Contributions to the Chemistry of Boron, 236[1]

In Quest of New and Stable Bis(organyloxy)boranes $(RO)_2BH$ for Catalytic Hydroboration☆

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New and stable bis(organyloxy)boranes, 1,3,2-dioxaborolanes and 1,3,2-dioxaborinanes have been prepared (i) from the corresponding diol and $BH_3 \cdot THF$ and (ii) from 1,2-diketones and $BH_3 \cdot THF$. They were characterized by spectroscopic techniques. The BH stretching frequency seems to be a measure of ring strain and Lewis acidity. The compounds have been qualitatively tested in the transition-metal-catalysed hydroboration of cyclopentene, and the dioxaborinane **11** proved to be superior to the 1,3,2-dioxaborolanes **9** and **18**.

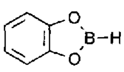
Since the discovery of catalytic hydroboration[2] several groups have been investigating the scope of this reaction[3]. In addition, interesting results related to the mechanism of this reaction were obtained[4], and two recent theoretical studies contributed to its understanding[5]. So far, catecholborane has proved to be the most versatile borane compound for this purpose. Catalysis is usually achieved by phosphane complexes of late transition metals, e.g. Wilkinson's complex[6]. However, nontransition metal catalysis is also possible[7a]. It is conceivable that many other boranes besides catecholborane will be suitable for catalytic hydroboration[7b], and optimal efficiency will not only depend on the borane component and on the transition metal compound, but also on the substrate to be hydroborated. This work presents results aimed at the synthesis of new stable boranes of the type $(RO)_2BH$ which may be useful in catalytic hydroboration.

Synthesis

Diorganyloxyboranes $(RO)_2BH$ have a tendency to decompose into triorganyloxyboranes $(RO)_3B$ and diborane[8]. This can be prevented to a certain extent by ring formation. Examples are catecholborane **1**, the tetramethyldioxaborolane **2**, or the 1,3,2-dioxaborolane **3** and the dioxaborinane **4**.

Another possibility is to use fairly large organyl groups in order to suppress dismutation of $(RO)_2BH$ into $(RO)_3B$ and B_2H_6. We used these two criteria for the synthesis of new diorganyloxyboranes.

The reaction of $BH_3 \cdot THF$ with triphenylcarbinol proceeds slowly at ambient temperatures. Even with an excess of the carbinol only the bis(triphenylmethoxy)borane **5** is formed as shown in eq. (1).



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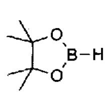

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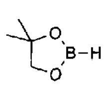

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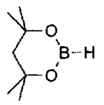


4

$$2\,Ph_3COH + BH_3 \cdot THF \longrightarrow \underset{\mathbf{5}}{(Ph_3CO)_2BH} + 2\,H_2 \tag{1}$$

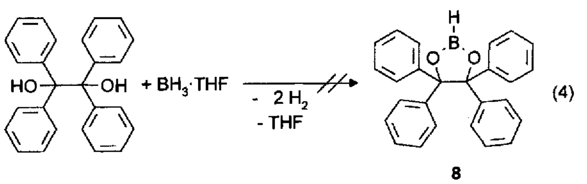
$$2\,Ph_2CO + BH_3 \cdot SMe_2 \longrightarrow \underset{\mathbf{6}}{(Ph_2CHO)_2BH} + SMe_2 \tag{2}$$

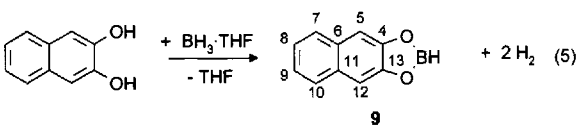
$$2\,PhCHO + BH_3 \cdot SMe_2 \longrightarrow \underset{\mathbf{7}}{(PhCH_2O)_2BH} + SMe_2 \tag{3}$$

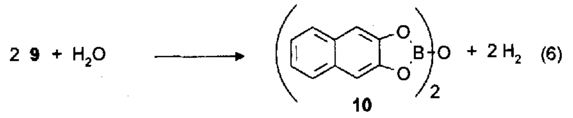
It is conceivable to use either diphenylcarbinol or benzyl alcohol for the preparation of the bis(diphenylmethoxy)borane **6** or the bis(benzyloxy)borane **7** by allowing these alcohols to react with either $BH_3 \cdot THF$ or $BH_3 \cdot SMe_2$. These reactions are, however, not straightforward. Unfortunately, this holds also for the hydroboration of benzophenone and benzaldehyde with $BH_3 \cdot SMe_2$. Compound **6** is indeed formed as shown in eq. (2), but $(Ph_2CHO)_3B$ is a by-product (ca. 20%). Separation of **6** from $(Ph_2CHO)_3B$ by fractional crystallization was not successful[9]. However, both products could be identified by their NMR spectra. An even larger proportion of $(PhCH_2O)_3B$ was formed besides **7** in the reaction described by eq. (3).

The synthesis of cyclic diorganyloxyboranes can be achieved in principle by the same methods. However, the reaction of tetraphenylglycol with $BH_3 \cdot THF$ proceeds slowly, even under reflux conditions. After 5 days, a signal at $\delta^{11}B = 14.3$ appears besides that of $BH_3 \cdot THF$. This does not signalize the formation of **8** but rather that of a boric ester, where the hydrogen atom in **8** is replaced by a BuO group resulting from THF cleavage.

In contrast, 2,3-dihydroxynaphthalene reacts smoothly with $BH_3 \cdot THF$, and compound **9** is formed almost quantitatively as depicted in eq. (5). **9** is susceptible to hydrolysis,

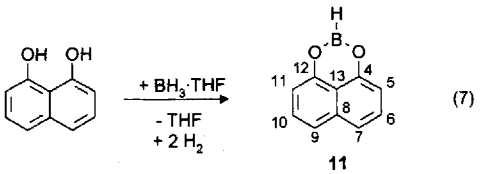


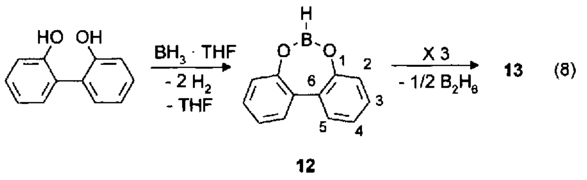


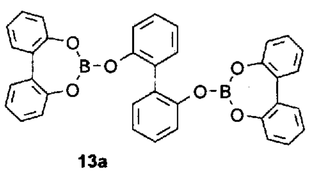


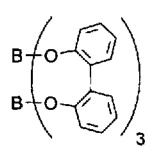
and the bis(dioxaborolanyl) oxide **10** is readily formed in the presence of small amounts of H_2O.

