First B-Organyloxy-Substituted Iminoboranes: Preparation, Stabilization, and Reactivity

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The amino(halo)(organyloxy)boranes ROB(X)N(H)R′ (R = 2,6-^{t}Bu$_2$C$_6$H$_3$, X = Cl, R′ = ^{t}Bu (**7**), SiMe$_3$ (**8**), 2,6-^{i}Pr$_2$C$_6$H$_3$ (**9**), 2,4,6-Me$_3$C$_6$H$_2$ (**10**), 2,4,6-^{t}Bu$_3$C$_6$H$_2$ (**11**); R = 2,6-(C$_6$H$_5$)$_2$C$_6$H$_3$, X = Cl, R′ = ^{t}Bu (**12**); R = 2,6-^{t}Bu$_2$C$_6$H$_3$, X = F, R′ = ^{t}Bu (**13**), 2,6-^{i}Pr$_2$C$_6$H$_3$ (**14**); R = ^{t}Bu$_3$C, X = F, R′ = ^{i}Pr (**15**), ^{t}Bu (**16**), SiMe$_3$ (**17**)) were dehydrohalogenated with *tert*-butyllithium at low temperature. The reaction involved the intermediate formation of an aryloxy(imino)-borane in the case of **7**, **9**, **11**, and **12**. The diazadiboretidines [ROB═NR′]$_2$ (R = 2,6-^{t}Bu$_2$C$_6$H$_3$, R′ = ^{t}Bu (**18**), SiMe$_3$ (**19**), 2,6-^{i}Pr$_2$C$_6$H$_3$ (**20**), 2,4,6-Me$_3$C$_6$H$_2$ (**21**); R = ^{t}Bu$_3$C, R′ = ^{i}Pr (**22**), SiMe$_3$ (**23**)) were isolated as the ultimate products of the reactions. The aryloxy(imino)-borane 2,6-^{t}Bu$_2$C$_6$H$_3$−O−B≡N-^{t}Bu (derived from **7**) was reacted with BEt$_3$ and Me$_3$SiN$_3$ to give the corresponding 1,2-addition products across the (B≡N) triple bond (**25** and **26**, respectively). The compounds were characterized by NMR spectroscopy (^{1}H, ^{11}B, ^{13}C, ^{29}Si), MS (EI and FI), and elemental analyses. X-ray structure determinations are presented for **18**, **22**, and **26**.

Introduction

In the past two decades a large number of new iminoboranes and amino(imino)boranes were prepared mainly by two types of elimination reactions with suitable amino(halo)boranes. Thermally induced elimination of a halogen(trimethyl)silane in the gas phase proved an effective method for the synthesis of organyl-(imino)boranes,[1] while many amino(imino)boranes could more successfully be prepared by dehydrohalogenation reactions, which can be performed at low temperature in the presence of strong Lewis bases with bulky substituents such as *tert*-butyllithium or lithium bis-(trimethylsilyl)amide.[2] These fundamental studies led to the conclusion that the stability of iminoboranes depends on the steric requirements of the substituents in the immediate vicinity of the (B≡N) triple bond.[1,2] Our group has added further details to this field, mainly by using *o*-substituted phenyl derivatives to stabilize such moieties.[3−6]

In view of the numerous successful syntheses of iminoboranes and amino(imino)boranes, it seemed promising to try the preparation of iminoboranes with elements other than carbon, silicon, or nitrogen attached to the multiply bonded center. A recent study dealt with borylhydroxylamines as precursors for N-oxygen-substituted iminoboranes.[7] Probably oxygen could also be a suitable neighbor for the boron atom in iminoboranes. The oxygen atom has two lone electron pairs and can therefore act as a π-donor toward boron, rather like the nitrogen atom in amino(imino)boranes. Moreover, the stability of the B−O bond should facilitate the synthesis of the starting materials needed. On the other hand, kinetic stabilization will be more difficult, as there is only one group on the oxygen atom to produce steric shielding (but two on the nitrogen atom of amino(imino)-boranes), and the shielding group is more distant from the center of unsaturation than in the organyl-substituted iminoboranes.

Our investigation concentrated on Lewis-base-induced dehydrohalogenation reactions with amino(halo)(organyloxy)boranes. Ideally, these reactions could lead to organyloxy(imino)boranes RO−B≡N−R′, a compound class that has so far been unknown. We also aimed to establish the influence of the substituents R and R′ on the stability of any unsaturated product and to describe the stabilization processes of unstable organyloxy-(imino)boranes. Finally, we hoped to gain some insight into the reactivity of the unsaturated target compounds. In this paper we present the findings of our study of B-oxygen-substituted iminoboranes.

Results and Discussion

Preparation of the Starting Materials. The amino (halo)(organyloxy)boranes which promised to be useful precursors for the synthesis of organyloxy(imino)-

(1) Paetzold, P. *Adv. Inorg. Chem.* **1987**, *31*, 123, and literature cited there.
(2) Nöth, H. *Angew. Chem.* **1988**, *100*, 1664, and literature cited there.
(3) Elter, G.; Meller, A.; Neuhaus, M.; Schmidt-Bäse, D. *J. Organomet. Chem.* **1990**, *381*, 299.
(4) Elter, G.; Heine, A.; Luthin, W.; Meller, A.; Sheldrick, G. M.; Stalke, D. *Z. Anorg. Allg. Chem.* **1992**, *608*, 147.
(5) Elter, G.; Geschwentner, M.; Meller, A. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1474.
(6) Elter, G.; Gornitzka, H.; Heine, A.; Luthin, W.; Meller, A.; Stratmann, J.-G. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1995.
(7) Albrecht, T.; Elter, G.; Meller, A. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1423.

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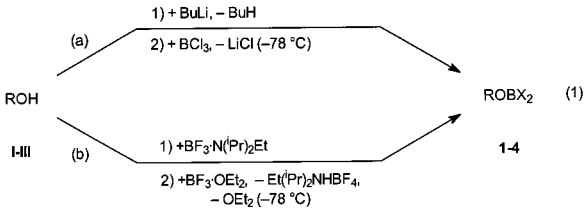
boranes were prepared in several steps from alcohols or phenols, respectively, boron trihalides, and a variety of amines.

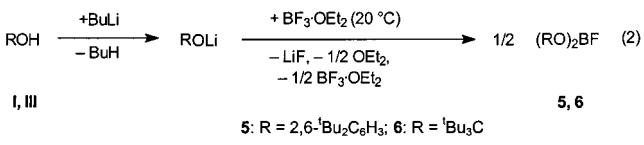
First the sterically hindered phenols 2,6-di-*tert*-butylphenol (**I**) and 2′-hydroxy-*m*-terphenyl (2,6-diphenylphenol, **II**) and the alcohol 1,1-di-*tert*-butyl-2,2-dimethylpropanol (tri-*tert*-butylmethanol, **III**) were reacted with boron trifluoride and/or boron trichloride to give organyloxy(dihalo)boranes. The syntheses of the dichlorophenoxyborane derivatives **1**[8] and **2** required the initial metalation of the respective phenols, while the fluorine compounds **3** and **4** could better be prepared from **I** and **III**, respectively, and boron trifluoride diethyl etherate in the presence of the adduct $BF_3{\cdot}N(^iPr)_2Et$.[9] The reactions were carried out at low temperature (eq 1).



starting material	X	R	path	product
I	Cl	2,6-^{t}Bu$_2$C$_6$H$_3$	(a)	**1**
II	Cl	2,6-Ph$_2$(C$_6$H$_5$)$_2$C$_6$H$_3$	(a)	**2**
I	F	2,6-^{t}Bu$_2$C$_6$H$_3$	(b)	**3**
III	F	^{t}Bu$_3$C	(b)	**4**

We were unable to isolate compound **4**, which decomposed when the solvent was removed in vacuo. However, it was possible to handle this compound in solution after filtering off the tetrafluoroborate. A characteristic peak around 40 ppm in the ^{19}F NMR spectrum of the reaction solution can be assigned to **4** (cf. ^{19}F chemical shift of **3**: 41.6 ppm). Our attempts to prepare a chloro-compound similar to **4** (tri-*tert*-butylmethoxy(dichloro)-borane) failed, too. We tried the reaction of boron trichloride with the alcohol **III** (in the presence of NEt_3) and with lithium tri-*tert*-butylmethanolate.

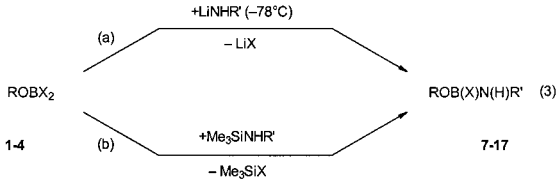
The reaction of the lithium derivatives of **I** and **III** with boron trifluoride diethyl etherate at room temperature led to the fluoro(diorganyloxy)boranes **5** and **6** (eq 2). The monosubstituted compound **3** could be observed only as a byproduct when the reaction with the phenol **I** was carried out at −78 °C.



(8) Compound **1** has been known for many years: (a) Hunter, D. H., Steinberg, H. US Pat. 3027397, 1962; *Chem. Abstr.* **1962**, *57*, 4595. (b) Steinberg, H. *Organoboron Chemistry. Vol. 1: Boron−Oxygen and Boron−Sulfur Compounds*; Wiley-Interscience: New York, London, Sydney, 1964; p 515. (c) Armbrecht, M.; Meller, A. *Chem. Ber.* **1986**, *119*, 1−8. We listed the compound in the Experimental Section since spectroscopic data and preparative details for **1** are missing in the literature.

(9) Harris, J. J.; Rudner, B. *Inorg. Chem.* **1969**, *8*, 1258.

In a second step the dihalo(organyloxy)boranes **1**−**4** were coupled with a number of lithiated or silylated amines. These reactions, which are summarized in eq 3, led to the amino(halo)(organyloxy)boranes **7**−**17**, which should allow a dehydrohalogenation reaction as a final step.



