

Cations Derived from BH_2^+ . Unsymmetrical Bis-Amine Substitution on Boron

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Abstract: Salts of boron cations, with two different tertiary amines coordinated to a BH_2^+ group, have been synthesized by displacement of iodide from adducts of monoiodoborane with trimethylamine, triethylamine, or pyridine. Pyridines substituted with a variety of functional groups, quinoline, *N,N*-dimethylaniline, and triethylamine were used as the second amine. The success of the preparation of these cations was found to depend on the basicity of the displacing amines and favorable steric factors. Carbonyl and nitrile substituents, which are normally reduced by B-H bonds, did not interfere with the synthesis. The cations could be converted to symmetrical derivatives by transamination. The compounds were stable at room temperature to Ag^+ , Hg^{2+} , Cu^{2+} , $\text{Cr}_2\text{O}_7^{2-}$, and H_2O_2 , as well as to acid or base. They decomposed slowly in hot HCl, water, or NaOH.

In a recent paper there was reported the successful synthesis of derivatives of BH_2^+ in which two identical alkylpyridines were bonded to boron.¹ The present paper reports the synthesis of singly charged boron cations of C_s symmetry, in which two different tertiary amines complete the coordination sphere around a BH_2^+ ion. Only two examples of this type of compound have been reported until now, *i.e.*, a boron cation with 4-methylpyridine and trimethylamine,² or with dimethylethylamine and trimethylamine³ coordinated to boron. The syntheses proceed most easily from amine-monoiodoboranes by displacement of iodide^{1,2,4,5} with various substituted pyridines, triethylamine, quinoline, and dimethylaniline. The synthesis is quite convenient and gives good yields with only minimum amounts of impurities or by-products. The compounds were characterized by elemental analysis of the hexafluorophosphates, and by their nmr and ir spectra. The reactivity of the cation was investigated with respect to thermal, oxidative, and hydrolytic degradation and with respect to transamination.

Experimental Section

Materials. Amine-boranes were obtained from Callery Chemical Co. and used without further purification. The various amines were obtained from commercial sources. All other chemicals and solvents were reagent grade and were used without any further purifications, but were dried over molecular sieve or sodium-lead alloy when appropriate.

Synthesis of Boron Cations from Trimethylamine-Borane. Trimethylamine-monoiodoborane was prepared as previously described^{1,2,6} and was allowed to react without isolation with various tertiary amines at room temperature to prepare the respective unsymmetrical boron cations. The synthesis is exemplified by the preparation of pyridinetrimethylaminedihydroboron(1+) ion, $(\text{CH}_3)_3\text{N}(\text{C}_5\text{H}_5\text{N})\text{BH}_2^+$.

Trimethylamine-borane, 2.198 g (30.19 mmoles), was dissolved in 35 ml of dry benzene. Solid iodine, 3.488 g (13.73 mmoles), was added in small portions while the solution was stirred and the flask was loosely stoppered between additions of iodine. The reaction was vigorous. After the additions of iodine, the solution was kept

stirred for about 10 min and 2.241 g (28.37 mmoles) of pyridine was added. A white precipitate gradually formed. The reaction mixture was kept stirred for about 5 hr at room temperature. It was then diluted with 40 ml of dry benzene, stirred for 10-15 min, filtered, and washed with 80 ml of dry benzene and a small amount of ether. The dried compound weighed 6.300 g (83% yield of iodide salt).

By this method iodide salts were easily prepared of cations where a $(\text{CH}_3)_3\text{NBH}_2^+$ group was attached to a variety of pyridine derivatives containing the following substituents: 4-methyl, 3,4-dimethyl, 4-methoxy, 4-phenyl, 4-benzoyl, 4-benzyl, 4-acetyl, 3-cyano-5-methyl, 3-bromo, and 3-iodo. In the synthesis of the quinoline derivative 24 hr was allowed for precipitation.

In all instances a little more than 2 moles of trimethylamine-borane was used per mole of iodine, and the amount of amine used was up to 15% in excess over the calculated amount of iodoborane.

A number of amines failed to give rapid precipitation at room temperature. These included *N,N*-dimethylaniline and pyridines with the following substituents: 2-fluoro, 2-chloro, 3-chloro, 4-cyano, and 2,4,6-trimethyl. In these instances the reaction mixture was heated for 3-4 hr at 65-70°. The yields of the iodide salts, based on the weight of dry product and the amount of iodine used, are given in Table I.

A direct comparison was made between the reactivity of 4-cyanopyridine and pyridine toward trimethylamine-iodoborane. Reaction with pyridine was carried out with the amounts and conditions as described above, but the mixture was filtered after only 1 hr. The yield of iodide salt was 57%. A reaction with 4-cyanopyridine under precisely the same conditions yielded only 16% of product after 1 hr at room temperature.

Attempted Synthesis of Triethylamine-Trimethylamine Cation from Trimethylamine-Borane. (a) A reaction mixture prepared from 27.47 mmoles of trimethylamine-borane and 13.73 mmoles of iodine in 35 ml of dry benzene was stirred for 15 hr at room temperature in a stoppered flask with 49.00 mmoles of dry triethylamine. Only a small quantity of precipitate was obtained (0.258 g) which was dissolved in 4 ml of water and treated with 1.5 ml of saturated NH_4PF_6 solution. The resulting precipitate weighed 0.136 g. Its nmr spectrum in CH_2Cl_2 showed only one absorption, a sharp singlet for δ 2.50 ppm upfield from the solvent, and was identical with the chemical shift for bis(trimethylamine)boronium hexafluorophosphate in the same solvent. Its infrared spectrum and melting point (205-206° dec) also agreed well with an authentic sample.

