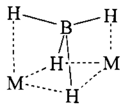
E $2\mu_1^1$-BH$_4$



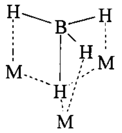
F μ_1^2-BH$_4$



G $2\mu_1^1, \mu_1^2$-BH$_4$



H $2\mu_1^1, \mu_1^2$-BH$_4$



I $3\mu_1^1, \mu_1^3$-BH$_4$

IR and NMR Spectra

In order to obtain some information on the interaction of the Li$^+$ center with the BH$_4{}^-$ anion, IR spectra were recorded of the solid compounds as Nujol/Hostaflon mulls. The data attributable to BH stretching vibrations are summarized in Table 1. There are four strong bands in this region, irrespective of the type of ether solvate molecule present, and the pattern observed is not characteristic for a BH$_4{}^-$ group of either T_d, C_{3v}, or C_{2v} symmetry. Bands due to ν^{10}BH$_4$ are not resolved. The strong band at 2240 ± 65 cm^{-1} seems to be the overtone of the δBH$_2$ vibration at 1130 ± 10cm^{-1}. The IR spectra of solid LiBH$_4$ and NaBH$_4$ do not differ significantly[15]. It is only the triglyme solvate that shows a better resolution. Obviously, the bonding between the BH$_4{}^-$ group and Li$^+$ is predominantly ionic, and the IR spectra do not allow any firm conclusions to be drawn regarding type of interaction of the BH$_4$ group with the Li center (μ_1, μ_2, or μ_3 bonding).

Table 1. IR bands in the stretching vibration region for the LiBH$_4$ ether solvates: crystalline material in Nujol/Hostaflon suspension

1[a]	**2**	**3**	**4**	**5**	**6**
2230 st	2180 m	2134	2198 m	2111 m	2180 st
2234 st	2277	2258	2264 st	2127 m	2256 st
2286 st	2306	2281	2295 st	2176 st	
2364 st	2320	2373	2560 st	2237 st	
	2410 sh		2330 m st	2272 st	2317 st
			2382 m st	2334 m st	
				2382 m st	

[a] In crystalline solid LiBH$_4$ the following bands were observed in the IR spectrum and assigned (in cm^{-1}): 2525 (2ν_2), 2408 (ν_2 + ν_4), 2308 (ν_3), 2182 (2ν_4)[15].

Likewise, the ^{11}B-NMR spectra of solutions of the LiBH$_4$ solvates in their respective ethereal solvents, or of the solid solvate in C$_6$D$_6$, did not yield any additional information (see Table 2). With the exception of LiBH$_4\cdot$TG, each solvate gave rise to a 1:4:6:4:1 quintuplet with $^1J(^{11}\mathrm{B}^1\mathrm{H})$ in the small range of 81−83 Hz, and δ^{11}B varying only within a range of ± 2.6 ppm. The shielding at the ^{11}B center decreases slightly when C$_6$D$_6$ is used as a solvent instead of the respective ether. This may be taken as evidence for a slightly stronger Li(BH$_4$) interaction within an ion pair. No NMR data could be recorded for LiBH$_4\cdot$1,4-dioxane, neither in dioxane nor in C$_6$D$_6$, due to its very low solubility in both solvents. This suggests that its structure in the solid state consists of an extended lattice. LiBH$_4\cdot$3 THF and LiBH$_4\cdot$1,3-dioxolane are also practically insoluble in deuterated benzene. However, for a solution of LiBH$_4$ in triglyme, two additional signals are observed at δ = +3.7 and δ = +7.5. The signals in this case are broad, even that for the BH$_4$ anion at δ = −39.7, and they show no resolved lines due to B-H coupling. The signal at δ = +3.7 may be due to the presence of a BH$_3$ adduct to the ether (cf. δ^{11}B = 2.5 for H$_3$B·OMe$_2$)[16].

Table 2. ^{11}B- and ^{7}Li-NMR data of LiBH$_4$ solvates [δ is given in ppm, the coupling constant $^1J(^{11}\mathrm{B}^1\mathrm{H})$ is given in Hz (in parentheses)

	LiBH$_4$ · OEt$_2$ **1**	LiBH$_4$ · DIV **2**	LiBH$_4$ · 2 DME **3**	LiBH$_4$ · TG **4**	LiBH$_4$ · 3 THF **5**	LiBH$_4$ · DIOXL **6**
δ^{11}B	−39.1 (81)[a]	−38.4 (81)[c]	−39.1 (83)[d]	−40.5, −14.6, −9.1 (br.)[e]	−41.0 (82)[e]	−40.4 (81)[g]
	−40.0 (87)[b]	−39.7 (br)[b]	−41.3 (82)[b]	−40.8 (71)[b]	−	−
δLi	1.78[a]	−1.83[c]	0.416[d]	1.300[e]	−2.331[f]	0.493[g]
	0.145[b]	0.119[b]	−0.154[b]	−0.679[b]	−	−

[a] In OEt$_2$. − [b] In C$_6$D$_6$. − [c] In diveron. − [d] In dimethoxyethane. − [e] In triglyme. − [f] In THF; in addition a weak doublet at δ^{11}B = 14 (64 Hz) is observed. − [g] − In 1,3-dioxolane.

