Metal Tetrahydroborates and Tetrahydroborato Metallates, 30 [1]. Alkoxo-Substituted Alkali Metal Tetrahydroborates: Studies in Solution and Structures in the Solid State

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Dedicated to Professor Kurt Dehnicke on the occasion of his 70^{th} *birthday*

Reactions of MBH_4 (M = Li, Na, K) with *t*BuOH, Ph_3COH, PhOH, F_5C_6OH, and 2,4-*t*$Bu_2C_6H_3OH$ in THF in a 1 : 1 ratio were followed by ^{11}B NMR spectroscopy. No $M[H_2B(OR)_2]$ species could be detected, but minor amounts of $M[H_3BOR]$ and larger amounts of $M[HB(OR)_3]$. In the reaction of $LiBH_4$ with 2,4-*t*$Bu_2C_6H_3OH$ also a fair proportion of $(RO)_2BH$ was generated. The perfluorophenolato borane $(F_5C_6O)_2BH{\cdot}THF$ was prepared from the phenol and $BH_3 \cdot THF$ in THF solution. It is unstable to disproportionation. Compound $(C_6F_5O)_3B{\cdot}THF$ was isolated and its crystal structure determined. Reaction of $LiBH_4$ with F_5C_6OH in hexane generated a solid that proved to be $Li[H_2B(OC_6F_5)_2]$. It is unstable in THF. On the other hand, 2,2'-dihydroxydiphenyl in the presence of secondary amines reacts to give $Li[C_{12}H_8O_2B(NR_2)_2]$ (**3 – 5**). $Li[B(O_2C_{12}H_8)_2]$, **2**, is formed when HN(*t*Bu)Ph is used as a secondary amine.

The unstable phthalatoborane $H\{C_6H_4[C(O)O]_2\}BH{\cdot}THF$ (**7**), is stabilized as its pyridine adduct (phth)BH·py (**8**). **7** reacts with 3 equivalents of Li*t*Bu to give $[Li(HBtBu)_3]$ (**11**), isolated as its tris(THF) solvate. Analogously, **7** reacts with LiNMePh to produce compound $Li[HB(NMePh)_3]$ (**10**). Similarly, **7** and NaO*t*Bu (molar ratio 1 : 3) give access to $Na[HB(OtBu)_3]$ (**9**). In attempts to grow single crystals, specimens resulting from a hexane solution showed that partial hydrolysis has occurred to give $Na[HB(OtBu)_3]{\cdot}Na[(tBuO)_2BO]{\cdot}Na[tBuOB(O)H]$, which crystallizes as a centrosymmetric dimer.

While catecholborane when treated with Li*t*Bu in THF and DME gave access to $(dme)_2Li[catB(tBu)_2]$, **12** $(dme)_2$, several compounds were observed when Li piperidide was used as nucleophile. Amongst these, the most interesting one was $(dme)(THF)Li_2(cat)(catBH)$, **13** (dme)THF, the crystal structure of which was determined. In all cases where the borate species carried OR groups the O atoms of the RO or PhO group coordinate with the alkali metal cation.

DFT calculations for the series of anions $H_{4-n}BX_n{}^-$ showed that $HBX_3{}^-$ is the most stable species for X = F, OH, NH_2. This confirms experimental results.

Key words: Hydridoborates, Catecholatohydridoborates, Aminohydridoborates, Alkali Metals, DFT Calculations

Introduction

It is well known that the reducing ability of alkali metal tetrahydroborates [2 – 4] depends on a number of factors, the most important one being the ionic character which increases as one moves from $LiBH_4$ to $CsBH_4$ while the reducing power decreases. The substitution of hydrogen atoms of the $BH_4{}^-$ unit by CN, OR, RC(O)O leads generally to higher selectivity. Compounds such as $NaBH_3CN$ [5], $Na[HB(O^tBu)_3]$ [6] or $Na[HB(OC(O)Me)_3]$ [7] are commercially available. Nevertheless, only few structures of the alkali metal salts in the solid state are known, as for example $LiBH_3CN$ [8], $(HO(CH_2)_2N(CH_2)_2]_2Na[BH_3CN]$ [9], or $[(HO(CH_2)_2]_3N \cdot Na[H_3BCN]$ [10], but little is known about their structures in solution [11].

Many reductions of organic functional groups with $NaBH_4$ are performed either in aqueous or alcoholic solutions, although $NaBH_4$ reacts with both solvents slowly with hydrogen evolution. In general, reactions in alcohols are preferred to reductions in other media [3, 4, 12]. It was suggested that this may be due to the formation of alkoxohydridoborates $[BH_{4-n}(OR)_n]^-$ [2 – 4, 13].

Santaniello *et al.* showed that $NaBH_4$ reacts with polyethyleneglycol (peg) with formation of the anion $[H_2B(peg)]^-$ [14, 15] as deduced from ^{11}B NMR studies. Kinetic studies of aqueous solutions of $NaBH_4$ showed that the anion $[H_2B(OH)_2]^-$ plays an important role [16]. However, this species could not be detected in solution by ^{11}B NMR in contrast to $[BH_3OH]^-$ and $BH(OH)_3]^-$ [16]. Moreover, there is evidence that $[BH_2(OR)_2]^-$ species are, in general, not very stable in solution [4, 13, 17–19].

Results

Reactions of alkalimetal alkoxides with borane-tetrahydrofuran

There are several routes to alkoxohydridoborates, the most convenient ones being reactions of alcohols with MBH_4, the addition of an alkali metal hydride MH to $BH_{3-n}(OR)_n$, or the addition of $BH_3{\cdot}THF$ to alkali metal alkoxides. In the latter case and using homogeneous conditions one can expect reactions according to eq. (1) by using equivalent amounts of the reagents. However, if there is a local excess of $BH_3{\cdot}THF$ hydride abstraction from $M(H_3BOR)$ as shown in eq. (2) can be expected as well as substituent exchange reactions as depicted by eq. (3). Continuous substituent exchange leads finally to MBH_4 and $M[B(OR)_4]$. This latter process is technically achieved in the synthesis of $NaBH_4$ from NaH and $B(OMe)_3$ which proceeds at elevated temperatures *via* $Na[HB(OMe)_3]$ [20]. The reaction according to eq. (2) can be suppressed to a certain extent by using high dilution and/or low temperatures [17].

$$M(OR) + H_3B \cdot THF \rightarrow M(H_3BOR) + THF \quad (1)$$

$$\begin{aligned} &M(H_3BOR) + H_3B \cdot THF \\ &\rightarrow M(BH_4) + H_2BOR \cdot THF \end{aligned} \quad (2)$$

$$2\,M(H_3BOR) \rightarrow M(BH_4) + M[H_2B(OR)_2] \quad (3)$$

$$2\,MOR + H_3B \cdot THF \rightarrow HB(OR)_2 + 2\,MH + THF \quad (4)$$

Reactions between $BH_3{\cdot}THF$ and MOR can be followed by ^{11}B NMR spectroscopy. The results listed in Table 1 were obtained with solutions of $M(OtBu)$ (M = Li, Na, K), $LiOCPh_3$ and $LiOC_6H_2(tBu)_3$ in THF in a 1 : 1 ratio. In none of the reactions studied could species of the type $M[H_2B(OR)_2]$ and $M[B(OR)_4]$ be detected. We were also unable to isolate $Na[H_3B(OR)]$ or $Na[HB(OR)_3]$ (R = *t*Bu) from the solutions although they contained 19% and 39% of these components, respectively. The main product was actually $NaBH_4$ [21]. This is also true for the reaction with KO*t*Bu. Potassium tetrahydridoborate precipitated from the solution. The main product in solution was $K[HB(OtBu)_3]$, and it is interesting that $B(OtBu)_3$ is formed in a significant amount (23%) in case of LiO*t*Bu, but not in the reactions with NaO*t*Bu or KO*t*Bu.

51% of $LiOCPh_3$ is converted into $LiBH_4$, and almost the same amount into $Li[HB(OCPh_3)_3]$ (47%). $Li[H_3BOCPh_3]$ is a minor product (2%). In contrast, the rather bulky 2,4,6-tri-*tert*-butylphenolate gave only 4% of $Li[HB(OC_6H_2tBu_3)_3]$ besides 41% of $LiBH_4$ and, rather unexpected 55% of the borane $HB(OC_6H_2tBu_3)_2$. These results show i) that the reactions do not stop at the adduct stage $M[H_3BOR]$, ii) that the hydride/OR exchange – by what mechanism whatsoever – has a driving force that favours MBH_4 and $M[HB(OR)_3]$. Moreover, the stoichiometry of the reaction products requires the formation of MH, in case of the reaction with $LiOC_6H_2tBu_3$ about 55% of LiH. We assume that it is formed in a reaction according to eq. (4), but alternatives are also feasible. Since in most reactions the solutions did not turn turbid, one has to assume that the alkali metal hydride is complexed by the alkoxohydridoborate molecules.

