Formation of a Pyridine Adduct of Dimethylaminoborane, an Important Intermediate

V. R. Miller and G. E. Ryschkewitsch

Contribution from the Department of Chemistry, University of Florida, Gainesville, Florida 32601. Received August 13, 1969

Abstract: Cations with pyridine or 4-methylpyridine coordinated to $(CH_3)_2HNBH_2^+$ were prepared from $(CH_3)_2$-$HNBH_2I$ and the respective amines. The first ion was also made from dimethylaminoborane and pyridinium ion. Reversible proton abstraction produced pyridine–boryl dimethylamine, a stronger base than triethylamine, which also can be considered as the pyridine adduct of dimethylaminoborane. This adduct was characterized in solution by its physical and chemical properties. Evidence is presented which indicates that this type of adduct plays a central role as intermediate in the reactions of boron cations derived from secondary or primary amines.

During the past few years boron cations of the type $R_1R_2BH_2^+$ have been prepared, where R_1 and R_2 may be aromatic heterocyclic amines, tertiary, secondary, and primary amines, and ammonia.[1] Those containing substituted pyridines and tertiary amines are quite unreactive toward water, acids, bases, and oxidizing agents.[1a] Those that contain secondary amines are reported to hydrolyze easier.[2] However, little has been published on the mechanisms of the reactions of boron cations containing secondary amines.
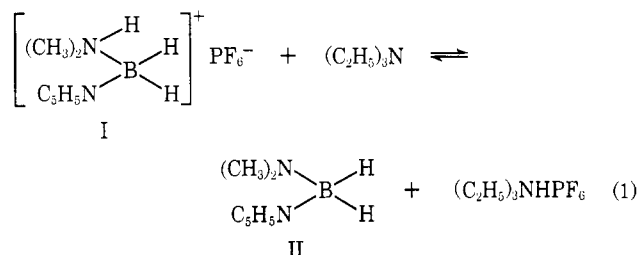
This paper demonstrates a path for the reactions of boron cations that contain secondary amines, which cannot be applied to cations containing only pyridines and tertiary amines. This path proceeds through a pyridine adduct of an aminoborane. There have been two reports of similar species.[3,4]

Results and Discussion

The proton magnetic resonance spectrum of $(CH_3)_2$-$HN(C_5H_5N)BH_2^+PF_6^-$ (I) in dichloromethane contains two peaks of equal areas at -2.49 and -2.58 ppm. These have been assigned to the hydrogens of the methyl groups, which are split into a doublet by spin–spin coupling with the hydrogen attached directly to nitrogen. When this compound is allowed to react with D_2O neat or in dichloromethane the disappearance of these two peaks and the appearance of a peak midway between them can be observed. This is evidence that the doublet is due to coupling with the hydrogen on nitrogen. A very broad band at -5.1 ppm is assigned to the N–H absorption.

When I is treated with an equimolar amount of triethylamine in dichloromethane at room temperature the two peaks in the methyl region merge instantly to one at -2.53 ppm. This could be due either to rapid exchange of the hydrogen on the secondary amine of I with triethylamine or the complete removal of this hydrogen. The spectrum contains only one set of
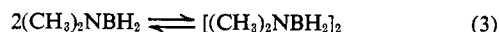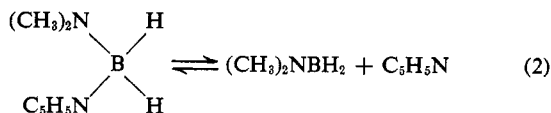
(1) (a) K. C. Nainan and G. E. Ryschkewitsch, *J. Amer. Chem. Soc.*, **91**, 330 (1969); (b) M. Inoue and G. Kodama, *Inorg. Chem.*, **7**, 430 (1968), and references therein.

(2) T. A. Shchegoleva, V. D. Sheludyakov, and B. M. Mikhailov, *Zh. Obshch. Khim.*, **35**, 1066 (1965); *J. Gen. Chem. USSR*, **35**, 1070 (1965).

(3) A. B. Burg and C. L. Randolph, Jr., *J. Amer. Chem. Soc.*, **73**, 953 (1951).