It is no surprise that 1,8-dihydroxynaphthalene reacts similarly with $BH_3 \cdot THF$, and the product is the naphtho-1,3,2-dioxaborinane **11**. This sublimable solid was obtained in 77% yield.

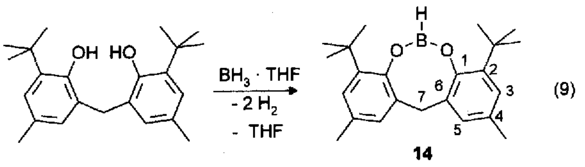





13a



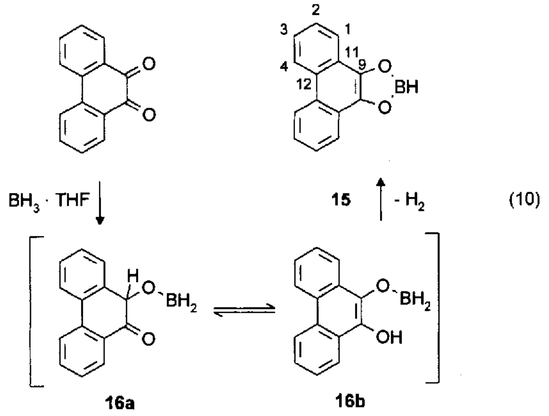
13b

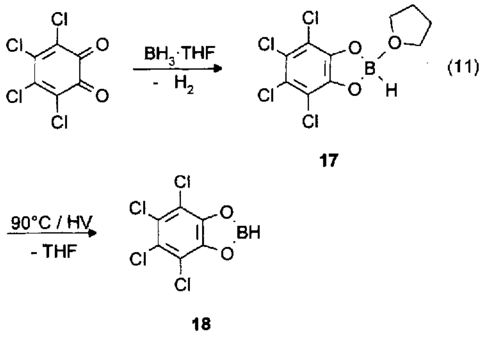


Similarly, the reaction of borane in THF with 2,2′-bis(hydroxy)diphenyl leads to the diorganyloxyborane **12**. However, ^{11}B-NMR data for this compound [$\delta^{11}B = 8.5$, $^1J(^{11}B^1H) = 140$ Hz] indicate tetracoordination of the boron atom, obviously resulting from THF addition. Compound **12** decomposes during removal of THF from its solution with formation of the boric acid ester **13** as shown in eq. (8). NMR data for **13** suggest a simple and rather symmetric structure.

In contrast to reaction (8) a rather straightforward reaction is observed between $BH_3 \cdot THF$ and 1,1-di(2-hydroxy-3-*tert*-butyl-5-methylphenyl)methane. The result is described by eq. (9). However, the reaction proceeds quite slowly and requires reflux conditions. Under these circumstances yields >90% for **14** can be achieved. The sluggishness of this reaction is certainly due to the proximity of the *tert*-butyl group to the OH functions.

In contrast, the reaction of $BH_3 \cdot THF$ with 9,10-phenanthrenoquinone proceeds smoothly, and the final product is the dioxaborolan **15**. Hydrogen gas is liberated during the course of this reaction. This indicates that BH_3 hydroborates a C=O bond followed by enolization to **16** and further hydrogen evolution. This behavior is described by eq. (10).





Attempts to obtain information about an intermediate by following the course of reaction (10) by ^{11}B-NMR spectroscopy failed, because no signal assignable to **16a** or to **16b** or another intermediate was observed. Similarly, *o*-chloroanil was reduced by $BH_3 \cdot THF$ resulting in a fair yield of the tetrachlorocatecholborane **18** as shown by eq. (11) and with discoloration of the quinone solution.

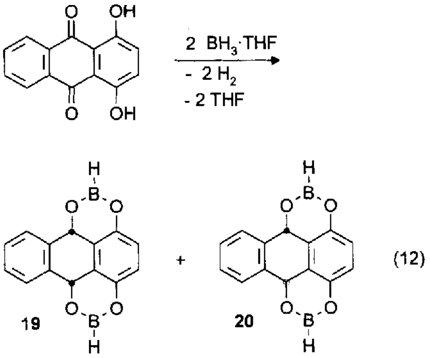
However, this reaction proceeds successfully only when the solid *o*-chloroanil is added to the $BH_3 \cdot THF$ solution. If the chloroanil is added as a THF solution to $BH_3 \cdot THF$, then polymerization is induced and a red gel is formed. This gel can be dissolved in $CHCl_3$. The ^{11}B-NMR spectrum of the resulting solution shows a signal at $\delta = 20.3$ which is typical of the BO_3-group of a boric acid ester.

In order to prevent polymerization of THF, $BH_3 \cdot SMe_2$ was used as a reducing agent in dimethylglycol ether or diethyl ether. In these cases, the formation of products with

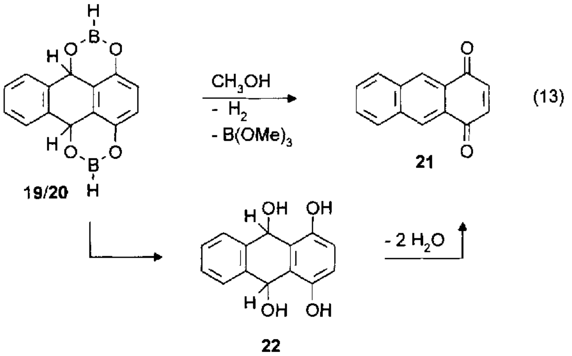
BO_3 units ($\delta^{11}B$ = 16–20) predominates even when an excess of $BH_3 \cdot SMe_2$ is employed.

As shown in eq. (11), the tetrachlorocatecholborane **18** forms as a THF adduct **17** which loses the ether during sublimation at 90°C in vacuo, demonstrating the remarkable Lewis acidity of compound **18** as well as its stability towards ligand exchange.

A compound of the dioxaborinane type was expected from the reaction of $BH_3 \cdot THF$ with 1,4-dihydroxy-9,10-anthraquinone. According to NMR data, the diastereomers **19** (*meso*-9*R*,10*S* or *meso*-9*S*,10*R*) and **20** (9*R*,10*R* or 9*S*,10*S*) are obtained. Evidence for this conclusion are two sets of ^1H- and ^{13}C-NMR signals with an additional splitting of the signals of the carbon atoms of the dioxaborinane ring system. This may be due to the presence of chair and boat conformers.