Lithium bis(pentafluorophenoxo)dihydridoborate

Brown *et al.* [22] have shown that the reaction of phenol with $LiBH_4$ in THF produces a mixture of $Li[HB(OPh)_3]$ and $Li[B(OPh)_4]$, We can confirm this. Neither $Li[H_3BOPh]$ nor $Li[H_2B(OPh)_2]$ could be detected by ^{11}B NMR. However, we expected that the synthesis of a $Li[H_2B(OAr)_2]$ species might be achieved by employing pentafluorophenolate as a less nucleophilic reagent [13]. In the hope to avoid substitutent exchange reactions we first studied the reaction of $HB(OC_6F_5)_2$ with LiH, expecting a reaction according to eq. (5). Compound $HB(OC_6F_5)_2$ was prepared as shown in eq. (6)

$$HB(O_6F_5)_2 + LiH \rightarrow Li[H_2B(OC_6F_5)_2] \quad (5)$$

$$\begin{aligned} &2\,HOC_6F_5 + H_3B \cdot THF \\ &\rightarrow HB(OC_6F_5)_2 \cdot THF + 2\,H_2 \end{aligned} \quad (6)$$

$$3\,HB(OR)_2 + THF \rightarrow 2\,B(OR)_3 + H_3B \cdot THF \quad (7)$$

$$LiBH_4 + 2\,HOC_6F_5 \rightarrow Li[H_2B(OC_6F_5)_2] + 2\,H_2 \quad (8)$$

$$3\,\mathrm{Li[H_2B(OC_6F_5)_2]} + 2\,\mathrm{THF} \rightarrow 2\,\underset{\mathbf{1}}{\mathrm{(F_5C_6O)_3B \cdot THF}} + \mathrm{LiBH_4} + 2\,\mathrm{LiH} \qquad (9)$$

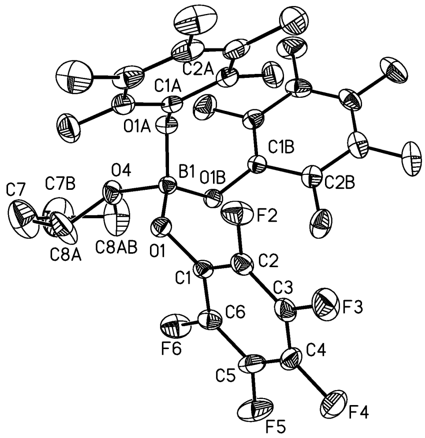


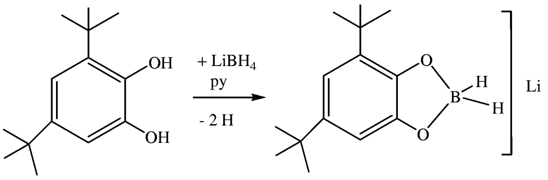
Fig. 1. Molecular structure of $(F_5C_6O)_3B{\cdot}THF$ (**1**). Thermal ellipsoids are depicted on a 25% probability level. Selected bond lengths (in Å) and bond angles (in °): B1–O1 1.431(4), B1–O4 1.558(9), O1–C1 1.348(5), O4–C8 1.47(2), O1–B1–O1A 113.8(3), O1–B1–O4 104.7(3), C8–O4–B1 121.1(6), B1–O1–C1 123.8(3), O1–C1–C6 123.6(4), O1–C1–C2 120.4(4). – Interplanar angles: C1 to C6/C1A to 6A 74.3°; C1O1B1/C1 to C6 103.6°.

An ^{11}B NMR signal at $\delta = 7.4$ [d, $^1J(^{11}B^1H) = 142$ Hz] has shown that the bis(pentafluoro-phenolato) borane was present in solution. Compared with δ values for other $HB(OR)_2$ species [23] the boron nucleus is better shielded by about 20 ppm, and this indicates to the formation of a THF adduct. On the other hand, the coupling constant fits better to a tri-coordinated boron atom. In addition, a singlet at $\delta = 3.1$ ($\sim$ 16%) has shown clearly the formation of $B(OC_6F_5)_3{\cdot}THF$, **1**. On standing over night the reaction mixture turned into a gel (THF polymerization) in which crystals were embedded. These were isolated and proved to be **1** by an X-ray structure determination (see Fig. 1). **1** is most likely generated by a substituent exchange as shown in eq. (7). Because $(C_6F_5O)_2BH{\cdot}THF$ could not be obtained in a pure state, we turned to the reaction of $LiBH_4$ with C_6F_5OH. This reaction in a polar solvent provided only $Li[HB(OC_6F_5)_3]$ [13]. In our case we avoided the presence of a polar solvent and treated a suspension of $LiBH_4$ in benzene with the phenol according to eq. (8) in hexane. Hydrogen was readily evolved. The solid was only sparingly soluble in $CDCl_3$, and exhibited an ^{11}B NMR signal at $\delta = 1.7$. This signal was rather broad and showed no clear triplet structure. Mass spectrometry led to signals at $m/e = 386/385$ corresponding to $(C_6F_5O)_2BH$. However, the elemental analysis of the solid fitted well with $Li[H_2B(OC_6F_5)_2]$. The compound is highly sensitive to moisture. Obviously, hydrolysis had occurred during the recording of its IR spectrum as the main band in the νBH region was at 2483 cm^{-1} with two weak bands at 2308 and 2275 cm^{-1}. The former would be compatible with $HB(OC_6F_5)_2$, the latter with $[H_2B(OC_6F_5)_2]^-$.

Attempted dissolution of the solid in THF resulted in a slurry. The supernatant solution showed a doublet at $\delta^{11}B = 6.1$, $^1J(^{11}B^1H) = 135$ Hz, corresponding to $(C_6F_5O)_2BH{\cdot}THF$. This result demonstrates that $Li[H_2B(OC_6F_5)_2]$ is unstable in polar solvents, but stable as a solid.

Lithium bis(catecholato)borates and related species

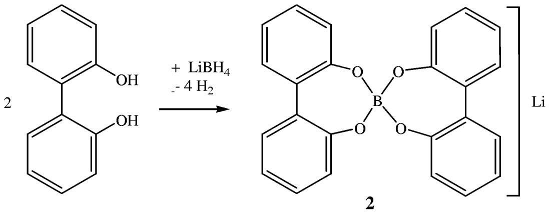
Although it is well known that catechol reacts with $LiBH_4$ in polar solvents to give lithium bis(catecholato)borate irrespective of the stoichiometry employed, we hoped that the introduction of bulky *t*butyl groups into the catechol, as in 4,6-$t\mathrm{Bu}_2H_2C_6O_2{}^-$ (cat') might retard or even prohibit the formation of a bis(catecholato)borate. If this could be achieved than a reaction according to eq. (10) might be realized.



(10)

Using pyridine as a solvent we observed the formation of $H_3B{\cdot}py$ by ^{11}B NMR. On heating the solution only $Li[B(O_2C_6H_2t\mathrm{Bu}_2)_2]$ and $LiBH_4$ could be detected. This suggests that in a first step the di-*tert*butylcatechol was monometallated by $LiBH_4$ with formation of hydrogen, $H_3B{\cdot}py$ and $Li[OC_6H_2(tBu)_2OH]$. These last two components then reacted at higher temperature with formation of $Li[Bcat'_2]$ and $LiBH_4$ probably *via* $Li[H_2Bcat']$.

A similar behaviour was observed for the reaction of $LiBH_4$ with 2,2'-dihydroxydiphenyl. In the presence of pyridine the formation of $H_3B{\cdot}py$ was noted. On heating, the final products were $Li[B(O_2R')_{2'}]$ (**2**) (R' = C_6H_4-C_6H_4) and $H_3B{\cdot}py$ (see eq. 11). However, when the reactions were performed in the presence of piperidine, pyrollidine, and morpholine then the Li salts of



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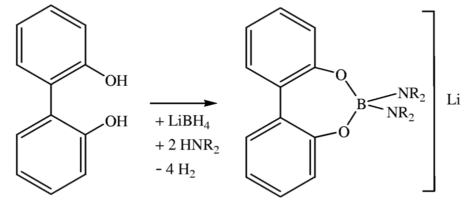


(12)

HNR$_2$ = HNC$_5$H$_{10}$ **3**
HNC$_4$H$_8$ **4**
HNC$_4$H$_8$O **5**
HN*t*BuPh **6**

the diphenylenedioxa-di(amino)borates **3**–**5** as shown in eq. (12) were formed. Due to their insolubility, these salts can be readily isolated. However, in the presence of NH*t*BuPh only **2** results but no **6**. Formation of these anions is an indication that during the course of the reaction of LiBH$_4$ with 2,2'-dihydroxydiphenyl the anion $[H_2BO_2R']^-$ is an intermediate.

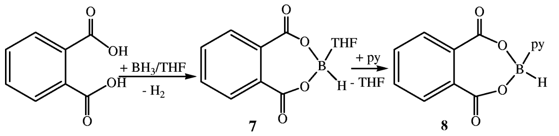
Reactions of phthalatoborane with nucleophiles

Because the reaction of phthalic acid with LiBH$_4$ led always to a mixture of products we synthesised the phthalatoborane $[C_6H_4(C(O)O]_2BH$ from phthalic acid and borane in THF as shown in eq. (13). ^{11}B NMR spectroscopy showed that this compound was present in solution only in minute amounts ($\sim$ 2%). The main product was the THF adduct **7**. However, **7** is not a stable compound, it decomposes in solution. Therefore, its reactions were studied by using only freshly prepared material. In contrast, the pyridine adduct **8** is perfectly stable.

1 : 1-Reactions of **7** with sodium *t*butylate, lithium amides or lithium *t*butyl resulted in the formation of various compounds. We found it essential that the solution of **7** is added to the solid alkali metal compounds in a 3 : 1 molar ratio in order to get reproducible results. Under these conditions reactions according to eq. (14) occurred.

Table 1. Reaction products (in % of B concentration) formed from MOR and BH$_3$ · THF (ratio 1 : 1) in THF solution.

MOR	M[BH$_4$]	M[H$_3$BOR]	M[HB(OR)$_3$	B(OR)$_3$	HB(OR)$_2$
LiO*t*Bu	26	7	44	23	–
NaO*t*Bu	43	19	38	–	–
KO*t*Bu	15 calcd.	35	65	–	–
LiOCPh$_3$	51	2	47	–	–
LiOC$_6$H$_2$*t*Bu$_3$	41	–	4	–	55



7 **8**

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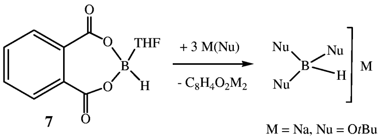

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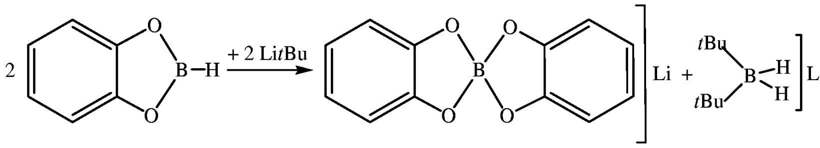
(14)

M = Na, Nu = O*t*Bu **9**
M = Li, Nu = NMePh **10**
M = Li. Nu = *t*Bu **11**

When **7** was treated with three equivalents of Li*t*Bu compound (THF)$_3$Li[HB(*t*Bu)$_3$] (**11**), could be isolated from the solution as colorless crystals. Its crystal structure was determined which is shown in Fig. 4. **11** could not be prepared from B*t*Bu$_3$ and LiH in THF [24, 25]. It is the previously missing link in the series of compounds Li[H$_{4-n}$B(*t*Bu)$_n$] [26, 27].

