# The Chemistry of Borinium and Borenium Ions[†]

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## Contents

## I. Introduction

Boron chemistry is characterized by neutral and anionic species and by a wealth of fascinating compounds, such as boranes, carboranes, and metallaboranes, where electron-deficient bonding prevails.[1] In contrast, cationic species of boron had received little attention until the structural elucidation of the "diammoniate of diborane" by Parry and co-workers.[2] This compound proved to be the bis(ammine)boronium tetrahydro-



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Prof. Dr. H. Nöth was born in 1928. He received his Ph.D. under the supervision of Professor E. Wiberg at the University of Munich. Professor Nöth was appointed Professor of Inorganic Chemistry at the University of Munich and Director of the Institute of Inorganic Chemistry, Ludwig-Maximilians-Universität in 1979 and is the author of over 350 publications. His current research interests involve the area of chemistry of hydrogen compounds, nitrogen-bonded compounds of boron, aluminum, phosphorus, and arsenic (particularly highly reactive species, cations, heterocycles, and cage compounds), coordination compounds with metal–boron bonding, heterocyclic π-complexes, $^{11}$B, $^{14}$N, and $^{27}$Al NMR spectroscopy, and infrared laser-induced reactions. In his spare time, he plays the piano and practices gardening.

[†] In this review the following abbreviations will be used throughout: R = general substituent; X = halogen substituent; Me = $CH_3$; Et = $C_2H_5$; Pr = $n$-$C_3H_7$; $i$-Pr = $i$-$C_3H_7$; $t$-Bu = $CMe_3$; tmp = 2,2,6,6-tetramethylpiperidino group; tfl = $O_3SCF_3^-$; D = neutral donor molecule; py = pyridine; pic = picoline; lut = lutidine; bpy = $\alpha,\alpha'$-bipyridyl. Double bond representations for BN or BO bonds in borinium cations are used throughout in this text. Formal charges which are associated with π-back donation ($>N^+=B^-=N^+<$ or $>N^+=B-R$) are avoided because they represent only charges due to π-bonding and neglect the σ-bond polarity which is opposite in sign to the π-bond. Arrows are also often used to indicate the origin of the π-bonding electron pair. Since this conflicts with the equivalence of the BN π-bonds in iminoboranes, this notation is also not used here.

borate (1). Both boron atoms in this salt are tetracoordinated and, therefore, coordinatively saturated. Subsequently, many cations containing tetracoordinated boron have been detected, and the chemistry of these boronium ions is adequately reviewed.[3] More recently, new types of cations containing boron in tricoordinate or dicoordinate environment have been detected. The general type 2 and 3 will be called borenium ion and borinium ion, respectively. A short summary on these cations has recently been published.[4]
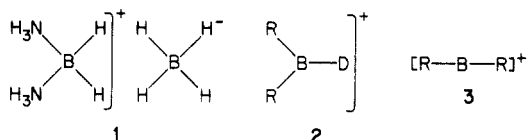
It is a generally recognized feature in boron chemistry that π-back-bonding plays an important role in the stabilization of tricoordinated species $BR_3$. Three of the valence orbitals of boron are involved in σ-bonding in these compounds making the $p_z$ orbital available for π-bonding. Typical examples are aminoboranes[5] and borazines[6] for which orbital representations are shown by 4 and 5. π-Bonding is very efficient in BN systems due to favorable overlap and energy matching of the atomic orbitals involved,[5a,7] and this helps the boron atom to become electronically saturated.

On the basis of MO principles, a concept for the synthesis of borenium and borinium ions has been developed. Considering tricoordinated cations of boron, three boron orbitals must be available for σ-bonding and one for π-bonding. Since boron in a $B^+$ species can supply only two valence electrons, it is necessary that the additional electron pair for one of the three σ-bonds must be supplied by an electron pair donor. Since π-bonding is expected to play an essential part in stabilizing these cations, at least one amino group (or another group capable of π-back-bonding) should be present. Species of type 6–8 exemplify this principle. A borenium ion of type 8 differs from 6 and 7 because the π-stabilization is provided by the ligand D. Pyridine is a good example. Its π-electrons may interact with the boron's $p_z$ orbital. Borenium ions of type 8 should allow a much larger variation of substituents R than in 6. Similarly, dicoordinated borinium ions are expected
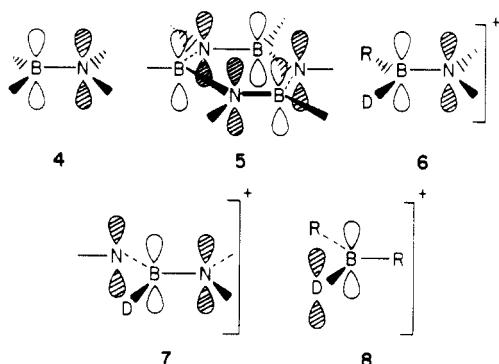
to be stable if the boron atom is sp-hybridized, and, therefore, two vacant p orbitals at boron are available for π-back-bonding. Taking into account that BN π-back bonding is very efficient, then a bis(amino)boron(1+) cation 9 is expected to be a good candidate for a stable borinium ion. It should certainly be much more stable than $H-B-H^+$, where no π-back-bonding is possible.[8] 9 is isoelectronic and should also be isostructural with an allene.
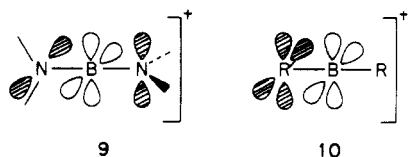
An alternative for a possible stable borinium ion is represented by 10: one substituent, R', would be re-

quired to involve both p orbitals at the boron atom in π-bonding; however, charge distribution is expected to be less favorable here than for the species of type 9.

Considering reasonable combinations of boron atoms with atoms or groups D, R, and X a large number of borenium and borinium ions are expected to be sufficiently stable to be detected by physical methods or even to be isolated as a salt. Until recently the literature contained scanty information on these cations. Furthermore, most of the ions described have not been adequately characterized, and some may exist only at moderate concentration in equilibrium with other species.

The formation of a bis(dimethylamino)(dimethylamine)borenium ion (11) was suggested in 1963 to explain the stoichiometry of the reaction of tris(dimethylamino)borane with hydrogen iodide.[9]
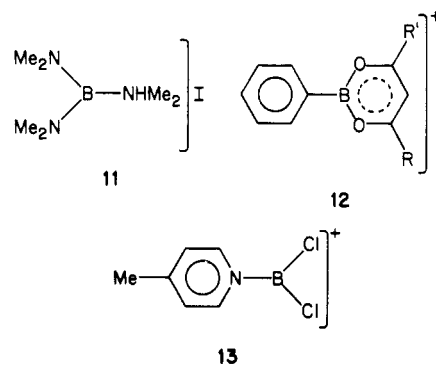
Several dioxaborenium ions of type 12 have been reported by Balaban and co-workers.[10] They treated arylboronic acids with acetylacetones, and the intermediates obtained were allowed to react with anhydrous $HClO_4$ or $HSbCl_6$ to provide cations of type 12, isolated as perchlorates or hexachloroantimonates. Evidence for their structure was deduced from UV and IR spectra. However, more recent work indicates that these compounds contain tetracoordinated boron atoms.[11] Finally, Ryschkewitsch and Wiggins[12] observed that $AlCl_3$ combines with (4-picoline)boron trichloride to produce a highly conducting solution in $CH_2Cl_2$. A low field shift of the $^{11}B$ NMR signal was observed, which was taken as evidence for the formation of cation 13.

The formation of a diphenylborinium ions was reported as early as 1958.[13] Diphenylboron chloride, dissolved in methyl ethyl ketone or nitrobenzene on addition of $AlCl_3$, produced a yellow solution of high electrical conductivity. This was attributed to the formation of a solvated diphenylborinium ion (14) (the original formulation is shown). However, on the basis of NMR data it was later concluded that tetracoordinated species were present in these solutions.[14] MO calculations led to the conclusion[15] that a planar diphenylborinium ion (15) is an unfavored species especially in the presence of a donor solvent, in contrast to the 9-borafluorenium ion 16, described by Köster and Willemsen[16] as a tetrachloroaluminate and a hexachloroantimonate.

In view of maximal π-interaction one would expect that a diphenylborinium ion in conformation 17 should be more stable than 15. In addition, 16 should have a high tendency to accept a pair of electrons and should therefore react with a base to form a tricoordinated borenium ion. Finally the borenium ion 18[17] and the

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17



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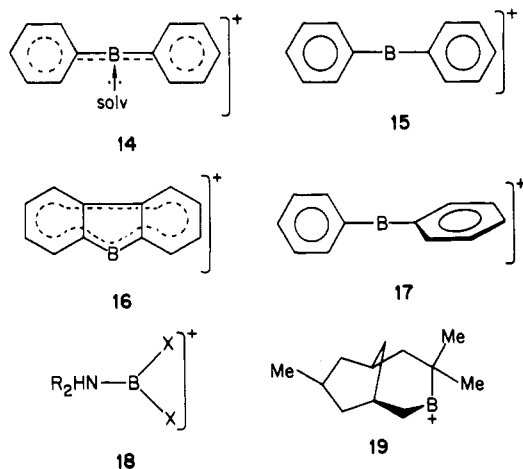
borinium ion 19[18] have been suggested as reactive intermediates.

## II. Preparation of Borinium and Borenium Salts

The methods for generating salts containing the dicoordinate borinium ion or the tricoordinate borenium ion can be classified into four categories: (a) boron–halogen bond heterolysis; (b) nucleophilic displacement; (c) electrophilic attack at BN bonds; (d) metathesis.

Cations which have so far been generated and isolated as salts and which can be considered well characterized are summarized in Tables I and II. Table III contains species which need confirmation or have been characterized in solution only.

### A. Boron–Halogen Bond Heterolysis

Tables I and II show that boron–halogen bond heterolysis is the most widely used and successful method for preparing borenium and borinium ions. A large range of halide acceptors can be applied; however, $AlCl_3$, $AlBr_3$, and $GaCl_3$ have so far been the preferred reagents for breaking a boron–halogen bond.

#### 1. Generation of Borinium Ions

Preparative procedures for the synthesis of borinium salts are very similar to those for phosphenium ions.[19] Parry et al.[20] allowed a 1:1 mixture of $(i\text{-}Pr_2N)_2BCl$ and $AlCl_3$ in $CH_2Cl_2$ to warm from −78 °C to room temperature in order to generate the borinium ion ($i\text{-}Pr_2N)_2B^+$. Since $AlCl_3$ is only slightly soluble in this solvent, reaction with the bis(amino)boron chloride is indicated by dissolution of $AlCl_3$. Reactions as shown in eq 1 can be monitored readily by ^{11}B and ^{27}Al NMR spectroscopy.[20–24] $AlBr_3$ and $GaCl_3$ offer the advantage that reactions according to eq 1 can also be conducted



$$R=Me, Et, i\text{-}Pr; R_2N=tmp, N(CMe_3)CH_2Ph; X=Cl, Br, I$$
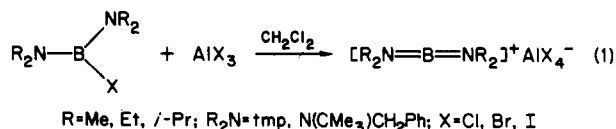
in nonpolar solvent such as pentane, hexane, or benzene. If bromoboranes and $AlBr_3$ are reacted to obtain tetrabromoaluminates,[21] it is advisable to use $CH_2Br_2$ instead of $CH_2Cl_2$ as solvent[22] in order to avoid Cl/Br exchange. If $CH_2Cl_2$ is used, rapid workup is necessary. Crystalline materials are more readily obtained from

$CH_2Cl_2$ solution than from any other solvent.

The interaction of a bis(amino)boron halide with a halide acceptor will not necessarily result in the formation of a bis(amino)boron(1+) cation. Actually, one would expect that a strong Lewis acid such as $AlCl_3$ or $GaCl_3$ should attack at the nitrogen atoms of bis(amino)boron halides. This mode of reaction is verified by using 1,3,2-diazaborolidines[25–27] as shown in eq 2.
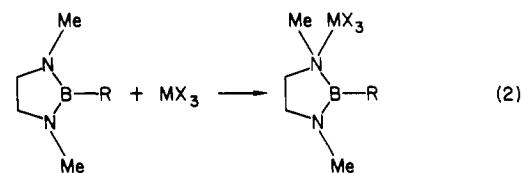


$$R=Me, NMe_2, Cl, Br, B(NMeCH_2)_2, M=B[26,27], Al[25,26], Ga[25,26], X=Cl, Br$$

There are three reasons for this behavior: (i) N adduct formation reduces the strain in the five-membered 1,3,2-diazaborolidines which contain $sp^2$-hybridized B and N atoms; (ii) the ammonium nitrogen atom generated by $MX_3$ addition inductively increases the electron acceptor potential of the boron atoms; (iii) BX bond heterolysis is unfavored because the resulting cation 21 would not be isostructural with an allene. The first two features find justification in the short B–N bond distance found in the X-ray structure of 20.[25]



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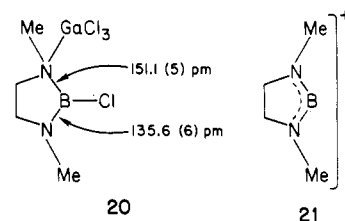
Increasing the ring size from five in 1,3,2-diazaborolidines to six in 1,3,2-diazaborinanes has no effect on the site of attack of $AlCl_3$ or $GaCl_3$: Al–N and Ga–N adducts are formed.[28] However, if the ring is expanded to nine members, ^{11}B NMR data indicate the formation of the borinium ion 22 as shown in eq 3.[29] Models show



22
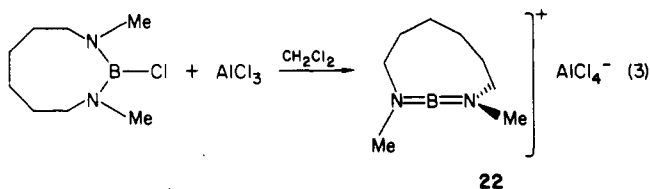
that an almost linear NBN skeleton can form under these circumstances. However, the salt has not yet been isolated. The formation of bis(amino)boron(1+) cations depends not only on geometrical but also on steric constraints: the bulkier the dialkylamino group, the easier are $(R_2N)_2B$ cations generated. So far, no salt containing cations 23 and 24 has been reported. This may be due to the lack of suitable starting compounds. However, the borinium ion 25 is formed, as an unstable
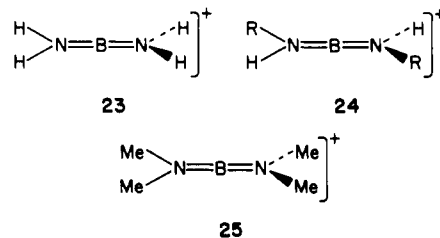