Table 3. Li···B atom distances in [Å] of the LiBH$_4$-ether solvates

	LiBH$_4$ · OEt$_2$	LiBH$_4$ · DIV	LiBH$_4$ · 2 DME	LiBH$_4$ · TG	LiBH$_4$ · 3 THF	LiBH$_4$ · DIOXL
Li···B	2.498(8)	2.560(4)	2.470(4)	2.478(6)	2.319(7)	2.445(3)
	2.53(1)	2.505(4)	−	−	−	2.447(3)
	2.54(1)	2.520(4)	−	−	−	2.431(3)

In benzene solution, the shielding of the ^{7}Li nucleus also varies considerably, but is more in line with the number of solvent molecules attached to the LiBH$_4$ molecule. This becomes evident by comparing the δ values for the DME and TG solvates with those of diethyl ether and diveron. The δ^7Li data for compounds **1**−**6** in their respective ether solutions are difficult to rationalize. The excellent shielding of the Li nucleus in **5** is most likely due to ion-pair formation [Li(THF)$_4$]BH$_4$, but then it is hard to understand why the Li center in **3** is less shielded than that in **2**, and why the Li resonance for **1** in diethyl ether solution is found at very low field. Since the degrees of association of LiBH$_4\cdot$OEt$_2$ and LiBH$_4\cdot$DIV in C$_6$D$_6$ solution are unknown, it is difficult to interpret the δ^7Li data, which suggest much stronger solvation in benzene (ratio Li/O only 1:1) than in ether. A better shielding in benzene can only be expected when strong interactions between $LiBH_4$ molecules remain, while the indications seem contrary to this. Therefore, association through the BH_4 groups must remain in benzene solution. As both compounds have been found to be moderately soluble, it is evident that the chain structures present for these compounds in the solid state (vide infra) must be broken down into smaller $[LiBH_4 \cdot Do]_n$ units (Do = coordinated solvent).

Crystal and Molecular Structures

Coordination Compounds of $LiBH_4$ with Noncyclic Ethers: Neither the NMR data of solutions of $LiBH_4$ in the respective ethers nor the IR data of the solid ether solvates allowed an unambiguous assignment of the structure of the $LiBH_4$-ether solvates, particularly with respect to the type of Li···H−B interaction. Therefore, it was necessary to determine the molecular structures of the ether solvates of $LiBH_4$ by X-ray diffraction analysis.

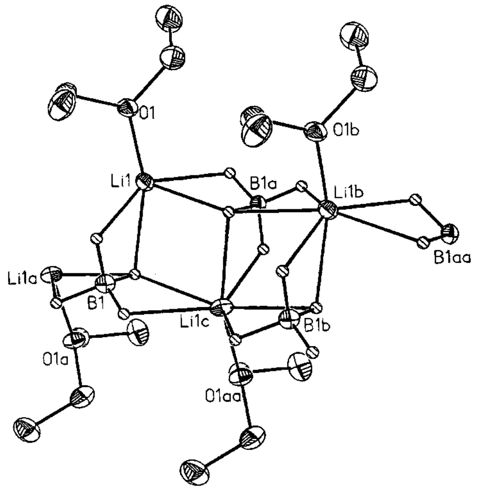
$LiBH_4 \cdot OEt_2$ (**1**), whose crystal structure has recently been reported[17], crystallizes from a diethyl ether solution in colorless needles of the orthorhombic system and, therefore, only a few features will be discussed.

Figure 1 shows that three of the four H atoms of the BH_4^- anion each interact with one Li center and that the fourth hydrogen atom coordinates to three Li^+ ions. This hydrogen atom is tetracoordinated. Moreover, each Li center is coordinated by six hydrogen atoms and one ether oxygen atom. The sum of bond angles subtended at the ether oxygen atoms is 359.8°. Li−H atom distances range from 1.94(5) to 2.25(5) A, while bond angles at Li span the wide range from 48.0 to 161.4°, with many falling in the interval 90 ± 15°. This shows that the coordination polyhedron can be described as a very strongly distorted octahedron. As expected, the coordination polyhedron around the boron atom is close to a tetrahedron.

The units shown in Figure 1 are the building blocks for the formation of doubly stranded chains in the lattice of **1** as depicted in Figure 2. In the lattice, each BH_4 group has to be described as $3\mu_1{}^1$, $\mu_1{}^3$, i.e. all four hydrogen atoms of the BH_4^- ion are involved in coordination to Li^+ ions, which are heptacoordinated. The ether molecules are arranged in such a manner that an organophilic "skin" partially shields the $(LiBH_4)_n$ core. This most probably explains why $LiBH_4 \cdot OEt_2$ not only dissolves in ether but also to a small extent in toluene. The structure in solution will, of course, differ significantly from that in the solid state.

$LiBH_4 \cdot DIV$ (**2**) crystallizes from toluene solution in thin monoclinic plates. Figure 3 depicts a single molecule, showing a doubly bridging BH_4 anion. These molecules are associated as shown in Figure 4a. Here, it can be seen that each Li center shares hydrogen atoms with three BH_4 groups, and this leads to heptacoordination at Li (6 H atoms and 1 O atom). Of the four hydrogen atoms of each BH_4^- anion, two are involved in bridging two Li centers, while the other two are involved in single B−H···Li interactions (2 $\mu_1{}^1$-, 2 $\mu_1{}^2$-BH_4). Figure 4a depicts the arrangement in a double-stranded chain. It also shows that the *tert*-butyl groups of the diveron molecules are ordered in such a manner that allows one methyl unit of each DIV molecule to be arranged in a zipper-like orientation. Thus, the organyl groups shield the $LiBH_4$ part of the $[(LiBH_4)_2]_\infty$ chain better than in **1** (Figure 4b). However, every second pair of *trans*-oriented ether molecules are turned by 69.7° to one another. Therefore, the arrangement of the molecules of **2** in the chain is different to that observed for **1**.

