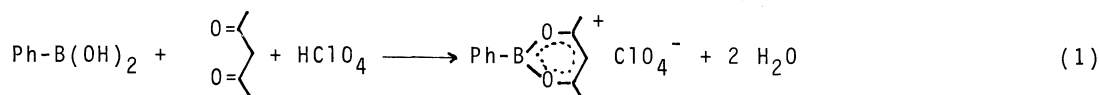


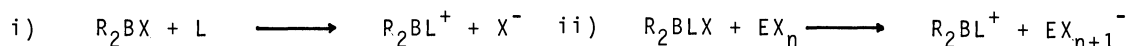
boronic acid with 1,3-diketones in the presence of anhydrous perchloric acid ⁶⁾:



Evidence presented for this type of compounds was a fairly high melting point, correct analysis and proton nmr. In addition $\delta^{11}\text{B}$ was reported as 32,8 ppm, which, of course, is typical for tricoordinated boron.

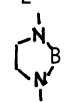
We have repeated Balaban's preparation, and, in addition also prepared the corresponding triflates. Our ^{11}B -nmr-data, however, clearly indicate the presence of tetracoordinated boron ($\delta^{11}\text{B}$ 5 - 7 ppm). Hydrolysis of the compounds in CH_2Cl_2 gives rise to an ^{11}B -nmr-signal at ~ 33 ppm, and this was confirmed as phenylboronic acid. There is therefore no evidence that Balaban's compounds are tricoordinated boronium salts, although we do not dispute that dioxaboronium salts may exist under certain conditions.

Considering possible routes to salts containing tricoordinated cations of boron two strategies can be developed: i) the nucleophilic displacement of a boron bonded anionic species X by a suitable base or ii) the removal of a group as an anion from a tetracoordinated borane adduct.



The nucleophilic displacement of a group X by a base L will certainly be favoured if X represents a good leaving group and if the bond to be broken is a weak bond. Amongst the halides iodine is of course suitable in terms of easy bond cleavage. A better leaving group, however, is triflate. Therefore, we investigated the action of various Lewis bases on a number of boron halides and boron triflates. There are two types of behaviour: i) the common simple addition and ii) the expected nucleophilic displacement. Table I summarizes some results, numbers 3 and 4 indicate that the reaction either leads to a tricoordinated or a tetracoordinated species.

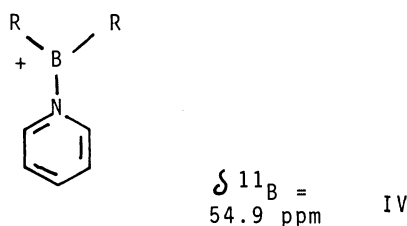
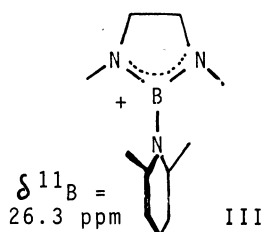
Table I: Results of the reactions of various boronchlorides and boron triflates with triethylamine, pyridine and 2,6-lutidine.

R ₂ BX	X = Cl			X = SO ₃ CF ₃		
	NEt ₃	py	lu	NEt ₃	py	lu
n-Bu	4	4	4	4	4	3
Ph ₂	4	4	4/3	4	3/4	3
	-	3	3	-	3	3

py = pyridine; lu = 2,6-lutidine

If triethylamine is used as a base 1:1 addition products containing tetracoordinated boron are formed. In the case of the aminoboron compounds adduct formation is prevented obviously for steric and electronic reasons. Pyridine, however, is a much more suitable base. Thus 1,3-dimethyl-1,3,2-diazaborolidine chloride forms a compound with tricoordinated boron at -30 °C.

