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Chemical Oxidation of 1,3,2-Diazaboroles and 1,3,2-Diazaborolidines

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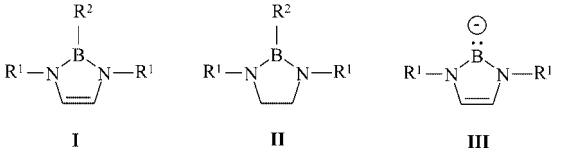
Oxidation of the 1,3,2-diazaborole *t*BuN^{a}CH=CHN^b(*t*Bu)-BBr(*N^a*–*B*) (**1h**) with $NO^+PF_6^-$ afforded the diazaborolium salts [*t*BuN^a=CH–CH=N^b(*t*Bu)BF_2(*N^a*–*B*)]$^+X^-$ (X = Br^-, Br_3^-, PF_6^-) (**3h**) as the result of different oxidation processes. The same product was obtained when the 1,3,2-diazaborolidine *t*BuN^aCH_2CH_2N^b(*t*Bu)BBr(*N^a*–*B*) (**2h**) was subjected to reaction with $NO^+PF_6^-$. In contrast to this, oxidation of **1h** and **2h** with $NO^+BF_4^-$ cleanly furnished [*t*BuN^{a}CH–CH=N^b(*t*Bu)-BFBr(*N^a*–*B*)]$^+BF_4^-$ (**6h**). Treatment of the 1,3,2-diazaboroles *t*BuN^{a}CH=CHN^b(*t*Bu)BR(*N^a*–*B*) [R = H (**1e**), CN (**1i**), C≡CH (**1j**)] with $NO^+PF_6^-$ under comparable conditions led to the borolium salts [*t*BuN^a=CH–CH=N^b(*t*Bu)BRF(*N^a*–*B*)]$^+PF_6^-$ [R = H (**3e**), CN (**3i**), C≡CH (**3j**)]. All the borolium salts investigated in this study were reversibly reduced by cyclic voltammetry. The novel products were characterized by elemental analyses and NMR spectra (^{1}H, ^{11}B, ^{13}C, ^{19}F, ^{31}P). The X-ray structure analysis of **3h** reveals two independent planar cations in the asymmetric unit, accompanied by one bromide and one tribromide ion.

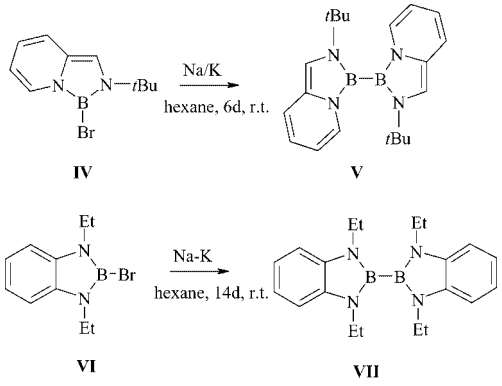
Introduction

The reactivity of the 1,3,2-diazaboroles **I** towards a broad range of nucleophiles has been investigated intensively and described in detail in the literature some years ago.[1] More recently, the redox chemistry of these compounds and of their saturated analogs, the 1,3,2-diazaborolidines **II** (Scheme 1), has been studied by cyclic voltammetry and He(I)-UV-photoelectron spectroscopy.[2]



Scheme 1. Diazaborole **I**, diazaborolidine **II** and boranide ion **III**.

The electrochemical reduction of diazaboroles to afford the boranide ion **III**, however, has never been observed. This is consistent with the results of their chemical reduction with sodium/potassium alloy, which also did not lead to anions of the type **III**. The latter would be analogous to Denk's silylene[3] or to the related germylene.[4] The alkali metal reduction of **IV**[5] and **VI**[6] afforded the diboranes(4) **V** and **VII**. Treatment of diazaborole **1h**, however, did not furnish the corresponding diborane(4) (Scheme 2).



Scheme 2. Chemical reduction of 1,3,2-diazaboroles **IV** and **VI**.