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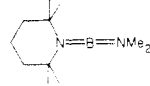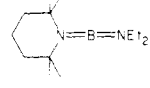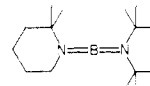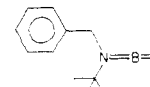## TABLE I. Synthetic Methods and Some Characterizing Data of Borinium Salts
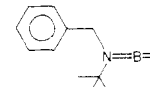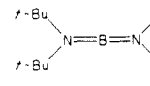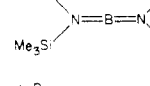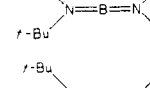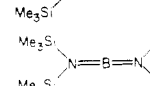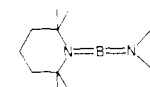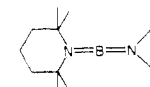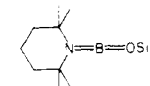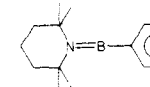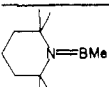
| cation | anion | Method[a] | $\delta(^{11}B)$ | $\nu(BN_2)$, cm$^{-1}$ | mp, °C | additional data | ref |
|---|---|---|---|---|---|---|---|
| $i\text{-}Pr_2N=B=N\text{-}i\text{-}Pr_2$ | AlCl$_4$ | A | 35.7 | 1830, 1850, 1900 | | $\delta(^{27}Al)$ 102.9 $\nu(AlCl_4)$ 500 cm$^{-1}$ | 20 |
| | AlBr$_4$ | A | 37.3 | | 58–64 | $\delta(^{27}Al)$ 80.2 | 22 |
| | GaBr$_4$ | A | 38.7 | 1830–1872 | 123–125 | $\delta(^{71}Ga)$ 76 | 22 |
| [structure: piperidine N=B=NMe$_2$] | AlBr$_4$ | A | 36.7 | 1850, 1872, 1908, 1925 | 112–114 | $\delta(^{27}Al)$ 80.7 | 21 |
| [structure: piperidine N=B=NEt$_2$] | BI$_4$ | A | 37.7 −127.1 | | | | 24 |
| | AlI$_4$ | A | 38.6 | | | $\delta(^{27}Al)$ ~23.2 | 24 |
| | AlCl$_4$ | A | 35.7 | | 58 | $\delta(^{27}Al)$ 102.8 | 24 |
| | AlBr$_4$ | A | 37.6 | 1835, 1895, 1910 | 90–95 | $\delta(^{27}Al)$ 80.7 | 21 |
| [structure: bis-piperidine N=B=N] | GaCl$_4$ | A | 37.3 | | 35 | | 24 |
| | GaBr$_4$ | A | 36.1 | | 140 dec | | 24 |
| | TaCl$_6$ | A | 35.7 | | 102–107 | | 24 |
| | TaBr$_6$ | A | 35.4 | | 149–151 | | 24 |
| | BF$_4$ | A | 35.0 0.9 | | 73–75 dec | | 24 |
| | BCl$_4$ | A | 35.8 7.2 | | 111–115 | | 24 |
| | BBr$_4$ | A | 35.4 −25.1 | | 195–198 | | 24 |
| | B(O$_3$SCF$_3$)$_4$ | D | 36.0 −3.1 | | 132–133 dec | | 24 |
| | AlCl$_4$ | A | 35.9 | | 165–168 | $\delta(^{27}Al)$ 102.8 | 24 |
| | GaCl$_4$ | A | 36.0 | | 138–140 | $\delta(^{71}Ga)$ 249 | 24 |
| | SbF$_6$ | A | 37.6 | | rapid dec 20 | | 23 |
| | O$_3$SCF$_3$ | D | 36.1 | 1787, 1800, 1830, 1860 | 103–105 | | 23, 24 |
| [structure: benzyl, t-Bu, N=B=N] | AlCl$_4$ | A | 38.7 | 1830, 1885 | 89–97 dec | $\delta(^{27}Al)$ 103 $\nu(AlCl_4)$ 490 cm$^{-1}$ | 54 |
| [structure: benzyl, t-Bu, SiMe$_3$, N=B=N] | BBr$_4$ | A | 35.8 −24.5 | 1810, 1860 | 90–93 | $\delta(^{29}Si)$ 16.55 | 33 |
| [structure: t-Bu$_2$ N=B=N t-Bu SiMe$_3$] | I | C | 36.1 | 1785, 1840 | 128–132 | $\delta(^{29}Si)$ 15.99 | 33 |
| [structure: t-Bu SiMe$_3$ Me$_3$Si t-Bu N=B=N] | I | C | 36.1 | 1760, 1780, 1835 | dec 0 | $\delta(^{29}Si)$ 15.1 | 33 |
| | BBr$_4$ | A | 35.2 −24.5 | 1750, 1780, 1830 | 116–118 | $\delta(^{29}Si)$ 15.45 | 33 |
| [structure: t-Bu$_2$ SiMe$_3$ N=B=N] | BBr$_4$ | A | 32.8[b] −24.5 | 1780, 1835 | 78–80 | $\delta(^{29}Si)$ 19.34 | 33 |
| [structure: t-Bu SiMe$_3$ Me$_3$Si SiMe$_3$ N=B=N] | BBr$_4$ | A | 33.3[b] −23.5 | 1760, 1780, 1830 | 83–84 | $\delta(^{29}Si)$ 19.02 14.01 | 33 |
| [structure: Me$_3$Si SiMe$_3$ N=B=N] | BBr$_4$ | A | 32.8[b] −24.5 | 1770, 1830 | 89–94 | $\delta(^{29}Si)$ 18.4 | 33 |
| [structure: piperidine N=B=N t-Bu SiMe$_3$] | I | C | 35.9 | 1795, 1850 | 92–95 dec | | 23, 48 |
| | O$_3$SCF$_3$ | C | 35.3 | 1796, 1848 | 111–115 | | 23, 48 |
| | BBr$_4$ | A | 36.5 −25.1 | | dec ~50 | | 23 |
| [structure: piperidine N=B=N SiMe$_3$ SiMe$_3$] | BBr$_4$ | A | 33.0 −24.7 | | dec >80 | | 23 |
| [structure: piperidine N=B=OSi-t-Bu$_3$] | AlCl$_4$ | A | 22.6 | 1885, 1950 | stable at −25 | $\delta(^{27}Al)$ 102.8 | 22 |
| [structure: piperidine N=B-phenyl] | AlBr$_4$ | A | 56.0 | | dec ambient temp | $\delta(^{27}Al)$ 81.3 | 21 |

TABLE I (Continued)

| cation | anion | method[a] | δ($^{11}$B) | ν(BN$_2$), cm$^{-1}$ | mp, °C | additional data | ref |
|---|---|---|---|---|---|---|---|
|  | AlBr$_4$ | A | 59.6 | | dec ambient temp | δ($^{27}$Al) 81.1 | 21 |

[a] A = halide abstraction; B = nucleophilic displacement; C = electrophilic attack; D = metathesis.  [b] Measured at −30 °C.

species[20] in CH$_2$Cl$_2$ solution from (Me$_2$N)$_2$BCl and AlCl$_3$. The solution, at 25 °C, shows an electrical conductivity close for a 1:1 electrolyte.[20] However, the $^{27}$Al NMR signal, although at the position expected for AlCl$_4^-$ is rather broad, and at −80 °C a second broad signal just upfield of AlCl$_4^-$ was also observed. The signal for AlCl$_4^-$ decreases gradually in intensity at room temperature while the upfield resonance became the major peak. Only a single broad $^{11}$B signal is then observed at δ($^{11}$B) +30.9 ppm, 3.3 ppm downfield of (Me$_2$N)$_2$BCl. In addition, a total of four $^{13}$C resonances are observed, which could not be assigned. The results indicate, at the present time, that [(Me$_2$N)$_2$B]AlCl$_4$ is first formed at low temperature but is unstable at ambient temperature.[20] The broad $^{27}$Al NMR signal for AlCl$_4^-$ suggests interaction with the cation, presumably through Cl bridges, thus reducing the $T_d$ symmetry of the anion which would be in agreement with its line width.[30]

At room temperature, a different species forms because the IR spectrum shows no bands in the typical "allene" region (1800–1900 cm$^{-1}$) which are characteristic for diaminoborinium ions.[20,21] (Me$_2$N)$_2$BBr·AlBr$_3$ behaves similarly.[20,31] The species 26–29 have been suggested as possibilities to account for the NMR and IR observations.[20]



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29 (S=solvent)
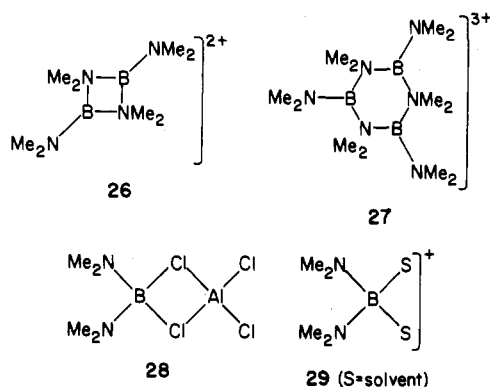
It becomes increasingly easy to isolate diaminoborinium salts as the bulk of the amino groups increases.[24] Thermal stability also increases, as shown for the tetrachloroaluminates of cations 30–32. Boron



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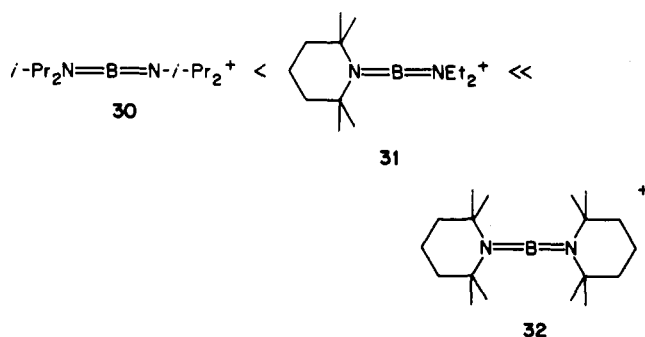
halogen bond heterolysis would be expected to become

more difficult with increasing the boron–halogen bond strength. Therefore, the interaction of various halide acceptors with (diethylamino)(2,2,6,6-tetramethyl-piperidino)boron halides was studied. Using the corresponding boron trihalide as a halide acceptor, it is found that the reaction of BF$_3$ with Et$_2$N(tmp)BF does not proceed according to eq 4, but BN bond cleavage is observed instead.[22] However, an equilibrium situation (4) results for X = Cl and Br, which lies on the right-hand side for X = I as shown by $^{11}$B NMR studies. The equilibrium (5) is already fully shifted to the side of the



(4)

X = F, Cl, Br, I



(5)

X = F, Cl
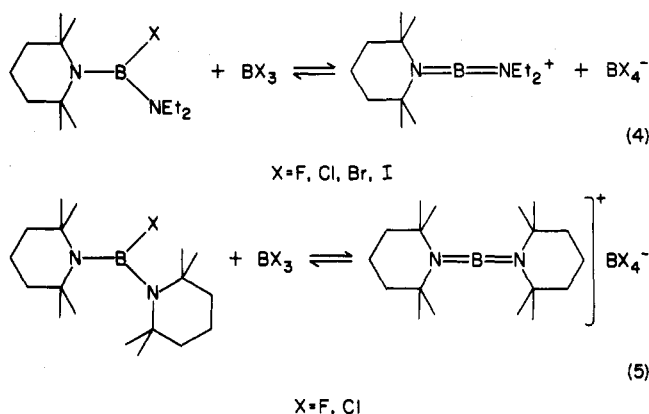
borinium ion in the case of (tmp)$_2$BX with X = F and Cl,[24] while (tmp)$_2$BBr and (tmp)$_2$BI have not been studied, because attempts to prepare them have so far failed.[22,24] It should be noted that bis(amino)boron(1+) tetrahaloborates are isomers of aminoboron dihalides.

