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Preparation and Characterization of Salts Containing Cations of Tricoordinate Boron[1]

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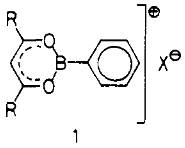
1,3-Dimethyl-2-triflato-1,3,2-diazaborolidine (**3**) reacts with various amines in a 1:1 ratio with displacement of the triflato group and formation of triflate salts containing cations with tricoordinate boron. α,α'-Bipyridyl in a 1:1 molar ratio gives a salt containing a tetracoordinated boron atom. *N,N,N',N'*-Tetramethylethylenediamine on the other hand produces a 1:1 adduct, which in CH_2Cl_2 solution provides evidence for an equilibrium between both types of cations. Similarly, tetrachloroaluminate salts have been obtained by the action of amines and triphenylphosphine on the 1:1 addition product **8** of $AlCl_3$ with 2-chloro-1,3-dimethyl-1,3,2-diazaborolidine. Although the constitution of the new salts could be deduced by IR and NMR data, final proof was achieved by an X-ray structure determination of the diphenylamine adduct **5c**. The compound crystallizes in the triclinic system, space group $P\bar{1}$, $Z = 2$. Refinement converged at $R = 0.056$ for 3043 unique reflections. There is no interaction of the triflate ion with the trigonal boron atom of the cation in the solid state, and three significantly different B–N bond lengths were determined (138.6, 141.2, and 154.7 pm).

Introduction

The chemistry of cations containing tetracoordinated boron is well established[2] since they were first discovered by Parry et al.[3] and Mikhailov et al.[4] More recently, the existence of salts containing two-coordinate boron in a cation has also been proved.[5,6] Therefore, it was to be expected that ionic compounds containing cations with tricoordinate boron should exist also. Some compounds of this type have been mentioned in the literature, but none are either convincingly characterized or have been properly isolated. This refers to the diphenylboron cation generated in nitrobenzene or ethyl methyl ketone solutions[7] for which NMR evidence favors a tetracoordinated rather than a tricoordinated species.[8] The formation of the cation $[Me_2NB(NHMe_2)_2]^{2+}$ (Me = CH_3) was postulated to explain the fact that $B(NMe_2)_3$ adds 2 equiv of HI without BN cleavage;[9] the structure of this cation was based primarily on IR evidence. Another class of reported compounds containing tricoordinate boron are the phenyl dioxaborinium(1+) cations (**1**), isolated as perchlorate and hexachloroantimonate salts.[10] However, we showed recently that these compounds have to be described as addition compounds of type **2** containing tetracoordinate boron.[11] Finally, good NMR evidence was presented for the existence of a cation $Cl_2B{\cdot}py^+$ in CH_2Cl_2 solution formed by chloride abstraction from $Cl_3B{\cdot}py$ (py = pyridine) by $AlCl_3$.[12] However, it appears that the salt $[Cl_2B{\cdot}py]AlCl_4$ could not be isolated.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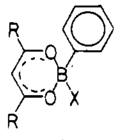
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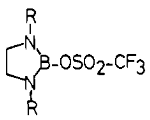
Considering the fact that boranes of type BX_3 are—formally—six-electron species gaining in stability by π back-bonding, one can envisage that $X_2B{\cdot}(donor)^+$ cations will be even more "electron deficient". The positive charge associated with a species of this type would almost certainly make it a very potent electrophile. Therefore, these cations are expected to gain in stability by groups X reducing the electron deficiency at boron. A group of this sort is pyridine because the π electrons of the ring can interact with the empty p_z orbital at the boron atom. Assuming that the groups X are themselves capable of back-donating electron density to boron, stabilization of the cation $X_2B{\cdot}(donor)^+$ is also to be expected. Since amino groups are well-known to exhibit this type of behavior, as exemplified in the stabilization of dicoordinated boron cations,[5,6] we expected the preferential formation of cations containing tricoordinate boron by the interaction of suitable donor molecules with diaminoboranes $(R_2N)_2BX$. Since, however, steric effects exerted by the group R prevent even in the case of R = Me maximal B–N π bonding, we chose 1,3,2-diazaborolidines as the model system for testing this hypothesis. Due to the experience that an excellent leaving group will favor salt formation, we investigated the triflatoborane **3** in preference to 1,3-dimethyl-2-halo-1,3,2-diazaborolidines (**4**) in its behavior toward various typical Lewis bases.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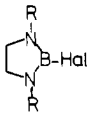
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R = CH_3

Experimental Section

All experimental manipulations were carried out under rigorously anhydrous conditions in a high-vacuum system and/or oxygen-free nitrogen gas using Schlenk techniques. Solvents were carefully dried and stored under N_2. 2,6-Lutidine, diethylamine, and pyridine were purified by distillation before use. Commercially available triflic acid and triphenylphosphine (reagent grade) were used as supplied. $AlCl_3$ was sublimed before use. $AgSO_3CF_3$ was prepared according to literature methods[13] and dried in vacuo.

NMR spectra were recorded on a JEOL FX 90 or Bruker WP 200 PFT multinuclei NMR spectrometers in CH_2Cl_2 solution. Chemical shifts refer to Me_4Si (^1H, ^{13}C), $BF_3{\cdot}OEt_2$ (^{11}B), and 1 M $Al(OH_2)_6^{3+}$, external (^{27}Al). IR spectra were obtained on a Perkin-Elmer 325 instrument; usually mulls in Nujol/Kel-F were used. Intensity data

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[†] Alexander von-Hümboldt Fellow.

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for the X-ray structure determination were collected with a Syntex P3 automated four-circle diffractometer. Calculations were performed on a NOVA 3 computer using the SHELXTL program package. Elemental analyses were obtained by the microanalytical laboratory, University of München. Carbon analysis was usually low due to slow or incomplete combustion. The reason why unsatisfactory N values were obtained for compounds **11** and **9b** remains obscure because NMR data showed no impurities.