The electrochemical oxidation of *N*,*N*-di-*tert*-butyldiazaboroles **1a**–**i** by cyclic voltammetry displayed clean, but irreversible waves, whereby the oxidation potentials $E_{ox,1/2}$ vary strongly in dependence of the substitution pattern at the boron center (Table 1). Thus, the amino-substituted borole **1a** as well as the methoxy-substituted heterocycle **1c** were oxidized much easier than the cyano- or bromodiazaboroles, **1h** or **1i**, which was rationalized by the donor and acceptor abilities of the functional groups at the boron atom. The corresponding saturated 1,3,2-diazaborolidines with identical ligands at the boron atom exhibited the same trend, but in general they were less easy oxidized. This trend was confirmed by photoelectron spectroscopy of the heterocycles in the gas phase.[2]

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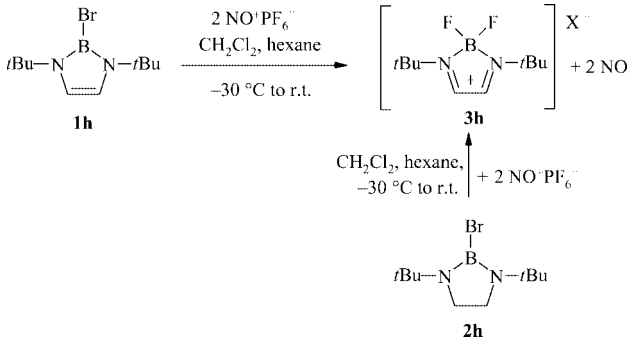
Table 1. Oxidation potentials of **1a**–**i** in CH_2Cl_2 vs. Fc/Fc$^+$.

1	a	b	c	d	e	f	g	h	i
R	NH_2	OMe	Me	NMe_2	H	SMe	$SnMe_3$	Br	CN
E_{ox} [mV]	–288	–58	124	158	310	354	396	576	752

Results and Discussion

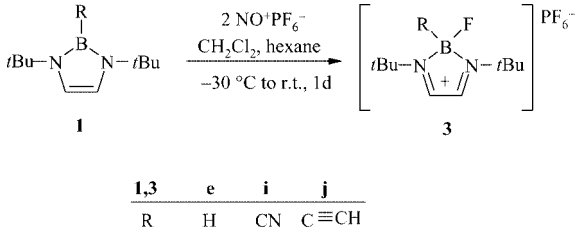
With respect to the irreversible electrochemical oxidation of diazaboroles, we were interested in the nature of the oxidation products and thus decided to oxidize these heterocycles chemically. The reaction of 1 equiv. of bromoborole **1h** with 2 equiv. of $NO^+PF_6^-$ in CH_2Cl_2/hexane led to the quantitative formation of the difluoroborolium salt **3h** as yellow crystals (Scheme 3). The counterion in the product, however, was not uniform. Obviously, the bromo ligand of **1h** was displaced by fluoride, which was released from a PF_6^- ion before, and serves now as a counterion in the salt in addition to the PF_6^- ion and the tribromide ion. The presence of a Br_3^- anion indicates that additional redox processes have taken place. It could be formed from Br^- by the oxidation with excessive $NO^+PF_6^-$. In contrast to other 1,3,2-diazaborolium salts with bromo or chloro substituents, **3h** was excellently soluble in dichloromethane and moderately soluble in toluene.



Scheme 3. Oxidation of the bromoborole **1h** and bromoborolidine **2h** with $NO^+PF_6^-$ (X = Br, Br_3, PF_6).

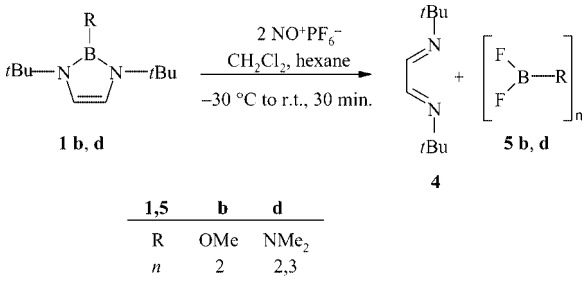
The reaction of the 1,3,2-diazaborolidine **2h** with $NO^+PF_6^-$ under the same conditions also led to the formation of product **3h** (Scheme 3). The employment of 4 equiv. of $NO^+PF_6^-$ did not lead to an improved yield. Instead 2 equiv. of the nitrosonium salt were recovered unaffected after the reaction.

Another situation was encountered when the 1,3,2-diazaborole was substituted by poor leaving groups, like the hydrido, ethynyl or cyano units. Here, only one fluoride atom was added to the boron center and borolium ions with two different ligands were formed. Thus, the reaction of the hydroborole **1e**, the cyanoborole **1i** or the ethynylborole **1j** with 2 equiv. of $NO^+PF_6^-$ afforded the intensely yellow (**3e**) or red borolium salts (**3i** and **3j**) in moderate to high yields (Scheme 4).



Scheme 4. Oxidation of diazaborole **1e**, **i**, **j** with $NO^+PF_6^-$.