The (diethylamino)(2,2,6,6-tetramethylpiperidino)-boron halides have also been used to study the behavior of various halide acceptors.[24,32] Although no definite compounds were isolated, $^{11}$B NMR data exclude the formation of Et$_2$N=B=tmp$^+$ from a mixture of SbF$_5$ with Et$_2$N(tmp)BF but show that B–N bond cleavage occurs. No reaction was observed by combining LiCl, BeCl$_2$, HgCl$_2$, CH$_3$HgCl, Hg(C≡CCH$_3$)$_2$, SnCl$_2$, ZnCl$_2$, PtCl$_2$, PtCl$_2$·2PhCN, Ph$_3$P·AuCl, or InCl$_3$ with Et$_2$N-(tmp)BCl in the presence of CH$_2$Cl$_2$.[24] Only AlCl$_3$, GaCl$_3$, and TaCl$_5$ initiated formation of the borinium ion. Products obtained with TiCl$_4$ and SbCl$_5$ as halide acceptors have not been characterized.[32] SnBr$_4$ and Et$_2$N(tmp)BBr interact, and NMR data suggest an equilibrium situation.[24] In contrast, Et$_2$N(tmp)B$^+$ salts can be isolated by using AlBr$_3$, GaBr$_3$, or TaBr$_5$ as the bromide acceptor. [Et$_2$N(tmp)B]AlI$_4$ results by reacting Et$_2$N(tmp)BI with AlI$_3$; this salt was characterized in solution only.[24] Although quantitative data are lacking, it appears that cation formation is favored for (R$_2$N)$_2$BX in the series X = F < Cl < Br < I, i.e., with decreasing boron–halogen bond strength. However, the halide acceptor strength is also important.[24]

Bulky amino groups prevent the synthesis of bis(amino)boron bromides and iodides, and even some chlorides are not accessible by standard procedures. For

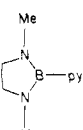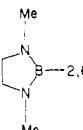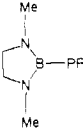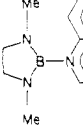TABLE II. Synthetic Methods and Some Characterizing Data of Borenium Salts
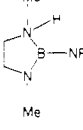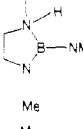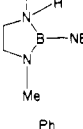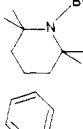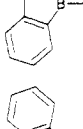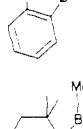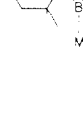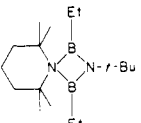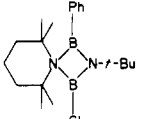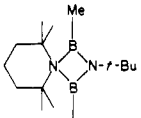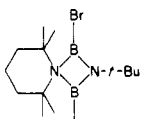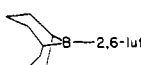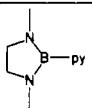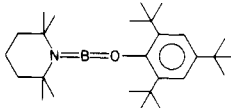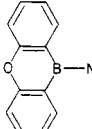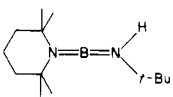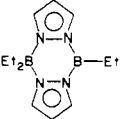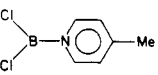
| cation | anion | method[a] | δ($^{11}$B) | mp, °C | remarks | ref |
|---|---|---|---|---|---|---|
| $(Me_2N)_2B\cdot py$ | $AlCl_4$ | A | 26.4 | 57 | δ($^{27}$Al) 102.6 | 22 |
| | $O_3SCF_3$ | B | 26.8 | 128–130 | | 22 |
| $(Me_2N)_2B\cdot 2,6$-lut | $O_3SCF_3$ | B | 25.5 | 90–92 | | 22 |
| $(i\text{-}Pr_2N)_2B\cdot py$ | Br | B | 30.2 | 161–163 | | 22 |
| | $O_3SCF_3$ | B | 29.0 | 121–125 | | 22 |
| | $AlCl_4$ | A | 29.8 | 107–109 | δ($^{27}$Al) 103.0 | 22 |
| $(i\text{-}Pr_2N)_2B\cdot 2,6$-lut | Br | B | 29.9 | 121 | | 22 |
| | $O_3SCF_3$ | B | 27.5 | 117–119 | | 22 |
| | $AlCl_4$ | A | 28.1 | 163–165 | δ($^{27}$Al) 102.9 | 22 |
| | $AlBr_4$ | A | 27.0 | 158–160 | δ($^{27}$Al) 80.2 | 22 |
|  | $O_3SCF_3$ | B | 26.7 | 38 | most often a yellow oil only | 47 |
|  | $O_3SCF_3$ | B | 26.7 | 51 | | 47 |
| | $AlCl_4$ | A | 26.3 | | δ($^{27}$Al) 103; oily material | 47 |
|  | $O_3SCF_3$ | B | 26.7 | | | 47 |
| | $AlCl_4$ | A | 26.5 | 66 | δ($^{27}$Al) 103; in solution equilibrium | 47 |
|  | $O_3SCF_3$ | B | 27.0 | 98 | X-ray structure | 53 |
|  | $O_3SCF_3$ | C | 25.8 | 108 | IR 1590, 1552 cm$^{-1}$ | 47 |
|  | $O_3SCF_3$ | C | 24.9 | | oily material | 47 |
|  | $AlCl_4$ | A | 25.0 | | δ($^{27}$Al) 103; oily material | 47 |
|  | $O_3SCF_3$ | B | 36.2 | | preliminary X-ray structure | 46 |
|  | $GaCl_4$ | A | | 142 dec | ν($GaCl_4^-$) 373 cm$^{-1}$ | 42 |
|  | $AlCl_4$ | A | 43.5 | | X-ray structure | 42 |
|  | Br | B | 48.9 | 108–110 dec | | 43 |
| | $AlBr_4$ | C | 47.8 | 151–152 dec | δ($^{27}$Al) 79.9 | 43 |

TABLE II (Continued)

| cation | anion | method[a] | δ($^{11}$B) | mp, °C | remarks | ref |
|---|---|---|---|---|---|---|
|  | Cl | B | 50.1 | | | 51 |
| | I | B | 50.2 | 105–110 dec | | 44, 51 |
| | O₃SCF₃ | B | 50.1 | 110 dec | | 51 |
|  | AlCl₄ | A | 37.6 46.4 | | δ($^{27}$Al) 103.7 | 43 |
|  | AlBr₄ | A | 36.5 47.8 | 117–118 dec | δ($^{27}$Al) 79.9 | 43 |
|  | AlBr₄ | A | 36.8 | 74–76 dec | δ($^{27}$Al) 79.7 | 43 |
| Bu₂B-2,6-lut | O₃SCF₃ | B | 54.7 | oil | | 42 |
|  | OSCF₃ | B | 59.2 | oil | 4, 42 | |
| | GaCl₄ | A | 58.5? | | | |

[a] See footnote a in Table I.

TABLE III.  Physical Data Related to Detected Borenium and Borinium Ions in Solution

| cation | anion | method of detection/remarks | ref |
|---|---|---|---|
|  | Cl | δ($^{11}$B) 26.3, stable only < −30 °C | 4 |
|  | Cl | δ($^{11}$B) NMR, stable only < −30 °C | 4 |
|  | AlBr₄ | δ($^{11}$B) in CH₂Cl₂ solution | 4 |
|  | ClO₄ | not precipitated from CH₃NO₂ solution with ether | 13b |
| i-Pr₂N=B=N-i-Pr₂ | AlCl₄ | stable in CH₂Cl₂ solution; see also Table I | 20 |
| Me₂N=B=NMe₂ | AlCl₄ | δ($^{11}$B) 30.9 (br); CH₂Cl₂ solution; shows conductivity 4.00 Ω⁻¹ cm²; no longer present at 25 °C | 20 |
|  | AlCl₄ | δ($^{11}$B) 35.7; δ($^{27}$Al) 101.4; rapid dec in CH₂Cl₂ solution, −40 °C | 23 |
|  | EtGaCl₃ | δ($^{11}$B) 3.6 (262 Hz), 35.3 (525 Hz); δ($^{13}$C) 144.8, 147.6, 113.3, 9.48, 8.36 (d) | 23 |
|  | Al₂Cl₇ | $^1$H, $^{11}$B (47.3 ppm, very br) | 17 |

example, (tmp)₂BCl cannot be prepared from BCl₃ and Litmp.[23]  However, bis(amino)boron fluorides may be obtained quite readily although they were originally regarded as unfavorable starting materials for (R₂N)₂B⁺

cations.[24]  This proved not to be true, as shown in eq 6 and 7.  The driving force behind these reactions is the formation of highly volatile BF₃ which results from rapid halogen exchange of the mixed species BFX₂ and

$(Me_3Si)_{4-n}(t\text{-}Bu)_nN_2BF \ + \ 2BBr_3 \ \longrightarrow$

$[(Me_3Si)_{4-n}(t\text{-}Bu)_nN_2B]BBr_4 \ + \ BFBr_2 \quad (6)$



$+ \ 2BX_3 \ \longrightarrow$



$BX_4 \ + \ BFX_2 \quad (7)$
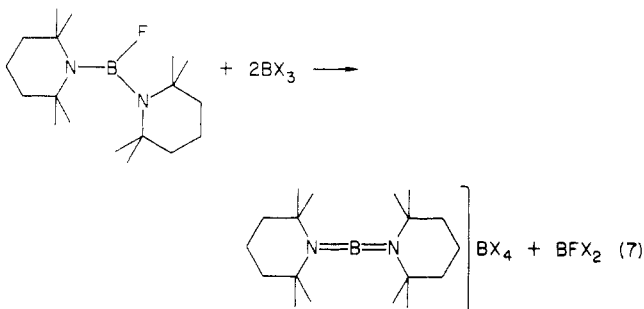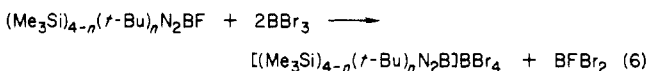
$BF_2X.$[34] Therefore, the number of BF bonds is retained in these reactions and, consequently, $\Delta G$ of the reaction is expected to be negative. All members of the series $[(Me_3Si)_{4-n}(t\text{-}Bu)_nN_2B]BBr_4$ could be prepared as described by eq 6 if an excess of boron tribromide is applied.[33] The two isomeric cations **33** and **34** were obtained by this method.[33] These reactions are of special interest because no SiN bond cleavage occurs under mild conditions.



**33**



**34**
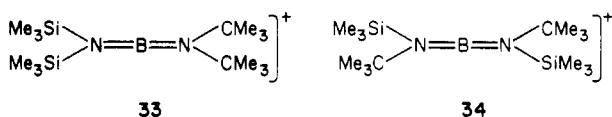
The bis(amino)boron fluorides can also be used to prepare tetrachloro- or tetrabromoaluminates and gallates.[24] This is due to the formation of thermodynamically favored AlF and GaF bonds. Reactions of type (8) have therefore been used to obtain tetrachloro-,



$+ \ 2AlX_3 \ \longrightarrow$



$AlX_4 \ + \ \text{"}AlFX_2\text{"} \quad (8)$

X = Cl, Br, I
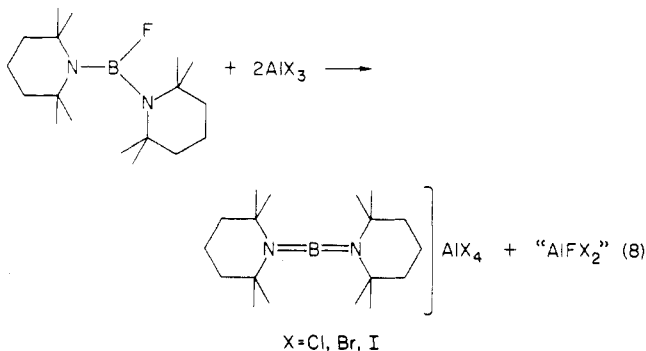
tetrabromo-, and tetraiodoaluminates where bis(dialkylamino) chlorides, bromides, and iodides are unknown or inaccessible. Attempts to synthesize dialkoxyborinium ions by chloride abstraction from dialkoxyboron chlorides with $AlCl_3$ or $GaCl_3$ were unsuccessful.[4a,22] However, organyloxy(2,2,6,6-tetramethylpiperidino)boron(1+) cations can be generated according to eq 9.[22] $AlCl_3$ dissolves at $-70$ °C in $CH_2Cl_2$ on



$+ \ AlCl_3 \ \rightleftharpoons$



$AlCl_4^-$

$(9)$

R = $t$-Bu, $t$-Bu$_3$C, Me$_3$Si, $t$-Bu$_3$Si
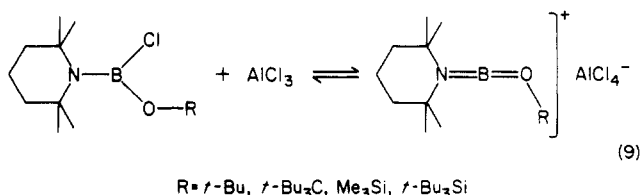
adding $t$-BuO(tmp)BCl or $t$-Bu$_2$HCO(tmp)BCl. The $^{11}$B NMR signal of the reaction mixture is shifted 3 ppm to lower field, but the $^{27}$Al NMR signal at 102 ppm is somewhat broader (50 Hz) than for free $AlCl_4^-$ (15–20

Hz).[35] Since more signals were observed in the $^{13}$C NMR spectrum (recorded at $-45$ °C) than expected for tmpBO-$t$-Bu$^+$, the conclusion was drawn that $AlCl_3$ may add to the oxygen atom of $t$-BuO(tmp)BCl. Therefore, the equilibrium situation as described by eq 9 seems to be involved.

A similar behavior was observed for $t$-Bu$_3$CO(tmp)-BF.[22] It reacts with $AlCl_3$, and a broad $^{27}$Al NMR signal is found at 106 ppm ($h(1/2) = 635$ Hz). At ambient temperature $\delta(^{27}Al)$ is typical for $AlCl_4^-$ (102.9 ppm), and the line width has considerably diminished ($h(1/2) = 63$ Hz).[22] In addition, a shoulder at 90 ppm appears. A broad $^{11}$B NMR signal at 20.2 ppm would be in accord with borinium ion formation, but $^{13}$C NMR data indicate that a more complex situation exists as described by eq 9.[22]

Surprisingly, the chloride abstraction by $AlCl_3$ from $Me_3SiO(tmp)BCl$ is readily achieved at $-50$ °C as shown by $^{11}$B, $^{27}$Al, and $^{13}$C NMR spectra. However, the $^{27}$Al NMR signal for $AlCl_4^-$ broadens increasingly as the temperature is raised to 20 °C. This can be explained by assuming an interaction between cation and anion.[22] This result, as compared to $t$-BuO(tmp)BCl, can be understood in terms of reduced basicity at the trimethylsiloxy group. Attack of $AlCl_3$ on the Cl atom is, therefore, favored. If the bulkiness of the siloxy group is further enhanced, the equilibrium (9) can be shifted to the side of the borinium salt: $t$-Bu$_3$SiO(tmp)BCl reacts quantitatively with $AlCl_3$ and the sharp signal of $AlCl_4^-$ ($\delta(^{27}Al)$ 102.8 ppm, $h(1/2) = 26$ Hz) is observed. $[t$-Bu$_3$SiO(tmp)B]AlCl$_4$ can be isolated. $CH_2Cl_2$ solutions show the conductivity expected for a 1:1 electrolyte.[22]

Attempts have also been made to detect cations of the type $[R_2N{=}BHal]^+$. Considering the stabilization of cations of this type the best choice would be $[R_2N{=}BF]^+$ due to the strong $\pi$-backbonding capability of fluorine. However, no evidence for a (2,2,6,6-tetramethylpiperidino)fluoroborinium ion has so far been obtained in reactions of tmpBF$_2$ with SbF$_5$ as a fluoride acceptor.[22] That $[R_2N{=}BHal]^+$ cations are involved in reactions of aminoboron dihalides can be demonstrated, e.g., by reaction of tmpBI$_2$ with BI$_3$.[22] At $-10$ °C two $^{11}$B NMR signals ($\delta$ $-7.6$ and $-2.3$ ppm) for the two components were recorded. However, a single signal at $\delta(^{11}B)$ $-10$ ppm was observed at ambient temperature. Therefore, an exchange reaction proceeds making the two different boron moieties magnetically equivalent. The reaction cannot be explained in terms of an iodide/amino group exchange as indicated by eq 10. Evidence for this interpretation is, inter alia, that the averaged $^{11}$B NMR signal is at *higher* field than any of the starting materials. $\delta(^{11}B)$ for BI$_4^-$ is reported at $-127.7$ ppm, and $\delta(^{11}B)$ for a tmpBI$^+$ cation is expected at $\sim$40 ppm. Therefore, the observed signal at $-10$ ppm is in accord with the suggested equilibrium.