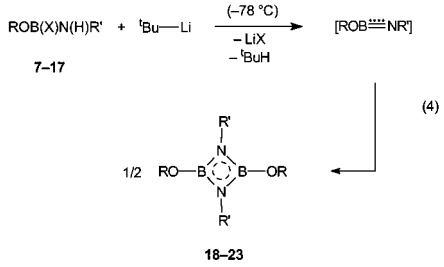
starting material	X	R	R'	path	product
1	Cl	2,6-^{t}Bu$_2$C$_6$H$_3$	^{t}Bu	(a)	**7**
1	Cl	2,6-^{t}Bu$_2$C$_6$H$_3$	SiMe$_3$	(b)	**8**
1	Cl	2,6-^{t}Bu$_2$C$_6$H$_3$	2,6-^{i}Pr$_2$C$_6$H$_3$	(a)	**9**
1	Cl	2,6-^{t}Bu$_2$C$_6$H$_3$	2,4,6-Me$_3$C$_6$H$_2$	(a)	**10**
1	Cl	2,6-^{t}Bu$_2$C$_6$H$_3$	2,4,6-^{t}Bu$_3$C$_6$H$_2$	(a)	**11**
2	Cl	2,6-(C$_6$H$_5$)$_2$C$_6$H$_3$	^{t}Bu	(a)	**12**
3	F	2,6-^{t}Bu$_2$C$_6$H$_3$	^{t}Bu	(a)	**13**
3	F	2,6-^{t}Bu$_2$C$_6$H$_3$	2,6-^{i}Pr$_2$C$_6$H$_3$	(a)	**14**
4	F	^{t}Bu$_3$C	^{i}Pr	(a)	**15**
4	F	^{t}Bu$_3$C	^{t}Bu	(a)	**16**
4	F	^{t}Bu$_3$C	SiMe$_3$	(b)	**17**

We did not succeed in coupling **3** with $(Me_3Si)_2NH$ (path (b)) or **4** with lithiated 2,6-diisopropylaniline (path (a)).

Reactions of the Amino(halo)(organyloxy)boranes 7−17 with *tert*-Butyllithium. The elimination of hydrogen chloride or fluoride, respectively, from the compounds **7**−**17** was achieved by treatment with *tert*-butyllithium at −78 °C (in hexane). While the reaction mixtures were allowed to warm to room temperature, their ^{11}B NMR spectra were continually monitored. We expected the formation of unsaturated intermediates or products to be observable in the ^{11}B NMR spectra because iminoboranes are known to have characteristic signals in the range 0−15 ppm.[1,2] The reactions are represented in eq 4.

It turned out that the reactions with the fluorine compounds started only when the temperature rose above 0 °C, and in some cases (**13** and **14**) moderate heating was necessary to initiate the dehydrofluorination. Under these conditions the intermediate formation of an organyloxy(imino)borane could not be observed. Apparently in these cases the organyloxy(imino)borane species is too short-lived and the corresponding cyclodimers are formed almost immediately.

The amino(chloro)(organyloxy)boranes, however, reacted with *tert*-butyllithium at temperatures below 0 °C, and the dehydrochlorination started at around −20 °C. With the compounds **7**, **9**, **11**, and **12** an organyloxy(imino)borane could be identified as a short-lived intermediate from the ^{11}B NMR spectra of the reaction solutions. Their NMR signals in the range 5−8 ppm could be observed for about 2 h but disappeared slowly



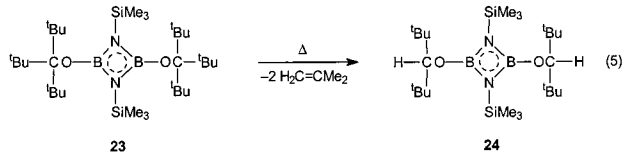
starting material	R	R'	[iminoborane]	product
7	2,6-^{t}Bu$_2$C$_6$H$_3$	^{t}Bu	δ^{11}B ≈ 5 ppm	**18**
8	2,6-^{t}Bu$_2$C$_6$H$_3$	SiMe$_3$	not detected	**19**
9	2,6-^{t}Bu$_2$C$_6$H$_3$	2,6-^{i}Pr$_2$C$_6$H$_3$	δ^{11}B ≈ 8 ppm	**20**
10	2,6-^{t}Bu$_2$C$_6$H$_3$	2,4,6-Me$_3$C$_6$H$_2$	not detected	**21**
11	2,6-^{t}Bu$_2$C$_6$H$_3$	2,4,6-^{t}Bu$_3$C$_6$H$_2$	δ^{11}B ≈ 7 ppm	
12	2,6-(C$_6$F$_5$)$_2$C$_6$H$_3$	^{t}Bu	δ^{11}B ≈ 7 ppm	
13	2,6-^{t}Bu$_2$C$_6$H$_3$	^{t}Bu	not detected	**18**
14	2,6-^{t}Bu$_2$C$_6$H$_3$	2,6-^{i}Pr$_2$C$_6$H$_3$	not detected	**20**
15	^{t}Bu$_3$C	^{i}Pr	not detected	**22**
16	^{t}Bu$_3$C	^{t}Bu	not detected	
17	^{t}Bu$_3$C	SiMe$_3$	not detected	**23**

when the reaction mixtures reached temperatures above 0 °C, giving way to the peaks around 25 ppm that can be associated with the respective cyclodimers. In combination with the 2,6-di-*tert*-butylphenoxy group the 2,6-diisopropylphenyl group seems to represent the borderline case as far as the bulkiness of the imino substituent is concerned. Less cumbersome substituents such as mesityl do not even temporarily stabilize the organyloxy(imino)borane.

We isolated the diazadiboretidines **18**−**23** as the ultimate products of the dehydrohalogenation of the investigated haloboranes. With their oxygen-substituted boron atoms they constitute a new type of diazadiboretidine. The uniform stabilization pattern observed is in full agreement with the established behavior of amino(imino)boranes. The presence of the oxygen atom does not alter the way in which the iminoboranes stabilize. However, it seems to have a strengthening effect on the boron−halogen bond in the starting compounds, so that their dehydrohalogenation requires higher temperatures than similar reactions with comparable bis(amino)(halo)boranes.[4,6]

No defined product was isolated from the reactions of the compounds **11**, **12**, and **16** with *tert*-butyllithium. In the case of **11** it is possible that the dehydrochlorination is followed by an intramolecular addition involving a methyl group of the bulky amino substituent.[3]

While the diazadiboretidines with the 2,6-di-*tert*-butylphenoxy group could easily be purified by sublimation, the tri-*tert*-butylmethoxy-substituted compounds displayed a tendency to split off isobutene when they were heated, due to the steric pressure that the three *tert*-butyl groups exert in the alkoxy substituents. Hence the compounds **22** and **23** were only obtained by crystallization. **22** decomposed in an irregular fashion when it was heated. When we attempted to sublime the diazadiboretidine **23** in vacuo, we obtained the related compound **24** (eq 5). The isobutene was collected in a



cold trap and identified by its ^{13}C NMR spectrum (see the Experimental Section). X-ray structure determinations were carried out with the compounds **18** and **22** (see below).

Reactions with Aryloxy(imino)boranes. Independent evidence for the temporary existence of the organyloxy(imino)boranes in the reactions presented above can be obtained when the reaction mixtures contain an additional reactant that offers an alternative reaction route for the unsaturated intermediate. Under such conditions, it should be possible to arrive at compounds other than the cyclodimers that are formed in the reactions according to eq 4.

A wide variety of reactions have been described both for iminoboranes and amino(imino)boranes; the extraordinary potential of these compound classes for synthetic purposes has thus been established.[1,2,10−15] However, the number of reaction types that can possibly be carried out with our organyloxy(imino)boranes is severely limited, mainly by the fact that the unsaturated species can only be handled (for a relatively short period of time) in the solution in which it was formed. A potential reaction partner for an organyloxy(imino)borane would therefore have to meet at least the following requirements:

(1) It must not react with the starting materials (*tert*-butyllithium and the organyloxy(amino)(halo)borane).

(2) Its reaction with the organyloxy(imino)borane has to be faster than the cyclodimerization of the iminoborane itself.

Consequently, many reactants are out of question to start with (e.g., all protic agents such as amines, alcohols, or thioles and most compounds containing halogen atoms). Among the remaining options the most promising reaction types include cycloadditions (with alkenes, alkynes, azides, dienes, etc.) and insertion reactions, e.g., with Lewis acids such as trialkylboranes.

We selected the chloroborane **7** as a model compound for our derivations and investigated the reactivity of its dehydrochlorinated form toward a range of substances, including unsaturated hydrocarbons, amino(imino)boranes, triethylborane, and azides.

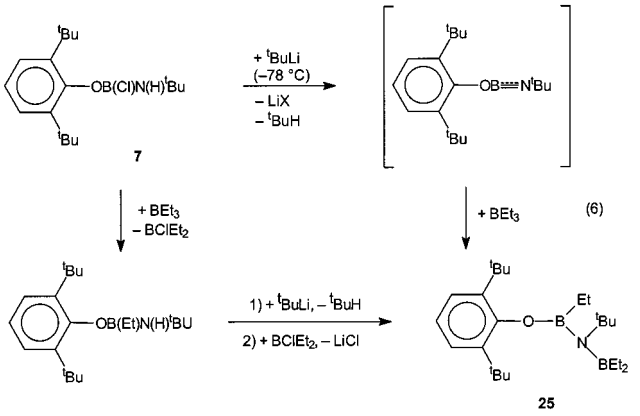
We could not observe cycloaddition reactions with 2,3-dimethyl-2-butene ([2+2]), 2-butyne ([2+2]), or 2,3-

(10) Geisberger, G.; Neukirchinger, K.; Nöth, H. *Chem. Ber.* **1990**, *123*, 455.
(11) Nöth, H.; Schübel, J. *Chem. Ber.* **1991**, *124*, 1687.
(12) Dreczewski, B.; Englert, U.; Hahnfeld, D.; Pawelec, Z.; Paetzold, P.; Walz, L.; Wojnowski, W. *Chem. Ber.* **1992**, *125*, 1073.
(13) Braunschweig, H.; Paetzold, P.; Spaniol, T. P. *Chem. Ber.* **1993**, *126*, 1565.
(14) Loderer, D.; Nöth, H.; Pommerening, H.; Rattay, W.; Schick, H. *Chem. Ber.* **1994**, *127*, 1605.
(15) Costisor, O.; Klöfkorn, C.; Paetzold, P.; Schmidt, M.; Spaniol, T.; Wagner, T.; *Chem. Ber.* **1995**, *128*, 1037.

dimethyl-1,3-butadiene (Diels−Alder or [2+2]). In all these cases the diazadiboretidine **18** was found to be the only product.