Compound Li[HB(NMePh)$_3$] (**10**), was the main product in the reaction of LiNMePh with **7**. However, **10** is unstable in solution decomposing slowly with elimination of LiH and formation of B(NMePh)$_3$. The structure of this tris(amino)borane is already known [28], and we characterized it by comparing the cell parameters of the crystal.

Also NaO*t*Bu reacted with **7** according to eq. (14). The main product ($\sim$ 80%) was Na[HB(O*t*Bu)$_3$], **9**, characterized by its ^{11}B NMR spectrum which showed a doublet at $\delta^{11}B = 0.4$ ppm, $^1J(^{11}B^1H) = 121$ Hz. It was accompanied by a second product ($\sim$ 20%) with $\delta^{11}B = 2.3$ ppm. This chemical shift corresponds with B(O*t*Bu)$_4^-$ [*e. g.* B(OMe)$_4^-$ shows a signal at $\delta^{11}B = 2.7$ ppm] [23]. Attempts to obtain single crystals of Na[HB(OtBu)$_3$] from the mixture of the two products by first extracting it with hexane followed by diethyl ether showed that most of the Na[B(O*t*Bu)$_4$] went into the ether phase. Storing the hexane solution at -80 °C and removing the solvent partially in several steps resulted in the formation of colorless crystals which deteriorated rapidly in a dry stream of N$_2$. Therefore, single crystals for a structure determination were selected at -30 °C. These proved to have the rather complex composition Na[HB(O*t*Bu)$_3$]·Na[OB-(O*t*Bu)$_2$]·Na[OB(O*t*Bu)OH$_{0.64}$H$_{0.36}$]$^{\cdot}$. Obviously hydrolysis of Na[HB(O*t*Bu)$_3$] had occurred to a certain



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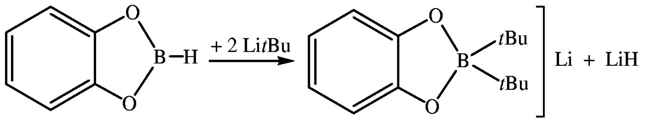

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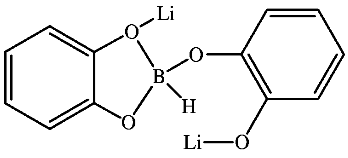

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Table 2. Reaction products observed by ^{11}B NMR of a 1 : 1 reaction of catecholatoborane with *t*BuLi in ether/hexane at −78 °C. Coupling constants $^1J(^{11}B^1H)$ in parentheses.

	^{11}B Chemical shift (ppm)	Percentage proportion
CatB*t*Bu	36.1 s	15
Li[CatB(*t*Bu$_2$)]	14.6 br	10
Li(BCat$_2$)	7.8 s	3
Li(H$_2$B*t*Bu$_2$)	−4.5 t (69 Hz)	50
Li(H$_3$B*t*Bu)	−20.3 quart. (79 Hz)	17
LiBH$_4$	−40.8 quint. (81 Hz)	5

Table 3. Reaction products observed by ^{11}B NMR of a 1 : 1 reaction of catecholatoborane with $LiNC_5H_{10}$ in ether/hexane at −78 °C. Coupling constants $^1J(^{11}B^1H)$ in parentheses.

	^{11}B Chemical shift (ppm)	Percentage proportion
$HB(NC_5H_{10})_2$	25.8 d (124 Hz)	34
Li(BCat$_2$)	8.4 s	22
Li(CatBH-OC$_6$H$_4$OLi)	6.5 br	38
Li(H$_3$BNC$_5$H$_{10}$) [29]	−16.3 br	6

degree. The compounds crystallized with 1 mol of hexane.

Reactions of catecholborane with nucleophiles

In analogy to the reactions of **7** with nucleophiles we also studied similar reactions with catecholatoborane. There is a high driving force for the formation of the alkali metal bis(catecholato)borate. Therefore, one may expect reactions according to eq. (15, 16).

The reaction of catecholborane with Li*t*Bu was performed in a mixture of diethyl ether and hexane at −78 °C. Table 2 shows that several compounds were formed, the main product being a dihydroborate, in this case the known $[BH_2(t\mathrm{Bu})_2]^-$ [26]. Addition of DME to the mixture led to the crystallization of one of the by products as (dme)$_2$Li[(C$_6$H$_4$O$_2$)B(*t*Bu)$_2$] (**13**) whose structure could be determined (see Fig. 4).

A totally different behavior was observed when lithium piperidide was used as the nucleophile. Once again a mixture of compounds was generated. In this case no dihydroborate was formed, but Li[H$_3$Bpip] appeared in small amounts (6%). The main components of the mixture were HB(pip)$_2$ (34%) and a catecholatoborate whose composition turned out to be (dme)Li[catB(H)O-C$_6$H$_4$OLi(THF)] (**13**) (38%). It was characterized by its crystal structure. Table 3 presents the result of this reaction.

Crystal structures

Although NMR data, in particular ^{11}B NMR data allow the assignment of most of the species by their chemical shifts and $^1J(^{11}B^1H)$ coupling constants, they give, however, no information as to the degree of association in solution which is expected particularly for the O and N containing products which may interact with the alkali metal ions [11]. Since a number of hitherto unknown borates were formed, X-ray structure determinations were essential.

Fig. 1 shows the structure of $(C_6F_5O)_3B\cdot THF$. The compound crystallized in space group R$\bar{3}$, and the boron atom and the oxygen atom of THF molecule oc-

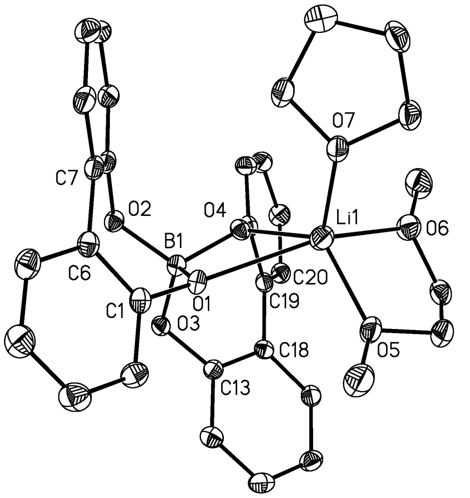


Fig. 2. Molecular structure of (dme·THF)Li[B($O_2C_{12}H_8)_2$], **2 · THF · dme**. Thermal ellipsoids are depicted on a 25% probability level. Selected bond lengths (in Å) and bond angles (in °): Li1–O1 2.510(4), Li1–O4 1.917(4), Li1–O5 1.931(4), Li1–O6 2.036(4), Li1–O7 1.920(4), B1–O1 1.454(3), B1–O2 1.438(3), B1–O3 1.429(3), B1–O4 1.464(3), O1–C1 1.356(2), O2–C12 1.345(2), C6–C7 1.459(3), O2–C12 1.345(2), O3–C13 1.353(2), O4–C24 1.360(2), C18–C19 1.458(3). – O1–Li1–O4 59.2(1), O1–Li1–O5 93.9(2), O1–Li1–O6 160.0(2), O1–Li1–O7 102.3(2), O4–Li1–O5 124.6(2), O4–Li1–O6 108.2(2), O4–Li1–O7 111.7(2), O5–Li1–O6 180.6(2), O5–Li1–O7 121.5(2), O6–Li1–O7 96.9(2), O1–B1–O2 112.5(2), O1–B1–O3 113.8(2), O1–B1–O4 100.7(2), O2–B1–O3 105.3(2), O2–B1–O4 112.7(2), O3–B1–O4 112.2(2), Li1–O1–B1 86.5(2), Li1–O1–C1 154.5(2), Li1–O4–B1 112.5(2), Li1–O4–C24 121.2(2). – Interplanar angles (in °): C1–C6/C7–C12 135.6, C13–C18/C19–C24 142.5, O1B1O4/O3B1O2 84.3, O1Li1O4/O1B1O4 128.2.

cupy a special position on the threefold axis. Therefore, the positions of the C atoms of the THF molecule are threefold disordered. Fig. 1 shows only one of these three orientations. The B–O bond lengths of the phenolic oxygen [1.431(4) Å] falls into the category observed for tetraorganyloxoborates. However the B–O bond to THF is longer, 1.557(9) Å. The C–O–B bond angles to the C_6F_5 group is quite open with 123.8(6)°, similar to the C–O–B bond angle of 124.7(7)° for the THF oxygen atom.

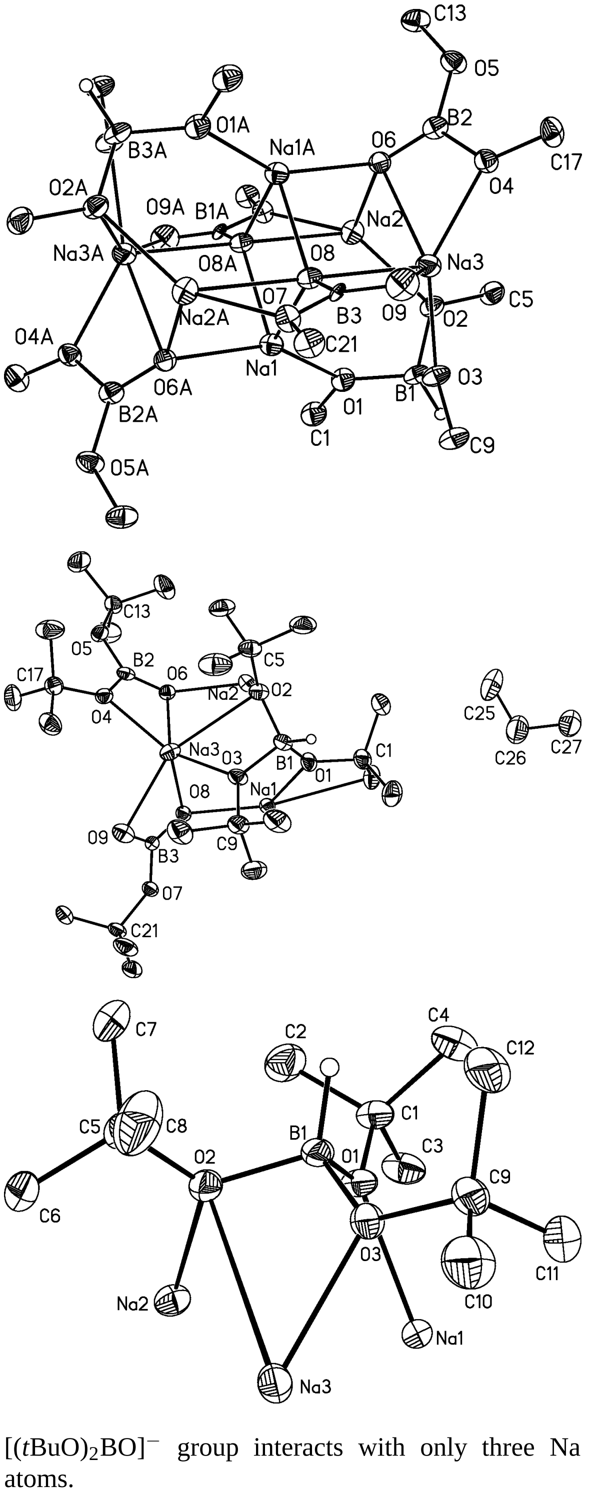
Fig. 2 shows the molecular structure of compound **2 · THF · DME**. It crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$. Its Li atom is pentacoordinated. The Li1-O bonds show that the coordination polyhedron around the Li center is a strongly distorted trigonal bipyramide with O-Li-O bond angles spanning the range from 59.2(1)° to 160.0(1)°. Also, Li-O bond lengths differ considerably: from 1.917(4) to 2.510(4) Å. The longest bond is to the oxygen atom O1. The surrounding about the boron center is also rather asymmetric. B-O bonds range from 1.429(3) to 1.464(3) Å, and O-B-O bond angles from 100.7(2)° to 112.7(2)°. While oxygen atoms of the 2,’2-dioxodiphenyl unit are bonded to the boron atom only two of them coordinate also to the Li1 atom.