$+ \ {}^*BI_3 \ \rightleftharpoons$



$+ \ BI_3 \quad (10)$



$+ \ {}^*BI_3 \ \rightleftharpoons$



$^*BI_4^- \quad (11)$
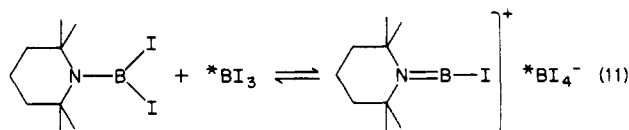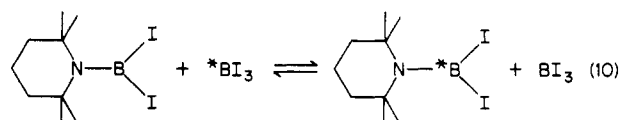
Reactions of this type can be monitored by using [10]B-labeled compounds, and these show that halogen transfer is much faster than tmp group transfer.[36] This situation can also be explained in terms of an intermediate, **35**. However, when reactions of type (12) are



**35**
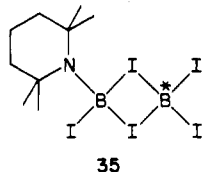
studied by ^{11}B NMR spectroscopy, signals for $BClBr_3^-$, $BCl_2Br_2^-$, and $BCl_3Br^-$ are easily detectable, and these provide very strong evidence for the existence of a (tetramethylpiperidino)haloborinium ion.[36]



(12)
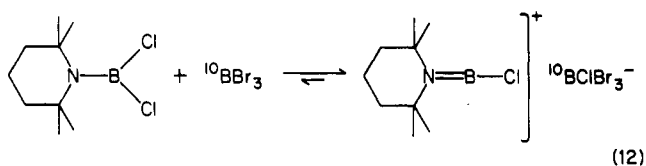
Two amino(organyl)boron(1+) cations have also been reported.[21] They were isolated as tetrachloroaluminates, obtained by chloride abstraction from R-(tmp)BCl (R = Me, Ph). Both salts are unstable at ambient temperature.

The highly conducting solutions of 1:1 mixtures of diphenylboron chloride and $AlCl_3$ in nitrobenzene or methyl ethyl ketone cited in section I were rationalized with the formation of a diphenylboron(1+) cation.[13] It was noted that diphenylboron chloride combines with $AgClO_4$ in nitrobenzene, nitromethane, or sulfolane with precipitation of AgCl and with formation of highly conducting solutions presumed to contain $[Ph_2B]ClO_4$. Similarities with the UV absorption spectra of diphenylmethyl bromide and $AlCl_3$ in the same solvents suggested the presence of solvated diphenylborinium cations. It was later shown that ^{1}H NMR data were in accord with a tetracoordinated diphenylboronium ion.[14] This interpretation contrasts sharply with the first report of an unsolvated $Ph_2B^+$ species.[37]

This interesting chemistry has been subsequently reinvestigated in our laboratory. Reactions of diphenylboron halides (Cl, Br) with aluminum trihalides in $CH_2Cl_2$ are very clearly complex.[38] Based upon ^{11}B NMR spectra no evidence for the formation of a $Ph_2B^+$ cation was found in solvents such as benzene or methylene chloride. BC bond cleavage is the preferred reaction which provides access to phenylboron dihalides,[38] detected in solution by ^{11}B NMR spectroscopy. However, Köster and Willemsen reported[16a] that 9-chloro-9-borafluorene reacts with $AlCl_3$ or $SbCl_5$ in $C_2H_2Cl_4$ solution. Dark blue solid compounds were obtained and described as 9-borafluorenium tetrachloroaluminates and hexachloroantimonates.[16b] The deep color of these materials does not exclude that stable radical cations are formed, because it has been shown that $AlCl_3$ in highly chlorinated hydrocarbons is capable of oxidizing organic materials if the binding energy of valence electrons is less than 7.9 eV.[40] Although He(I) PE spectra of 9-borafluorenes are not yet reported, it is to be expected that less energy than 7.9 eV is required for their ionization, and, therefore, oxidation of the 9-borafluorene system is not unlikely.[41]

## 2. Generation of Borenium Ions

A tetracoordinated boron atom is required for the synthesis of a borenium ion by boron–halogen bond heterolysis. Potential starting materials are, therefore, Lewis acid–base adducts of boron halides, which are abundant. However, it should be kept in mind that the halide acceptor necessary for inducing the BX heterolysis may not only break the boron halogen bond but also the donor acceptor bond. The two reactions (13) and (14) may compete with one another. Reactions of
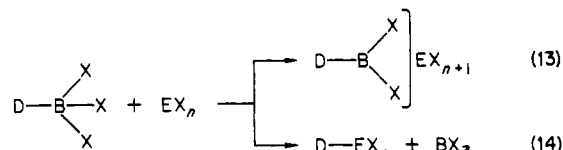


type (14) will dominate if the original donor–acceptor bond is weak, while a reaction according to (13) should be favored when the cation is stabilized by $\pi$-back-bonding as described in section I.

The latter principle has been nicely demonstrated by Ryschkewitsch and Wiggins.[12] They observed no reaction between $Me_3N \cdot BCl_3$ and $AlCl_3$ in $CH_2Cl_2$ in contrast to 4-pic$\cdot BCl_3$. NMR data and conductivity studies revealed the presence of an equilibrium, (15) $K_{eq}$ = 20 ± 3; at 25 °C. No salt has been isolated.
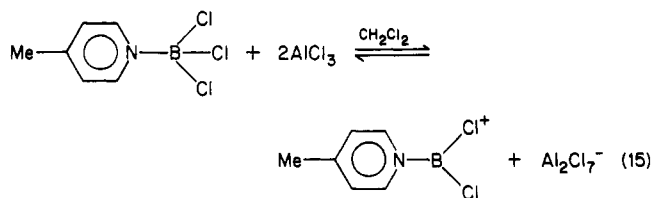


Pyridine or 2,6-lutidine adducts of dibutylboron chloride or 9-chloro-9-borabicyclo[3.3.1]nonane (9-Cl-9-BBN) react with $AlCl_3$ in $CH_2Cl_2$ solution according to eq 14 because the stability of the complexes is low due to the weak Lewis acidity of the borane derivatives and steric hindrance exerted by the lutidine.[42] If $GaCl_3$ is used as the halide acceptor, reaction 13 is observed in addition to (14) (ratio ~3:7) for the pyridine adduct of 9-Cl-9-BBN.[42] The pyridine adduct of diphenylboron chloride behaves similarly.[39] Reaction 13 proceeds quantitatively for the pyridine adduct of 9-chloro-9-borafluorene with $GaCl_3$ as halide acceptor. The red salt **36** can be isolated.[42] Similarly, the action of $AlCl_3$ on the acridine adduct of 9-chloro-9-borafluorene produces the dark red salt **37** besides some yellow acridine$\cdot AlCl_3$ and a third, orange component which has not been identified.[42] Unexpectedly a new type of bore-



**36**                    **37**
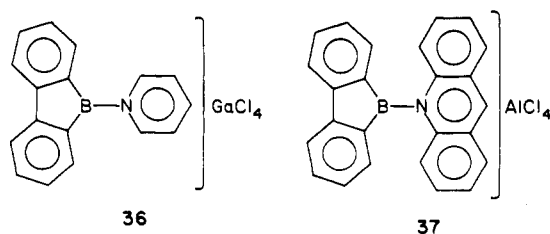
nium ion has been found by halide abstraction from the cyclic haloboration products of (tert-butylimino)-(2,2,6,6-tetramethylpiperidino)borane (**38**). Equation 16 describes the synthesis of the tetrabromoaluminate

**39.**[43] Similarly, phenylboron dichloride reacts with **38** to give a mixture of the two isomers **40** and **41**. On treatment with $AlCl_3$ in $CH_2Cl_2$ these produce only the salt **42** by boron–chlorine bond heterolysis.[43] Analogous reactions were performed by using $MeBBr_2$ and $AlBr_3$[43] or $EtBCl_2$ and $AlCl_3$.[44] The ease of formation of cations of type **39** and **42** is attributed to their electronic structure which resembles that of allyl cations.[43]
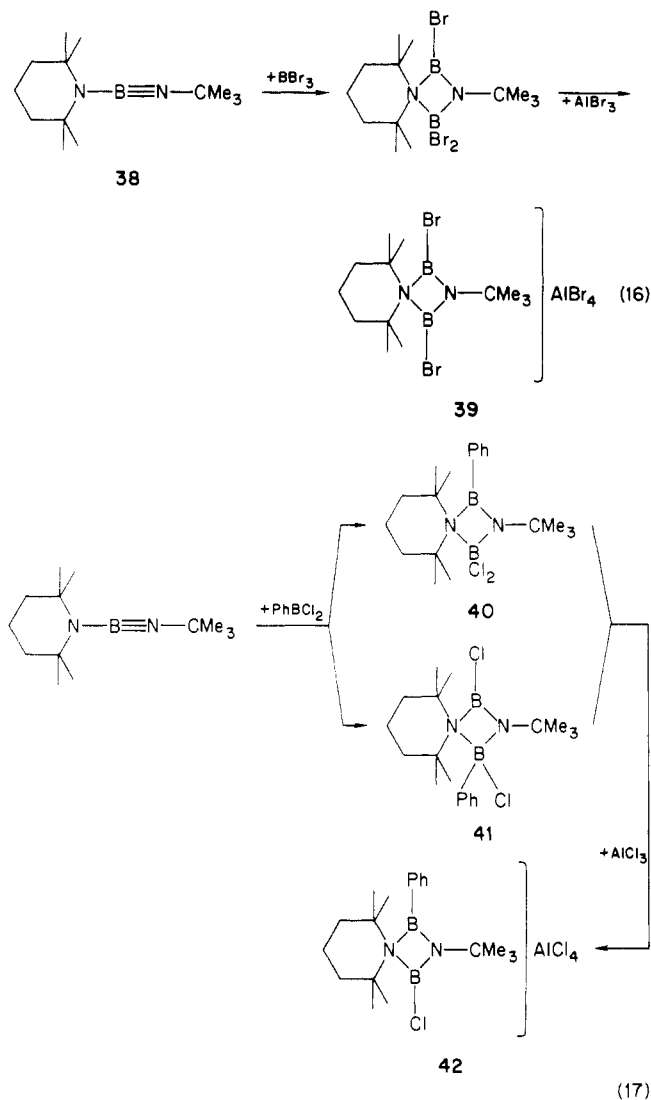


B. **Protic Attack of the Boron–Nitrogen Bond**

Diaminoborenium ions can be generated by proton addition to a BN bond of a tricoordinated aminoborane. Such a reaction, as outlined in eq 18, is most likely the first step in the protolytic cleavage of a BN bond.[45] The salts **43** and **44** have been suggested as structures for the products obtained from anhydrous HI and B-$(NMe_2)_3$.[9] However, apart from analysis of the prod-



ucts and the observation of a different stoichiometry for the reaction between HI and $B(NMe_2)_3$ as compared to $HCl/B(NMe_2)_3$, no convincing evidence for the existence of these ions has been presented. Repetition of this work showed that BN cleavage cannot be exclud-



ed.[46] However, if 2-(dialkylamino)-1,3-dimethyl-1,3,2-diazaboretidines, which can be considered as cyclic triaminoboranes, are treated with triflic acid, salts of a diazaboretidinium ion are obtained.[47]
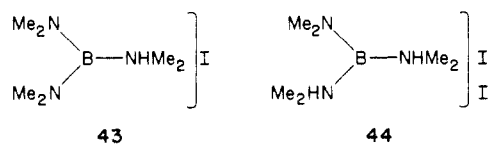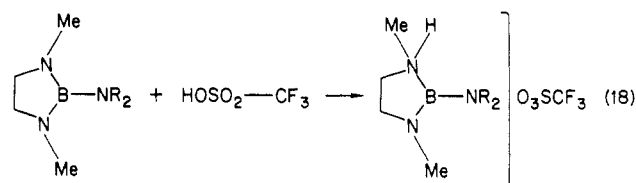
C. **Electrophilic Attack at Boron–Nitrogen Bonds**

(Dialkylamino)borinium salts should be readily accessible by addition of a suitable electrophile on the nitrogen atom of an iminoborane. Indeed, reactions of type (19) have been realized by using an aminoiminoborane and trimethylsilyl triflate or iodide.[48] $CH_3OS-$ $O_2CF_3$ produces a neutral bis(amino)((trifluoromethyl)sulfonyloxy)borane, because steric requirements allow the attack of the triflate ion on the boron center.[48]
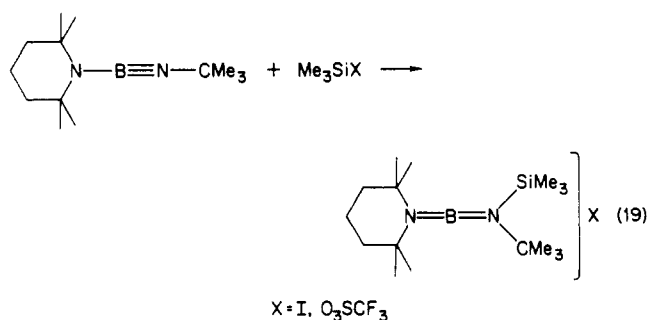