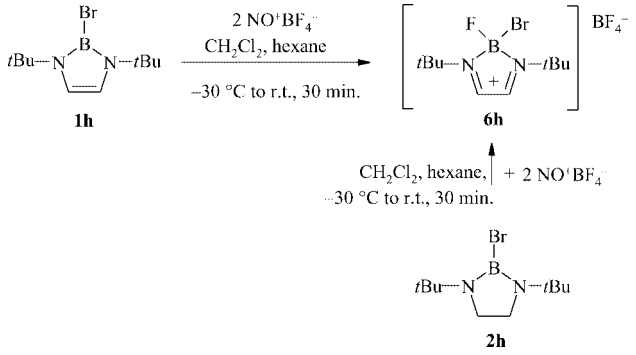
Here, the hexafluorophosphate was observed as the sole counterion. The formation of the different diazaborolium salts studied here requires a twofold electron transfer. Principally, this could lead to the liberation of 2 equiv. of NO. At the top of the reaction vessel, where the released gases came into contact with air, an acidic reaction at a moist indicator paper was observed (HNO_3). The oxidation of the diazaborolidine **2h** to **3h**, however, required the removal of four electrons. According to experimental evidence this is accomplished by only 2 equiv. of the nitrosonium salt. Obvioulsy, here NO^+ is reduced to a nitrogen species with an oxidation number smaller than +II (N_2?). The treatment of diazaboroles containing electron-donating substituents on the boron atom, like dimethylamino- or methoxy-functionalized derivatives **1d** and **1b** with $NO^+PF_6^-$, did not lead to the borolium salts. Here, a ring opening took place with the formation of *N*,*N*′-di-*tert*-butyldiazabutadiene (**4**), $[Me_2NBF_2]_2$ (**5d**) or $[MeOBF_2]_n$ (**5b**), which were identified by comparison of their ^1H and ^{11}B NMR spectra with those of authentic samples (Scheme 5).



Scheme 5. Oxidation of diazaboroles **1b**, **d** with $NO^+PF_6^-$.

The 1,3,2-diazaboroles **1c**, **1k** (R = Ph) with methyl or phenyl substituents at the boron center were reluctant towards oxidation with $NO^+PF_6^-$ despite the fact that the methyl-substituted diazaborole **1c** and its saturated analog were easily oxidized electrochemically. Even an excess of the oxidant and stirring in boiling toluene for hours did not lead to the oxidation of the heterocycle.

Some of these experiments were repeated with $NO^+BF_4^-$ and $AgPF_6$ With the hexafluorophosphate, the results of the reaction with $NO^+PF_6^-$ were reproduced. In contrast to this, the reaction of **1h** and **2h** with $NO^+BF_4^-$ led to the mixed borolium salt **6h** (Scheme 6). In addition to elemental analysis, the identity of **6h** was evidenced by ESI mass spectroscopy. The signal of the cation of **6h** (*m*/*z* = 356 [M$^+$]) was observed with the correct isotopic distribution.



Scheme 6. Reaction of **1**, **2h** with $NO^+BF_4^-$.

With $AgPF_6$ as an oxidation agent, side reactions were observed depending on the stoichiometry of both reactants. Equimolar amounts of bromoborole **1h** and $AgPF_6$ led to the formation of equal portions of *t*BuN^{a}CH=CHN^b(*t*Bu)-BF(N^a–*B*) (**1l**) and salt **3h**. The formation of the fluoroborole **1l** was avoided by the use of 2 equiv. of $AgPF_6$, and borolium salt **3h** was then isolated as the only product.

Spectra and Structural Data

The $^{11}B\{^1H\}$ NMR spectrum of **3h** displays several signals in the typical area for tetracoordinate boron ($\delta \approx$ 6 ppm), due to the various borolium salts present.[7] In the ^1H NMR spectrum the ring protons absorb as broad singlets at δ = 8.87 ppm. The NMR spectroscopic data of the other borolium salts **3e**,**i**,**j** and **6h** are similar. ESI mass spectra of all the different borolium salts were obtained, whereby the cations represent the base peak. The products of the reaction of 1,3,2-diazaboroles with electron-donating groups (**1b**,**d**) were identified by comparison of the ^1H and $^{11}B\{^1H\}$ NMR spectroscopic data with authentic samples. In both cases, the ^1H NMR spectrum displays two characteristic singlets at δ = 1.10 and 8.09 ppm for the free *N*,*N*′-di-*tert*-butyldiazabutadiene. In addition to that, in the ^1H NMR spectrum of the reaction of **1b** with $NO^+PF_6^-$, another singlet at δ = 1.24 ppm is present, which belongs to the boron-bound methoxy group of the difluoro(methoxy)-borane **5b**. The product of the reaction of **1d** with $NO^+PF_6^-$, the difluoro(dimethylamino)borane **5d**, shows in the ^1H NMR spectrum a singlet at δ = 1.36 ppm. In the $^{11}B\{^1H\}$ NMR spectrum, the signals for $[F_2BOMe]_n$ (n = 2,3) are observed at δ = 0.66 ppm and for $[F_2BNMe_2]_2$ at δ = 1.08 ppm, in agreement with the data of authentic samples.