A similar pattern occurred when a cross-dimerization of our aryloxy(imino)borane with other iminoboranes was attempted. The relatively stable amino(imino)-borane $(Me_3Si)_2N-B{\equiv}N$-(2,6-^{i}Pr$_2$C$_6$H$_3$)[6] was recovered intact from the reaction mixture alongside the cyclodimer **18**. The more reactive compound (2,6-^{i}Pr$_2$C$_6$H$_3$)-$(SiMe_3)N-B{\equiv}N$-(2,6-^{i}Pr$_2$C$_6$H$_3$) did not react with the model aryloxy(imino)borane either; instead it gave the diazasilaboretidine that has been described as its intramolecular stabilization product.[6]

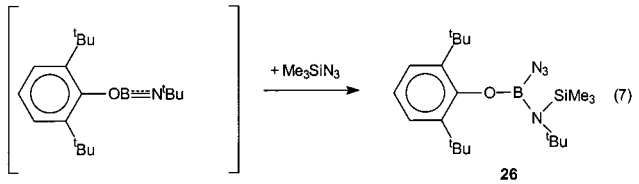
These observations made us look for a reaction partner with a stronger affinity toward the (B≡N) triple bond in the organyloxy(imino)borane, which ought to be the case with Lewis acids. Accordingly, the reaction of the aryloxy(imino)borane derived from **7** with an excess of triethylborane led to the insertion product of the organyloxy(imino)borane into one of the B−C bonds **25** (eq 6).



As indicated in eq 6, there are two possible routes leading from **7** to **25**. The chloroborane **7** could theoretically be alkylated by BEt_3 prior to any metalation of the nitrogen atom. We reckoned that in this case it should be possible to isolate the intermediate amino(ethyl)borane. In a separate experiment we therefore added BEt_3 to the chloroborane **7** at −78 °C; the workup of this reaction mixture gave the starting compound **7** in quantitative yield. This is further evidence for the intermediate formation of the organyloxy(imino)borane in the reaction according to eq 6.

The analogous reaction of **7** with trimethylaluminum did not deliver an amino−alane derivative similar to **25**. Instead a mixture of the starting compound **7** and the corresponding B-methyl-substituted derivative was recovered and was identified by the mass and NMR spectra of the distilled product. All our efforts to separate the two components were foiled by their similar boiling points. However, this outcome might indicate that the alkylation represented in eq 6 must indeed be considered an alternative to the formation of the organyloxy(imino)borane.

Another successful addition resulted with trimethylsilyl azide. According to eq 7 the azide was added across the (B≡N) bond of our aryloxy(imino)borane, giving the B-azido derivative **26**; the structure of this compound was determined by an X-ray structure analysis. A



similar reaction was tried with phenyl azide, but the product could not be purified by sublimation because it decomposed upon heating.

The reactions according to eqs 6 and 7 are again in full agreement with the established behavior of amino(imino)boranes.[1,2] The excessive sterical hindrance in **26** prevents a cyclization to give a tetrazaboroline.

Crystal Structures. X-ray structure analyses were performed with the compounds **18**, **22**, and **26**. The results are depicted in the Figures 1−3, respectively. Selected atomic distances and angles are summarized in Table 1, and crystallographic data are compiled in Table 2. Among the diazadiboretidines it shows that **18** is exactly planar and has a symmetry center in the center of the ring. In **22** the four-membered ring deviates somewhat from a planar geometry: the folding angle is 174.9° and the torsion angle 3.8°. This may be due to the extreme sterical crowding among the oxygen atoms. Until now there are five X-ray structure determinations of diazadiboretidines reported in the literature: those of the B-amino-substituted species [TMPB-NBu]$_2$ (**A**)[16] (TMP = 2,2,6,6-tetramethylpiperidine) and [$(Me_3Si)_2$NBNSiMe$_3$]$_2$ (**B**)[17] and those of the B-organyl-substituted [$F_5C_6BN^tBu]_2$ (**C**),[18] [^{t}BuBN^{t}Bu]$_2$,[19] and [BuN^tBu]$_2$ (**E**).[20] Of these **A**, **B**, **C**, and **E** are planar, **D** is folded (folding angle 155°, torsion angle 18°). The mean BN distances in the respective rings are 1.460 Å in **18**, 1.470 Å in **22**, 1.468 Å in **A**, 1.458 Å in **B**, 1.430 Å in **C**, 1.486 Å in **D**, and 1.456 Å in **E**. The exocyclic BN bond lengths are 1.465 Å in **A** and 1.441 Å in **B**. The (exocyclic) BO distances are 1.365 Å in **18** and 1.355 Å (mean) in **22**. The BO distances are slightly larger than the exocyclic BO bonds in trihydroxyboroxine (about 1.349 Å).[21] All six diazadiboretidines have slightly rhomboidal shaped ring systems: the angles about the ring N atoms vary between (mean) 82.1° in **B** and 88.0° in **D**. It shows that regardless of the type of substituents bonded to the boron atoms (i.e., RO, C_6H_5, Bu, and ^{t}Bu; there are planar and folded ring systems), only the two amino-substituted species (**A** and **B**) both have planar rings. This could lead to the assumption that exocyclic π-bonding might play an important role. However, in both B-aminodiazadiboretidines (as well as the C_6F_5 group in **C**) the substituents are twisted out of the B_2N_2 plane and cannot overlap to form π-bonds. The longest BN distance in the ring (1.486 Å) is found in [^{t}BuBN^t-Bu]$_2$ (**D**), and the shortest in [$C_6F_5BN^tBu]_2$ (**C**). This all indicates that exocyclic π-bonding between the boron atom and its substituent (when it exists) is just one of

(16) Nöth, H.; Schwartz, M.; Weber, S. *Chem. Ber.* **1985**, *118*, 4716.
(17) Hess, H. *Acta Crystallogr., Sect. B* **1969**, *25*, 2342.
(18) Paetzold, P.; Richter, A.; Thijssen, T.; Würtenberg, S. *Chem. Ber.* **1979**, *112*, 3811.
(19) Paetzold, P.; von Plotho, C.; Schmid, G.; Boese, R.; Schrader, B.; Bougeard, D.; Pfeiffer, U.; Gleiter, R.; Schäfer, W. *Chem. Ber.* **1984**, *117*, 1089.
(20) Paetzold, P.; Schröder, E.; Schmid, G.; Boese, R. *Chem. Ber.* **1985**, *118*, 3205.
(21) Peters, C. R.; Milberg, M. E. *Acta Crystallogr.* **1964**, *17*, 229.

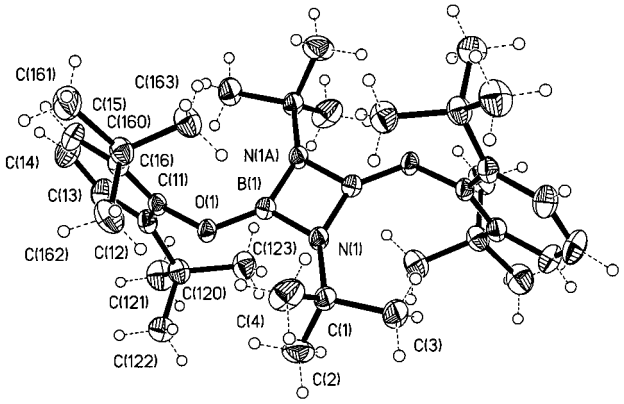


Figure 1. Crystal structure of the diazadiboretidine **18**.

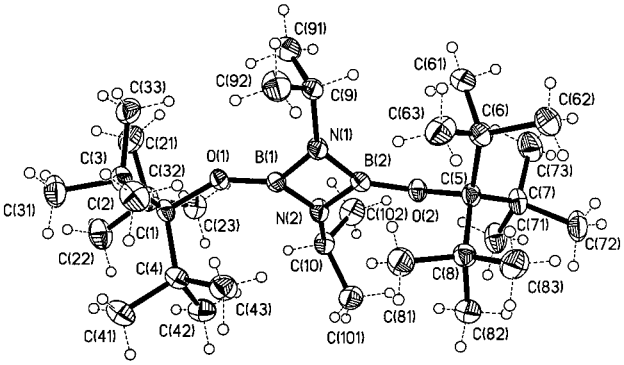


Figure 2. Crystal structure of the diazadiboretidine **22**.

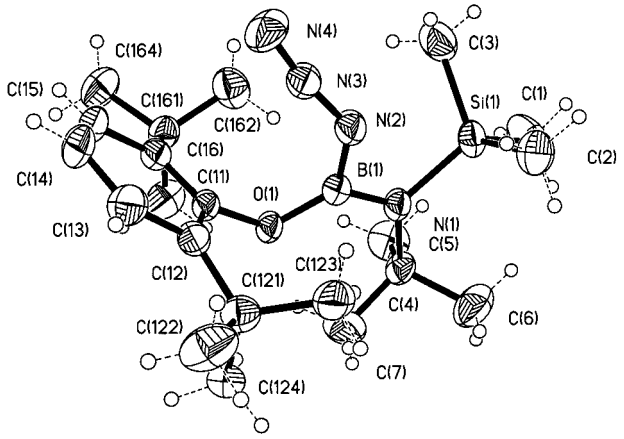


Figure 3. Crystal structure of the azidoborane **26**.

several factors that influence the structure of diazadiboretidines. Polarization in the σ-system due to the electronegativity of the substituents and—most importantly—packing effects of the overcrowded molecules in the solid state apparently play an important role.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of dry nitrogen in dry solvents. NMR: Bruker AM 250, reference $SiMe_4$ internal (^1H, ^{13}C, ^{29}Si), $BF_3{\cdot}OEt_2$ external (^{11}B), C_6F_6 internal (^{19}F), 5% solutions for ^1H, ^{19}F, 20% for ^{11}B, ^{13}C, ^{29}Si. MS: Finnigan MAT 8230. Elemental analyses (C/H/N) were carried out at the analytical laboratory of the Institut für Anorganische Chemie, Universität Göttingen; to allow a distinction between different phenyl groups, the ^1H and ^{13}C positions of the substituents have been numbered in the following way: 1−6 refer to the oxygen-bonded phenyl group, starting with the carbon atom attached to oxygen. 7−12 refer to the other phenyl group(s), starting with the atom that is connected to the rest of the molecule.