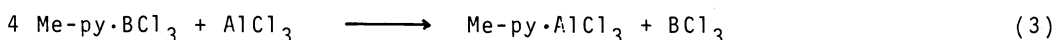
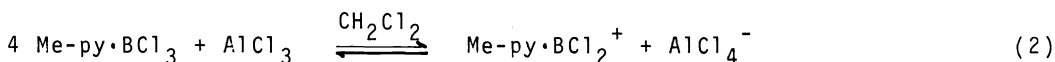
In contrast, all triflates form salts with 2,6-lutidine. This demonstrates that a good leaving group is very helpful in producing boronium(1+) salts. The most stable salts are those derived from the diazaborolidine. This enhanced stability e.g. over the dibutyl derivative is due to a better charge stabilisation as described by the formulae III, and ^{11}B -, ^{14}N - and ^{13}C -nmr-data are in consonance with the suggested structure and bonding.



Coplanarity of the pyridine base in III is prevented by the bulk of the N-methylgroups of the diazaborolidine ring. In contrast, the pyridine heterocycle approaches coplanarity with the C_2BN plane in the diorganyl compounds thus providing π -back donation from the rings π -charge with concomitant increase of electron density at boron.

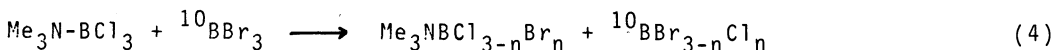
There is fairly little change ($\Delta^{11}\text{B} = -3 \text{ ppm}$) in the formation of III from 1,3-dimethyl-2-triflato-1,3,2-diazaborolidine ($\delta^{11}\text{B} = 23.3 \text{ ppm}$) in contrast to $\Delta^{11}\text{B} + 8 \text{ ppm}$ for IV, while the ^{11}B -nmr signal of tetracoordinated $\text{Bu}_2\text{B}\cdot\text{trif}\cdot\text{py}$ is found at 12.2 ppm. In addition to nmr data, electrical conductance in CH_2Cl_2 fully supports the ionic nature of the compounds.

Abstraction of a halide from a tetracoordinated boron adduct has first been described by Ryschkewitsch ³⁾, and ^{11}B nmr evidence was given for the equilibrium (2)

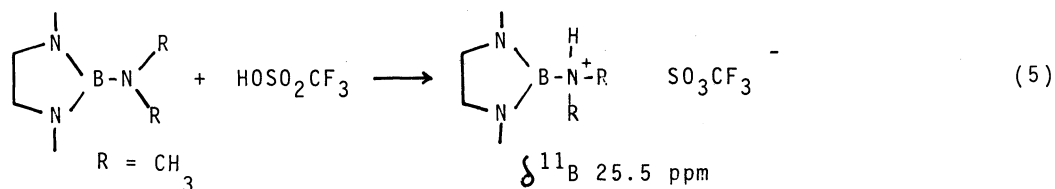


However, a base displacement (3) may also occur as well as a one electron oxidation. Such behaviour was observed in the reaction of $\text{ph}_2\text{BCl}\cdot\text{py}$ with AlCl_3 ⁷⁾.

Reactions of type (2), even if stable salts cannot be isolated, play an important role in substitution reactions of tetracoordinated boron, e.g. for halide displacements under acidic conditions as can be demonstrated by ^{10}B labeling experiments. A typical example is provided for by equation (4).



In addition to the two methods discussed a third method may be fairly general too: the addition of a proton to a tris(amino)borane. A stable, solid salt results on treating 2-dimethylamino-diazaborolidine with 1 mole of triflic acid:

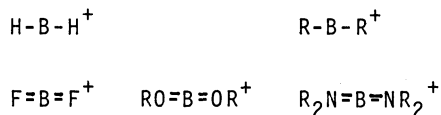


The stability of this salt can again be attributed a) to stabilisation by π -back bonding and b) the presence of a weak nucleophilic anion. This result indicates, that tricoordinated boronium(1+) ions may be intermediates in many protolysis reactions of boron compounds.

Dicoordinate Boron Cations

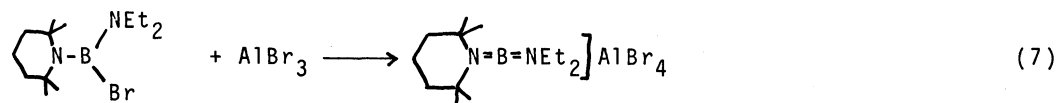
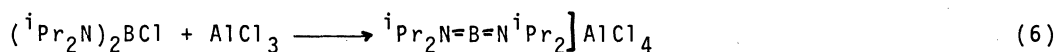
Tricoordinated boron cations, though still rare, are not very exotic because boron exhibits its usual coordination. Dicoordinated boron cations, on the contrary, should be exceedingly difficult to make due to the notorious electron deficiency at the boron atom. Indeed, the first proposal for the possible existence of a dicoordinated diphenyl boron cation by Davidson and French in 1958 ⁴⁾, was shown by later work to be a solvated species.