(4) C. A. Brown and R. C. Osthoff, *ibid.*, **74**, 2340 (1952).

ethyl peaks, the position of which is intermediate between those of triethylamine and triethylammonium ion. From this it is concluded that triethylamine abstracts a proton from I in a rapid, reversible reaction, and that the value of the equilibrium constant is within an order of magnitude of one. Equation 1 shows this reaction and the expected boron-containing product II. Using the chemical shifts of the ethyl peaks to

$$\left[\begin{array}{c} (CH_3)_2N \diagdown_{\displaystyle B} \diagup^{\displaystyle H} \diagdown H \\ C_5H_5N \diagup \diagdown H \end{array} \right]^+ PF_6^- \;+\; (C_2H_5)_3N \;\rightleftharpoons$$

$$I$$

$$(CH_3)_2N \diagdown_{\displaystyle B} \diagup^{\displaystyle H} \diagdown H \;+\; (C_2H_5)_3NHPF_6 \quad (1)$$

$$C_5H_5N \diagup$$

$$II$$

calculate the ratios of the various species, an equilibrium constant of 0.1 at 20° was calculated.

When pyridine or 4-picoline is used instead of triethylamine the doublet does not collapse and the chemical shift of the added pyridine peaks are within experimental error of those of free pyridine. This is in agreement with pyridine being a weaker base than triethylamine. The nmr spectrum of a solution of I and pyridine in dichloromethane shows no change on standing for 3 days at 25°.

Addition of gaseous hydrogen chloride to this $(C_2H_5)_3N$ solution immediately restores the doublet ($J = 5.5$ Hz) in the methyl region corresponding to I, and to the same intensity and line width as in the original solution before addition of triethylamine. From the neutralized solution pure starting material was indeed isolated, but the yield was only 20% because of work-up difficulties in the separation from triethylammonium salts. These findings are additional evidence that the reaction represented by eq 1 is in fact reversible. Lowering the temperature of a solution of the cation I and triethylamine to $-37°$ also restores the doublet in the methyl region, while the ethyl peaks shift only a few cycles and remain quite different in chemical shift from pure triethylamine. The reappearance of the doublet is therefore caused by a slowing of the exchange rate rather than by a substantial shift in the equilibrium

Although II is the conjugate base of I it might be unstable and dissociate as in eq 2. The dimethyl-aminoborane could then dimerize as in eq 3.

$$\underset{C_5H_5N}{\overset{(CH_3)_2N}{\diagdown}}\overset{H}{\underset{H}{\diagup}}B \rightleftharpoons (CH_3)_2NBH_2 + C_5H_5N \qquad (2)$$

$$2(CH_3)_2NBH_2 \rightleftharpoons [(CH_3)_2NBH_2]_2 \qquad (3)$$

Using infrared spectroscopy it is possible to show that the concentration of free pyridine in the solution is very low. The infrared spectra of I, and of I with an equimolar concentration of triethylamine, are compared with that of free pyridine. The 1700–1500- and 1100–900-cm^{-1} regions are shown in Figure 1. Although the positions of the bands at 1582 and 1000 cm^{-1} in the mixture of I and triethylamine are slightly different from those in free pyridine, the difference is not much greater than experimental error. However, when free pyridine is added to the mixture of I and triethylamine a change in relative intensities is observed in the 1600-cm^{-1} region and a new band appears at 995 cm^{-1}. Thus, the bands at 1582 and 1000 cm^{-1} of curve c are not due to free pyridine, and the concentration of free pyridine must be quite low. The increase in the intensity of the band at 1067 cm^{-1} upon addition of triethylamine is due to the triethylamine.

The nmr spectrum of I plus triethylamine shows only one set of pyridine peaks. When free pyridine is added no new peaks appear. Instead, the original peaks shift upfield, toward free pyridine. The two paths for this exchange are nucleophilic substitution and dissociation (eq 2). To provide evidence for the dissociation path a solution of I and tri-n-butylamine in nitrobenzene was subjected to vacuum fractionation at room temperature. The infrared spectrum showed the −78° fraction to be a mixture of free pyridine and dimethylaminoborane. This evidence supports the contention that although the concentrations of free pyridine and monomeric dimethylaminoborane are low, they are in relatively rapid equilibrium with the neutral adduct, II.