Starting Materials. 1,1-Di-*tert*-butyl-2,2-dimethylpropanol **III**[22] and phenyl azide[23] were prepared according to the literature. All other starting materials were commercially available. Concentrations: butyllithium 15% in hexane, *tert*-butyllithium 1.5 M in pentane, triethylborane 1 M in hexane, trimethylaluminum 2 M in heptane.

Preparation of the Dichloroboranes 1 and 2. A 0.1 mol sample of 2,6-di-*tert*-butylphenol **I** (20.6 g) or 2,6-diphenylphenol **II** (24.6 g), respectively, was dissolved in 100 mL of hexane. An equimolar amount of butyllithium was added to this solution, which was then refluxed for 3 h. After cooling to −78 °C a freshly prepared solution of 0.2 mol boron trichloride (23.2 g) in 100 mL of hexane was added dropwise. The reaction mixture was stirred for another 2 h at low temperature and then allowed to warm. The solvent was removed at reduced pressure and the residue separated from the lithium chloride by distillation in vacuo. The crude product was purified by a second distillation.

2,6-Di-*tert*-butylphenoxy(dichloro)borane (1): colorless liquid, bp 84 °C/0.01 Torr. Yield: 22.4 g (78%). Anal. Calcd for $C_{14}H_{21}BCl_2O$ (287.04 g/mol): C, 58.57; H, 7.39. Found: C, 58.49; H, 7.38. MS (EI, 70 eV): *m/e* (rel intensity) 286 (10) ($C_{14}H_{21}11B^{35}Cl_2O$) [$M^+$], 271 (60) [$M^+ - Me$], 57 (100) [$CMe_3^+$]. ^1H NMR ($CDCl_3$, 25 °C): δ 7.27 (AB_2, 2H, 3/5), 7.06 (AB_2, 1H, 4), 1.39 (s, 18H, CMe_3). ^{13}C NMR ($CDCl_3$, 25 °C): δ 151.3 (1), 139.8 (2/6), 126.3 (3/5), 124.5 (4), 35.4 (CMe_3), 31.7 (CMe_3). ^{11}B NMR ($CDCl_3$, 25 °C): δ 31.8.

Dichloro(2,6-diphenylphenoxy)borane (2): colorless solid, bp 140 °C/0.01 Torr, mp 39 °C. Yield: 22.4 g (58%). Anal. Calcd for $C_{18}H_{13}BCl_2O$ (327.02 g/mol): C, 66.11; H, 4.01. Found: C, 66.42; H, 4.50. MS (EI, 70 eV): *m/e* (rel intensity) 326 ($C_{18}H_{13}$-$11B^{35}Cl_2O$) (100) [M^+], 290 (85) [$M^+ - HCl$]. ^1H NMR ($CDCl_3$, 25 °C): δ 7.1−7.6 (m, 13H, 3−5 and 8−12). ^{13}C NMR ($CDCl_3$, 25 °C): δ 147.3 (1), 137.0 (2/6 or 7), 133.6 (2/6 or 7), 130.2 (3/5 or 10), 129.4 (8/12 or 9/11), 128.5 (8/12 or 9/11), 127.7 (3/5 or 10), 125.7 (4). ^{11}B NMR ($CDCl_3$, 25 °C): δ 31.3.

Preparation of the Difluoroboranes 3 and 4. At 0 °C a solution of 0.1 mol ethyldiisopropylamine (12.9 g) in 100 mL of diethyl ether was added to a solution of 0.2 mol of boron trifluoride diethyl etherate (28.4 g) in 100 mL of diethyl ether. The mixture was stirred for 2 h at room temperature and then cooled to −78 °C. A solution of 0.1 mol of 2,6-di-*tert*-butylphenol **I** (20.6 g) or 1,1-di-*tert*-butyl-2,2-dimethylpropanol **III** (20.0 g), respectively, in 100 mL of diethyl ether was added; the reaction mixture was stirred for another 4 h at low temperature and for 12 h at room temperature. Then the solid precipitate was filtered off. In the case of **4** the clear filtrate was used directly for further reactions (we assumed the yield to be 70%). For **3** the solvent was removed at reduced pressure, and the residue was separated from the lithium fluoride by distillation in vacuo. The crude product was purified by a second distillation.

2,6-Di-*tert*-butylphenoxy(difluoro)borane (3): colorless liquid, bp 52 °C/0.01 Torr. Yield: 19.2 g (76%). Anal. Calcd for $C_{14}H_{21}BF_2O$ (254.13 g/mol): C, 66.16; H, 8.35. Found: C, 66.18; H, 8.40. MS (EI, 70 eV): *m/e* (rel intensity) 254 (15) [M^+], 239 (100) [$M^+ - Me$]. ^1H NMR ($CDCl_3$, 25 °C): δ 7.18 (AB_2, 2H, 3/5), 6.95 (AB_2, 1H, 4), 1.43 (s, 18H, CMe_3). ^{13}C NMR ($CDCl_3$, 25 °C): δ 149.4 (t, 1, $^3J_{CF} = 2.9$ Hz), 140.6 (2/6), 125.9 (3/5), 124.4 (4), 35.1 (CMe_3), 31.2 (CMe_3). ^{11}B NMR ($CDCl_3$, 25 °C): δ 12.4. ^{19}F NMR ($CDCl_3$, 25 °C): δ 41.5.

Preparation of the Bis(phenoxy)boranes 5 and 6. The compounds were not intentionally prepared but obtained from the following procedure: 0.1 mol of 2,6-di-*tert*-butylphenol **I** (20.6 g) or 1,1-di-*tert*-butyl-2,2-dimethylpropanol **III** (20.0 g),

(22) Anwander, R.; Herrmann, W. A.; Kleine, M.; Scherer, W. *Chem. Ber.* **1992**, *125*, 1971.
(23) Allen, C. F. H.; Lindsay, R. O. *Org. Synth. Collect. Vol.* **1955**, *3*, 710.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 18, 22, and 26

			Compound **18**				
O(1)−B(1)	1.365(2)	N(1)−B(1)	1.465(2)	N(1A)−B(1)	1.454(2)	N(1)−C(1)	1.475(2)
O(1)−C(11)	1.399(2)	B(1)−B(1A)	1.948(3)				
N(1A)−B(1)−N(1)	96.29(12)	B(1A)−N(1)−B(1)	83.71(12)	N(1)−B(1)−O(1)	124.37(14)	N(1A)−B(1)−O(1)	139.33(14)
B(1)−O(1)−C(11)	126.33(12)	O(1)−C(11)−C(12)	118.33(13)	O(1)−C(11)−C(16)	117.92(13)	C(16)−C(11)−C(12)	123.61(13)
O(1)−B(1)−B(1A)	172.3(2)						
			Compound **22**				
B(1)−N(1)	1.481(2)	N(1)−B(2)	1.459(2)	B(2)−N(2)	1.474(2)	N(2)−B(1)	1.455(2)
B(1)−O(1)	1.351(2)	O(1)−C(1)	1.459(2)	B(2)−O(2)	1.360(2)	O(2)−C(5)	1.462(2)
N(1)−C(9)	1.465(2)	N(2)−C(10)	1.461(2)	B(1)−B(2)	1.994(3)		
N(1)−B(2)−N(2)	94.30(13)	B(1)−N(1)−B(2)	85.42(12)	B(1)−N(2)−B(2)	85.82(12)	C(9)−N(1)−B(1)	129.90(14)
C(9)−N(1)−B(2)	137.24(14)	C(10)−N(2)−B(1)	140.12(14)	C(10)−N(2)−B(2)	133.57(14)	O(1)−B(1)−N(1)	124.99(15)
O(1)−B(1)−N(2)	140.8(2)	O(2)−B(2)−N(1)	140.4(2)	O(2)−B(2)−N(2)	125.25(15)	B(1)−O(1)−C(1)	146.24(13)
B(2)−O(2)−C(5)	142.92(13)	O(1)−C(1)−C(2)	105.87(12)	O(1)−C(1)−C(3)	101.82(12)	O(1)−C(1)−C(4)	108.28(12)
O(1)−B(1)−B(2)	170.82(14)	O(2)−B(2)−B(1)	170.76(14)				
			Compound **26**				
B(1)−N(1)	1.416(4)	B(1)−O(1)	1.376(4)	B(1)−N(2)	1.475(4)	O(1)−C(11)	1.401(3)
N(1)−C(4)	1.515(4)	N(1)−Si(1)	1.802(3)	N(2)−N(3)	1.220(4)	N(3)−N(4)	1.129(4)
N(1)−B(1)−N(2)	114.3(2)	N(1)−B(1)−O(1)	125.1(3)	N(2)−B(1)−O(1)	120.6(2)	B(1)−O(1)−C(11)	121.3(2)
B(1)−N(1)−C(4)	124.3(2)	B(1)−N(1)−Si(1)	115.1(2)	Si(1)−N(1)−C(4)	120.6(2)	B(1)−N(2)−N(3)	128.9(3)
N(2)−N(3)−N(4)	171.5(3)						