(b) A similar reaction mixture was refluxed with protection from the atmosphere for 5 hr. There was isolated 5.401 g of benzene-insoluble crystalline material, which was converted to hexafluorophosphate as described above. This product melted at 110-112° and had a complex nmr spectrum in CH_2Cl_2 : a triplet (1:2:1, δ 4.12, $J = 7$ Hz), a singlet (δ 2.50), and a quartet (1:3:3:1, $J = 7$ Hz), centered at δ 2.30, whose upfield low-intensity portion was covered by the singlet (chemical shifts upfield of the solvent peak). The integrated intensities of the triplet and the sum of the integrals of the quartet and the singlet were in the ratio of 9:20.7. The downfield half of the quartet had one-third the intensity of the triplet. The observed pattern and the chemical shifts corresponded to a mixture of bis(trimethylamine) cation and the triethylamine-

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Table I. Yields of Unsymmetrical Boronium Salts of BH_2^+

Compounds	Yield of iodide salt, % ^a	Conversion to PF_6^- salt, %	Yield of PF_6^- salt, overall, % ^a
Amines coordinated to $(CH_3)_3NBH_2^+$			
Pyridine	83	93	77
4-Methylpyridine	96	84	81
3,4-Dimethylpyridine	98	96	94
Quinoline	99 ^c	33	33
3-Bromopyridine	74	82	61
3-Iodopyridine	81	82	66
3-Chloropyridine ^d	93	76	71
2-Fluoropyridine ^d	67	85	57
2-Chloropyridine ^d	63	91	57
4-Cyanopyridine ^d	86	93	80
3-Methyl-5-cyanopyridine	67	84	56
4-Phenylpyridine	87	89	77
4-Benzylpyridine	94	68	64
4-Benzoylpyridine	84	87	73
4-Acetylpyridine	79	75	59
4-Methoxypyridine	80	95	76
2,4,6-Trimethylpyridine ^d	73	77	56
2-Methoxypyridine	34	94	32
N,N-Dimethylaniline ^d	52	30	16
Amines coordinated to $PyBH_2^+$			
Triethylamine	90	90	81
2,4,6-Trimethylpyridine	93	81	75
4-Methylpyridine ^b	96	87	84
2-Methoxypyridine	99 ^c	67	66
Amines coordinated to $(C_2H_5)_3NBH_2^+$			
Pyridine	79	96	76
Trimethylamine	64	66	42

^a Based on iodoborane. ^b Prepared by Dr. S. Chandra. ^c After drying for 48 hr by vacuum pumping these iodides contained a liquid impurity. ^d Reaction temperature 65–70°.

trimethylamine cation, prepared pure as described below; only one N-methyl peak was observed since both compounds have identical chemical shifts for this group. The proportions of the symmetrical and the unsymmetrical cations, calculated from the integrals, were 39 and 61 mole %, respectively. Two recrystallizations from hot water increased the melting point to 126–128° and the proportion of bis(trimethylamine) cation to 53 mole %.

Preparation of Bis(trimethylamine) Cation. A 0.500 M solution of trimethylamine-iodoborane prepared from stoichiometric amounts of iodine and trimethylamine-borane was saturated for 10 min at room temperature with gaseous trimethylamine. Precipitation started rapidly. After standing overnight the precipitate was filtered, washed with benzene, and redissolved in chloroform to remove a small amount of insoluble trimethylammonium iodide. The final product weighed 43.39 g (88% yield of boronium iodide). A portion of the product was converted to the hexafluorophosphate salt, mp 201–203° dec (lit.³ 200–205°). Another portion was treated with a solution of mercuric iodide in excess potassium iodide. The resulting precipitate was recrystallized from hot 1,2-dichloroethane-carbon tetrachloride. The light yellow product softened and melted *in vacuo* around 180° with formation of Hg, HgI₂, and $(CH_3)_3N$. *Anal.* Calcd for $C_{12}H_{20}B_2N_4HgI_4$: Hg, 20.68; I, 52.32. Found: Hg, 20.35; I, 52.36. The ir spectrum of the tetraiodomercurate was identical with the spectrum of the iodide except for the differences due to anions.

Synthesis of Boron Cations from Pyridine-Borane. The procedure followed was essentially the same as described for trimethylamine-borane as the starting material. Iodination of the borane proceeded more vigorously, and precipitation of the cation was very rapid in all instances and was noticeably exothermic. Derivatives were isolated at room temperature from 4-methylpyridine, 2-methoxypyridine, 2,4,6-trimethylpyridine, and triethylamine. Yields are given in Table I.

Synthesis of Boron Cations from Triethylamine-Borane. Triethylamine-iodoborane was prepared from 3.151 g (27.45 mmoles)

of triethylamine-borane, dissolved in 35 ml of benzene, and 3.119 g (12.28 mmoles) of iodine; the iodine color was discharged more slowly than with trimethylamine-borane and produced a reddish solution. After addition of 2.607 g (33.00 mmoles) of pyridine and 5 hr at room temperature, 6.344 g of boronium iodide was isolated (81% yield). The compound was identical with the one obtained from the reaction of pyridine-iodoborane and triethylamine.