Figure 1. ORTEP plot of four $LiBH_4 \cdot OEt_2$ (**1**) molecules; estimated standard deviations in parentheses[a]



[a] Selected bond lengths and atom distances [A]: Li1−O1 1.927(6), Li1−H1 1.97(3), Li1−H2 2.11(3), Li1−H 42.08(3), B1−H1 1.12(3), B1−H2 1.14(3), B1−H3 1.01(5), B1−H4 1.19(4), Li1···B1 2.53(1), Li1···B1B 2.54(1). − Selected bond angles [°]: C1−O1−C3 115.0(3), C11−O1−Li1 122.3(4), C3−O1−Li 122.5(3), H1−B1−H3 109(3), H1−B1−H2 107(2), H1−B1−H4 110(3), H2−B1−H3 116(3), H2−B1−H4 107(3), H3−B1−H4 108(2), O1−Li1···B1 122.5(3), O1−Li1···B1A 106.2(4), Li1−H2−Li1A 161(2), Li1−H1−B1 105(2), Li1A−H3−B1 104(3), B1−H4−Li1B 105(3). − Atom Li1B is part of the adjacent chain (see Figure 2).

$LiBH_4 \cdot 2$ DME (**3**) forms colorless monoclinic crystals. There is half a molecule in the asymmetric unit. The Li and B atoms occupy special positions on a C_2 axis. Figure 5 depicts the molecular structure of compound **3**.

It is apparent that the hexacoordinated Li atoms are surrounded by four oxygen atoms of two DME molecules and two hydrogen atoms from a $\mu_2{}^1$-BH_4 group.

The B−H bonds to the bridging hydrogen atoms are slightly, although not significantly, longer than those to the terminal hydrogen atoms. In the case of the Li−O coordination, one Li−O distance is significantly shorter than the other [2.058(2) A for O2, 2.133(1) A for O1]. The rather acute O1−Li−O2 bond angle is due to the small bite angle of the DME molecule. Consequently, the deviation from octahedral symmetry around the Li ion is substantial; the smallest bond angle is 55.9(9)° (H2−Li1−H2a), the largest 150.8(5)° (H2−Li1−O2). Bond angles subtended at atoms O1 and O2 are rather different, the largest C−O−Li bond angles being those to the methyl groups of the DME molecule, which range from 122.0(1) to 126.30(9)°. More interesting in terms of the coordination geometry is the fact that the bond angle sums at atoms O1 and O2 are 321.1(3)° and 349.5(3)°, respectively. Considering the C−O−C bond

Figure 2. A space-filling model of a chain of $LiBH_4 \cdot OEt_2$

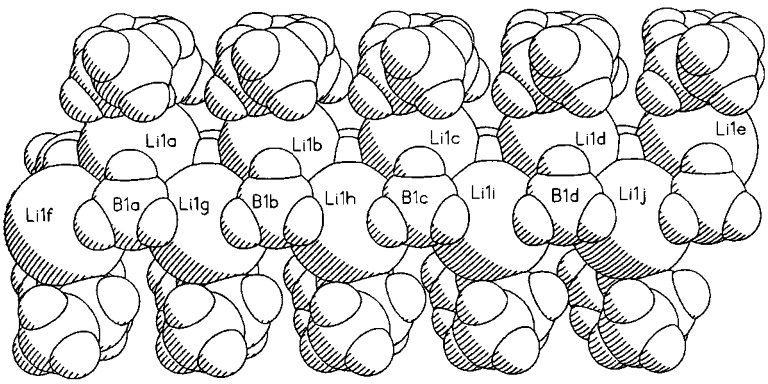
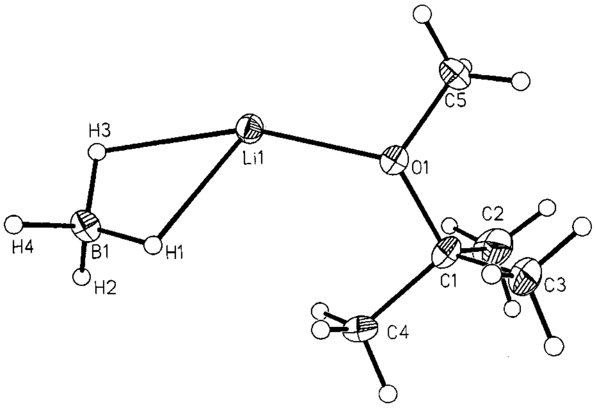


Figure 3. ORTEP plot of $LiBH_4 \cdot OMe(CMe_3)$ (**2**) in the asymmetric unit[a]



[a] Selected bond lengths and atom distances [A]: Li1−O1 2.000(4), Li1−H1 2.11(2), Li1−H3 2.16(2), Li1B−H1 2.16(2), H2−Li1A 2.00(2), H3−Li1A 2.08(2), Li1−H4B 2.08(2), Li1−HaB 2.16(2), B1−H1 1.11(2), B1−H2 1.12(3), B1−H3 1.14(2), B1−H4 1.11(3), Li1···B1 2.560(4), Li1−B1A 2.505(4), Li1−B1B 2.529(4). − Selected bond angles [°]: O1−Li1−H1 110.9(6), O1−Li1−H3 159.1(6), H1−B1−H2 110(2), H1−B1−H3 110(2), H1−B1−H4 108(2), H2−B2−H3 106(2), H2−B1−H4 114(2), H3−B1−H4 109(2), B1−H1−Li1 101(1), B1−H3−Li1 97(1), B1−H4−Li1B 100(1), B1−H2−Li1A 104(2) Σ∠ at O1: 356.0°.

angles of 112.6 and 111.3(3)°, respectively, it would appear that these oxygen atoms are best described as being sp^3-hybridized. The O1−Li−O2 bond angle of 79.49(6)° as well as the Li1−O1−C2 and Li1−O2−C3 bond angles [112.6(1)° and 111.87(8)°] indicate that the Li···O interaction is predominantly polar. However, it should be borne in mind that **3** is nevertheless a molecular compound.