Table 2. Crystallographic Data for the Compounds 18, 22, and 26

	18	**22**	**26**
empirical formula	$C_{36}H_{60}B_2N_2O_2$	$C_{32}H_{68}B_2N_2O_2$	$C_{21}H_{39}BN_4OSi$
fw	574.48	534.50	402.46
temperature (K)	153(2)	203(2)	203(2)
wavelength (Å)	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a (Å)	9.040(2)	11.2304(9)	12.651(6)
b (Å)	11.653(2)	25.997(6)	11.653(4)
c (Å)	16.955(4)	11.456(2)	16.858(13)
α (deg)	90	90	90
β (deg)	99.42(2)	97.171(11)	91.11(4)
γ (deg)	90	90	90
V (Å^3)	1762.0(6)	3318.5(9)	2485(2)
Z	2	4	4
density$_{calcd}$ (Mg m^{-3})	1.083	1.070	1.076
abs coeff (mm^{-1})	0.065	0.064	0.112
F(000)	632	1200	880
cryst size (mm^3)	0.70 × 0.60 × 0.40	0.80 × 0.70 × 0.40	0.90 × 0.80 × 0.80
θ range (deg)	3.52−25.12	3.59−25.02	3.67−25.06
limiting indices	$-10 \le h \le 10$	$-13 \le h \le 13$	$-15 \le h \le 15$
	$-13 \le k \le 13$	$-14 \le k \le 30$	$-13 \le k \le 13$
	$-20 \le l \le 20$	$-13 \le l \le 13$	$-19 \le l \le 20$
no. of reflns collected	5734	9601	11 136
no of ind reflns	3138	5834	4375
R_{int}	0.0372	0.0309	0.0715
refinement method		full-matrix-least squares on F^2	
no. of data/restraints/params	3133/0/199	5818/0/365	4369/0/265
goodness-of-fit on F^2	1.037	1.056	1.105
final R indices [$I>2\sigma(I)$]	R1=0.0459	R1=0.0500	R1=0.0679
	wR2=0.1094	wR2=0.1232	wR2=0.1878
R indices (all data)	R1=0.0622	R1=0.0644	R1=0.0761
	wR2=0.1236	wR2=0.1420	wR2=0.2089
largest diff peak/hole [e nm^{-3}]	212/−210	269/−184	463/−296

respectively, was solved in 100 mL of hexane. An equimolar amount of butyllithium was added to this solution, which was then refluxed for 3 h. A solution of 0.1 mol of boron trifluoride diethyl etherate (14.2 g) in 100 mL of diethyl ether was added dropwise. The reaction mixture was stirred for another 2 h. The solvent was removed at reduced pressure, and the residue was separated from the lithium fluoride by sublimation in vacuo. The crude product was purified by a second sublimation in vacuo.

Bis(2,6-di-*tert*-butylphenoxy)(fluoro)borane (5): colorless solid, sublp 90 °C (bath temperature)/0.01 Torr, mp 151 °C. Yield: 16.7 g (76%, reaction ratio taken into account). Anal. Calcd for $C_{28}H_{42}BFO_2$ (440.45 g/mol): C, 76.34; H, 9.71. Found: C, 76.10; H, 9.71. MS (EI, 70 eV): *m/e* (rel intensity) 440 (45) [M$^+$], 425 (10) [M$^+$ − Me], 219 (100) [M$^+$ − ^{t}Bu$_2$PhO, −Me, −H]. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.27 (AB_2, 4H, 3/5), 7.02 (AB_2, 2H, 4), 1.45 (s, 36H, CMe_3). ^{13}C NMR ($CDCl_3$, 25 °C): δ 149.6 (d, 1, $^3J_{CF}$ = 2.5 Hz), 141.3 (2/6), 126.2 (3/5), 123.2 (4), 35.8 (*C*Me$_3$), 32.1 (d, C*Me*$_3$, $^6J_{CF}$ = 1.3 Hz). ^{11}B NMR ($CDCl_3$, 25 °C): δ 14.0. ^{19}F NMR ($CDCl_3$, 25 °C): δ 55.4.

Bis(1,1-di-*tert*-butyl-2,2-dimethylpropoxy)(fluoro)borane (6): colorless solid, sublp 130 °C (bath temperature)/0.01 Torr, mp 206 °C. Yield: 10.1 g (47%, reaction ratio taken into account). Anal. Calcd for $C_{26}H_{54}BFO_2$ (428.52 g/mol): C, 72.88; H, 12.70. Found: C, 72.67; H, 12.80. MS (EI, 70 eV): *m/e* (rel intensity) 371 (5) [M$^+$ − CMe_3], 57 (100) [CMe_3^+]. ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.34 (s, 54H, CMe_3). ^{13}C NMR ($CDCl_3$, 25 °C): δ 93.7 (d, *C*CMe_3, $^3J_{CF}$ = 1.2 Hz), 45.8 (C*C*Me$_3$), 32.9 (CC*Me*$_3$). ^{11}B NMR ($CDCl_3$, 25 °C): δ 11.5. ^{19}F NMR ($CDCl_3$, 25 °C): δ 66.1.

Preparation of the Amino(halo)(organyloxy)boranes 7 and 9−16. A 0.1 mol sample of the relevant amine (**7**, **12**,

13, **16**: 7.3 g of *tert*-butylamine; **9**, **14**: 17.7 g of 2,6-diisopropylaniline; **10**: 13.5 g of 2,4,6-trimethylaniline; **11**: 26.1 g of 2,4,6-tri-*tert*-butylaniline; **15**: 5.9 g of isopropylamine) was solved in 100 mL of hexane. An equimolar amount of butyllithium was added to these solutions, which were then refluxed for 3 h. After cooling to −78 °C a solution of 0.1 mol of the relevant dihalogeno-oxyborane (**7**, **9**−**11**: 28.7 g of **1**; **12**: 32.7 g of **2**; **13**, **14**: 25.4 g of **3**; **15**, **16**: 24.8 g of **4**) in 100 mL hexane was added dropwise. The reaction mixture was stirred for another 2 h at low temperature and then allowed to warm. The solvent was removed at reduced pressure and the residue separated from the lithium halide by distillation (**7**, **10**, **12**, **13**, **15**, **16**) or sublimation (**9**, **11**) in vacuo. This process was then repeated to purify the crude product. **10** and **14** crystallized after the distillation.

(*tert*-Butylamino)(2,6-di-*tert*-butylphenoxy)(chloro)borane (7): colorless liquid, bp 110 °C/0.01 Torr. Yield: 18.4 g (57%). Anal. Calcd for $C_{18}H_{31}BClNO$ (323.78 g/mol): C, 66.77; H, 9.67; N, 4.33. Found: C, 66.67; H, 9.75; N, 4.03. MS (EI, 70 eV): *m*/*e* (rel intensity) 323 (10) [M^+], 308 (15) [M^+ − Me], 57 (100) [CMe_3^+]. There are two isomers of the compound at room temperature due to the inhibited rotation around the B−N bond (ratio **7a**/**7b** ca. 5:4); the rotational barrier is eliminated at 80 °C. ^{1}H NMR (C_6D_6, 25 °C): δ 7.2 (AB_2, 2H, 3/5/**7a** and **7b**), 6.9 (AB_2, 1H, 4/**7a** and **7b**), 3.24 (br, 1H, NH/**7a**), 3.04 (br, 1H, NH/**7b**), 1.48 (s, 18H, $CCMe_3$/**7a**), 1.46 (s, 18H, $CCMe_3$/**7b**), 1.20 (s, 9H, $NCMe_3$/**7a**), 1.08 (s, 9H, $NCMe_3$/**7b**); (C_6D_6, 80 °C) δ 7.2 (AB_2, 2H, 3/5), 6.9 (AB_2, 1H, 4), 3.0−3.2 (br, 1H, NH), 1.45 (s, 18H, $CCMe_3$), 1.16 (br, 9H, $NCMe_3$). ^{13}C NMR (C_6D_6, 25 °C): δ 153.9 (1/**7a**), 151.7 (1/**7b**), 141.4 (2/6/**7b**), 140.9 (2/6/**7a**), 126.5 (3/5/**7b**), 126.1 (3/5/**7a**), 123.6 (4/**7b**), 123.5 (4/**7a**), 50.4 ($NCMe_3$/**7a**), 49.2 ($NCMe_3$/**7b**), 35.7 ($CCMe_3$/**7a**), 35.6 ($CCMe_3$/**7b**), 32.3 ($NCMe_3$/**7a**), 31.9 ($CCMe_3$/**7b**), 31.8 ($CCMe_3$/**7a**), 31.6 ($NCMe_3$/**7b**). ^{11}B NMR (C_6D_6, 25 °C): δ 25.1.

(2,6-Di-*tert*-butylphenoxy)(chloro)(2,6-diisopropylphenylamino)borane (9): colorless solid, sublp 175 °C (bath temperature)/0.01 Torr, mp 114 °C. Yield: 25.2 g (59%). Anal. Calcd for $C_{26}H_{39}BClNO$ (427.86 g/mol): C, 72.99; H, 9.19; N, 3.27. Found: C, 72.42; H, 9.35; N, 3.40. MS (EI, 70 eV): *m*/*e* (rel intensity) 427 (50) [M^+], 57 (100) [CMe_3^+]. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.28 (AB_2, 2H, 3/5), 7.2 (AB_2, 3H, 9−11), 7.02 (AB_2, 1H, 4), 4.89 (br, 1H, NH), 3.53 (sep, 2H, C*H*Me$_2$, $^3J_{HH}$ = 6.9 Hz), 1.49 (s, 18H, CMe_3), 1.20 (d, 12H, CH*Me*$_2$, $^3J_{HH}$ = 6.9 Hz). ^{13}C NMR ($CDCl_3$, 25 °C): δ 151.9 (1), 146.2 (8/12), 141.0 (2/6), 134.0 (7), 127.0 (10), 126.0 (3/5), 123.3 (9/11), 123.2 (4), 35.5 (*C*Me$_3$), 31.8 (C*Me*$_3$), 28.2 (*C*HMe$_2$), 23.7 (CH*Me*$_2$). ^{11}B NMR ($CDCl_3$, 25 °C): δ 26.1.