1,3-Dimethyl-2-triflato-1,3,2-diazaborolidine (3). To a suspension of $AgSO_3CF_3$ (1.00 g, 3.89 mmol) in 25 mL of CH_2Cl_2 was added dropwise a solution of 2-chloro-1,3-dimethyl-1,3,2-diazaborolidine (**4**)[14] (0.51 g, 3.85 mmol) in 25 mL of CH_2Cl_2 with stirring at −78 °C. After complete addition, stirring was continued for 1 h. The insoluble product (AgCl: found 0.5 g; calcd 0.56 g) was removed, the solvent stripped from the filtrate at room temperature, and the product was then kept for 2 h under a high vacuum to remove all volatile materials. **3** remains as a white solid: yield 0.93 g (96%); mp 59 °C; δ (^{11}B) 23.4 in CH_2Cl_2. Anal. Calcd for $C_5H_{10}BF_3N_2O_3S$: C, 24.41; H, 4.10; N, 11.39. Found: C, 24.1; H, 5.1; N, 11.0.

In most cases only the CH_2Cl_2 solution of **3** was prepared and used as such to investigate reactions of **3** with electron-pair donors.

2,6-Lutidine(*N*–*B*)-1,3-dimethyl-1,3,2-diazaborolidinium(1+) Triflate (5b). **3** was prepared as described from 0.86 g (6.49 mmol) of **4** and 1.67 g (6.56 mmol) of silver triflate. The CH_2Cl_2 solution was then cooled in a dry ice/acetone bath and a solution of 2,6-lutidine (0.69 g) in 25 mL of CH_2Cl_2 added dropwise with stirring. After 1 h the mixture was brought to ambient temperature. Solvent was then removed, but no crystalline material formed. A thick oil remained after removal of all solvent. It solidified on cooling to ~−10 °C. Crystallization of **5b** was induced by treatment with pentane, hexane, or benzene but was not always successful; mp 51 °C. Anal. Calcd for $C_{12}H_{19}BF_3N_3O_3S$: C, 40.81; H, 5.42; N, 11.89. Found: C, 38.0; H, 5.6; N, 11.5.

Pyridine(*N*–*B*)-1,3-dimethyl-1,3,2-diazaborolidinium(1+) Triflate (5a). (i) The compound was prepared as described for **3** with 0.85 g (6.41 mmol) of **4**, 1.64 g (6.40 mmol) of silver triflate, and 0.51 g (6.4 mmol) of pyridine. Spectra were recorded rapidly on the freshly prepared solution. Additional signals appeared in spectra taken at later times, and often a brown oil separated from the solution. A yellow oily solid remained after removal of CH_2Cl_2 at 0 °C; yield 1.79 g (86%).

(ii) **3** was made from 0.257 g (1.94 mmol) of **4** and 0.50 g of silver triflate (1.94 mmol) in 10 mL of CH_2Cl_2 at −78 °C. After removal of AgCl, 0.153 g (1.93 mmol) of pyridine was added at −78 °C with stirring. This produced a yellow color of the solution. Removal of solvent left behind a yellow oily solid, which on dissolving in $CDCl_3$ showed the following NMR spectra: $\delta(^{11}B)$ = 25.8, 11.8 (very little intensity); $\delta(^1H)$ = 2.49 (6 H), 3.33 (4 H), 7.72–8.74 (5 H) together with two more small signals.

(iii) After **3**, was prepared exactly according to (ii), 2 mol equiv of pyridine was added at −78 °C. Exactly the same ^{11}B and ^1H NMR spectra were recorded from the isolated sample after stripping off solvent and excess pyridine.

(iv) **3**, prepared from 0.257 g (1.94 mmol) of **4** was dissolved in 10 mL of pentane, and 0.153 g (0.93 mmol) of pyridine in 30 mL of pentane was added at −78 °C with stirring. When the mixture was warmed to ambient temperature, a pale yellow precipitate formed. The supernatant liquid was removed and the solid dried: mp 38 °C; $\delta(^{11}B)$ = 27.0 in CH_2Cl_2 together with an extremely small signal at 5 ppm. After 2–3 h the product showed the same ^{11}B NMR spectrum as obtained in the above experiments. The solid was not sufficiently soluble in pentane, cyclohexane, or benzene to record good NMR spectra.

1,3-Dimethyl-2-(diphenylamino)-1,3,2-diazaborolidinium(1+) Triflate (5c). **3** was prepared from 0.87 g (6.57 mmol) of **4** and 1.69 g (6.59 mmol) of silver triflate in CH_2Cl_2. A 1.11-g sample (6.56 mmol) of diphenylamine, dissolved in 30 mL of CH_2Cl_2, was added with stirring at −78 °C. The volume of the mixture was then reduced to ~20 mL in vacuo, layered with 30 mL of *n*-hexane, and then left overnight at 0 °C. The crystals formed were isolated by syringing off the supernatant liquid. After the crystals were washed with 10 mL of hexane and dried, 1.74 g of **5c** (64%) was obtained; mp 108 °C. The product contained a reasonable amount of suitable single crystals. Anal. Calcd for $C_{17}H_{21}BF_3N_3O_3S$: C, 49.17; H, 5.10; N, 10.12. Found: C, 43.5; H, 5.2; N, 10.4. IR (cm^{-1}): 3200 (b), 1590 (b), 1552 (s), 1495 (s), 1485 (s), 1240 (sb), 1662 (sb), 1030 (vs), 758 (s), 702 (s), 635 (s), 515 (m).

