boron atom in aminomethyleneborane prompts for steric shielding, i.e., the concept used successfully in this study.

Conclusions

The results described in the Discussion demonstrate convincingly that $AlBr_3$ attacks specifically at the bromine atoms of the amidoboron bromides investigated, removing it as $AlBr_4^-$ with formation of amidoboron(1+) cations of dicoordinate boron. The thermal stability of the salts decreases in the order **6** ≥ **5** > **7** > **8**, i.e., with decreasing electronic and steric shielding of the boron atoms. A similar situation holds for dicoordinate phosphorus cations[46] with bis(amido)phosphorus cations forming the most stable salts. However, attempts to prepare tricoordinate tris(amido)silicon cations have failed so far.[47] This indicates that presently our understanding of the governing factors that will lead to nonmetal cations of low coordination numbers is still incomplete.

The remarkable stability of the diamidoboron(1+) cations is due to the fact that these are isoelectronic with allenes, providing an all-octet situation for the NBN skeleton. π bonding between B and N is certainly stronger than in neutral BN compounds but is still weaker than in allenes in spite of the positive charge. Nevertheless it may be expected that other species isoelectronic with allenes may be prepared with use of the principles outlined in this work, e.g., aminomethyleneboranes $R_2N{-}B{=}CR_2$. This type of compound is a missing link and a challenge, too, because it is a molecule with the still rather rare BC double bond.[48] In contrast, the isomeric ketimino- or aldiminoboranes possessing an allene type structure but tricoordinate boron are well-known.[49,50]

If BX π bonding contributes significantly to the stabilization of dicoordinate boron cations, then one may expect boron cations of this type containing BO and BF bonds. The cations R_2NBOR^+ and R_2NBF^+ should form more readily than $ROBOR^+$. The cation FBF^+ is another possible candidate and should be an extremely strong electrophile. Since its boron atom cannot be sterically shielded, it is quite unlikely that stable salts containing this cation can be made. However, it cannot be excluded from the present experiments that salts of diarylboron cations may be made under certain experimental conditions. On the other hand, dialkylboron cations will possess only an electron quartet and will be most likely too strong an electrophile to be either formed or detected. We are presently engaged in testing these hypotheses and believe that the result of these investigations will be of importance to the understanding of reaction pathways in boron chemistry.

Acknowledgment. A grant by Deutsche Forschungsgemeinschaft for purchasing the Bruker WP 200 instrument is gratefully acknowledged as is the support for this work. In addition we thank Fonds der Chemischen Industrie and BASF-Aktiengesellschaft for financial assistance. Miss H. Wagner and cand. chem. D. Neumeier helped with the experiments, Mrs. G. Hanatschek recorded the IR spectra, and Mrs. L. Moser and Mr. K. Schönauer are responsible for the elemental analysis. We gratefully acknowledge their assistance. Thanks are due also to Dr. U. Schubert and Mr. H. Riedl for permission to use the Syntex $P2_1$ equipment and help in the low-temperature study. This work was carried out at TU Garching. Dr. R. Schell and Dr. P. Konrad conducted similar though less definite experiments as described in this work in the late 1960s; it is due to their observations that our interest in the possibility of finding the dicoordinate boron cation continued.

Registry No. **1**, 78837-58-8; **2**, 78837-59-9; **3**, 78837-60-2; **4**, 78837-61-3; **5**, 78870-24-3; **6**, 78870-26-5; **7**, 78870-28-7; **8**, 78870-30-1; (tmp)Li, 38227-87-1; Me_2NBBr_2, 7360-64-7; Et_2NBBr_2, 868-29-1; CH_3BBr_2, 17933-16-3; $Ph{-}BBr_2$, 4151-77-3; $AlBr_3$, 7727-15-3; (tmp)BCl_2, 79855-29-1; (tmp)H_2^+, 79855-30-4; (tmp)H, 768-66-1; CH_4, 74-82-8; $H_3C{-}CH_3$, 74-84-0; Me–Ph, 108-88-3; $Me{-}NH_2$, 74-89-5; Me_3N, 75-50-3; CH_3^+, 14531-53-4; $CH_3{-}CH_2^+$, 14936-94-8; $Ph{-}CH_2^+$, 6711-19-9; $H_2N{-}CH_2^+$, 54088-53-8; $Me_2N{-}CH_2^+$, 77267-03-9; BH_2^+, 15194-16-8; $Me{-}BH^+$, 79855-31-5; $Ph{-}BH^+$, 79855-32-6; $H_2N{-}BH^+$, 79855-33-7; $Me_2N{-}BH^+$, 79855-34-8; $H_2N{-}B^+{-}Me$, 79855-35-9; $H_2N{-}B^+{-}Ph$, 79855-36-0; $H_2N{-}B^+{-}NH_2$, 79855-37-1; $Me_2N{-}B^+{-}NH_2$, 79855-38-2; $Me_2N{-}B^+{-}Me$, 79855-39-3; $Me_2N{-}B^+{-}Ph$, 79855-40-6; $Me_2N{-}B{-}NMe_2$, 79840-42-9; BH_3, 13283-31-3; $Me{-}BH_2$, 12538-96-4; $Ph{-}BH_2$, 45481-30-9; $H_2N{-}BH_2$, 14720-35-5; $Me_2N{-}BH_2$, 1838-13-7; $H_2N{-}BH{-}Cl$, 47938-17-0; $H_2N{-}BCl{-}Me$, 79855-41-7; $H_2N{-}BCl{-}Ph$, 79855-42-8; $H_2N{-}BCl{-}NH_2$, 79855-43-9; $H_2N{-}BCl{-}NMe_2$, 79855-44-0; $Me_2N{-}BCl_2$, 1113-31-1; Ph–CO–Cl, 98-88-4; $Ph{-}CO^+$, 19270-10-1; $H_2N{-}B{=}CH_2$, 79855-45-1.