A solution of triethylamine-iodoborane was prepared from 4.39 mmoles of iodine and a slight excess of triethylamine-borane, as above, and gaseous trimethylamine was passed through the solution. Within 5 min a white precipitate appeared. After 1 hr the product was isolated by filtration and washed; 1.658 g of dry product was obtained, which contained an impurity of 25% trimethylammonium iodide, as indicated by an additional singlet absorption in the nmr spectrum. Precipitation with NH_4PF_6 gave the hexafluorophosphate salt free of ammonium ion. The over-all yield was 66%.

Derivatives. The water-soluble iodide salts were readily converted to insoluble salts of PF_6^- , AsF_6^- , Br_3^- , complex iodo-mercurates HgI_3^- or HgI_4^{2-} , or $B(C_6H_5)_4^-$. All but the last of these anions were useful for clean separation of boron cation from any ammonium salt impurities, which remained in solution.

Pyridinetrimethylaminedi-hydroboron(1+) iodide, 2.435 g, was dissolved in 5 ml of water, and 3.5 ml of saturated NH_4PF_6 solution was added. The hexafluorophosphate precipitated immediately and was washed, in portions, with 20 ml of water and 15 ml of ether. The dry product weighed 2.414 g (83% yield). Derivatives of all other boron cations were prepared in similar fashion. Their yields are given in Table I.

Elemental analyses and melting points of salts recrystallized from hot water or water-acetone are listed in Table II.

Transamination. Pyridinetrimethylaminedi-hydroboron(1+) iodide, 1.779 g, was heated with 4.079 g of pyridine at 100–110° for 4 hr. After the reaction mixture was cooled, 40 ml of a 1:1 benzene-ether mixture was added. The precipitate was filtered, washed with benzene and ether, and dried. The weight of the product, 1.907 g, corresponded to a 99% yield of bis(pyridine)-boronium iodide. The compound in 3 ml of water was precipitated with 2 ml of saturated NH_4PF_6 solution. After washing with 10 ml of water and 15 ml of ether, 1.667 g (83%) of $(C_5H_5N)_2BH_2PF_6$ was obtained. The hexafluorophosphate salt was identical with that reported in the literature.⁴

In similar experiments, the iodide salts of the cations derived from trimethylamine and 4-methylpyridine, or from trimethylamine and 4-benzoylpyridine, were refluxed with 4-methylpyridine. Both salts gave bis(4-methylpyridine)boronium iodide in 78 and 82% yields, respectively, based on the weight of recovered product. The derived hexafluorophosphate salts were identical in melting point and nmr and ir spectra with an authentic sample.¹

Hydrolytic Stability. A 1-ml portion of freshly prepared 0.94 M aqueous 4-methylpyridinetrimethylaminedi-hydroboron iodide was diluted with 1 ml of water, or with 1 M HCl or 1 M NaOH in two volume ratios (1:1 and 1:3). At room temperature no change was observed in the nmr spectrum in any of the solutions after 9 hr. On heating at 100° slow gas evolution was observed and there appeared new sets of absorption which were identical with those of the free amines or their ammonium salts. The extent of degradation was estimated from the integrated proton nmr spectra of the mixtures in the aliphatic region for the acid solution and in the aromatic region for the neutral and basic solutions. In all solutions the sum of the free and coordinated 4-methylpyridine absorptions remained constant. In basic solution some trimethylamine was lost. The percentages of decomposition are given in Table III.

Stability toward Oxidizing Agents. An aqueous solution of 4-methylpyridinetrimethylaminedi-hydroboron iodide was converted to the nitrate by precipitation of iodide with excess silver nitrate. There was no evidence of reduction of silver ion. The excess silver ion was precipitated by addition of sodium hydroxide. After filtration the solution was acidified with H_2SO_4 and was approximately 1 M in boron cation. One milliliter of this solution was mixed, respectively, with 2 ml of 1 M $AgNO_3$, $CuCl_2$, or $HgCl_2$, or with 2 ml of 30% H_2O_2 , 0.1 M $K_2Cr_2O_7$, or 0.1 M $KMnO_4$, and kept for 24 hr at room temperature. No change was observed in the nmr spectra of the first five solutions. Permanganate ion was rapidly decolorized; 4-methylpyridine also reacted with MnO_4^- under similar conditions.

Infrared Spectra. All the boronium salts had similar infrared spectra except for the expected differences caused by the known absorptions of the anions and substituents on the amines. The

