SYNTHESES OF BORANE ADDUCTS AND OF BORON CATIONS DERIVED FROM BH_2^+

By

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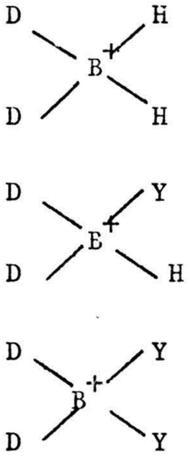
CHAPTER I

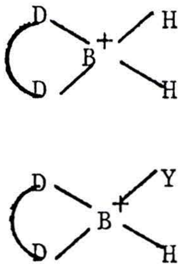
INTRODUCTION

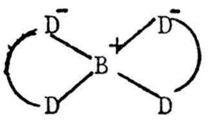
In the classic work of Parry and Shore,(1) the structure of "diammoniate of diborane" was shown to be the tetrahydroborate salt of the boron cation, diaminedihydroboron (+1). Since that time the chemistry of boron cations has been developed rapidly and a great number of boron cations have been reported.(2-26) According to the number of cationic boron nuclei present in the molecule, the various cations reported in the literature and prepared in this laboratory can be classified as mononuclear, binuclear and polynuclear cations. Depending on the number of charges, mononuclear cations may be further classified as monocations, dications and trications. The binuclear boron cations so far known are dications. The number of charges on the polynuclear cations is not certain, but tentatively they are considered as polycations.(7) These classifications are structurally represented as follows:

<u>Mononuclear Cations</u>

<u>Monocations</u>

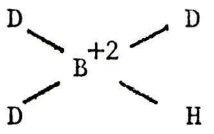


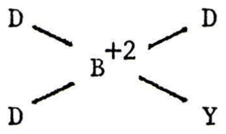




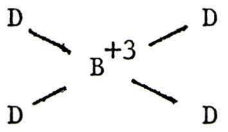
D = donor bases
Y = organo groups
or halogen

Dications

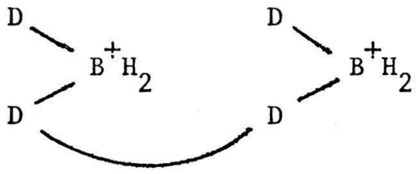




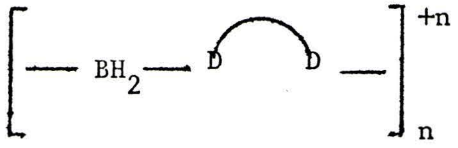
Trications



Binuclear Cations



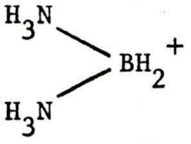
Polynuclear Cations

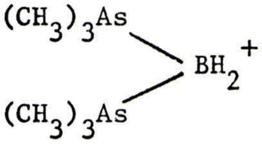


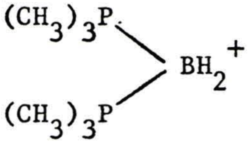
n is uncertain

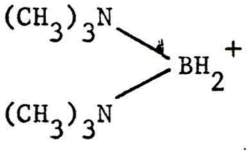
In general the donor bases coordinated to boron cations are either neutral or negatively charged. The bases commonly used are amines, phosphines, arsines, amine oxides or phosphine oxides. According to the number and kinds of ligands used, boron cations can be classified into many groups which of course, may include mono-, di-, and trications, mono-,bi-, and polynuclear cations. Their examples with appropriate references are given in the following pages.

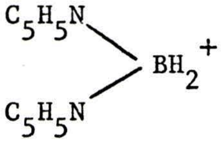
$(base)_2BH_2^{+}$ (2-5)

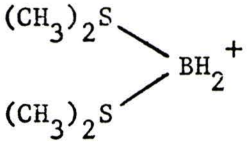


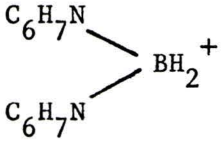






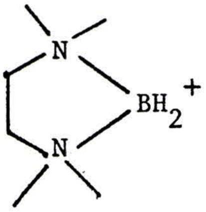


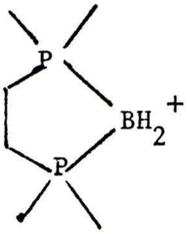


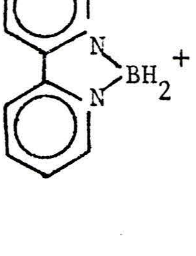


C_6H_7N = 2-picoline,
3-picoline,
or 4-picoline

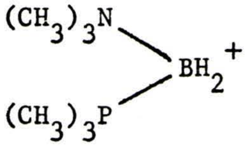
$(dibase)BH_2^{+}$ (3,7)

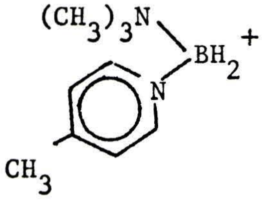


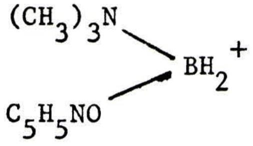


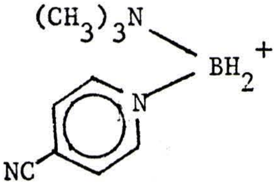


$(\mathrm{base})(\mathrm{base}^1)\mathrm{BH}_2^+$ (3,6,8-11)

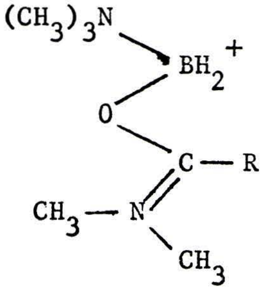


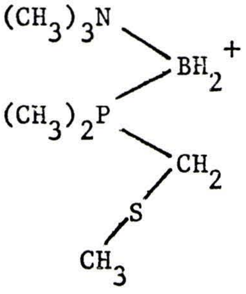


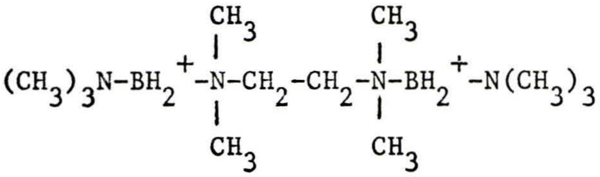




$(\mathrm{base})(\mathrm{dibase})\mathrm{BH}_2^+$ (10,12)

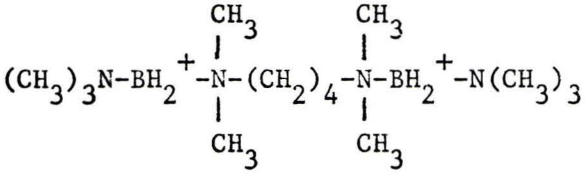






$$(CH_3)_3N{-}BH_2^{+}{-}\underset{CH_3}{\overset{CH_3}{N}}{-}CH_2{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{N}}{-}BH_2^{+}{-}N(CH_3)_3$$

$(base)BH_2^{+}(dibase)BH_2^{+}(base)$(7,11)



$$(CH_3)_3N{-}BH_2^{+}{-}\underset{CH_3}{\overset{CH_3}{N}}{-}(CH_2)_4{-}\underset{CH_3}{\overset{CH_3}{N}}{-}BH_2^{+}{-}N(CH_3)_3$$

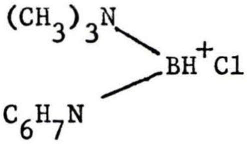
$(base)_2YBH^{+}$(2,3,13,14) e.g.

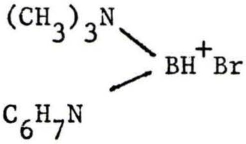
$(C_5H_5N)_2BH^{+}(C_6H_{13})$

$(C_6H_7N)_2BH^{+}Cl$

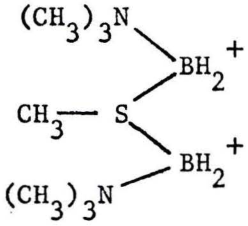
C_6H_7N = 4-picoline

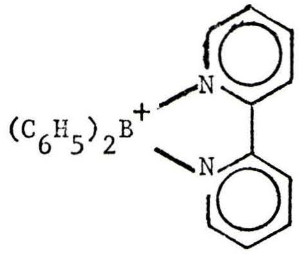
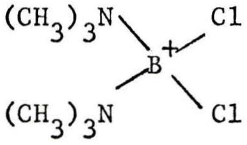
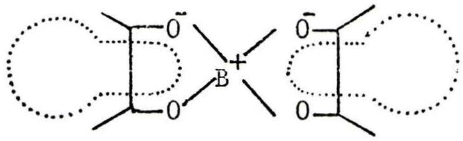
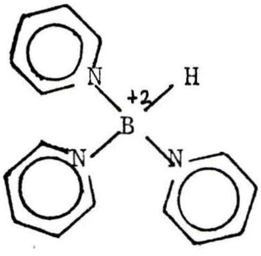
$(base)(base^1)BH^{+}Y$(9,14,15)



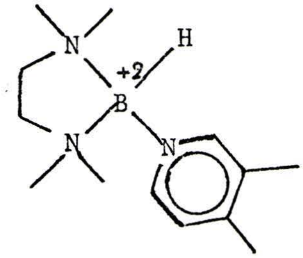


$(base)BH_2^{+}{-}S(R)\ BH_2^{+}\ (base)^{+}$(17,18)

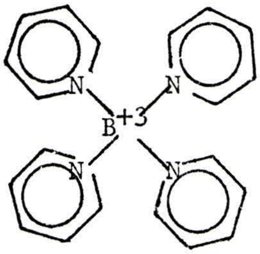


(dibase) BY_2^+(19,20)	
(solvent)Y_2B^+(21)	$(C_6H_5)_2B^+$ (ethyl methyl ketone)
$(base)_2BY_2^+$(3,22-24)	
$(dibase)_2B^+$(16)	$(C_5H_5N)_2B^+$ $(C_6H_{11})_2$ 
$(base)_3BH^{+2}$(18,25)	 $(C_6H_7N)_3BH^{+2}$
$(base)_3BY^{+2}$(26)	$(C_5H_5N)_3B\ Br^{+2}$

$(base)(dibase)BH^{+2}$(7)



$(base)_4B^{+3}$(18,26)



$(dibase\ BH_2)_n^{+n}$(7)

$(TMBD\ BH_2)^{+n}$

$(TMPD\ BH_2)_n^{+n}$

n is uncertain, TMBD = tetramethylbutylene-diamine, TMPD = tetramethylpropylene-diamine.

In the previous examples base and base^1 represent amines, phosphines, arsines, amine oxides, or phosphine oxides, and Y an organo group or halogen.

Along with a variety of compounds, a number of synthetic routes have also been developed.

Boron cations belonging to the class, $(\text{base})_2BH_2^+$ where base represents tertiary amines, have been prepared by the following methods

$$2\ Ph_3C^+ + BH_4^- + 2\ \text{Amine} \xrightarrow[-50\ \text{to}\ 25°]{CH_3CN} 2\ Ph_3CH + (\text{Amine})_2BH_2^{+}\ ^{(27)}$$

Miller and Muetterties(3) prepared them using high temperature reaction of base-boranes with "onium" salts of large anions.

$$A{\cdot}BH_3 + AH^+X^- \xrightarrow{100-180°} (A)_2BH_2^+\ X^- + H_2$$

A = tertiary amine; X= halogen

The method pioneered by Douglass(13,28) in the preparation of boronium ions of the type, $(\text{base})_2\overset{+}{B}YH$ where Y represents organo groups, was developed by Ryschkewitsch(4) to prepare $(C_5H_5N)_2BH_2^+$ cation.

$$(CH_3)_3NBH_3 + I_2 + 2\ C_5H_5N \xrightarrow{70°} (CH_3)_3NH^+\ I^- + (C_5H_5N)_2BH_2^+I^-$$

Starting with sodium borohydride, iodine and pyridine, $(C_5H_5N)_2BH_2^+I$ was prepared in high yield in this laboratory.(4)

$$2BH_4^- + 2C_5H_5N + I_2 \rightarrow 2C_5H_5NBH_3 + 2I^- + H_2$$

$$C_5H_5N{\cdot}BH_3 + I_2 + 2C_5H_5N \rightarrow (C_5H_5N)_2BH_2^+I^- + C_5H_5NH^+I^-$$

Noth and co-workers(2,8) prepared a number of boron cations, $(\text{base})_2BH_2^+$ where base represents mainly aliphatic primary or secondary amines, by nucleophilic displacement reaction on monohalo-amineboranes

$$A\ BH_2X + A \rightarrow (A)_2BH_2^+X^-$$

A = amines; X = halogen

Boron cations, (base)(base^1)BH_2^+ where two different tertiary amines complete the coordination sphere around a BH_2^+ ion were rarely known until 1968. Actually only two examples were reported, i.e., a boron cation with 4-methylpyridine and trimethylamine,(9) or with dimethylethylamine and trimethylamine coordinated to boron.(3)

It was one of the objectives of the present work to prepare a series of new boron cations of the types, (base)$_2BH_2^+$, (base)(base^1)BH_2^+ and (base)(dibase)BH_2^+ by simple methods with good yields. In this context it may be worth mentioning that a number of boron cations, whose structural representations are given in the preceding pages, were actually reported in the literature as a result of the work of this author, or were prepared by others who used the basic method developed in this laboratory.(4,5,9) The reactive properties of the cations were also investigated with respect to thermal, oxidative and hydrolytic degradation, and with respect to transamination.

Closely related to boron cations, amine-boranes constitute an important class of boron-nitrogen compounds since they or their derivatives provide a direct entry to the synthesis of amino-boranes or borazines,(29,30) or to boron cations.(3,4,28) It is therefore of considerable importance to develop simpler and more convenient methods of synthesis of amine-boranes from readily available starting materials. Present methods involve either direct combination of amine and diborane reaction of ethereal lithium borohydride with ammonium salts,(31) transamination of an already formed amine-borane,(32,33) or less direct methods like reduction of an appropriate boron compounds using hydrogen or borohydride.(34-36)

Therefore it was another objective of the present work to develop a convenient one-step synthesis of borane adducts using sodium borohydride, appropriate donors and iodine. The new method was successfully worked out for the synthesis of ammonia-borane, boranes of different aliphatic amines which include primary and secondary monoamines, tertiary di- and tri-amines, boranes of substituted pyridines, and for the synthesis of phenyl-substituted phosphine boranes.(37)

The reaction of $NaBH_4$ and I_2 in glyme gives diborane in high yield.(38) Therefore it was thought that if BH_4^- could react with the diborane produced by BH_4^- and I_2 *in situ*, $B_3H_8^-$ might be prepared.

The triborohydride ion, $B_3H_8^-$, is an important intermediate for the synthesis of polyhedral borane, $B_{12}H_{12}^{-2}$. On heating $B_3H_8^-$ ion, it decomposes to $B_{12}H_{12}^{-2}$ and BH_4^-.(39) $B_3H_8^-$ ion has been prepared previously from different starting materials, such as sodium amalgam and diborane,(40) degradation of decaborane,(41) sodium and diborane,(42) and sodium borohydride and diborane,(42) but these are not very convenient methods.

Synthesis of $B_3H_8^-$ was a subsidiary objective of the present research program. An attempt was made to prepare $B_3H_8^-$ from the readily available starting materials, $NaBH_4$ and I_2. Even though the yields were not very high, both $B_3H_8^-$ and $B_{12}H_{12}^{-2}$ were prepared successfully.

CHAPTER II

MATERIALS AND INSTRUMENTATION

Materials

Amine-boranes were obtained from Callery Chemical Co.,and used without further purification. Sodium borohydride was supplied in good purity by Metal Hydrides, Inc.

Ammonium hexafluorophosphate was obtained from the Ozark-Mahoning Company.

Trimethylamine and dimethylamine gases were obtained from the Matheson Company.

The various amines and phosphines were obtained from commercial sources, namely; Eastman Organic Chemicals, K. & K. Laboratories, and Aldrich Chemical Co., Inc. Amines were distilled when necessary and dried and stored over calcium hydride or molecular sieve 3A.

Monoglyme (1,2-dimethoxyethane), obtained from Matheson Coleman and Bell, was dried by calcium hydride and diglyme (diethylene glycol dimethyl ether), obtained from the Ansul Chemical Company, was stored over calcium hydride for two days, and then fractionally distilled from lithium aluminum hydride.

All solvents supplied from various commercial sources were used without purification except for drying over calcium hydride, molecular sieve or "dri-Na" when appropriate.

Instrumentation

Infrared spectra were obtained on either Beckman IR-10 or Perkin-Elmer 137 instruments. Samples were prepared as KBr pellets with occasional use of a mineral oil (Nujol) mull. In the case of liquid amines, spectra were run as a liquid film using sodium chloride plates.

Proton nmr spectra were taken on a Varian A-60 instrument with tetramethylsilane as external or internal reference and B^{11} nmr spectra were obtained at 19.3 or 32.1 Mc with trimethylborate as the external reference. Methylene chloride, nitromethane or acetone was used as the solvent.

Ultraviolet spectra were obtained in 95 per cent ethyl alcohol with a Cary 14 spectrophotometer.

Elemental analyses were obtained from Galbraith Laboratories, Inc., or Peninsular ChemResearch, Inc.

Melting points were taken on a Thomas-Hoover apparatus and were not corrected.

Sodium borohydride was handled either in a dry box or in a nitrogen atmosphere.

CHAPTER III

SYNTHESES OF BORON CATIONS AND BORANE ADDUCTS

Syntheses of Boron Cations, BH_2^+

Syntheses of Bis-amine BH_2^+

Bis-amine boron cations, where two alkylpyridines coordinated to a $>BH_2^+$ group, are prepared by three apparently general synthetic methods.(5) The syntheses proceed from (1) sodium borohydride, iodine and an appropriate alkylpyridine (2) trimethylamine borane, iodine and alkylpyridine or (3) trimethylamine iodoborane and alkylpyridine. The general procedure and usefulness of each synthetic method are illustrated as follows.