(2,6-Di-*tert*-butylphenoxy)(chloro)(2,4,6-trimethylphenylamino)borane (10): colorless solid, bp 190 °C (bath temperature)/0.01 Torr, mp 113 °C. Yield: 30.7 g (80%). Anal. Calcd for $C_{23}H_{33}BClNO$ (385.78 g/mol): C, 71.61; H, 8.62; N, 3.63. Found: C, 71.59; H, 8.64; N, 3.62. MS (EI, 70 eV): *m*/*e* (rel intensity) 385 (55) [M^+], 57 (100) [CMe_3^+]. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.3 (AB_2, 2H, 3/5), 7.0−7.1 (AB_2, 1H, 4), 6.91 (s, 2H, 9/11), 4.85 (s, 1H, NH), 2.31 (s, 6H, 8/12), 2.28 (s, 3H, 10), 1.50 (s, 18H, CMe_3). ^{13}C NMR ($CDCl_3$, 25 °C): δ 151.8 (1), 141.0 (2/6), 135.3 (10), 135.0 (8/12), 134.7 (7), 129.0 (9/11), 125.9 (3/5), 123.1 (4), 35.5 (*C*Me$_3$), 31.8 (C*Me*$_3$), 20.8 (C10*Me*), 19.4 (C8/12*Me*). ^{11}B NMR ($CDCl_3$, 25 °C): δ 25.8.

(2,4,6-Tri-*tert*-butylphenylamino)(2,6-di-*tert*-butylphenoxy)(chloro)borane (11): yellow solid, sublp 190 °C (bath temperature)/0.01 Torr, mp 168 °C. Yield: 22.6 g (44%). Anal. Calcd for $C_{32}H_{51}BClNO$ (512.02 g/mol): C, 75.07; H, 10.04; N, 2.74. Found: C, 74.32; H, 9.85; N, 2.72. MS (EI, 70 eV): *m*/*e* (rel intensity) 510 (60) [$C_{32}H_{51}{}^{11}B^{35}ClNO^+$−H], 191 (100) [$^tBu_3C_6H_3NH_2^+$−Me]; (FI): 511 (100) [$C_{32}H_{51}{}^{11}B^{35}ClNO$; M^+]. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.38 (s, 2H, 9/11), 7.27 (AB_2, 2H, 3/5), 7.00 (AB_2, 1H, 4), 5.09 (br, 1H, NH), 1.54 (s, 18H, 2/6CMe_3 or 8/12CMe_3), 1.50 (s, 18H, 2/6CMe_3 or 8/12CMe_3), 1.31 (s, 9H, 10CMe_3). ^{13}C NMR ($CDCl_3$, 25 °C): δ 151.8 (1), 147.9 (8/12), 147.4 (10), 141.4 (2/6), 134.3 (7), 126.1 (3/5), 123.1 (9/11), 122.9 (4), 37.2 (8/12*C*Me$_3$), 35.9 (2/6*C*Me$_3$), 34.7 (10*C*Me$_3$), 32.9 (2/6C*Me*$_3$ or 8/12C*Me*$_3$), 32.4 (2/6C*Me*$_3$ or 8/12C*Me*$_3$), 31.4 (10C*Me*$_3$). ^{11}B NMR ($CDCl_3$, 25 °C): δ 25.6.

(*tert*-Butylamino)(chloro)(2,6-diphenylphenoxy)borane (12): colorless liquid, bp 200 °C (bath temperature)/0.01 Torr. Yield: 23.4 g (64%). Anal. Calcd for $C_{22}H_{23}BClNO$ (363.69 g/mol): C, 72.66; H, 6.37; N, 3.84. Found: C, 72.52; H, 6.21; N, 3.97. MS (EI, 70 eV): *m*/*e* (rel intensity) 363 (5) [M^+], 348 (15) [M^+ − Me], 246 (100) [$(C6H5)_2C_6H_3OH^+$]. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.2−7.6 (m, 13H, 3−5 and 8−12), 3.12 (br, 1H, NH), 1.05 (s, 9H, CMe_3). ^{13}C NMR ($CDCl_3$, 25 °C): δ 148.7 (1), 138.5 (2/6 or 7), 134.8 (2/6 or 7), 130.0 (3/5 or 10), 129.7 (8/12 or 9/11), 128.0 (8/12 or 9/11), 127.0 (3/5 or 10), 123.8 (4), 49.6 (*C*Me$_3$), 31.3 (C*Me*$_3$). ^{11}B NMR ($CDCl_3$, 25 °C): δ 23.5.

(*tert*-Butylamino)(2,6-di-*tert*-butylphenoxy)(fluoro)borane (13): colorless liquid, bp 80 °C/0.01 Torr. Yield: 16.2 g (53%). Anal. Calcd for $C_{18}H_{31}BFNO$ (307.26 g/mol): C, 70.35; H, 10.19. Found: C, 70.40; H, 9.96. MS (EI, 70 eV): *m*/*e* (rel intensity) 307 (10) [M^+], 292 (25) [M^+ − Me], 57 (100) [CMe_3^+]. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.32 (AB_2, 2H, 3/5), 7.05 (AB_2, 1H, 4), 2.64 (d, 1H, NH, $^3J_{HF}$ = 17.8 Hz), 1.48 (s, 18H, $CCMe_3$), 1.29 (s, 9H, $NCMe_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 150.9 (d, 1, $^3J_{CF}$ = 5.0 Hz), 141.3 (2/6), 125.7 (3/5), 122.8 (4), 48.3 (d, N*C*Me$_3$, $^3J_{CF}$ = 2.4 Hz), 35.2 (C*C*Me$_3$), 31.9 (d, NC*Me*$_3$, $^4J_{CF}$ = 2.4 Hz), 31.3 (CC*Me*$_3$). ^{11}B NMR ($CDCl_3$, 25 °C): δ 18.9. ^{19}F NMR ($CDCl_3$, 25 °C): δ 37.7.

(2,6-Di-*tert*-butylphenoxy)(fluoro)(2,6-diisopropylphenylamino)borane (14): colorless solid, bp 160 °C/0.01 Torr, mp 89 °C. Yield: 34.2 g (83%). Anal. Calcd for $C_{26}H_{39}BFNO$ (411.41 g/mol): C, 75.89; H, 9.57. Found: C, 76.50; H, 9.84. MS (EI, 70 eV): *m*/*e* (rel intensity) 411 (100) [M^+]. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.28 (AB_2, 2H, 3/5), 7.1 (AB_2, 3H, 9−11), 7.02 (AB_2, 1H, 4), 4.30 (d, 1H, NH, $^3J_{HF}$ = 15.4 Hz), 3.50 (sep, 2H, C*H*Me$_2$, $^3J_{HH}$ = 6.9 Hz), 1.47 (s, 18H, CMe_3), 1.20 (d, 12H, CH*Me*$_2$, $^3J_{HH}$ = 6.9 Hz). ^{13}C NMR ($CDCl_3$, 25 °C): δ 150.6 (d, 1, $^3J_{CF}$ = 3.7 Hz), 145.0 (8/12), 141.2 (2/6), 133.4 (7), 126.1 (10), 125.8 (3/5), 123.3 (9/11), 123.2 (4), 35.2 (*C*Me$_3$), 31.3 (C*Me*$_3$), 28.1 (*C*HMe$_2$), 23.8 (CH*Me*$_2$). ^{11}B NMR ($CDCl_3$, 25 °C): δ 18.3. ^{19}F NMR ($CDCl_3$, 25 °C): δ 37.6.

(1,1-Di-*tert*-butyl-2,2-dimethylpropoxy)(fluoro)(isopropylamino)borane (15): colorless liquid, bp 71 °C/0.01 Torr. Yield: 16.6 g (58%). Anal. Calcd for $C_{16}H_{35}BFNO$ (287.27 g/mol): C, 66.90; H, 12.28; N, 4.88. Found: C, 67.56; H, 12.18; N, 4.92. MS (EI, 70 eV): *m*/*e* (rel intensity) 230 (10) [M^+ − CMe_3], 174 (70) [M^+ − CMe_3, −H_2C=Me_2], 57 (100) [CMe_3^+]. ^{1}H NMR ($CDCl_3$, 25 °C): δ 3.5 (br, 1H, C*H*Me$_2$), 3.3 (br, 1H, C*H*Me$_2$), 2.1 (br, 1H, NH), 1.31 (br, 27H, CMe_3), 1.06 (d, 6H, CH*Me*$_2$, $^3J_{HH}$ = 6.9 Hz); at 60 °C only one peak for C*H*Me$_2$: 3.4 (br, 2H). ^{13}C NMR ($CDCl_3$, 25 °C): δ 94.2 (*C*CMe$_3$), 93.6 (*C*CMe$_3$), 45.8 (*C*HMe$_2$), 41.5 (br, *C*CMe$_3$), 32.9 (br, CC*Me*$_3$), 26.4 (CH*Me*$_2$); at 60 °C only one peak for *C*CMe$_3$: 94 (br). ^{11}B NMR ($CDCl_3$, 25 °C): δ 17.1. ^{19}F NMR ($CDCl_3$, 25 °C): δ 42.6, 44.5; ($CDCl_3$, 60 °C) δ 43.8.

(*tert*-Butylamino)(1,1-di-*tert*-butyl-2,2-dimethylpropoxy)(fluoro)borane (16): colorless liquid, bp 68 °C/0.01 Torr. Yield: 21.6 g (72%). Anal. Calcd for $C_{17}H_{37}BFNO$ (301.29 g/mol): C, 67.77; H, 12.38; N, 4.65. Found: C, 67.75; H, 12.32; N, 5.41. MS (EI, 70 eV): *m*/*e* (rel intensity) 244 (2) [M^+ −CMe_3], 188 (10) [M^+ − CMe_3, −H_2C=CMe_2], 57 (100) [CMe_3^+]. ^{1}H NMR ($CDCl_3$, 25 °C): δ 2.43 (d, 1H, NH, $^3J_{HF}$ = 18.0 Hz), 1.29 (s, 27H, $CCMe_3$), 1.19 (d, 9H, $NCMe_3$, $^5J_{HF}$ = 1.0 Hz). ^{13}C NMR ($CDCl_3$, 25 °C): δ 93.6 (*C*CMe$_3$), 47.3 (d, N*C*Me$_3$, $^3J_{CF}$ = 2.6 Hz), 45.8 (C*C*Me$_3$), 32.9 (CC*Me*$_3$), 32.2 (d, NC*Me*$_3$, $^4J_{CF}$ = 2.6 Hz). ^{11}B NMR ($CDCl_3$, 25 °C): δ 17.2. ^{19}F NMR ($CDCl_3$, 25 °C): δ 50.5.