(12)



(13)

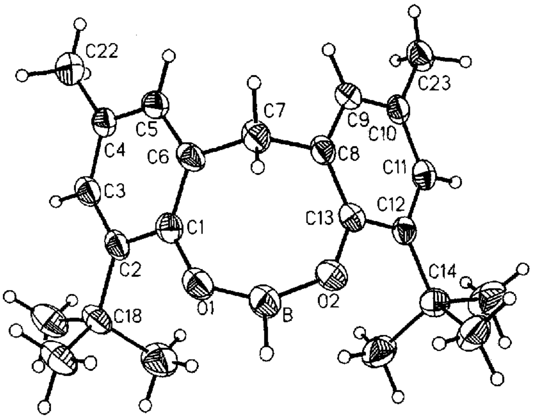
The product mixture obtained in a reaction according to eq. (12) shows a tendency to decompose into an insoluble product. No mass spectrum (electron impact) could be recorded due to very low volatility, but the IR spectrum of the insoluble product still reveals a band at $\tilde{\nu}$ = 2578 cm^{-1} which indicates the presence of a BH bond. Treatment of **19/20** with $CHCl_3/CH_3OH$ yields the crystalline 1,4-anthraquinone **21** as shown by eq. (13), with **22** as a probable intermediate.

The reaction (13) reminds one of the result of the reaction of 1,4-dihydroxy-9,10-anthraquinone with $NaBH_4$, which also leads to **21**[10]. Moreover, compounds **19** and **20** are thermally unstable. Heating of the mixture to 180°C produces a red solid product which consists primarily of the quinone **21**. This requires the loss of "HBO"[11] or the boroxine (in a next step). However, under the reaction conditions these products should decompose into B_2H_6 and B_2O_3[12].

Molecular Structure of 14 and NMR Spectra

Molecular Structure of Compound **14**: Although NMR data and mass spectral information are in accord with the constitution of **14**, bonding parameters were obtained from an X-ray structure determination. Relevant data are found in the legend of Figure 1.

Figure 1. The molecular structure of compound **14** in the crystal; thermal ellipsoids represent a 25% probability[a]



[a] Selected bond lengths [Å] and angles [°]: H–B 1.14(5), B–O1 1.343(7), B–O2 1.351(6), O1–C1 1.393(5), O2–C13 1.394(5), C1–C6 1.401(6), C8–C13 1.377(5), C6–C7 1.514(6), C7–C8 1.521(5); H–B–O1 115(2), H–B–O2 114(2), O1–B–O2 130.6(6), B–O1–C1 136.5(4), B–O2–C13 133.6(4), O1–C1–C6 119.4(5), O2–C13–C8 119.7(4), C1–C6–C7 121.2(5), C7–C8–C13 121.2(4), C6–C7–C8 109.6(3).

As expected, the boron atom resides in a planar environment but the two B–O bonds are slightly different. Surprisingly, the O–B–O bond angle [131.1(7)°] is rather large. This is true also for the B–O–C bond angles [136.6(5)° for O1, 132.8(5)° for O2] while the C6–C7–C8 bond angle is perfectly tetrahedral [109.6(4)°]. Bond angles subtending at atoms C1, C6, C8, and C13 are close to the expected 120°.

The seven-membered dioxaborocin ring adopts a tub conformation with C1/C6/C8 and C13 atoms lying in a plane, as well as atoms B1/O1/O2/C1 and C13. The two planes form an interplanar angle of 133.3°, while the C6/C7/C8 plane includes an angle of 115.0° with the C1/C6/C8/C13 plane. On the other hand, the folding angle between the two phenyl rings is 100.2°, making the compound **14** butterfly-shaped with C_s point group symmetry, and giving it a rather open structure. This conformation brings the *tert*-butyl group into the proximity of the boron atom shielding it sterically from one side, while the other side remains open, e.g. for nucleophilic attack. Moreover, it is conceivable that the molecule possesses a static structure, and any change in ring conformation would be a high-energy process.

NMR Spectra: The ^{11}B-NMR data of the di(organyloxy)boranes exhibit with doublets in the range of $\delta^{11}B$ = 21–30 the presence of tricoordinated boron atoms. A closer look reveals the effect of structural differences on the shielding. The five-membered 1,3,2-dioxaborolanes are characterized by $\delta^{11}B = 25 \pm 2$ while the signals of the six-membered 1,3,2-dioxaborinanes appear as doublets at $\delta = 29 \pm 2$ and those of the eight-membered 1,3,2-dioxaborocine at $\delta = 22$. $\delta^{11}B = 28 \pm 1$ is typical of noncyclic members. The BH coupling spans a range from 148 to 205 Hz. For the noncyclic members, a comparatively small coupling (<148 Hz) or even unresolved signals are observed, while $^1J(^{11}B^1H)$ for the five- and six-membered rings are recorded in the range of 160–180 Hz. An exceptionally large $^1J(^{11}B^1H)$ value of 205 Hz is observed for the eight-membered compound **14**. This large coupling is most likely due to the wide O–B–O bond angle found for this compound.

The main differences in the ^{1}H- and ^{13}C-NMR spectra of the noncyclic $(RO)_2BH$ compounds **5** and **6** are that the *para*-H atoms of $(Ph_3CO)_2BH$ are deshielded by $\delta = 0.23$ relative to $(Ph_2HCO)_2BH$, and a deshielding is also observed for the carbon atom next to the oxygen atom. This deshielding corresponds with the series $Ph_{4-n}CH_n$ ($n = 1, 2, 3, 4$) and is explained by an electron-withdrawing effect due to the increasing number of phenyl substituents[13]. The shift difference between compounds **5** and **6** is $\delta = 7.6$, but $\delta = 14.7$ between Ph_2CH_2 and Ph_3CH.