Dicoordinated cations of boron are to be expected to be unique for a number of reasons. To understand this let us consider a series of such ions. A dihydrido- or dialkylboron cation would be highly electron deficient and therefore an extremely strong Lewis acid and an electrophile. They represent systems with electron quartets. And it is difficult to envisage that proper conditions can be established to generate a salt of the free dihydridoboron-(1+) ion.



There is a slightly higher probability for the existence of a diorganylboron cation, because attack of the counterion at the boron center can be blocked by steric hindrance. So far however, we have been unable to detect a bis(tert-butyl)boron or even a bis(mesityl)boron cation. In the series difluoro-, dialkoxy and dialkylamino boron cations one may expect electronic stabilisation of the dicoordinated boron cation by π -back bonding. In addition, steric shielding increases as we pass along this line. It was the combined forces of electronic and steric factors that led professor Parry and his group as well as ours to the detection and finally to the isolation of dicoordinated bis-(amino)cations of boron, as salts. The first reports on these results appeared last year ⁵⁾.

Both groups used the method of halide abstraction from a bis(dialkylamino)-boronhalide by a strong halide acceptor. The aminoborane used by Parry was either bis(diisopropylamino)boronchloride or bis(dimethylamino)boron chloride, while we chose a more bulky system, 2,2,4,4-tetramethylpiperidino-diethylamino-boron bromide (tmpBNEt₂Br).

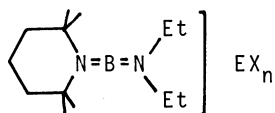


These reactions and the allenic structure of the boron cations formed were proved by a variety of methods, with multinuclear nmr spectroscopy providing conclusive evidence for the exclusive formation of tetrahaloaluminates and ^{13}C -nmr for the high symmetry of the cations. Final proof came from an X-ray structure determination. This study showed a linear NBN skeleton with short BN distances and orthogonal arrangement of the C_2N moiety of the amino groups. Thus these cations are truly isoelectronic and isostructural with allenes.

Since the formation of a bis(amino)boron salt from a bis(amino)boronhalide requires the breaking of a boron halogen bond, it is to be expected that boron iodides will be favoured over fluorides in salt formation because the boron iodine bond is the weakest in the series. Indeed, aluminium iodide readily reacts with tetramethyl-piperidino-diethylaminoboron iodide yielding the corresponding tetraiodoborate salt. This is another of the hitherto still rare examples of salts where boron is the central atom in both, the cation and anion, the classical example being Parry's $[\text{H}_2\text{B}(\text{NH}_3)_2]^+\text{BH}_4^-$. However, the new example is the first one in which the boron in the cation is dicoordinated.

A large number of halide acceptors allow boron halogen bond breaking, according to equation (6), and the results are summarized in Table II.

Table II: List of salts formed in the reaction of 2,2,6,6-tetramethylpiperidino-diethylamino-boronhalides with the appropriate halide acceptor.



EX_n^-	EX_n^-	EX_n^-
AlI_4^-	AlBr_4^-	AlCl_4^-
BI_4^-	GaBr_4^-	GaCl_4^-
HgI_3^-	TaBr_6^-	TaCl_4^-