It is well known that the two phenyl rings of diphenyl are twisted against each other. In **2** the interplanar angles are 135.6 and 142.5°, respectively. Moreover, the central LiO_2 B ring is not planar as shown by an interplanar angle O1Li1O4/O1B1O4 of 128.2°. The point group symmetry of the molecule is C_1.

Fig. 3 (top) depicts the rather unusual structure of a dimeric sodium hydrido-tris(*tert*-butoxo) borate {Na[HB(O*t*Bu)$_3$]·Na[OB(O*t*Bu)$_2$]·Na[OB(O*t*Bu)OH$_{0.64}$H$_{0.36}$]}$_2$. For the sake of clarity the Me groups have been omitted. The molecule is centrosymmetric and contains a Na_6O_6 core. All of its oxygen atoms except O5 and O5A coordinate with sodium ions. The Na_6O_6 core can be viewed as two face sharing cubes with two opposite corners missing. However, the two missing sites could be assumed as filled in by atoms O3/O3A but the Na1–O3 distance is 3.272 Å, and this excludes a sufficiently strong interaction.

While Fig. 3 (middle) shows the asymmetric unit of the molecule including half of the hexane solvent molecule, one can readily note the Na[HB(O*t*Bu)$_3$] building block in Fig. 3 (bottom). The Na[HB(O*t*Bu)$_3$ part of the molecule coordinates with its three O atoms to three different Na atoms. The sum of the O–B–O bond angles is 317.4°, about 10° less than for an ideal tetrahedral arrangement. The average B–O bond length is 1.495(5) Å. This lies well in the range of B–O bond lengths found for alkoxoborates (1.42 to 1.59 Å).

In addition to this building block there are two different anionic groups containing tri-coordinated boron atoms: [(*t*BuO)$_2$BO]$^-$ and [*t*BuOB(OH,H)O]$^-$. The second of these showed an unusually high thermal parameter for its O9 atom suggesting that close to its position an other lighter atom was present. Therefore, we placed a hydrogen atom closer to the boron atom and refined the site occupation factors for H and OH. A reasonable solution resulted for the composition [*t*BuOB(OH)$_{0.64}$H$_{0.36}$O]$^-$. The unique O atoms in these two anions coordinate differently with Na atoms. Atom O8 of the anion [*t*BuOB(OH)$_{0.64}$H$_{0.36}$O]$^-$ coordinates to four Na atoms while atom O6 of the



⟵ Fig. 3. *Top:* Molecular structure of $\{Na[HB(OtBu)_3]\cdot[Na[(tBuO)2BO]\cdot[Na(tBuOB(O)(OH)_{0.64}H_{0.36})]\}_2$. Only one C atom for each *tert*-butoxy group shown. Thermal ellipsoids are depicted on a 25% probability level. Selected bond lengths (in Å) and bond angles (in °): Na1–O1 2.286(3), Na1–O8 2.319(3), Na1–O8A 2.397(3), Na1–O6A 2.233(3), Na2–O2 2.249(3), Na2–O6 2-223(3), Na2–O7A 2.297(3), Na2–O8A 2.434(3), Na3–O4 2.278(3), Na3–O3 2.292(3), Na3–O8 2.491(2), Na3–O9 2.513(5), Na3–O2 2.866(3), B1–O1 1.498(6), Na–O2 1.510(5), B1–O3 1.476(5), B2–O4 1.406(5), B2–O5 1.392(5), B2–O6 1.319(5), B3–O7 1.389(6), B3–O8 1.269(5), B3–O7 1.389(5), B1–H1 1.11(1). – O6A–Na1–O1 144.8(1), O6A–Na1–O8 92.1(1), O1–Na1–O8 121.7(1), O6A–Na1–O8A 88.6(1), O6–Na2–O2 103.4(1),O6–Na2–O7A 118.4(1), O2–Na2–O7A 138.3(1), O6–Na2–O8A 89.3(1), O2–Na2–O8A 127.2(1), O7A–NA2–O8A 567.0(1), O4–Na3–O3 143.3(1), O4–Na3–O6 58.7(1), O3–Na3–O6 131.2(1), O4–Na3–O8 119.3(1), O3–Na3–O8 97.4(1), O6–Na3–O8 85.8(1), O4–Na3–O9 116.2(1), O8–Na3–O9 102.7(1), O4–Na3–O2 106.2(1), O1–B1–O2 105.3(4), O1–B1–O3 107.6(3), O2–B1–O3 104.5(3), O5–B2–O6 128.3(5), O4–B2–O6 117.5(4), O4–B2–O5 114.2(4), O8–B3–O9 123.9(5), B1–O1–Na1 121.6(2), B1–O2–Na2 117.4(2), B1–O2–Na3 85.3(2), B2–O4–Na3 94.8(2), B2–O6–Na2 136.3(3), B3–O8–Na1 134.1(2), B3–O8–Na2A 91.3(3), B3–O8–Na1 134.4(3). Torsion angles (in °): Na1O1B1O2 −86.6, Na3O3B1O2 150.9, Na2O2B1O1 21.4. Interplanar angles (in °): Na1AO6Na2/O6B2O4 49.4, Na1AO8Na1/O8B3O2 82.7, Na3O6Na2/O6B2O4 136.5.

Middle: The $Na[HB(OtBu)_3]$ part of the structure shown above.

Bottom: The $Na[HB(OtBu)_3]$ building block of the structure shown above. C25 – C27 shows one half of the hexane solvent.

$[(tBuO)_2BO]^-$ group interacts with only three Na atoms.

Fig. 4 shows the molecular structure of $(THF)_3Li[HB(tBu)_3]$. As expected the anion coordinates to the solvated Li ion *via* its hydrogen atom. The Li1–H1–B1 bond angle is 153(1)°. Steric repulsion between the *t*Bu groups opens the C–B–C bond angles on average to 113°. However, this type of interaction becomes more significant when looking at the B–C bond lengths. Within the series $Li[H_3BtBu]$<$Li[H_2BtBu_2]$<$Li[HBtBu_3]$ there is a constant increase of the B–C bond lengths from 1.625(3) *via* 1.643(3) to 1.71(1) Å [26, 27]. The B–H bond length is on the long side of those known in organylhydridoborates, but the Li–H distance falls well within those found in other lithium hydridoborates.

Fig. 5 depicts the structure of compound $(dme)_2Li[catB(tBu)_2]$ (**12**). Its structure is rather simple compared to those shown in Fig. 3a but nevertheless provided a surprise, because one of the two DME ligands is monodentate while the other is bidentate. This is due to the fact that one oxygen atom of the catecholato unit binds to the Li center resulting in the shortest of the four Li–O bonds. The longest

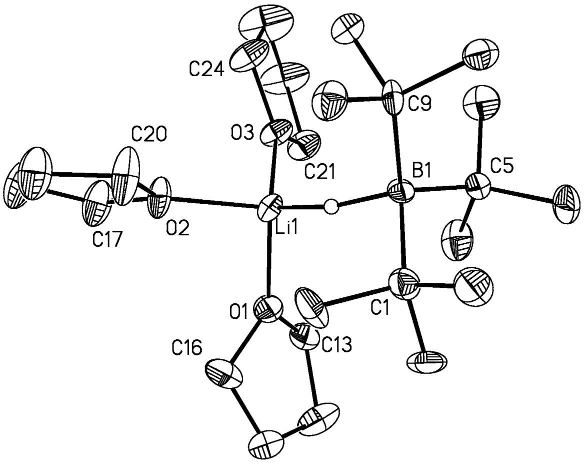


Fig. 4. Molecular structure of (THF)$_3$Li[HB(tBu)$_3$], **11**·**3**THF. Thermal ellipsoids are depicted on a 25% probability level. Selected bond lengths (in Å) and bond angles (in °): Li1–O1 1.97(1), Li1–O2 1.94(2), Li1–O3 1.96, B1–C1 1.71(1), B1–C5 1.73(1), B1–C9 1.69(1), Li1–H1 1.81(2). – C1–B1–C5 113.2(6), C1–B1–C9 113.8(7), C5–B1–C9 112.7(7), C1–B1–O4 1.464(3).