Several reactions were run which, although they do not prove the existence of II, do show that the boron cation, I, is stable relative to a mixture of dimethylaminoborane dimer, pyridine, and an ammonium salt. In the first reaction, equimolar amounts of pyridine, triethylammonium hexafluorophosphate, and dimethylaminoborane were allowed to stand in dichloromethane for 7 weeks. Although the products could not be separated, the nmr spectrum showed the presence of I. In a similar experiment dimethylaminoborane and pyridinium hexafluorophosphate were heated in acetonitrile for 1.5 hr. The nmr spectrum again showed the presence of I. A 45% yield of I was isolated from this solution. Thus, the reaction shown in eq 4 proceeds in the direction indicated.
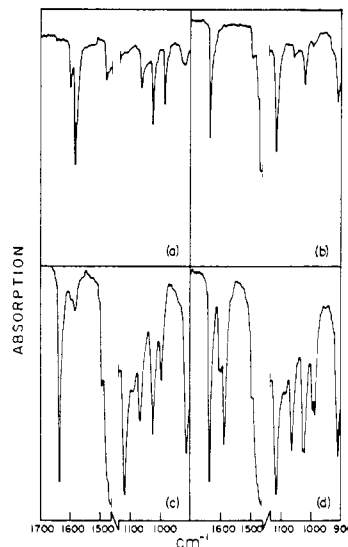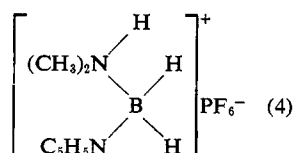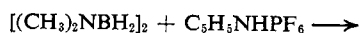
$$[(CH_3)_2NBH_2]_2 + C_5H_5NHPF_6 \longrightarrow$$

$$\left[\underset{C_5H_5N}{\overset{(CH_3)_2N}{\diagdown}}\overset{H}{\underset{H}{\diagup}}\overset{\overset{H}{\diagup}}{\underset{\diagdown}{B}}\right]^+ PF_6^- \qquad (4)$$

Figure 1. Infrared spectra of the 1700–1500- and 1100–900-cm^{-1} regions of (a) 0.1 M pyridine; (b) 0.050 M $(CH_3)_2HN(C_5H_5N)BH_2$-PF_6 (I); (c) 0.25 M I and 0.25 M triethylamine; and (d) 0.25 M I, 0.25 M triethylamine, and pyridine in dichloromethane.

The value for the equilibrium constant associated with eq 1, 0.1, indicates that the pyridine adduct of dimethylaminoborane is a substantially stronger base than triethylamine. Thus the boryl group appears to enhance the base strength of a nitrogen atom relative to an alkyl group, as might have been expected from consideration of electronegativities and the associated inductive effects. It might be argued that the true value for eq 1 is not that which was calculated, but is actually smaller, because the presence of reaction 2 has lowered the concentration of II and displaced eq 1 to the right. This is negated by the conclusion that the concentration of free pyridine is very low.

The above conclusions are also in accord with an estimate of the stability of the amine–aminoborane adduct with respect to dissociation, which is based on bond energy approximations. Taking a value between 25 and 30 kcal/mol[5] for the dissociation energy of the bond to pyridine (without rearrangement of the aminoborane), and 15 kcal for the stabilization resulting from π bonding in the aminoborane,[6] one estimates a new dissociation enthalpy of +10 to +15 kcal/mol for eq 2. An alternate estimate is provided by the dissociation enthalpy of 0.5 mol of the dimer of dimethylaminoborane, +10 kcal/mol.[3] The latter reaction is similar to eq 2 in that a σ bond to nitrogen in tetrahedral boron is cleaved while a σ bond is made. Enthalpy differences of this magnitude are sufficiently large to preclude ready detection of both reactants and products, but are small enough to allow rapid interconversion. In this light it is not surprising that attempts to isolate pure compound II were not successful.

The nmr spectrum of II can be calculated using the value of the equilibrium constant and the observed

(5) E. R. Birnbaum and G. E. Ryschkewitsch, Inorg. Chem., 4, 575 (1965).

(6) W. S. Brey, Jr., M. E. Fuller, II, G. E. Ryschkewitsch, and A. S. Marshall in "Boron–Nitrogen Chemistry," R. F. Gould, Ed., Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p 101.
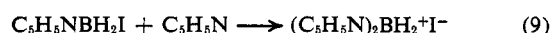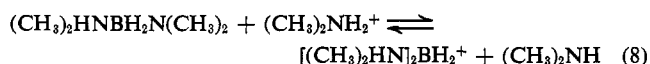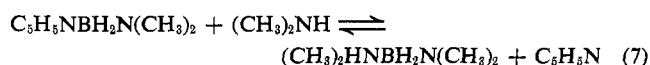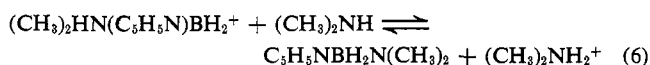
Table I. Proton Nmr Data in Dichloromethane