1. Synthesis of bis(4-picoline)boronium iodide from sodium borohydride, iodine, and 4-picoline.--Sodium borohydride (94% hydride purity), 0.793 g (19.7 mmoles), was slurried with 24 ml of 4-picoline taken in a 250 ml round bottom flask. Iodine solution, 7.290 g (29.0 mmoles) in 190 ml of benzene, was added very slowly while the picoline-borohydride slurry was stirred by a magnetic stirrer. During the addition of iodine, hydrogen gas was evolved, and in the early stages the reaction was very fast. The solution was heated gradually to 70°, and the addition of iodine was continued. When all the iodine had been added, a permanent iodine color developed and on further heating for 1 hour, the color still persisted. The amount of iodine used corresponded closely to the quantities calculated according to the equation.

$$2NaBH_4 + 6\ C_6H_7N + 3I_2 \rightarrow 2NaI + 2\ (C_6H_7N)_2BH_2^+I^- + 2\ C_6H_7NH^+I^-$$

The reaction mixture was then evaporated to dryness by vacuum pumping, and the resulting solid mixture was extracted with 100 ml of dry chloroform and filtered. The leftover solid, after washing with warm chloroform and drying, weighed 3.007 g, and was identified by infrared spectrum and qualitative analysis as sodium iodide (20.0 mmoles). The filtrate was treated with trimethylamine gas to convert the picolinium salt to the less soluble trimethylammonium iodide. The ammonium salt weighed 2.850 g and had an ir spectrum identical with that of an authentic sample. The remaining solution was evaporated to dryness, affording 6.075 g of bis(4-picoline)boronium iodide (89% yield).

Bis(2-picoline)boronium and bis(3-picoline)boronium salts were prepared by similar procedures, and their yields are reported in Table I.

2. Synthesis of bis(2-picoline)boronium iodide from trimethylamine-borane, iodine and 2-picoline.--Trimethylamine-borane, 2.100 g (27.5 mmoles), was dissolved in 25 ml of 2-picoline. Solid iodine, 6.978 g (27.5 mmoles), or iodine in benzene solution, was added in small portions over a 15-minute period. An exothermic reaction started immediately. The reaction mixture was heated gradually to 70° and heating was continued until the iodine color was discharged (about 1 hour). The temperature was then raised to 110° and the mixture was refluxed for 2 hours. After evaporation to dryness, the solid mixture was extracted with 100 ml of chloroform. The less soluble $(CH_3)_3NH^+I^-$ was filtered off (4.382 g, 23.4 mmoles). On saturating the filtrate with trimethylamine gas an additional crop of trimethylammonium iodide was obtained (1.172 g, 6.2 mmoles). The solution was then evaporated at room temperature, affording 8.016 g (90% yield) of bis(2-picoline)boronium iodide. Thus reaction had occured according to

$$(CH_3)_3NBH_3 + I_2 + 2\ C_6H_7N \rightarrow (CH_3)_3NH^+I^- + (C_6H_7N)_2BH_2^+I^-$$

By a similar procedure, boronium salts of 3-picoline, 4-picoline, 2,4-lutidine, and 3,4-lutidine were prepared; their yields are given in Table 1.

3. Synthesis of bis(3-picoline)boronium iodide from trimethylamine-monoiodoborane.--The iodoborane adduct was prepared by a modification of the method of Noth.(2)

$$2\ (CH_3)_3NBH_3 + I_2 \rightarrow 2\ (CH_3)_3NBH_2I + H_2$$

A sample of trimethylamine-borane, 1.902 g (26.1 mmoles), was dissolved in 30 ml of dry benzene in a 125 ml conical flask. To this solution, 2.774 g (10.9 mmoles) of iodine was added in small portions while the solution was stirred, and the flask was loosely stoppered between additions of iodine to avoid loss of hydrogen iodide. The reaction was very vigorous. After all of the iodine had been added, the solution attained a very light violet color. The resulting solution was stirred for 10 minutes. Then 20 ml of 3-picoline was added to this solution. The benzene was then distilled off and the mixture was heated to 110° for 3-4 hours. A precipitate was formed during this time.

After cooling, about 30 ml of benzene was added and filtered. The solid residue was washed with benzene and a small amount of ether. The dried product of bis(3-picoline)boronium iodide weighed 6.480 g (92% yield). By this method boron cations of all picolines and lutidines were prepared. The yields are given in Table 1.

Conversion of boronium iodides to salts of PF_6^-, AsF_6^-, and $B(C_6H_5)_4^-$.--Metathesis of boronium iodide to the hexafluorophosphate was accomplished by adding excess of ammonium hexafluorophosphate to a solution of iodide until precipitation was complete. The precipitated hexafluorophosphate was collected by filtration and recrystallized from hot water.

In order to determine the yields of conversion of boronium iodide to hexafluorophosphate, some of the iodides prepared from iodoborane adducts were converted to $> BH_2^+ PF_6^-$ and the general details were typified by conversion of bis(4-picoline)boronium iodide to boronium hexafluorophosphate. A sample of iodide salt, 0.500 g,was dissolved in 12 ml of distilled water, and 0.525 g (3.22 mmoles) of NH_4PF_6 was added to precipitate the boronium hexafluorophosphate. The precipitate was washed with 8 ml of water and 20 ml of ether, and was dried and weighed. Yields are given in Table II. Elemental analyses of the hexafluorophosphate salts are given in Table III.

Preparation of $> BH_2^+AsPF_6^-$ and $> BH_2^+B(C_6H_5^-)_4$.--By metathetical reactions boronium iodides could also be converted to derivatives such as salts of AsF_6^- and $B(C_6H_5)_4^-$. Hexafluorophosphate and hexafluoroarsenate salts of boron cations are especially useful for separation of boronium ions from ammonium salts which tend to be the principal impurities in the iodides prepared by either of the above methods. When sodium tetraphenylborate is used to precipitate boronium ions, ammonium salts also tend to be precipitated and therefore its use is of limited value. Bis(4-picoline)boronium hexafluoroarsenate was prepared from boronium iodide solution and its analyses and m.p. are reported in Table III. From an aqueous solution of bis(2-picoline)boronium iodide, prepared from sodium borohydride, iodine and 2-picoline, boronium tetraphenylborate was precipitated by adding an aqueous solution of $Na\ B(C_6H_5)_4$. The dry compound started shrinking and softening at 135° and melted at 145°.

TABLE I

YIELDS OF BIS-AMINE $BH_2^+I^-$ SALTS

Amine	From $NaBH_4$, %	From $(CH_3)_3NBH_3$, %	From $(CH_3)_3NBH_2I$, %
2-Picoline	83	90	90
3-Picoline	88	96	92
4-Picoline	89	86	91
2,3-Lutidine			93
2,4-Lutidine		62	89
2,5-Lutidine			91
2,6-Lutidine			84
3,4-Lutidine		70	97
3,5-Lutidine			98

TABLE II

YIELDS OF BIS-AMINE $BH_2^+PF_6^-$ SALTS[a]

Amine	Based on I^- salts,[b] %	Over-all, based on $(CH_3)_3NBH_3$, %
3-Picoline	96	88
4-Picoline	93	84
2,3-Lutidine[c]	77	72
2,5-Lutidine	89	81
2,4-Lutidine	91	88

[a] The salts were readily recrystallized from hot water.

[b] Prepared from $(CH_3)_3NBH_2I$. [c] Only 0.250 g of B^+ salt was used.

TABLE III

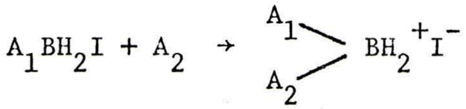
ANALYSES OF BIS(ALKYLPYRIDINE)BORONIUM SALTS

		%C	%H	%N	%B	%P	%F	Mp, °C
$C_{12}H_{16}N_2BPF_6$	Calcd	41.89	4.65	8.15	3.15	9.02	33.16	
$(2\text{-pic})_2BH_2^+PF_6^-$	Found	42.04	4.74	8.31	3.24	8.95	32.96	155-155.5
$(3\text{-pic})_2BH_2^+PF_6^-$	Found	41.96	4.77	8.20	3.03	8.93	33.05 q	94.5-95
$(4\text{-pic})_2BH_2^+PF_6^-$	Found	41.80	4.80	8.01	3.20	9.20	32.93	132.5-133
$C_{12}H_{16}N_2BAsF_6$	Calcd	37.15	4.12	7.22	2.79	19.32[a]	29.42	
$(4\text{-pic})_2BH_2^+AsF_6$	Found	37.30	4.21	6.98	2.96	19.05[a]	29.16	140-141
$C_{14}H_{20}N_2BPF_6$	Calcd	45.19	5.38	7.53	2.91	8.34	30.66	
$(2,3\text{-lut})_2BH_2^+PF_6^-$	Found	45.37	5.49	7.36	2.89	8.56	30.24	148.5-149.5
$(2,4\text{-lut})_2BH_2^+PF_6^-$	Found	45.16	5.52	7.62	2.75	8.48	30.39	113-114
$(2,5\text{-lut})_2BH_2^+PF_6^-$	Found	45.16	5.46	7.36	2.87	8.40	30.41	147.5-148.5
$(2,6\text{-lut})_2BH_2^+PF_6^-$	Found	45.49	5.47	7.38	2.81	8.28	30.91	133.5-134.5
$(3,4\text{-lut})_2BH_2^+PF_6^-$	Found	45.14	5.53	7.42	3.06	8.46	30.39	133.5-134
$(3,5\text{-lut})_2BH_2^+PF_6^-$	Found	45.12	5.49	7.31	2.76	8.60	30.70	203.5-204

[a] % As.

Syntheses of $(Amine_1)(Amine_2)BH_2^+$

The present section deals with syntheses of singly charged boron cations having two different tertiary amines coordinated to BH_2^+ group. The synthesis in general is accomplished by nucleophilic displacement of iodide from amine-monoiodoboranes by various tertiary amines.



$$A_1BH_2I + A_2 \rightarrow (A_1)(A_2)BH_2^+I^-$$

$A_1$and A_2 are different tertiary amines.

A_1BH_2I used in these syntheses are trimethylamine-monoiodoborane, triethylamine-monoiodoborane, and pyridine-monoiodoborane, whereas tertiary amines used as nucleophiles include various substituted pyridines, triethylamine, trimethylamine, dimethylamine and quinoline. In general, synthesis is quite convenient and gives good yields with minimum amounts of impurities or by products.

Reactions were done either at room temperature or at 65-70°. The general procedure and its variations is illustrated in the following sections.

1. Synthesis of boron cations from trimethylamine-borane.-- Trimethylamine-monoiodoborane was prepared as previously described and was allowed to react without isolation with various tertiary amines at room temperature to prepare the respective unsymmetrical boron cations. The synthesis is typified by the preparation of $(C_5H_5N)(CH_3)_3NBH_2^+I$, the iodide salt of (pyridine)(trimethylamine) boron cation.

Trimethylamine-borane, 2.198 g (30.2 mmoles) was dissolved in 35 ml of dry benzene in a 125 ml conical flask. Solid iodine, 3.488 g (13.7 mmoles),was added in small portions while the solution was stirred and the flask was loosely stoppered between additions of iodine to avoid the loss of hydrogen iodide. The reaction was vigorous. After the additions of iodine, the solution was kept stirred for about 10 minutes and 2.24 g (28.4 mmoles) of pyridine was added. A white precipitate gradually formed. The reaction mixture was kept stirred for about 5 hours at room temperature. During this time more precipitate was formed. It was then diluted with 40 ml of benzene, stirred for 10-15 minutes, 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).

The reactions may be represented as

$$2(CH_3)_3NBH_3 + I_2 \rightarrow 2(CH_3)_3NBH_2I + H_2$$

$$2(CH_3)_3NBH_2I + 2C_5H_5N \rightarrow 2(C_5H_5N)(CH_3)_3NBH_2{}^+I^-$$

Boron cations, where a $(CH_3)_3NBH_2{}^+$ group was attached to a number of substituted pyridines, were prepared at room temperature by a similar method starting from trimethylamine-monoiodoborane. Pyridines had the following substituents: 4-methyl, 3,4-dimethyl, 4-methoxy, 2-methoxy, 4-phenyl, 4-benzoyl, 4-benzyl, 4-acetyl, 3-cyano- 5-methyl, 3-boromo, and 3-iodo. The precipitation time was about 5 hours. In the synthesis of the quinoline derivative 24 hours were allowed for precipitation.

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 hours at 60-70° in an oil bath.

In all instances, a little more than 2 moles of trimethylamine-borane was used (as starting material) per mole of iodine and the amount of amine used as starting material was up to 15% in excess over the

TABLE IV

YIELDS OF $(AMINE_1)(AMINE_2)$BORONIUM SALTS

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-Methoxypridine	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

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[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°.

calculated amount of iodoborane. The yields of the boronium iodide salts, based on the weight of dry product and the amount of iodine used, are given in Table IV.

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

Actual amounts of reactants, solvents etc.,taken in this experiment are given in the following Table.

TABLE V

COMPARATIVE YIELDS OF $(TMA)(PY)BH_2^+$ AND $(TMA)(4\text{-}CYPY)BH_2^+$ SALTS

Reactants, solvents and conditions	$(TMA)^a(4\text{-}Cypy)BH_2^+I^-$	$(TMA)^a(Py)BH_2^+I^-$
TMA BH_3	2.195 g (30.2 mmoles)	2.195 g (30.2 mmoles)
I_2	3.488 g (13.7 mmoles)	3.488 g (13.7 mmoles)
Amine	2.984 g (28.7 mmoles of 4-cyanopyridine)	2.266 g (28.7 mmoles of pyridine)
Time for precipitation	1 hour	1 hour
Benzene for dilution	30 ml	30 ml
Benzene for washing ppt.	50 ml	50 ml
Ether for washing ppt.	15 ml	15 ml
Time for drying	5 hours	5 hours
Amount of iodide salt obtained	1.333 g (16%)	4.375 g (57%)
Amount of iodide converted to > $BH_2^+PF_6^-$	1.265 g	3.525 g
% of conversion of $BH_2^+I^-$ to $BH_2^+ PF_6^-$	92	91

a = trimethylamine

Attempted synthesis of triethylamine-trimethylamine cation from trimethylamine-borane.--(a) A reaction mixture prepared from 27.5 mmoles of trimethylamine-borane and 13.7 mmoles of iodine in 35 ml of dry benzene was stirred for 15 hours at room temperature in a stoppered flask with 49.0 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. The expected reaction should have produced 8.210 g of iodide salt. Its nmr spectrum in CH_2Cl_2 showed only one absorption, a sharp singlet at 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 hours. There was isolated 5.401 g of benzene insoluble crystalline material, which was converted to hexafluorophosphate as described above. This product melted at 110-120° and had a complex nmr spectrum in CH_2Cl_2: a triplet (1:2:1, δ = 4.12 ppm, J = 7 Hz), a singlet (δ = 2.50 ppm), and a quartet (1:3:3:1, J = 7 Hz), centered at δ 2.30 ppm, 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)boron cation and the (triethylamine)(trimethylamine)boron 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)boron cation to 53 mole %.

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 pyridine-borane proceeded more vigorously, and the precipitation of the cation was very rapid in all instances and was noticeably exothermic.

For example, (pyridine)(2,4,6-collidine)boronium iodide was prepared from 2.305 g (25.1 mmoles) of pyridine-borane, 2.740 g (10.8 mmoles) of iodine, and 2.763 g (22.8 mmoles) of collidine. After iodination, the reaction mixture was stirred for 15 minutes, collidine was added, and the mixture was stirred for 4 hours. The precipitate was filtered out, washed with benzene and dried. It weighed 6.800 g (93% yield). The entire iodide was converted to boronium hexafluorophosphate, and the yield of conversion was 81%.

By a similar procedure, boron cations, where $C_5H_5NBH_2^+$ coordinated with 4-picoline, 2-methoxy pyridine and triethylamine, were prepared at room temperature. Their yields are given in Table IV.

Synthesis of boron cations from triethylamine-borane.--Triethylamine-monoidoborane was prepared from 3.151 g (27.5 mmoles) of triethylamine-borane, dissolved in 35 ml of dry benzene, and 3.119 g (12.3 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

(33.0 mmoles) of pyridine, the reaction mixture was kept stirred for 5 hours 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-monoiodoborane and triethylamine.

Preparations of (triethylamine)(trimethylamine)boronium salt from triethylamine-iodoborane.--A solution of triethylamine-monoiodoborane was prepared from 1.201 g (10.5 mmoles) of triethylamine-borane dissolved in 35 ml of benzene and 1.116 g (4.4 mmoles) of iodine. The solution was light-reddish colored. Gaseous trimethylamine was passed through this solution. Within 5 minutes a white precipitate appeared and the color of the solution was discharged. The gas was passed for 1 hour; thereafter the precipitate was filtered, washed and dried; 1.658 g of dry product was obtained, which contained as impurity of 25% trimethylammonium iodide, as indicated by an additional singlet absorption in the nmr spectrum. Precipitation of NH_4PF_6 gave the hexafluorophosphate salt free of ammonium ion. The over-all yield was 66%.