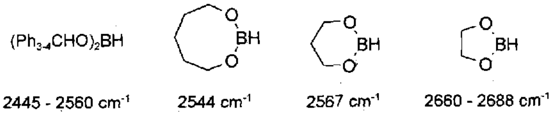
The aryl protons as well as the carbon nuclei of **9** and **10** are deshielded with respect to 2,3-dihydroxynaphthalene, particularly noticeable for the carbon atoms next to the oxygen atoms ($\Delta\delta = 2.8$ and 4.7 for **9** and **10**, respectively). This reflects the electron-withdrawing effect of the boron atom due to B–O σ-bonding. For this reason it is surprising that the dioxaborinane **11** shows almost no change in the shielding of the hydrogen atoms of the naphthalene structure compared to the parent compound. Moreover, the respective carbon atoms in **11** gain in shielding by 2–4 ppm compared to 1,8-dihydroxynaphthalene. Substitution effects in monosubstituted a-naphthalene particularly influence the H atoms at positions 2 and 4. However, these are almost not influenced in **11** compared with the 1,8-dihydroxynaphthalene. This is most likely due to a cumulative effect caused by 1,8-substitution. For instance, atom C-9 is in an *ortho* position with respect to the oxygen atoms, while C-3 is in the *meta* position. Compared to the "catecholboranes" **1** and **9** with $\delta^{11}B = 29.0$ and 29.2 as well as $\delta^{17}O = 159.0$ and 159.2 we not only observe a better shielded ^{11}B nucleus for the dioxaborinan **11** ($\delta^{11}B = 26.5$) but also a much better shielded ^{17}O atom ($\delta = 128.1$). This indicates a higher degree of BO π-bonding in the latter[14].

The bis(organyloxy)borane **12** is unstable, and its ^{11}B-NMR spectrum ($\delta^{11}B = 8.5$ in THF, $^1J(^{11}B^1H) = 140$ Hz) is indicative of the formation of a THF adduct. Due to its rapid decomposition, no ^{1}H- and ^{13}C-NMR data could be recorded. However, the boric acid ester **13**, which forms easily, shows by its ^{1}H- and ^{13}C-NMR spectra that it must have a fairly high symmetry in solution because only six ^{13}C-NMR signals are observed. This excludes the possible structure **13a** and makes **13b** the more likely alternative.

In contrast to compound **12**, the eight-membered borane **14** is quite stable, and the ^{1}H- and ^{13}C-NMR spectra are in accord with a molecule that has a C_s point group symmetry. There are two non-equivalent CH_2 protons, and this excudes a planar eight-membered ring-system. However, the data allow no decision between a "chair"-, "boat"- or "tub"-shaped molecule. For this reason, it was a lucky coincidence that compound **14** crystallized readily and could therefore be subjected to a crystal structure analysis (v.s).

IR Spectra: The IR bands of di(organyloxy)boranes are of diagnostic value. Two characteristic bands due to ^{10}B–H and ^{11}B–H stretching vibrations are expected. These can be readily observed in the region of 2400–2800 cm^{-1}. Nevertheless, BH stretching bands cannot always be recognized, particularly in compounds like **5** or **6** where the BH content is low and where even the more dominant ^{11}BH vibration is of low intensity. It can now be shown that the ν-BH bands allow us to differentiate between noncyclic and cyclic $(RO)_2BH$ compounds, and, in addition, between five-, six- and eight-membered rings. The bands observed for the ^{11}BH stretching vibrations are listed in Figure 2.

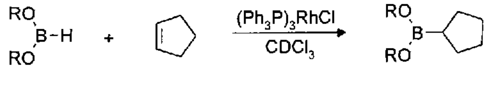
Figure 2. B–H stretching frequencies of several organyldioxoboranes[a]



[a] Substituents are not shown.

The B–H bond is weaker in noncyclic bis(organyloxy)boranes as well as in the eight-membered ring system, and is stronger for the five-membered 1,3,2-dioxaborolanes. This is in line with the fairly high degree of Lewis acidity of 1,3,2-dioxaborolanes which is particularly pronounced in compound **18**.

Hydroboration: Catalytic hydroboration has become a synthetic method[3,4] and its scope has considerably extended since its discovery[2]. Emphasis has been concentrated both on substrates and on catalysts. In the present study the variation of the hydroborating agent was qualitatively evaluated by using $(Ph_3P)_3RhCl$ as catalyst and cyclopentene as substrate as shown in eq. (14).

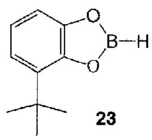


(14)

Typically, the disappearance of the alkene protons was taken as a measure of the hydroboration activity of the $(RO)_2BH$ compound. Table 1 summarizes the results.

Table 1. Catalytic hydroboration of cyclopentene by various organyldioxoboranes at ambient temperature

	11[a]	**9**[b]	**18**[a]	**1**[a]	**23**[a]	**7**[a]	**15**[a]
50-% "yield" [min]	1	4	10	30	30	[c]	[d]
> 90-% "yield" [min]	4	10	30	90	110	[c]	[d]



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[a] No reaction observed in the absence of catalyst at 20 °C. – [b] Colorless needles formed in the absence of catalyst within 24 h. – [c] No reaction within 24 h in the presence of catalyst. – [d] Formation of a solid, gas evolution but no hydroboration observed.

It is surprising that the six-membered 1,3,2-dioxaborinane **11** reacts faster than the five-membered 1,3,2-dioxaborolanes, and amongst these the compounds **9** and **18** react even faster than the "standard" compound, benzo-1,3,2-dioxaborolanene **3**, while the 5-*tert*-butylbenzo-1,3,2-dioxaborolane **22** exhibits about the same hydroboration activity as **3**. This shows that the "remote" bulky *tert*-butyl group exerts no effect on the rate of the hydroboration. However, neither the noncyclic dioxaborane $(Ph_3CO)_2BH$ nor the phenanthro[9,10-*d*]-1,3,2-dioxaborolane can be – as suggested – a hydroboration reagent.

These results stress the point that the boron atom of the diorganyloxyborane must be sufficiently Lewis-acidic in order to be catalytically activated for hydroboration. This can be readily rationalized for the five-membered C_2O_2B systems in comparison with the noncyclic system because there is little strain at the boron atom of the latter group considering that the first step in the catalytic hydroboration is the oxidative addition of the borane to the metal center. In the Lewis acid-base interaction the ring strain is particularly reduced for the five-membered 1,3,2-dioxaborolanes and this favors the addition step. The higher reactivity of **11** is probably not due to a release of the strain at the boron atom on addition but to a higher stability of the oxidative addition product.