Compounds	(CH$_3$)$_2$N δ, ppm	J, Hz	Pyridine substituent δ, ppm	Pyridine ring	δ, ppm
(CH$_3$)$_2$HN(C$_5$H$_5$N)BH$_2^+$PF$_6^-$ (I)	−2.53^a	5.5		H$_{2,6}$	−8.64^b
				H$_{3,5}$	−7.88^b
				H$_4$	−8.33^b
(CH$_3$)$_2$HN(4-CH$_3$C$_5$H$_4$N)BH$_2^+$PF$_6^-$	−2.48^a	5.5	−2.60	H$_{2,6}$	−8.51^a
				H$_{3,5}$	−7.78^a
(CH$_3$)$_2$HN(4-CH$_3$C$_5$H$_4$N)BH$_2^+$I$^-$	−2.40^a	5.5	−2.63	H$_{2,6}$	−8.92^a
				H$_{3,5}$	−7.73^a
[(CH$_3$)$_2$HN]$_2$BH$_2^+$PF$_6^-$	−2.61^a	5.5			
(CH$_3$)$_2$HN(C$_5$H$_5$N)BH$_2$ (II)^c	−2.5			H$_{2,6}$	−8.5^b
				H$_{3,5}$	−7.4^b
				H$_4$	−7.8^b

^{a} Doublet. ^{b} Center of multiplet. ^{c} Calculated from an equimolar mixture of I and triethylamine.

chemical shifts obtained from the spectrum of an equimolar mixture of I and triethylamine. The values are shown in Table I. Except for a small band at 1580 cm^{-1} all the bands in the infrared spectrum of a mixture of I and triethylamine can be assigned to either I, triethylamine, or triethylammonium hexafluorophosphate. The ratio of I:II in these solutions is 4:1.

The existence of the amine–aminoborane II and the properties deduced for it offer an explanation for a number of reactions in which this compound apparently functions as an important intermediate. For example, when dimethylamine is added to C$_5$H$_5$NBH$_2$I, a substantial amount of (C$_5$H$_5$N)$_2$BH$_2^+$I$^-$ is isolated. As shown in eq 5–9 the first step would be the displacement of iodide by dimethylamine, producing the expected cation. This would react with more dimethylamine to give the neutral species II. An exchange of amines, eq 7, would produce (CH$_3$)$_2$HNBH$_2$N(CH$_3$)$_2$, which on protonation would give the symmetrical cation [(CH$_3$)$_2$HN]$_2$BH$_2^+$ and free pyridine. Pyridine is known to react rapidly with C$_5$H$_5$NBH$_2$I to give (C$_5$H$_5$N)$_2$BH$_2^+$I$^-$. The products would thus be a mixture of the two symmetrical cations and the unsymmetrical cation.

$$C_5H_5NBH_2I + (CH_3)_2NH \longrightarrow (CH_3)_2HN(C_5H_5N)BH_2^+I^- \quad (5)$$

$$(CH_3)_2HN(C_5H_5N)BH_2^+ + (CH_3)_2NH \rightleftharpoons$$
$$C_5H_5NBH_2N(CH_3)_2 + (CH_3)_2NH_2^+ \quad (6)$$

$$C_5H_5NBH_2N(CH_3)_2 + (CH_3)_2NH \rightleftharpoons$$
$$(CH_3)_2HNBH_2N(CH_3)_2 + C_5H_5N \quad (7)$$

$$(CH_3)_2HNBH_2N(CH_3)_2 + (CH_3)_2NH_2^+ \rightleftharpoons$$
$$[(CH_3)_2HN]_2BH_2^+ + (CH_3)_2NH \quad (8)$$