Synthesis of bis-amine boron cations by transamination.--(Pyridine)(trimethylamine)boronium iodide, 1.779 g, was heated with 4.079 g of pyridine at 100-110° for 4 hours. 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 saturated NH_4PF_6. After washing with 10 ml of water and 15 ml of ether, 1.667 g (83%) $(C_5H_5N)_2BH_2PF_6$ was obtained. The hexafluorophosphate salt was identical to that reported in the literature.(4)

In similar experiments, the iodide salts of the cations derived from trimethylamine and 4-picoline, or from trimethylamine

TABLE VI

ANALYSES OF $(\mathrm{AMINE}_1)(\mathrm{AMINE}_2)$BORONIUM SALTS

Compounds		%C	%H	%N	%B	%X	Mp, °C^b
$\mathrm{TMABH_2(py)^+PF_6^-}$	Calcd	32.45	5.41	9.46	3.65		
	Found	32.57	5.60	9.25	3.48		94.5-95
$\mathrm{TMABH_2(py)^+AsF_6^-}$	Calcd	28.49	4.90	8.07	3.29		
	Found	28.26	4.74	8.24	3.18		85-85.5
$\mathrm{TMABH_2(4\text{-}CH_3py)^+PF_6^-}$	Calcd	34.83	5.81	9.03	3.48		
	Found	34.92	5.96	8.92	3.39		147-148
$\mathrm{TMABH_2[3,4\text{-}(CH_3)_2py]^+PF_6^-}$	Calcd	37.06	6.18	8.65	3.34		
	Found	37.26	6.19	8.80	3.53		81-82.5
$\mathrm{TMABH_2NC_9H_7{}^+PF_6^-}$	Calcd	41.65	5.21	8.01	3.12		
	Found	41.72	5.36	8.24	3.31		98.5-99.5
$\mathrm{TMABH_2(3\text{-}Brpy)^+PF_6^-}$	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
$\mathrm{TMABH_2(3\text{-}Ipy)^+PF_6^-}$	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
$\mathrm{TMABH_2(3\text{-}Clpy)^+PF_6^-}$	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
$\mathrm{TMABH_2(2\text{-}Fpy)^+PF_6^-}$	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
$\mathrm{TMABH_2(2\text{-}Clpy)^+PF_6^-}$	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
$\mathrm{TMABH_2(4\text{-}CNpy)^+PF_6^-}$	Calcd	33.67	4.68	13.09	3.36		
	Found	33.84	4.84	13.24	3.11		135-137.5

TABLE VI (continued)

Compounds		%C	%H	%N	%B	%X	Mp, °C^b
$TMABH_2(3\text{-}CH_3\text{-}5\text{-}CNpy)^+PF_6^-$	Calcd	35.82	5.07	12.54	3.22		
	Found	35.35	5.01	12.20	3.03		113.5-114.5
$TMABH_2(4\text{-}C_6H_5py)^+PF_6^-$	Calcd	45.16	5.38	7.53	2.90		
	Found	44.98	5.26	7.45	2.79		139.5-140.5
$TMABH_2(4\text{-}C_6H_5CH_2py)^+PF_6^-$	Calcd	46.63	5.69	7.25	2.79		
	Found	46.79	5.66	7.23	2.64		113-114.5
$TMABH_2(4\text{-}C_6H_5COpy)^+PF_6^-$	Calcd	45.02	5.00	7.00	2.70		
	Found	44.99	5.09	6.84	2.86		163-165
$TMABH_2(4\text{-}CH_3COpy)^+PF_6^-$	Calcd	35.53	5.33	8.29	3.19		
	Found	35.00	5.24	8.21	3.02		147-148
$TMABH_2(4\text{-}CH_3Opy)^+PF_6^-$	Calcd	33.13	5.52	8.59	3.31		
	Found	33.64	5.56	8.54	3.06		111-112
$TMABH_2[2,4,6\text{-}(CH_3)_3py]^+PF_6^-$	Calcd	39.05	6.51	8.23	3.20		
	Found	38.38	6.59	8.09	3.27		104-105
$TMABH_2(2\text{-}CH_3Opy)^+PF_6^-$	Calcd	33.13	5.52	8.59	3.31		
	Found	33.64	5.44	8.64	3.08		134.5-135.5
$TMABH_2(N,N\text{-dimethylaniline})^+PF_6^-$	Calcd	39.07	6.51	8.28	3.20		
	Found	39.07	6.64	8.24	3.37		106.5-107.5
$TMABH_2ITEA)^+PF_6^-$	Calcd	33.98	8.18	8.18			
	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

TABLE VI (continued)

Compounds		%C	%H	%N	%B	%X	Mp, °C[b]
$pyBH_2[2,4,6-(CH_3)_3py]^+PF_6^-$	Calcd	43.58	5.03	7.82	3.02		
	Found	43.51	5.13	7.74	3.09		119.5-120.5
$pyBH_2(4-CH_3py)^+PF_6^-$	Calcd	40.00	4.24	8.48	3.27		
	Found	39.80	4.20	8.24	4.49		67-68
$pyBH_2-(2-CH_3Opy)^+PF_6^-$	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; NC_9H_7 = quinoline; py = pyridine. [b] Uncorrected.

and 4-benzoylpyridine, were refluxed with 4-picoline. Both salts gave bis(4-picoline)boronium iodide in 78% and 82% yields, respectively, based on the weight of recovered product. The derived hexafluorophosphate salts were identical in melting and infrared spectrum to an authentic sample.

Derivatives.--The water soluble iodide salts were readily converted to insoluble salts of PF_6^-, AsF_6^-, Br_3^-, complex iodomercurates 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.

(Pyridine)(trimethylamine)boronium iodide, 2.435 g, was dissolved in 5 ml of water and 3.5 ml 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 IV.

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

Synthesis of Boron Cations, (Amine)(Phosphine)BH_2^+

Boron cations with ligands coordinated to a BH_2^+ group through two different group V elements, namely nitrogen and phosphorus, were prepared by the same general method used for the syntheses of amine-coordinated cations. Amine-borane was iodinated to prepare monoiodoborane and then it was allowed to react with phosphines to get the unsymmetrical dihydroboron cations. Reactions were carried out either at room temperature or in refluxing benzene.

Synthesis of (dimethylamine)(triphenylphosphine)boronium iodide.--Dimethylamine-borane, 1.060 g (18.0 mmoles), was iodinated in 50 ml of dry benzene by adding 2.160 g (8.5 mmoles) of solid iodine during a period of 10 minutes. The solution was stirred for about 10 minutes after iodination and the solution was colorless. Triphenylphosphine, 4.595 g (17.5 mmoles), was added and a pale yellow color was developed. No immediate precipitation was observed, but during the next 3 hours a good amount of white precipitate was formed. The reaction mixture was kept stirred at room temperature for about 22 hours and then it was filtered. The precipitate was washed with 50 ml of benzene, dried and weighed 6.707 g (88% yield).

The crude iodide salt shrank at 100°, softened at 110° and melted at 117-123° with decomposition. The ir and nmr spectra of the boronium salt showed the absorptions characteristic to $(CH_3)_2NH_2^+$ ion as an impurity. A sample of the crude iodide was twice recrystallized from methylene chloride-ether mixture, but still the impurity was not removed completely as indicated by ir and nmr spectra. So 1.004 g of the crude iodide was stirred with 30 ml of 0.3N hydrochloric acid solution for about 1 minute, rapidly filtered and washed with 10 ml of 0.2N hydrochloric acid solution and 30 ml of ether. The precipitate was then dissolved in minimum amount of methylene chloride and reprecipitated by adding excess ether (approximately 100 ml ether), filtered, dried and weighed 0.760 g. The ir and nmr spectra still showed the presence of very small impurity. It melted at 136.5-138° with decomposition to an orange-red liquid. Analysis calculated for iodide salt: C, 53.69%; H, 5.37%; N, 3.13%; Found: C, 53.54%; H, 5.10%; N, 3.06%.

The ir and nmr spectra of the hexafluorophosphate salt prepared from an acidified aqueous solution of the iodide showed that the compound was free of impurities.

Synthesis of (trimethylamine)(1,2-bis(diphenylphosphino)ethane) boronium salts.--The molar ratio of trimethylamine-monoiodoborane and diphosphine used in this synthesis was 2:1 to get a dication having two BH_2^+ groups in the molecule.

$$2\ (CH_3)_3NBH_2I + (Ph)_2P\text{-}CH_2\text{-}CH_2\text{-}P(Ph)_2 \rightarrow$$
$$(CH_3)_3NBH_2^+\text{-}P(Ph)_2\text{-}CH_2\text{-}CH_2\text{-}(Ph)_2P\text{-}BH_2^+N(CH_3)_2\ 2I^-$$

Trimethylamine-borane, 0.561 g (7.7 mmoles), dissolved in 25 ml of dry benzene was iodinated, as described in previous experiments, using 0.869 g (3.4 mmoles) iodine. 1,2-bis(diphenylphosphino)ethane, 1.372 g (3.5 mmoles), was added to the iodoborane adduct and kept stirred for 4.5 hours at room temperature. On addition of phosphine, there was an immediate color change from pale yellow to colorless, but precipitation was very slow during a period of 4.5 hours. The reaction mixture was then heated in an oil bath at 60° for 17 hours. The resulting precipitate was filtered off, washed with 40 ml of benzene, and dried; it weighed 2.102 g (77% yield).

The iodide salt was sparingly soluble in water like other phosphine-containing boronium salts. A sample of iodide salt, 0.410 g, was dissolved in 110 ml of water and the hexafluorophosphate was precipitated by adding excess NH_4PF_6 salt solution. The hexafluorophosphate salt isolated weighed 0.357 g (83% recovery, mp. 149.5-152 dec.). The product was dissolved in methylene-chloride and reprecipitated by adding excess ether. The pure hexafluorophosphate salt melted at 157-158° with decomposition.

Analysis calculated for PF_6^- salt: C, 46.15%; H, 5.53%; N, 3.37%; Found: C, 46.09%; H, 5.58%; N, 3.35%.

Synthesis of (pyridine)(triphenylphosphine)boronium salts.--Salts containing this ion were prepared by the reaction between pyridine-monoiodoborane and triphenylphosphine. Pyridine-borane, 1.200 g (12.9 mmoles), dissolved in 40 ml of benzene was iodinated by 1.381 g (5.4 mmoles) of iodine. When 2.901 g (11.1 mmoles) of phosphine was added, precipitation was immediate with some evolution of heat. Benzene, 40 ml, was added to make the reaction mixture less viscous, and the mixture was stirred for 7.5 hours at room temperature. Before filtration it was further diluted with 20 ml of benzene. The precipitate was washed with 100 ml of benzene and dried; it weighed 5.736* g. The expected yield was 5.229 g.

A sample of the iodide salt was converted to PF_6^- salt, and recrystallized in acetone-water mixture. mp. 128-129°; Analysis calculated for PF_6^- salt: C, 55.31%; H, 4.41%; N, 2.81%; Found: C, 55.57%; H, 4.53%; N, 2.71%.

Synthesis of (trimethylamine)(triphenylphosphine)boronium salts.--Compounds of this type were prepared by the reaction between triphenylphosphine and trimethylamine-monoiodoborane. The reaction proceeded very slowly at room temperature. Even though heating improved the yield, the total yield was not very high.

In one experiment, 1.218 g (16.7 mmoles) of trimethylamine-borane in 30 ml of benzene was iodinated by 1.740 g (6.9 mmoles) of iodine and 3.737 g (14.3 mmoles) of phosphine was added to the iodoborane. Within 5 minutes the color of the solution was discharged. No immediate

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*The nmr spectrum showed that the iodide salt contained some benzene which could not be removed by vacuum pumping for 24 hours.

precipitation was observed. The reaction flask was kept closed while the reaction mixture was being stirred for 16 hours at room temperature. The iodide salt isolated by filtration weighed 0.920 g. The filtrate was heated in an oil bath at 70° for 3 hours. By filtration, 0.965 g of precipitate was isolated and thus a total of 1.885 g of boronium iodide was obtained from this experiment. The expected yield was 6.316 g.

A sample of iodide salt was converted to hexafluorophosphate salt, recrystallized and analyzed. Analysis calculated for PF_6^-: C, 52.61%; H, 5.43%; N, 2.92%; Found: C, 52.61%; H, 5.31%; N, 2.87%. mp. 163.5-165° dec.

In another experiment, 0.571 (7.8 mmoles) of trimethylamine-borane in 35 ml of benzene was iodinated by 0.872 g (3.4 mmoles) of iodine. Triphenylphosphine, 1.917 g (7.3 mmoles), was added and the reaction mixture was stirred at room temperature for about 5 hours. There was only slight precipitation. On heating in an oil bath at 65° for 16 hours more precipitate was formed. The temperature was then raised to 83° and heating was continued for 24 hours. Boronium iodide isolated was 0.827 g. The expected yield was 3.165 g.

Attempt to prepare (trimethylamine)(triphenylamine)boron cation.-- Trimethylamine-iodoborane, resulting from iodination of borane adduct, 0.571 g (7.8 mmoles), in 35 ml of benzene with 0.872 g (3.4 mmoles) of iodine, was treated with 1.792 g (7.3) mmoles of triphenylamine. It took 20 minutes to discharge the color of the iodoborane adduct after the addition of triphenylamine. After 24 hours heating in an oil bath at 83°, 0.151 g of precipitate was isolated. Their spectrum of the solid was identical with the spectrum of the trimethylammonium iodide salt. There was no characteristic doublet of BH_2^+ in the region 2500 cm^{-1}.

This small amount of ammonium salt might have been formed by incidental hydrolysis of iodoborane adduct even though the reaction flask was kept closed during heating. The theoretical yield of the expected iodide salt was 3.049 g. The filtrate, on further refluxing for about 20 hours, yielded 0.186 g of a solid which had an ir spectrum identical to that of trimethylammonium salt. Thus this reaction did not give any boron cation.

Synthesis of (4-picoline)(triphenylphosphine)boronium salts.-- 4-picoline-borane, 0.630 g (5.90 mmoles) 40 ml of benzene was iodinated by 0.597 g (2.35 mmoles) of iodine. When 1.279 g (4.88 mmoles) of triphenylphosphine was added to the iodoborane adduct, there was an immediate precipitation. The precipitate had a slight orange-yellow color. After stirring the reaction mixture for about 7 hours, the mixture was filtered. The washed and dried precipitate weighed 2.131 g.

Due to the poor solubility of the boronium iodide in water a PF_6^- salt could not be prepared. A sample of the boronium iodide was washed with acidified water and some ether; it was then dissolved in methylene chloride and reprecipitated by adding excess ether. The nmr spectrum confirmed the presence of the expected boron cation but the spectrum did show some extra peaks. When the compound was dissolved in methylene chloride the solution was clear immediately after mixing. On standing slow evolution of a gas was, however, observed with precipitation of a solid. The ir spectrum showed a distinct doublet near 2500 cm^{-1}, which is the characteristic stretching frequency of BH_2^+ group, a strong peak near 1635 cm^{-1} for the coordinated pyridine ring, a medium peak near 1165 cm^{-1} for BH_2^+ deformation, a medium peak near 1125 cm^{-1} for B-N stretch, a sharp, strong peak near 1110 cm^{-1} for tetra-coordinated phenyl-substituted phosphine, and other known absorptions belonging to the ligands. The ir spectrum showed no characteristic absorption near 2700 cm^{-1} for the N-H stretch of the picolinium salt. The compound was not analyzed, but the spectral evidence strongly supports the presence of the expected boronium salt in the reaction product.

Syntheses of Borane Adducts

Synthesis of Amine and Phosphine Boranes

A new, rapid and high-yield synthesis of borane adducts with amines and tertiary phosphines will be described in this section. It is based on the reaction of sodium borohydride and iodide in the presence of a donor. The procedure is applicable to the syntheses of borane adducts of ammonia, primary, secondary and tertiary amines, di-and triammines, pyridines, and phenyl-substituted phosphines.

General procedure of synthesis.--The apparatus consists of a nitrogen-flushed 250 ml two-necked flask fitted with a pressure-compensated-dropping funnel and an outlet tube leading to a bubbler containing a benzene-amine mixture (see Figure I). In a typical experiment a stoichiometric quantity of iodine in 1,2-dimethoxyethane (monoglyme) was added dropwise to a stirred mixture of sodium borohydride (15-20% excess) and the amine (7-10% excess) with monoglyme. Quantities were calculated on the basis of the equation:

$$2\ NaBH_4 + 2\ R_3N + I_2 \rightarrow 2\ NaI + 2\ R_3NBH_3 + H_2$$

R_3N = amine

The general work-up of this preparative method is exemplified by the synthesis of 2-picoline-borane.