Discussion

New bis(organyloxy)boranes were prepared by two routes. a) by reaction of $BH_3 \cdot THF$ with a "diol" and b) by oxidation of $BH_3 \cdot THF$ (or $BH_3 \cdot SMe_3$) with *o*-quinones. Reactions of type a) are sterically controlled: 2,3-dihydroxynaphthalene reacts like catechol quantitatively with borane in THF, and this is also observed for 1,8-dihydroxynaphthalene. Also, 2,2′-bisphenol reacts slowly with BH_3 in THF but the seven-membered ring is unstable. It is a fairly strong Lewis acid as it forms an adduct with THF. Removal of the solvent obviously induces a dismutation into "BH_3" and the boric acid ester **13**. Most likely, this ester has the same constitution and a similar structure as found for the corresponding 1,1′-dihydroxy-2,2′-dinaphthalene derivative[14,15]. In contrast, the eight-membered 1,3,2-dioxaborocin **14** forms readily although slowly, and we regard this as evidence for the steric shielding of the oxygen atoms by the *tert*-butyl groups. That steric effects influence the rate of H_2 evolution significantly is demonstrated by the slow reaction of triphenylmethanol with $BH_3 \cdot THF$ while tetraphenylglycol has not reacted with $BH_3 \cdot THF$ within 5 days.

The reaction of $BH_3 \cdot L$ (L = THF, SMe_2) with carbonyl compounds provides a different entry into the synthesis of di(organyloxy)boranes. In the case of a ketone, the hydroboration is straightforward, and even by using of an excess of borane, e.g. in the reaction of benzophenone with $BH_3 \cdot SMe_2$, it is not possible to stop the reaction at the $(Ph_2CHO)_2BH$ stage because the remaining BH bond is still highly reactive towards the ketone to produce $(Ph_2CHO)_3B$. Therefore, the rates of reaction leading to $(Ph_2CHO)BH_2$, $(Ph_2CHO)_2BH$ and $(Ph_2CHO)_3B$ do not differ considerably. The formation of phenanthro[9,10-*d*]-1,3,2-dioxaborolane **15** from phenanthroquinone proceeds in high yield. No hydroboration of the keto group is observed. This is in line with the reduction of *p*-benzoquinone due to rearomatization. No intermediates could be detected by ^{11}B-NMR spectroscopy during the reaction described by eq. (10). Therefore, the course of the reaction, as depicted in eq. (10), remains speculative. One can estimate that the rearomatization energy would be in the order of ca. 80 kJ/mol[16].

The observed course of reaction (10) is unique in the sense that anthraquinone is quantitatively reduced by $NaBH_4/BF_3$ in diglyme to anthracene[11a]. In contrast, $BH_3 \cdot THF$ hydroborates 1,4-dihydroxy-9,10-anthraquinone at the C=O groups with concomitant reaction of the intermediate at the OH group and hydrogen evolution. This course of the reaction may be due to the smaller resonance energy of anthracene compared to phenanthrene.

The new di(organyloxy)boranes provide a range of reagents for catalytic hydroboration, and it remains to be seen whether they are superior to catecholborane not only by reactivity but also by selectivity.

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Experimental Section

All experiments were conducted under anhydrous conditions in flame-dried Schlenk glassware under oxygen-free dinitrogen or in a vacuum apparatus. Solvents were dried by standard procedures, distilled and stored under N_2. $BH_3 \cdot THF$ was prepared by dissolving freshly generated diborane gas in THF. $NaBH_4$ was used as supplied by Chemetall GmbH. The alcohols, ketones and quinones were of commercial grade. The catalyst $(Ph_3P)_3RhCl$ was prepared by the method of Wilkinson[17] and stored under dinitrogen gas. – Elemental analyses were performed in the microanalytical laboratory of the institute. IR: Perkin-Elmer TF; MS: Varian CH7 (70 eV); NMR: Jeol 270 (^1H, ^{13}C), Jeol 400 (^{13}C), Bruker AP 200 (^{11}B), standards: TMS (^1H, ^{13}C), C_6D_6 (^{13}C), $BF_3 \cdot Et_2O$ (^{11}B); positive δ values refer to frequencies higher than the standard. X-ray structure analysis: A Siemens P4 four-circle diffractometer operating with Mo-K_α radiation was used and a graphite monochomator. Data collection was performed in the ω-scan mode; the structure was solved by direct methods using the SHELXTL-Plus program[18]. Refinement of the structure was on F^2 as implemented in the SHELX 93 program[19].

Bis(diphenylmethoxy)borane (**6**): $BH_3 \cdot SMe_2$ (1.26 g, 16.6 mmol) was dissolved in ether (10 ml), the solution cooled to 0 °C and a solution of benzophenone (5.93 g, 32.5 mmol) in 30 ml of ether was slowly added with stirring. Stirring was continued at ambient temperature and a slow formation of a suspension was observed. After 20 h, no ^{11}B-NMR signal of $BH_3 \cdot SMe_2$ could be detected. The crystalline precipitate of **6** which had formed was isolated at 0 °C and washed with small amounts of ether. Yield 5.13 g of **6** (82%), m.p. 96 °C with decomposition. – NMR ($CDCl_3$): δ^1H = 4.4 (q, 1 H, BH), 6.29 (s, 2 H, OCH), 7.02 (t, 4 H, *p*-H), 7.08 (t, 8 H, *m*-H), 7.27 (δ, 8 H, *o*-H). – $\delta^{11}B$ = 27.3 (br., BH coupling could not be resolved). – $\delta^{13}C$ = 79.2 (BOC), 126.5 (*p*-C), 127.4 (*o*-C), 128.4 (*m*-C), 143.1 (*i*-C). – IR (cm^{-1}): $\tilde{\nu}$ = 3106 w, 3072 w, 3064 w, 2943 w, 2927 w, 2916 w, 2526 m (ν-BH), 2481 w, 2445 vw, 1493 m, 1456 m, 1421 m, 1389 st (ν-BO_2), 1342 st, 1007 m, 760 m, 747 m, 704.6 st, 697 m. – $C_{26}H_{23}BO_2$ (378.28): calcd. C 82.55, H 6.13; found C 82.95, H 6.10.

Tris(diphenylmethoxy)borane: Benzophenone (10.2 g, 56 mmol) was dissolved in 20 ml of THF and a solution of BH_3 (42 mmol) in 40 ml of THF was added at 0 °C within 5 min. All volatile components were removed shortly after addition. The residue was recrystallized from hot toluene and afforded 10.55 g of $(Ph_2CHO)_3B$ (100%) as hexagonal prisms of m.p. 163 °C. – NMR ($CDCl_3$): δ^1H = 6.37 (s, 1H, CH), 7.25 (m, 5H, Ph). – d^{11}B ($CDCl_3$): 18.6. – δ^{13}C ($CDCl_3$): 77.1 (OC), 126.3 (*m*-C), 127.0 (*p*-C), 128.2 (*o*-C), 143.6 (*i*-C). – IR (cm^{-1}): $\tilde{\nu}$ = 3064 w, 3029 w, 2929 w, 1494 m, 1456 m, 1417 st, 1391 st (ν-BO_2), 1343 st, 1333 st, 1325 st, 1306 m, 1036 m, 1019 m, 758 m, 746 m, 706 st, 696 m. – $C_{39}H_{33}BO_3$ (560.50): calcd. C 83.57, H 5.93; found C 83.70, H 5.90.