---

(46) Thomas, M. C.; Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1977**, *16*, 994 and literature cited therein.

(47) Cowley, A. H.; Cushner, M.; Riley, P. E. *J. Am. Chem. Soc.* **1981**, *102*, 624.

(48) (a) Species containing (partial) BC double bonds are formed on α-deprotonating sterically hindered organoboranes[41b] or by BC cleavage of polyborylmethanes.[41c] (b) Wilson, J. W., private communication. (c) Matteson, D. S. *Synthesis* **1975**, *14*, 375.

(49) Hess, H. *Acta Crystallogr., Sect. B* **1969**, *B25*, 2334.

(50) Collies, M. R.; Lappert, M. F.; Snaith, R.; Wade, K. *J. Chem. Soc., Dalton Trans.* **1972**, 370. Dorokhov, V. A.; Lappert, M. F. *J. Chem. Soc. A* **1969**, 433.

Contribution from the Department of Chemistry,
University of Utah, Salt Lake City, Utah 84112

Synthesis and Characterization of Salts of the Bis(diisopropylamido)boron(III) Cation and Attempted Reactions To Make the Corresponding Bis(dimethylamido)boron(III) Cation[1]

JOHN HIGASHI, ALAN D. EASTMAN, and R. W. PARRY*

Received June 1, 1981

Bis(diisopropylamino)chloroborane and pure $AlCl_3$ react under rigorously anhydrous conditions in a one to one ratio to give an ionic compound that can be formulated as $[(i\text{-}Pr)_2N{=}B{=}N(i\text{-}Pr)_2]^+[AlCl_4]^-$. This representation is supported by ^{27}Al, ^1H, ^{13}C, and ^{11}B NMR data as well as by IR absorption bands at 1830–1900 cm^{-1} assigned to the B=N double bond. Conductivity data are also given for the related compound made from bis(dimethylamino)chloroborane. The $[Me_2N{=}B{=}NMe_2]^+$ cation was not stable in solution. Evidence is interpreted in favor of either its condensation to bigger units and/or the formation of a molecular compound with the $AlCl_4^-$ anion. Lewis base molecules will add to the tetramethyl cation to give a four-coordinate boron cation.

The bis(dimethylamido)phosphorus cation, $[(Me_2N)_2P]^+$, was described in papers from this laboratory.[2] The existence of that species, a coordinately unsaturated system stabilized by extensive $p\pi{-}p\pi$ bonding, in this case across the N–P–N

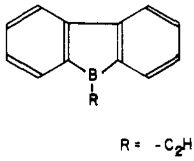
0020-1669/82/1321-0716$01.25/0

chain, suggested that the analogous boron cation might also be stable. Such a system would formally have sp hybridization on the boron atom, allowing delocalization of the two nitrogen lone pairs into the two empty 2p orbitals of boron; the N–B–N$^+$ system would be isoelectronic and isostructural with the C–C–C system in allene and would be the first example of a two-coordinate boron cation.

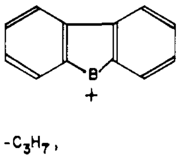
Tetrahedral four-coordinate boron cations are well-known and thoroughly characterized,[3] but earlier reports describing the synthesis of a two-coordinate cation have been questioned. The bulk of the work toward that end has been performed on the chlorodiphenylborane Lewis acid system. Davidson and French[4] observed that the equivalent conductance of methyl ethyl ketone solutions containing chlorodiphenylborane and aluminum chloride was 36.6 Ω^{-1} cm^2 (0.047 M), whereas solutions of chlorodiphenylborane alone had an equivalent conductance of 0.0379 Ω^{-1} cm^2 (0.0356 M). Conductivities of comparable solutions of aluminum chloride were not reported. They also noted that addition of silver perchlorate to solutions of chlorodiphenylborane in nitrobenzene resulted in immediate precipitation of silver chloride. They observed that the foregoing metathesis reaction occurred only in basic solvents and that the cationic boron species could be isolated only as the 2,2′-bipyridyl complex $[(C_6H_5)_2B(bpy)]^+X^-$. The counterion X^- could be Cl^-, Br^-, I^-, $[B(C_6H_5)_4]^-$, etc. When the silver perchlorate metathesis reaction was run in dioxane, the product was not a good electrolyte even though it appeared to be identical in all other respects with the product made in nitrobenzene.