1,3-Dimethyl-2-(dimethylamino)-1,3,2-diazaborolidinium(1+) Triflate (7a). A 0.91-g portion (6.46 mmol) of 1,3-dimethyl-2-(dimethylamino)-1,3,2-diazaborolidine[15] was dissolved in 25 mL of CH_2Cl_2. At −78 °C a solution of 0.97 g (6.46 mmol) of triflic acid in 50 mL of dichloromethane was added dropwise with stirring. An oily material was left after removal of solvent. It was treated with hexane but proved insoluble, and no crystalline material formed; yield 1.8 g of **7a** (95%). Anal. Calcd for $C_7H_{17}BF_3O_3N_3S$: C, 28.88; H, 5.89; N, 14.44. Found: C, 28.3; H, 5.8; N, 14.1.

1,3-Dimethyl-2,2-(α,α'-bipyridyl)-1,3,2-diazaborolidinium(1+) Triflate (10). To a pentane solution of **3**, made from 0.257 g (1.94 mmol) of **4** and 0.5 g (1.94 mmol) of silver triflate in CH_2Cl_2 was added 0.30 g (1.92 mmol) of α,α'-bipyridyl in 20 mL of pentane. A white solid formed at −78 °C, which acquired an orange color on warming to ambient temperature. The solution was decanted off, leaving a precipitate that was washed twice with pentane: yield 0.62 g of **10** (79%); $\delta(^{11}B)$ ($CDCl_3$) = 12.2. Anal. Calcd for $C_{15}H_{18}BF_3N_4O_3S$: C, 44.79; H, 4.51; N, 13.92. Found: C, 40.6; H, 4.7; N, 13.2.

Attempt To Prepare 1,3-Dimethyl-2,2-(*N*,*N*,*N′*,*N′*-tetramethylethylendiamine)-1,3,2-diazaborolidinium(1+) Triflate (11). A 40-mL portion of a CH_2Cl_2 solution containing 0.47 g (1.91 mmol) of **3** was cooled to −78 °C, and 0.22 g (1.9 mmol) of tetramethylethylenediamine was added under vigorous stirring. The reaction mixture was warmed to ambient temperature. A low-melting solid remained after stripping off the solvent; yield 0.61 g (88%).

Its solution in CH_2Cl_2 showed ^{11}B NMR signals at 26.4 and 10.5 ppm in an intensity ratio of 1:5 concurrent with monodentate and bidentate behavior of the diamine. ^1H NMR was not very informative—a larger number of signals were observed in the region 1.56–2.41 ppm as expected for equilibrium 8.

Anal. Calcd for $C_{11}H_{20}BF_3N_4O_3S$: C, 36.47; H, 7.23; N, 15.47. Found: C, 33.9; H, 7.0; N, low results (13.5).

Aluminum Trichloride(*Al*–*N*)-2-chloro-1,3-dimethyl-1,3,2-diazaborolidine (8). (i) A 0.48-g sample of $AlCl_3$ (3.55 mmol) was suspended in 25 mL of CH_2Cl_2, and 0.47 g (3.54 mmol) of **4** in 20 mL of CH_2Cl_2 was added at −78 °C while stirring. Most of the $AlCl_3$ dissolved within 15 min. A clear solution resulted in 2 h. On warming, a pink color appeared at about −50 °C, and the product became dark red at ambient temperature. Solutions of **8** can only be used at temperatures <−50 °C.

(ii) With toluene as a solvent, 0.59 g (4.4 mmol) of $AlCl_3$ and 0.59 g (4.45 mmol) of **4** reacted at −78 °C to form a clear solution. On addition of pentane to the stirred reaction mixture, a solid precipitated that was filtered, washed twice with 20 mL of pentane at −78 °C, and dried in vacuo: yield 40%; $\delta(^{11}B)$ = 31; $\delta(^{27}Al)$ = 108.6 (line width 75 Hz), 103.6 (small amount of $AlCl_4^-$). Anal. Calcd for $C_4H_{10}AlBCl_4N_2$: N, 10.39. Found: N, 10.5.

2,6-Lutidine(*N*–*B*)-1,3-dimethyl-1,3,2-diazaborolidinium(1+) Tetrachloroaluminate (9b). When 1.01 g (7.62 mmol) of **4** in 20 mL of CH_2Cl_2 was added to a stirred suspension of 1.00 g (7.56 mmol) of $AlCl_3$ in 25 mL of CH_2Cl_2 at −78 °C a clear solution resulted in approximately 2 h. Then, a solution of 0.81 g (7.57 mmol) of 2,6-lutidine in 25 mL of CH_2Cl_2 was added dropwise. After 1 h the solution was warmed, solvent stripped off, and the oily residue washed with pentane and benzene. The oil failed to crystallize; yield 2.71 g of **9b** (94%). Anal. Calcd for $C_{11}H_{19}AlBCl_4N_3$: C, 35.43; H, 5.13; N, 11.26. Found: C, 32.7;, H, 5.2; N, 8.7.

1,3-Dimethyl-2-(diethylamino)-1,3,2-diazaborolidinium(1+) Tetrachloroaluminate (9d). This compound was prepared analogously from 0.61 g (4.60 mmol) of **4**, 0.60 g (4.5 mmol) of $AlCl_3$, and 0.33

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(16) The experimental results of this and related studies comprising bis(dimethylamino)boron halides (Cl, Br, I), bis(diethylamino)boron bromide, bis(diisopropylamino)boranes $(R_2N)_2BX$ (X = Cl, Br, SO_3CF_3), and (2,2,6,6-tetramethylpiperidino)(dialkylamino)boranes will be published in a forthcoming paper. See: Weber, S. Diploma Thesis, University of München, 1981. Rasthofer B. Ph.D. Thesis, University of München, 1984.