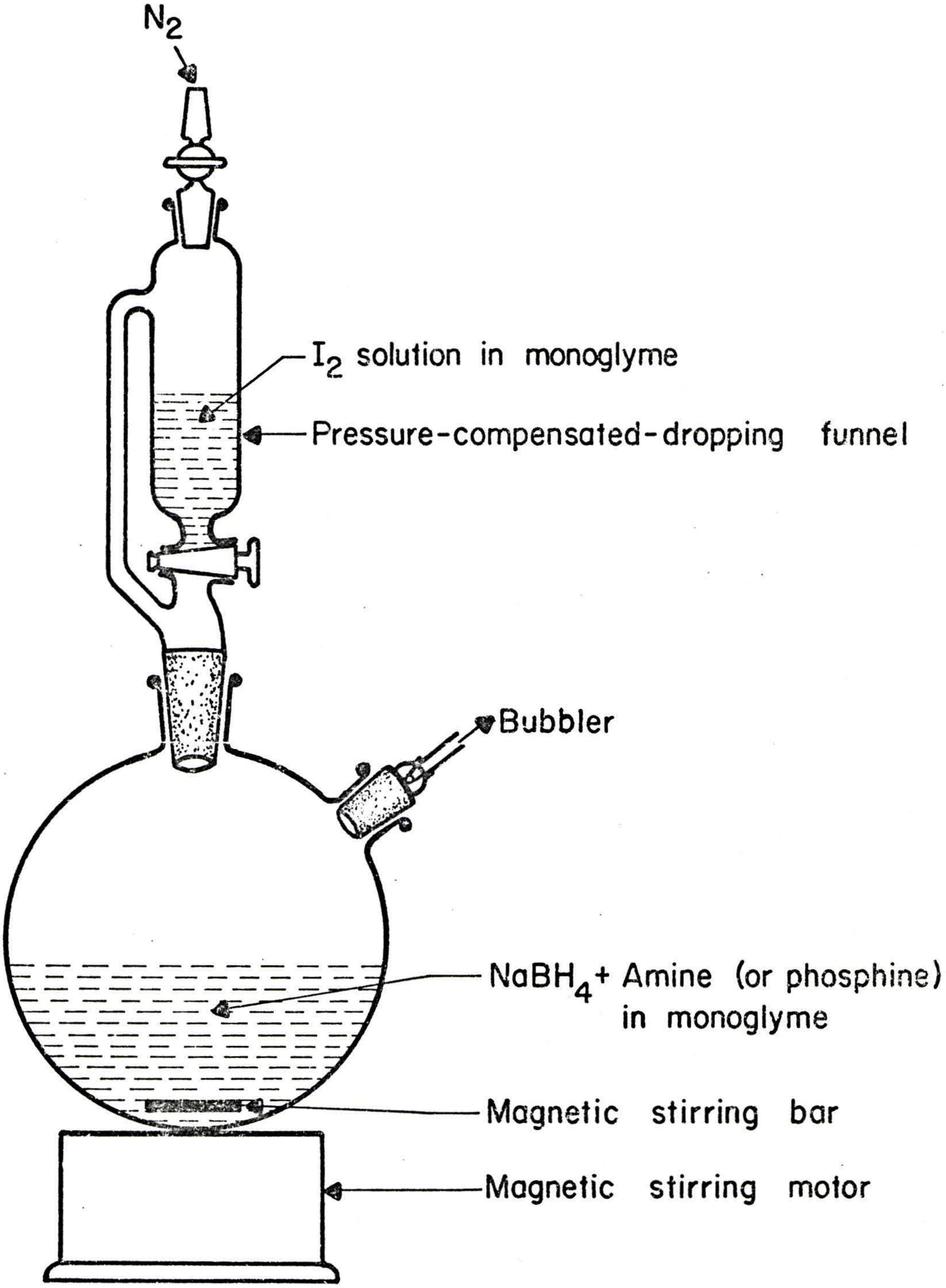

Figure I, Apparatus for the syntheses of borane adducts and polyhedral boranes.

Synthesis of 2-picoline-borane.--To sodium borohydride, 1.390 g (36.8 mmoles) and 3.000 g (32.3 mmoles) of 2-picoline in 40 ml of dry monoglyme, iodine, 3.855 g (15.2 mmoles) in 35 ml of monoglyme were added dropwise over a period of about three hours. The reaction mixture was kept stirred throughout the experiment, while the hydrogen gas was escaping through the bubbler. About 5 ml of monoglyme was used to wash down the sides of the funnel at the end of the reaction. The solvent was then removed by pumping and the resulting solids were extracted with 130 ml of dry benzene to separate the soluble amine-borane from sodium iodide and unreacted sodium borohydride. The insoluble solid (NaI and $NaBH_4$) was dried and weighed 4.700 g (expected from stoichiometry: 4.800 g). An acidified aqueous solution of the solid did not give a precipitate with excess ammonium hexafluorophosphate. The infrared spectrum of the solid did not show any characteristic absorptions for amine derivatives and the proton nmr was blank. Thus no bis-amine boron cation was present.

The filtrate, evaporated to dryness, weighed 3.056 g (94% yield), mp 44-45.5° (lit. 46-48°; Table VII). The H^1 and B^{11} nmr and infrared spectra were identical with an authentic sample prepared from diborane. Shortening the period of iodine addition to 20 minutes under otherwise identical conditions did not change the yield.

A portion of the product (1.121 g), dissolved in 50 ml of benzene, was precipitated with 20 ml of hexane. The recovered material (0.759 g, 68%) melted at 45-46.5°.

Synthesis of ammonia-borane.--The apparatus and general work-up of the preparation of NH_3BH_3 were similar to those of 2-picoline borane. Ammonia, 0.350 g, was passed into 50 ml of monoglyme and 1.143 g (30.2

mmoles) of sodium borohydride was added to it. Iodine, 2.538 g (10.0 mmoles) dissolved in 40 ml of monoglyme was added dropwise over a period of about 45 minutes. After reaction, the solvent was pumped off and 150 ml of anhydrous diethyl ether (dried over calcium hydride for several days) was added to extract the ammonia-borane. The filtrate, evaporated to dryness, weighed 0.450 g (73% yield). The properties and infrared spectrum of the white crystalline residue were identical to that reported in literature.(43,44)

Calculated hydridic hydrogen, 9.79%; Found, 9.62.(45)

The infrared spectrum of the ether-insoluble residue indicates absorptions of unreacted borohydride overlapped by absorptions of diamminedihydriodoboron(1^+) cation. The cation might have been formed by decomposition of ammonia-borane at room temperature.

Synthesis of the other amine-boranes was accomplished as with 2-picoline borane. Pentamethyldiethylenetriamine tris(borane) was obtained as the insoluble residue when the solids remaining after evaporation of the monoglyme were extracted with water. The borane adduct of 2,2'-dipyridyl was only slightly soluble in benzene. A preparation from 3.095 g (19.3 mmoles) amine and a slight excess I_2 gave 0.568 g benzene-soluble extract, mostly unreacted amine, and after water extraction, 2.441 g (13.2 mmoles, 68%) of the 1:2 adduct.

The yields of boranes and the melting points of the crude and recrystallized products are given in Table VII. Analytical data for new compounds are listed in Table VIII. Analyses were performed by Peninsular ChemResearch, Inc., Gainesville, Florida.

<u>Synthesis of triphenylphosphine-borane</u>.--To triphenylphosphine, 9.157 g (35.0 mmoles) and sodium borohydride, 1.569 g (41.5 mmoles) in 40 ml of monoglyme, iodine, 4.296 g (16.9 mmoles) in 40 ml of glyme was

added dropwise over about 3 hours. After the solvent was evaporated, triphenylphosphine-borane was extracted with 200 ml of benzene; on evaporation 7.750 g of borane was obtained (83%, mp. 182-186°). A second extraction with 200 ml of methylene chloride yielded an additional 1.231 g of borane (mp. 183-186°). The total yield of triphenylphosphine-borane was about 96%.

A portion of the crude product (1.812 g) was treated with 35 ml of dry hexane and filtered. The hexane insoluble portion, dissolved in 70 ml of benzene ,was precipitated with 80 ml of hexane (recovery 66%, mp. 189°). Analyses for new phosphorus-containing boranes are given in Table VIII.

TABLE VII

YIELDS AND MELTING POINTS OF AMINE-AND PHOSPHINE-BORANES

Compounds	Yield of Borane %[h]	Mp. C° of Crude Product	Mp. C° of Recrystallized Product	Lit. Mp. C°
Ammonia-borane	73			
2-Picoline-borane	94	44-45.5	45-46.5	46-48[a]; 40[b]
4-Picoline-borane	80	64-67	72-73	72-73[b]
2,4,6-Collidine-borane	91	96-97	98-100	99.2-100.3[a]
2-Methoxy pyridine-borane	81	63-66	69-70	
Di-n-propylamine-borane	88	28-29	28.5-29.5	30[c]
Dimethylamine-borane	62	33-34.5	35	36[d]
Isopropylamine-borane	84	60-61.5	61.5-62.5	65[c]
TMED.2BH$_3$	81	177-182.5	181-183	182.5-184[e]
PMDET.3BH$_3$	91	170-175 dec.	182-188.5	185-186[f]
2,2'-Dipyridyl bis(borane)	67	*	*	
Triphenylphosphine-borane	96	183-186	189	189[g]
Bis(diphenylphosphino)methane bis(borane)	87	185-186.5 dec.	186.5-188 dec.	
1,2-Bis(Diphenylphosphino)ethane bis(borane)	97	159.5-167.5 dec.	162-167.5 dec.	

TMED = tetramethylethylene diamine; PMDET = pentamethyldiethylenetriamine; [a]. E. R. Birnbaum, Doctoral Dissertation, University of Florida 1961; [b]. J. A. Bigot, Th. J. deBoar and F. L. J. Sixma, Rec. Trav. Chim., 76, 996 (1957); [c]. H. Noth and H. Beyer, Chem. Ber., 93, 928 (1960); [d]. D. R. Alton, R. D. Brown, J. C. Carter and R. C. Taylor, J. Am. Chem. Soc., 81, 3550 (1953); [e]. N. E. Miller and E. L. Muetterties, ibid., 86, 1033 (1964); [f]. F. E. Walker and R. K. Pearson, J. Inorg. Nucl. Chem., 27, 1981 (1965); [g]. M. A. Frisch, H. G. Heal, H. Mackle and I. O. Madden, J. Chem. Soc. (London), 899 (1965); [h]. based on iodine; * white crystalline compound turns light brown at 129-131°C, becomes dark brown on continuous heating, and does not melt even at 300°C.

TABLE VIII

ANALYSES OF NEW BORANE ADDUCTS

Compounds		%C	%H	%N
2-CH_3O Py · BH_3	Calcd	58.63	8.14	11.40
	Found	58.61	8.05	11.38
$C_{10}H_8N_2$ · 2 BH_3	Calcd	65.26	7.67	15.23
	Found	65.11	7.54	15.02
$(C_6H_5)_2P-CH_2-CH_2-P(C_6H_5)$ · 2 BH_3	Calcd	73.23	7.09	-
	Found	72.97	7.20	-
$(C_6H_5)_2P-CH_2-P(C_6H_5)_2$ · 2 BH_3	Calcd	72.88	6.80	-
	Found	72.70	6.68	-

Py = Pyridine; $C_{10}H_8N_2$ = 2,2' Dipyridyl.

CHAPTER IV

PHYSICAL, CHEMICAL AND SPECTRAL PROPERTIES OF BORANE ADDUCTS AND BORON CATIONS

Physical and Chemical Properties

The borane adducts of various amines and phosphines prepared in this study are white and crystalline solids. In general, they all have some solubility in methylene chloride, benzene, nitromethane, chloroform and monoglyme. Poly-borane adducts are less soluble than mono-adducts in the same solvent.

The boronium iodides prepared are soluble in water, chloroform, acetone and methylene chloride, but insoluble in carbon tetrachloride, benzene and diethyl ether. Bis(3,5-lutidine)boronium iodide and (amine)(phosphine)boronium iodides are less soluble in water than other iodides. The iodide salts tend to absorb moisture. Many of the boronium iodides in the solid state are nearly white, while there are some iodides which have distinct colors, ranging from light yellow to orange-red.

Absorption in the visible region appears only if a pyridine ring is present and shifts to longer wave lengths 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 orange-red in methylene chloride, but the color fades to yellow on addition of ethanol; very 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 suggests that charge-transfer transitions occur from iodide ion to the pyridine ring, as has been observed in N-alkylpyridinium iodides.(46,47) Charge transfer may be responsible for the origin of color and the observed spectral changes. Muetterties(16) observed that bis(tropolono)boronium hexafluorophosphate and chloride salts are colorless, while the bromide is pale yellow and the iodide is orange-red. He also suggested that the origin of color in this case is due to charge-transfer from the anion to the chelate cation.

Electron withdrawing substituents in pyridine increases 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. Pronounced charge-transfer phenomenon may be the reason for the distinct color of boronium iodide salts derived from 4-cyano or 4-acetylpyridine,while 4-picoline or pyridine boronium iodides do not have pronounced colors. 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.*

Derivative Chemistry of Boronium Salts

The boron cations form sparingly water-soluble salts with large anions such as PF_6^-, AsF_6^-, $B(C_6H_5)_4^-$, $B_{12}H_{12}^{-2}$, Br_3^-, complex iodomercurates HgI_3^- or HgI_4^{-2}. By metathetical reaction, boronium iodides

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*Research on the problem of charge-transfer complexes of boronium iodides is currently in progress in this laboratory.

could be converted to these less soluble derivatives, and the general details of conversion of boronium iodides to hexafluorophosphates were already given in the last chapter. The high yields of boronium hexafluorophosphates obtained from boronium iodides by metathetical reaction (Tables II and IV) show that the iodides are substantially pure; in fact, the losses can be accounted for by the slight solubility of the boronium hexafluorophosphates in water, which is of the order of 0.01 M at room temperature but substantially larger near the boiling point.

Boronium hexafluorophosphates are white solids which can be readily crystallized from methylene chloride-ether mixture, acetone-water mixture or from hot aqueous solutions. It would be safer to use non-aqueous medium to recrystallize the salts containing phosphine as one of the ligands on boron cations, because they do have a tendency to decompose in aqueous medium.

The hexafluorophosphate and hexafluoroarsenate salts are particularly useful for the separation of boronium ions from ammonium salts which may be present as impurities in the iodides synthesized by the various methods given in the last chapter. Tetraphenylborate ion precipitates both boron cations and ammonium salts and, therefore, its use is limited as far as the separation is concerned. The water-insoluble boronium tribromide can be converted to water-soluble bromide by treating with $Na_2S_2O_5$ solution.(15) The iodomercurates can be decomposed to a soluble salt by concentrated nitric acid.

Thermal Stability of Boronium Salts

The hexafluorophosphate salts are indefinitely stable at room temperature in the solid state. (Trimethylamine)(N, N' dimethylaniline) boronium hexafluorophosphate, which was originally white, slowly developed a violet color during one year's time. A number of boronium iodide salts 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 $[(CH_3)_3N]_2BH_2^+Cl^-$ at high temperature reported by Muetterties,[3,16] or whether decomposition is caused by the presence of water in the hydroscopic salts, is not certain. Boronium iodides with phosphine ligands, on standing at room temperature, slowly change their color from white to yellow.

Hydrolytic Stability

The symmetrical and unsymmetrical boronium salts with amines as the ligands 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 reported(3,16) that $[(CH_3)_3N]_2BH_2^+$ on heating with 10% sodium hydroxide or hydrochloric acid at 100°C for long periods of time, did not show a noticeable reaction. The following experiment demonstrates that the replacement of one trimethylamine by 4-picoline decreases the stability of the cation to hydrolysis.

One milliliter of freshly prepared 0.94 M aqueous (trimethylamine)(4-picoline)boronium iodide was diluted with 1 ml of water, or with 1 M HCl or 1 M HaOH 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 hours. On heating at 100° slow gas evolution was observed and there appeared new sets of absorptions which were identical to 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 the aromatic region of the proton spectra was used for the neutral and basic solutions. In all solutions the sum of the free and coordinated 4-picoline absorptions remained constant. In basic solution some trimethylamine was lost. The percentages of decomposition are given in Table IX.

TABLE IX

HYDROLYSIS OF (TRIMETHYLAMINE)(4-PICOLINE)BORONIUM IODIDE

	1 M HCl		H_2O	1 M NaOH	
Dilution ratio	1:1	1:3	1:1	1:1	1:3
8 1/2 hours, 100°	45%	46%	52%	57%	69%
15 1/2 hours, 100°	54%	88%	57%[x]	77%	93%

[x] Difficult to estimate due to broadening and poor resolution

Substitution by a second molecule of 4-picoline gives a further decrease in stability: 85% decomposition occured in 30 minutes 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 may be noted that either steric inhibition of the hydrolysis by the bulky ligand of trimethylamine,(16) or rate enhancement through electronic factors in the pyridine ligand,could account for the observed trend.(14)

Even though no quantitative experiments were done on the hydrolytic stability of boron cations with phosphine as one of the ligands, during the work-up of the syntheses it was observed that they are less stable to hydrolysis than are boronium iodides with amines as the ligands. Similar observations were reported by Muetterties(16) and Kelly.(11) Thus the kind of the ligand site also determines the hydrolytic stability of the boronium salts.

Stability Towards Oxidizing Agents

An aqueous solution of (trimethylamine)(4-picoline)boronium 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 was precipitated by addition of sodium hydroxide. After filtration the solution was acidified with sulphuric acid; the resulting solution was approximately 1M in boron cation. From this solution 1 ml was mixed, respectively, with 2 ml of 1M $Ag\ NO_3$, $Cu\ Cl_2$ or $HgCl_2$, or with 2 ml of 30 per cent H_2O_2, 0.1M $K_2Cr_2O_7$ or 0.1M $KMnO_4$, and kept for 24 hours at room temperature. No change was observed in the nmr spectra of any of these solutions except in the case of potassium permanganate solution. Permanganate ion was rapidly decolorized. 4-picoline also reacted with permanganate ion under similar condition.

Thus the cation was quite inert to a number of oxidizing agents which normally react rapidly in the cold with neutral boranes. Ag^+, Hg^{+2} . Cu^{+2}, $Cr_2O_7^{-2}$ and H_2O_2 failed to react. Permanganate reacted, but not noticeably faster than 4-picolinium ion itself, which is oxidized by permanganate at the methyl group. Moreover, it has been reported,(16) bis-amine cations, $(NR_3)_2BH_2^+$, failed to react with concentrated sulphuric and nitric acids, salts of Au^{+3} ion and 30% hydrogen peroxide.

Transamination

The amine substituent on boron cations can be replaced by other amines under appropriate conditions. Actually, the success of the syntheses of bis(alkylpyridine)boronium iodide from trimethylamine-borane and iodine depends on transamination. The unsymmetrical cation formed as an intermediate is transaminated to bis(alkylpyridine)boronium iodide by displacement of trimethylamine with the appropriate alkylpyridine. The following experiment demonstrates transamination of (trimethylamine)(4-benzoyl pyridine)boronium iodide to bis(4-picoline)boronium iodide by 4-picoline at high temperature.