Armstrong and Perkins[5] used a Pariser–Parr–Pople LCAO–MO–SCF method to calculate the electronic structure of both solvated and unsolvated diphenylboron cations. The UV spectrum, calculated for the solvated ion, was closer to the observed spectrum; thus, they concluded that Davidson and French's ion contained four-coordinate boron. In a related NMR study Moodie, Ellul, and Conner[6] reported that addition of $AgClO_4$ to sulfolane solutions of $(C_6H_5)_2BCl$ gave a change in chemical shift for the phenyl protons of only 0.07 ppm (−7.29 to −7.36 ppm vs. Me_4Si). Addition of a Lewis base to the cation also gave a very small change in δ. These data were interpreted as indicating that very little electron density was transferred in π bonds from the phenyl rings to the boron; thus, coordination of solvent molecules to give a four-coordinate species was assumed. Köster and Benedikt[7] prepared substituted 9-borafluorenes (**1**). Köster later prepared the cyclic cation (**2**). Armstrong and Perkins[5] concluded that such a cation would not be solvated in weakly basic solvents and that the positive charge on the boron would be dispersed over the aryl ring system. As yet experimental evidence on this point is not available. Nöth[8] suggested that the bis(dimethylamido)boron(III) cation might be isolable, but his group obtained negative results when they attempted the synthesis using SbF_6^- as the counterion. Recently Nöth and Staudigl[9] have been successful in synthesizing a cation with $AlCl_4^-$. The reports from our two laboratories are complementary.

1



2



In this report we describe the reaction between $(Me_2N)_2BCl$ and $AlCl_3$ and $[(i\text{-}Pr)_2N]_2BCl$ and $AlCl_3$ as well as the reaction between $[(Me)_2N]_2BBr$ and $AlBr_3$. The evidence provides strong support for a linear $[(i\text{-}Pr)_2N{=}B{=}N(i\text{-}Pr)_2]^+$ ion, but the methyl compound appears to be less stable.

Experimental Section

General Procedures and Instrumentation. Reactions were run with use of vacuum-line and drybox techniques. Exposure of reagents and products to air and moisture was rigorously avoided. NMR spectra were taken with a Varian FT-80A multinuclear spectrometer with a variable-temperature probe. Infrared spectra were taken with a Beckman IR-20 spectrometer. Gases were contained in an 8-cm glass cell with KBr windows. Liquids were either run as solutions or as capillary films between KBr plates. Solids were either run as KBr pellets or as Nujol or Kel-F mulls. All conductivity measurements were made on either an Industrial Instrument Model RC-1B bridge or a Yellow Springs Instrument Co. Model 31 conductivity bridge. The cell (constant = 0.277 cm^{-1}) was designed to permit attachment to the vacuum line to avoid any exposure of the system to air or water vapor.

Materials. All materials were reagent grade unless specifically noted. BCl_3, from Matheson Coleman and Bell (MCB), was fractionated on the vacuum line before use. The −120 °C fraction was used. Amines from MCB were dried over NaOH before use. Solvents were dried over Linde 4A molecular sieves. Ethers were checked for peroxide content with use of aqueous acidic iodide solution. Peroxides were removed by refluxing with CuCl.[10] Peroxide-free ethers were stored over $LiAlH_4$.

Bis(diisopropylamino)chloroborane, $[(i\text{-}Pr)_2N]_2BCl$. A 2.34-mol sample of diisopropylamine in 500 mL of hexane was cooled in a dry ice–2-propanol bath. A 0.58-mol sample of BCl_3 was vaporized, condensed on a cold finger, and allowed to drip into the stirred solution. Addition was complete in 1 h. After the system stood overnight, the solid (R_2NH_2Cl) was filtered off, solvent was distilled out, and the residue was vacuum-distilled at 55–65 °C (0.2–0.5 mmHg).

Tris(dimethylamino)borane and bis(dimethylamino)chloroborane were synthesized by literature methods.[11] The reactions used were

$$BCl_3 + 6HN(CH_3)_2 \xrightarrow[\text{pentane}]{-80\ ^\circ C} [(CH_3)_2N]_3B + (CH_3)_2NH_2Cl$$

$$2B[N(CH_3)_2]_3 + BCl_3 \xrightarrow[\text{pentane}]{-80\ ^\circ C} 3ClB[N(CH_3)_2]_2$$

The bromo compound could be made with use of BBr_3. The purity of the product was monitored by ^1H NMR. Freshly purified aliquots were distilled directly into the reaction vessels.

Aluminum chloride and aluminum bromide were reagent grades from MCB and Fisher Scientific, respectively. Each was carefully purified just before use by vacuum sublimation from a 10:1 mixture of the trihalide and potassium halide.[12] The solids were always manipulated under N_2 or in a vacuum line.