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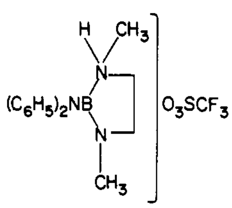
(18) For a discussion of the structures of Lewis acid adducts of diazaborolidines see: Anton, K.; Nöth, H. *Chem. Ber.*, in press.

Table I.[a] Crystal Data for



5c = 12

formula	$C_{17}H_{21}BF_3N_3O_3S$
mol wt	415.24
cell parameters	
a, Å	9.256 (2)
b, Å	10.741 (2)
c, Å	11.482 (2)
α, deg	68.69 (1)
β, deg	77.86 (2)
γ, deg	71.27 (1)
V, Å^3	1001.5 (3)
Z	2
ρ(calcd), g cm^{-3}	1.377
space group	$P\bar{1}$
cryst dimens, mm	0.7 × 0.5 × 0.4
temp, °C	20
radiation	Mo Kα
μ, cm^{-1}	20.1
2θ range, deg	2-50
scan rate, deg min^{-1}	1.2-29.3
no. of indep reflcns	3776
no. of reflcns with $I > 3\sigma(I)$	3043
no. of refined parameters	316
final R	0.056
final R_w	0.059

[a] Estimated standard deviations in parentheses; graphite-monochromatized Mo Kα radiation (0.710 69 Å) used.

Table II. List of Fractional Atomic Coordinates (×10^4) and U_{eq} (Å^2 × 10^3) Values, Defined as One-Third of the Diagonal U_{ij} Tensor of the Anisotropic Temperature Parameters

atom	x	y	z	U_{eq}, Å^2
S	12832 (1)	4921 (1)	7453 (1)	59 (1)
N(1)	7583 (2)	3035 (2)	9081 (2)	56 (1)
N(2)	8973 (2)	4182 (2)	7281 (2)	47 (1)
N(3)	9275 (2)	1602 (2)	7689 (2)	46 (1)
O(1)	14339 (3)	4036 (3)	7460 (3)	126 (2)
O(2)	12119 (3)	5065 (3)	8638 (2)	107 (1)
O(3)	11848 (2)	4748 (2)	6757 (2)	80 (1)
F(1)	14060 (3)	6932 (2)	7022 (2)	125 (1)
F(2)	13608 (3)	6726 (3)	5388 (2)	141 (1)
F(3)	11802 (3)	7579 (2)	6527 (3)	147 (1)
C	13102 (4)	6598 (3)	6549 (3)	74 (2)
C(1)	7036 (3)	4508 (3)	8955 (2)	69 (1)
C(2)	8296 (3)	5094 (3)	8104 (3)	68 (1)
C(3)	6778 (3)	2115 (4)	10078 (3)	84 (2)
C(4)	8251 (3)	4739 (2)	6081 (2)	60 (1)
C(21)	8571 (2)	481 (2)	8104 (2)	47 (1)
C(22)	9426 (3)	−870 (3)	8633 (2)	65 (1)
C(23)	8744 (3)	−1949 (3)	9068 (3)	76 (1)
C(24)	7215 (3)	−1693 (3)	8985 (3)	74 (1)
C(25)	6378 (3)	−364 (3)	8447 (3)	72 (1)
C(26)	7039 (3)	733 (2)	7985 (2)	58 (1)
C(11)	10628 (2)	1476 (2)	6797 (2)	48 (1)
C(12)	11957 (2)	1659 (3)	7001 (2)	62 (1)
C(13)	13217 (3)	1588 (3)	6088 (3)	80 (1)
C(14)	13161 (4)	1312 (3)	5029 (3)	84 (1)
C(15)	11851 (4)	1109 (3)	4845 (3)	82 (1)
C(16)	10584 (3)	1188 (3)	5724 (2)	64 (1)
B	8639 (3)	2781 (3)	8087 (2)	44 (1)

g (4.5 mmol) of $HN(C_2H_5)_2$. It is an oily liquid, soluble in chlorinated hydrocarbons; yield 1.48 g of **9d** (95%). Anal. Calcd for $C_8H_{20}AlBCl_4N_3$: C, 28.43; H, 5.96; N, 12.43. Found: C, 30.5; H, 6.7; N, 12.9.

Reaction of 8 with Diethylamine. When **8** (prepared from 0.39 g (2.94 mmol) of **4** and 0.40 g of $AlCl_3$ (2.99 mmol) in 30 mL of toluene and suspended in 40 mL of pentane) is treated with 2 equiv of diethylamine (0.43 g, 5.98 mmol) in 20 mL of pentane at −78 °C, a white fluffy precipitate formed. When the reaction mixture was slowly warmed to room temperature, the precipitate disappears and a brown oil forms. The supernatant liquid was decanted off and the residual oil was washed twice with pentane. It appears from NMR spectra ($\delta(^1H)$ = 1.39 (t), 3.19 (q), 8.23 (b); $\delta(^{27}Al)$ = 103 ($h_{1/2}$ = 25 Hz)) that the oil is $(Et_2NH_2)AlCl_4$. The supernatant liquid shows only one signal at $\delta(^{11}B)$ = 26.5, which is consistent with a BN_3 environment,[19] as expected for 2-(diethylamino)-1,3-dimethyl-1,3,2-diazaborolidine.

1,3-Dimethyl-2-(triphenylphosphino)-1,3,2-diazaborolidinium(1+) Tetrachloroaluminate (9e). **8** prepared from 0.56 g (4.2 mmol) of $AlCl_3$ and 0.56 g (4.23 mmol) of **4** in toluene was reacted with 1.10 g (4.20 mmol) of $P(C_6H_5)_3$. After the solvent was stripped off at ambient temperature, an oil remained that solidified after 1 week. It was washed with hexane and dried: yield 2.04 g of **9e** (92%); mp 66 °C. Anal. Calcd for $C_{22}H_{25}AlBCl_4N_2P$: C, 50.04; H, 4.77; N, 5.30. Found: C, 47.5; H, 5.1; N, 4.9.