Boron cation, (trimethylamine)(4-benzoyl pyridine)boronium iodide, 0.788 g (2.06 mmoles), was refluxed in 4-picoline for about 4 hours. It was then diluted with benzene and ether to precipitate the boronium iodide. The salt was filtered, dried and weighed 0.549 g (1.68 mmoles). So the recovery of bis(4-picoline)boronium iodide is about 82%. The iodide salt was characterized by nmr, which was identical to the spectrum of an authentic sample. The reaction may be represented in the following equation:

$$\mathrm{TMABH_2(4\text{-}C_6H_5COPy)^+I^- + 2(4\text{-}CH_3Py)} \overset{\Delta}{\rightarrow}$$
$$\mathrm{TMA + 4\text{-}C_6H_5COPy + (4\text{-}CH_3Py)_2BH_2{}^+I^-}$$

TMA = trimethylamine

In contrast, 4-acetylpyridine, which is a weaker base than 4-picoline, did not react with (trimethylamine)(4-benzoyl pyridine)boronium iodide on refluxing in benzene for about 4 hours. The unsymmetrical boronium iodide, 1.002 g (2.62 mmoles), and 3.626 g (30.22 mmoles) of 4-acetylpyridine were refluxed in 35 ml of dry benzene. After the reaction, the isolated product had the same nmr spectra as those of the starting material.

Thus amine displacement offers a convenient route to prepare bis-amine boronium salts, provided that the displacing amine is sufficiently basic and the proper reaction temperature is maintained.

Spectral Properties of Borane Adducts and Boron Cations

Ultraviolet Spectra

The uv spectra of the bis(amine)boronium hexafluorophosphates were taken in 95 per cent ethyl alcohol with a Cary 14 spectrophotometer. The general procedure is exemplified by the following details for bis(4-picoline) boronium hexafluorophosphate.

A sample of the salt, 21 mg (0.0610 mmoles), was dissolved in a volumetric flask and diluted with alcohol to 25 ml solution, solution #1. From this, 5 ml of the solution was taken and diluted to exactly 50 ml in another flask, solution #2. From solution #2, 10 ml was diluted to 30 ml, solution #3, and another 10 ml portion of solution from solution #2 was diluted to 100 ml, solution #4. The spectra were run on solutions #3 and #4. Their results are given in Table X.

The uv spectra of boronium salts are similar to the spectra of the free amines, a short wavelength band and a central more intense band with a shoulder on either side. In boronium salts the absorptions are shifted to longer wavelengths generally by about 50 A°.

Infrared Spectra of Borane Adducts and Boron Cations

KBr pellets of the compounds were used for infrared spectra. For the liquid amines, spectra were run as a liquid film using sodium chloride plates. All the spectra were obtained on either Beckman IR-10 or Perkin-Elmer 137 instruments. Vibrational assignments were based on IR-10

TABLE X

ULTRAVIOLET SPECTRA OF BIS-AMINE $BH_2^+PF_6^-$ SALTS

Amine	Molar absorptivity x 10^{-3}	Wavelength, Å
2-Picoline	9.44	2625
	10.85	2680
	8.68	2725
3-Picoline	8.77	2660
	9.42	2670
	6.58	2750
4-Picoline	6.15	2509[a]
	7.43	2562
	5.22	2637
2,3-Lutidine	10.38	2692
	11.52	2726
	9.09	2795
2,4-Lutidine	9.13	2630
	9.53	2640
	8.53	2700
2,5-Lutidine	10.54	2723[b]
	11.15	2750
	8.71	2809
2,6-Lutidine	10.54	2683
	9.73	2735[c]
3,4-Lutidine	7.43	2608[b]
	7.62	2626
	5.95	2683
3,5-Lutidine	8.08	2667[b]
	9.20	2715
	6.83	2781

[a] Small shoulder. [b] Broad shoulder. [c] Long tail at higher wavelength.

spectra, which were usually the best resolved.

In general, the vibrational frequencies of the BH_3 group of the borane adducts are similar to the infrared data reported in the literature.(44,48) The infrared spectrum of the triphenylphosphine-borane is identical to the published spectrum,(49) 608 cm^{-1} for B-P stretching, very near to 2400 cm^{-1} and 2240 cm^{-1} for asymmetric and symmetric B-H stretching respectively, 1135 cm^{-1} for BH_3 bending and 1060 cm^{-1} for BH_3 wagging. A new, strong absorption at 1100 cm^{-1} was found in the infrared spectra of the phosphine-boranes and phosphine-containing boron cations, and it may be assigned as the characteristic band for phenyl-substituted tetracoordinate phosphorus.(50,51) Infrared spectra of 4-picoline-borane and 1,2-bis(diphenylphospniho)ethane bis(borane) are reproduced in Figures II and III respectively as typical spectra of an amine-borane and phosphine-borane.

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 various ligands. The assignments of the various bands were made by a straight-forward comparison between the spectra of the boronium complexes and the spectra of the uncoordinated amines and phenyl-substituted phosphines.

Two B-H stretching vibrations, symmetrical and antisymmetrical, as well as a symmetrical deformation vibration are expected for a BH_2 grouping. In general the asymmetric stretch will occur at higher frequency than the symmetric stretch, and the stretching modes will occur at much higher frequencies than bending modes. The B-H stretching vibrations of the BH_2 grouping are found in the region 2400-2500 cm^{-1} as a strong doublet, and the deformation of HBH is found as an intense band near 1160 cm^{-1}.(3,10)

In the region 2250-2400 cm^{-1} two weak absorptions are observed in many of the spectra. No definite assignments have so far been made for these absorptions.

The B-H stretching vibrations of the BH_2^+ group in boron cations are shifted to higher frequencies compared to the B-H stretching frequencies of the BH_3 group of the borane adducts. For example, asymmetric and symmetric stretching of pyridine-borane are assigned at 2350 cm^{-1} and 2280 cm^{-1} respectively,$^{(48)}$ while in the case of BH_2^+ group of bis(pyridine) boronium salt, the asymmetric stretch falls at 2500 cm^{-1} and symmetric stretching at 2470 cm^{-1}. Similar observations are found in the case of other boron cations. There is little difference between the deformation frequency of BH_2^+ and BH_3 groups.

The B-N stretching vibrations in boronium salts are contradictorily reported in literature. There is one report stating that B-N stretching appears in the region 1450-1465 cm^{-1} comparable to a band found in bis-aminoboranes and in borazines,$^{(28)}$ while Miller and Muetterties$^{(3)}$ suggest that B-N stretching in bis(trimethylamine)boronium salts appears at a lower region 725-900 cm^{-1}. In the classic work of Taylor,$^{(44)}$ B-N stretching in alkylamine-boranes has been definitely assigned in the region 650-750 cm^{-1} contrary to the previously reported assignments at 1110-1250 cm^{-1}.$^{(48)}$ Taylor also suggested that the strong band observed at 1100-1250 cm^{-1} in amine-boranes might have been the result of coupling of B-N motion with other skeletal motions.

In the infrared spectra of all the boron cations having pyridine or substituted pyridine as a ligand, there is a strong new absorption near 1100 cm^{-1} which is characteristic of coordination of pyridines to BH_2^+ (Tables XI and XII). This may be designated to an absorption related to B-N stretching, probably B-N motion coupled with any skeletal motion or uncoupled B-N stretching.

One of the characteristic absorptions of the free pyridines, appearing in the region 1500-1600 cm^{-1} (ring stretch), is shifted to higher wave numbers. When the amine is coordinated to BH_2^+ group, the shifts are larger than those observed when the amine is coordinated to BH_3 group. The ring-breathing frequency observed in the region 980-1020 cm^{-1} is also shifted upfield on coordination to BH_2^+ group (Table XI).

In the spectrum of free pyridine the strong band at 1578 cm^{-1} has a shoulder at 1593 cm^{-1}. On coordination this shoulder disappears while the band at 1578 cm^{-1} shifts to a higher wave number depending on the nature of Lewis acid to which coordination takes place.(48,52,53) For example, when pyridine is coordinated to BH_3, BF_3, BCl_3, BBr_3 and H^+ (in PyHCl), the band at 1578 cm^{-1} is shifted to 1624 cm^{-1}, 1630 cm^{-1}, 1636 cm^{-1} (and 1621 cm^{-1}), 1630 cm^{-1} and 1631 cm^{-1} respectively, while in $(Py)_2BH_2^+$ it shifts to 1628 cm^{-1} and in $(Py)_3BH^+$ it shifts to 1632 cm^{-1}. It is also interesting to note that when pyridine coordinates to metals, such as Co^{+2}, Mn^{+2}, Fe^{+2}, Ni^{+2}, Ag^{+1}, or Hg^{+2}, the highest shift observed is only up to 1615 cm^{-1}.(52)

When 4-picoline is coordinated to BH_3, the strong band near 1605 is shifted to near 1630 cm^{-1}, while in bis(4-picoline)BH_2^+, it is shifted to 1632 cm^{-1}. On chlorination, it shifts to 1639 cm^{-1} as observed in bis(4-picoline)BCl_2^+,(14) while in 4-picoline-boron trichloride it shifts to 1641 cm^{-1} with a shoulder at 1606 cm^{-1}.(48)

When pyridine and 4-picoline are coordinated to the same BH_2^+ as in the case of (pyridine)(4-picoline)BH_2^+, the characteristic strong ring-stretching bands of both pyridine and 4-picoline appear as an

TABLE XI

INFRARED DATA OF BIS(ALKYLPYRIDINE)BORON CATIONS

Compounds (PF_6^- Salts)	Asymmetric B-H stretch cm^{-1}	Symmetric B-H stretch cm^{-1}	Ring stretch 1575-1640 cm^{-1}	BH_2 deformation near 1160 cm^{-1}	B-N stretching 1095-1145 cm^{-1}	Ring breathing 1030-1050 cm^{-1}
$(2\text{-pic})_2BH_2^+$	2530	2440	1625 (1593)	1160	1115	1030 (1000)
$(3\text{-pic})_2BH_2^+$	2490	2450	1630 (1578)	1150	1130	1032 (1027)
$(4\text{-pic})_2BH_2^+$	2480	2460	1632 (1605)	1150	1095	1040 (995)
$(2,3\text{-lut})_2BH_2^+$	2490	2465	1615 (1575)	1150	1105	1038 (1025)
$(2,4\text{-lut})_2BH_2^+$	2490	2465	1640 (1605)	1168	1100	1038 (1035)
$(2,5\text{-lut})_2BH_2^+$	2500	2440	1630 (1601)	1162	1105	1040 (1035)
$(2,6\text{-lut})_2BH_2^+$	2535	2520	1620 (1575)	1175	1140	1045 (1030)
$(3,4\text{-lut})_2BH_2^+$	2483	2448	1633	1160	1113	1033 (1025)
$(3,5\text{-lut})_2BH_2^+$	2480	2460	1620 (1580)	1165	1145	1050 (1035)

The wave numbers in parentheses correspond to the values of free amines. All the spectra were taken on IR-10. Due to the limited resolving power of IR-10, there may be some uncertainty in the values reported.

TABLE XII

INFRARED DATA OF UNSYMMETRICAL BORON CATIONS

Compounds	Asymmetric B-H stretch cm^{-1}	Symmetric B-H stretch cm^{-1}	Pyridine ring stretch 1575-1640 cm^{-1}	BH_2 deformation near 1160 cm^{-1}	B-N stretching 1095-1145 cm^{-1}
$(Py)(4\text{-pic})BH_2^+PF_6^-$	2490	2460	1635 (4-picoline) 1623 (pyridine)	1155	1105
$(TMA)(2\text{-}Fpy)BH_2^+PF_6^-$	2505	2480	1633	1170	1130 1120[a]
$(TEA)(Py)BH_2^+PF_6^-$	2490	2470	1625	1190 1175[a]	1140 1120[a]
$(TMA)(4\text{-}Cypy)BH_2^+PF_6^-$	2500	2465	1635	1162	1105
$(TMA)(Quinoline)BH_2^+PF_6$	2465	2420		1160	1110
$(PPh_3)(CH_3)_2NBH_2^+PF_6^-$	2455	2420		1160	
$(PPh_3)(4\text{-pic})BH_2^+I^-$	2470	2425	1635	1165	1125

Py = pyridine; TMA = trimethylamine; TEA = triethylamine; PPh_3 = triphenylphosphine

[a] Shoulder

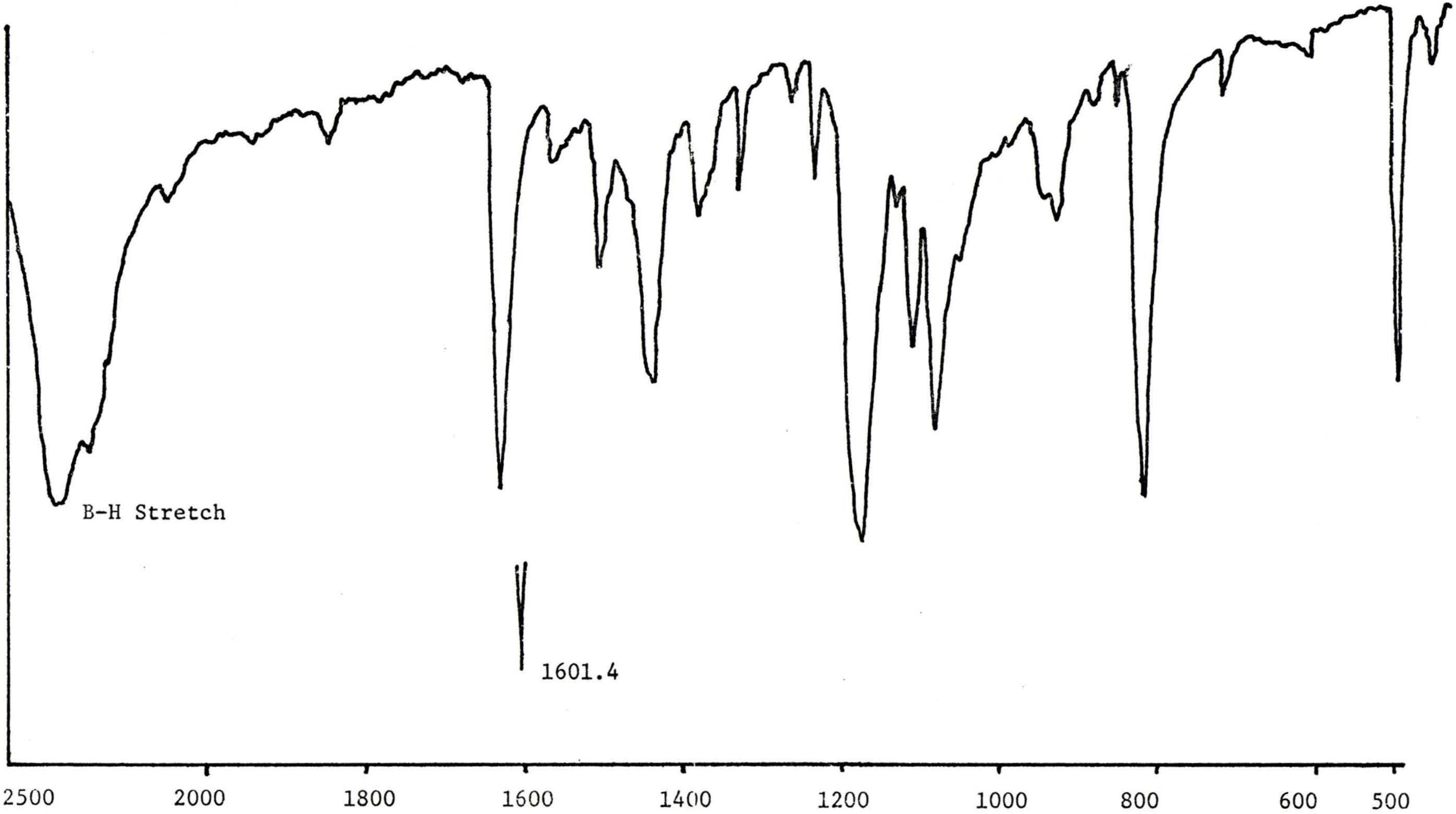


Figure II. Infrared spectrum of 4-picoline-borane.