Table II. Elemental Analyses^a

Compounds		% C	% H	% N	% B	% X	Mp, °C ^b
TMABH ₂ (py)+PF ₆ ⁻	Calcd	32.45	5.41	9.46	3.65		
	Found	32.57	5.60	9.25	3.48		94.5-95
TMABH ₂ (py)+AsF ₆ ⁻	Calcd	28.49	4.90	8.07	3.29		
	Found	28.26	4.74	8.24	3.18		85-85.5
TMABH ₂ (4-CH ₃ py)+PF ₆ ⁻	Calcd	34.83	5.81	9.03	3.48		
	Found	34.92	5.96	8.92	3.39		147-148
TMABH ₂ (3,4-(CH ₃) ₂ py)+PF ₆ ⁻	Calcd	37.06	6.18	8.65	3.34		
	Found	37.26	6.19	8.80	3.53		81-82.5
TMABH ₂ NC ₉ H ₇ +PF ₆ ⁻	Calcd	41.65	5.21	8.01	3.12		
	Found	41.72	5.36	8.24	3.31		98.5-99.5
TMABH ₂ (3-Brpy)+PF ₆ ⁻	Calcd	25.62	4.00	7.47	2.89	21.34 (Br)	
	Found	25.45	4.12	7.57	2.68	21.14	103-104
TMABH ₂ (3-Ipy)+PF ₆ ⁻	Calcd	22.77	3.56	6.64	2.57	30.11 (I)	
	Found	22.65	3.69	6.56	2.49	30.02	112.5-114
TMABH ₂ (3-Clpy)+PF ₆ ⁻	Calcd	29.04	4.54	8.48	3.28	10.75 (Cl)	
	Found	28.94	4.65	8.32	3.07	11.03	106-107.5
TMABH ₂ (2-Fpy)+PF ₆ ⁻	Calcd	30.60	4.78	8.93	3.45	42.39 (F)	
	Found	30.38	4.53	9.11	3.45	42.50	108-109
TMABH ₂ (2-Clpy)+PF ₆ ⁻	Calcd	29.04	4.54	8.48	3.28	10.75 (Cl)	
	Found	29.18	4.67	8.60	3.52	10.66	104.5-105.5
TMABH ₂ (4-CNpy)+PF ₆ ⁻	Calcd	33.67	4.68	13.09	3.36		
	Found	33.84	4.84	13.24	3.11		135-137.5 (dec)
TMABH ₂ (3-CH ₃ -5-CNpy)+PF ₆ ⁻	Calcd	35.82	5.07	12.54	3.22		
	Found	35.35	5.01	12.20	3.03		113.5-114.5
TMABH ₂ (4-C ₆ H ₅ py)+PF ₆ ⁻	Calcd	45.16	5.38	7.53	2.90		
	Found	44.98	5.26	7.45	2.79		139.5-140.5
TMABH ₂ (4-C ₆ H ₅ CH ₂ py)+PF ₆ ⁻	Calcd	46.63	5.69	7.25	2.79		
	Found	46.79	5.66	7.23	2.64		113-114.5
TMABH ₂ (4-C ₆ H ₅ COpy)+PF ₆ ⁻	Calcd	45.02	5.00	7.00	2.70		
	Found	44.99	5.09	6.84	2.86		163-165
TMABH ₂ (4-CH ₃ COpy)+PF ₆ ⁻	Calcd	35.53	5.33	8.29	3.19		
	Found	35.00	5.24	8.21	3.02		147-148
TMABH ₂ (4-CH ₃ Opy)+PF ₆ ⁻	Calcd	33.13	5.52	8.59	3.31		
	Found	33.64	5.56	8.54	3.06		111-112
TMABH ₂ (2,4,6-(CH ₃) ₃ py)+PF ₆ ⁻	Calcd	39.05	6.51	8.23	3.20		
	Found	38.38	6.59	8.09	3.27		104-105
TMABH ₂ (2-CH ₃ Opy)+PF ₆ ⁻	Calcd	33.13	5.52	8.59	3.31		
	Found	33.64	5.44	8.64	3.08		134.5-135.5
TMABH ₂ (N,N-dimethylaniline)+PF ₆ ⁻	Calcd	39.07	6.51	8.28	3.20		
	Found	39.07	6.64	8.24	3.37		106.5-107.5
TMABH ₂ (TEA)+PF ₆ ⁻	Calcd	33.98	8.18	8.81			
	Found	33.99	8.14	8.56			102.5-103.5
pyBH ₂ (TEA)+PF ₆ ⁻	Calcd	39.05	6.51	8.28	3.20		
	Found	38.98	6.22	8.16	3.30		154.5-155.5
pyBH ₂ (2,4,6-(CH ₃) ₃ py)+PF ₆ ⁻	Calcd	43.58	5.03	7.82	3.02		
	Found	43.51	5.13	7.74	3.09		119.5-120.5
pyBH ₂ (4-CH ₃ py)+PF ₆ ⁻	Calcd	40.00	4.24	8.48	3.27		
	Found	39.80	4.20	8.24	4.49		67-68
pyBH ₂ (2-CH ₃ Opy)+PF ₆ ⁻	Calcd	38.15	4.05	8.09	3.12		
	Found	37.88	4.24	8.02	3.08		116-118

^a Performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and Peninsular ChemResearch, Inc., Gainesville, Fla. X = F, Cl, Br, or I; TMA = trimethylamine; TEA = triethylamine; NC₉H₇ = quinoline; py = pyridine. ^b Uncorrected.

Table III. Hydrolysis of 4-Methylpyridinetrithylamine-BH₂⁺ Cation (%)

Time, hr	Temp, °C	1 M HCl		H ₂ O	1 M NaOH	
		1:1 ^a	1:3 ^a	1:1 ^a	1:1 ^a	1:3 ^a
8.5	100	45	46	52	57	69
15.5	100	54	88	57 ^b	77	93

^a Dilution ratios. ^b Difficult to estimate due to broadening and poor resolution.

assignments of the various bands were made by a straightforward comparison between the spectra of the coordinated amines and the spectra of the free amines. The stretching vibrations for BH₂ grouping are doublets found in the region 2400-2500 cm⁻¹, and the deformation of the HBH angle is found as an intense band near 1160 cm⁻¹. An additional intense broad band, often resolved into a doublet, appears between 1100 and 1250 cm⁻¹. It may be assigned to the B-N valence stretch, as reported by Greenwood and Wade,⁷ even though this has been disputed by Taylor and Cluff.⁸

In pyridine and substituted-pyridine complexes, in the region 1430-1640 cm⁻¹, there are four characteristic principal bands, as

(7) N. N. Greenwood and K. Wade, *J. Chem. Soc.*, 1130 (1960).