Synthesis of $[(R_2N)_2]^+[AlCl_4]^-$. Approximately 5 mL of CH_2Cl_2 was added to freshly sublimed $AlCl_3$. A 2-g quantity of $ClB[N(i\text{-}Pr)_2]_2$ was then added, and the solution was stirred. Although $AlCl_3$ is only slightly soluble in CH_2Cl_2, the amount of solid $AlCl_3$ definitely de-

---

(1) Presented in part before the 4th International Meeting on Boron Chemistry, Salt Lake City/Snowbird, Utah, July 1979.

(2) Thomas, M. G.; Kopp, R. W.; Schultz, C. W.; Parry, R. W. *J. Am. Chem. Soc.* **1974**, *96*, 2646. Thomas, M. G.; Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1977**, *16*, 994.

(3) Shultz, D. R.; Shore, S. G.; Kodama, G.; Giradot, P. R.; Parry, R. W. *J. Am. Chem. Soc.* **1958**, *80*, 1. Taylor, R. C.; Schultz, D. R.; Emery, A. R. *J. Am. Chem. Soc.* **1958**, *80*, 27. Nordman, C. E.; Peters, C. R. *Ibid.* **1959**, *81*, 3551. Parry, R. W. *Inorg. Synth.* **1970**, *12*, 126. Miller, J. E.; Muetterties, E. L. *J. Am. Chem. Soc.* **1964**, *86*, 1033. Douglass, J. E. *Ibid.* **1964**, *86*, 5431. Shitov, O. P.; Ioffe, S. L.; Tartakovskij, V. A.; Novikov, S. S. *Russ. Chem. Rev.* (*Engl. Transl.*) **1970**, *39*, 905.

(4) Davidson, J. M.; French, C. M. *J. Chem. Soc.* **1958**, 114; **1962**, 3364.

(5) Armstrong, D. R.; Perkins, P. G. *J. Chem. Soc. A* **1966**, 1026.

(6) Moodie, R. B.; Ellul, B.; Connor, T. M. *Chem. Ind.* (*London*) **1966**, 767.

(7) Köster, R.; Benedikt, G. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 323.

(8) Nöth, H. *Prog. Boron Chem.* **1970**, *3*, 248.

(9) Nöth, H.; Staudigl, R.; Wagner, H.-U. *Inorg. Chem.*, preceding paper in this issue.

(10) Jolly, W. L. "The Synthesis and Characterization of Inorganic Compounds"; Prentice-Hall; Englewood Cliffs, NJ, 1970; p 116.

(11) Steinberg, J. J.; Brotherton, R. J. "Organoboron Chemistry"; Vol. II, Interscience: New York, 1966; p 12.

(12) Jones, D. E. H.; Wood, J. L. *J. Chem. Soc. A* **1966**, 1448.

creased after a few minutes. The solution was filtered in the vacuum system to remove any excess $AlCl_3$. A sample was prepared for NMR measurements and stored at -80 °C. The NMR spectra showed that the product was stable for days in a sealed tube. On exposure of the product to air a solid was formed that was insoluble in CH_2Cl_2.

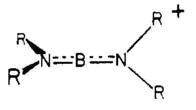
Similar procedures were used in the $ClB(NMe_2)_2$ reaction, but the product was not stable after synthesis. The NMR spectra changed as the product was warmed. Chemical analysis of the solution (1 to 1.99 for N to Cl) showed the reaction stoichiometry to be 1 to 1 for $AlCl_3$ to $ClB(NMe_2)_2$.

Reactions of $(Me_2N)_2BCl{\cdot}AlCl_3$ with Lewis Bases—Formation of Four-Coordinate Cation. In a typical preparation, 1 mmol of Lewis base was introduced into an NMR tube containing 0.5 mmol of $(Me_2N)_2BCl{\cdot}AlCl_3$ in 1 mL of CH_2Cl_2 at 25 °C. NMR and IR data were then obtained.

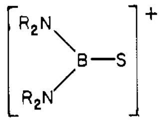
Results and Discussion

NMR Spectra for $[((i\text{-Pr})_2N)_2B]^+[AlCl_4]$. Proton, carbon-13, boron-11, and aluminum-27 spectra were run on a CH_2Cl_2 solution of $[((i\text{-Pr})_2N)_2B]^+[AlCl_4]^-$ at ambient temperature. Data are shown in Table I. The existence of the $AlCl_4^-$ ion in solution is clearly and unequivocally established by the ^{27}Al spectrum, which matches an authentic spectrum made as part of this study on a sample of $Me_4N^+AlCl_4^-$. Both spectra agree very well with earlier literature reports on $AlCl_4^-$.[13] Further, the sharpness of the spectrum indicates that the regular tetrahedral geometry of the $AlCl_4^-$ has not been disturbed significantly in solution (low field gradients).