X-ray Structure Determination of 5c. Single crystals of **5c** were obtained from CH_2Cl_2/hexane. The crystals were well shaped and indicated a triclinic system. A suitable crystal was then mounted under argon in a glass capillary that was dried in vacuo before use. The crystal was sealed in the capillary under argon and mounted on the diffractometer. Unit cell dimensions were determined by a least-squares fit from the settings of 25 automatically centered high-angle reflections (2θ = 25–42.2°). Crystal data information is presented in Table I. The intensities of two standard reflections were recorded after every 48 reflections. Their intensity varied no more than 2.2% during data collections. The intensities of the reflections were adapted to the changes in the intensities of the standard reflections. The corrected intensity data were then converted into structure factors through applications of Lorentz and polarization factors. No absorption correction was applied. Fractional coordinates are listed in Table II.

The structure was solved by direct methods. The best E-map revealed all non-hydrogen atoms with the exception of two oxygen atoms, which were located from a Fourier-difference map. Isotropic refinement proceeded in four cycles to R = 0.174. Refinement with anisotropic temperature factors brought R to 0.0885 in eight cycles. The positions of all hydrogen atoms were then located from a difference-Fourier map. They were included in the final refinement with fixed U_1 = 0.08. The calculations used the blocked-cascade procedure. The final discrepancy factors for 3043 observed reflections with $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.0562$ and $R_w = \sum(||F_o| - |F_c||w^{1/2})/\sum(|F_o|w^{1/2}) = 0.0594$ with $w = 1/(\sigma^2(F_o) + 0.0003(F_o^2))$.

Discussion

2-Chloro-1,3-dimethyl-1,3,2-diazaborolidine (**4**) adds 1 equiv of pyridine at −30 °C, and ^{11}B NMR data of the product suggested the formation of a tricoordinate species, tentatively formulated as pyridine(N–B)-1,3-dimethyl-1,3,2-diazaborolidinium(1+) chloride.[16] We therefore expected that a better leaving group at the boron atom might help in generating more stable cations containing tricoordinate boron. Such a group would be present in the 2-triflato derivative, **3**, readily available through reaction 1.

Addition of a stoichiometric amount of a nitrogen base L to a solution of **3** in dichloromethane furnishes the salts **5** as described by eq 2. According to ^{11}B NMR data the cations containing 2,6-lutidine (**5b**) and diphenylamine (**5c**) are stable in contrast to the pyridine-containing cation of **5a**, which decomposes in CH_2Cl_2 solution. No cation of type **6** is formed, however. Triphenylphosphine, on the other hand, is incapable of replacing the triflato group in **3**, a result that can be explained in terms of the HSAB theory.

Salts of a diazaborolidinium(1+) cation can also be prepared by adding triflic acid to the 2-dimethylamino derivative **7** as shown in eq 3. This stands in sharp contrast to the behavior

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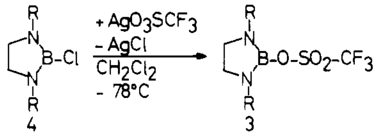
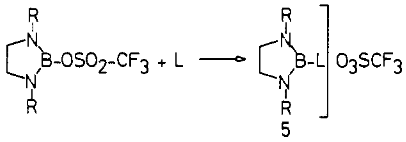
(19) Nöth, H.; Wrackmeyer, B. "Nuclear Magnetic Resonance Spectroscopy of Boron Compounds"; Springer-Verlag: Berlin, Heidelberg, New York, 1978.


(1)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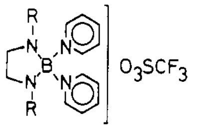
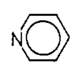
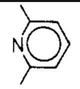
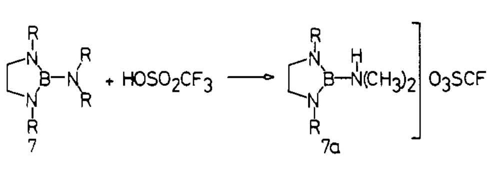

6

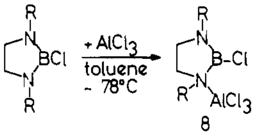
	5a	5b	5c
L			$NH(C_6H_5)_2$

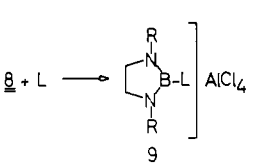

(3)

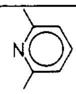
R = CH_3

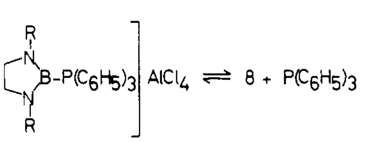
of **7** toward HCl, where B–N cleavage occurs rapidly and at low temperature even in exces of **7**.[17]

Finally, we observed the formation of 1,3-dimethyl-1,3,2-diazaborolidinium(1+) ions in the base attack on the aluminum chloride adduct of 2-chloro-1,3-dimethyl-1,3,2-diazaborolidine (**8**),[18] which forms according to eq 4. Although one could envisage that an amine or phosphine would displace $AlCl_3$ from the diazaborolidine due to their greater base strength, such a reaction was not observed. Rather, the boron-bonded chlorine atom is displaced, and the chloride formed attacks at the coordinated $AlCl_3$ with formation of $AlCl_4^-$. Equation 5 summarizes these results.