(8) R. C. Taylor and C. Cluff, *Nature*, **182**, 390 (1958).

expected,⁹⁻¹¹ which are due to C-C and C-N stretching vibrations, two of which are symmetric and two of which are antisymmetric in-plane ring deformations. The distinct band near 1600 cm⁻¹ in free pyridines is shifted to near 1640 cm⁻¹ by about 30-40 cm⁻¹ on complexing to the BH₂⁺ group. The weak band near 1580 cm⁻¹ in the spectrum of free pyridines remains nearly constant on coordination. The two bands near 1490 and 1430 cm⁻¹ in the free pyridines, which have been assigned to ring vibrations, are obscured by superposition of the C-H deformations when aliphatic groups are present. In bis(pyridine) derivatives the lower frequency band is shifted to 1450-1460 cm⁻¹, while the higher frequency band remains nearly invariant.

Nmr Spectra. Proton nmr spectra of the boronium hexafluorophosphates were taken in CH₂Cl₂ with the Varian A-60 instrument with tetramethylsilane as an external reference, and B¹¹ nuclear resonance spectra were obtained at 19.3 Mc with trimethyl borate as the external reference. The chemical shifts, δ , in parts per million, and observable B-H coupling constants, J , in cycles per second, are reported in Table IV. In general, B¹¹ resonances are triplets, as expected, but there are a few instances where broadening obscures the multiplicity. Due to excessive line broadening, hydrogens attached to boron could not be detected in the proton spectra. The integrated intensities of the proton spectra agreed well with the expected values. Resonances belonging to the pyridine ring protons were assigned on the basis of their relative intensities, their multiplicity, and their relative chemical shifts.^{12,13} There is a definite downfield chemical shift in all the proton resonances on coordination to a BH₂⁺ group when compared to the proton resonances of the free amines. The chemical shifts of the protons of (CH₃)₃N (a singlet) fall at δ 2.75 \pm 0.08 ppm downfield of tetramethylsilane in all the mixed compounds, provided the same solvent CH₂Cl₂ is used. Changes in the anion and solvents may cause changes in the values reported in the table.

Results and Discussion

The unsymmetrical boron cations prepared in this study are white, easily crystallizable stable solids when isolated in the form of their hexafluorophosphate salts. The iodide salts are extremely soluble in water and range in color, in the solid state, from pure white to orange-red. Absorption in the visible region appears only if a pyridine ring is present and shifts to longer wavelengths as the electron-withdrawing power of the substituent on pyridine increases, *e.g.*, from methyl to 4-acetyl or 4-cyano. Salts containing the latter two substituents on pyridine are also orange-red in methylene chloride, but the color fades to yellow on addition of ethanol; dilute aqueous solutions are colorless but turn yellow on addition of potassium iodide, even if hexafluorophosphates are used. The changes in the absorption spectrum parallel the visual changes. This behavior confirms our earlier suggestion¹ that charge-transfer transitions from iodide ion to the pyridine ring are responsible for the observed spectral changes, in analogy to the behavior of pyridinium salts.¹⁴ Electron-withdrawing substituents in pyridine increase the electron affinity of the ring and should, therefore, produce a red shift in the charge-transfer absorption. In the solid state, or in a solvent where extensive ionic association can take place, the probability of charge-transfer absorption would be high and the effect on the visible spectrum more pronounced. The charge-transfer spectra which have been observed so far are

very broad but do show some discernible fine structure. The question whether stable ion complexes or loose "contact" complexes are responsible for the spectra is at present unsolved.

The hexafluorophosphate salts are indefinitely stable at room temperature in the solid state. A number of iodide salts, however, had extensively decomposed after 8 months in the dark in a closed bottle. In fact, even in freshly prepared and recrystallized samples the odor of amine can often be noticed. Whether this behavior is caused by a slow displacement of amine by iodide, analogous to the decomposition of bis(trimethylamine)-dihydroboron chloride at high temperature reported by Muetterties,³ or whether decomposition is caused by the presence of water in the hygroscopic salts, is not certain.

The cations are quite stable to acid or base in the cold, but they are slowly hydrolyzed to amine and hydrogen in boiling water. Acid in low concentration appears to retard the hydrolysis while base accelerates the reaction. It has been reported³ that [(CH₃)₃N]₂BH₂⁺, on heating with 10% sodium hydroxide or hydrochloric acid at 100° for long periods of time, did not show a noticeable change. As is demonstrated in Table III, replacement of one trimethylamine by 4-methylpyridine decreases the stability of the cation to hydrolysis. Substitution by a second molecule of 4-methylpyridine gives a further decrease in stability; 85% decomposition occurred in 0.5 hr at 100° in 1 M NaOH. The nature of the coordinated amine thus can produce very drastic changes in the reactivity of the cation. It should be noted that either steric inhibition of the hydrolysis by trimethylamine or rate enhancement *via* electronic factors in the pyridine ligand could account for the observed trend.¹⁵

The cation from 4-methylpyridine and trimethylamine was quite inert to a number of oxidizing agents which normally react rapidly in the cold with neutral boranes. Thus Ag⁺, Hg²⁺, Cu²⁺, Cr₂O₇²⁻, and H₂O₂ failed to react. Permanganate reacted, but not noticeably faster than 4-methylpyridinium ion itself, which is oxidized by permanganate at the methyl group.