Many other compounds possessing Lewis acidic properties react similarly with the iminoborane **38** but not with formation of true salts but rather of adducts which can be regarded as "internal salts" **45**. Equation 20 summarizes some results, which will not be discussed here any further.[49] The only exception which seemed to lead to a true borinium ion involved $SnBr_4$. However, compound **46** could not be isolated.
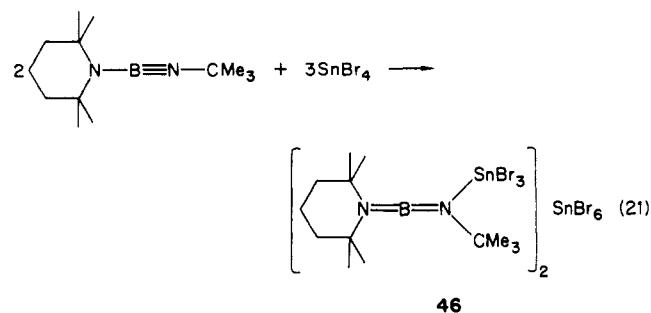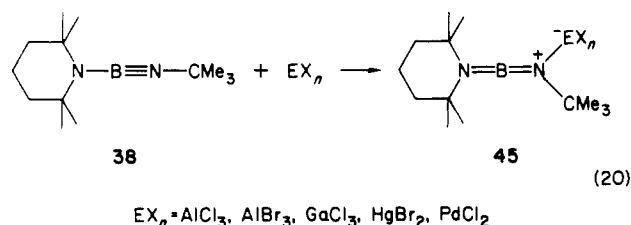


D. **Nucleophilic Displacements**

The best studied reactions in boron chemistry are those involving a base or a nucleophile and a tricoor-

dinated boron compound. Usually 1:1 addition compounds containing tetracoordinated boron are obtained. Furthermore, if an excess of pyridine is used, nucleophilic displacement of a halide ion can lead to bis-(pyridine)boronium salts.[3] However, it has recently been shown that a 1:1 reaction will not necessarily produce 1:1 acid–base adducts but, by nucleophilic displacement of a good anionic leaving group, also borenium ions.[22,47] Therefore, the two competing reactions (22) and (23) have to be considered besides the formation of [R$_2$BD$_2$]X.



$$(25)$$

**49**
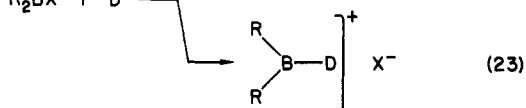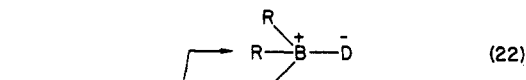
Reactions of 1,3-dimethyl-2-((trifluoromethyl)-sulfonyloxy)-1,3,2-diazaborolidine with pyridine, 2,6-lutidine, or diphenylamine (mole ratio 1:1) readily produce the corresponding 1,3,2-diazaborolidinium triflates.[47] The first two cations are described by the formula **47**, while the proton of the diphenylamine migrates to a ring nitrogen atom,[20] generating the cation **48**. Chloride is a much less favorable leaving group



**47**          **48**
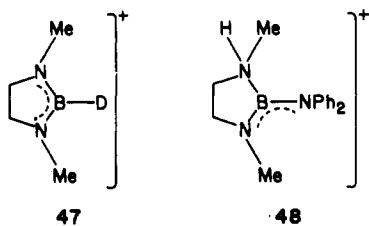
than triflate. It can, therefore, be understood that diethylamine, 2,6-lutidine, or triphenylphosphine will not displace a chloride ion from 2-chloro- or 2-bromo-1,3-dimethyl-1,3,2-diazaborolidine,[50] although pyridine is capable of doing so as shown in eq 24.[47,50] However,



$$(24)$$

X = Cl, Br
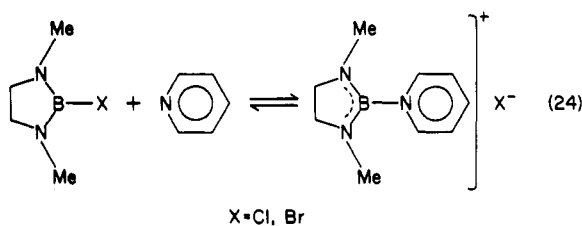
if the AlCl$_3$ adduct of this diazaborolidine is used, rapid formation of the diazaborolidinium tetrachloroaluminate **49** is observed by using 2,6-lutidine, diethylamine, or triphenylphosphine as a base. Obviously, the addition of AlCl$_3$ at a ring nitrogen atom renders the boron center more acidic and therefore favors the attack of a base (or nucleophile), generating a salt whose chloride ion then displaces the coordinated AlCl$_3$ with tetrachloroaluminate formation.[47] Equation 25 describes this sequence of reactions.

Nucleophilic displacements are also readily encountered with noncyclic bis(amino)boranes. Pyridine or 2,6-lutidine displace the triflato group from bis(diisopropylamino)boron triflate, and no bis(diisopropyl-

amino)bis(pyridine)boronium triflate is formed in the presence of excess pyridine (eq 26 and 27). However,
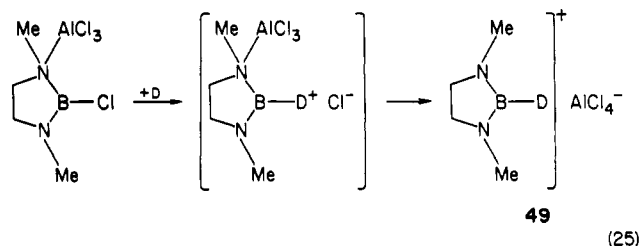


$$(26)$$



$$(27)$$

D = py, 2,6-lut
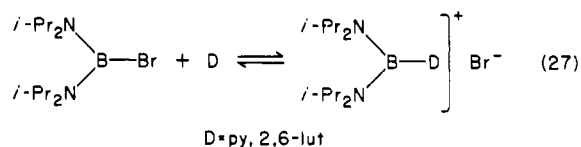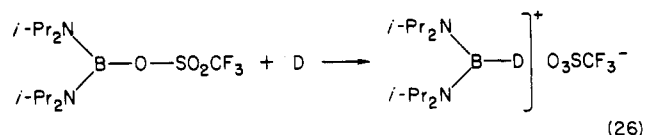
the broad ^{11}B NMR signal observed under these conditions indicate rapid pyridine exchange.[22] Only exchange equilibria are observed by NMR spectroscopy in the case of bis(diisopropylamino)boron bromide, and the CH$_2$Cl$_2$ solution shows only low conductivity. No reaction was observed between bis(diisopropylamino)-boron chloride and 2,6-lutidine.[22] This series of experiments convincingly demonstrates the importance of a good leaving group for borenium ion formation.

Competition between adduct and borenium ion formation has been studied also for a series of diorganylboron halides and triflates, employing pyridine and 2,6-lutidine as nucleophiles.[47] Lewis acid–base adducts were obtained from pyridine or 2,4-lutidine and dibutylboron triflate or 9-((trifluoromethyl)sulfonyloxy)-9-borabicyclo[3.3.1]nonane. In contrast 2,6-lutidine displaces the triflato group as shown in eq 28. This demonstrates that steric shielding is necessary for stabilizing the borenium cation.



$$(28)$$
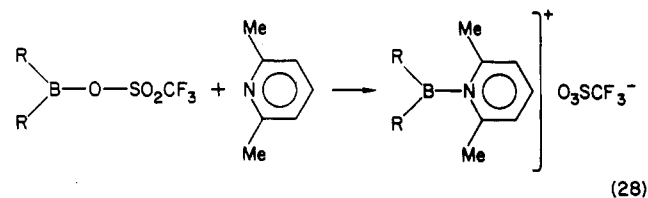
In contrast, 9-((trifluoromethyl)sulfonyloxy)- as well as 9-chloro-9-borafluorene gives 1:1 adducts not only with pyridine or 2,4-lutidine but also with 2,6-lutidine. Incorporation of the boron atom into a five-membered ring system is obviously insufficient to prevent the formation of a coordination compound.[47] As pointed out earlier, an appropriate acceptor is necessary to heterolytically break the bond to the electronegative substituent.[47]

A nucleophilic displacement reaction is also involved in the reaction of (tert-butylimino)(2,2,6,6-tetramethylpiperidino)borane with dialkylboron halides,[43,51] which proceeds according to eq 29. If we assume that organoboration occurs faster than haloboration the diborylamine **50** should be an intermediate. Intramolecular nucleophilic displacement of a halide would then
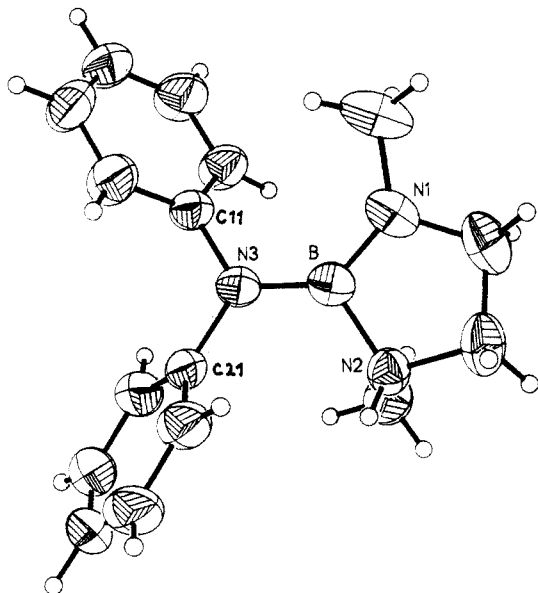
**Figure 1.** ORTEP plot of the 2-(diphenylamino)-1,3-dimethyl-1,3,2-diazaborolidinium ion **55**. Important parameters:[47] B–N1 = 1.386 (3) Å, B–N2 = 1.547 (3) Å, B–N3 = 1.412 (3) Å; N1–B–N2 = 106.1 (2)°, N1–B–N3 = 132.9 (2)°; N2–B–N3 = 120.7 (2)°; $\tau$(BN3C11C12/BN1N2N3) = 39°.

produce the final product. Diborylamines of type **50** are readily formed by combining the iminoborane **38** with $BR_3$.[23,24]



$$R = Me, Et; X = Cl, Br, I$$



**50**
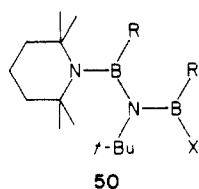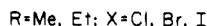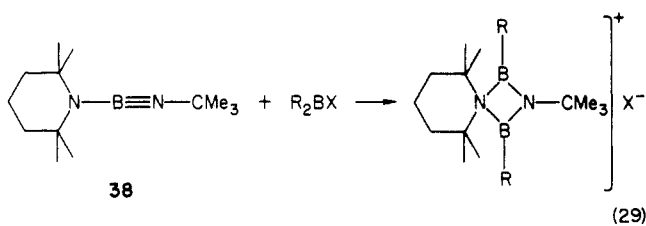
### E. Base Addition to Borinium Ions

A general route to borenium salts should be provided by the addition of a base to a borinium salt as described in eq 30. However, there may be severe steric re-



striction as demonstrated for $(tmp)_2B^+$ which does not add $NEt_3$[23] or pyridine.[24] Pyridine induces substituent exchange in $(Me_2N)_2BCl$ to give $B(NMe_2)_3$ and $Me_2NBCl_2 \cdot py$. If, however, $AlCl_3$ is first combined with $(Me_2N)_2BCl$ in $CH_2Cl_2$ and 1 mol of pyridine is subsequently added, the borenium salt **51** is formed quantitatively (eq 31).[22] $[(i\text{-}Pr_2N)_2B]X$ (X = $AlCl_4^-$, $AlBr_4^-$) behaves similarly[22] on adding pyridine or 2,6-lutidine. Reactions of this type will also be discussed in section VI.B.1.
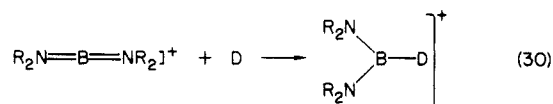


**51**
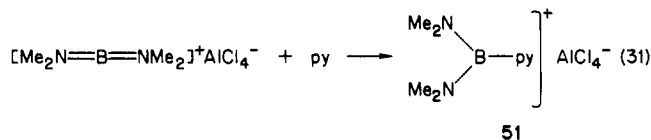
### F. Metathesis

Most of the reactions described in the previous sections produce borenium or borinium salts containing a complex anion. Attempts have been made to exchange these anions by metathesis. It is feasible that this method may generate borenium salts from coordination compounds as described by eq 32, which can be regarded as a metathetical reaction. Reactions of this type, using $KBPh_4$, $LiBPh_4$, $AgBPh_4$, or $AgPF_6$, have so far been unsuccessful. However, silver triflate converted the tetrabromoborate **52** into the tetrakis-((trifluoromethyl)sulfonyloxy)borate **53**, described by eq 33.[23,24]

$$R_2BX \cdot D + AgY \longrightarrow [R_2B \cdot D]Y + AgX \qquad (32)$$



**52**



**53**
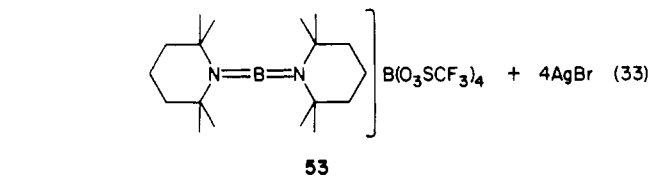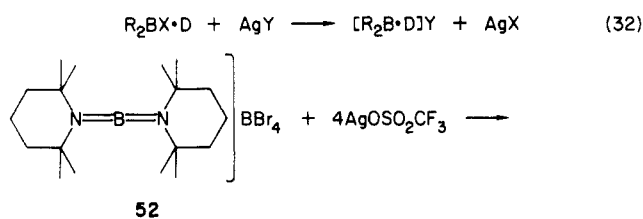
Similarly, $(tmp)_2BCl$ undergoes metathesis with Ag triflate to produce bis(tetramethylpiperidino)boron(1+) triflate in high yield (eq 34).[24] This, to our knowledge,
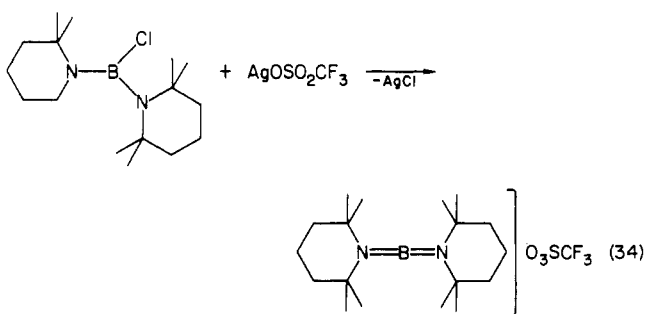


is the first example, in which a borane derivative is converted into a salt by metathesis with a concurrent decrease in coordination number at the boron center. The high steric potential of the tmp group is essential for this type of reaction, because $(i\text{-}Pr_2N)_2BCl$ or $(Me_2N)_2BCl$ readily give access to the corresponding bis(amino)boron triflate.[22]

### G. Other Methods

Since substituent exchange reactions are quite common in the chemistry of tri- and tetracoordinated mononuclear boron compounds, it is likely that—favorable conditions given—these proceed via cationic boron species. One such reaction is the bromination of tetraethylpyrazabole, and evidence has been presented that mono- mono- and dibromination proceeds via a
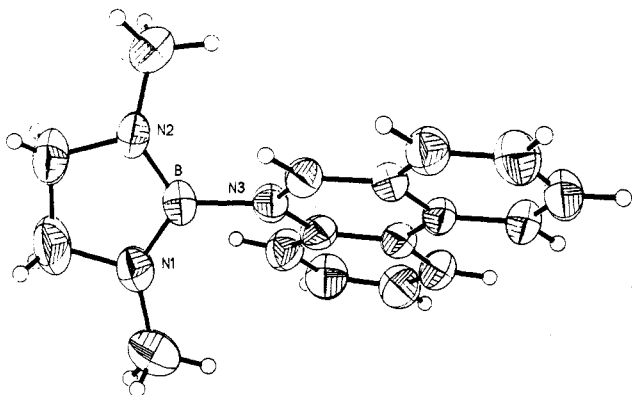
**Figure 2.** ORTEP plot of the 1,3-dimethyl-2-phenanthridin-5-yl-1,3,2-diazaborolidinium ion **56.** Important parameters:[53] B–N1 = 1.390 (5) Å, B–N2 = 1.379 (6) Å, B–N3 = 1.530 (6) Å; N1–B–N2 = 112.8 (4)°, N2–B–N3 = 122.6 (3)°, N1–B–N3 = 124.6 (4)°; $\tau$(phenanthridine plane/BN1N2N3) = 55.0°.

tricoordinated cation.[52] This type of reaction has been substantiated by using $GaCl_3$ as the electrophile. Under these conditions the cation of **54** is sufficiently stable in solution to allow the recording of $^{11}B$ and $^{13}C$ NMR spectra, which are in accord with the suggested structure for the cation.[29] No boron exchange is involved in this process.[52] The same mechanism was discussed for the stepwise bromination of pyrazabole with boron tribromide to 4,4,8,8-tetrabromopyrazabole. The first step is represented by eq 36, and **54a** is a suggested intermediate.