Bis(triphenylmethoxy)borane (**7**): A solution of triphenylmethanol (10.4 g, 40 mmol) in 50 ml of THF was slowly added to a solution of BH_3 in THF (15 ml, 31 mmol) with stirring. Hydrogen evolution started immediately but slowly: after 1 h only 60% of the borane had reacted. Stirring was continued for 24 h and all volatile components were then removed from the clear solution in vacuo. The solid that remained was recrystallized from hexane. Yield 8.78 g of **7** (83%); m.p. 158–160 °C. – NMR ($CDCl_3$): δ^1H = 4.2 (br. q, 1H, BH), 7.19 (m, 24H, *o*-, *p*-H), 7.25 (m, 6H, *p*-H). – δ^{11}B = 28.9 [d, $^1J(^{11}B^1H)$ = 148 Hz]. – δ^{13}C = 86.4 (OC), 127.0 (*p*-C), 127.9 (*o*-C), 128.4 (*m*-C), 145.9 (*i*-C). – IR (cm^{-1}, nujol, Hostaflon): $\tilde{\nu}$ = 3085 w, 3054 m, 3024 w, 2557 w (ν-BH), 1599 w, 1490 st, 1447 st, 1394 st, 1356 st, br., 760 st, 700 st, 637 st. – MS; *m/z*: 530 [$M^{+\bullet}$], 259 [$Ph_3CO^{+\bullet}$], 243 [$Ph_3C^{+\bullet}$], 182 [$Ph_2CO^{+\bullet}$], 166 [$Ph_2C^{+\bullet}$], 111* [243^2/530], 104 [$C_6H_4CO^{+\bullet}$], 76 [$C_6H_4^{+\bullet}$]. – $C_{38}H_{31}BO_2$ (530.47): calcd. C 86.04, H 5.89; found C 84.13, H 5.94.

Naphtho[2,3-d]-1,3,2-dioxaborole (**9**): A suspension of 2,3-dihydroxynaphthalene (3.08 g, 19 mmol) in 50 ml of THF was rapidly added to a stirred BH_3 solution of THF (10 ml, 19 mmol) at 0 °C. Gas evolution began immediately and the naphthol dissolved slowly. After 1 h, the reaction mixture was allowed to attain ambient temperature and a clear solution formed within 2 h. At this stage an ^{11}B-NMR signal at δ = 15, $^1J(^{11}B^1H)$ = 158 Hz, was recorded as a doublet. The solvent was removed in vacuo to yield almost pure **9**, which after sublimation at 110 °C/6 mbar gave 3.08 g of **9** (95%); m.p. 78 °C. – NMR (in $CDCl_3$): δ^1H = 4.8 (br. q, 1H, BH), 7.24 (dd, 2H, 7,6-H), 7.59 (s, 2H, 4,9-H), 7.81 (dd, 2H, 8,5-H). – δ^{11}B = 29.2 [d, $^1J(^{11}B^1H)$ = 175 Hz]. – δ^{13}C = 108.8 (C-5,12), 125.0 (C-8,9), 127.7 (C-7,10), 130.4 (C-6,11), 146.8 (C-4,13). – IR (cm^{-1}): $\tilde{\nu}$ = 3057 m (νCH), 2683 m, 2664 st (ν-BH), 1511 m, 1483 w, 1467 st, 1457 st, 1438 m, 1416 m, 1313 st, 1292 st, 1242 st, br., 860 st, 764 m, 747 st, 501 st, 467 m, 386 m. – MS; *m/z*: 170 [$M^{+\bullet}$], 141 [$C_{10}H_6O^+$], 114 [$C_9H_6^{+\bullet}$], 88 [$C_7H_4^{+\bullet}$], 63 [$C_5H_3^+$]. – $C_{10}H_7BO_2$ (169.97): calcd. C 70.66, H 4.15; found C 69.60, H 4.42.

Bis{naphtho[2,3-d]-1,3,2-dioxaborol-2-yl}Ether (**10**): On attempts to crystallize **9** from CH_2Cl_2 a compound was formed that showed no doublet in the ^{11}B-NMR spectrum. It turned out that the CH_2Cl_2 solvent used contained H_2O, and the addition of a small amount of H_2O to a CH_2Cl_2 solution of **9** provided the same result. MS showed that compound **10** had formed; m.p. 246–248 °C. The yield was not determined. – NMR ($CDCl_3$): δ^1H = 7.33 (s, 4H, 5,12′-H), 7.40 (dd, 4H, 8,9′-H), 7.72 (dd, 4H, 7,10′-H). – δ^{11}B = 16.4. – δ^{13}C = 106.7 (C-5,12), 123.9 (C-8,9), 127.0 (C-7,10), 130.0 (C-7,12), 148.7 (C-4,13). – IR (cm^{-1}): ν = 3076 w, 3053 w, 1617 m, 1556 st, 1450 st, 1429 st, 1308 m, 1290 m, 1232 st, br., 984.5 st, 883.7 st, 746.8 m, 645.0 m, 485.2 m. – MS (*m/z*): 354 [100, $M^{+\bullet}$], 212, 186, 114 [$C_9H_6^{+\bullet}$]. – $C_{20}H_{12}B_2O_5$ (353.93): calcd. C 67.87, H 3.42; found C 68.00, H 3.52.