The amine substituents on boron can be replaced by other amines under appropriate conditions. Thus, trimethylamine was readily replaced by pyridine or 4-methylpyridine at 100°. Likewise, the cation derived from trimethylamine and 4-benzoylpyridine was cleanly transaminated by 4-methylpyridine with replacement of both ligands by the latter amine. In contrast, the rather weak base 4-acetylpyridine did not react with this unsymmetrical ion on refluxing in benzene for 4 hr; only starting material was recovered. Amine displacement thus offers a good route to symmetrical bis-amine cations, provided that the displacing amine is sufficiently basic.

The synthesis of the new cations proceeded, in most instances, rapidly and with very high yields. Yields were reproducible in duplicate runs. In general, pyridine-iodoborane appeared to be more reactive than either trimethylamine or triethylamine-iodoborane, a difference which parallels the distinction in reactivity between benzyl and primary alkyl halides in nucleo-

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(14) E. M. Kosower, *J. Am. Chem. Soc.*, **77**, 3883 (1955).

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Table IV. Proton and B¹¹ Nmr Data of Boronium Salts^a

Compounds (PF ₆ ⁻ salts)	H ¹ resonances					B ¹¹ resonances			
	Aliphatic amines TMA or TEA δ, ppm	Pyridine substituents δ, ppm	H ¹	Pyridine ring δ, ppm	J _{B-H} , cps	M	δ, ppm	J _{B-H} , cps	M
TMABH ₂ (4-CH ₃ py) ⁺	TMA, 2.67	CH ₃ , 2.63	H _{2,6}	8.55	7	2	15.8	90 ± 5	3
TMABH ₂ (4-CH ₃ Opy) ⁺	TMA, 2.67	OCH ₃ , 4.12	H _{3,5} H _{2,6}	7.78 8.46	7 7.5	2	16.9 ± 0.5 ^c	100	3
TMABH ₂ (4-CNpy) ⁺ (in methylene chloride)	TMA, 2.77		H _{3,5} H _{2,6}	7.35 8.92	7.5 7	2	14.5 ± 0.5 ^b	(≈370) ^f	B
TMABH ₂ (4-CNpy) ⁺ • (in acetone)	TMA, 2.27		H _{3,5} H _{2,6}	8.26 8.64	7 7	2			
TMABH ₂ (4-C ₆ H ₅ COpy) ⁺	TMA, 2.80	C ₆ H ₅ , 7.81	H _{3,5} H _{2,6}	7.91 8.86	7 7	2	16.1 ± 1 ^c	(350 ± 50) ^f	B
TMABH ₂ (4-C ₆ H ₅ CH ₂ py) ⁺	TMA, 2.68	C ₆ H ₅ , 7.36	H _{3,5} H _{2,6}	8.17 8.52	7 7	2	16.4 ± 1 ^c	(350 ± 50) ^f	3
TMABH ₂ (4-C ₆ H ₅ py) ⁺	TMA, 2.73	CH ₂ , 4.28 C ₆ H ₅ , 7.77	H _{3,5} H _{2,6}	7.74 8.67	7 7	2	16.6 ± 1 ^c	(350 ± 50) ^f	B
TMABH ₂ (4-CH ₃ COpy) ⁺ (in methylene chloride)	TMA, 2.73	COCH ₃ , 2.77	H _{3,5} H _{2,6}	8.14 8.86	7 7	2			
TMABH ₂ (4-CH ₃ COpy) ⁺ • (in nitromethane)	TMA, 2.08	COCH ₃ , 2.08	H _{3,5} H _{2,6}	8.36 8.29	7 7	2	16.4 ± 1 ^c	(330 ± 30) ^f	3
TMABH ₂ (3,4-(CH ₃) ₂ py) ⁺	TMA, 2.68	3-CH ₃ , 2.45	H _{3,5} H _{2,6}	7.67 8.38	7	2	15.6	110	3
TMABH ₂ (2,4,6-(CH ₃) ₃ py) ⁺	TMA, 2.74	4-CH ₃ , 2.55 2,6-CH ₃ , 2.94	H ₅ H _{3,5}	7.71 7.48	7	2	21.6 ± 0.5	99 ± 10	3
TMABH ₂ (3-Clpy) ⁺	TMA, 2.80		H _{2,6} H ₄ H ₅	8.78 8.56 8.10			15.9	(300) ^f	B
TMABH ₂ (3-Brpy) ⁺	TMA, 2.78		H _{2,6} H ₄ H ₅	8.82 8.62 8.03			16.4	(280) ^f	B
TMABH ₂ (3-Ipy) ⁺	TMA, 2.77		H _{2,6} H ₄ H ₅	8.90 8.77 7.86			16.2	(280) ^f	B
TMABH ₂ (3-CH ₃ -5-CNpy) ⁺ (in methylene chloride)	TMA, 2.82	3-CH ₃ , 2.73	H _{2,6} H ₄	8.78 8.53					
TMABH ₂ (3-CH ₃ -5-CNpy) ⁺ • (in nitromethane)	TMA, 2.13	3-CH ₃ , 1.98	H _{2,6}	8.17			10.4 ± 2.6 ^d		B
TMABH ₂ (2-Fpy) ⁺	TMA, 2.78		H ₄ H _{4,6}	7.85 8.56			14.0 ± 0.5	(≈300) ^f	B
TMABH ₂ (2-Clpy) ⁺	TMA, 2.75		H _{3,5} H ₆ H ₄	7.79 8.76 8.38	7	2	18.2	120	3
TMABH ₂ (2-CH ₃ Opy) ⁺	TMA, 2.74	OCH ₃ , 4.23	H _{3,5} H _{4,6}	7.90 8.41			18.3		3
TMABH ₂ (quinoline) ⁺	TMA, 2.78		H _{3,5} H ₂ H _{4,8}	7.43 9.2 8.96			19.3	120	3
TMABH ₂ (py) ⁺	TMA, 2.71		H _{5,6,7,8} H _{2,6} H ₄ H _{3,5}	8.17 8.74 8.43 8.00	5.5	2	16.4		3
TMABH ₂ (N,N-dimethylaniline) ⁺	TMA, 2.52 N(CH ₃) ₂ , 3.33	C ₆ H ₅ , 7.65					14.6	115	3
TMABH ₂ (TEA) ⁺	TMA, 2.85 CH ₃ , 1.27 (triplet, J = 7) CH ₂ , 3.05 (quartet, J = 7)								
pyBH ₂ (2-CH ₃ Opy) ⁺		OCH ₃ , 4.05	H _{4,6} (*py) H _{3,5} (*py) H _{2,6} (py) H ₄ (py) H _{3,5} (py)	8.23 7.35 8.67 8.46 7.83	5.5	2	16.4 ± 1.6		B