(4)


(5)

	9b	9d	9e
L		$NH(C_2H_5)_2$	$P(C_6H_5)_3$

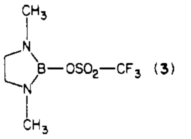
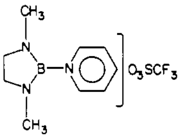
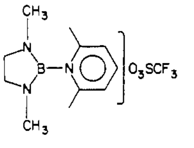
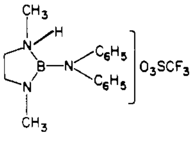
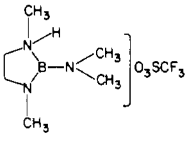
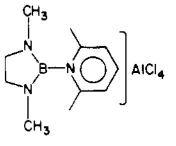
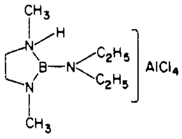
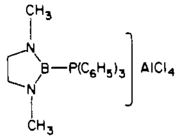
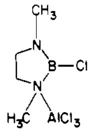

(6)

R = CH_3

The nitrogen base adducts **9b** and **9d** are stable in solution according to NMR evidence, in contrast to the triphenylphosphine product **9e**. Two ^{11}B NMR signals for the CH_2Cl_2 solution indicate an equilibrium situation as described by eq 6, and ^{27}Al NMR data show the absence of $Ph_3P{\cdot}AlCl_3$. Only one ^{31}P NMR signal is observed, which is shifted from −1.02 to −2.9 ppm when the **8**:$P(C_6H_5)_3$ ratio is increased from 1:0.5 to 1:2 (free $P(C_6H_5)_3$: $\delta(^{31}P) = -5.49$ in CH_2Cl_2). The $\delta(^{27}Al)$ NMR spectrum shows two signals at 103 and 109 ppm; they are practically not affected by the triphenylphosphine concentration, but more **9e** is present at higher phosphine ratios as evidenced by an increase of the $AlCl_4^-$ signal intensity at $\delta(^{27}Al)$ = 103. Therefore, phosphine exchange proceeds primarily at **9e**.

Freshly prepared solutions from solid **9e** gave only weak signals in the ^1H and ^{11}B NMR spectra attributable to **8**, increasing in intensity to a final value within 1 h. This behavior can be regarded as evidence that **9e** is a salt in the solid state. Nevertheless, it is surprising that **8** will react with $P(C_6H_5)_3$ while **3** does not. We believe that this difference is due to the higher Lewis acidity at boron in **8**, a compound that can be

Table III. ^1H, ^{11}B, and ^{27}Al NMR Data of 1,3-Dimethyl-1,3,2-diazaborolidinium(1+) Salts and Related Compounds[a]

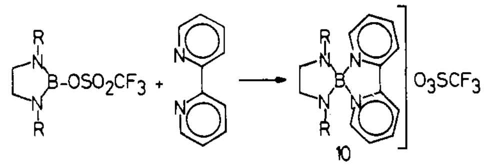
	$\delta(^{11}B)$	$\delta(^{27}Al)$	$\delta(^1H)$
	23.3		2.59 (br, 6 H), 3.21 (br, 4 H)
	26.7		2.49 (6 H), 3.33 (4 H), 7.72-8.74 (m, 5 H)
	26.5		2.55 (6 H), 2.76 (6 H), 3.55 (4 H), 7.35-7.95 (m, 3 H)
	25.8		2.33 (3 H), 2.64 (3 H), 2.96 (2 H), 3.33 (2 H), 6.99 (1 H), 7.07-7.49 (m, 10 H)
	24.9		2.67 (6 H), 2.73 (6 H), 3.26 (4 H), 7.89 (br, 1 H)
	26.3	103 (25)	2.57 (6 H), 2.82 (6 H), 3.62 (4 H), 7.7-8.53 (m, 3 H)
	25.0	103 (28)	1.12 (t, 6 H), 2.82 (6 H), 3.00 (q, 4 H), 3.40 (4 H), 6.48 (1 H)
	30.0 26.5	109 (62) 103 (22)	1.98 (d), 2.71, 3.17, 3.28, 7.1, 7.49
	31.0	108.6 (75)	2.87 (6 H), 3.38 (b, 4 H)

[a] Line width in Hz; br = broad, m = multiplet, t = triplet, d = doublet.

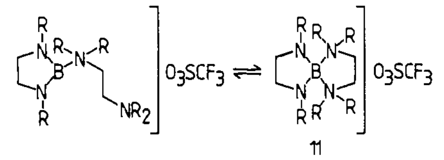
regarded as a monoaminoborane in contrast to the diaminoborane **3**.

All the compounds that we considered as salts containing a tricoordinated boron atom in the cation could also be described as simple Lewis acid–base adducts involving tetracoordinated boron atoms. What, then, gives evidence or even proves them to be ionic as suggested? Strong evidence comes from ^{11}B NMR data, summarized in Table III. The parent compound, **3**, exhibits a fairly sharp ^{11}B NMR signal at 23.3 ppm.