The $LiBH_4 \cdot TG$ solvate **4** forms colorless, orthorhombic crystals. There are four molecules in the unit cell. However, the triglyme ligand does not coordinate to only one Li center. As shown in Figure 6, the triglyme ligand binds to *two* different Li centers through two of its four oxygen donor atoms. Therefore, a chain structure results, in which the Li centers are hexacoordinated. The Li ions are coordinated by four oxygen atoms of *two* different triglyme molecules, as well as by a $\mu_2{}^1$-bonding BH_4 group.

The C−O atom distances in **4** fall in the fairly narrow range from 1.425(2) (O1−C2) to 1.432(2) A (O2−C4). However, the sum of bond angles at atom O1 is only 335.4°, in contrast to atom O2, where the sum is 359.3°. This points to two different bonding situations for O1 and O2, as suggested also by the *shorter* Li1−O2 atom distance. On the other hand, the O2−Li1−O1 bond angle of 79.67(8)° does not deviate at all from the analogous bond angle in **3** [79.49(8) A], and we take this as evidence that the Li···O interactions in **4** are again primarily determined by polar factors, irrespective of the bond angle sums at the O atoms.

Coordination Compounds of $LiBH_4$ with Cyclic Ethers: Cyclic ethers such as THF, 1,4-dioxane, 1,3,5-trioxolane, and many others add to $LiBH_4$. However, to date we have been unsuccessful in obtaining good single crystals of these solvates, apart from the case of THF and 1,3-dioxolane solvates.

$LiBH_4 \cdot 3$ THF (**5**) crystallizes from a THF solution at −40°C in extensively intergrown platelets. Crystal selection at low temperature was difficult, as was the mounting using oxygen-free perfluoroether oil. Several crystals had to be examined and even the best one was comparatively weakly diffracting. Consequently, the quality of the structure determination is less than satisfactory. Nevertheless, a model structure was found that seems to be reliable, even though the hydrogen atoms at the boron center had to be fixed in their found positions in the final cycles of refinement. Figure 7 shows the result.

It is apparent that **5** is a molecular compound that may be regarded as a contact ion pair. The Li center is hexacoordinated by three oxygen atoms and three hydrogen atoms. Thus, the BH_4 group acts as a $\mu_3{}^1$-ligand. Li−O atom distances vary significantly, ranging from 1.952(6) to 2.017(6) A, while the O−Li−O bond angles span the small range from 100.6(3) to 102.5(3)°. On the other hand, the bite of the BH_4 group is very small, as exemplified by H−Li−H bond angles in the range 45.5−54.4°. The Li···B atom distance is 2.319(7) A, which is shorter than the Li···B distances found for $\mu_2{}^1$-BH_4 groups.

$LiBH_4 \cdot$ 1,3-DIOXL (**6**) separates from saturated 1,3-dioxolane solutions. The crystals are monoclinic. The contents of the asymmetric unit is depicted in Figure 8. The structure features tricoordinated Li ions, which are, of course, coordinatively unsaturated. These units associate to

Figure 4. a) Four molecules of **2** in a chain; b) space-filling model

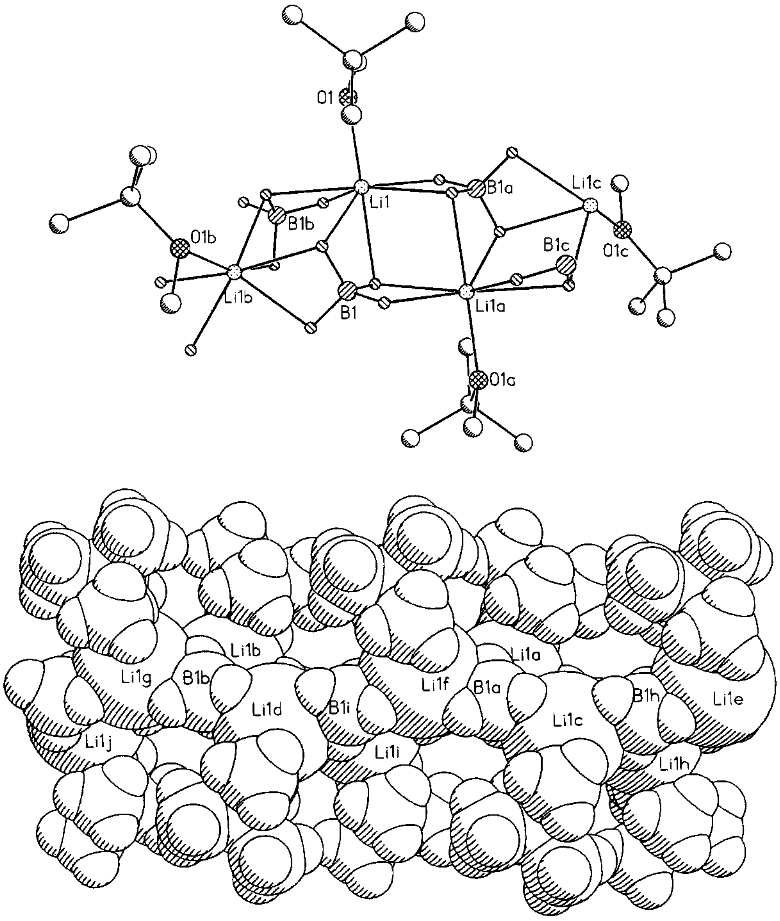
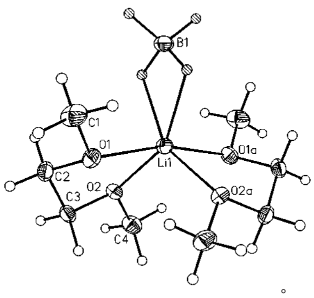


Figure 5. ORTEP plot of the molecular structure of $LiBH_4 \cdot 2$ DME (**3**)[a]



[a] Selected bond lengths and atom distances [A]: Li1−O1 2.133(1), Li1−O2 2.058(2), Li1−H2 1.17(2), B1−H1 1.15(2), B1−H2 1.17(2), Li1···B1 2.470(4). − Selected bond angles [°]: O1−Li1−O2 79.49(6), O1−Li1−O1a 165.9(2), O1−Li1−O2a 92.60(7), O2−Li1−O1a 92.60(7), O2−Li1−O2a 111.9(2), Li1−H2−B1 98.1(9), H1−B1−H1a 110(2), H1−B1−H2 111(1). Σ∠ O1 = 341.2°, O2 = 349.5°.

form an extended structure, as shown in Figure 9. The BH_4 groups join strands of Li(1,3-dioxolane) units.