Table IV (Continued)

Compounds (PF ₆ ⁻ salts)	H ¹ resonances				B ¹¹ resonances		
	Aliphatic amines TMA or TEA δ, ppm	Pyridine substituents δ, ppm	H ¹	Pyridine ring δ, ppm, J _{H-H} , cps, M	δ, ppm	J _{B-H} , cps	M
pyBH ₂ (4-CH ₃ py) ⁺		4-CH ₃ , 2.58	H _{2,6} (py) H ₄ (py) H _{3,5} (py) H _{3,5} (*py) H _{2,6} (*py)	8.67 8.30 7.70 7.96 7 2 8.67	16.7 ± 0.5	105	3
pyBH ₂ (2,4,6-(CH ₃) ₃ py) ⁺		4-CH ₃ , 2.53 2,6-CH ₃ , 2.67	H _{3,5} (*py) H _{2,4,6} (py) H _{3,5} (py) H _{2,6}	7.42 8.28 7.85 8.68 5.5 2	18.1		B
pyBH ₂ (TEA) ⁺	CH ₃ , 1.30 (triplet, J = 7) -CH ₂ , 2.90 (quartet, J = 7)		H ₄ H _{3,5}	8.58 8.01	20.6 ± 0.5 ^a	88 ± 10	3

^a All the δ values represent the centers of the resolvable or complex multiplets. Except where stated, all H¹ and B¹¹ spectra are of boronium hexafluorophosphates in methylene chloride. H¹ and B¹¹ are referred to external tetramethylsilane and trimethyl borate, respectively. Symbols: B, broad; M, multiplicity; TMA, (CH₃)₃N; TEA, (C₂H₅)₃N; py, C₅H₅N; *py, substituted pyridine. ^b Iodide in methylene chloride. ^c Iodide in nitromethane. ^d Hexafluorophosphate in acetone. ^e Because of the low solubility of the boronium hexafluorophosphate salts in methylene chloride nitromethane and acetone were used for better spectra. ^f Full width at half maximum intensity. ^g Iodide in water.

philic substitution. In comparison to organic halides, however, the boron compounds are vastly more reactive: they react rapidly with amines even in solvents of low dielectric constant which generally inhibit the rates of reactions leading to charged species.¹⁶ This difference is vividly demonstrated by the high reactivity of trimethylamine-iodoborane which is isoelectronic and isosteric with neopentyl iodide. The latter compound undergoes nucleophilic substitution only slowly.¹⁷

With trimethylamine-iodoborane as the starting material, it was possible to observe differences in the ease with which product was formed as a function of the nature of the second amine. Substituents *ortho* to the pyridine nitrogen atom sharply decreased the rate of product formation, as evidenced by the low yield with 2-methoxypyridine, and by the necessity of employing elevated temperatures for complete reaction. Since 2,4,6-trimethylpyridine, with a pK_a for the ammonium ion of 6.75,¹⁸ reacted much slower than 4-methylpyridine, a weaker base (pK_a = 6.03), it is concluded that the formation of boron cation is subject to steric inhibition if the attacking amine is sufficiently bulky. With pyridine-iodoborane as its starting material, the generally very high reactivity precluded similar observations.

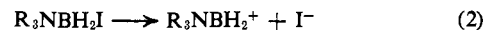
The formation of the boron cations also appeared to be influenced by electronic factors in the nitrogen base substituting on the amine-iodoborane. Both 3-chloro- and 4-cyanopyridine, which are markedly less basic than pyridine, and whose substituents should not interfere sterically, reacted sluggishly at room temperature with trimethylamine-iodoborane. Carefully obtained yield data indicated that pyridine reacted at least four times faster than 4-cyanopyridine. Although the reaction rates unquestionably decreased with lowered base strength, the sensitivity of the reaction to variation in this parameter is not very pronounced; even 2-fluoro-

pyridine, an extremely weak base (pK_a = -0.44) with an *ortho* substituent, did not fail to give a reasonable product yield on heating to 70°.

The yields of iodide salts quoted in Table I were obtained either at 25° or at 70°, but under otherwise identical reaction conditions. Since the conversion to pure hexafluorophosphates was nearly quantitative for most cations (indicating substantial purity in the primary product), the yields represent a measure of relative rates of the general reaction



where R₃N represents a tertiary amine or pyridine. This reaction could proceed *via* nucleophilic attack on boron by the amine nitrogen leading to displacement of iodide ion. On the other hand, primary ionization of the boron-iodine bond followed by addition of amine to the resulting three-coordinate cation would not be implausible in view of an expected high ionic character of this bond.