Naphtho[1,8-de]-1,3,2-dioxaborinane (**11**): As described for compound **9** a BH_3 solution in THF (17 ml, 32 mmol) was allowed to react with 1,8-dihydroxynaphthalene (4.23 g, 26.4 mmol) dissolved in 30 ml of THF at 0 °C. After hydrogen gas evolution had ceased the solution was allowed to attain ambient temperature. A brown solid residue was obtained after all volatile components had been removed in vacuo. Distillation at 67 °C/0.003 bar gave 3.46 g of **11** (77%) as a colorless liquid which solidified quickly; m.p. 125 °C. – NMR ($CDCl_3$): δ^1H = 4.2 (br. q, 1H, BH), 6.72 (d, 2H, 6,7-H), 7.20 (t, 2H, 5,8-H), 7.27 (d, 2H, 4,9-H). – δ^{11}B = 26.5 [d, $^1J(^{11}B^1H)$ = 177 Hz]. – δ^{13}C = 109.4 (C-4,9), 118.1 (C-9b), 121.3 (C-6,7), 127.6 (C-5,8), 134.9 (C6a), 146.7 (C-3a, 9a). – IR (cm^{-1}): $\tilde{\nu}$ = 3057 st, 3016 w (ν-CH), 2626 st, 2567 st (ν-BH), 1636 m, 1610 st. – MS; *m/z*: 170 [$M^{+\bullet}$], 141 [$C_{10}H_6O^+$], 114 [$C_9H_6^{+\bullet}$], 88 [$C_7H_4^{+\bullet}$], 63 [$C_5H_3^+$]. – $C_{10}H_7BO_2$ (169.97): calcd. C 70.66, H 4.15; found C 69.88, H 4.02.

Boric Acid Ester of 2,2′-Dihydroxy-1,1′-biphenyl (**13**): A solution of BH_3 (10 ml, 19.0 mmol) in THF was dropped into a stirred solution of 2,2′-bisphenol (3.3 g, 18.8 mmol) in 30 ml of THF at −20 °C. 800 ml of H_2 gas (36 mmol) was liberated and a microcrystalline product had precipitated. Then the suspension was stirred for 2 h at ambient temperature. The clear solution showed a doublet at δ^{11}B = 8.5, $^1J(^{11}B^1H)$ = 142 Hz, indicating the quantitative formation of a diorganyloxyborane $(RO)_2BH$. THF was then removed in vacuo. An oil remained that started foaming in vacuo. No product distilled or sublimed up to 180 °C/8 mbar. The nonvolatile solid was then dissolved in CH_2Cl_2. Addition of pentane to the solution caused precipitation of compound **13**. Yield 3.44 g of **13** (96%), m.p. 149–153 °C. – NMR ($CDCl_3$): δ^1H = 6.96 (d, 6H, 2,2-H), 7.14 (t, 6H, 4,4′-H), 7.27 (dd, 6H, 5,5′-H), 7.35 (td, 6H, 3,3′-H). – δ^{11}B = 19.5 ($h_{1/2}$ = 1110 Hz). – δ^{13}C = 120.9 (C-2,2′), 123.9 (C-4,4′), 127.8 (C-6,6′), 129.0 (C-5,5′), 130.0 (C-3,3′), 151.2 (C-1,1′). – MS; *m/z*: 574 [$M^{+\bullet}$], 558, 406, 380, 238, 212, 195, 183, 168, 139. – $C_{36}H_{24}B_3O_6$ (574.21): calcd. C 73.91, H 4.14; found C 72.98, H 4.21.

4,8-Di-1-tert-butyl-2,10-dimethyl-12H-dibenzo[d,g][1,3,2]-dioxaborocin (**14**): A solution of 1,1-bis(2-hydroxy-3-*tert*-butyl-5-methylphenyl)methane (3.4 g, 10 mmol) in 40 ml of THF was added to a solution of BH_3 (10 mmol) in 4.6 ml of THF with stirring. During this process the yellow solution turned colorless, and H_2 gas (450 ml, 20 mmol) was liberated. The residue which remained after removal of all volatile components in vacuo was heated at 100 °C for 90 min without losing B_2H_6. Crystallization from hexane gave 3.2 g of **14** (91%) as colorless needles. **14** sublimes at 220 °C, 10 mbar, m.p. 140–148 °C (dec.). – NMR ($CDCl_3$): δ^1H = 1.34 (s, 18H, 13,17-H), 2.23 (s, 6H, 14,15-H), 3.79 [d, ^2J(H,H) = 13.7 Hz, 1H, 12-H], 4.18 [d, ^2J(H,H) = 13.7 Hz, 1H, 12-H], 6.92 (s, 2H, 1,11-H), 6.92 (s, 2H, 3,9-H). – δ^{11}B = 21.9 [d, $J(^{11}B^1H)$ = 205 Hz], $h^{1/2}$ = 577 Hz. – δ^{13}C = 21.0 (C-14,15), 29.6 (C-13,17), 34.6 (C-12,16), 35.0 (C-12), 126.1 (C-3,9), 127.7 (C-1,11), 130.8 (C-2,10), 132.2 (C-11a,12a), 139.5 (C-4,8), 148.1 (C-4a,7a). – IR (cm^{-1}): $\tilde{\nu}$ = 3001 w, 2986 w, 2956 st, 2920 st, 2878 st, 2544 st (ν-BH), 1602 w. – MS; *m/z*: 350 [$M^{+\bullet}$], 335 [M – Me]$^{+\bullet}$, 279 [M – C_4H_8]$^{+\bullet}$. – $C_{23}H_{31}BO_2$ (350.31): calcd. C 78.86, H 8.92; found C 78.74, H 9.14.

Phenanthro[9,10-d]-1,3,2-dioxaborolane (**15**): A solution of BH_3 (20.5 mmol) in 5.7 ml of THF was cooled to 0 °C and a suspension of 9,10-phenanthrenoquinone (3.89 g, 18.6 mmol) in 30 ml of THF was added with stirring within 4 min. A clear red-brown solution resulted with some gas evolution. After stirring for 1 h at ambient temperature, all volatile components were removed in vacuo. The off-white residue was subjected to sublimation at 10 mbar. At

140–145 °C (oil bath temperature) 1.66 g of **15** (40%), m.p. 128 °C, was isolated. 1.42 g of a greenish residue remained which was not identified. – NMR (C_6D_6): $\delta^1H = 5.1$ (q, br., 1 H, BH), 7.6 (m, 4 H, 4,5,9,10-H), 8.21 (dd, 2 H, 4,11-H), 8.71 (d, 2 H, 7,8-H). – $\delta^{11}B = 28.4$ [d, $^1J(^{11}B^1H) = 150$ Hz]. – $\delta^{13}C = 120.3$ (C-7,8), 122.5 (C-3b,11a), 123.3 (C-5,10), 125.5 (C-6,9), 127.1 (C-4,11), 127.8 (C-7a,7b), 139.4 (C-3a,11b). – IR (cm^{-1}): $\tilde{\nu} = 3068$ w, 2660 st (ν-BH), 1651 w, 1615 w, 1519 m, 1450 m, 1358 st (ν-BO_2), 1133 st (ν-BO_2), 847 st, 764 st, 724 st. – MS; *m/z*: 220 [$M^{+\cdot}$], 191 [$C_{14}H_7O^+$], 164 [$C_{13}H_8^+$], 163 [$C_{13}H_7^{+\bullet}$]. – $C_{14}H_9BO_2$ (220.04): calcd. C 76.42, H 4.12; found C 76.29, H 4.25.