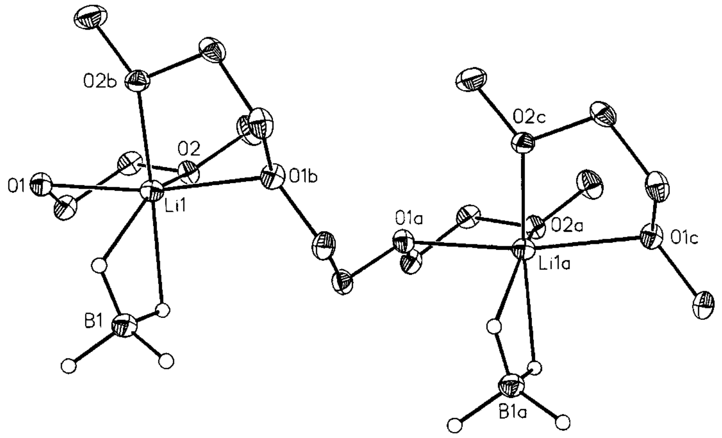
The BH_4 groups are of the $4\mu_1{}^1$-type, i.e. there are four singly bridging hydrogen atoms to 4 Li centers. Moreover, both oxygen atoms of the 1,3-dioxolane are involved in coordination. This leads to hexacoordinated Li ions with an H_4O_2 environment. The two Li−O distances are 1.993(3) and 2.031(3) A, and the O−Li−O bond angles are 94.6(1)° for Li1 and 96.2(1)° for Li2. It is also interesting to note that the Li···B atom distances are 2.445(3) and 2.439(3) A, respectively. These are definitely longer than the Li···B distance in **4** as a result of the "unusual" Li−H−B interactions. The two OCO planes of the dioxolane molecules coordinated to a Li center are twisted by almost 90° with respect to one another. The symmetry at atom Li2 is higher than that at atom Li1. Moreover, the Li···B···Li angles differ considerably, amounting to 174.1(1)° at atom B1 and 162.8(1)° at atom B2.

Discussion

It is well known that $LiBH_4$ forms many well-defined solvates with various kinds of ethers[2]. Although the compositions of some of these solvates have been determined, their structures in the solid state and in solution have never been adequately described.

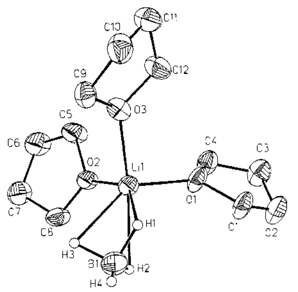
In the present study, it is demonstrated that an IR-spectroscopic investigation does not allow unambiguous conclusions to be drawn concerning the coordination mode of the anion BH_4^- to the Li centers. Such information can only be obtained from X-ray structure determinations, which are of course confined to the solid state. Thus, the structure of $(LiBH_4)_2 \cdot 18$-crown-6 has been determined, which reveals $\mu_1{}^1$-BH_4 interactions with the Li centers[4].

Figure 6. ORTEP plot of two molecules of $LiBH_4 \cdot TG$ (**4**)[a]



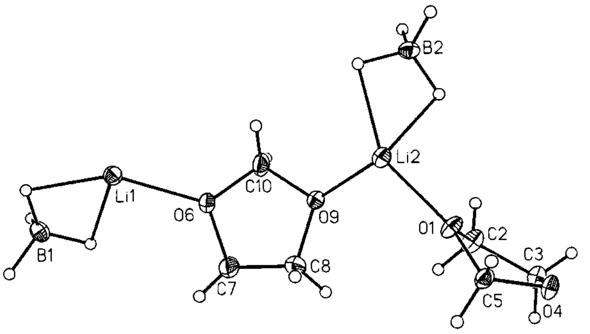
[a] Selected bond lengths and atom distances [A]: Li1−O1 2.192(2), Li1−O2 2.035(3), Li1−O1B 2.192(2), Li1−O2B 2.035(3), Li1···B1 2.487(6). − Selected bond angles [°]: O1−Li1−O2 79.67(8), O1−Li1−O2B 94.1(1), O1−Li1−O1B 169.6(2), O2−Li1−O1B 94.1(1), O2−Li1−O2B 107.3(2), O1B−Li1−O2B 79.68(8).