Preparation of the Amino(chloro)(phenoxy)borane 8. A 0.1 mol sample of the dichloroborane **1** was mixed at room temperature with 0.1 mol of 1,1,1,3,3,3-hexamethyldisilazane (16.1 g) without a solvent. The mixture was refluxed for 2 h.

The chlorosilane formed was removed at reduced pressure, and the residue was twice distilled in vacuo.

(2,6-Di-*tert*-butylphenoxy)(chloro)(trimethylsilylamino)borane (8): colorless liquid, bp 80 °C/0.01 Torr. Yield: 23.2 g (68%). Anal. Calcd for $C_{17}H_{31}BClNOSi$ (339.79 g/mol): C, 60.09; H, 9.20; N, 4.12. Found: C, 60.55; H, 9.00; N, 4.65. MS (EI, 70 eV): *m/e* (rel intensity) 339 (60) [M^+], 324 (10) [$M^+ - Me$], 236 (100) [$M^+ - Me, -NHSiMe_3$]. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.26 (AB_2, 2H, 3/5), 7.02 (AB_2, 1H, 4), 2.6 (br, 1H, NH), 1.41 (s, 18H, CMe_3), 0.20 (s, 9H, $SiMe_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 151.7 (1), 141.1 (2/6), 126.0 (3/5), 123.2 (4), 35.4 (CMe_3), 31.6 (CMe_3), 1.0 ($SiMe_3$). ^{11}B NMR ($CDCl_3$, 25 °C): δ 27.2. ^{29}Si NMR ($CDCl_3$, 25 °C): δ 7.3.

Preparation of the Amino(fluoro)(alkoxy)borane 17. A 0.1 mol sample of 1,1,1,3,3,3-hexamethyldisilazane (16.1 g, without a solvent) was added at room temperature to a freshly prepared solution of 0.1 mol of the difluoroborane **4** in diethyl ether. The mixture was stirred for 6 h at 25 °C, after which the ether and the fluorosilane formed were removed at reduced pressure. The residue was twice distilled in vacuo.

(1,1-Di-*tert*-butyl-2,2-dimethylpropoxy)(fluoro)(trimethylsilylamino)borane (17): colorless liquid, bp 75 °C/0.01 Torr. Yield: 12.8 g (40%). Anal. Calcd for $C_{16}H_{37}BFNOSi$ (317.37 g/mol): C, 60.55; H, 11.75; N, 4.41. Found: C, 60.97; H, 12.01; N, 4.72. MS (EI, 70 eV): *m/e* (rel intensity) 260 (10) [$M^+ - CMe_3$], 204 (65) [$M^+ - CMe_3, -H_2C{=}CMe_2$], 57 (100) [$CMe_3^+$]; (CI, isobutene) 318 ($M^+ + 1$). ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.8 (br, 1H, NH), 1.29 (s, 27H, CMe_3), 0.10 (d, 9H, $SiMe_3$, $^5J_{HF} = 0.9$ Hz). ^{13}C NMR ($CDCl_3$, 25 °C): δ 94.0 (d, $CCMe_3$, $^3J_{CF} = 1.2$ Hz), 45.7 (d, $CCMe_3$, $^4J_{CF} = 0.3$ Hz), 32.8 ($CCMe_3$), 1.0 (d, $SiMe_3$, $^4J_{CF} = 1.3$ Hz). ^{11}B NMR ($CDCl_3$, 25 °C): δ 18.0. ^{19}F NMR ($CDCl_3$, 25 °C): δ 54.5. ^{29}Si NMR ($CDCl_3$, 25 °C): δ 4.6.

Preparation of the Diazadiboretidines 18−23. A 0.1 mol sample of *tert*-butyllithium (66.7 mL) was added dropwise to a solution of 0.1 mol of the relevant amino(halo)(organyloxy)borane (**18**: 32.3 g of **7** or 30.7 g of **13**; **19**: 34.0 g of **8**; **20**: 42.8 g of **9** or 41.1 g of **14**; **21**: 38.6 g of **10**; **22**: 28.7 g of **15**; **23**: 31.7 g of **17**) in 100 mL of hexane at −78 °C. The reaction mixtures were allowed to warm to room temperature, and stirring was continued until the temperature reached 0 °C. When **13** or **14** was used as the starting material, the reaction mixture was then refluxed for 2 h. The procedure then varied for the different compounds. **18**: After 24 h a layer of colorless crystals formed on top of the lithium halide. With a sufficiently large-pored filter the crystals could be separated from the powdery salt. They were washed twice with hexane, and the remaining solvent was removed in vacuo. **19−21**: The solvent was removed at reduced pressure, and the residue was separated from the lithium halide by sublimation in vacuo. The crude product was purified by a second sublimation. **22**, **23**: The lithium fluoride was filtered off from the reaction solution, and the solvent was then removed in vacuo. The residue was recrystallized from hexane (**22**) or toluene (**23**).

1,3-Di-*tert*-butyl-2,4-bis(2,6-di-*tert*-butylphenoxy)-1,3-diaza-2,4-diboretidine (18): colorless solid, mp 290 °C. Yield: 17.8 g (62%). Anal. Calcd for $C_{36}H_{60}B_2N_2O_2$ (574.63 g/mol): C, 75.24; H, 10.52; N, 4.88. Found: C, 74.47; H, 10.64; N, 5.00. MS (EI, 70 eV): *m/e* (rel intensity) 574 (5) [M^+], 559 (100) [$M^+ - Me$]. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.20 (AB_2, 4H, 3/5), 6.93 (AB_2, 2H, 4), 1.45 (s, 36H, $CCMe_3$), 0.85 (s, 18H, $NCMe_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 154.2 (1), 140.8 (2/6), 125.4 (3/5), 122.5 (4), 48.7 ($NCMe_3$), 35.6 ($CCMe_3$), 32.6 ($NCMe_3$), 31.2 ($CCMe_3$). ^{11}B NMR ($CDCl_3$, 25 °C): δ 25.0.

1,3-Bis(trimethylsilyl)-2,4-bis(2,6-di-*tert*-butylphenoxy)-1,3-diaza-2,4-diboretidine (19): colorless solid, sublp 190 °C/0.01 Torr, mp 276 °C. Yield: 7.0 g (23%). Anal. Calcd for $C_{34}H_{60}B_2N_2O_2Si_2$ (606.65 g/mol): C, 67.32; H, 9.97; N, 4.62. Found: C, 66.84; H, 9.43; N, 5.16. MS (EI, 70 eV): *m/e* (rel intensity) 606 (1) [M^+], 591 (1) [$M^+ - Me$], 401 (100) [$M^+ - {}^tBu_2C_6H_3O$]. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.24 (AB_2, 4H, 3/5), 6.98 (AB_2, 2H, 4), 1.41 (s, 36H, CMe_3), −0.28 (s, 18H, $SiMe_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 152.7 (1), 141.3 (2/6), 125.7 (3/5), 123.2 (4), 35.5 (CMe_3), 31.2 (CMe_3), 1.5 ($SiMe_3$). ^{11}B NMR ($CDCl_3$, 25 °C): δ 26.3. ^{29}Si NMR ($CDCl_3$, 25 °C): δ −4.0.

2,4-Bis(2,6-di-*tert*-butylphenoxy)-1,3-bis(2,6-diisopropylphenyl)-1,3-diaza-2,4-diboretidine (20): colorless solid, sublp 250 °C/0.01 Torr, mp 255 °C. Yield: 5.4 g (14%). Anal. Calcd for $C_{52}H_{76}B_2N_2O_2$ (782.80 g/mol): C, 79.79; H, 9.79; N, 3.58. Found: C, 79.19; H, 9.63; N, 3.58. MS (EI, 70 eV): *m/e* (rel intensity) 782 (100) [M^+], 726 (20) [$M^+ - CMe_3$], 57 (100) [CMe_3^+]. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.13 (AB_2, 4H, 3/5), 7.0 (AB_2, 6H, 9−11), 6.86 (AB_2, 2H, 4), 3.25 (sep, 4H, $CHMe_2$, $^3J_{HH} = 6.7$ Hz), 1.17 (d, 12H, $CHMe_2$, $^3J_{HH} = 6.7$ Hz), 1.16 (s, 36H, CMe_3), 0.65 (d, 12H, $CHMe_2$, $^3J_{HH} = 6.7$ Hz). ^{13}C NMR ($CDCl_3$, 25 °C): δ 149.8 (1), 143.9 (8/12), 140.3 (2/6), 135.7 (7), 127.8 (3/5), 124.3 (10), 124.2 (9/11), 123.1 (4), 36.1 (CMe_3), 32.1 (CMe_3), 28.0 ($CHMe_2$), 25.6 ($CHMe_2$), 24.2 ($CHMe_2$). ^{11}B NMR ($CDCl_3$, 25 °C): δ 25.0.

2,4-Bis(2,6-di-*tert*-butylphenoxy)-1,3-bis(2,4,6-trimethylphenyl)-1,3-diaza-2,4-diboretidine (21): colorless solid, sublp 240 °C/0.01 Torr, mp 200 °C. Yield: 18.5 g (53%). Anal. Calcd for $C_{46}H_{64}B_2N_2O_2$ (698.64 g/mol): C, 79.08; H, 9.23; N, 4.01. Found: C, 79.24; H, 9.27; N, 4.07. MS (EI, 70 eV): *m/e* (rel intensity) 698.5 (100) [M^+], 641.4 (10) [$M^+ - CMe_3$]. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.1 (AB_2, 4H, 3/5), 6.9 (AB_2, 2H, 4), 6.62 (s, 4H, 9/11), 2.16 (s, 6H, 10), 1.88 (s, 12H, 8/12), 1.13 (s, 36H, CMe_3). ^{13}C NMR ($CDCl_3$, 25 °C): δ 150.4 (1), 141.1 (2/6), 135.5 (10), 133.4 (8/12), 132.4 (7), 128.4 (9/11), 126.0 (3/5), 122.8 (4), 35.6 (CMe_3), 31.5 (CMe_3), 20.6 (C10*Me*), 19.4 (C8/12*Me*). ^{11}B NMR ($CDCl_3$, 25 °C): δ 25.6.