4,5,6,7-Tetrachloro-1,3,2-benzodioxaborolane (**18**): To a solution of BH_3 (38 mmol) in 20 ml of THF *o*-chloroanil (2.80 g, 11.4 mmol) was added via a solid dispenser. The quinone dissolved and the resulting red solution decolorized with H_2 evolution (1700 ml, 75 mmol). Workup in the usual way resulted in 3.85 g (102%) of an off-white solid, which, according to the ^{11}B-NMR spectrum [$\delta^{11}B = 15.7$, d, $^1J(^{11}B^1H) = 110$ Hz] was a THF adduct of the borolane. There was also a small amount (ca. 1%) of a product with $\delta^{11}B = 5.7$ [t, $^1J(^{11}B^1H) = 133$ Hz] having a BH_2 group. During sublimation of the solid THF was lost at 90 °C/10 mbar, and **18** was formed in clusters of very fine needles, m.p. 95 °C. **18** is very sensitive to hydrolysis. – NMR ($CDCl_3$): $\delta^1H = 4.85$ (q, BH). – $\delta^{11}B = 30.2$ d, $^1J(^{11}B^1H) = 177$ Hz. – $\delta^{13}C = 116.9$ (C-2), 127.6 (C-3), 143.6 (C-1). – IR (cm^{-1}): $\tilde{\nu} = 2703$ w, 2688 st (ν-BH), 1600 w, 1602 w, 1417 st, 1392 st (ν-BO_2), 1150 m, 1127 m, 1012 m, 806 m, 795 m, 663 m, 474 w. – MS; *m/z*: 256 [$M^{+\bullet}$], 228 [$C_6Cl_4O^+$], 221 [$M^{+\bullet} - Cl^\bullet$] [$C_5Cl_2^{+\bullet}$], 200 [$C_5Cl_4^{+\bullet}$], 193 [$C_6Cl_3O^+$], 165 [$C_5Cl_3^+$], 130 [$C_5Cl_2^{+\bullet}$], 95 [$C_5Cl^+$], 60 [$C_5^{+\bullet}$]. – $C_6HBCl_4O_2$ (257.69): calcd. C 27.97, H 0.39; found C 28.06, H 0.68.

5-tert-Butyl-1,3,2-benzodioxaborolan (**22**): Prepared by allowing 2-*tert*-butylcatechol (10 mmol) to react with a BH_3 solution in THF (10 mmol). The yield was not determined. NMR ($CDCl_3$): $\delta^1H = 1.32$ (s, 2 H, Me), ca. 4.8 (q, 1 H, BH), 7.16 (m, 2 H), 7.33 (d, 1 H, H-5). – $\delta^{11}B = 29.2$ q, $^1J(^{11}B^1H) = 175$ Hz. – $\delta^{13}C = 31.7$ (q, Me), 34.8 (s, *C*Me$_3$), 110.0 (dd, C-6), 111.7 (d, C-3), 119.8 (dd, C-5), 145.1 (s, C-1), 146.8 (s, C-5), 147.3 (s, C-7). – IR (cm^{-1}): $\tilde{\nu} = 3076$ m, 2965 s, 2990 m, 2869 m, 2653 s (B–H), 1613 w, 1492 s, 1488 s, 1465 m, 1426 m, 1365 m, 1311 m, 1287 s, 1280 s, 1255 s, 1226 s, 1161 m, 1154 m, 1133 s, 925 w, 864 s, 826 s, 814 ms, 654 m.

Catalytic Hydroboration of Cyclopentene: Two equivalents of a sample of 100–200 mmol of the corresponding hydroborane were added to one equivalent of a solution of cyclopentene in $CDCl_3$ (0.2 mol/l), and samples were transferred to the NMR spectrometer. Additionally, each time a control sample was prepared and investigated by ^1H- and ^{11}B-NMR reference spectra. No reaction occurred in absence of the catalyst. After addition of 0.1 ml of a 0.05 M solution of $(PPh_3)_3RhCl$ in $CDCl_3$ to the borane/cyclopentene mixture, the disappearance of the signal of the alkene proton ($\delta = 5.7$) was observed quantitatively. The time interval between the addition of the catalyst and the first recording of the spectrum was about 25 s. – ^1H-NMR data of cyclopentene: $\delta = 1.80$ (quint, 2 H), 2.27 (t, 4 H), 5.70 (s, 2 H); cyclopentyl group: $\delta = 1.70$ (m, 8 H), 1.94 (m, 1 H).

X-ray Structure Determination of (**14**): Crystal size: 0.33 × 0.35 × 0.4 mm, $C_{23}H_{31}BO_2$, mol. mass 350.3 g/mol, colorless prism, triclinic, $a = 9.427(5)$, $b = 9.500(6)$, $c = 12.307(7)$ Å, $\alpha = 82.95(1)$, $\beta = 83.57(3)$, $\gamma = 88.73(3)°$, $V = 1087(2)$ Å^3, space group $P\bar{1}$ (No. 2), $Z = 2$, $F(000) = 380$, $\mu = 0.066\ mm^{-1}$. – Data collection: $T = 293$ K, ω-scans, scan speed 2.5–60°/min, 2Θ-range = 2.0–47.5° in h, $\pm k$, $\pm l$, 3819 reflections measured, 3155 independent and 1600 observed reflections [$I > 2.5\ \sigma(I)$]. – Structure solution: Direct methods, refinement by least-squares methods on F^2, nonhydrogen atoms refined anisotropically, H atoms were placed in calculated positions and refined with the riding model. A boron-bonded H atom was found in the difference Fourier map and its position freely refined with U_i fixed. $R = 0.0617$, GOF (on F^2) = 1.021, variables refined: 246, largest difference peak 0.14 e/Å^3, $wR_2 = 0.1482$, $w^{-1} = \sigma^2F_o^2 + (0.0890\ P)^2 + 0.1295\ P$ with $P = (F_o^2 + 2F_c^2)/3$. Ctystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. 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: teched@chemcrys.cam.ac.uk), by quoting the deposition number CCDC-100056.

☆ Dedicated to Prof. Dr. *Marianne Baudler* on the occasion of her 75th birthday.

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