N3-2

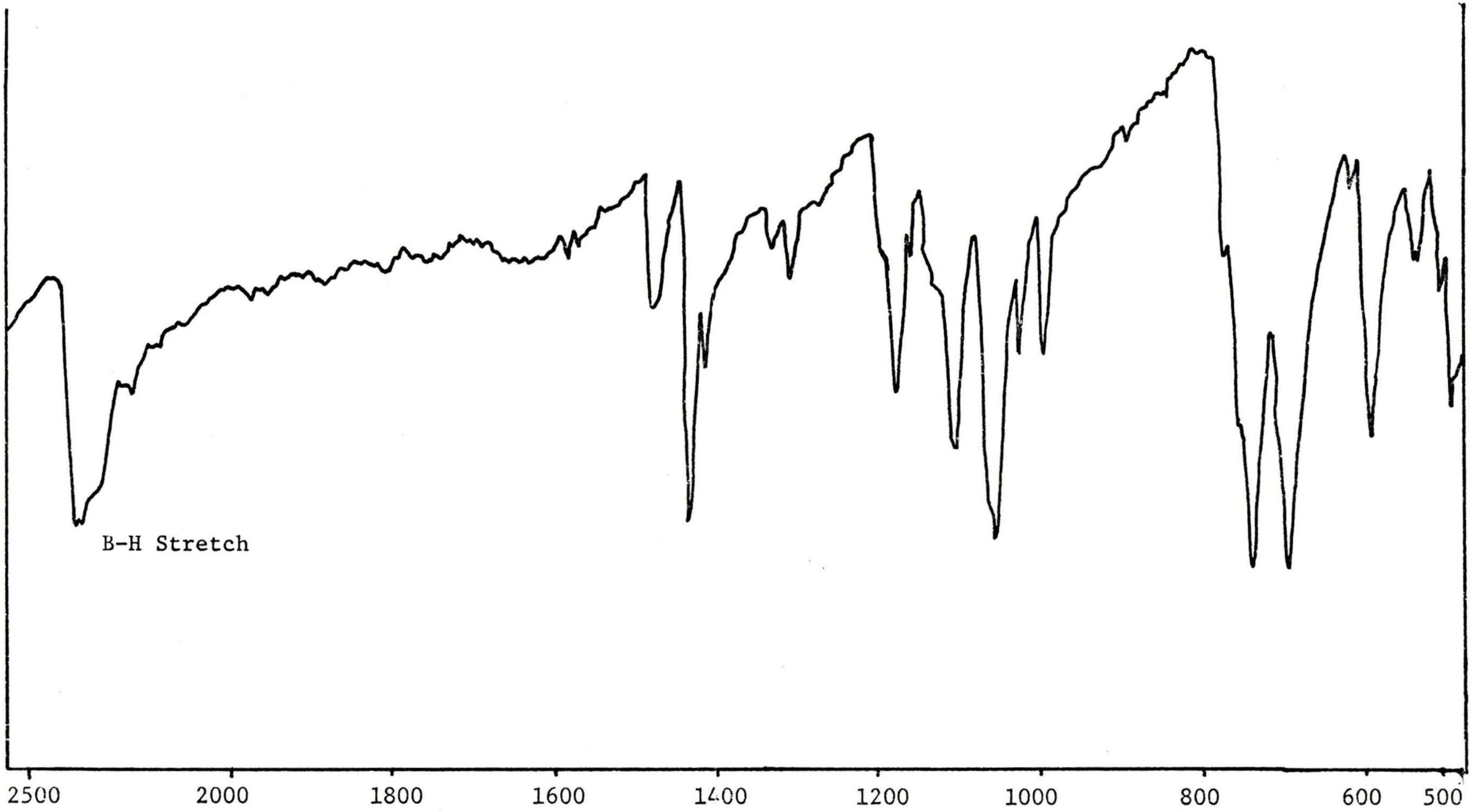


Figure III. Infrared spectrum of 1,2-bis(diphenylphosphino)ethane bis(borane).

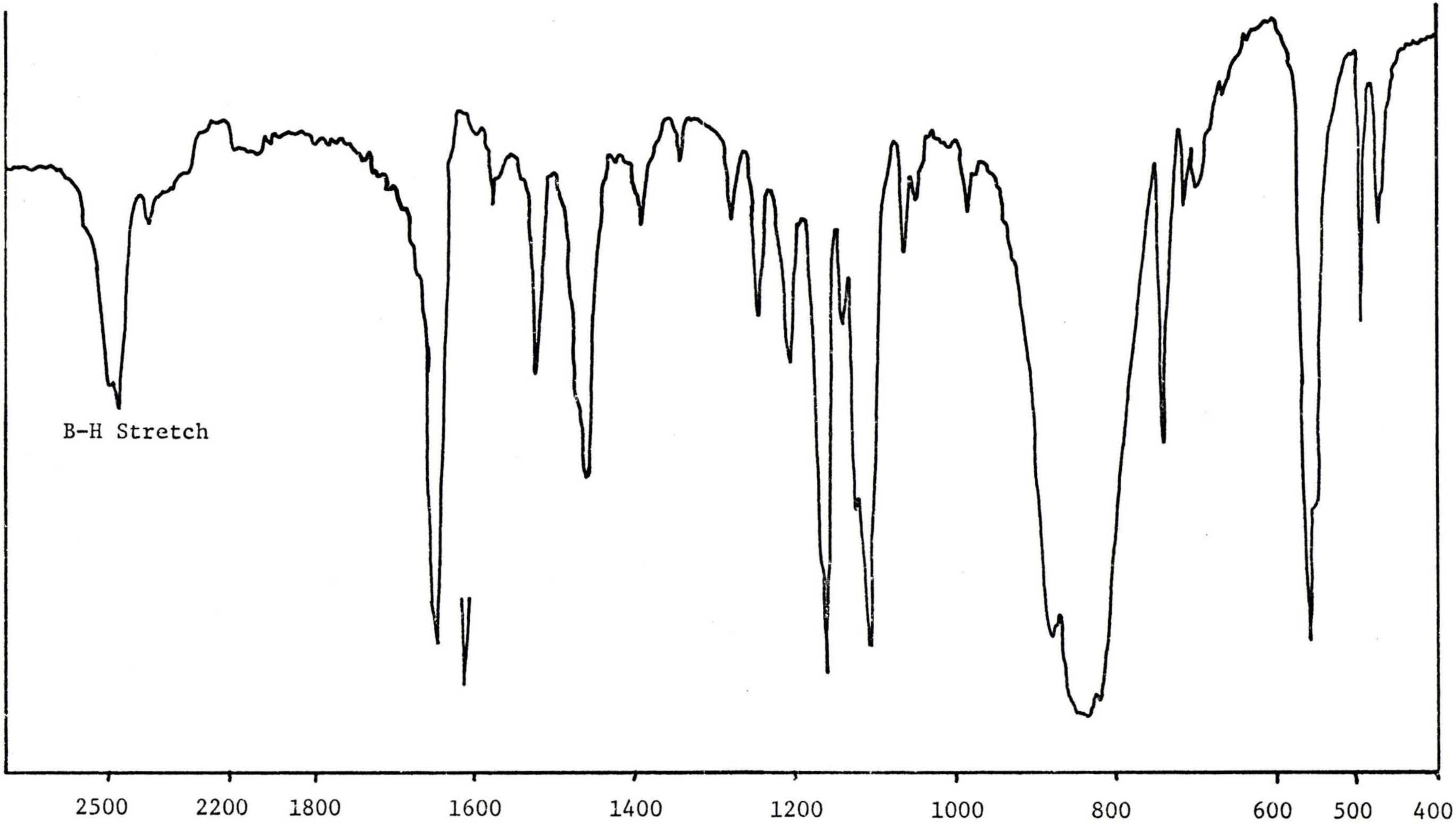


Figure IV. Infrared spectrum of bis(4-picoline)boronium hexafluorophosphate.

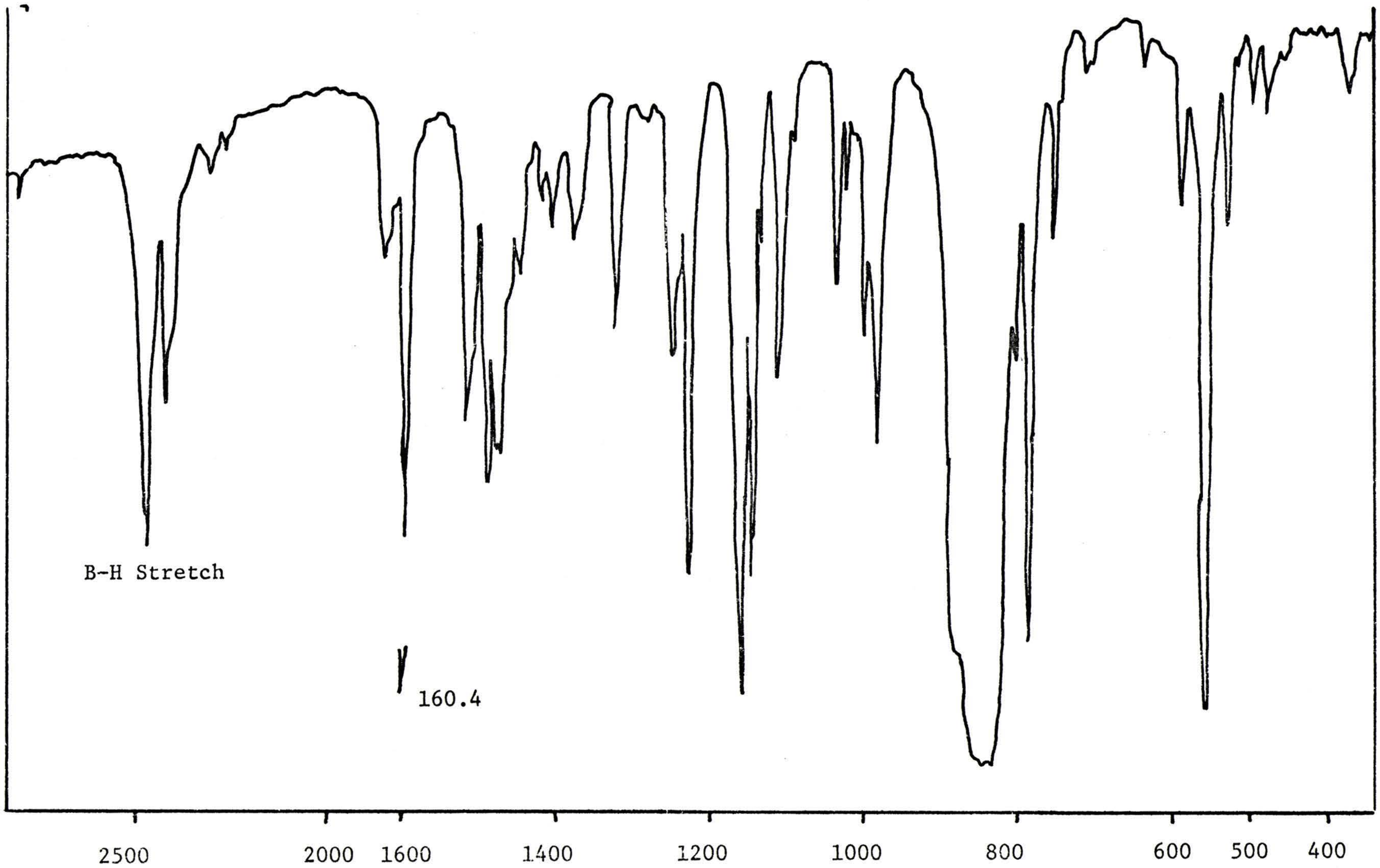


Figure V. Infrared spectrum of (trimethylamine)(quinoline)boronium hexafluorophosphate.

unsymmetrical doublet, the upfield one for coordinated 4-picoline and the downfield one for coordinated pyridine.

In the hexafluorophosphate salts, the characteristic absorption for PF_6^- is found in the region 800-900 cm^{-1} as a very strong, broad band. Various infrared assignments are given in Tables XI and XII. Spectra of bis(4-picoline)BH_2^+ and (trimethylamine)(quinoline)BH_2^+ salts are reproduced in Figures IV and V as examples for infrared spectra of boronium salts.

Nuclear Magnetic Resonance Spectra

Proton nmr spectra of the borane adducts and boronium salts were taken on the Varian-A60 instrument with tetramethylsilane as an internal or external reference and B^{11} spectra were taken at 19.3 Mc or 32.1 Mc with trimethylborate as the external reference. In most of the cases, methylene chloride was the solvent, but occasionally other solvents, such as nitromethane, acetone or water, were used to get better spectra when the compound was found to be less soluble in methylene chloride. The chemical shifts, δ, in parts per million and coupling constants, J, in cycles per second, of proton resonances and boron resonances are reported in Tables XIII to XVI. The integrated intensities of the proton spectra of the ligands of borane adducts and of boron cations agreed well with the expected values, and thus nmr was an extremely useful and easy device to characterize the compounds prepared in this research program.

In general, there is a definite downfield chemical shift in all the proton resonances of the ligand on coordination to BH_3 and BH_2^+ groups. Resonances belonging to the pyridine ring protons were assigned on the basis of their relative intensities, their multiplicity, and their relative chemical shifts.(54,55)

The proton nmr spectra of the phenyl-substituted diphosphine-boranes are noteworthy. The bis(phosphine)methane-borane shows the triplet (Table XIII) for the CH_2 group expected from coupling of both phosphorus atoms to the protons as does the parent donor. The bis(phosphino)ethane-borane shows only a doublet (sometimes called "deceptive doublet") for the CH_2 group, whereas the uncoordinated phosphine shows a triplet. The latter pattern corresponds to virtual coupling of both phosphorus atoms to the protons.(56,57) On coordination to BH_3 this coupling was not observed, a phenomenon which also has been observed on coordination of bis(phosphino)ethane, to alkyl groups or sulfur or oxygen.(56,57) In the boron cation with bis(phosphino)ethane coordinated to two BH_2^+ groups, a similar doublet for CH_2 protons is observed.

In uncoordinated 2,2'-dipyridyl, $H_{3,3'}$, the protons attached to the 3 position, in the ring have unusual downfield chemical shifts compared to other α-substituted pyridines. This has been attributed to partial ring current effect and the lone pair effect of nitrogen on the hydrogen of the adjacent pyridine rings when the pyridine rings are coplanar as is true for the free base.(58,59) In 2,2'-dipyridyl bis(borane), $H_{3,3'}$ has shifted to upfield compared to free base while other protons have shifted to downfield on coordination to BH_3 group. This upfield shift is reasonable for the bis-borane adduct which contains no lone pair electrons on nitrogen and has presumably lost coplanarity.

In the unsymmetrical boronium salts, (trimethylamine)(amine)BH_2^+, the chemical shifts of the protons of $(CH_3)_3N$ (a singlet) fall at $\delta = 2.75 \pm 0.08$ ppm downfield of tetramethylsilane (external), provided CH_2Cl_2 is the solvent (Table XV).

The basicity of the 4-substituted pyridines decreases from 4-OCH_3 to 4-CN, -OCH_3>-CH_3>-Ph>-H>-$COCH_3$>-CN. The nmr Table XV shows that in the case of 4-substituted pyridines coordinated to $(CH_3)_3NBH_2^+$, there is an increasing downfield shift of both α and β protons with decreasing basicity. A similar observation has been reported for 4-substituted pyridine complexes of platinum (II).(60)

In the boronium salts with triphenylphosphine as a ligand it is observed that there is long-range phosphorus-proton coupling. In the case of (trimethylamine)(triphenylphosphine)boronium and (dimethylamine)(triphenylphosphine)boronium salts, the methyl protons are coupled to phosphorus (J = 1.5 cps) which is a four-bond phosphorus-proton coupling. In (4-picoline)(triphenylphosphine)boronium salt the methyl protons of 4-picoline are also coupled to phosphorus (J = 1.5 cps), which is a seven-bond phosphorus-proton coupling. These results show that phosphorus can couple to protons at a long range when they are separated by P-B-N bonds.

In general, the B^{11} resonances are quartets for all the amine-boranes, as expected. The B^{11} spectrum of triphenylphosphine-borane is more complex than that of amine-boranes due to additional B-P coupling (Figures VI and VII). It is an octet composed of overlapping quartets with JB-H = 98Hz and JB-P = 57Hz. A similar complexity is observed in the B^{11} spectra of other phenyl-substituted phosphine-boranes; but due to lack of resolution coupling constants are not reported.

The B^{11} spectra of the boronium salts are triplets as expected for BH_2^+ group. There are some cases where broadening has obscured the multiplicity. Due to excessive line broadening, hydrogens attached to BH_2^+ could not be detected in the proton spectra under normal operating conditions. The chemical shift of B^{11} resonances in BH_2^+ is in the range of 15-22 ppm, while in amine-boranes it is in the range of 28-38 ppm. Thus, as expected in cations there is a definite downfield shift to the B^{11} resonances compared to that of borane adduct.

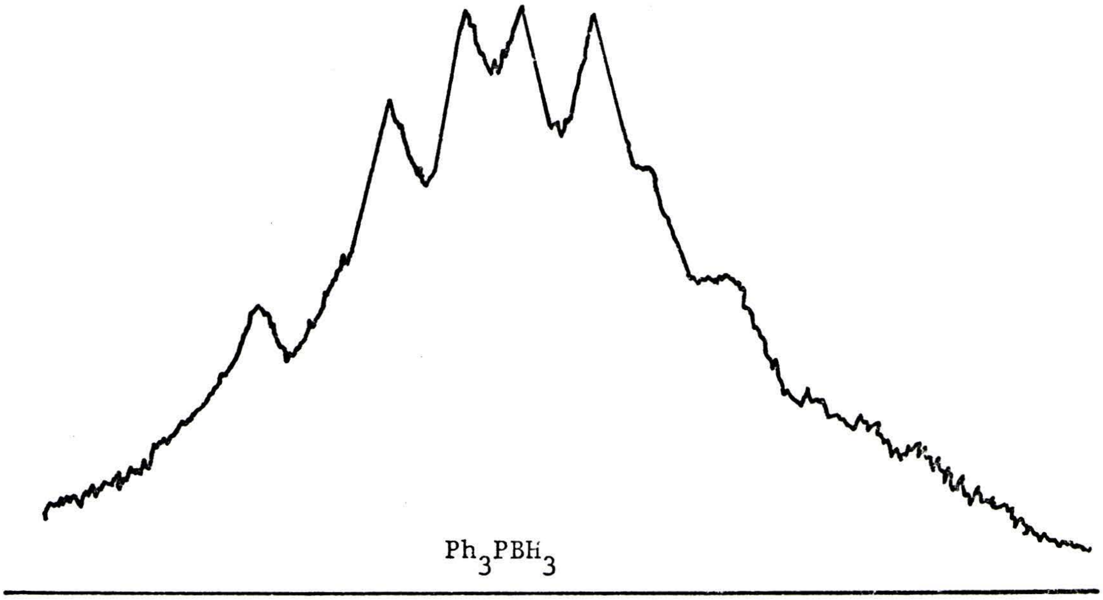


Figure VI. B^{11} nmr spectrum of triphenylphosphine-borane.