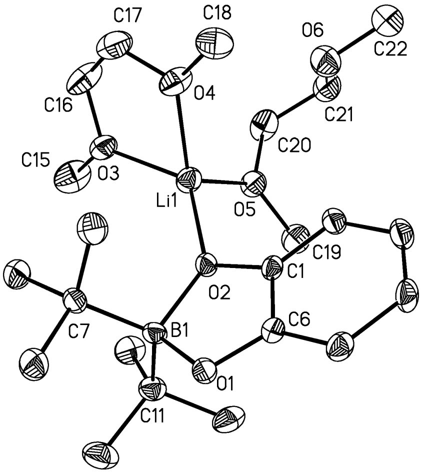


Fig. 5. Molecular structure of (dme)$_2$Li[tBu$_2$Bcat] (**12**). Thermal ellipsoids are depicted on a 25% probability level. Selected bond lengths (in Å) and bond angles (in °): Li1–O2 1.936(5), Li1–O3 2.013(6), Li1–O4 2.010(6), Li1–O5 1.966(6), B1–O1 1.531(4), B1–O2 1.589(4), B1–C7 1.646(5), B1–C11 1.644(5), O2–C1 1.361(3), O1–C6 1.350(3), O3–C16 1.382(4), O4–C17 1.385(4), O4–C18 1.415(4), O5–C19 1.428(4), O4–C20 1.445(4), O6–C21 1.415(5), O6–C22 1.411(4). – O4–Li1–O5 117.1(3), O4–Li1–O2 116.2(3), O4–Li1–O3 81.2(2), O2–Li1–O3 131.8(3), O2–Li1–O5 108-8(3), O3–Li1–O5 99.8(2), O4–Li1–O5 117.1(3), Li1–O2–B1 133.8(2), Li1–O2–C1 118.0(2), B1–O1–C6 108.9(2), B1–O2–C1 107.1(2), O1–B1–C7 121.8(3), O1–B1–C11 108.8(2), C7–B1–C11 121.8(3). – Interplanar angles (in °) O3L1O4/O5Li1O2 75.9, O1B1O2/B1C7C11 88.4, O1B1O2/C1-C6 2.9.

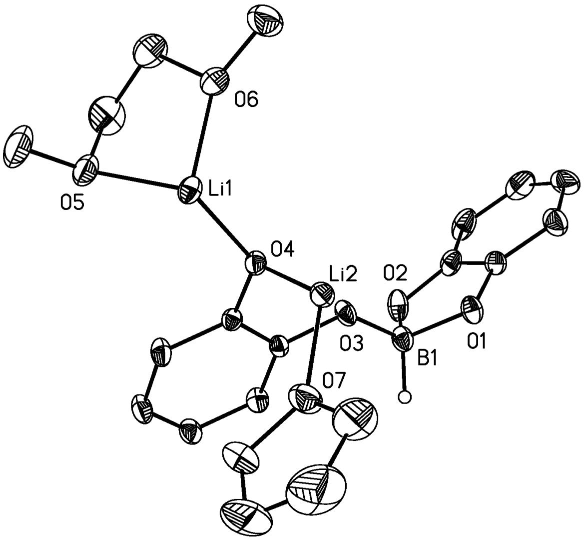


Fig. 6a. The asymmetric unit of **13**.

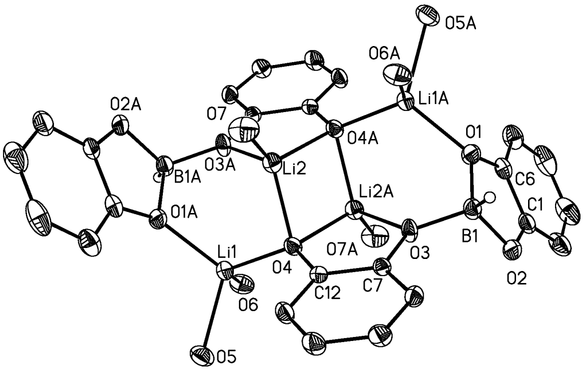


Fig. 6b. Molecular structure of {(thf·Li)(dme·Li)[(catBH)-(cat)]}$_2$, (**13**)$_2$. Thermal ellipsoids are depicted on a 25% probability level. Selected bond lengths (in Å) and bond angles (in °): Li1–O4 1.887(4), Li1–O5 2.022(4), Li1–O6 2.010(4), Li1–O1A 1.953(5), Li2–O4 1.940(4), Li2–O7 1.910(4), Li2–O7 1.910(4), Li2–O3A 1.944(4), B1–O1 1.519(3), B1–O2 1.466(4), B1–O3 1.471(4). – O1–B1–O2 104.1(2), O1–B1–O3 113.0(1), O2–B1–O3 111.6(2), H1–B1–O2 112(1), O4–Li1–O5 118.6(2), O4–Li1–O6 112.0(2), O4–Li1–O1A 112.6/(2), O4–Li2–O7 120.1(2), O4–Li2–O4A 99.5(2), O4–Li2–O3A 106.5(2), O3A–Li2 –O4A 85.2(2), O7–Li2–O4A 124.5(2), O7–Li2–O3a 114.9(2), O3A–Li2–O4A 85.2(2). Interplanar angles (in °): Li2O4Li2AO2A/O4Li2AO3 38.8, O4Li2AO3/BaO1O2 69.7, B1O1O2/C1-C6 2.4, O4O3Li2A/O4ALi1AO1 71.3.

Li–O bonds are those to the chelated DME molecule. As expected, there are two different B–O bond lengths for the catecholato unit: 1.531(4) and 1.589(4) Å. Coordination to the Li atom lengthens the B–O bond. The two B–C bonds are of equal lengths. They are shorter by 0.06 Å than in compound **11**. Although the

O–B–C bond angles are close to 110° the C–B–C bond angle is quite open and corresponds with 121.8(3)° to an sp^2 type boron atom.

An interesting structure is also provided by compound **13**. Fig. 6a shows the asymmetric unit. The low coordination of the Li atoms suggest that it is associated. One of the two Li atoms interacts with a chelating DME molecule while the other one binds one THF molecule. Indeed, the molecule is dimeric in the solid sate. The association to a centrosymmetric dimer is represented in Fig. 6b. Now the Li atoms are tetra-coordinated. The structure of the dimer reveals that one catecholate unit is doubly deprotonated, one Li atom forms an almost planar five-membered LiO_2C_2 ring while the chatecholatoborane unit coordinates with one of its O atoms to a Li atom (O1A-Li1). The molecule can be looked at as a lithium tri(organyloxo)hydridoborate, because its boron atom binds to three oxygen atoms and one hydrogen atom.

Stability of substituted hydridoborates

Previous work [6–8, 12–14, 26, 27, 29–32] has shown that substituted hydridoborates have a tendency to substituent exchange where the species $[HBX_3]^-$ seems to be the most stable for X = F, OR and NR_2. In contrast, all members of the alkali metal alkyl substituted hydridoborates with different R groups are readily accessible and for some of them the crystal structures have been determined [26, 32–38]. In this study the missing member in the series $Li[H_{4-n}B(t\mathrm{Bu})_n]$, the compound with $n = 3$ was prepared, and structurally characterized. As far as we are aware no theoretical study has been performed which could give evidence that the cited tendencies of substitutent exchange to give finally BH_4^- and BX_4^- is thermodynamically or kinetically controlled. Therefore, we performed DFT calculations at the B3LYP/6-311++G(d,p) level for a series of substituted hydridoborate species. Solvent and cation effects were not taken into account. Table 4 lists the point group symmetry for these species. Calculations for these geometries showed no imaginary frequencies, *i. e.* the calculations refer to minima on the local hypersurface.

The calculated ΔH_f energies for the species allow an estimation of the reaction energies for the isodesmic reactions summarized in Table 5. Because the number of bonds remain the same in the ligand exchange reactions, systematic errors are compensated [38]. The energies quoted in Table 5 refer to one mole of the substituted hydridoborate.

Table 4. Point group symmetry for a series of substituted hydridoborates.

	F, Cl	OMe	CN	NCS	Me	NH_2
H_3BX^-	C_{3v}	C_1	C_{3v}	C_1	C_{3v}	C_1
$H_2BX_2^-$	C_{2v}	C_2	C_{2v}	C_{2v}	C_{2v}	C_1
$HBHX_3^-$	C_{3v}	C_s	C_{3v}	C_{3v}	C_{3v}	C_1
BX_4^-	T_d	D_{2d}	T_d	D_{2d}	T	C_1

Table 5. Calculated reaction energies (in kJ/mol for 1 mole of $H_{4-n}BX_n^-$) for the disproportionation of substituted hydridoborate anions.

X =	F	Cl	OMe	CN	NCS	Me	NH_2
$4\,H_3BX^- \rightarrow BX_4^- + 3\,BH_4^-$	−43	+25	−38	+53	+49	−9	−31
$2\,H_2BX_2^- \rightarrow BX_4^- + BH_4^-$	−44	+18	−26	+68	+56	−4	−32
$4\,HBX_3^- \rightarrow 3\,BX_4^- + BH_4^-$	−19	+29	−13	+49	+37	−5	−21

The data show that there are two types of substituents X. Substituents F, OMe and NH_2 favor the disproportionation to BH_4^- and BX_4^-, while substituents Cl, CN and NCS favor the mixed hydridoborate species. The data for X = Me show that the energy differences in the series $BMe_{4-n}H_n^-$ are rather small. This could indicate that disproportionation equilibria are established. However, since all members of the series could be isolated and structurally characterized, it is most likely that their stabilities are kinetically controlled. Because examples are known for M = Li, Na, and K, the cation has no influence on the stability. The calculated data for X = F, OMe and NH_2 are in accord with the preferred formation of HBX_3^- species, while for X = CN and NCS it is the species $H_2BX_2^-$. The substituents F, OMe and NH_2 are π-donors. Obviously this property is one factor that destabilizes the $H_{4-n}BX_n^-$ $(n = 1, 2)$ species. There is no correlation with electronegativity.

The type and number of substituents should influence the B–H and B–X bond lengths. Calculated bond lengths for the $H_{4-n}BX_n^-$ anions as a function of n and X are listed in Tables 6 and 7. In most cases the B–H distance decreases with increasing numbers of X. The differences are small for X = OMe, Me and NH_2, but significant for X = F, Cl and CN. In case of X = Me the B–H bond length increases as the number of Me groups increases. Amongst the X groups studied, the low electronegativity of the Me group with its electron donating function results obviously in bond lengthening. For X = F, Cl, OMe, NH_2, and NCS the B–X bond lengths decrease with increasing n while the B–C bond lengths of the cyanohydridoborate and the methylhydridoborate remain almost constant. So, only strong electronegative groups have a significant influence on the bond lengths.