X-ray Structural Analysis of 3h

Yellow single crystals of **3h** suitable for an X-ray diffraction study (Table 2) were grown from a dichloromethane/hexane (1:1) mixture. Two independent diazaborolium cations are in the asymmetric unit in addition to one bromide and one tribromide anion. There are no bonding contacts between the cations and anions. The tribromide ion is slightly bent [Br(3)–Br(2)–Br(4) 175.65(1)°] with bond lengths Br(2)–Br(3) of 2.5811(4) Å and Br(2)–Br(4) of 2.5325(4) Å. In the symmetric anion of $(Me_3NH)Br_3$ the Br–Br bond length amounts to 2.54 Å (Br–Br–Br 171°), whereas in the nonsymmetric anion of $(PBr_4)Br_3$ (Br–Br–Br 177.3°) the Br–Br bond lengths are 2.39(1) and 2.91(1) Å.[8]

As the bonding parameters of both cations do not differ significantly, only the ring constructed of the atoms B(1), N(1), N(2), C(1) and C(2) is discussed in detail (Figure 1). The structure features a planar five-membered heterocycle (sum of bond angles 539.9°) with a tetracoordinate boron atom. The bond lengths B(1)–F(1) [1.366(3) Å] and B(1)–F(2) [1.369(3) Å] are slightly shorter than the B–F contacts in the BF_4^- ion of $[\{Mes^*P{=}C(NMe_2)\}_2Cu]BF_4$, which range from 1.379(2) to 1.403(2) Å.[9] The boron–nitrogen bonds [B(1)–N(1) 1.607(3) Å, B(1)–N(2) 1.611(3) Å] are significantly longer than the average B–N single-bond of 1.59 Å found in amine–boranes.[10] Consistently, in compound **VIII** the B–N distance amounts to 1.588(3) Å.[11] An extremely long B–N bond was found in the Dewar borazine **IX** [1.752 Å].[12]

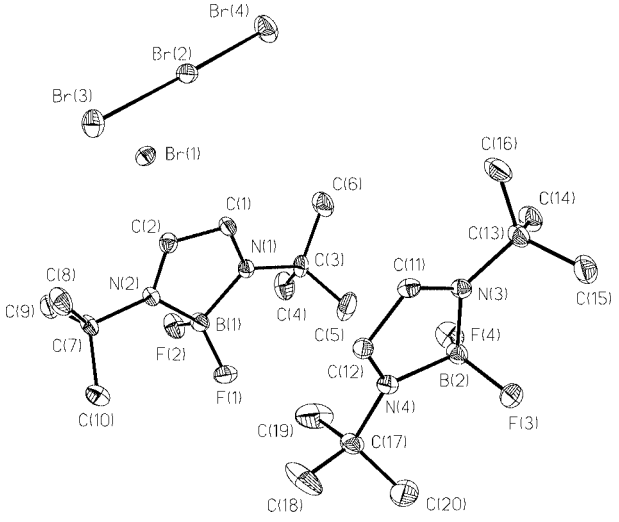
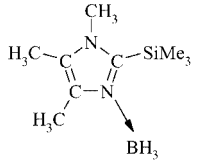
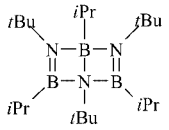


Figure 1. Crystal structure of **3h**; H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: B(1)–N(1) 1.607(3), B(1)–N(2) 1.611(3), B(1)–F(1) 1.366(3), B(1)–F(2) 1.369(3), N(1)–C(1) 1.282(3), N(2)–C(2) 1.290(3), N(1)–C(3) 1.513(3), N(2)–C(7) 1.511, C(1)–C(2) 1.491(3); N(1)–B(1)–N(2) 97.2(2), B(1)–N(1)–C(1) 110.4(2), B(1)–N(2)–C(2) 109.8(2), N(1)–C(1)–C(2) 111.0(2), N(2)–C(2)–C(1) 111.2(2), N(1)–B(1)–F(1) 110.9(2), N(1)–B(1)–F(2) 112.1(2), N(2)–B(1)–F(1) 112.4(2), N(2)–B(1)–F(2) 109.7(2), F(1)–B(1)–F(2) 113.3(2), B(1)–N(1)–C(3) 124.9(2), B(1)–N(2)–C(7) 125.2(2), C(1)–N(1)–C(3) 124.7(2), C(2)–N(2)–C(7) 124.4(2).