**54**

$$Et_2B \quad BEtBr \quad (35)$$



$$H_2B \quad BH_2 \ + \ ^{10}BBr_3 \ \longrightarrow \ H_2B \quad BHBr \ + \ ^{10}BHBr_2 \quad (36)$$



**54a**
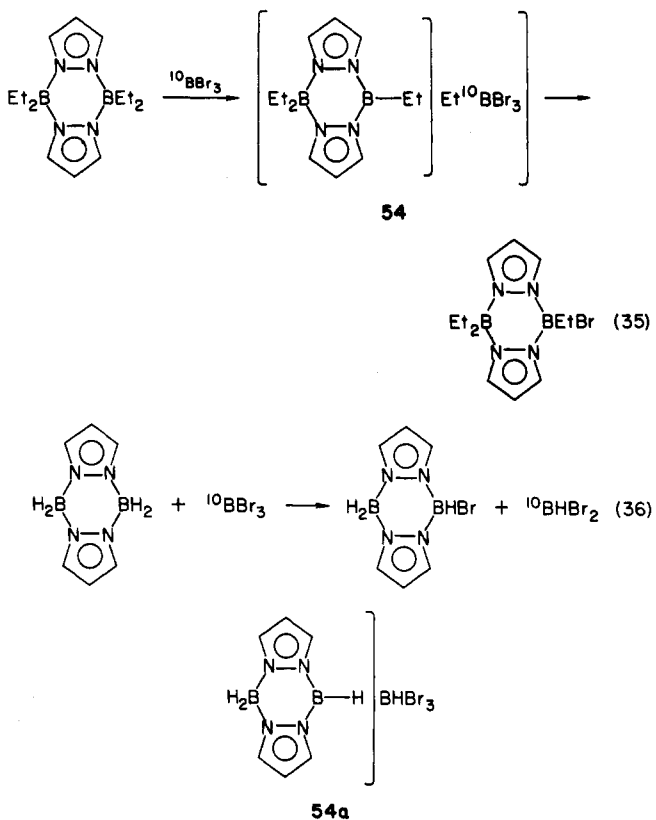
## III. Structures of Borinium and Borenium Ions

The preparative results would not be unambiguous, especially in the case of borenium ions, if X-ray structures were not available. Five structures have so far been published, and Figures 1–5 show ORTEP plots of the cations.
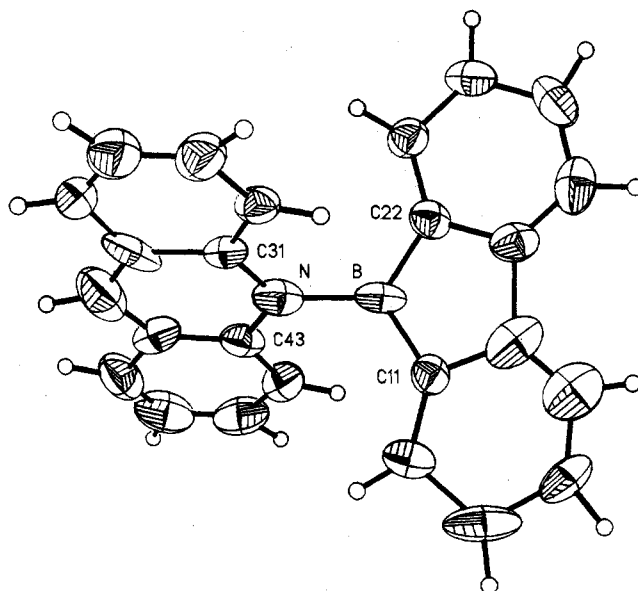


**Figure 3.** ORTEP plot of the acridin-9-yl-9-borafluorenium ion **57.** Important parameters:[42] B–N = 1.650 (11) Å, B–C11 = 1.450 (12) Å, B–C22 = 1.476 (13) Å; N–B–C11 = 123.2 (8)°, N–B–C22 = 121.6 (7)°, C11–B–C22 = 115.2 (7)°; $\tau$(acridine/BC11C22N) = 62°.
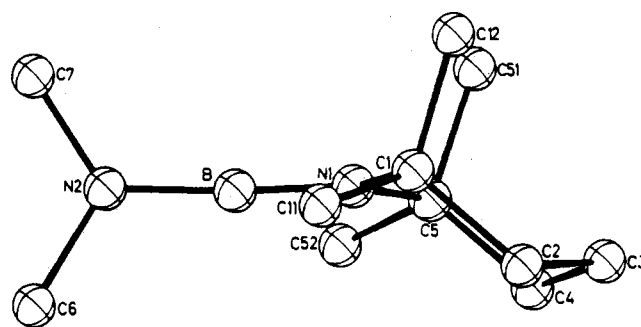


**Figure 4.** ORTEP plot of the (dimethylamino)(2,2,6,6-tetramethylpiperidino)borinium(1+) cation **58.** Important parameters:[21] B–N1 = 1.30 (4) Å, B–N2 = 1.42 (4) Å; N1–B–N2 = 176 (3)°; $\tau$(C1N1C5/C6N2C7) = 87°.
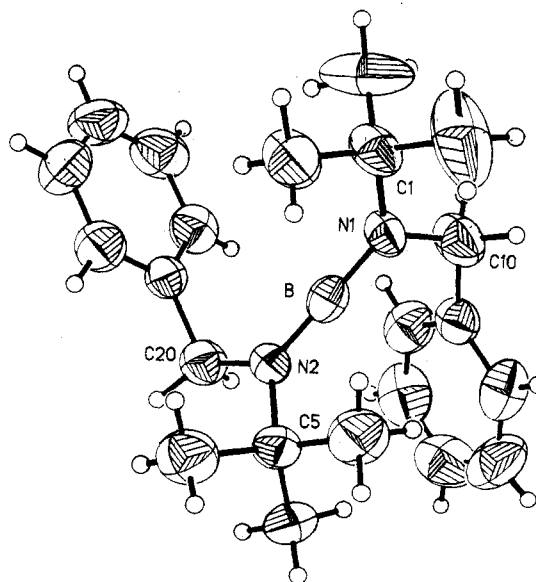


**Figure 5.** ORTEP plot of the bis(benzyl-*tert*-butylamino)borinium(1+) cation **59.** Important parameters:[54] B–N1 = 1.331 (5) Å, B–N2 = 1.334 (5) Å; N1–B–N2 = 179.5 (4)°; $\tau$(C1N1C10/C5N2C20) = 86.4°. For the sake of clarity H atoms have been omitted and only a part of the carbon atoms are represented by thermal ellipsoids (30% probability).

The crystal structures of the borenium ions 55,[47] 56,[53] and 57[42] clearly show the absence of the interaction with the anion. Consequently, the tricoordinated boron atoms are surrounded by three atoms generating a plane including the boron atom, which is sp²-hybridized. The BN bond to the ammonium type nitrogen in 55 is fairly long. The remaining endocyclic BN bond in this cation is 0.026 Å shorter than the exocyclic bond to the diphenylamino group. This shorter ring BN bond is a bit longer (0.03 Å) than found in the GaCl₃ adduct 20 (1.356 Å).[25] This reflects the fact that two BN bonds contribute to diminish the electron deficiency at the boron atom in 55, while only a single BN π-bond can be generated in 20. The diphenylamino group is twisted out of the BN₃ plane by 39° due to steric crowding, and this results in reduced π-overlap to the exocyclic amino group.

The structure of 56 is closely related to the structure of 55, the main difference being that the two endocyclic BN bonds are now expected to be equivalent. This is indeed the case (within experimental error), and these two bonds are not very much longer on average than the shortest BN bond in 55. The structure shows, however, a fairly long BN bond to the phenanthridine molecule which is twisted out of the diazaborolidine plane by 55°, and this considerably weakens a possible BN π-interaction.

This conclusion is substantiated by comparison with the BN bond length in 57: 1.650 (11) Å can be considered a fairly long BN bond, and it is, to our knowledge, the longest BN bond reported.[42] This indicates weak bonding of the acridine molecule to the borafluorenium ion, the result of the strongly twisted planes of these two molecular moieties. The borafluorenium ion contains quite short BC bonds, suggesting considerable BC π-bonding. The bonding situation in the central BC₄ ring of this system is very similar to that of the cyclopentadienyl cation.[55]
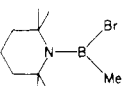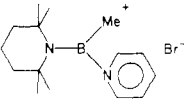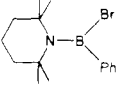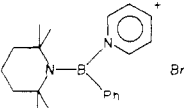
The prediction that bis(dialkylamino)borinium ions are isoelectronic and isostructural with allenes has been proved by two X-ray structures. The R value obtained for [(tmp)BNMe₂]AlBr₄ is only 0.104, and all bond lengths are associated with fairly high standard deviations. The two rather different BN bond lengths may therefore be artefacts. Although an in depth discussion of bonding has to be excluded for this reason, the topology of the cation clearly shows a linear NBN skeleton and almost perpendicular C₂N groups. In contrast, the structure of [(PhCH₂(Me₃C)N)₂B]AlCl₄[54] refined to R = 0.078. The two BN bonds in this cation are equally long, and their mean value of 1.332 (3) Å is very close to the 1.325 Å calculated for (Me₂N)₂B⁺ by the STO-3G method.[21] This bond length corresponds with the CC double bond. Nevertheless, in spite of the equal numeric numbers, the two systems cannot directly be compared with one another, because two sp² carbon atoms contribute to the bonding in olefins, while a sp-hybridized boron atom and a sp²-hybridized nitrogen form the BN bond in the diaminoborinium ions.

## IV. Spectroscopic Properties

### A. IR Spectra

The tricoordinated borenium ions structurally re-

**TABLE IV. Some IR Data for Aminoboron Bromides and Their (Pyridine)borenium Ions (cm⁻¹)**

| | $\nu$(BN) | $\nu$(BBr) |
|---|---|---|
| | 1380, 1410 | 492 |
| | 1430, 1460 | |
| | 1385, 1420 | 510 |
| | 1440, 1470 | |

semble bis(amino)- or monoaminoboranes. Comparable molecules are shown in 60–63. Therefore the IR
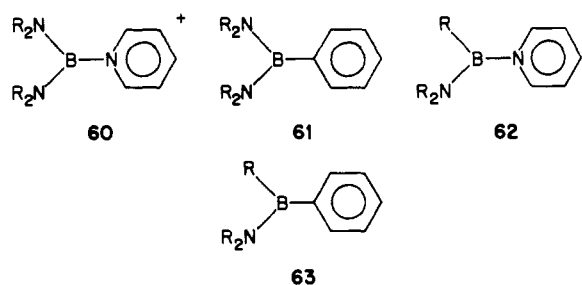
spectra should be similar, e.g., the bis(dialkylamino)-(pyridine)borenium ions should be comparable to bis-(dialkylamino)phenylboranes. Indeed, the bands attributable to BN vibrations are found in the same frequency range as for aminoboranes.[22] Table IV lists some representative data. It therefore appears that cation formation is accompanied by an increase in the BN stretching frequency. However, this cannot be taken as unequivocal evidence for stronger BN bonding in the borenium ions because coupling between the two BN vibrations in the cation has to be taken into account. An interesting additional conclusion can be drawn from the infrared data. Although Davidson and Phillips[56] assigned bands at 331 and 361 cm⁻¹ to the $\nu_{as}$(BBr) stretching vibrations, the alternative is that bands at 492 and 510 cm⁻¹ listed in Table IV result from this group in aminobromoboranes. These bands are absent in the IR spectra of (pyridine)borenium ions. Furthermore, no bands of suitable intensity are present in the range between 500 and 300 cm⁻¹, leading evidence that borenium salts are present.[22]

A much more dramatic change in the frequencies of the BN vibrations is observed when borinium ions are formed, in accord with their allenic-type structure.[20,21] In addition, bands typical of free AlX₄⁻ or GaX₄⁻ anions are also observed, thus ascertaining the proposed structures.[20,21] Some relevant data are summarized in Table I. The IR spectra of all diaminoborinium salts show strong bands in the region of 1800–1900 cm⁻¹. Although one expects only two IR bands for $\nu_{as}$(¹⁰BN₂) and $\nu_{as}$(¹¹BN₂) of a linear NBN skeleton, the spectra often contain up to four bands. A Fermi resonance has been offered as a source of the additional bands;[21]

however, an unambiguous rationale has yet to be provided. While there is little variation in both intensity and frequency of IR bands for bis(amino)borinium ions the (tmp)BOSi-t-Bu$_3$ cation[22] definitely shows a high frequency shift; this indicates a strong contribution of the BO vibration to $\nu$(NBO) which is probably due to a very strong BO bond.[22]

## B. NMR Spectra

Borenium and borinium ion formation has been monitored predominantly by NMR methods, and for most compounds $^1$H, $^{11}$B, $^{13}$C, $^{14}$N, $^{19}$F, $^{27}$Al, $^{29}$Si, or $^{77}$Ga data have been recorded. Only some features of the boron and aluminum resonances will be discussed here, although $^{13}$C NMR data are also very helpful for structural assignments.[20,21,22,23,57] Relevant data are collected in Tables I and II.