Table 6. Calculated B–H bond lengths (in Å) for $H_{4-n}BX_n{}^-$ as a function of *n* and X.

X =	F	Cl	OMe	CN	NCS	Me	NH_2
H_3BX^-	1.240	1.215	1.242	1.224	1.222	1.243	1.245[a]
$H_2BX_2{}^-$	1.238	1.200	1.238	1.215	1.213	1.245	1.246[b]
$HBX_3{}^-$	1.228	1.191	1.242	1.210	1.208	1.249	1.241

[a] Average value of 1.239, 1.239 and 1.256 Å; [b] average value of 1.241, 1.251 Å.

Table 7. Calculated B–X bond lengths (in Å) for $H_{4-n}BX_n{}^-$ as a function of *n* and X.

X =	F	Cl	OMe	CN	NCS	Me	NH_2
H_3BX^-	1.483	2.012	1.506	1.590	1.548	1.657	1.577
$H_2BX_2{}^-$	1.456	1.941	1.499	1.589	1.535	1.653	1.570[a]
$HBX_3{}^-$	1.433	1.901	0.484	1,t591	1.525	1,654	1.566
$BX_4{}^-$	1.417	1.882	1.479	1.596	1.518	1.658	1.565

[a] Average value of 1.556 and 1.583 Å.

Two, respectively three, different bond lengths for $H_2BX_2{}^-$ and H_3BX^- result from the different orientations of the lone pair of electrons of the NH_2 group relative to the H or X atoms.

Discussion

It is well known that organyl hydroborates $M[H_{4-n}BR_n]$ are less prone to a substituent exchange than alkoxohydroborates $M[H_{4-n}B(OR)_n]$ [39]. Amongst the latter the tris(organyloxo)hydroborates $M[HB(OR)_3]$ seem to be the most stable ones in this series. However, their stability against ligand exchange depends on the size of the R group and the metal atom: the stability increases in the series Li < Na < K while it decreases with increasing size of the organyl group [26, 39]. Brown *et al.* detected that substituent exchange of the alkoxohydrido borates $K[HB(OR)_3]$ could be prevented by an excess of KH in THF solution [8, 29, 32]. On the other hand, alkoxohydridoborates $M[H_3BOR]$ and $M[H_2(OR)_2]$ are the least stable species in the series of $[H_{3-n}B(OR)_{n+1}]^-$ anions $(n = 1, 2, 3)$. An alkali metal salt of the catecholatodihydroborate anion $[H_2B(O_2C_6H_4]$ is unknown, but it can be stabilized by coordination to a transition metal fragment. Coordination involves two MHB bonds [40 – 43].

Our study supports previous investigations in this field [12, 13, 16]. The formation of $B(OtBu)_3$ in the reaction of BH_3·THF with LiO*t*Bu shows that an elimination of LiH occurs during the reaction, and regarding the results by Brown *et al.* [44] in the stabilization of $K[HB(OiPr)_3]$ by KH it may well be that this holds also for the $Li[HB(OtBu)_3]$ system. In the series Li < Na < K the formation of $M[H_3B(OtBu)]$ compounds is favored, showing that substituent exchange is retarded with increasing ionic character of the compounds. Also noteworthy is the observation that lithium tris(2,4-di[*tert*-butyl)phenolato]-hydrido borate is converted to a large extent not only into $LiBH_4$ but also into $HB[OC_6H_3(tBu)_2]_2$. This latter compound may result from a reaction according to eq. (17)

$$\begin{aligned} &BH_3 \cdot THF + Li[H_2B(OR)_2] \\ &\rightarrow HB(OR)_2 + LiBH_4 + THF \end{aligned} \tag{17}$$

While Singaram *et al.* [13] observed that $LiBH_4$ reacted with C_6F_5OH in THF with formation of $Li[HB(OC_6F_5)_3]$ only, we obtained good evidence that in non polar solvents the reaction provides $Li[H_2B(OC_6F_5)_2]$ which decomposes in THF to $Li[HB(OC_6F_5)_3]$. On the other hand, the reaction of $HB(OC_6F_5)_2$·THF with LiH in THF gave only $(C_6F_5O)_3B$·THF as an identifiable product. It is one of the rare examples that a borane $(RO)_3B$ forms an adduct with THF. There is only one compound known which is comparable, the dimeric $[N(1,3\text{-}O_2C_6H_3)_3]B$·THF [45].

2,2'-Dihydroxydiphenyl reacts with $LiBH_4$ in THF to give the lithium borate **2**. However in the presence of secondary amines, borates of the type $Li[(OC_6H_4\text{-}C_6H_4O)B(NR_2)_2]$ are readily accessible, and this is an indication that $Li[(OC_6H_4\text{-}C_6H_4O)BH_2]$ is an intermediate. Normally, secondary and primary amines, under ambient conditions, form only adducts with alkali metal tetrahydridoborates [46].

The formation and stability of the phthalatoborane **7** is similar to the diacylboranes described by H. C. Brown derived from dichloroacetic acid, benzoic acid and *p*-chlorobenzoic acid. These also form THF adducts [47]. Compound **7** reacts easily with nucleophiles to give hydridoborates of type $M[HB(Nu)_3]$. Thus the reaction with Li*t*Bu generated $Li[HB(tBu)_3]$·3 THF, which could so far not be observed by other routes [48]. With NaO*t*Bu we obtained in THF solution $Na[HB(OtBu)_3]$. Upon attempts to isolate it in the form of single crystals we obtained $Na[HB(OtBu)_3]\cdot Na[B(OtBu)_2O]\cdot Na[(H,OH)B(OtBu)O]_2$ as an unexpected hydrolysis product, which has an unprecedented Na_6O_6 core structure. The O atoms of the $HB(OtBu)_3$ anion bind to three different Na atoms.

The structure of the comparable centrosymmetric phenolate $\{Na[HB(OPh)_3](THF)_2\}_2$ is a dimer. Its phenoxy oxygen atoms coordinate to the Na atoms, two forming B–O–Na bridges and one a B–O(Na)$_2$ bridge [49]. The B–O bond of this unit is 0.3 Å longer than the other two, and it may well be that these interactions favor the substituent exchange of the organyloxo hydrido borates. Alkali metal alkoxoborates offer a fair number of structural motifs. These range from solvent separated ion pairs [5] *via* dimers [50] to catena type structures [50].

Although a number of interesting new compounds could be characterized there remain still a number of questions to be answered in order to better understand the governing principles of these reactions. The calculational results give a hint to the thermodynamics involved, but it appears that kinetic control is at least as essential.

Experimental Section

All reactions were carried out under dry nitrogen gas using the Schlenk technique. Stock solutions were prepared by dissolving diborane generated in the reaction of $NaBH_4$ with BF_3 in diglyme. $LiBH_4$, $NaBH_4$, and Li*t*Bu were obtained from Chemetall GmbH. The metallated alcohols, phenols and amides were prepared by standard methods. All other reagents were commercially available.

NMR spectra were measured with Jeol GSX 270 or Jeol EX 400 instruments. The chemical shifts are referenced to the usual standards either internal or external (^{11}B, ^{7}Li, ^{19}F). Data sets for the crystal structure determinations were collected with a Siemens P4 diffractometer equipped with an area detector and a low temperature device LT2. Elemental analyses were performed in the Department's microanalytical laboratory.

Reactions of $H_3B{\cdot}THF$ with alkali metal alkoholates and phenolates: (see also Table 1)

To 50 ml of a 0.064 M solution of $BH_3{\cdot}THF$ was added at -78 °C 25 ml of a THF solution containing LiO*t*Bu (283 mg, 3.54 mmol). While stirring, this mixture was allowed to warm to r. t. A sample was investigated by ^{11}B NMR which showed signals at -41.2 (26%), -15.0 (7%), -0.6, 1.2 and 3.5 (together 44%) and 16.1 ppm (23%). Signals in the region -0.6 to 3.5 ppm overlapped; insufficient resolution did not allow the determination of the number of H atoms at these boron atoms. The same result was obtained when the reagents were mixed at ambient temperature. Table 1 lists the results of analogous reactions with alkali metal alkoholates and phenolates.

*Bis(pentafluorophenoxy)borane tetrahydrofuran and tris(pentafluorophenoxy)borane tetrahydrofuran (**1**)*

To 8.03 ml of a stirred solution of BH_3 in THF (21.7 mmol) was added slowly a solution of pentafluorophenol (7.98 g, 43.4 mmol) in THF (20 ml). After 2 h the hydrogen gas evolution had ceased. The ^{11}B NMR spectrum of the solution showed signals at $\delta = 3.1$ [s, 16%, **1**] and 7.4 ppm [d, $^{1}J(^{11}B^{1}H) = 142$ Hz), 84%, $(C_6F_5O)_2BH{\cdot}THF$]. A gel formed overnight in which crystals of octahedral shape were present. They proved to be **1**. These were isolated, but not all of the gel could be properly removed.

$C_{22}H_8BF_{15}O_4$ (632.10): calcd. C 41.80, H 1.27; found C 40.54, H 1.72.

^{1}H NMR (270 MHz, C_6D_6, $SiMe_4$): $\delta = 1.33$, 1.67 (m, CH_2-CH_2), 3.30, 3.52 (m, O-CH_2). – $^{13}C\{^{1}H\}$ NMR (C_6D_6): $\delta = 25.42$ (OCH_2CH_2), 26.97 (OCH_2CH_2), 68.07 (OCH_2), 70.78 (OCH_2). ^{13}C NMR signals for the aryl group could not be observed. – ^{19}F NMR (C_6D_6, $CFCl_3$): $\delta = -176.0$ (unresolved triplet, *p*-F), 170.6 (t, $^{3}J(^{19}F^{19}F) = 20$ Hz, *m*-F), -168.8 (d, $^{3}J(^{19}F^{19}F) = 20$ Hz). – ^{11}B NMR (THF, $BF_3{\cdot}OEt_2$) $= 3.1$ (s).

1 : 1 Reaction of $LiBH_4$ with phenol: 67 mg (3.1 mmol) of $LiBH_4$ was dissolved in THF (40 ml). To the stirred solution was added a solution of phenol (275 mg, 2.92 mmol) in THF (20 ml). A rapid gas evolution ceased within 15 min. Stirring was continued for 1 h. Then the ^{11}B NMR spectrum of the solution showed only the presence of $Li[HB(OPh)_3]$ [$\delta^{11}B = 2.6$ (d, $^{1}J(^{11}B^{1}H) = 115$ Hz, 33%] and $LiBH_4$ [$\delta^{11}B = -41$, quint., $^{1}J(^{11}B^{1}H) = 81$ Hz, 67%].