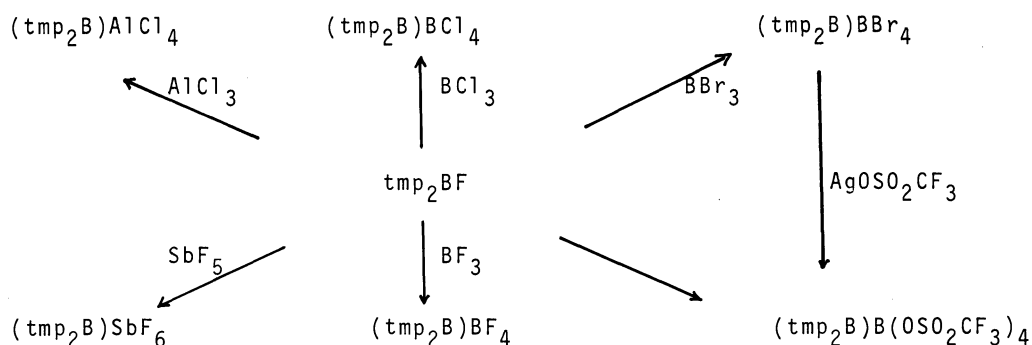
Halogen Exchange via Cationic Intermediate



The results, especially those with boron halides as halogen acceptors gives clear evidence that the boron halogen bond strength is an important factor for the formation of a bis(dialkylamino)boron(1+)-cation because no stable salts can be isolated with BBr_3 and BCl_3 as acceptors.

It was therefore not surprising that the fluoride, $\text{tmpB}(\text{NEt}_2)\text{F}$, underwent BN cleavage in its reaction with SbF_5 .

Parry has shown that a solution of bis(dimethylamino)boron(1+)tetrachloroaluminate decomposed quickly at ambient temperature in contrast to the bis(diisopropylamino)boron salt. Our tetramethylpiperidino-dimethylaminoboron-tetrabromoaluminate was stable for several weeks in the crystalline state. Therefore, increasing bulkiness of the boron ligands should lead to increased stability of the salts. This assumption as well as the need for an additional crystal structure determination led to us to investigate the chemistry of bis(tetramethylpiperidino)boranes. To cut a long story short: the only compound of this class to be fairly readily accessible is $(\text{tmp})_2\text{BF}$. However, this is an excellent starting material for salts containing $(\text{tmp})_2\text{B}$ -cations. Results are summarized as follows.



Aluminium chloride reacted readily producing, in CH_2Cl_2 solution, bis(tmp)boron(1+)-tetrachloroaluminate. The driving force for this reaction is, of course, provided by the formation of insoluble aluminium fluorides.

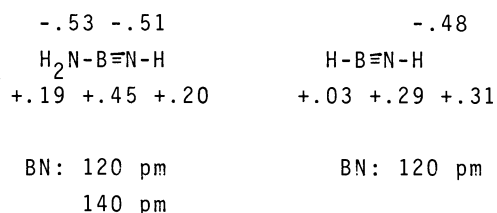
Similarly, the tetrachloro- and tetrabromoborates are easily accessible by treating tmp_2BF with excess BCl_3 or BBr_3 , and gaseous BF_3 is produced. The tetrabromoborate can be converted into a tetratriplatoborate by silver triflate. This compound provides nice crystals. Unfortunately, however, we failed to determine its X-ray structure because the reflexions were very diffuse and typical for plastic crystals.

Interestingly, tmp_2BF not only reacted with SbF_5 resulting in BF bond breaking and formation of the hexafluoro-antimonate but even with BF_3 to yield the tetrafluoroborate. This result indicates that the driving force of the formation of bis(dialkylamino)boron cations is astonishingly high.

Halide abstraction from a boron halide R_2BX is certainly a general method for producing dicoordinated boron cations. So far, however, only a few species other than the diamino boron cations could be reliably detected. Treatment of aminoalkoxyboronhalides with aluminiumhalides produces multicomponent mix-

Verification of equation (8) proved more difficult than anticipated. Methyl-iodide and tert.-butylbromide were unreactive. Methyltriflate on the other hand provided bis(amino)triflatoboranes. Obviously steric factors are again of great importance.

One might argue that the charge density at the imino nitrogen is unfavourable for attack of the electrophile on this nitrogen atom. MO calculations on the STO-3G level for iminoboranes show fairly high negative net charges with only little differences between the two nitrogen atoms.