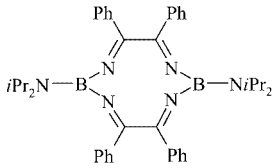
VIII



IX

In the precursor molecules, the 1,3,2-diazaborole B–N bond lengths range from 1.40–1.45 Å [e.g., (trimethylstannyl)diazaborole **1g**: B–N 1.439(7) and 1.450(7) Å].[1b] The

endocyclic C–N bond lengths [C(1)–N(1) 1.282(3) Å; C(2)–N(2) 1.290(3) Å] are characteristic for double bonds which are well comparable with those in the cyclic ketiminoborane **X** [1.273(3)–1.277(2) Å].[13]



X

The carbon–carbon bond length in the cation [1.491(3) Å] indicates a bond order of unity, whereas in the precursor diazaboroles double bonds [e.g., 1.344(8) Å in **1g**] are typical. In the course of the oxidation process the angle at the boron atom N(1)–B(1)–N(2) (in diazaboroles ca. 105°) was compressed to 97.42(16)° in **3h**, whereas the endocyclic angles B(1)–N(1)–C(1) [110.41(17)°], B(1)–N(2)–C(2) [109.8(2)°], N(1)–C(1)–C(2) [111.0(2)°] and N(2)–C(2)–C(1) [111.2(2)°] are similar to those in **1g** [107.1(4)–110.2(5)°].

Electrochemical Data

The established protocol for the synthesis of 2-halo-1,3,2-diazaboroles involves the reduction of the corresponding diazaborolium salts with a strong reducing agent, e.g. sodium amalgam.[1d] This preparative result is supported by reductive cyclovoltammetric experiments. All borolium salts **3e**,**h**,**i**,**j** and **6h** show a clean, reversible curve in the range of 0 to –2 V, performed in dichloromethane or acetonitrile as a solvent. The reductive cyclovoltammogram of **3j** is shown as a representative in Figure 2 with scan rates from 10 to 100 mV/s.

The distance between the two extrema (120 mV) exceeds the theroretical value of 58 mV and could be an indicator for quasireversibility.

The reductive potentials $E_{1/2}$ of the various borolium salts, taken from square-wave voltammetry, vary from –731 mV (**3e**) to –742 mV (**3j**), vs. the ferrocene/ferrocinium standard. As expected, no electrochemical oxidation was observed in the range of 0–3.2 V.

Conclusions

A number of 1,3,2-diazaboroles with different substituents at the boron atom can be irreversibly oxidized using cyclic voltammetry; the potentials E^o, taken from square-wave voltammetry, vary strongly, subject to the functional group at the boron atom. We were interested in the nature of the oxidation products and decided to study the chemical oxidation of a series of 1,3,2-diazaboroles **1b**–**e** and **1h**,**i**,**j**. The products were either borolium salts with two fluoride ligands at the boron atom as given with **3h**, or borolium salts with one fluoride substituent in addition to the functional group at the boron center. The latter situation was observed with diazaboroles containing poor leaving groups as given in **1e**,**i**,**j**. With electron-donating groups at the boron atom (**1b**,**d**) oligomers of difluoroboranes were detected as products. Interestingly, the alkyl- or aryl-substituted diazaboroles can not be oxidized chemically, although the oxidative cyclovoltammogram of the methyl-substituted borole **1c** shows a clean, irreversible signal. The chemical oxidation of the 2-bromodiazaborolidine **2h** suprisingly led to the same product **3h** as in the case of the unsaturated analog.