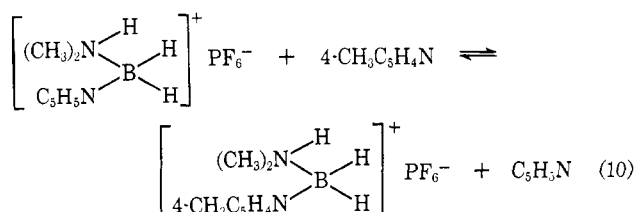$$C_5H_5NBH_2I + C_5H_5N \longrightarrow (C_5H_5N)_2BH_2^+I^- \quad (9)$$
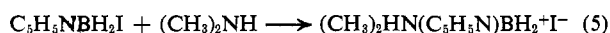
This reaction scheme has important consequences for the synthesis of boron cations by nucleophilic substitution on boron when one of the amines which is to be bonded to boron carries a hydrogen atom. The intermediate formation of an amine–aminoborane adduct activates the boron compound toward loss of amine, and it is best to start with the primary or secondary amine already attached to boron. Thus no difficulties were encountered when the synthesis of I was carried out starting with dimethylamine–iodoborane and pyridine.
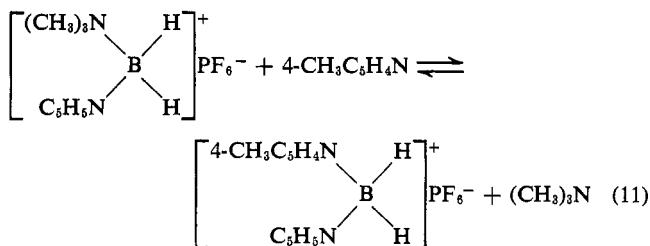
Intermediate formation of the amine–aminoborane adduct also provides an explanation for the rapid formation of (CH$_3$)$_2$HN(4-CH$_3$C$_5$H$_4$N)BH$_2^+$PF$_6^-$ from I and 4-picoline. The nmr spectrum of equimolar amounts, 0.6 M, of I and 4-picoline in dichloromethane 1 min after mixing contains bands in the methyl region at −2.35, −2.47, and −2.58 ppm with relative areas of 1:5:8, respectively. There is no further change in the spectrum on standing for an hour. When pyridine is added to (CH$_3$)$_2$HN(4-CH$_3$C$_5$H$_4$N)BH$_2^+$PF$_6^-$ in the mole ratio of 0.4 to 1, bands at −2.34, −2.45, −2.55, and −2.58 ppm are observed with approximate relative areas of 1:5:5:5.

These are assigned to free 4-picoline, the methyl doublet, and the methyl of the coordinated picoline, respectively. Addition of another 0.8 equiv of pyridine gives a spectrum very similar to that obtained by the addition of 4-picoline to an equivalent amount of I. It is apparent that the methyl of the coordinated picoline and half the dimethylamine doublet now overlap. This shift is attributed to the presence of more free pyridine as the chemical shifts of these boron cations appear to be sensitive to the presence of other species. When a similar solution was evaporated to dryness the nmr spectrum of the residue showed it to be the dimethylamine, 4-picoline cation. Thus, the equilibrium shown in eq 10 is rapidly established. Assuming that the fraction of 4-picoline that is uncoordinated is equal
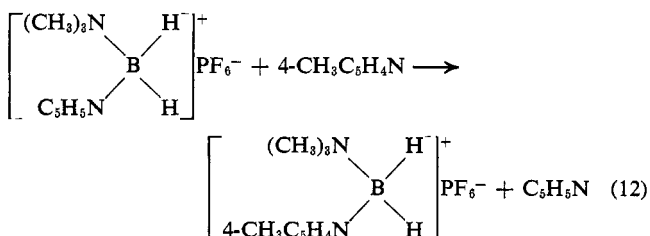
$$\left[\begin{array}{c} (CH_3)_2N \diagdown \!\!\! \diagup^{H} \\ C_5H_5N \diagdown^{B} \diagdown \!\!\! \diagup^{H}_{H} \end{array} \right]^+ PF_6^- + 4\text{-}CH_3C_5H_4N \rightleftharpoons$$

$$\left[\begin{array}{c} (CH_3)_2N \diagdown \!\!\! \diagup^{H} \\ 4\text{-}CH_3C_5H_4N \diagdown^{B} \diagdown \!\!\! \diagup^{H}_{H} \end{array} \right]^+ PF_6^- + C_5H_5N \quad (10)$$

to the area of the free 4-picoline peak (−2.35 ppm) divided by one-third of the total methyl area, a value of 10 was calculated for the equilibrium constant at 37°. There was no evidence for the displacement of dimethylamine.

When the corresponding reaction was performed using 0.6 M $(CH_3)_3N(C_5H_5N)BH_2^+PF_6^-$ instead of I different results were obtained. The first reaction observed was the displacement of trimethylamine by 4-picoline, eq 11. After 22 min at 37° only 6% of the

$$\left[\begin{array}{c} (CH_3)_3N \quad\quad H \\ \diagdown\quad\diagup \\ B \\ \diagup\quad\diagdown \\ C_5H_5N \quad\quad H \end{array}\right]^+ PF_6^- + 4\text{-}CH_3C_5H_4N \rightleftharpoons$$