2,4-Bis(1,1-di-*tert*-butyl-2,2-dimethylpropoxy)-1,3-diisopropyl-1,3-diaza-2,4-diboretidine (22): colorless solid, mp 158 °C (decomp). Yield: 6.0 g (22%). Anal. Calcd for $C_{32}H_{68}B_2N_2O_2$ (534.52 g/mol): C, 71.91; H, 12.82; N, 5.24. Found: C, 71.23; H, 12.20; N, 4.74. MS (EI, 70 eV): *m/e* (rel intensity) 534 (1) [M^+], 421 (10) [$M^+ - CMe_3, -Me_2C{=}CH_2$], 405 (15) [$M^+ - 2CMe_3, -Me$], 57 (100) [$CMe_3^+$]; (FI) 534 (30) [$M^+$], 478 (100) [$M^+ - Me_2C{=}CH_2$], 421 (20) [$M^+ - CMe_3, -Me_2C{=}CH_2$]. ^{1}H NMR ($CDCl_3$, 25 °C): δ 3.69 (sep, 2H, $CHMe_2$, $^3J_{HH} = 6.9$ Hz), 1.39 (s, 54H, CMe_3), 1.14 (d, 12H, $CHMe_2$, $^3J_{HH} = 6.9$ Hz). ^{13}C NMR ($CDCl_3$, 25 °C): δ 97.7 ($CCMe_3$), 45.8($CCMe_3$), 41.2 ($CHMe_2$), 33.4 ($CCMe_3$), 24.4 ($CHMe_2$). ^{11}B NMR ($CDCl_3$, 25 °C): δ 24.2.

2,4-Bis(1,1-di-*tert*-butyl-2,2-dimethylpropoxy)-1,3-bis(trimethylsilyl)-1,3-diaza-2,4-diboretidine (23): colorless solid, mp 130 °C (decomp). Yield: 26.5 g (90%). Anal. Calcd for $C_{32}H_{72}B_2N_2O_2Si_2$ (594.72 g/mol): C, 64.63; H, 12.20; N, 4.71. Found: C, 63.78; H, 11.29; N, 5.94. MS (EI, 70 eV): *m/e* (rel intensity) 537 (10) [$M^+ - CMe_3$], 57 (100) [CMe_3^+]; (FI) 594 (100) [M^+]. ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.37 (s, 54H, CMe_3), 0.15 (s, 18H, $SiMe_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 101.4 ($CCMe_3$), 46.3 ($CCMe_3$), 33.8 ($CCMe_3$), 3.4 ($SiMe_3$). ^{11}B NMR ($CDCl_3$, 25 °C): δ 25.4. ^{29}Si NMR ($CDCl_3$, 25 °C): δ −7.6.

Preparation of the Diazadiboretidine 24. See **22**; instead of recrystallization the residue was purified by sublimation in vacuo. The isobutene formed is collected in a cold trap with 1 mL of $CDCl_3$. The ^{13}C NMR spectrum of this solution displays two peaks (δ 111, 142 ppm) assigned to the sp^2-hybridized carbon atoms of isobutene.

2,4-Bis(1-*tert*-butyl-2,2-dimethylpropoxy)-1,3-bis(trimethylsilyl)-1,3-diaza-2,4-diboretidine (24): colorless solid, sublp 160 °C/0.01 Torr, mp 135 °C. Yield: 8.7 g (36%). Anal. Calcd for $C_{24}H_{56}B_2N_2O_2Si_2$ (482.51 g/mol): C, 59.74; H, 11.70; N, 5.81. Found: C, 59.51; H, 11.26; N, 5.78. MS (EI, 70 eV): *m/e* (rel intensity) 482 (3) [M^+], 425 (10) [$M^+ - CMe_3$], 57 (100) [CMe_3^+]; (FI) 482 (100) [M^+]. ^{1}H NMR ($CDCl_3$, 25 °C): δ 3.63 (s, 2H, OCH), 1.02 (s, 36H, CMe_3), 0.14 (s, 18H, $SiMe_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 87.3 ($CCMe_3$), 37.6 ($CCMe_3$), 28.9 ($CCMe_3$), 3.1 ($SiMe_3$). ^{11}B NMR ($CDCl_3$, 25 °C): δ 25.6. ^{29}Si NMR ($CDCl_3$, 25 °C): δ −5.8.

Preparation of the Diborylamine 25. A solution of 0.05 mol of **7** (16.2 g) in 50 mL of hexane was cooled to −78 °C; to this solution was added first 0.1 mol of triethylborane (100 mL) and then 0.05 mol of *tert*-butyllithium (33.3 mL). The mixture was then allowed to warm to room temperature while stirring was continued. The solvent was removed at reduced pressure, and the residue was separated from the lithium chloride by distillation in vacuo. The crude product was purified by a second distillation.

***tert*-Butyl[2,6-di-*tert*-butylphenoxy(ethyl)boryl](diethylboryl)amine (25)**: yellow liquid, bp 160 °C/0.01 Torr. Yield: 10.4 g (54%). Anal. Calcd for $C_{24}H_{45}B_2NO$ (385.25 g/mol): C, 74.83; H, 11.77; N, 3.64. Found: C, 74.55; H, 11.53; N, 3.60. MS (EI, 70 eV): *m/e* (rel intensity) 385 (2) [M^+], 370 (5) [M^+ − Me], 356 (15) [M^+ − Et], 57 (100) [CMe_3^+]. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.2 (AB_2, 2H, 3/5), 6.9 (AB_2, 1H, 4), 1.48 (s, 9H, $NCMe_3$), 1.41 (s, 18H, $CCMe_3$), 1.22 (q, 6H, CH_2, $^3J_{HH}$ = 7.5 Hz), 0.98 (t, 9H, CH_2CH_3, $^3J_{HH}$ = 7.4 Hz). ^{13}C NMR ($CDCl_3$, 25 °C): δ 155.3 (1), 140.9 (2/6), 125.2 (3/5), 121.4 (4), 52.1 (N*C*Me$_3$), 35.8 (C*C*Me$_3$), 32.6 (NC*Me*$_3$), 31.7 (CC*Me*$_3$), 22.2 (B(*C*H$_2$CH$_3$)$_2$), 11.8 (B*C*H$_2$CH$_3$), 9.6 (BCH$_2$*C*H$_3$), 9.0 (B(CH$_2$*C*H$_3$)$_2$). ^{11}B NMR ($CDCl_3$, 25 °C): δ 74.1 (NBC_2), 30.1 (OB(N)C).

Preparation of the Azidoborane 26. A solution of 0.05 mol of **7** (16.2 g) in 50 mL of hexane was cooled to −78 °C; to this solution was added first 0.075 mol of trimethylsilyl azide (8.6 g) and then 0.055 mol of *tert*-butyllithium (36.7 mL). The mixture was then allowed to warm to room temperature while stirring was continued. The solvent was removed at reduced pressure, and the residue was separated from the lithium chloride by sublimation in vacuo. The crude product was purified by a second sublimation.

Azido(2,6-di-*tert*-butylphenoxy)[*tert*-butyl(trimethylsilyl)amino]borane (26): colorless solid, sublp 90 °C (bath temperature)/0.01 Torr, mp 93 °C. Yield: 12.7 g (63%). Anal. Calcd for $C_{21}H_{39}BN_4OSi$ (402.46 g/mol): C, 62.67; H, 9.77; N, 13.92. Found: C, 62.82; H, 9.54; N, 13.67. MS (EI, 70 eV): *m/e* (rel intensity) 402 (1) [M^+], 387 (10) [M^+ − Me], 359 (10) [M^+ − Me, $-N_2$], 303 (100) [M^+ − CMe_3, $-N_3$]. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.23 (AB_2, 2H, 3/5), 7.04 (AB_2, 1H, 4), 1.52 (s, 9H, $NCMe_3$), 1.43 (s, 18H, $CCMe_3$), 0.30 (s, 9H, $SiMe_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 152.3 (1), 142.0 (2/6), 125.9 (3/5), 123.8 (4), 54.5 (N*C*Me$_3$), 35.5 (C*C*Me$_3$), 34.1 (NC*Me*$_3$), 31.4 (CC*Me*$_3$), 6.6 ($SiMe_3$). ^{11}B NMR ($CDCl_3$, 25 °C): δ 21.7. ^{29}Si NMR ($CDCl_3$, 25 °C): δ 7.6. IR (in KBr): ν_{as} (N_3) 2139 cm^{-1}.

X-ray Structure Determinations for 18, 22, and 26. Data were collected on a Stoe-Siemens diffractometer with monochromated Mo Kα radiation (λ = 71.03 pm). The temperatures of the measurements are listed in Table 2. The structures were solved by direct methods using SHELXS-90.[24] All non-hydrogen atoms were refined anisotropically. For the hydrogen atoms the riding model was used. The structures were refined against F^2 with a weighting scheme of $w^{-1} = \sigma^2(F_o^2) + (g_1P)^2 + g^2P$, with $P = (F_o^2 + 2F_c^2)/3$ using SHELXL-93.[25] The R values are defined as $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{0.5}$. Figures 1−3 (hydrogen atoms omitted) show 50% probability displacement ellipsoids. Crystal data and structure refinement details are listed in Table 2.

Summary

The first B-2,6-disubstituted aryloxy(imino)boranes were detected as intermediates in the dehydrohalogenation of the corresponding amino(aryloxy)chloroboranes by ^{11}B NMR and addition reactions across the B≡N triple bond. The as yet undescribed B-organyloxy-substituted diazadiboretidines are the stable, final products formed by the dimerization of the organyloxy(imino)boranes.

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Supporting Information Available: Tables of crystal data, complete fractional coordinates and U values, bond lengths and angles, and anisotropic displacement parameters, and fully labeled figures of 50% anisotropic displacement parameters of the structures **18**, **22**, and **26**. This material is available free of charge via the Internet at http://pubs.acs.org.

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