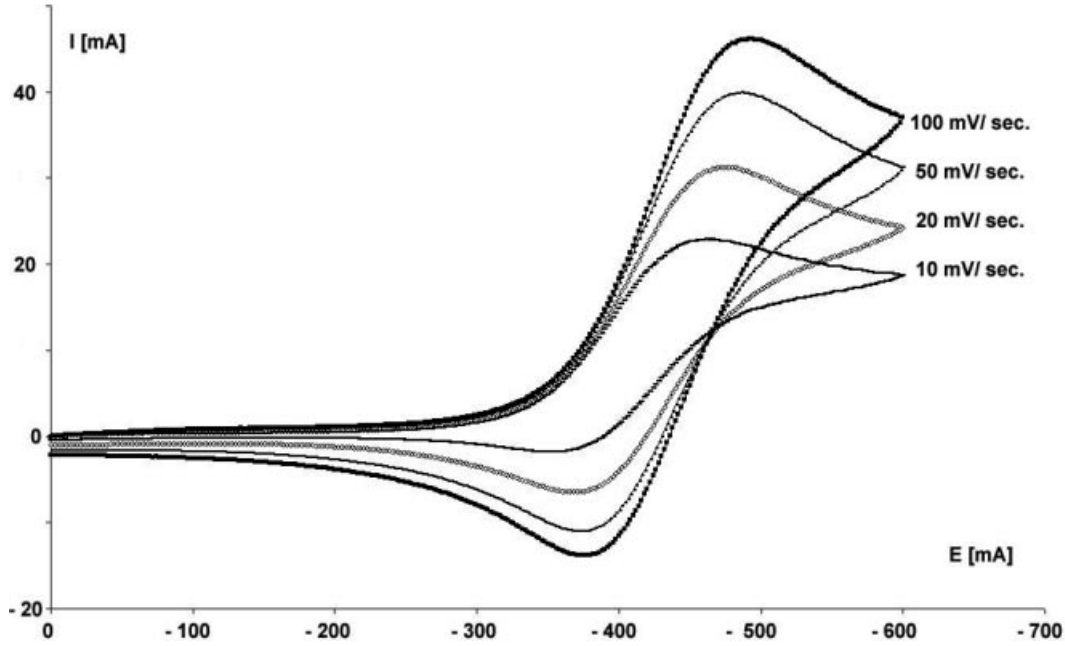


Figure 2. Reductive multiscan cyclovoltammogram of the borolium salt **3j**, 0 to –700 mV, CH_2Cl_2 with TBAPF at scan rates 10, 20, 50 and 100 mV/s.

The borolium salts **3e**,**h**,**i**,**j** and **6h** are deeply colored, air-stable compounds and prone for reduction by cyclic voltammetry. Hereby, the values of $E_{1/2}$ [ca. –735 mV] do not vary significantly.

Experimental Section

General: All manipulations were performed under dry nitrogen. Solvents were rigorously dried with appropriate drying agents and distilled before use. The boron-containing heterocycles were prepared as described in the literature: *t*BuN^a=CH–CH=N^b(*t*Bu)-BR(*N*^{a}–*B*) (**1b**–**e**,**h**,**i**,**j**; R = OMe,[5] Me,[14] NMe$_2$,[1a] H,[1b] Br,[1d] CN,[1a] C$_2$H[1a]) and *t*BuN^{a}CH$_2$CH$_2$N^b(*t*Bu)BBr(*N*^{a}–*B*) (**2h**).[2] NMR spectra were recorded in CD_2Cl_2 with a Bruker AM Avance DRX 500 spectrometer (^{1}H, ^{11}B, ^{13}C, ^{19}F) using $SiMe_4$, $BF_3{\cdot}OEt_2$ and $CFCl_3$ as external standards, mass spectra with a VG Autospec sector-field mass spectrometer (Micromass). The electrochemical experiments were performed with a PAR Model 270A instrument and the relevant software (Model 270). A system of microelectrodes with a three-electrode array was used. As working electrode a platinum wire was used (1.5 cm length, 0.5 mm diameter), which was formed to a helix around the counter electrode. A silver wire (1.5 cm length, 1 mm diameter) served as pseudo-reference electrode. All experiments were conducted in a glass device, which was flame dried prior to use and filled with dry dinitrogen. The determinations were performed in a 0.1 M solution of tetrabutylammonium hexafluorophosphate (TBAPF) in CH_2Cl_2 and MeCN with concentrations of the analyte of ca. $1{\cdot}10^{-4}$ mol L^{-1} in the range of 0–3 V. The cyclovoltammograms were recorded with scan rates of 5–700 mV s^{-1}, whereby the results presented here were obtained with scan rates of 10, 20, 50 and 100 mV s^{-1}. All published potentials were confirmed by square-wave voltammetry (frequency: 5 Hz). The oxidation potentials were referenced vs. the ferrocene/ferrocinium couple (E_{ox} = 0 eV) as a standard.

[(*t*BuN^a=CH–CH=N^b*t*Bu)BF$_2$(*N*^{a}–*B*)]X (X = Br$^-$, Br$_3^-$, PF$_6^-$) (3h). Path a: Compound **1h** (1.00 g, 3.86 mmol) was dissolved in a mixture of 20 mL of CH_2Cl_2 and 20 mL of hexane and cooled to –30 °C. Then solid $NOPF_6$ (1.36 g, 7.72 mmol) was added. The color of the solution turned pale yellow and after 2 h at 20 °C to orange. After 2 d at 4 °C, the product **3h** crystallized with different counterions (1.61 g). **Path b:** Analogous protocol with **2h** instead of **1h**. **Path c:** Analogous protocol with $AgPF_6$ instead of $NOPF_6$. ^{1}H NMR: δ = 1.54 (s, 18 H, *t*Bu), 8.87 (s, 2 H, NCH) ppm. ^{13}C NMR (CD_2Cl_2): δ = 27.7 [s, C(*C*H$_3$)$_3$], 60.8 [s, *C*(CH$_3$)$_3$], 151.2 (s, NCH) ppm. ^{11}B{^{1}H} NMR: δ = 6.1 ppm. ^{19}F{^{1}H} NMR: δ = –69.7 (d, ^2J = 710.0 Hz, PF$_6^-$), –148.8 (s, BF) ppm. ^{31}P{^{1}H} NMR: δ = –144 (sept, ^2J = 710.0 Hz, PF$_6$) ppm. Due to different counterions the elemental analysis was meaningless. ESI MS: *m*/*z* = 217 [*t*BuN^a=CH–CHN^b(*t*Bu)BF$_2$(*N*^{a}–*B*)]$^+$.