$$\left[\begin{array}{c} 4\text{-}CH_3C_5H_4N \quad\quad H \\ \diagdown\quad\diagup \\ B \\ \diagup\quad\diagdown \\ C_5H_5N \quad\quad H \end{array}\right]^+ PF_6^- + (CH_3)_3N \quad (11)$$

trimethylamine had been displaced. After another 4 hr at 25° it appeared as though pyridine was also being displaced, but at a slower rate, eq 12. The nmr spec-

$$\left[\begin{array}{c} (CH_3)_3N \quad\quad H \\ \diagdown\quad\diagup \\ B \\ \diagup\quad\diagdown \\ C_5H_5N \quad\quad H \end{array}\right]^+ PF_6^- + 4\text{-}CH_3C_5H_4N \longrightarrow$$

$$\left[\begin{array}{c} (CH_3)_3N \quad\quad H \\ \diagdown\quad\diagup \\ B \\ \diagup\quad\diagdown \\ 4\text{-}CH_3C_5H_4N \quad\quad H \end{array}\right]^+ PF_6^- + C_5H_5N \quad (12)$$

trum after 20 hr confirmed the idea that both reactions were occurring. These conclusions are based on the aromatic and methyl regions of the nmr spectra and the known chemical shifts.[1a]

Thus, the large difference in the rate constants (substantially greater than 10^3 assuming a second-order rate law) and the different products (substitution of only pyridine vs. preferential substitution of trimethylamine and subsequent substitution of pyridine) indicate different mechanisms for the two reactions. The most reasonable explanation for this is the ability of I to form the neutral species II.

Amine–aminoborane adducts are also important in the solvolysis of boron cations. The cation derived from 4-methylpyridine and dimethylamine is rapidly hydrolyzed at room temperature in basic solution, but much more slowly in acidic solution. In contrast, cations containing only tertiary amines, and specifically the cation containing 4-methylpyridine and trimethylamine, are quite stable under similar conditions.[1a] This strongly implicates the neutral amine–dimethylaminoborane as the first intermediate in the solvolysis. Mikhailov and coworkers have studied the kinetics of hydrolysis and alcoholysis of a number of symmetrical boron cations derived from primary or secondary amines and from pyridine, and have proposed a mechanism which involves displacement of an amine from the cation by solvent.[2] They eliminated from consideration proton loss from amine because they reported that the bis(pyridine) cation, $(C_5H_5N)_2BH_2^+$, which has no acidic proton, evolved hydrogen at 20° with a half-life of about 4 min. We observed that the hexafluorophosphate salt of this ion survives heating at 60° in the same solvent mixture as was used by Mikhailov, and that the half-life is greater than 2 hr at this temperature. Mikhailov's mechanism is thus deprived of the key argument in its favor and it appears most likely that the solvent, alcohol or water, serves as a Brønsted base rather than as a nucleophile in the initial step of solvolysis. Compound I indeed exchanges hydrogen with D_2O, even in slightly acidic solution, and does so very rapidly.

Finally, the results presented here provide strong support for the general mechanism proposed by Shore for the formation of cycloborazanes from diborane and sodium amide in liquid ammonia.[7] This mechanism involves in the first step proton abstraction from $(NH_3)_2\text{-}BH_2^+$, an ion which is formed from diborane and ammonia and which is analogous to the cation described here. The intermediate $(NH_3)BH_2NH_2$ thus formed is analogous to the compound II. Our results confirm that the formation of Shore's intermediate should be thermodynamically favorable and very rapid. In view of the rapid transamination of compound II with 4-methylpyridine it seems likely that the polyborazanes are formed by displacement of amine from an amine–aminoborane rather than from a bis(amine) boron cation. The latter reaction was suggested by Shore as a second possibility, but can now be excluded.

Experimental Section

The solvents and pyridine were reagent grade and dried over molecular sieves (3A). Triethylamine, tri-n-butylamine, and 4-picoline were from Eastman Organic Chemicals. Dimethylamine-borane and pyridine–borane were obtained from Callery Chemical Company.

The nmr spectra were recorded on a Varian A-60 instrument. Chemical shifts were measured from tetramethylsilane (TMS) or from the ^{13}C side band of the solvent, dichloromethane. All are reported from TMS using -3.85 ppm as the chemical shift of the ^{13}C side band of CH_2Cl_2. The infrared spectra were recorded on a Beckman IR-10 spectrophotometer using sodium chloride windows. They were calibrated using the polystryrene bands at 1601 and 906.5 cm^{-1}.