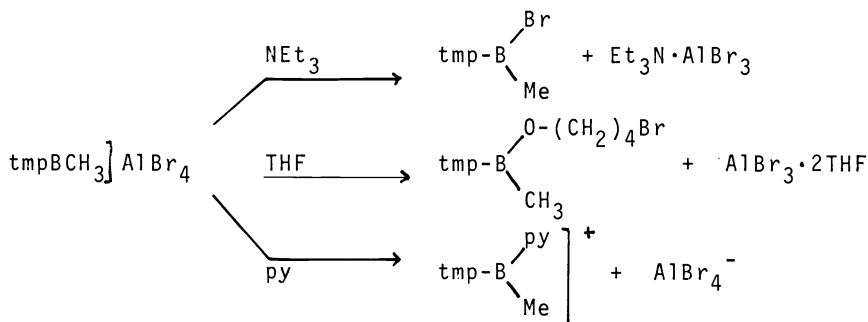


Thus, it is to be expected that the electrophile will add at the imido nitrogen because of the high stability of the bis(diamino)boron(1+) cations⁵⁾.

Reactions of bis(amino)boron cations

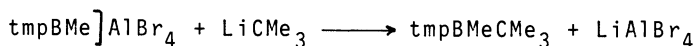
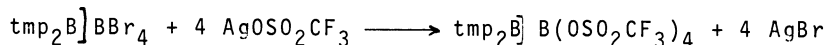
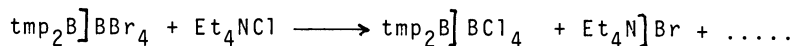
It is obvious that two types of reactions may be expected from dicoordinated boron cations: i) attack of an anion at the boron center to produce a bis-(amino)borane derivative, ii) allene type behaviour e.g. addition reactions on one of the two BN double bonds.

tmpBCH₃AlBr₄ shall serve as an example. Triethylamine will react quickly with this salt. However, attack of the base occurs at the aluminium rather than the boron center. Simple bromide transfer is therefore achieved. Tetrahydrofuran is cleaved by the salt and a ω-chlorobutoxy group is in-



roduced. Pyridine on the other hand produces a salt containing a tricoordinated boron cation. This, therefore, is another route to this type of boron cations.

Similarly, if we start from the sterically more hindered bis(tmp)boron cation, nucleophiles usually attack only at the anion. Typical examples are:



The first of these reactions clearly states that it will be very difficult to prepare either bis(tetramethyl-piperidino)boron chloride or bromide, even by this electrophilic route. Therefore, it may be postulated, that these compounds may be ionic rather than covalent, and this would provide another type of isomerism in boron chemistry.

It is evident from the preparative results presented that there is a high probability of cation formation in reactions where boron compounds are treated with a strong Lewis acid. Examples that require these ions as intermediates are the formation of bis(diethylamino)boron chloride from bis(diethylamino)boron fluoride and aluminium chloride or the formation of tmp_2B^+ in the reaction of tmpBCl_2 with BBr_3 . Moreover, the rate of reactions of aminoborohalides with Lewis acids depends on the polarity of the solvent thus indicating that ionic or highly polar states are favoured.

REFERENCES

1. B.M. Mikhailov and N.S. Fedotov, Bull. Acad. Sci. USSR, **1**, 1788 (1961).
2. S.G. Shore and R.W. Parry, J. Am. Chem. Soc. **80**, 8 (1958);
D.R. Schultz and R.W. Parry, J. Am. Chem. Soc. **80**, 4 (1958).
3. G.E. Ryschkewitsch, Boron Hydrides, Editor: E.L. Muetterties, Academic Press, New York (1975).
4. J.M. Davidson and C.M. French, J. Chem. Soc. 114 (1958).
5. J. Higashi, A.D. Eastman and R.W. Parry, Inorg. Chem. **21**, 716 (1982);
H. Nöth, R. Staudigl and H.-U. Wagner, Inorg. Chem. **21**, 706 (1982).
6. A.T. Balaban, A. Arsene, I. Bally, A. Barabas and M. Paraschiv, Tetrahedron Letters 3917 (1965).
7. A. Konstantinov, Diploma Thesis, University of Munich.(1982).
8. P.I. Paetzold, private communication (1982).