Figure 7. ORTEP plot of the molecular structure of $LiBH_4 \cdot 3$ THF (**5**); thermal ellipsoids are represented at the 25% probability level[a]



[a] Selected bond lengths and atom distances [A]: Li1−O1 1.952(6), Li1−O2 1.968(5), Li1−O3 2.017(6), Li1−H1 2.02(4), Li1−H2 2.10(5), Li1−H3 2.12(4), Li1···B1 2.319(7), B1−H1 1.15(3), B1−H2 1.15(3). − Selected bond angles [°]: O1−Li1−O2 102.5(3), O1−Li1−O3 100.6(3), O2−Li1−O3 101.4(2), O1−Li1···B1 114.2(3), O2−Li1···B1 117.8(3), O3−Li1···B1 117.8(3), H1−B1−H2 110.2(3), H1−B1−H3 102.7(3), H1−B1−H4 117.3(8), H2−B1−H3 90.3(3), H2−B1−H4 90.3(3), H3−B1−H4 115.7(3); $\Sigma\angle$ at O atoms: O1: 358.1°, O2: 357.6°, O3: 354.9°

Figure 8. ORTEP plot of the molecular structure of $LiBH_4 \cdot 1,3$-dioxolane (**6**)[a]

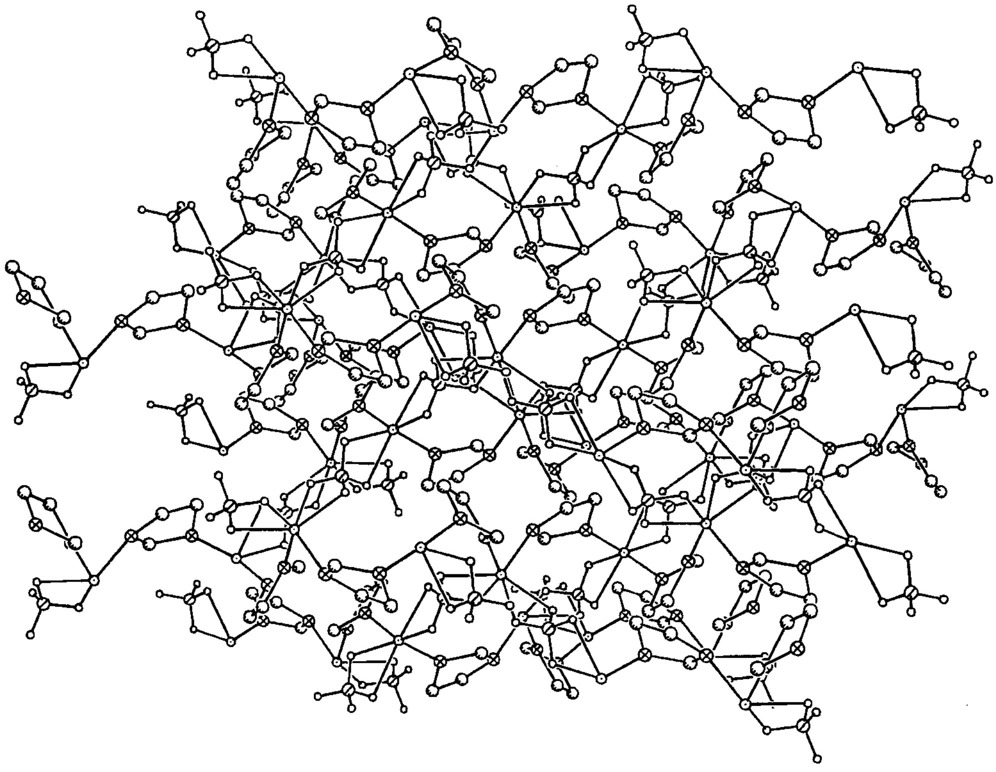


[a] Selected bond lengths and atom distances [A]: Li1−O6 2.004(3), Li1−O4A 1.993(3), Li1···B1 2.445(3), Li1−B2B 2.447(3) Li2···B2 2.431(3), Li2C−B1 2.428(3), Li2−O1 1.984(3), Li2−O9 2.031(3). Selected bond angles [°]: O6−Li1−B1 117.4(1), B1−Li1−O4A 100.6(1), O6−Li1−O4A 96.2(1), O4A−Li1···B2B 118.6(1), O6−Li1···B2B 98.7(1).

The compound can therefore be regarded as a "double" contact ion pair, in which each Li atom is coordinated by a hydrogen atom and four oxygen atoms. Although all the molecular solvates described herein, such as $LiBH_4 \cdot 2$ DME and $LiBH_4 \cdot 3$ THF, may also be regarded as contact ion pairs, this seems to be an inadequate description as the BH_4 group definitely favors μ_1, μ_2, or μ_3 interactions with the Li^+ center. The structure determinations presented in this study clearly show a preferential orientation of the BH_4 moiety. Using Edelstein's correlation of metal−boron distances as a measure of the denticity of the BH_4 group[18], it is shown that this holds not only for typical covalent metal tetrahydridoborates, but also for more polar metal tetrahydridoborates.

It is also evident that strongly coordinating ether ligands such as THF and DME lead to the formation of molecular $LiBH_4$ complexes, while more weakly bound ethers such as OEt_2 or diveron lead to polymers. This is apparent from ether/Li ratios of 1:1 with weak donors and ratios of up to 4:1 with strong donor molecules. As the O/Li ratio decreases, coordination unsaturation at the Li ion increases and this is counterbalanced by additional Li···H interactions. Therefore, we observe BH_4 groups of type **A** ($\mu_3{}^1$-BH_4) for $LiBH_4 \cdot 3$ THF, of type **B** ($\mu_2{}^1$-BH_4) for $LiBH_4 \cdot 2$ DME and $LiBH_4 \cdot TG$, and $4\mu_1{}^1$-BH_4 for $LiBH_4 \cdot 1,3$-DIOX. Type-**D** BH_4 groups ($2\mu_1{}^1,2\mu_1{}^1$-BH_4) are present in $LiBH_4 \cdot DIV$ and $3\mu_1{}^1,\mu_1{}^3$-bonding is found in $LiBH_4 \cdot OEt_2$. Thus, in these cases, each hydrogen atom of the BH_4 group is involved in interactions with the Li^+ ions. Amongst the $LiBH_4$−ether complexes described here, there are hydrogen atoms of the BH_4 group that coordinate to three Li centers, as for example, in **1**. Consequently, these are H^- ions in a tetracoordinated environment. However, in complexes of $LiBH_4$ with nitrogen ligands, the interaction of BH_4 hydride with three Li centers is more common than with ethers[19], and we have recently found an example where even four metal centers coordinate to one hydride, namely $LiAl_3H_5(OR)_5$[20].