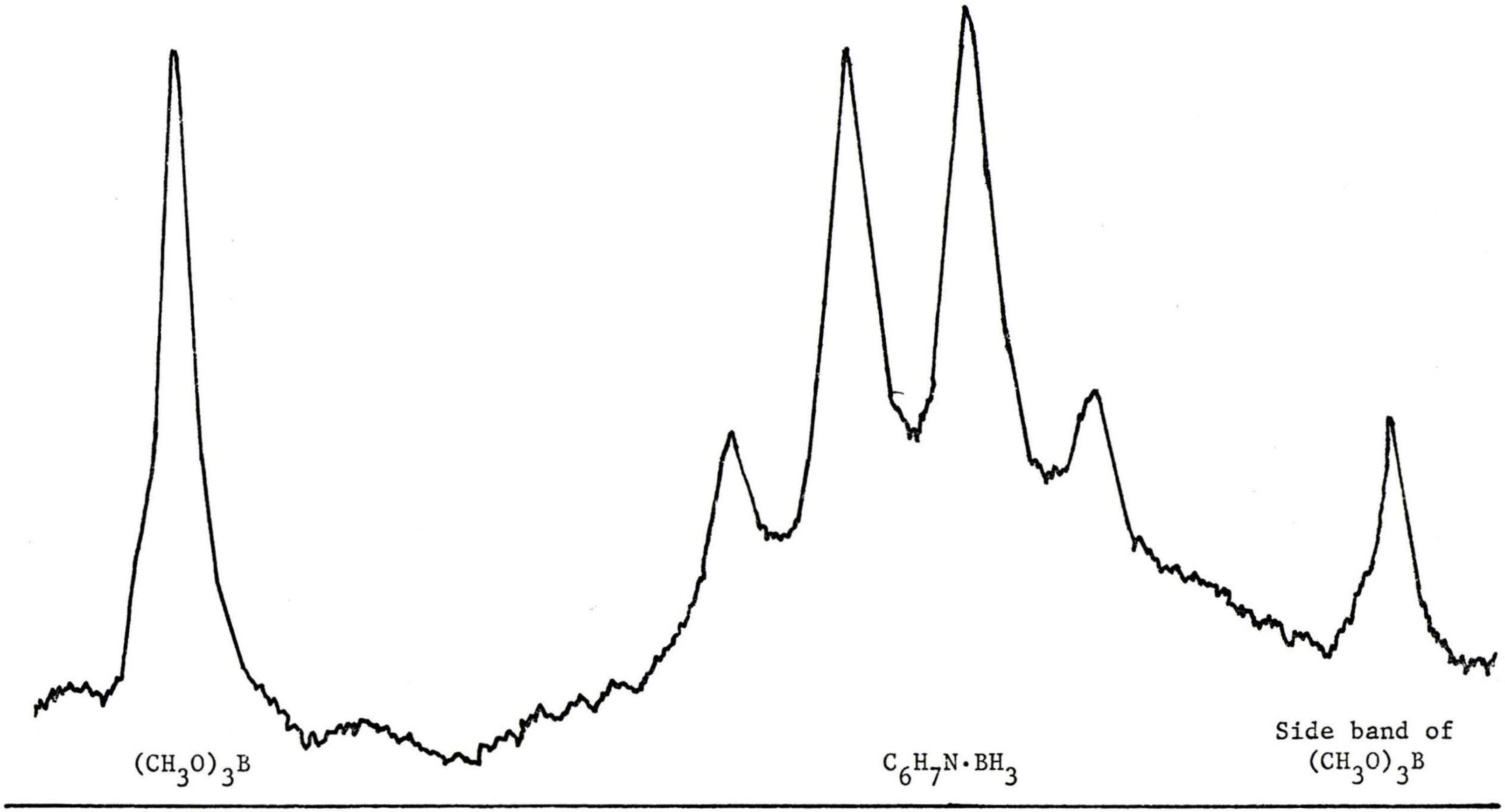


Figure VII. B^{11} nmr spectrum of 4-picoline-borane.

TABLE XIII

PROTON AND B^{11} NMR DATA OF AMINE AND PHOSPHINE BORANES

Compounds	H^1 resonances δ, ppm		B^{11} resonances δ, ppm	Multiplicity	J_{B-H}, cps
$2\text{-}CH_3py \cdot BH_3$	$2\text{-}CH_3$	2.72	31.9	4	101
	$H_{3,5}$	7.33			
	H_4	7.88			
	H_6	8.72			
$4\text{-}CH_3py \cdot BH_3$	$4\text{-}CH_3$	2.48	30.6	4	100
	$H_{3,5}$	7.33			
	$H_{2,6}$	8.40			
$2\text{-}OCH_3py \cdot BH_3$	$2\text{-}OCH_3$	4.07	32.9	4	100
	$H_{3,5}$	7.05			
	H_4	8.00			
	H_6	8.45			
$2,4,6\text{-}(CH_3)_3py \cdot BH_3$	$4\text{-}CH_3$	2.33	36.2	4	98
	$2,6\text{-}CH_3$	2.70			
	$H_{3,5}$	7.07			

TABLE XIII (continued)

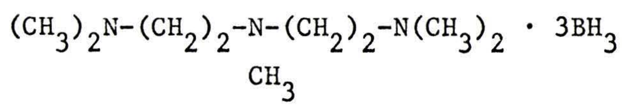
Compounds	H^1 resonances δ, ppm		B^{11} resonances δ, ppm	Multiplicity	J_{B-H}, cps
$CH_3-\overset{\beta}{CH_2}-\overset{\alpha}{(CH_2)}_2NH \cdot BH_3$	α-CH_2	1.72	34.2	4	95
	β-CH_2	2.68			
	$-CH_3$	0.98			
$(CH_3)_2NH \cdot BH_3$	$-CH_3$	2.48	32.4	4	94
$(CH_3)_2-CNH_2 \cdot BH_3$	$-CH_3$	1.25	38.5	4	95
	$-CH$	3.02			
$(CH_3)_2N-(CH_2)_2-N(CH_3)_2 \cdot 2BH_3$	$-CH_3$	2.62	28.7	4	100
	$-CH_2$	3.15			
$2,2'-C_5H_4N \cdot 2BH_3$	$H_{3,3',5,5'}$	7.66	30.7_*	4	99
	$H_{4,4'}$	8.11			
	$H_{6,6'}$	8.83			
 $(CH_3)_2N-(CH_2)_2-\underset{CH_3}{N}-(CH_2)_2-N(CH_3)_2 \cdot 3BH_3$	$-CH_3$	2.65	29.5^{a}_{*}	4	96±4
	$-CH_2$	3.21			
$(C_6H_5)_3P \cdot BH_3$	$-C_6H_5$	7.47	55.8	8	$J_{B-H}=98$ $J_{B-P}=57$

TABLE XIII (continued)

Compounds	H^1 resonances δ, ppm		B^{11} resonances δ, ppm	Multiplicity	J_{B-H}, cps
$(C_6H_5)_2P\text{-}CH_2\text{-}P(C_6H_5)_2 \cdot 2BH_3$	$-C_6H_5$	7.46	55.4		
	$-CH_2$	3.27			
	(triplet, J=11.5 cps)				
$(C_6H_5)_2P\text{-}CH_2\text{-}CH_2\text{-}P(C_6H_5)_2 \cdot 2BH_3$	$-C_6H_5$	7.49	58.4		
	$-CH_2$	2.38			
	(doublet, J=3.0 cps)				

All the δ values represent the centers of the resolvable or complex multiplets; H^1 and B^{11} spectra were run in methylene chloride; H^1 chemical shifts are measured relative to tetramethylsilane, internal, and B^{11} with respect to trimethylborate, external; Py=pyridine: 2,2'-C_5H_4N=2,2'-dipyridyl. a. in nitromethane; * B^{11} nmr obtained at 32.1 Mc.

TABLE XIV

NMR DATA FOR BIS-AMINE $BH_2^+PF_6^-$ SALTS

Compounds	CH_3	Aromatic protons			B^{11} resonance
	δ, ppm	δ, ppm	J_{H-H}	M^a	δ, ppm J_{B-H}, cps
$(2\text{-pic})_2BH_2^+$	2.68	$H_{3,5}$ 7.77		m	22.3 ± 1.1, J = 90 cps
		$H_{4,6}$ 8.27		m	
$(3\text{-pic})_2BH_2^+$	2.55	H_5 7.80		Q	23.1 ± 0.8 b
		H_4 8.18	8	D	
		$H_{2,6}$ 8.57		bD	
$(4\text{-pic})_2BH_2^+$	2.58	$H_{2,6}$ 8.53	6	D	19.2 ± 1.1 b
		$H_{3,5}$ 7.67	6	D	
$(2,3\text{-lut})_2BH_2^+$	$2\text{-}CH_3$ 2.63	H_5 7.60	6	T	20.0 ± 0.5
	$3\text{-}CH_3$ 2.53	$H_{4,6}$ 8.20	6	D	
$(2,4\text{-lut})_2BH_2^+$	$2\text{-}CH_3$ 2.62	$H_{3,5}$ 7.50	6	D	22.0 ± 0.8, J = 90 cps
	$4\text{-}CH_3$ 2.57	H_6 8.10	6	D	
$(2,5\text{-lut})_2BH_2^+$	$2\text{-}CH_3$ 2.62	H_3 7.63	8	D	22.0 ± 0.8, J = 90 cps
	$5\text{-}CH_3$ 2.45	$H_{4,6}$ 8.00		b	

TABLE XIV (continued)

	CH_3	Aromatic protons			B^{11} resonance	
	δ, ppm	δ, ppm	J_{H-H}	M^a	δ, ppm	J_{B-H}, cps
$(2,6\text{-lut})_2BH_2^+$	$2,6\text{-}CH_3$ 1.88	$H_{3,5}$ 6.93	8	D	26.6 ± 1, J = 110 cps	
		H_4 7.46		m		
$(3,4\text{-lut})_2BH_2^+$	$3\text{-}CH_3$ 2.43	H_5 7.62	6	D	18.9 ± 0.8 b	
	$4\text{-}CH_3$ 2.50	$H_{2,6}$ 8.4		b		
$(3,5\text{-lut})_2BH_2^+$	$3,5\text{-}CH_3$ 2.50	H_4 7.97		bS	20 ± 2	
		$H_{2,6}$ 7.37		bS		

[a] Symbols: M, multiplicity; S, singlet; D, doublet; T, triplet; Q, quartet; m, complex multiplet; b, broad. [b] In nitromethane.

TABLE XV

NMR DATA OF (AMINE$_1$)(AMINE$_2$)BORONIUM SALTS

	H^1 resonances						B^{11} resonances		
Compounds (PF_6^- salts)	Aliphatic amines TMA or TEA δ, ppm	Pyridine substituents δ, ppm	H^1	Pyridine ring δ, ppm	Pyridine ring J_{H-H}, cps	M	δ, ppm	J_{B-H}, cps	M
$TMABH_2(4\text{-}CH_3py)^+$	TMA, 2.67	CH_3, 2.63	$H_{2,6}$	8.55	7	2	15.8	90 ± 5	3
			$H_{3,5}$	7.78	7	2			
$TMABH_2(4\text{-}CH_3Opy)^+$	TMA, 2.67	OCH_3, 4.12	$H_{2,6}$	8.46	7.5	2	16.9 ± 0.5^g	100	3
			$H_{3,5}$	7.35	7.5	2			
$TMABH_2(4\text{-}CNpy)^+$ (in methylene chloride)	TMA, 2.77		$H_{2,6}$	8.92	7	2	14.5 ± 0.5^b	$(\approx 370)^f$	B
			$H_{3,5}$	8.26	7	2			
$TMABH_2(4\text{-}CNpy)^{+e}$ (in acetone)	TMA, 2.27		$H_{2,6}$	8.64	7	2			
			$H_{3,5}$	7.91	7	2			

TABLE XV (continued)

	H^1 resonances						B^{11} resonances		
Compounds (PF_6^- salts)	Aliphatic amines TMA or TEA δ, ppm	Pyridine substituents δ, ppm	H^1	Pyridine ring δ, ppm	Pyridine ring J_{H-H}, cps	M	δ, ppm	J_{B-H}, cps	M
$TMABH_2(4-C_6H_5COpy)^+$	TMA, 2.80	C_6H_5, 7.81	$H_{2,6}$	8.86	7	2	16.1 ± 1^c	$(350 \pm 50)^f$	B
			$H_{3,5}$	8.17	7	2			
$TMABH_2(4-C_6H_5CH_2py)^+$	TMA, 2.68	C_6H_5, 7.36	$H_{2,6}$	8.52	7	2	16.4 ± 1^c	$(350 \pm 50)^f$	3
		CH_2, 4.28	$H_{3,5}$	7.74	7	2			
$TMABH_2(4-C_6H_5py)^+$	TMA, 2.73	C_6H_5, 7.77	$H_{2,6}$	8.67	7	2	16.6 ± 1^c	$(350 \pm 50)^f$	B
			$H_{3,5}$	8.14	7	2			
$TMABH_2(4-CH_3COpy)^+$ (in methylene chloride)	TMA, 2.73	$COCH_3$,22.77	$H_{2,6}$	8.86	7	2			
			$H_{3,5}$	8.36	7	2			
$TMABH_2(4-CH_3COpy)^{+e}$	TMA, 2.08	$COCH_3$, 2.08	$H_{2,6}$	8.29	7	2	16.4 ± 1^c	$(330 \pm 30)^f$	3
			$H_{3,5}$	7.67	7	2			

TABLE XV (continued)

	H^1 resonances						B^{11} resonances		
	Aliphatic amines TMA or TEA	Pyridine substituents		Pyridine ring					
Compounds (PF_6^- salts)	δ, ppm	δ, ppm	H^1	δ, ppm	J_{H-H}, cps	M	δ, ppm	J_{B-H}, cps	M
$TMABH_2[3,4-(CH_3)_2py]^+$	TMA, 2.68	$3-CH_3$, 2.45	$H_{2,6}$	8.38			15.6	110	3
		$4-CH_3$, 2.55	H_5	7.71	7	2			
$TMABH_2[2,4,6-(CH_3)_3py]^+$	TMA, 2.74	$2,6-CH_3$, 2.94	$H_{3,5}$	7.48			21.6 ± 0.5	99 ± 10	3
		$4-CH_3$, 2.56							
$TMABH_2(3-Clpy)^+$	TMA, 2.80		$H_{2,6}$	8.78			15.9	$(300)^f$	B
			H_4	8.56					
			H_5	8.10					
$TMABH_2(3-Brpy)^+$	TMA, 2.78		$H_{2,6}$	8.82			16.4	$(280)^f$	B
			H_4	8.62					
			H_5	8.03					

TABLE XV (continued)

	H^1 resonances						B^{11} resonances		
				Pyridine ring					
Compounds (PF_6^- salts)	Aliphatic amines TMA or TEA δ, ppm	Pyridine substituents δ, ppm	H^1	δ, ppm	J_{H-H}, cps	M	δ, ppm	J_{B-H}, cps	M
$TMABH_2(3\text{-}Ipy)^+$	TMA, 2.77		$H_{2,6}$	8.90					
			H_4	8.77			16.2	$(280)^f$	B
			H_5	7.86					
$TMABH_2(3\text{-}CH_3\text{-}5\text{-}CNpy)^+$ (in methylene chloride)	TMA, 2.82	$3\text{-}CH_3$, 2.73	$H_{2,6}$	8.78					
			H_4	8.53					
$TMABH_2(3\text{-}CH_3\text{-}5\text{-}CNpy)^{+e}$ (in nitromethane)	TMA, 2.13	$3\text{-}CH_3$, 1.98	$H_{2,6}$	8.17			10.4 ± 2.6^d		B
			H_4	7.85					
$TMABH_2(2\text{-}Fpy)^+$	TMA, 2.78		$H_{4,6}$	8.56			14.0 ± 0.5	$(\approx 300)^f$	B
			$H_{3,5}$	7.79					
$TMABH_2(2\text{-}Clpy)^+$	TMA, 2.75		H_6	8.76	7	2			
			H_4	8.38			18.2	120	3
			$H_{3,5}$	7.90					

TABLE XV (continued)

	H^1 resonances						B^{11} resonances		
Compounds (PF_6^- salts)	Aliphatic amines TMA or TEA δ, ppm	Pyridine substituents δ, ppm	H^1	Pyridine ring δ, ppm	Pyridine ring J_{H-H}, cps	M	δ, ppm	J_{B-H}, cps	M
$TMABH_2(2\text{-}CH_3Opy)^+$	TMA, 2.74	OCH_3, 4.23	$H_{4,6}$	8.41			18.3		3
			$H_{3,5}$	7.43					
$TMABH_2$ (quinoline)$^+$	TMA, 2.78		H_2	9.2			19.3	120	3
			$H_{4,8}$	8.96					
			$H_{5,6,7,3}$	8.17					
$TMABH_2(py)^+$	TMA, 2.71		$H_{2,6}$	8.74	5.5	2	16.4		3
			H_4	8.43					
			$H_{3,5}$	8.00					
$TMABH_2$(N,N-dimethylaniline)$^+$	TMA, 2.52 $N(CH_3)_2$, 3.33 C_6H_5, 7.65						14.6	115	3

TABLE XV (continued)

	H^1 resonances						B^{11} resonances		
Compounds (PF_6^- salts)	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
$TMABH_2(TEA)^+$	TMA, 2.85								
	CH_3, 1.27 (triplet, J = 7)								
	CH_2, 3.05 (quartet, J = 7)								
$pyBH_2(2\text{-}CH_3Opy)^+$		OCH_3, 4.05	$H_{4,6}$ (*py)	8.23					
			$H_{3,5}$ (*py)	7.35					
			$H_{2,6}$ (py)	8.67	5.5	2	16.4 ± 1.6		B
			H_4 (py)	8.46					
			$H_{3,5}$ (py)	7.83					
$pyBH_2(4\text{-}CH_3py)^+$		4-CH_3, 2.58	$H_{2,6}$ (py)	8.67					
			H_4 (py)	8.30			16.7 ± 0.5	105	3
			$H_{3,5}$ (py)	7.70					
			$H_{3,5}$ (*py)	7.96	7	2			
			$H_{2,6}$ (*py)	8.67					

TABLE XV (continued)

	H^1 resonances						B^{11} resonances		
Compounds (PF_6^- salts)	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
$pyBH_2[2,4,6-(CH_3)_3py]^+$		4-CH_3, 2.53	$H_{3,5}$ (*py)	7.42					
		2,6-CH_3, 2.67	$H_{2,4,6}$ (py)	8.28			18.1		B
			$H_{3,5}$ (py)	7.85					
$pyBH_2(TEA)^+$	CH_3, 1.30 (triplet, J = 7)		$H_{2,6}$	8.68	5.5	2			
			H_4	8.58			20.6 ± 0.5[g]	88 ± 10	3
	-CH_2, 2.90 (quartet, J = 7)		$H_{3,5}$	8.01					

[a] All the δ values represent the centers of the resolvable or complex multiplets. Except where states, all H^1 and B^{11} spectra are of boronium hexafluorophosphates in methylene chloride. H^1 and B^{11} are referred to external tetramethylsilane and trimethyl borate, respectively. Symbols: B, broad; M, multiplicity; TMA, $(CH_3)_3N$; TEA, $(C_2H_5)_3N$; py, C_5H_5N; *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.