The data presented here allow one to make judgments concerning these alternatives.

First, if eq 2 represented the rate-determining step in the over-all reaction, one should expect that trimethylamine-iodoborane should react at the same rate, regardless of the amine entering in eq 3, and identical product yields should be obtained. This is contrary to our observations.

If ionization of the iodoborane were not rate determining, then the subsequent amine addition to the three-coordinate intermediate would have to be the slow step. In this case, the extremely slow reactions of trimethylamine-iodoborane with triethylamine or *ortho*-substituted or weakly basic pyridine derivatives would imply that addition of the amine to the hypothetical (CH₃)₃NBH₂⁺ ion is also slow at room temperature. This assumption is in disagreement with the general observation that Lewis acid-base additions are very fast in the absence of extensive molecular rearrange-

(16) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 32.

(17) Reference 16, p 53.

(18) D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solutions," Butterworth and Co., Ltd., London, 1965, p 141.

ments. Direct experiments concerning this point have been made with boron trifluoride and various amines. They showed that the addition in these cases proceeded essentially without activation energy.¹⁹ One might reasonably expect that a three-coordinate positively charged borane should thermodynamically be even a stronger acceptor than boron trifluoride, and therefore should react at least as rapidly as boron trifluoride. A reversible equilibrium in eq 3 is ruled out by the fact that the cations are stable at room temperature. The foregoing argument effectively eliminates a mechanism involving ionization of the iodoborane and leaves the likelihood that the boron cations are formed by a bimolecular nucleophilic substitution represented by eq 1.

Displacement of one amine by another is an alternate nucleophilic substitution which, in principle, should be a possible reaction competing with iodide displacement. In only one instance was there evidence that this occurred. If, in general, amine exchange had occurred to a significant extent, one should have isolated symmetrically bis-amine cations in mixture with the unsymmetrical ones. Such a side reaction should have been especially noticeable in the reaction of trimethylamine-iodoborane with pyridines, since the proposed intermediate pyridine-iodoborane, produced by amine exchange, is more reactive in cation formation than the trimethylamine derivative. The nmr spectra and other properties of the hexafluorophosphate salts, which were isolated in almost quantitative yield and high purity, showed no evidence whatever of the presence of bispyridine cations. One must thus conclude that displacement of iodide from boron is considerably faster than displacement of amine. As a corollary, the results also imply that simple dissociation of the boron-nitrogen bond, unaided by external amine, is a slower process than iodide displacement in the three amine-iodoboranes studied here.

The one example in which loss of an amine from an iodoborane adduct apparently took place is the attempted synthesis of an unsymmetrical cation, with triethylamine- and trimethylamine-iodoborane as reactants. The reaction at room temperature was extremely slow and gave exclusively a low yield of the symmetrical cation derived from trimethylamine. At 80° more extensive reaction occurred but still gave a substantial proportion of symmetrical product. The net transfer of an originally coordinated amine to another boron atom must mean that a boron-nitrogen bond had been cleaved. The resulting trimethylamine then could combine with unreacted starting material, as was demonstrated by direct reaction of trimethylamine- and trimethylamine-iodoborane in a separate

(19) G. B. Kistiakowsky and C. E. Klots, *J. Chem. Phys.*, **34**, 715 (1961).

experiment. With more extensive reaction at elevated temperature triethylamine-iodoborane accumulated in the reaction mixture and could compete with trimethylamine-iodoborane for trimethylamine, giving the unsymmetrical cation in mixture with the bis(trimethylamine)boron cation. This reaction was also demonstrated by direct experiment. It is of course possible that at higher temperature direct iodide displacement by triethylamine on trimethylamine-iodoborane proceeds competitively with amine displacement. If so, iodide displacement must have a higher activation energy than amine displacement.

Although the unsymmetrical cation could not be obtained pure starting with trimethylamine-borane, the inverse procedure, starting with triethylamine-iodoborane and trimethylamine, cleanly gave the desired compound. This discrepancy in results was unexpected, since one might reasonably expect that the transition states for either iodide displacement have similar conformation and similar steric interactions between coordinated amine and incoming nucleophile. Examination of molecular models reveals, however, that triethylamine coordinated to iodoborane must have the terminal CH₃ in the ethyl groups folded away from iodine, and therefore from the boron atom, if repulsions are to be avoided. In fact, the molecule appears very much like trimethylamine-iodoborane if one considers only the disposition of atoms in the immediate vicinity of boron. Uncoordinated triethylamine, on the other hand, easily allows conformations which place the bulk of the terminal methyl groups around the reaction site, the electron pair on nitrogen. Thus successful iodide displacement from trimethylamine-iodoborane by triethylamine must achieve the minimum free energy for the transition state by striking a balance between an unfavorable activation entropy associated with restricted conformations of the ethyl groups, which are sterically unfavorable for reaction, and an activation enthalpy increased by steric repulsions, for those conformations which do not suffer from the entropy disadvantage. In triethylamine-iodoborane the conformation of the ethyl groups is already largely fixed and offers no barrier to an approaching trimethylamine molecule. This line of reasoning leads to the inference that the iodination of triethylamine-borane should be subject to inhibition relative to the iodination of trimethylamine-borane, since it is primarily the presence of the large iodine substituent on boron which freezes the conformations of the ethyl groups. Iodination of triethylamine-borane indeed is visibly slower than the corresponding reaction of trimethylamine-borane.

Acknowledgment. The authors express their appreciation to the National Institutes of Health, who supported this research under Grant GM-13650.