### 1. NMR Data of Borinium Salts

Halide abstraction from a bis(amino)boron halide is associated with a downfield shift of the $^{11}$B NMR signal by 5–8 ppm.[20-22] A $\delta$($^{11}$B) range of 35–38 ppm is typical for bis(amino)borinium ions as is the increased line width which covers typically 400–800 Hz. This increase in width is associated with an increase in the field gradient and a resulting rapid relaxation.[22,57] Silyl substitution at the nitrogen atoms deshields the boron atom, indicating a further decrease in electron density at the boron atom.[33] This interpretation is substantiated by a low frequency shift of $\nu_{as}$(BN$_2$). Anions have no marked influence on $\delta$($^{11}$B), as expected for separated ions.

Substitution of one R$_2$N group for the t-Bu$_3$SiO group results in a high field shift of the $^{11}$B resonance. The better shielding is not unexpected for the exchange of R$_2$N vs. the substituent RO.[58] However, the observed high field shift is more pronounced than in aminoalkoxyboranes, and this can be taken as evidence that the RO moiety contributes strongly to the electron density at boron.

In contrast, the boron atom in aminoorganylborinium salts is strongly deshielded.[22] This is in agreement with the (formal) electron sextet structure for these cations.

The diaminoborinium tetrahaloborates exhibit a second narrow $^{11}$B NMR signal for the anionic species.[24] However, if the tetrahaloborate anion exchanges a halide ion with the cation, the $^{11}$B NMR signals are observed at higher frequencies than for free BX$_3$. In case of rapid exchange only a single averaged signal can be recorded. Typical examples are the reactions of (tmp)B(Br)NMe$_2$ with BBr$_3$,[23] (tmp)B(Cl)NEt$_2$ and BCl$_3$,[32] or (tmp)B(Br)R with BBr$_3$.[21,22,57] In contrast, these aminoboranes form cations on treatment with AlX$_3$ due to its increased halide acceptor strength. The formation of tetrahaloaluminates is indicated by strong $^{27}$Al NMR signals typical for AlCl$_4^-$ or AlBr$_4^-$.[35] If (tmp)B(Br)NEt$_2$ is treated with AlCl$_3$, the full series of $^{27}$Al NMR signals for AlCl$_{4-n}$Br$_n^-$ is observed.[21]

$^{27}$Al NMR spectroscopy is an even better method than $^{11}$B NMR spectroscopy for testing the borinium ion formation,[20,21] both by the chemical shift and, more importantly, by the line width. If the width found falls in the range of 15–25 Hz, free AlX$_4^-$ is present. Line widths up to ~80 Hz indicate weak interactions with the borinium ion (e.g., in the case of [(tmp)BMe]AlBr$_4$.

### 2. NMR Data of Borenium Salts

Inspection of Table II demonstrates that the diaminoborenium salts show $\delta$($^{11}$B) values typically in the range of 25–30 ppm. This corresponds to that of tris-(amino)boranes and bis(amino)boron halides (24–32 ppm).[58] Therefore, only small changes in $\delta$($^{11}$B) are observed when bis(amino)boranes are combined, e.g., with pyridine to generate a borenium ion. However, the reaction is always associated with a considerable increase of the $^{11}$B line width.[22]

Chemical shifts in the 25–30 ppm range were also observed on adding 2 mol of a nitrogen base to a solution of Me$_2$N=B=NMe$_2^+$. This shift was taken as evidence for the formation of a tetracoordinated borenium salt.[20] The $\delta$($^{11}$B) values reported for these CH$_2$Cl$_2$ solutions fall, however, into the range for tricoordination at the boron atom. Therefore, it is more likely that borenium ions of type (Me$_2$N)$_2$BD$^+$ are present in solution.[23] This is ascertained not only by isolation of salts and by the X-ray structure of representative compounds[47] but also by the coherent NMR data of multinuclear NMR studies.[23,47] If indeed stable ions of type [(Me$_2$N)$_2$BD$_2$]$^+$ (D = NH$_3$, Me$_2$NH, 0.5 en) were formed, an $^{11}$B NMR signal in the $\delta$ range observed for 64[22] (2.2 ppm) should result. Such a conclusion seems



64                    65
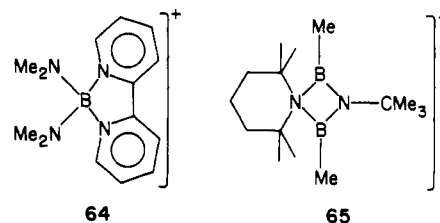
to be justified because species carrying only nitrogen substituents are compared. A much larger variation of $^{11}$B chemical shifts has been observed for cyclic borenium salts.[43] Nevertheless, it is interesting to note that the $\delta$($^{11}$B) values correspond closely to those of the comparable monoaminoboranes. Thus the boron atoms in 65 show practically the same shielding as found for Me$_2$BNMe$_2$[58] or 39 as observed for Br$_2$BNMe$_2$.[58] This indicates strong $\pi$-bonding between boron and nitrogen; a conclusion that should be further confirmed, e.g., by an X-ray structure determination.

$^{11}$B NMR spectroscopy proved also very helpful in following the borenium ion formation according to eq 17 or 37 by halide abstraction. The initial mixture in CH$_2$Cl$_2$ shows several $^{11}$B NMR signals. After halide abstraction, e.g., with AlCl$_3$ only two boron resonances in the tricoordinated region are observed.[51]



$$ (37) $$
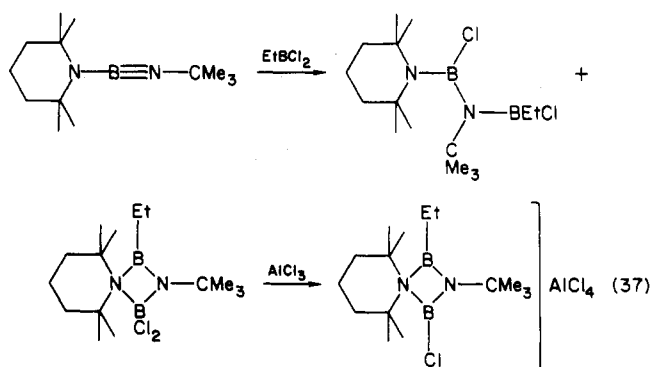
## C. Dynamic Processes

Very few detailed studies on dynamic processes involving borinium and borenium ions are presently available. Considering the short BN bond lengths observed for the bis(benzyl-*tert*-butylamino)borinium ion, one would expect a higher barrier to rotation than in monoaminoboranes. Temperature-dependent $^1$H NMR spectra of this cation led to a lower limit of $\Delta E_A = 85$ kJ/mol,[54] which is in the range observed for monoaminoboranes. However, since collapse of the AB pattern for the $CH_2$ groups in this cation has not been fully achieved, the true value may be higher by 10–15 kJ/mol, and this, then, would be in accord with a higher BN bond strength. On the other hand, a barrier to rotation of $\Delta E_A = 92$ kJ/mol has been calculated[21] for $Me_2N=B=NMe_2^+$.

Rapid proton migration has been observed for the cyclic borenium ion **66**; only one signal each for the exocyclic and endocyclic MeN groups[47] were recorded in $CH_2Cl_2$ solutions even at –60 °C. Two other types of dynamic processes, observed by means of $^{11}$B NMR spectroscopy, are described by eq 38 and 39.[23,42] An equilibrium of type (39) exists for $[Bu_2B-2,6-lut]O_3SCF_3$ and $[9-BBN-2,6-lut]O_3SCF_3$,[42] while an equilibrium of type (38) is observed for reactions of diphenylboron triflate with 2,4-lutidine and 2,6-lutidine.[42]



**66**



$$(38)$$



$$(39)$$

## V. Theoretical Aspects

Borinium ions $BR_2^+$ carrying a wide range of substituents R have been observed in the gas phase. They often appear as very stable ions in the fragmentation process of the parent ion $BR_3^+$ in mass spectrometric investigations.

The smallest possible borinium ion is the dihydrido species $BH_2^+$. Its formation according to eq 40 is unfavorable, and an energy of 12.0–12.5 eV is required for this process.[59] The energy needed cannot be provided
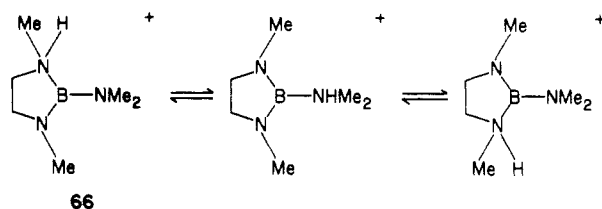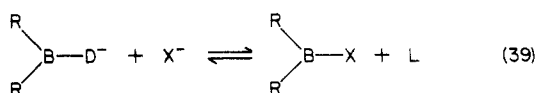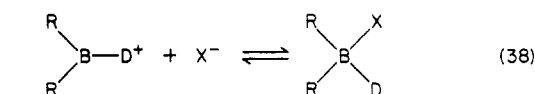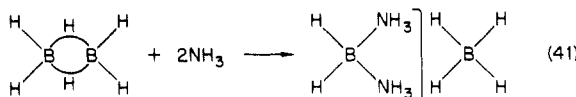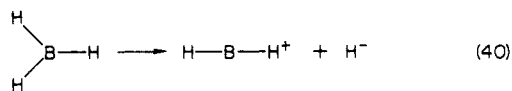


$$(40)$$



$$(41)$$

by adding a ligand D to produce $BH_2 \cdot D^+$, and consequently no such borenium ion has yet been prepared. If, however, 2 mol of D are added to $BH_2^+$ and $H^-$ is complexed by $BH_3$, then heterolysis is a possible and energetically feasible route (see eq 41).[2]

**TABLE V. Calculated BH Distances (Å) and Total Energies (au) for $BH_2^+$.**

| | method | | |
|---|---|---|---|
| | UHF/STO-3G[8] | UHF/4-31G[8] | IEPA[60] |
| $d_{B-H}$ | 1.187 | 1.162 | 1.174 |
| total energy | -25.174 43 | -25.432 88 | |

Relevant molecular data of $BH_2^+$ obtained by three different MO methods are summarized in Table V. Its ground-state structure is $^1\Sigma_g^+$, and a $D_{\infty h}$ point-group symmetry is assumed.[60] Two different unrestricted Hartree–Fock calculations[8] gave good agreement with BH distances calculated by the IEPA method[60] (extensive basis set with inclusion of correlation). Total energies calculated by various methods comprise values between –25.174 and –25.743 au.[8] For other data see reference 61. Calculations have also been performed for the borinium ions $BF_2^+$, $BFCl^+$, and $BCl_2^+$.[62] These cations should be linear like $BH_2^+$, and they also possess a $^1\Sigma_g^+$ electronic ground state.[63] Calculated bond lengths[64] are 1.31 Å for $BF_2^+$ and 1.74 Å for $BCl_2^+$. According to these data the BF bond in the difluoroborinium ion would correspond with the BX bond length in $BF_3$ (1.3131 (11) Å)[64] and $BCl_3$ (1.7421 (44) Å).[65]

HMO theory predicts that the diphenylborinium ion of point-group symmetry $C_{2h}$[15] is less stable than the uncoordinated 9-borafluorenium ion **16**. More recent calculations using the STO-3G method on the diphenylborinium ion **17** of $D_{2d}$ point-group symmetry show that this conformation is more stable by 3.1 kcal/mol than the $D_{2h}$ conformation **15**.[21] This is an astonishing small energy difference considering that only *one* p orbital of boron is involved in $\pi$-bonding in **15** in contrast to *two* in **17**. The better stability of the 9-borafluorenium ion **16** as compared to **15** is due to the incorporation of the boron atom into a delocalized $\pi$-electron system.[15] However, it should be noted that the geometry used in the calculations, especially the BC bond distance, has not been optimized.

A more extensive series of MO calculations using the STO-3G method[21] produced the results shown in Table VI. The energies listed refer to the isodesmic reaction (42), negative values corresponding to a stabilization of

$$X-H + H_3C-R \rightleftharpoons X-R + H_3C-H \qquad (42)$$
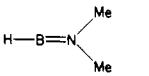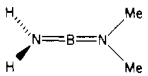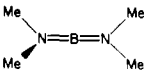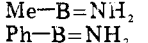
the system X by the substituent R. Me is the standard in this system. The data reveal that stability increases in the series R = H < Me < Ph < $NH_2$ < $NMe_2$. The linear arrangement, e.g., presence of sp-hybridized boron atoms, is the preferred configuration of the borinium ions,[21] and allenic type conformations of symmetry $D_{2d}$ are more stable than linear conformations of symmetry $D_{2h}$ (18 kcal/mol for $H_2N=B=NH_2^+$ and 22 kcal/mol for $Me_2N=B=NMe_2^+$[21]).