[(*t*BuN^a=CH–CH=N*t*Bu)BBrF(*N*^{a}–*B*)]BF$_4$ (6a): To a chilled solution (–30 °C) of **1h** (1.00 g, 3.86 mmol) in a mixture of CH_2Cl_2 (20 mL) and hexane (20 mL), solid $NOBF_4$ (0.90 g, 7.72 mmol) was added. The color of the solution turned pale yellow and after 2 h at room temp. it changed to orange. After 3 d at 4 °C, pure **6a** (1.24 g, 88%) was collected as yellow crystals. ^{1}H NMR: δ = 1.44 (s, 18 H, *t*Bu), 8.80 (s, 2 H, NCH) ppm. ^{13}C NMR: δ = 27.9 [s, C(*C*H$_3$)$_3$], 61.2 [s, *C*(CH$_3$)$_3$], 151.7 (s, NCH) ppm. ^{11}B{^{1}H} NMR: δ = 5.2 ppm. ^{19}F{^{1}H} NMR: δ = –69.7 (d, ^2J = 710.0 Hz, PF$_6^-$), –148.5 (s, BFBr) ppm. $C_{10}H_{20}B_2BrF_5N_2$ (364.80): calcd. C 32.92, H 5.53, N 7.68; found C 33.44, H 6.13, N 7.99. ESI MS: *m*/*z* = 278 [*t*BuN^a=CH–CHN^b(*t*Bu)BBrF(*N*^{a}–*B*)]$^+$.

[(*t*BuN^a=CH–CH=N^b*t*Bu)BHF(*N*^{a}–*B*)]PF$_6$ (3e): Solid $NOPF_6$ (1.94 g, 11.10 mmol) was added to a solution (–30 °C) of **1e** (1.00 g, 5.55 mmol) in CH_2Cl_2 (20 mL) and hexane (20 mL). Again, the color of the solution changed during the reaction from colorless to orange. After 2 d of stirring at room temp., the solution was stored at –4 °C for 4 d, and 1.28 g (67%) was obtained as yellow crystals. ^{1}H NMR: δ = 1.41 (s, 18 H, *t*Bu), 3.75 (br. s, BH), 8.53 (s, 2 H, NCH) ppm. ^{13}C NMR: δ = 27.3 [s, C(*C*H$_3$)$_3$], 60.8 [s, *C*(CH$_3$)$_3$], 158.3 (s, NCH) ppm. ^{11}B{^{1}H} NMR: δ = 5.2 ppm. ^{19}F{^{1}H} NMR: δ = –69.7 (d, ^1J = 710.0 Hz, PF$_6^-$), –147.7 (s, BFBr) ppm. ^{31}P{^{1}H} NMR: δ = –144 (sept, ^1J = 710.0 Hz, PF$_6^-$) ppm. No reliable analysis was obtained. ESI MS: *m*/*z* = 199 [*t*BuN^a=CH CHN^b(*t*Bu)-HBF(*N*^{a}–*B*)]$^+$.

[(*t*BuN^a=CH–CH=N^b*t*Bu)B(CN)F(*N*^{a}–*B*)]PF$_6$ (3i): A solution of **3i** (1.00 g, 4.88 mmol) and $NOPF_6$ (1.70 g, 9.76 mmol) was stirred in a mixture of CH_2Cl_2/hexane (1:1) for 3 d, whereby the color changed from yellow to red. The solution was stored at 4 °C for at least 5 d; then 1.39 g of the product (77%) was obtained as a red solid. ^{1}H NMR: δ = 1.45 (s, 18 H, *t*Bu), 7.81 (s, 2 H, NCH) ppm. ^{13}C{^{1}H} NMR: δ = 28.9 [s, C(*C*H$_3$)$_3$], 59.6 [s, *C*(CH$_3$)$_3$], 155.1 (s, NCH) ppm. ^{11}B{^{1}H} NMR: δ = 5.1 ppm. ^{19}F{^{1}H} NMR: δ = –69.7 (d, ^1J = 710.0 Hz, PF$_6^-$), –148.5 (s, BFCN) ppm. ^{31}P{^{1}H} NMR: δ = –144 (sept, ^1J = 710.0 Hz, PF$_6$) ppm. $C_{11}H_{20}BF_7N_3P$ (369.11): calcd. C 35.79, H 5.46, N 11.38; found C 35.38, H 6.11, N 11.99. ESI MS: *m*/*z* = 224 [*t*BuN^a=CH CHN^b(*t*Bu)B(CN)F(*N*^{a}–*B*)]$^+$.