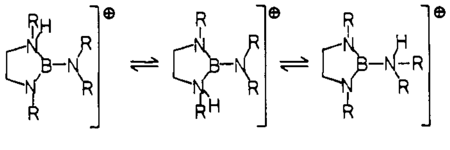
Addition of pyridine, 2,6-lutidine, or diphenylamine in a 1:1 ratio causes a slight downfield shift of this signal to 26–27 ppm. If the base would simply add to the boron atom making it tetracoordinated one would certainly expect a high-field shift by at least several ppm as observed for the majority of Lewis acid–base adducts of boron compounds.[19] In reaction 3 a small high-field shift is observed for the formation of **7a**. The parent compound **8** exhibits an ^{11}B NMR signal at 31.0 ppm, its adducts **9b** and **9d** at 30.0 and 26.5, respectively. All these chemical shifts remain in the region for tricoordinated boron compounds. That these assignments are correct can be substantiated by looking at the ^{11}B chemical shifts observed for the α,α'-bipyridyl and *N,N,N',N'*-tetramethylethylenediamine adducts with **3**. The former forms in pentane as a colorless solid −78 °C but turns orange at ambient temperature, thus resembling the product obtained by Banford and Coates[20] from α,α'-bipyridyl and bis(dimethylamino)boron chloride. It exhibits an ^{11}B NMR signal at 12.2 ppm in freshly prepared $CDCl_3$ solution. It is, therefore, justified to describe its formation by eq 7. In contrast, the adduct **11**, produced from **3** and tetramethylethylenediamine, gave rise to two ^{11}B NMR signals at 26.4 and 10.5 ppm (1:5 ratio) in CH_2Cl_2 solution, and this can be explained by an equilibrium of type 8. Further addition of base to the solutions causes a remarkable change: the signals shift to 24 and 19.5 ppm, respectively, and on warming, they merge into a broad peak. Therefore, a rapid exchange of the base occurs in addition to the equilibrium involving tri- and tetracoordinated boron.



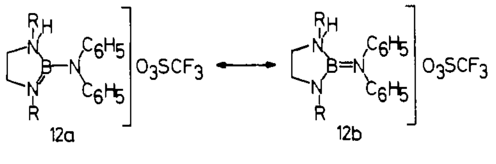
(7)



(8)



(9)



R = CH_3

Additional information is gained in the case of the tetrachloroaluminates by the ^{27}Al NMR spectra and IR data: there is a single, sharp line at ~103 ppm as well as a strong band at 500 cm^{-1}. Both chemical shift and line width are typical for free $AlCl_4^-$ [21] as is the IR band. In contrast, addition of triphenylphosphine to **8** results in two overlapping ^{27}Al NMR signals. One, at 103 ppm (22 Hz), clearly indicates the formation of $AlCl_4^-$; the other, at 109 ppm (62 Hz), results from the starting material.

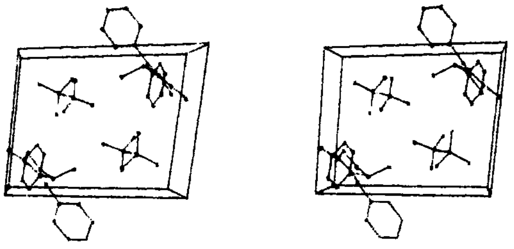


Figure 1. Stereopolot of the unit cell of **5c**. View is down the *b* axis. H atoms have been omitted.

A comparison of the proton NMR data of **5a** and **5b** reveals differences in the shielding of the diazaborolidine protons. The protons are better shielded in the pyridine adduct, and this may indicate a different orientation of the pyridine ring relative to the diazaborolidine as compared with the lutidine. Models show that the methyl groups of 2,6-lutidine strongly interact with those of the diazaborolidine ring, and therefore, it is to be expected that the 2,6-lutidine ring will orient itself more or less perpendicularly to the N_3B plane. Consequently, the CH_3 groups of the diazaborolidine unit will be deshielded by the lutidine's ring current. No B–N π interaction is to be expected, therefore, between boron and 2,6-lutidine. In contrast, the pyridine ring in **5a** may adopt coplanarity with the diazaborolidine ring system and therefore contributes to the electron density at boron via π bonding. Nevertheless, electron density at the boron atom is comparable for **5a** and **5b**.

For the cation in **7a** two sets of CH_3 proton NMR signals are observed, and only one is observed for the CH_2 group. This would be in accord with structure **7a**, but fluxional behavior according to eq 9 cannot be ruled out. A prototropism seems plausible, because similar base strengths are to be expected for all three nitrogen centers in **7**.

This situation holds no longer for **5c**, where the diphenylamino moiety will certainly be less basic then the diazaborolidine nitrogens. Indeed, proton NMR data show two pairs of chemically nonequivalent CH_3 and CH_2 groups, and this indicates a nonfluxional structure. Therefore, the cation is represented by **12 a/b**.

That the proton remains fixed at one ring nitrogen is somewhat surprising but can be rationalized by assuming strong B–N π back-bonding from the second ring nitrogen to boron, making this center therefore very weakly basic. Evidence for this situation comes from a study of 1:1 Lewis acid–base adducts of diazaborolidines[18,22] and from IR data of **5c** exhibiting a "doublet" at 1490 cm^{-1} characteristic of a B–N bond of high bond order.

Since the chemical shifts for comparable compounds **5** and **9** are identical within experimental error, it would be difficult to understand this fact were the compounds obtained as Lewis acid–base adducts rather than salts. The ^{11}B chemical shifts for the diazaborolidinium salts described here are quite similar to those observed by the addition of 2 mol of a base such as NH_3 or ethylendiamine to $[(CH_3)_2N]_2BCl{\cdot}AlCl_3$, which is present as a bis(dimethylamido)boron(1+) cation in CH_2Cl_2 solution,[6] and it was suggested that cations containing tetracoordinated boron atoms are formed in these reactions.[16] On the basis of the behavior of **8** toward diethylamine it appears

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[20] Banford, L.; Coates, G. E. *J. Chem. Soc.* **1964**, 3564.

[21] Kidd, R. G.; Truax, D. R. *J. Am. Chem. Soc.* **1968**, *90*, 6867.

[22] Anton K.; Euringer, Ch.; Nöth, H. *Chem. Ber.* **1984**, *117*, 1222.

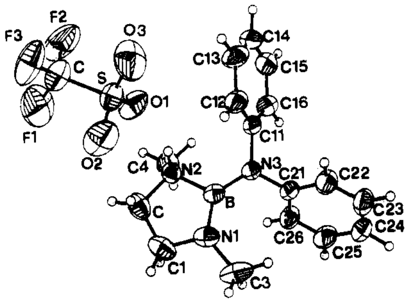

Figure 2. ORTEP plot of the cation of **5c**.