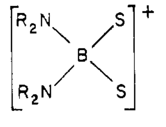
NMR data on the cation are instructive but less definitive than the ^{27}Al spectrum on $AlCl_4^-$. Structural possibilities for the cation include the three models shown:



linear tetraisopropyl-allene analogue; two-coordinate boron



solvated, three-coordinate boron



solvated, four-coordinate boron

R=-i-Pr S=SOLVENT

The proton spectrum shows the isopropyl group clearly and indicates that all isopropyl groups are equivalent since only two signals, a doublet and a septet in a ratio of 6 to 1, are seen. No signal corresponding to bound CH_2Cl_2 is seen; thus if solvent is involved in the structure, it would have to be exchanging rapidly with bulk solvent. Both sets of protons are shifted to higher δ values by about 0.4 ppm as a result of the cation formation.

The carbon-13 spectrum confirms the conclusions from the ^1H spectrum. The central single carbon of the isopropyl group is shifted downfield (+δ values) by 4.7 ppm as a result of ion formation. The methyl carbons are shifted only -0.1 ppm by this process. Again no signal is seen to indicate coordinated, nonexchanging solvent. The carbon-13 data also indicate clearly that all isopropyl groups are equivalent. This suggests that there is considerable freedom of motion around the N–C bond. The ^{11}B spectrum of the cation shows a single broad peak at +35.7 ppm from $F_3B{\cdot}OEt_2$. The starting borane has a signal at +29.6 ppm; thus formation of the cation results in a shift of 6.1 ppm downfield from the starting material. This shift on cation formation is small in comparison to the shift observed when the phosphorus compound $[(R_2N)_2P]^+$ is formed from $(R_2N)_2PCl$ (from 160 to 264 ppm).[2] On the other hand, a deshielded (large δ value) phosphorus atom is not always seen for a dicoordinate phosphorus cation. Dimroth[14] reported a chemical shift of about 35 ppm for his dicoordinate phosphorus cation. Very extensive electron delocalization was possible. Similarly, in the dicoordinate, linear boron cation very extensive electron delocalization over the N–B–N framework is to be anticipated and a marked shift of the boron resonance downfield is *not* to be anticipated.

In a later phase of this work (this paper) authentic four-coordinate boron cations were prepared by adding 2 mol of base to $(1/n)[Me_2N{=}B{=}NMe_2]_n^{n+}$. The ^{11}B chemical shift

Table I. NMR Data for $[(i\text{-Pr})_2N{=}B{=}N(i\text{-Pr})_2]^+[AlCl_4]^-$

	nucleus		δ	area
$((i\text{-Pr})_2N)_2BCl$	^1H	septet	3.3[a] (J = 7.0 Hz)	1.0
	^1H	doublet	1.0 (J = 7.0 Hz)	5.9
$[((i\text{-Pr})_2N)_2B]^+$-$[AlCl_4]^-$	^1H	septet	3.7 (J = 6.5 Hz)	1.0
	^1H	doublet	1.4 (J = 6.5 Hz)	6.1
$((i\text{-Pr})_2N)_2BCl$	^{13}C	singlet	6.9[b]	1
	^{13}C	singlet	31.0	2
$[((i\text{-Pr})_2N)_2B]^+$-$[AlCl_4]^-$	^{13}C	singlet	-2.2	1
	^{13}C	singlet	-31.1	2
$((i\text{-Pr})_2N)_2BCl$	^{11}B	broad singlet	+29.6[c]	
$[((i\text{-Pr})_2N)_2B]^+$-$[AlCl_4]^-$	^{11}B	broad singlet	+35.7	
$AlCl_3$ in CH_2Cl_2	^{27}Al	very broad singlet	+111.7[d]	
$[((i\text{-Pr})_2N)_2B]^+$-$[AlCl_4]^-$	^{27}Al	sharp singlet	+102.9	
$[Me_4N]^-[AlCl_4]^-$	^{27}Al	sharp singlet	+102.4	
lit.[e] for $[AlCl_4]^-$	^{27}Al	sharp singlet	+102.4	

[a] Proton standard = tetramethylsilane. [b] Carbon standard = CH_2Cl_2; add +54.0 to convert to carbon in Me_4Si. [c] Boron standard = $F_3B{\cdot}O(C_2H_5)_2$. The spectrum is not changed in either case by ^1H spin decoupling. [d] Aluminum standard = $Al(H_2O)_6^{3+}$. For $AlCl_3$ the width at half-height was 300 Hz, for $[(R_2N)_2B]^+$-$[AlCl_4]^-$ the value was 40 Hz, and for $[Me_4N]^+[AlCl_4]^-$ the value in this laboratory was 60 Hz. The literature value for the $AlCl_4^-$ width at half-height was 15 Hz.

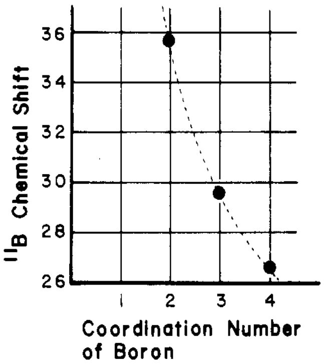


Figure 1. Chemical shift of ^{11}B for $[((i\text{-Pr})_2N)_2B]^+$, $((i\text{-Pr})_2N)_2BCl$, and $[(Me_2N)_2B(N\text{–base})_2]^+$ plotted against the coordination number of boron.