$(CH_3)_2HN(C_5H_5N)BH_2^+$. The method developed by Ryschkewitsch and coworkers[1a,8,9] was used to prepare an 86% yield of crude hexafluorophosphate salt. Since this compound is hydrolyzed fairly easily the water was made slightly acidic with HCl and contact with such solutions was minimized. The crude product was purified by repeated precipitation from 1,2-dichloroethane with petroleum ether (bp 65–110°), mp 90.5–91.5°. The nmr data are given in Table I.

Anal. Calcd for $C_7H_{14}BF_6N_2P$: C, 29.82; H, 5.00; N, 9.94. Found: C, 29.89; H, 4.95; N, 9.94.

$(CH_3)_2HN(4\text{-}CH_3C_5H_4N)BH_2I$. In a similar procedure the reaction of dimethylamine–borane, iodine, and 4-picoline gave a 91% yield of the crude iodide salt. Crystallization from acetone and precipitation from methylene chloride with petroleum ether (bp 20–40°) gave an analytically pure sample, mp 139–140°.

Anal. Calcd for $C_8H_{16}BIN_2$: C, 34.57; H, 5.80; N, 10.08. Found: C, 34.66; H, 5.86; N, 10.06.

The hexafluorophosphate salt could be prepared in water, as above, or by stirring with ammonium hexafluorophosphate in acetonitrile, filtering of the ammonium iodide, evaporating, dissolving in methylene chloride, and filtering to remove excess ammonium hexafluorophosphate. In contrast to other cations this compound could only be obtained as an oil. The nmr spectra of both the iodide and hexafluorophosphate salts, given in Table I, are in complete agreement with the proposed cation. The difference in chemical shift values due to different anions has been observed with other boron cations.

(7) K. W. Böddeker, S. G. Shore, and R. K. Bunting, *J. Amer. Chem. Soc.*, **88**, 4396 (1966).

(8) G. E. Ryschkewitsch and J. M. Garrett, *ibid.*, **89**, 4240 (1967).

(9) K. C. Nainan and G. E. Ryschkewitsch, *Inorg. Chem.*, **7**, 1316 (1968).

[(CH₃)₂HN]₂BH₂PF₆. In a similar manner equivalent amounts of dimethylamine–borane, iodine, and dimethylamine were allowed to react to give a 95% yield of crude iodide salt. Conversion to the hexafluorophosphate salt in dilute acid gave a 30% yield, mp 100–104°. Concentration of the filtrate gave another 37% of the cation, mp 87–93°. Repeated precipitation from methylene chloride with petroleum ether gave a sample melting at 102–104°.

Anal. Calcd for C₄H₁₆BF₆N₂P: C, 19.38; H, 6.50; N, 11.30. Found: C, 19.37; H, 6.59; N, 10.97.

The Reaction of Pyridine–Monoiodoborane with Dimethylamine. A sample of 1.65 g (17.7 mmol) of pyridine–borane was dissolved in 30 ml of benzene and 2.10 g (8.3 mmol) of I₂ added slowly. The reaction mixture was stirred for 10 min and then 16.8 mmol of dimethylamine in 34 ml of benzene was added. After stirring for another hour the benzene layer was decanted off and the remaining oil dried under vacuum giving 4.27 g of product. This was dissolved in 10 ml of 0.1 *M* HCl and treated with 18.7 mmol of ammonium hexafluorophosphate. The precipitate was filtered, rinsed with water and ether, and dried under vacuum to give 2.37 g (7.5 mmol) of (C₅H₅N)₂BH₂⁺PF₆⁻, mp 103–109° (lit.[10] 116°). Except for a small impurity the nmr spectrum was identical with that of an authentic sample. The washings were evaporated under reduced pressure to give 0.42 g of an oil. The nmr spectrum showed this oil to be about half [(CH₃)₂HN]₂BH₂PF₆ and part (C₅H₅N)₂BH₂PF₆. The filtrate was evaporated under reduced pressure and the resulting solid extracted with dichloromethane. Evaporation of this solution gave 1.61 g of an oil which the nmr spectrum showed to be about 90% [(CH₃)₂HN]₂BH₂PF₆. Thus, of the expected 16.5 mmol of boron cation, 7.5 mmol (46%) can be accounted for as (C₅H₅N)₂BH₂PF₆ and 6.6 mmol (40%) as [(CH₃)₂HN]₂BH₂PF₆. There was no evidence for the mixed cation, (CH₃)₂HN(C₅H₅N)BH₂PF₆.