*Lithium (2,2'-dioxodiphenylene)bis(piperidino)borate (**3**)*

53 mg of $LiBH_4$ (2.4 mmol) were dissolved in piperidine (15 ml). To the stirred solution was added solid 2,2'-dihydroxy-diphenyl (459 mg, 2.46 mmol). After gas evolution had ceased the turbid solution was heated for 12 h at reflux. The solid that had formed was removed by filtration and dried. Only a single ^{11}B NMR signal could then be detected in the solution at $\delta^{11}B = 26.9$ [d, $^{1}J(^{11}B^{1}H) = 118$ Hz] which is due to $HBpip_2$. Yield of **3**: 430 mg (48%), m. p. ∼ 150 °C.

^{1}H NMR (400 MHz, d^6-DMSO): $\delta = 1.37$ (m, 8H), 1.45 (m, 4H), 2.62 (m, 8H), 6.88 [d, 2H, $^{3}J(^{1}H^{1}H) = 7.9$ Hz], 6.96 [t, 2H, $^{3}J(^{1}H^{1}H) = 7.5$ Hz], 7.23 [t, 2H, $^{3}J(^{1}H^{1}H) = 7.9$ Hz], 7.33 [d, 2H, $^{3}J(^{1}H^{1}H) = 7.5$ Hz]. – ^{13}C NMR (101 MHz, d^6-DMSO): $\delta = 25.1$, 26.8, 46.9, 120.1, 122.3, 128.0, 128.7, 132.1, 157.4. – ^{11}B NMR (97 MHz. d^6-DMSO): $\delta = 7.3$.

$C_{22}H_{28}O_2N_2Li$ (369.99): calcd. C 71.43, H 7.63, N 7.52; found C 71.46, H 7.73, N 6.85.

*Lithium-(2,2'-dioxodiphenyl)bis(pyrrolidino)borate (**4**)*

124 mg of $LiBH_4$ (5.69 mmol) were dissolved in pyrrolidine (25 ml). After addition of 2,2'-dihydroxydiphenyl

(1.06 g, 5.69 mmol) the mixture was stirred for 1 h. No gas evolution was noted, but commenced on heating to reflux. A solid started separating after about 30 min. Refluxing was continued for another 3.5 h. Then the supernatant solution showed an ^{11}B NMR signal at $\delta = -17.3$ (quart.) due to $H_3B{\cdot}HNC_4H_8$. The solid was isolated and washed with hexane to give **4** as a white powder. Yield: 660 mg (34%), m. p. 180 °C dec.

^{1}H NMR (270 MHz, d^6-DMSO): $\delta = 1.54$ (m, 8H), 2.62 (m, 8H), 6.88 [d, $^3J(^1H^1H) = 7.6$ Hz, 2H], 6.96 [t, $^3J(^1H^1H) = 7.6$ Hz, 2H], 7.23 [t, $^3J(^1H^1H) = 7.6$ Hz, 2H], 7.32 [d, $^3J(^1H^1H) = 7.6$ Hz, 2H]. – ^{13}C NMR [68 MHz, d^6-DMSO): $\delta = 25.8, 47.1, 120.4, 122.6, 128.2, 128.7, 132.3, 157.7$. – ^{11}B NMR (87 MHz, d^6-DMSO): $\delta = 7.5$ (s). – ^{7}Li NMR (105 MHz, LiCl in D_2O): $\delta = -1.1$.

$C_{20}H_{24}O_2N_2BLi$ (342.21): calcd. C 71.41, H 7.80, N 8.19; found C 71.41, H 7.60, N 8.07.

*Lithium (2,2'-dioxodiphenyl)bis(morpholino)borate (**5**)*

387 mg of $LiBH_4$ (17.8 mmol) were dissolved in morpholine (50 ml). After addition of 2,2'dihydroxydiphenyl (3.297 g, 17.71 mmol) gas evolutions set in. Stirring was continued for 1 h and the resulting suspension was then heated to reflux for 4 h. The solid **5** was isolated and washed twice with hexane (50 ml) and dried. Yield: 3.93 g (59%), m. p. 170 °C dec.

^{1}H NMR (270 MHz, d^6-DMSO): $\delta = 2.67$ (m, 8H), 3.51 (m, 8H), 6.93 [d, $^3J(^1H^1H) = 7.8$ Hz, 2H], 6.99 [d, $^3J(^1H^1H) = 7.6$ Hz, 2H], 7.26 [t, $^3J(^1H^1H) = 7.6$ Hz, 2H], 7.36 [d, $^3J(^1H^1H) = 7.8$ Hz, 2H]. – ^{13}C NMR (68 MHz; d^6-DMSO): $\delta = 46.7, 68.0, 120.4, 122.6, 128.2, 128.7, 132.4, 157.7$. – ^{11}B NMR (97 MHz, d^6-DMSO): $\delta = 7.5$ (s). – ^{7}Li NMR (105 MHz, d^6-DMSO): $\delta = -0.9$.

$C_{20}H_{24}O_4N_2BLi$ (374.20): calcd. C 64.20, H 6.47, N 7.49; found C 64.87, H 7.07, N 7.43.

*Lithium bis(2,2'-dioxodiphenyl)borate (**2**)*

To a stirred solution of $LiBH_4$ (44 mg, 2.02 mmol) in benzyl-*tert*-butylamine (20 ml) was added 2,2'-dihydroxydiphenyl (2.02 mmol). No gas evolution set in. On heating to reflux for 8 h a voluminous colorless precipitate was present. It was isolated by filtration and washed with hexane. Yield: 480 mg of **2** (62%), m. p.>200 °C.

^{1}H NMR (270 MHz, d^6-DMSO): $\delta = 6.87$ [d, $^3J(^1H^1H) = 7.5$ Hz. 4H], 6.96 [t, $^3J(^1H^1H) = 7.5$ Hz, 4H], 7.23 [t, $^3J(^1H^1H) = 7.5$ Hz, 4H], 7.32 [$^3J(^1H^1H) = 6.6$ Hz, 4H]. – ^{13}C NMR (101 MHz, d^6-DMSO): $\delta = 120.3, 122.6, 128.2, 128.7, 132.2, 157.7$. – ^{11}B NMR (64 MHz, d^6-DMSO): $\delta = 9.0$ (s). – ^{7}Li NMR (105 MHz, d^6-DMSO): $\delta = -1.1$.

$C_{24}H_{16}O_2N_2BLi$ (386.13): calcd. C 74.65, H 6.25; found C 74.24, H 6.13.

Lithium bis(pentafluorophenolato)dihydridoborate

To a stirred suspension of $LiBH_4$ (240 mg, 11.2 mmol) in benzene (25 ml) was added a solution of C_6F_5OH (4.12 g, 22.4 mmol) in benzene (50 ml). Hydrogen gas was generated slowly. After 19 h the H_2 evolution had ceased. 3/4 of the benzene was removed from the suspension and the solid isolated. Yield: 3.4 g (79%), m. p. 219 – 220 °C.

NMR: ^{13}C and ^{1}H NMR signals could not be detected in d^6-DMSO solutions. – ^{11}B NMR (87 MHz, $CDCl_3$) = 1.7 (br, $^{11}B^1H$ coupling could not be observed); (in THF): $\delta = 6.1$ [d, $^1J(^{11}B^1H) = 135$ Hz] assigned to $(C_6F_5O)_2BH{\cdot}THF$.

$C_{12}H_2O_2BF_{10}Li$ (385.89): calcd. C 37.35, H 0.52; found C 35.76, H 0.64.

Reaction of $LiBH_4$ with 3,5-di(tert-butyl)catechol in pyridine

61 mg of $LiBH_4$ were dissolved in pyridine (5 ml). To the stirred solution was added 612 mg of 3,5-di(tert-butyl)catechol. A rapid gas evolution started. After 10 h the suspension showed only ^{11}B NMR signals for BH_3.py: $\delta^{11}B = -12.0$ [quart., $^1J(^{11}B^1H) = 93$ Hz, 80%] and $LiBH_4$ [$\delta^{11}B = -39.1$ ppm (quint., $^1J(^{11}B^1H) = 81$ Hz, 20%]. The suspension was heated to reflux for 20 h. Then the supernatant solution showed the presence of BH_3.py [$\delta^{11}B = -12.0$ ppm (quart., $^1J(^{11}B^1H) = 93$ Hz, 20%] and Li[Bcat(tBu$_2$)$_2$] [$\delta^{11}B = -14.2$ ppm (s, 70%)] besides some minor other signals.

Phthalatohydroborane

To a 2.12 M solution of BH_3 in THF were added 9 ml of THF. Stirring was then started and a solution of phthalic acid (0.30 g, 1.8 mmol) dissolved in 15 ml of THF was added. Gas evolution set in rapidly. After 15 min gas evolution had ceased. The ^{11}B NMR spectrum of the solution showed a doublet at $\delta^{11}B = 4.1$ [d, $^1J(^{11}B^1H) = 143$ Hz] assigned to **7**. Two more signals at $\delta^{11}B = 18.0$ [s, 18%, a $B(OR)_3$ species] and at $\delta^{11}B = 27.1$ (d, 163 Hz, 2%, most likely phthalBH) were also noted.

Addition of pyridine to the solution led to a single ^{11}B NMR signal at $\delta^{11}B = 3.0$ [d, $^1J(^{11}B^1H) = 133$ Hz)], which corresponds to the pyridine adduct **8** of the phthalatohydroborane.

While **7** is stable in solution for several hours, removal of the solvent produced a white powder which was hardly soluble in deuterobenzene, and this solution showed two ^{11}B NMR signals as singlets at $\delta^{11}B = 18.0$ and 3.7 in a 1 : 1 ratio.

Reaction of sodium tert-butylate with phthalatohydroborane in THF

NaOtBu (0.534 g, 5.56 mmol) was placed in a 50 ml bulb flushed with N_2. While stirring a solution of phthalatohydroborane (1.8 mmol) in 25 ml of THF was added. The suspension turned immediately yellow. Checking the

Table 8. Crystallographic data and parameters for data collection and structure solutions.