---

(13) Kidd, R. G.; Truax, D. R. *J. Am. Chem. Soc.* **1968**, *90*, 6867.

(14) Dimroth, K.; Hoffman, P. *Chem. Ber.* **1966**, *99*, 1325. Dimroth, K. *Fortschr. Chem. Forsch.* **1973**, *38*, 1.

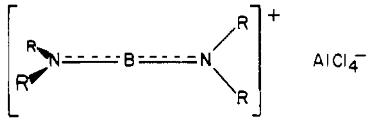
Table II. Infrared Spectra (cm^{-1}) of $((i\text{-Pr})_2N)_2BCl$ and $[((i\text{-Pr})_2N)_2B]^+[AlCl_4]^-$

$((i\text{-Pr})_2N)_2BCl$	$[((i\text{-Pr})_2N)_2B]^+[AlCl_4]^-$
510 (w)	500 (vs) [$(AlCl_4]^-$)
570 (w)	
620 (w)	675 (w)
	800 (w)
	850 (w)
900 (m)	900 (w)
	980 (s)
1000 (m, sh)	1010 (m, sh)
1040 (sh)	
1070 (s)	
1130 (s)	1100-1180 (s, br)
1180 (s)	
1325 (vs)	1330 (vs)
1360 (m)	1380-1400 (s)
1420 (m)	1450 (s)
1445 (s)	1510 (m)
	1830-1850 (vs) (N=B=N)
	1900 (s, sp)
2890 (vs)	2930 (vs)
2940 (vs)	2980 (vs)

value for these compounds where the ligand was a nitrogen base was about δ 26.5 ± 0.6 (Table V). If the chemical shift for ^{11}B is plotted against coordination number of boron in the species (ion or molecule), the curve shown in Figure 1 is obtained. This plot indicates that the assignment of a coordination number of 2 to the boron cation is consistent with ^{11}B NMR data but, taken by itself, is not proof of the existence of a dicoordinate ion.

In summary the ^{27}Al NMR data conclusively establish the existence of the $AlCl_4^-$ ion in CH_2Cl_2 solution. The sharp signal indicates that the tetrahedral symmetry is retained. The ^1H, ^{13}C, and ^{11}B data are most consistent with a tetraisopropylallene type of linear N═B═N cation with the planes of the two N═B double bonds at right angles to each other. Although the data support the allene structure, the NMR data alone can not eliminate conclusively a tricoordinate or tetracoordinate solvate in which there is rapid exchange between the coordinated solvent and the bulk solvent in the solution. Infrared data address this latter point.

Infrared Spectra of $[(i\text{-Pr})_2N{=}B{=}N(i\text{-Pr})_2]^+[AlCl_4]^-$. The infrared spectrum of $[((i\text{-Pr})_2N)_2B]^+[AlCl_4]^-$ differs dramatically from that of $[(i\text{-Pr})_2N]_2BCl$ in two important respects. First, the absorption for $AlCl_4^-$ at 500 cm^{-1} in the ionic compound is clear and definitive, confirming the identification of $AlCl_4^-$ by NMR.[15] The absorption at 500 cm^{-1} is not seen in the parent borane, since $AlCl_4^-$ was not present there. Second, absorptions in the region between 1830 and 1900 cm^{-1} are strong in the ionic compound and do not appear in the parent borane. This band is most logically attributed to the asymmetric stretching frequency of the B═N double bonds. This motion is probably coupled quite strongly to the N–C carbon motions. The C═C═C stretching vibration in the comparable allenes occurs as a strong band in the range 1920–2000 cm^{-1},[16] although in a few of the tetrasubstituted allenes this absorption is very weak.[17] In certain cases, particularly when the substituent is a carbonyl or nitrile group, the characteristic allene band appears as a well-defined doublet.[16] Whether or not the absorptions at 1800–1900 cm^{-1} represent a similar doubling, an overtone, or a combination band is still indefinite. Regardless of this more detailed question, the strong absorption at 1800–1900 cm^{-1} provides strong support for an N═B═N linkage. The IR and NMR data strongly support the structure



3

The B–N bond in bis(amino)boranes is usually assigned in the region 1300–1600 cm^{-1}[18] and is probably also coupled quite strongly to carbon motions. In the parent borane the band at 1445 is tentatively assigned as the B–N stretching frequency.

The Aluminum Trichloride Adduct of Bis(dimethylamino)chloroborane and the Aluminum Trichloride Adduct of Bis(dimethylamino)bromoborane. Although $(Me_2N)_2BCl$ will react with dry $AlCl_3$ in CH_2Cl_2 solution to give an ionic species, the product is much less stable and appears to undergo secondary reactions. The solvent and $(Me_2N)_2BCl$ were condensed onto a sample of $AlCl_3$ at −196 °C, and the sample was warmed gradually. NMR was used to monitor reaction progress. It was found that results varied depending on reaction conditions. A mixture was indicated by NMR data, and a precipitate formed in the sealed NMR tube if the system was allowed to stand at room temperature for several days.