[(CH₃)₂NBH₂]₂. To 3.00 g (50.9 mmol) of resublimed (CH₃)₂HNBH₃ in 15 ml of dichloromethane and 15 ml (108 mmol) of triethylamine was added 12.7 g (50.0 mmol) of solid iodine in small portions over 15 min. The stirred solution was cooled in an ice bath. After stirring for another 10 min the reaction vessel was attached to the vacuum line and cooled to −45°; the more volatile components were removed. The remaining solid was warmed to 25° and the [(CH₃)₂NBH₂]₂ removed and purified by trap to trap fractionation. The product, 1.28 g (12.4 mmol), was characterized by the nmr spectrum, comparison with the published infrared spectrum, and vapor pressure of 8 mm at 20° (8 mm reported[11]).

Distillation of Dimethylaminoborane and Pyridine from I and Tri-*n*-butylamine. A sample of 0.50 g of I was dissolved in 2.0 ml of tri-*n*-butylamine (dried over molecular sieves) and 50 ml of nitrobenzene. After several minutes the slight gas evolution stopped. The solution was held at 25° and fractionated through −15° and −78° traps for 5 min. The contents of the traps were discarded and the process repeated for 10 min. Except for the appearance of a few small extra bands the infrared spectrum of the −78° trap was a simple summation of the spectra of dimethylaminoborane and pyridine.

Preparation of I from Dimethylaminoborane and Pyridinium Hexafluorophosphate. A sample of 0.058 g (1.02 mmol) of dimethylaminoborane dimer and 0.180 g (0.80 mmol) of pyridinium hexafluorophosphate was heated at 70° in acetonitrile for 1.5 hr. The solvent was removed and the remaining oil recrystallized from 3 *M* HCl to give 0.10 g (0.35 mmol) of I, mp 84–86°.

Attempts to Isolate (CH₃)₂N(C₅H₅N)BH₂. The reaction of I with NaBH₄ in acetonitrile gave pyridine–borane and dimethylamine–borane, identified by the nmr spectrum. A slight evolution of a gas was observed.[12] The reaction of I with LiAlH₄ gave dimethylamine–borane but no pyridine–borane, as shown by nmr.

The nmr spectrum of the reaction mixture of the iodide salt of I with a deficiency of *n*-butyllithium showed apparent doublets in the methyl region (*J* = 5.5 Hz) and absorptions in the pyridine region besides the peaks due to unreacted I. The presence of II is thus denied, since exchange would collapse the doublets.

A solution of I in CH₂Cl₂ was allowed to react with solid, anhydrous K₂CO₃. The infrared and nmr spectra could be interpreted as showing the presence of II along with several other major components. However, changes in the nmr spectrum upon the addition of HCl did not indicate the expected production of I from II.

In another approach an acetonitrile solution of dimethylaminoborane and pyridine was heated. The changes in the nmr spectrum showed several reactions occurring. The addition of HCl produced no I.

(10) G. E. Ryschkewitsch, *J. Amer. Chem. Soc.*, **89**, 3145 (1967).

(11) E. Wiberg, A. Bolz, and P. Buchheit, *Z. Anorg. Allg. Chem.*, **256**, 285 (1948).

(12) A similar behavior reported for the bis-*t*-butylamine boron cation: H. Noth, H. Beyer, and H. Vetter, *Chem. Ber.*, **97**, 110 (1964).

The Preparation of Borane in High Absolute Yield from Borane Carbonyl[1]

G. W. Mappes and T. P. Fehlner

Contribution from the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556. Received August 30, 1969

Abstract: Borane, BH₃, has been produced in yields of 60% from borane carbonyl, BH₃CO. BH₃CO diluted to a high degree in an inert carrier gas is thermally decomposed in a tubular fast flow reactor. Analysis of the products is accomplished utilizing a mass spectrometer with molecular beam sampling. An absolute sensitivity for borane has been obtained by a kinetic method and streams containing up to 50 mTorr of BH₃ have been produced. Purities of up to 84% based on total boron hydrides have been achieved.

The chemical and physical nature of the borane species, BH₃, has been the subject of considerable interest for many years. It appears that borane, in the absence of any form of coordination, may be viewed as a small planar molecule with a singlet ground state.

It has an empty p orbital which, in contrast to that of BF₃, is not involved in π bonding. The electronic structure of BH₃ is essentially different from that of other reactive species, *e.g.*, free radicals. Thus experimental information on the nature of this species serves to illuminate a new facet of chemistry.

The direct identification of small quantities of BH₃ in the gas phase by a number of groups[2–10] was the