Figure 9. View of the three-dimensional array of compound **6**



It is evident that the BH_4 group is a very versatile ligand, and it can be expected to show still further variations in coordination mode as a ligand in competition with ethers or other donor ligands. Studies in this area are currently in progress in our laboratory.

We thank *Chemetall GmbH* for support of this study. Moreover we are indebted to the *Fonds der Chemischen Industrie* for unbureaucratic help over many years, and we are also grateful to Mrs. *E. Kiesewetter* and Mrs. *G. Hanatschek* for recording the IR spectra.

Experimental Section

The hydrolytic sensitivity of $LiBH_4$ requires the exclusion of moisture in all experiments. Therefore, the Schlenk-tube technique was used with N_2 or Ar as the protecting gas. All solvents were carefully dried, and only flame-dried glassware was used. $LiBH_4$ (Chemetall GmbH) was crystallized from diethyl ether and dried in vacuum. NMR spectra were recorded with Jeol EX 270 and EX 400 instruments [standards: TMS (^1H, ^{13}C), 1 M LiCl (^7Li), $BF_3 \cdot OEt_2$ (^{11}B)]. – IR: Nicolet FT-IR.

Lithium Tetrahydridoborate–Diethyl Ether (**1**): Diethyl ether (35 ml) was added to $LiBH_4$ (0.94 g, 43 mmol) at 20°C with stirring. After heating to reflux for 4 h, a turbid solution formed, from which the insoluble material was removed by filtration (G3 glass frit). On cooling to 5°C, needles formed which were not suitable for X-ray crystallography. Yield: 3.36 g of **1** (81%), m.p. ca. 5°C. The ether adduct was dissolved in a minimum amount of an Et_2O/toluene (5:3) mixture. Single crystals of sufficient quality grew at −20°C. Isolation and the selection of suitable crystals was carried out at this temperature. **1** was found to be readily soluble in Et_2O and benzene, but insoluble in hexane. – $C_4H_{14}BLiO$ (95.91): calcd. B 11.27, Li 7.24; found B 11.09, Li 7.11 (by titration); B 10.33, Li 6.92 (by AAS).

Lithium Tetrahydridoborate–tert-Butyl Methyl Ether (**2**): Prepared analogously to **1** from $LiBH_4$ (0.76 g) and diveron (25 ml). **2** crystallized from the solution in very thin, interwoven needles. Yield: 3.07 g (79%), dec. 283°C. Single crystals were obtained from the saturated solution at 20°C by cooling to 5°C. The compound was found to be soluble in diveron and benzene, but insoluble in hexane. – $C_5H_{16}BLiO$ (128.08): calcd. B 9.83, Li 6.31; found B 9.69, Li 6.22 (by titration); B 8.93, Li 6.43 (by AAS).

Lithium Tetrahydridoborate–Bis(dimethoxyethane) (**3**): Prepared analogously to **1** from $LiBH_4$ (0.61 g, 28 mmol) and dimethoxyethane (60 ml). A clear solution resulted after heating. Since no crystals separated at 20°C, the solution was cooled to −20°C. Well-shaped needles separated. Yield: 2.4 g of **3** (42%). The compound was found to be soluble in DME, THF (reaction), and benzene, but insoluble in hexane. – $C_8H_{24}BLiO$ (154.03): calcd. B 5.35, Li 3.44; found B 5.41, Li 3.53 (by titration); B 5.45, Li 3.41 (by AAS).

Lithium Tetrahydridoborate–Triglyme (**4**): Obtained by dissolving $LiBH_4$ (250 mg, 11.5 mmol) in 10 ml of triglyme. After heating to reflux (20 min), the hot suspension was filtered and the clear solution was cooled to −20°C. Well-shaped needles formed, which were isolated by filtration. Yield: 600 mg of **4** (26%), m.p. 59°C. The compound was found to be soluble in triglyme and benzene, but insoluble in hexane. – $C_8H_{22}BLiO$ (152.01): calcd. B 5.41, Li 3.47; found B 5.40, Li 3.42 (by titration); B 5.28, Li 3.24 (by AAS).

Lithium Tetrahydridoborate–Tris(tetrahydrofuran) (**5**): To $LiBH_4$ (3.2 g, 146 mmol), tetrahydrofuran (50 ml, 615 mmol) was added with stirring. Most of the $LiBH_4$ dissolved exothermically. The turbid solution was heated to reflux for 10 min, and any insoluble material was then removed at ambient temperature by fil-

Table 4. Data relevant to crystallography, data collection and refinement of the structures of the $LiBH_4$-ether adducts