BN bond lengths should be shorter in aminoborinium ions than in monoaminoboranes. The BN bond length calculated for $(Me_2N)_2B^+$ is in excellent agreement with that found for **59**.[54]

The calculated charge densities for the borinium ions clearly show that the boron atom carries a positive charge varying from +0.613 unit for $HB=NH_2^+$ to +0.725 in $MeB=NMe_2^+$, and this charge is considerably higher than in neutral aminoboranes.[21] It should be noted that the polarity of the BN $\sigma$-bond is opposite to the polarity of the BN $\pi$-bond which transfers elec-

Table VI. Calculated STO-3G Total Energies $E$ (au) for Geometry-Optimized Structures RX and $\Delta E$ Values (kcal/mol) for the Isodesmic Reaction (42).[21]  Calculated Bond Length and Charge at the Boron Atom (in e Units)

| X | | R | | | | |
|---|---|---|---|---|---|---|
| | | H | Me | Ph | NH₂ | NMe₂ |
| BH⁺ | $E$ | −25.174 43 | −63.816 78 | −252.022 81 | −79.629 55 | −156.807 18 |
| | $\Delta E$ | 0 | −40 | −63 | −104 | −116 |
| BNH₂⁺ | $E$ | −79.629 55 | −118.254 18 | −306.448 77 | −134.054 74 | −211.224 05 |
| | $\Delta E$ | 0 | −26 | −45 | −85 | −95 |
| BNMe₂⁺ | $E$ | −156.807 19 | −195.426 54 | −383.616 59 | −211.224 05 | −288.390 77 |
| | $\Delta E$ | 0 | −23 | −39 | −80 | −86 |

| cation | d(BN), Å | q | cation | d(BN), Å | q |
|---|---|---|---|---|---|
| H—B=N(Me)(Me) | 1.306 | 0.613 | H(H)N=B=N(Me)(Me) | 1.330 (NH₂) 1.321 (NMe₂) | 0.693 |
| (Me)(Me)N=B=N(Me)(Me) | 1.325 | 0.650 | Me—B=NH₂ Ph—B=NH₂ | 1.322 1.327 | 0.725 0.638 |

tron density from nitrogen to boron.

The CH₃ group stabilizes the cation MeB=NH₂⁺ better than a comparable carbenium ion due to increased hyperconjugation. This is made possible by the boron atom which supplies two p orbitals for this interaction.[21] Furthermore, it has been shown that there is a striking analogy for the heterolysis reactions 43 and 44. The electron densities at the phenyl substituents
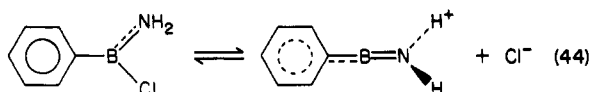


change for both compounds by about the same amount during this process. This is experimentally verified by appropriate changes in $\delta(^{31}C)$ for the ipso and para carbon atoms of the phenyl groups.[21]

## VI.  Reactions of Borinium and Borenium Salts

The borinium and borenium ions are coordinatively unsaturated. This and the positive charge makes them a stronger acid and electrophile as compared to similar neutral species. Nucleophilic attack of reagents on the boron atom should, therefore, be characteristic for these classes of compounds, and reported reactions are generalized by eq 45–48.

$$R_2B^+ + D \rightarrow R_2BD^+ \quad (45)$$

$$R_2BD^+ + D \rightarrow R_2BD_2^+ \quad (46)$$

$$R_2B^+ + R^- \rightarrow R_3B \quad (47)$$

$$R_2BD^+ + R^- \rightarrow R_3B \cdot D \quad (48)$$
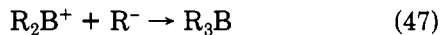
### A.  Thermal Stability

Although data reporting the thermal stability of borinium ions are only qualitative and, hence, thermodynamic and kinetic stabilities are difficult to discern, it appears that borinium salts are preferably kinetically stabilized.

The most stable salts containing borinium ions are those of the (tmp)₂B⁺ cation. Melting points are fairly high (see Table I), and decomposition of the tetrahalometalates is usually only observed on melting.[21,22,24]

R₂N(tmp)B halometalates are also fairly stable,[21,22,24] and in the case of (tmp)B(NEt₂)⁺ the tetrabromoaluminate[24] is definitely more stable than the tetrachloroaluminate[20] (decomposition slowly at ~50 °C). Very slow decomposition of [(tmp)BMe]AlCl₄ and [(tmp)BPh]AlCl₄ was observed in solution at −30 °C, although the solid salts can be isolated. The latter two deliquesce at ambient temperature to a red oily material.[21]

Trimethylsilyl halides are formed on heating ((trimethylsilyl)amino)borinium tetrahaloborates;[33] but again, no quantitative data are available in contrast to the thermal decomposition of [(tmp)BN(CMe₃)SiMe₃]I which quantitatively splits off Me₃SiI at 120 °C in a high vacuum as shown in eq 49.[68]  Although (2,2,6,6-



$$2 Me_3SiI \quad (49)$$
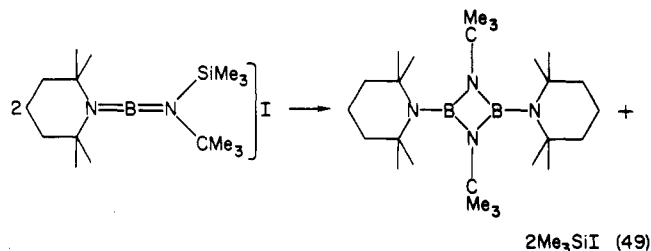
tetramethylpiperidino)boron dihalides are isomeric to bis(2,2,6,6-tetramethylpiperidino)boron(1+) tetrahaloborates, no conversion of these isomers in any of the two directions as shown in eq 50 have been observed.[23,24]



$$X = F, Cl, O_3SCF_3$$
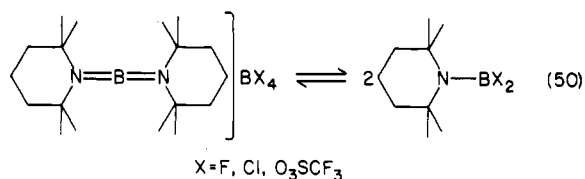
### B.  Reactions with Neutral Donor Molecules

#### 1.  Borinium Salts

Reactions of the type described in eq 45 lead to borenium ions and have already been discussed in section II.E. Salts of the (tmp)₂B⁺ ion do not react with pyridine, dimethylamine, and ammonia[23] due to the sterically shielded boron atom. In contrast, (i-Pr₂N)₂B⁺ readily adds pyridine and even 2,6-lutidine furnishing borenium salts.[22]  However, (i-Pr₂N)₂BCl is not attacked by these bases,[22] demonstrating that the borinium ion is a much stronger acid. Similarly, the unstable salt

$[(Me_2N)_2B]AlCl_4$ reacts readily with pyridine, and only a 1:1 reaction occurs even in the presence of excess pyridine as shown in eq 51.[20,22] $\alpha,\alpha'$-Bipyridyl adds to $(Me_2N)_2B^+$ to yield the red cation **64**.[20,22,68] $(Me_2N)_2B$-$(py)^+$ and $(Me_2N)_2B(bpy)^+$ are easily discernible by their [11]B chemical shifts (25.7 and 2.2 ppm, respectively[22]). ^{11}B NMR signals in the range of 25.9–27.7 ppm are reported, when 2 molar equiv of a base ($NH_3$, $HNMe_2$, $H_2NCH_2CH_2NH_2$, $PPh_3$) were allowed to react with a $CH_2Cl_2$ solution of $[(Me_2N)_2B]AlCl_4$.[20] Therefore, tricoordinated borenium salts are formed in these reactions[22] but not tetracoordinated boronium salts.[20]

$$[R_2N\!\!=\!\!B\!\!=\!\!NR_2]AlCl_4 \ + \ D \ \longrightarrow \ \begin{bmatrix} R_2N \\ B-D \\ R_2N \end{bmatrix} AlCl_4 \quad (51)$$

R=/-Pr, Me, D=py, 2,6-lut

$$[Me_2N\!\!=\!\!B\!\!=\!\!NMe_2]^+ \ + \ bpy \ \longrightarrow \quad (52)$$

**64**

Base attack has also been studied by using $[(tmp)-BN(CMe_3)SiMe_3]I$, **67**, as a model compound because the anion cannot compete with the cation in nucleophilic reaction as can $AlCl_4^-$ or $GaCl_4^-$.[68] Diethylamine reacts according to eq 53 by cleavage of the SiN bond



(53)

and with formation of a tris(amino)borane. The stoichiometry of eq 53 was also observed in 1:1 reactions. It is very likely that the first step in this reaction leads to the borenium ion **68**. The inductive effect of the ammonium-type nitrogen should increase the Lewis acidity of the $Me_3Si$ group which is then attacked by the amine, followed by HI elimination from **69** by the base. This route is substantiated by the observation that $NH_3$ forms an unstable borenium salt **70**, while an excess of $NH_3$ initiates a reaction analogous to (53). On the other hand, pyridine adds readily to **67** giving access to the salt **71**.[50] A behavior similar to the salt **67** has been observed for $[(tmp)BMe]AlBr_4$.[50] Pyridine adds in a 1:1 molar ration: the salt **72** can be isolated. Triethylamine is too bulky to attack at the boron center



**70**          **71**

**72**

of this borinium salt but displaces a bromide ion from the tetrabromoaluminate which attacks the borinium ion. The result of this reaction is described by eq 54.



$Et_3N\cdot AlBr_3$  (54)

^{11}B NMR spectroscopy did not prove unambiguously the formation of the borenium salt $(tmp)B(THF)Me^+$ from addition of 1 mol of THF to a $[(tmp)BMe][AlBr_4]$ solution in $CH_2Cl_2$ at –60 °C. When an excess of THF is used, fairly rapid ether cleavage occurs as shown in eq 55.[50]



(55)

## 2. Borenium Salts

The acid–base chemistry of borenium salts has not yet been studied in much detail. It appears that base exchange as depicted in eq 56 involving a boronium ion is rather general. Although no boronium salt has been isolated, $\alpha,\alpha'$-bipyridyl displaces pyridine from bis(amino)(pyridine)borenium salts as described in eq 57.[51] Addition of an excess of $NMe_3$ to a $CH_2Cl_2$ solution of $[4\text{-pic}\cdot BCl_2]Al_2Cl_7$ produces the boronium salt, which was isolated as the hexafluorophosphate.[12] Reaction 58 was taken as chemical evidence for the formation of the borenium ion in question, because the neutral adduct $Cl_3B\cdot4\text{-pic}$ will not add $NMe_3$.

## C. Reactions with Anionic Donor Molecules

### 1. Borinium Salts

Anion attack on borinium ions should produce neutral borane derivatives, as outlined in the general eq 47. Since salts of borinium ions are accessible only if bulky anions of low nucleophilicity are present, it appears that these salts will only be attacked at the boron center if

$$\text{(56)}$$



$$\text{(57)}$$



$$\text{(58)}$$

the anion is rather small. This has been demonstrated for reaction 59, where the fluoride ion produces $(tmp)_2BF$. In contrast, $[Et_4N]Cl$ does not attack the tetrabromoborate **73** at the boron center but exchanges halide ions with the $BBr_4^-$ anion, while no reaction is observed by using $[Et_4N]Br$.[24] Obviously higher tem-



$$\text{(59)}$$



**73**



$$\text{(60)}$$





$$\text{(61)}$$
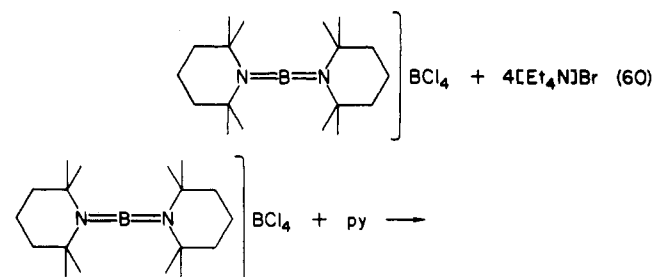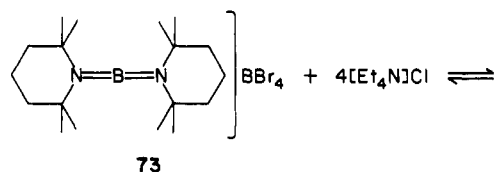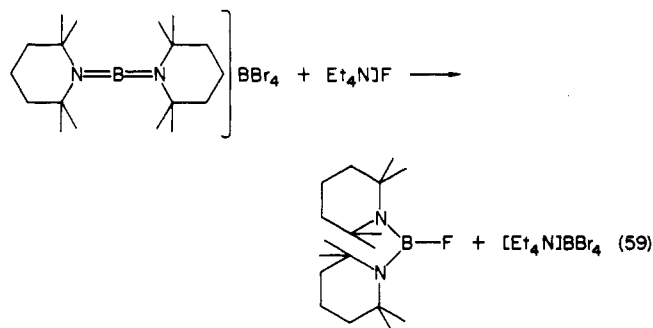
peratures are required to induce chloride attack on $(tmp)_2B^+$ because $[(tmp)_2B]BCl_4$ produces $(tmp)_2BCl$ in boiling pyridine, and the reaction is described by eq 61.[24] $[(tmp)_2B]BBr_4$ will not react similarly under the

same conditions, and this suggests that $(tmp)_2BBr$ may not exist in this form but rather as $[(tmp)_2B]Br$.[24] $[tmpBMe]AlBr_4$ reacts with Li-$t$-Bu to produce $(tmp)BMe(t\text{-}Bu)$.[4,50]

### 2. Borenium Salts

Only reaction 62 has been reported that falls into the category discussed here. Addition of $[Et_4N]Cl$ to a solution of 4-pic-$BCl_2^+$ completely restores the $^1H$ NMR multiplet pattern of the neutral $BCl_3$ adduct.[12]



$$\text{(62)}$$
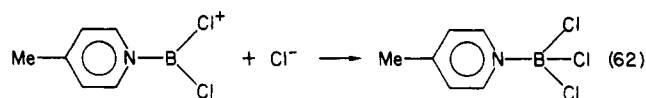
## D. Other Reactions

Many of the reactions of borinium salts proceed by metathesis at their complex anions and this leads to the formation of new anions as generalized in eq 63. Reactions of this type have already been discussed in section II.C.

$$[R_2N\!\!=\!\!B\!\!=\!\!NR_2]EX_n + nMY \rightarrow$$
$$R_2N\!\!=\!\!B\!\!=\!\!NR_2]EY_n + nMX \quad \text{(63)}$$
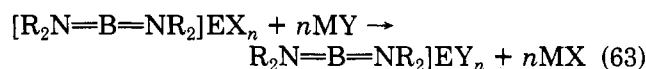
## VII.  Conclusion

The discovery of borinium and borenium ions shows that the element boron has an unexpectedly variable and interesting cation chemistry of its own and that many reactions of borane derivatives with electrophilic reagents may more likely proceed via ionic intermediates rather than neutral coordination compounds.[4] Moreover, also the solution chemistry of boranes may not only involve tetracoordinated species (boronium salts or Lewis acid–base adducts) but also borenium salts. To prove or disprove this prediction requires many additional experiments, and hopefully this Review will stimulate research in this area.

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