Compound	**1**	**2**	**9**	**11**	**12**	**13**
Chem. formula	$C_{22}H_8BF_{15}O_4$	$C_{32}H_{34}BLiO_7$	$C_{27}H_{62.36}B_3Na_3O_{8.64}$	$C_{24}H_{52}BLiO_3$	$C_{22}H_{42}BLiO_6$	$C_{20}H_{27}BLi_2O_7$
Form. wght.	632.09	548.34	626.33	406.41	420.31	404.11
Cryst. size [mm]	0.15 × 0.32 × 0.45	0.10 × 0.10 × 1.00	0.10 × 0.10 × 0.30	0.05 × 0.20 × 0.20	0.05 × 0.10 × 0.20	0.20 × 0.20 × 0.20
Cryst. system	hexagonal	monoclinic	triclinic	orthorhombic	monoclinic	triclinic
Space group	R-3	P2(1)/c	P-1	Pna2(1)	P2(1)/c	P-1
a [Å]	13.40(1)	15.551(9)	12.707(1)	17.281(3)	9.8850(9)	9.5059(9)
b [Å]	13.40(1)	8.955(5)	13.678(2)	10.1769(18)	12.707(1)	10.643(1)
c [Å]	21.82(2)	19.576(1)	13.806(2)	14.989(3)	20.742(2)	11.967(1)
α [°]	90.00	90.00	66.858(2)	90.00	90.00	70.656(2)
β [°]	90.00	94.261(9)	63.218(2)	90.00	100.3580(1)	72.608(2)
γ [°]	120.00	90.00	69.529(2)	90.00	90.00	82.998(1)
V [Å^3]	3395(4)	2718(3)	1925.0(4)	2636.1(9)	2562.9(4)	1089.76(18)
Z	6	4	2	4	4	2
ρ (calcd.), [mg/m^3]	1.855	1.340	1.081	1.024	1.089	1.232
μ [mm^{-1}]	0.206	0.092	0.104	0.063	0.075	0.089
F(000)	1872	1160	682	912	920	428
Index range	$-7 < h < 13$ $-13 < k < 4$ $-26 < l < 7$	$-20 < h < 19$ $-11 < k < 10$ $-25 < l < 25$	$-13 < h < 16$ $-16 < k < 18$ $-17 < l < 17$	$-17 < h < 17$ $-10 < k < 10$ $-15 < l < 15$	$-10 < h < 10$ $-14 < k < 14$ $-22 < l < 20$	$-11 < h < 12$ $-13 < k < 13$ $-15 < l < 13$
2 θ [°]	54.80	58.80	58.02	42.52	46.50	57.64
Temp, [K]	193	193(2)	193(2)	183(2)	193(2)	193(2)
Refl. collected	1067	15649	11215	9048	11149	6234
Refl. unique	993	5546	5907	2913	3516	3276
Refl. observed (4σ)	931	2801	2668	1288	2008	2267
R (int.)	0.0123	0.0615	0.0751	0.1910	0.0636	0.0216
No. variables	143	382	400	272	281	277
Weight.[a] x/y	0.1744/12.3827	0.2401/0.000	0.0731/0.000	0.050/0.000	0.0799/0.000	0.0809/0.2540
GOOF	1.132	0.896	0.938	0.944	0.985	1.032
Final R (4σ)	0.0921	0.0496	0.0612	0.0741	0.0561	0.0509
Final $wR2$	0.2699	0.0972	0.1275	0.1254	0.1300	0.1339
Larg. res. peak [e/Å^3]	0.487	0.193	0.207	0.176	0.196	0.187

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

resulting solution by ^{11}B NMR showed the formation of NaHB(O*t*Bu)$_3$ [δ^{11}B $= 0.4$ ppm, d, $^1J(^{11}B^1H) = 121$ Hz] and a "contamination" [δ^{11}B $= 2.3$, s; NaB(O*t*Bu)$_4$] in the ratio of ∼ 4 : 2. After removal of the solvent the slightly yellow powder was first treated with some hexane and the solid extracted with diethyl ether. The diethyl ether contained most of the NaB(O*t*Bu)$_4$. The hexane phase was stored at −80 °C. After two weeks crystals had separated, which became opaque in a stream of dinitrogen. Therefore, crystals for a structure determination were selected at −30 °C. According to the X-ray structure determination they had the composition Na[HB(O*t*Bu)$_3$]-[NaOB(O*t*Bu)-(OH)$_{0.64}$(H$_{0.36}$)]·0.5 C_6H_{14}. The ^{11}B NMR spectrum of the supernatant hexane solution showed two signals in a 1 : 1 ratio at δ^{11}B $= 25.5$ [d, $^1J(^{11}B^1H) = 163$ Hz], and a singlet at δ^{11}B $= 16.0$ indicating the presence of HB(O*t*Bu)$_2$ and B(O*t*Bu)$_3$, respectively.

*Lithium tris(tert-butyl)hydroborate tris(tetrahydrofuran) (**11**)·(THF)$_3$*

At −78 °C a solution of Li*t*Bu in pentane (2.0 mmol, 2.65 M) was diluted with hexane (20 ml). To the stirred solution was slowly added a solution of phthalatoborane in THF (25 ml, 5.3 mmol) diluted with diethyl ether (50 ml). The solution turned immediately red. After addition was completed, stirring was continued at −78 °C for 30 min. An ^{11}B NMR spectrum of the solution showed ^{11}B NMR signals at 5.6 (d), −0.4 (d), −4.5 (t) and 83 ppm (s). Most of the solvents were stripped off *in vacuo*. The residue was dissolved in 5 ml of hexane and then kept at −30 °C. After several days crystals of (THF)$_3$LiHB(*t*Bu$_3$) (**11**) had separated. The filtrate showed an ^{11}B NMR signal at 83.0 ppm for B*t*Bu$_3$.

Lithium tris(methylphenylamino)hydridoborate and tris(methylphenylamino)borane

At −78 °C 700 mg of LiNMePh (6.19 mmol) was dissolved in THF (20 ml). To the solution was added 25 ml of a THF solution of phthalatoborane (18 mmol). After several hours the solvents were removed *in vacuo* from the slightly yellow solution. The yellow residue was washed with diethyl ether and then dissolved in THF. The ^{11}B NMR spectrum showed the presence of Li[HB(NMePh)$_3$)] [doublet at −2.1 ppm, $^1J(^{11}B^1H) = 111$ Hz] besides an ^{11}B NMR signal at 30 ppm for $B(NMePh)_3$. The solution was stored at -20 °C. The crystal that separated proved to be $B(NMePh)_3$ as shown by the determination of its unit cell [28].

*Lithium di(tert-butyl)catecholatoborate bis(dimethoxyethane) (**10**)·(dme)$_2$*

1.8 ml of a pentane solution of Li*t*Bu (1.65 M, 3.0 mmol) was diluted with hexane (10 ml). Drop wise addition of a catecholato borane solution (0.30 g, 2.8 mmol) in diethyl ether (10 ml) resulted in the formation of a yellow precipitate. The solution showed the following ^{11}B NMR signals: 36.1 (s, 15%), 14.6 (s, 10%), 7.8 (s, 3%), -4.5 [t, 69 Hz, 50%, $Li(H_2BtBu_2)$], -20.3 (quart., 79 Hz, 17%), -40.8 (quint., 81 Hz, 5%). The solid (predominantly $LiBcat_2$ was isolated by filtration. DME (5 ml) was added to the filtrate. Within several hours colorless needles of $(dme)_2Li[catB(tBu)_2]$, crystallized. Yield: 78 mg (7%). It was characterized by its crystal structure. Compound $Li(H_2BtBu_2)$ could not be isolated.

^{1}H NMR (400 MHz, C_6D_6): $\delta = 1.34$ (12 H, CMe_3), 2.96 (12 H, OMe), 3.00 (8 H CH_2O), 6.8 (m, 4H). – ^{13}C NMR (101 MHz, C_6D_6): δ = 30.3 CMe_3, 58.7 (OCH_3), 70.8 (OCH_2), 108.0, 117.3. – ^{11}B NMR (87 MHz, C_6D_6): δ = 14.6.

*Dilithium di(catecholato)hydroborate (**13**)·THF·dme*

0.169 g lithium piperidide (1.86 mmol) was suspended at -78 °C in THF (15 ml). This suspension was treated with a solution containing 0.2 ml (1.9 mmol) of catecholato borane in THF (10 ml). The ^{11}B NMR spectrum of the solution showed at r.t. ^{11}B NMR signals at 25.8 (d, 124 Hz, 34%), 12.4 (s, 22%), 7.2 (br, 38%), and -16.3 ppm (quart. 95 Hz, 6%). After adding DME (2 ml) to the solution a colorless precipitate formed which dissolved on addition of THF (20 ml). Within 12 h crystals of **13 · THF · dme** together with a powder had separated. One of the clear crystals was used for structure determination. A quantitative separation from byproducts by extraction with benzene or hexane was not achieved. Only THF dissolved the solid. The ^{11}B chemical shift for **13** was 7.2 ppm (br). BH coupling could not be resolved.

Crystal structure determination

Crystals were placed in perfluoroether oil and suitable specimens selected and placed on the tip of a glass fiber. They were cooled to -80 °C. The reflections on a total of 60 frames were used to determine the dimension of the unit cell. Data were recorded on a total of 1200 frames with a speed of 5 s/frame. Data reduction was performed with the program SAINT [53], and the SHELX93 [54] programs were used for structure solution and refinement. All non-hydrogen atoms were refined with anisotropic parameters and hydrogen atoms bound to carbon atoms were placed in calculated positions. Positions of BH hydrogen atoms were found in difference Fourier maps. Relevant crystallographic data are summarized in Table 8.

In compound **1** the boron atom and the oxygen atom of THF occupied special position at the threefold axis. Consequently this thf molecule was triply disordered, and no H atoms could be found for its C atoms. In compound **8** the oxygen atom of the assumed OH group had an unusually large thermal parameter suggesting that a H atom was positioned close to it. Therefore, we refined the site occupation factors which improved the R value, but the B–O distance turned out to be too short.

Crystallographic data for the structure determinations have been deposited with the Cambridge Crystallographic Data Centre, CCDC 612051- 612056. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code +(1223)336 033; e-mail: fileserv@ccdc.cam.ac.uk).

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