NMR Spectra for $(Me_2N)_2BCl{\cdot}AlCl_3$ in CH_2Cl_2. A sample of $(Me_2N)_2BCl{\cdot}AlCl_3$ made at very low temperature and allowed to warm up to −80 °C showed a relatively broad Al signal in the position attributable to $AlCl_4^-$ and a second broad signal of lower intensity just upfield from the $AlCl_4^-$ signal. The existence of the peak for $AlCl_4^-$ indicated initial formation of an ionic product. This fact was confirmed by conductivity measurements shown in Table III. If the sample was allowed to stand for several hours at room temperature, the $AlCl_4^-$ signal got smaller and the other signal grew to be the major peak. The signal for ^{11}B in the parent borane was a fairly broad peak at +27.6 ppm from $F_3B{\cdot}OEt_2$. For the $AlCl_3$ adduct the ^{11}B signal was again a broad peak at +30.9 ppm. The low-temperature NMR showed several peaks, which were poorly resolved.

Table III. Conductivity Measurements in Dry CH_2Cl_2 at 25 °C[a]

compd	Λ, Ω^{-1} cm^2	compd	Λ, Ω^{-1} cm^2
$(Me_2N)_2BCl$	2.85×10^{-2}	$[(n\text{-Bu})_4N]^+I^-$	1.98
$AlCl_3$	0.235	$(Me_2N)_2BCl{\cdot}AlCl_3$	4.00
$[Me_4N]^+[AlCl_4]^-$	5.36		

[a] As NMR data show, if the sample is run very promptly at room temperature $AlCl_4^-$ is still present. It soon decreases in amount as a precipitate forms.

The carbon-13 spectrum showed one large peak at −14.9 ppm from CH_2Cl_2, very small peaks at −10.3 and −13.4 ppm, and a moderately large peak at −7.9 ppm. As the temperature was raised, no clearly defined pattern of changes in the ^{13}C peak heights could be detected, but the spectral pattern was far more complex than would be expected for the dicoordinate linear boron cation. In fact a number of different patterns were obtained, suggesting competing processes.

The NMR and conductivity evidence suggest quite strongly that initially the ionic material $[Me_2N{=}B{=}NMe_2]^+[AlCl_4]^-$ is formed at low temperature, but the system with methyl groups on the cation is unstable, presumably because the alkyl groups are not large enough to block reactions, giving boron

---

(15) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley: New York, 1978; p 136.

(16) Bellamy, L. J. "Advances in Infrared Group Frequencies"; Methuen and Co. Ltd.: London, 1968; p 65.

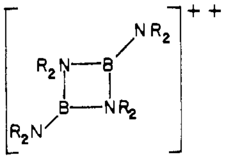
(17) Wotiz, J.; Mancuso, D. *J. Org. Chem.* **1957**, *22*, 207.

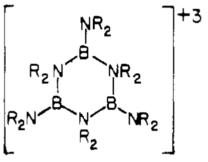
(18) Niedenzu, K.; Beyer, H.; Dawson, J. W. *Inorg. Chem.* **1962**, *1*, 738. Bruch, J. E.; Gerrard, W.; Goldstein, M.; Mooney, E. F.; Willis, H. A. *Spectrochim. Acta* **1962**, *18*, 1403.

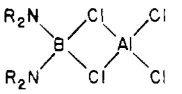
Table IV. Infrared Spectra of $(Me_2N)_2BCl$, $(Me_2N)_2BBr$, $(Me_2N)_2BCl\cdot AlCl_3$, and $(Me_2N)_2BBr\cdot AlBr_3$ (All Values in cm^{-1})

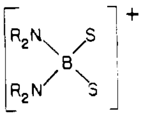
$(Me_2N)_2BCl$	$(Me_2N)_2BCl\cdot AlCl_3$	$(Me_2N)_2BBr$	$(Me_2N)_2BBr\cdot AlBr_3$
2980 (m)	3000 (m)	2984 (m)	3000 (m)
2850 (s, br)	2910 (s, br)	2850 (s, br)	2910 (s, br)
2735 (sh)	2805 (m)	2800 (s)	2803 (m)
2440 (w)			
1555 (sh)	1610 (sh)	1555 (sh)	1610 (sh)
1532 (vs)	1565 (vs)	1532 (vs)	1556 (vs)
1465 (vs)	1470 (vs)	1465 (vs)	1470 (vs)
1415 (vs)	1410 (s)	1410 (vs)	1410 (s)
1400 (sh)		1385 (s)	
1360 (s)	1360 (s)	1355 (s)	1360 (ms)
1215 (s)	1205 (s)	1215 (s)	1210 (s)
1190 (m)	1195 (m)	1190 (m)	1195 (m)
1137 (s)	1145 (s)	1140 (s)	1146 (s)
1070 (s)	1065 (s)	1067 (s)	1065 (s)
1015 (sh)	1020 (w)	1018 (sh)	1020 (w)
915 (sh)	930 (w)	915 (sh)	930 (w)
890 (ms)	900 (m)	983 (ms)	901 (m)
840 (w)		860 (m)	705 (m)
	703 (m)		
	660 (w)		660 (w)
582 (s)		585 (sh)	
	550 (vs, br)	562 (m)	
			405 (s, br)

a higher coordination number. Several possibilities exist. These include









4

R=-CH_3 S=SOLVENT

It is currently not possible to differentiate between these species, but the possibility of a solvate (**4**) can be minimized by the fact that the infrared spectra are identical in CH_2Cl_2 and in $C_2H_4Cl_2$ and is almost identical neat.