Compound	**1**	**2**	**6**	**4**	**9**	**3**
Chem. formula	$C_4H_{14}BLiO$	$C_5H_{16}BLiO$	$C_3H_{10}BLiO_2$	$C_8H_{22}BLiO_4$	$C_{12}H_{28}BLiO_3$	$C_8H_{24}BLiO_4$
Form. wght.	95.90	109.93	95.86	200.01	238.09	202.02
Cryst. size [mm]	0.15 × 0.2 × 0.4	0.3 × 0.4 × 0.55	0.33 × 0.4 × 0.6	0.1 × 0.15 × 0.3	0.1 × 0.3 × 0.9	0.2 × 0.3 × 0.3
Cryst. system	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic	Tetragonal	Monoclinic
Space group	*Pna*2(1)	*I*2/*a*	*P*2(1)/*n*	*Pbcn*	*I*4(1)*cd*	*C*2/*c*
a [Å]	11.806(12)	9.2598(7)	7.1656(5)	6.395(2)	18.2973(3)	14.376(5)
b [Å]	13.617(9)	12.3190(9)	12.9452(9)	15.078(7)	18.2973(3)	7.895(3)
c [Å]	4.531(5)	14.4108(14)	13.2702(8)	12.798(7)	18.4226(4)	12.258(5)
α [°]	90.00	90.00	90.00	90.00	90.00	90.00
β [°]	90.00	94.159(1)	101.523(1)	90.00	90.00	105.59(2)
γ [°]	90.00	90.00	90.00	90.00	90.00	90.00
V [$Å^3$]	728.4(12)	1639.5(2)	1206.1(1)	1234.1(10)	6167.7(2)	1340.1(9)
Z	4	8	8	4	16	4
ρ(calcd.) [Mg/m^3]	0.875	0.891	1.056	1.076	1.026	1.001
μ [mm^{-1}]	0.053	0.053	0.076	0.079	0.068	0.073
F(000)	216	496	416	440	2112	448
Index range	$-13 \leq h \leq 13$ $-10 k \leq \leq 10$ $-5 \leq l \leq 5$	$-11 \leq h \leq 11$ $-14 \leq k \leq 14$ $-17 \leq l \leq 17$	$-7 \leq h \leq 7$ $-14 \leq k \leq 14$ $-13 \leq l \leq 14$	$-5 \leq h \leq 8$ $-18 \leq k \leq 18$ $-15 \leq l \leq 15$	$-20 \leq h \leq 18$ $-20 \leq k \leq \leq 20$ $-20 \leq l \leq 20$	$-15 \leq h \leq 18$ $-10 \leq k \leq 10$ $-15 \leq l \leq 15$
2 θ [°]	46.50	56.26	46.50	58.12	46.48	57.52
Temp. [K]	193(4)	173(4)	203	173	153(5)	193
Refl. collected	2821	4174	4690	6273	12493	3729
Refl. unique	867	1518	1706	1184	2215	1295
Refl. observed (4σ)	714	1026	1548	627	1938	1140
R (int.)	0.0825	0.0555	0.0332	0.0650	0.1845	0.0216
No. variables	82	93	188	74	166	113
Weighting scheme[a] *x*/*y*	0.0000/0.5250	0.0728/2.2374	0.0409/0.5497	0.0281/0.4510	0.0835/3.1079	0.0341/0.6213
GOOF	1.219	1.089	1.076	1.164	1.122	1.235
Final *R* (4σ)	0.0627	0.0647	0.0386	0.0400	0.0658	0.0415
Final *wR*2	0.1109	0.1668	0.0943	0.0813	0.1697	0.0978
Larg. res. peak [e/A°^{3}]	0.150	0.660	0.183	0.124	0.196	0.098

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

tration. A 25-ml aliquot of the solution was cooled to −75°C. Extensively intergrown crystals were deposited. Single crystals were selected at −75°C and investigated crystallographically. The crystals, which proved to be $LiBH_4 \cdot 3$ THF, melted at ca. −60°C. The remaining solution was subjected to NMR (^7Li, ^{11}B) and IR analysis. The compound loses THF readily at ambient temperature, and finally gives $LiBH_4 \cdot$THF[8]. As yet, we have not been able to obtain the latter in the form of single crystals.

Lithium Tetrahydridoborate−1,3-Dioxolane (**6**): $LiBH_4$ (780 mg, 35.8 mmol) was added to 1,3-dioxolane (40 ml). The suspension was heated to reflux for 20 min, and insoluble material was removed by filtration at −30°C. On storing the clear solution at −30°C, colorless crystals formed within 3 d. Yield: 2.67 g of **6** (78%). Recrystallization from 20 ml of toluene at −30°C gave well-shaped single crystals of **6**. − $C_3H_{10}BLiO_2$ (95.86): calcd. C 37.62, H 10.44, B 11.27; found C 36.93, H 10.43, B 11.15.

Crystal-Structure Determinations: Single crystals were grown by slow evaporation of the solvent from the ethereal solutions ($LiBH_4 \cdot OEt_2$, $LiBH_4 \cdot$DIV, $LiBH_4 \cdot 3$ THF) or by cooling solutions in toluene (all others) to low temperatures. The crystals of **1**, **2**, and **5** were removed from the cold solution and transferred directly into precooled perfluoroether oil at −60°C. The selected specimen was mounted on a glass fiber, which was rapidly transferred to the goniometer head. The crystal was cooled in an N_2 cold stream to −100°C. Most crystals of $LiBH_4 \cdot$DIV and $LiBH_4 \cdot 3$ THF were found to be weakly diffracting. Only the best data obtained are reported here. A Siemens P4 four-circle diffractometer equipped with a SMART-CCD detector was used for data collection with graphite-monochromated Mo-K_α radiation. Preliminary determinations of the cell constants used reflections of 4 different sets of 15 frames. The dimensions of the unit cell reported in Table 4 are those calculated from all data. Data reduction was performed using the program SAINT[21]. The structures were solved by the direct methods implemented in the SHELXTL and SHELX-93 program packages[22]. Hydrogen atoms bonded to the boron atom were refined freely, except for those in **3**. Non-hydrogen atoms were described anisotropically. Hydrogen atoms bonded to carbon atoms were placed in calculated positions and refined with a riding model. The positions of hydrogen atoms bonded to boron atoms were taken from difference Fourier maps. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-101311. Copies of the data can be obtained free of charge on application to CCCD, 12 Union Park, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44(0)1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

☆ Dedicated to my colleague Prof. Dr. *K.-H. Kompa* on the occasion of his 60th birthday.

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