[(*t*BuN^a=CH–CH=N^b*t*Bu)B(C$_2$H)F(*N*^{a}–*B*)]PF$_6$ (3j): Neat $NOPF_6$ (1.72 g, 9.80 mmol) and **3j** (1.00 g, 4.90 mmol) were stirred in a mixture of CH_2Cl_2/hexane (1:1) for 1 d, whereby the solution turned from colorless to cherry-red. After 4 d at 4 °C, 1.25 g of the product was collected as a red solid (69%). ^{1}H NMR: δ = 1.69 (s, 18 H, *t*Bu), 2.51 (s, C$_2$CH), 8.77 (s, 2 H, NCH) ppm. ^{13}C NMR: δ = 29.0 [s, C(*C*H$_3$)$_3$], 66.0 [s, *C*(CH$_3$)$_3$], 89.8 (s, C$_2$H), 161.3 (s, NCH) ppm. ^{11}B{^{1}H} NMR: δ = 5.1 ppm. ^{19}F{^{1}H} NMR: δ = –69.7 (d, ^1J = 710.0 Hz, PF$_6^-$), –148.5 (s, BFC$_2$H) ppm. ^{31}P{^{1}H} NMR: δ

Table 2. Crystal data and collection parameters.

	3h
Empirical formula	$C_{10}H_{20}BBr_3F_2N_2$
M_r [mg mol^{-1}]	1.621
Crystal dimensions [mm]	0.30 × 0.21 × 0.15
Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	10.1840(12)
b [Å]	11.5580(11)
c [Å]	14.1300(10)
α [°]	84.033(7)
β [°]	69.445(7)
γ [°]	83.944(8)
V [Å^3]	1544.6(3)
Z	2
$\rho_{calcd.}$ [Mg·m^{-3}]	1.621
μ [mm^{-1}]	5.251
F(000)	748
Θ [°]	2.14–30.00
No. refl. collected	61803
No. refl. unique	8984
R(int)	0.0523
No. refl. [$I > 2\sigma(I)$]	6835
Refined parameters	468
GOF	1.048
R_F [$I > 2\sigma(I)$]	0.0308
wR_{F2} [$I > 2\sigma(I)$]	0.0517
$\Delta\rho_{max/min}$ [e·Å^{-3}]	0.770/–0.705

= –144 (sept, ^1J = 710.0 Hz, PF_6) ppm. $C_{12}H_{21}BF_7N_2P$ (368.12): calcd. C 39.15, H 6.15, N 7.61; found C 39.33, H 6.12, N 7.78. ESI MS: *m*/*z* = 223 [*t*BuN^a=CH CHN^b(*t*Bu)B(C_2H)F(N^a–*B*)]$^+$.

Reaction of 1b with $NOPF_6$: Compound **1b** (1.00 g, 4.48 mmol) and neat $NOPF_6$ (1.72 g, 9.80 mmol) were stirred in a mixture of hexane/CH_2Cl_2 (1:1) for 7 d. The solvent was removed in vacuo and 0.18 g (50%) of $[F_2BOMe]_n$ (*n* = 2, 3) was collected as a yellow oil. ^{1}H NMR: δ = 1.24 (s, 3 H, OMe) ppm. ^{11}B{^{1}H} NMR: δ = 0.66 ppm. ^{19}F{^{1}H} NMR: δ = –152.6 ppm.

Reaction of 1d with $NOPF_6$: Compound **1d** (1.00 g, 4.75 mmol) and neat $NOPF_6$ (1.67 g, 9.5 mmol) were stirred in a mixture of hexane/CH_2Cl_2 (1:1) for 9 d. The solution turned red after minutes (a borolium salt is formed, but not stable). After removal of the solvent, 0.40 g (98%) of **5d** was collected as a colorless solid. ^{1}H NMR: δ = 1.36 (s, 6 H, NMe_2) ppm. ^{11}B{^{1}H} NMR: δ = 1.09 ppm. ^{19}F{^{1}H} NMR: δ = –162.6 ppm.

X-ray Structural Analysis: Details are listed in Table 2. CCDC-292358 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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