Infrared Data on $(Me_2N)_2BCl\cdot AlCl_3$. The infrared spectrum of the adduct taken after warming to 25 °C shows virtually the same absorptions as the starting bis(dimethylamino)chloroborane except that a strong absorption at 498 cm^{-1} attributable to $AlCl_4^-$ appears. Significantly the bands at 1800 and 1900 cm^{-1} attributable to a $B{=}N$ stretching mode in the isopropyl ion do *not* appear. This fact argues strongly for a cyclic species without double bonds. Data are shown in Table IV. The data for the corresponding $AlBr_4^-$ salt are also shown. The $AlBr_4^-$ absorptions appear at 405 cm^{-1}.[15]

Table V. Lewis Base Adducts of $(Me_2N)_2BCl\cdot AlCl_3$

base	$\delta(^1H)^a$	$\delta(^{11}B)^b$	$\nu_{as}(B\text{-}N)^c$
none	3.03	31.0	1580
NH_3	2.78	26.3	1565
Me_2NH	2.75	27.3	1570
$H_2NCH_2CH_2NH_2$	2.76	25.9	1557
$(i\text{-}Pr)_2O$	2.61		
Ph_3P	2.53	27.7	

[a] δ of ^1H in the methyl groups of $(Me_2N)_2BCl\cdot AlCl_3$; reference = Me_4Si. [b] Reference = $F_3B\cdot OEt_2$. [c] Frequency assigned to N-B stretch by analogy to parent borane.

Lewis Acid Chemistry of $(Me_2N)_2BCl\cdot AlCl_3$. If indeed the bis(dimethylamido)boron(III) cation dimerizes or trimerizes with itself, it would appear that addition of a Lewis base might break up the aggregates and generate normal, four-coordinate boron cations:

$$[(Me_2N)_2B]_n^{n+}[AlCl_4]^-_n + 2nL \rightarrow n[[(Me_2N)_2BL_2]^+[AlCl_4]^-]$$

Several Lewis bases were added to $(Me_2N)_2BCl\cdot AlCl_3$. Evidence for uptake of 2 mol of base and formation of the four-coordinate cation was obtained and is summarized in Table V. In one case where the base was 2,2′-bipyridyl, the complex $[(Me_2N)_2B(bpy)]^+Cl^-$ was synthesized and compared to the corresponding $AlCl_4^-$ salt. The cations were identical. The $[(Me_2N)_2B(bpy)]^+$ cation has been reported by Banford and Coates.[19]

Very small changes in the B–N stretching frequency and a boron chemical shift value below that for the parent borane in each case indicate that the four-coordinate species has been formed and has broken up the aggregates.

Acknowledgment. Support of this work by the National Science Foundation through Grant No. GP 32079 and CHE 7920313 to the University of Utah is gratefully acknowledged. The authors are also grateful to the Colorado State University Regional NMR Center funded by National Science Foundation Grant No. CHE 7818581 for obtaining some of the NMR spectra used in this study.

Registry No. $[(i\text{-}Pr)_2N\text{-}B\text{-}N(i\text{-}Pr)_2]^+[AlCl_4]^-$, 79840-41-8; $(Me_2N)_2BCl\cdot AlCl_3$, 79840-43-0; $(Me_2N)_2BBr\cdot AlBr_3$, 79896-47-2; $[(i\text{-}Pr)_2N]_2BCl$, 28049-80-1; $(Me_2N)_2BCl$, 6562-41-0; $(Me_2N)_2BBr$, 6990-27-8; $AlCl_3$, 7446-70-0; $[Me_4N]^+[AlCl_4]^-$, 21481-78-7; $[(n\text{-}Bu)_4N]^+I^-$, 311-28-4; diisopropylamine, 108-18-9; BCl_3, 10294-34-5; $(Me_2N)_2B(NH_3)_2^+\cdot AlCl_4^-$, 79840-31-6; $(Me_2N)_2B(Me_2NH)_2^+\cdot AlCl_4^-$, 79840-33-8; $(Me_2N)_2B(H_2NCH_2CH_2NH_2)^+\cdot AlCl_4^-$, 79840-35-0; $(Me_2N)_2B((i\text{-}Pr)_2O)_2^+\cdot AlCl_4^-$, 79840-37-2; $(Me_2N)_2B(PPh_3)_2^+\cdot AlCl_4^-$, 79840-39-4.

---

(19) Banford, L.; Coates, G. E. *J. Chem. Soc.* **1964**, 3564.