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) in 5c

	Distances		
S-O1	1.416 (2)	C-F1	1.328 (5)
S-O2	1.421 (2)	C-F2	1.289 (4)
S-O3	1.425 (3)	C-F3	1.321 (4)
S-C	1.794 (3)		
B-N1	1.386 (3)	N1-C1	1.462 (4)
B-N2	1.547 (3)	N1-C3	1.463 (4)
B-N3	1.412 (3)	N2-C2	1.510 (4)
N3-C21	1.437 (3)	N2-H	0.864 (26)
N3-C11	1.447 (2)		
	Angles		
N1-B-N2	106.1 (2)	C4-N2-B	110.0 (2)
N1-B-N3	132.9 (2)	C4-N2-H2	108.6 (17)
N2-B-N3	120.7 (2)	B-N2-H2	112.6 (16)
C1-N1-C3	116.7 (2)	C2-N2-C4	112.5 (2)
C1-N1-B	112.4 (2)	C2-N2-B	104.3 (2)
C3-N1-B	129.9 (3)	C2-N2-H2	108.9 (22)
O1-S-O2	115.3 (2)	O2-S-O3	113.5 (1)
O1-S-O3	115.5 (2)	O2-S-C	104.1 (2)
O1-S-C	103.3 (2)	O3-S-C	103.0 (2)

[a] C–C bond lengths of the phenyl rings were found in the range from 1.366 to 1.390 (6) Å.

that the species observed in solution are aminolysis products.

The NMR arguments provided here for tricoordinate boron in the cations are convincingly supported by the result of a single-crystal X-ray structure determination of **5c** = **12**. The compound crystallizes in the triclinic system, space group $P\bar{1}$. Figure 1 shows a stereoplot of the unit cell, indicating that there are no interactions of the triflate group with the boron atoms. Therefore, the compound is truly ionic. Hydrogen-bridge bonding seems to occur between the unique hydrogen bond and O(3) of the triflato group but is very weak as evidenced by a H···O(3) distance of 200.3 pm.

The bond characteristics of the triflate anion match perfectly with bond distances and angles found in other triflate salts.[23] On the other hand, fairly large U_{ii} values both for the oxygen and fluorine atoms indicate some disorder of the anion due to rotation.

Figure 2 depicts the molecular structure of the cation in **5c**, and Table IV lists selected bond distances and angles. The principal feature of the cation is a planar boron atom surrounded asymmetrically by three nitrogen atoms (sum of bond angles at boron 359.7°). The nitrogen atom N2 carries the added proton and is, therefore, tetracoordinated, as is of course apparent from the bond angles. The fairly wide bond angle N1–B–N3 is due to steric repulsion between the C1CH$_3$ group and the adjacent phenyl group. The bond angle N1–B–N2 (106.1°) remains virtually unaffected as compared with the structure of neutral 1,3,2-diazaborolidines[24,25] and their EX$_3$ addition products.[18,23] Moreover, the ring conformation of the diazaborolidinium ion resembles also closely those of the EX$_3$ addition products. The ring adopts an envelope conformation with the carbon atom next to the tetracoordinated nitrogen bending out from the ring's plane.

The average B–N bond in diazaborolidines is 1.41 Å. Three significantly different B–N bonds are observed in **5c**: a rather long B–N bond to the tetracoordinated nitrogen atom, a fairly "normal" B–N bond to the diphenylamino group, and a shorter ring B–N bond (1.39 Å). This bond is somewhat longer as those found for the GaCl$_3$ adducts of 2-chloro-1,3-dimethyl-1,3,2-diazaborolidine[18] or the *B,B'*-bis(1,3-dimethyl-1,3,2-diazaborolidin-2-yl)[26] (1.356 and 1.369 Å), respectively. We attribute this to the fact that the exocyclic nitrogen atom contributes π-electron density to the boron atom, though less effectively than the ring nitrogen N2 because the atoms C2/C4/N2/B1 lie essentially in a plane while the B/N3/C11/C21 plane is twisted by ~39° with respect to the B/N1/N2/N3 plane, thus making B–N π overlap less effective. **12a/b** gives a valence-bond description of the bonding in the cation of **5c**, where the canonical form **12a** contributes more strongly than **12b**.

The results presented in this study indicate that cations of the type $(R_2N)_2B{\cdot}L^+$ may play an important role in aminolysis processes of boron derivatives and in the cleavage of B–N bonds by protic reagents. Moreover, scattered information in the literature and unpublished material from our laboratory indicate that tricoordinated boron cations are fairly abundant.[16]

Acknowledgment. C.K.N. thanks Humboldt-Stiftung for an award that made this study possible. In addition, thanks are due to Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, and BASF-Aktiengesellschaft for continuous support.

Registry No. **3**, 92669-29-9; **4**, 17739-11-6; **5a**, 92641-80-0; **5b**, 92641-82-2; **5c**, 92641-84-4; **7a**, 92641-86-6; **8**, 92641-87-7; **9b**, 92641-88-8; **9d**, 92641-90-2; **9e**, 92669-28-8; **10**, 92641-92-4; **11**, 92641-94-6; AgSO$_3$CF$_3$, 2923-28-6; triflic acid, 1493-13-6; 1,3-dimethyl-2-(dimethylamino)-1,3,2-diazaborolidine, 26944-84-3.

Supplementary Material Available: Listings of bond distances and bond angles, anisotropic thermal parameters, hydrogen atom positions, observed and calculated structure factors, and fractional atomic coordinates and a figure and a probability plot for the tricoordinated boron cation (36 pages). Ordering information is given on any current masthead page.

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