TABLE XVI

PROTON NMR DATA OF (AMINE)(PHOSPHINE)BORONIUM SALTS

Compounds	H^1 resonances δ, ppm	Multiplicity	Coupling constants, J, cps
$(CH_3)_3NBH_2PPh_3^+PF_6^-$	$N(CH_3)_3$, 2.73	D	$J_{PBNCH} = 1.5$
	C_6H_5, 7.68	C	
$(CH_3)_3NBH_2^+P(Ph)_2-CH_2-CH_2-(Ph)_2PBH_2^+N(CH_3)_3 2PF_6^-$	$N(CH_3)_3$, 2.63	S	
	C_6H_5, 7.50	C	
	CH_2, 2.43	D	$J_{PCH} = 3.0$
$(CH_3)_2NBH_2PPh_3^+I^-PF_6^-$	$(CH_3)_2$, 2.41	Q	$J_{HNCH} = 5.5$ $J_{PBNCH} = 1.5$
	C_6H_5, 7.56	C	
$C_5H_5NBH_2PPh_3^+PF_6^-$	C_6H_5, 7.63	C	
	$H_{2,6,4}$, 8.27	BD	
	$H_{3,5}{}^a$		

TABLE XVI (continued)

Compounds	H^1 resonances δ, ppm	Multiplicity	Coupling constants, J, cps
$C_6H_7NBH_2PPH_3^+I^-$	CH_3, 2.58	D	$J_{PBNCCCCH} = 1.5$
	C_6H_5, 7.59	C	
	$H_{2,6}$, 8.35	D	
	$H_{3,5}$[a]		

All the spectra were run in methylene chloride using tetramethylsilane as the internal reference. The δ values represent the centers of the resolvable or complex multiplets. C_6H_7 = 4-picoline; [a], the peaks were covered by the peaks of the phenyl groups; D = doublet; S = singlet; Q = quartet; BD = broad doublet; C = complex.

CHAPTER V

DISCUSSION ON SYNTHESES OF BORANE ADDUCTS AND BORON CATIONS

Syntheses of Borane Adducts

The results of the synthetic method developed for borane adducts show that it is a very convenient, rapid and quite general method which may be used for the preparation of amine- and phosphine-boranes in high yields. The reactions involved in this synthesis proceed essentially quantitatively according to the following equation.

$$2NaBH_4 + I_2 + 2A \xrightarrow[\text{monoglyme}]{\text{R. T.}} 2A\cdot BH_3 + H_2 + 2NaI \qquad (1)$$

A = amine or phosphine

It has been reported$^{(38)}$ that diborane could be prepared in excellent yield (98%) by the reaction of sodium borohydride and iodine in diglyme at room temperature. The most likely reaction path in the borane synthesis is an initial hydride abstraction from BH_4^- by iodine to produce the strong Lewis acid, BH_3, which is then trapped by the donor bases present in the reaction mixture.

$$BH_4^- + I_2 \rightarrow BH_3 + HI \qquad (2)$$

$$BH_3 + \text{base} \rightarrow \text{base}\cdot BH_3 \qquad (3)$$

$$BH_4^- + HI \rightarrow H_2 + BH_3 \xrightarrow{\text{base}} \text{base}\cdot BH_3 \qquad (4)$$

$$HI + \text{base} \rightarrow \text{"Onium" salt} \qquad (5)$$

$$\text{"Onium" salt} + BH_4^- \rightarrow \text{base}\cdot BH_3 + H_2 \qquad (6)$$

Whether HI reacts directly with an additional mole of BH_4^- (equation 4) or whether it is temporarily trapped by the base to form the "onium" salts (equation 5) does not affect the eventual results because "onium" salts are known to react with BH_4^- (equation 6) to yield base-boranes.(31) At least in the preparation of one of the amine-boranes, 2,2'-dipyridyl bis(borane), there was an indication that ammonium salt might have been formed as an intermediate product according to equation 5. When the addition of iodine solution was started, a reddish color was developed and the color deepened when more iodine was added, but the color started fading towards the end of the reaction. When hydrogen iodide solution in water was mixed with dipyridyl, a similar color was observed. In other preparations no color was developed. Probably dipyridyl among all other bases used for syntheses gives colored iodide salt and therefore the formation of ammonium salt could be observed during the preparation. This color may be due to the charge-transfer phenomenon as observed in the case of other pyridinium salts.(46,47)

In spite of serious efforts to detect boronium salt in the reaction products none, except in the preparation of ammonia-borane, were found. Ammonia-borane is known to decompose slowly to give the bis-amine boron cation. If the amine-borane were iodinated by I_2 or HI in the presence of amines, boron cations would had been formed. So the lack of formation of boron cations strongly suggests that borohydride ion reacts much more rapidly with iodine than do amine-boranes, and this is chemically in agreement with the expected higher hydride activity of BH_4^-.

Intermediate formation of diborane as a significant reaction path can be ruled out on the basis that no bis(dimethylamine)boronium salt was detected.* The cation should have been formed in mixture with demethylamine-borane, had molecular diborane been present.(61)

Diglyme or triglyme in which borohydride has greater solubility, can be used instead of monoglyme, but the low boiling point of monoglyme is a definite advantage over the use of other ethers since it can be readily removed from the reaction products, and apparently the lower solubility of borohydride in monoglyme does not interfere with the reaction yields as indicated by the high yields obtained in all the preparations.

Syntheses of Boron Cations

The unsymmetrical boron cations reported in Chapter III (Table IV) were prepared by nucleophilic substitution reactions on tetrahedral boron. Amine-monoiodoboranes in benzene solutions were allowed to react with various amines or phenyl-substituted phosphines either at room temperature or refluxing benzene, and thus boronium salts were prepared. The general reaction can be summed up in the following equation.

$$A_1BH_2I + A_2 \rightarrow A_1A_2B^+H_2I^- \qquad (7)$$

A_1 = trimethylamine, dimethylamine, triethylamine, pyridine or 4-picoline.

A_2 = Various tertiary amines, or phenyl-substituted phosphines.

The synthesis of the new cations proceeded, in most cases, rapidly and with high yields. Yields were reproducible in duplicate runs. The yields of iodide salts quoted in Table IV were obtained either at 25° or at 70°, but under otherwise identical reaction conditions. Since there are no side reactions and the conversion to pure hexafluorophosphates

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*The lower yield of the dimethylamine-borane was caused by losses during vacuum evaporation of the solvent, and not by side reactions.

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 represented in equation 7.

In general, iodoboranes of aromatic amines were found to be more reactive than the alkylamine-iodoboranes. This difference is parallel to the differences found in the nucleophilic substitution reactions of benzyl halide (isoelectronic and isosteric with pyridine-iodoborane) and neopentyl halide(isoelectronic and isosteric with trimethylamine-iodoborane) of carbon chemistry. It has been estimated that the ratio of average relative rates of SN_2 reactions of benzyl halide and neopentyl halide is about $1.2x10^7$:1.(62) Though no definite kinetic experiments were done in this research program, it has been observed during syntheses that pyridine-iodoborane was more reactive than other alkylamine-iodoboranes under the same experimental conditions. For example, triethylamine readily reacted with $PyBH_2I$ (Py = pyridine) at room temperature and gave $(Py)(TEA)BH_2^+I^-$ (TEA = triethylamine), in good yield (90%, Table IV),while the TEA reacted very little with $TMABH_2I$ (TMA = trimethylamine) at room temperature as described in Chapter III. However, in comparison with organic halides, the boron compounds are more reactive; they react rapidly with amines even in less polar solvents like benzene, which generally inhibit the rates of nucleophilic substitution reactions involving an ionic transition state.(62)

When the same nucleophiles are used, the difference between the reactivity of $PyBH_2I$ and $TMABH_2I$ can be explained in terms of steric and electronic factors. In the case of $TMABH_2I$, the methyl groups of nitrogen which is next to the nucleophilic substitution site, boron, can severely hinder the incoming nucleophile during the transition state and thus the activation energy is raised and reactivity is lowered. A similar explanation is given for the low reactivity of neopentyl compounds. But in $PyBH_2I$, like benzyl halide, in addition to less steric hindrance compared to $TMABH_2I$, electronic factors also play an important part in determining higher reactivity. First of all, pyridine being planar, the steric hindrance to the incoming nucleophile during transition state will be less than what may be present in the case of $TMABH_2I$. Secondly, in the transition state of the nucleophilic reaction the boron being substituted is sp^2 hybridized, and can use its other p orbital (Figure VIII) to conjugate with the π electron system in addition to its use for bonding the leaving iodide group and the incoming nucleophile; this conjugation would stablize the transition state and consequently the reaction rate would be increased. A similar explanation is given for the higher reactivity of allyl and benzyl halides.(62)

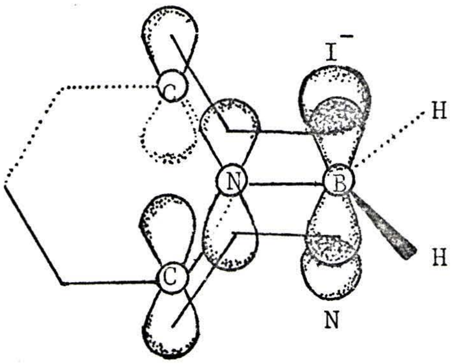

Figure VIII. Transition state for an SN_2 substitution in $PyBH_2I$.

Based on the steric factors, one may argue that dimethylamine-iodoborane may be more reactive than trimethylamine-iodoborane if the same nucleophile and experimental conditions are used: this was observed when triphenylphosphine was allowed to react with $DMABH_2I$ (DMA = dimethylamine) or $TMABH_2I$. In the case of $DMABH_2I$ the reaction proceeded at room temperature and gave $(DMA)(PPh_3)BH_2^+$ (88% yield) while the reaction with $TMABH_2I$ at room temperature was very slow and on refluxing in benzene the yield was not very high (about 30%). When one of the methyl groups of TMA is replaced by hydrogen, as in DMA, steric hindrance is reduced and consequently reactivity is stepped up. This behavior is again parallel to what is reported in carbon chemistry. Isobutyl halide, isoelectronic and isosteric with $DMABH_2I$, is much more reactive than neopentyl halide in SN_2 reactions and the ratio of average relative rates of isobutyl halide and neopentyl halide is about $3x10^3$:1.(62)

The formation of the boron cations appeared to be influenced by the nature of the incoming nucleophiles. With trimethylamine-iodoborane as the starting material, it was possible to observe differences in the ease with which the product was formed as a function of the nature of the incoming amines and phosphines. Substituents *ortho* to the pyridine nitrogen atom sharply decreased the rate of product formation, as evidenced by the low yield with 2-methoxy pyridine (pKa = 3.28) while 4-benzoyl pyridine, with a similar basicity (pKa = 3.35), gave a higher yield at room temperature (Table IV). Similarly, 2,4,6-collidine with a high basicity, (pKa = 7.45), needed heating to complete the reaction while pyridine, which is less basic (pKa = 5.17) proceeded at room temperature and gave high yields. It may be concluded now that the steric environment of the incoming amine has some influence on the formation of boron cations. If the attacking amine is sufficiently bulky, then the formation of boron cations is subject to steric inhibition. With pyridine-iodoborane as the starting material, the high reactivity precluded similar observations.

The formation of boron cation can also be influenced by the electronic factors of the incoming nucleophile substituting on the amine-iodoborane. For a given group of nucleophiles containing the same nucleophilic atom, and where the steric features in the immediate vicinity of the nucleophilic atom are similar, nucleophilic reactivity may be correlated with basicities. It is observed that basicities of the attacking amines having similar steric environments influenced the cation formation. Both 3-chloro- and 4-cyanopyridine, which are markedly less basic than pyridine and 4-picoline and whose substituents should not interfere sterically, reacted sluggishly at room temperature with $TMABH_2I$. 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 the parameter is not very pronounced; even 2-fluoropyridine, an extremely weak base (pKa = -0.44) with an *ortho* substituent, did not fail to give a reasonable product yield on heating to 70°. Acetonitrile which is an extremely weak base (pKa = -10.13) was also found to react with $TMABH_2I$ and gave the boron cations.(63)

Some of the amines used as nucleophiles in this study have two unlike nucleophilic sites, either of which (but not both simultaneously) may attack the electrophilic center of the iodoborane adducts. Pyridines with substituents like $-CN$, $-OCH_3$, $-COCH_3$ are the ambident nucleophiles used in this study. In their SN_2 reactions the more basic end may react preferentially with a substrate whose electrophilic atom acquires a significant positive charge in the transition state, while the more polarizable end would react with a substrate whose electrophilic atom has many electrons in the outer orbitals.(64) Therefore, one would expect that the nitrogen of these substituted pyridines (ambident nucleophiles), being more basic sites than their respective substituents, would have preferentially coordinated to boron (a member of the second row elements) which has no electrons in the outer orbitals.

Few phenyl-substituted phosphine-containing cations have been prepared using phosphines as nucleophiles while amine-iodoboranes were the substrates. When $TMABH_2I$ was reacted with triphenylphosphine, the reaction proceeded very sluggishly at room temperature, but on refluxing in benzene the yield was improved. When the analogous nitrogen compound, triphenylamine, was reacted with $TMABH_2I$, no reaction was observed even on refluxing. This is parallel to the observations that phosphines have higher nucleophilic reactivity in many reactions than corresponding amines.(65) The inertness of triphenylamine has been attributed to the high conjugation energy, and greater steric hindrance. It may be worth mentioning in this context that triphenylphosphine reacts rapidly with methyl iodide, whereas triphenylamine is inert.(65)

It has been reported that when $TMABH_2I$ was treated with a diamine, N,N,N',N'-tetramethylethylene diamine (TMED), a mixture of $(TMA)_2BH_2^+$ and $TMEDBH_2^+$ (chelated boron cation) was produced at room temperature.(7) When $TMABH_2I$ was reacted with a diphosphine, bis(diphenylphosphino)ethane, the product obtained was only a non-chelated boron cation, $TMABH_2^+P(Ph)_2-CH_2-CH_2-(Ph)_2P-BH_2^+TMA$. Of course, for a strict comparison of a diamine and a diphosphine for their chelating ability, $(CH_3)_2P-CH_2-CH_2P(CH_3)_2$ would have been the best analogue of TMED $(CH_3)_2N-CH_2CH_2N(CH_3)_2$. Still, this experimental observation seems to suggest that chelation in the case of diphosphine may not take place readily.

The general reaction of the synthetic procedure represented in equation 7 could proceed via nucleophilic attack on the tetrahedral boron of the amine-iodoborane by the amines (or phosphines) leading to displacement of iodide ion. This type nucleophilic substitution reaction would be the SN_2 type reaction. On the other hand, primary ionization of the boron-iodine bond followed by addition of amine to the resulting three-coordinate cation would be another possible path to form the boron cation when one considers the expected high ionic character of the B-I bond (SN_1 type reaction). The data presented in this study could allow one to make judgements concerning these two alternatives, SN_2 or SN_1 reactions.

$$A_1BH_2I \rightarrow A_1BH_2^+ + I^- \qquad (8)$$

$$A_1BH_2^+ + A_2 \rightarrow A_1A_2BH_2^+I^- \qquad (9)$$

A_1 and A_2 = amines

First, in the SN_1 reactions the nucleophile attacks after the rate-determining step, and therefore it cannot alter the rate of the reaction. If equation 8 represents 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 equation 9, and identical product yields should be obtained. This is contrary to the observations in this study. It was already pointed out that the nature of the incoming amines influences the yields when trimethylamine-iodoborane was the substrate.

If ionization of the iodoborane were not the rate-determining step, 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 $(CH_3)_3NBH_2^+$ ion* is also slow at room temperature. This assumption is in disagreement with the general observation that Lewis

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*The formation of three-coordinate boron cation as an intermediate has been recently demonstrated in this laboratory. In the presence of a strong Lewis acid like $AlCl_3$, $(CH_3)_3NBCl_3$ was found to undergo ionization to $(CH_3)_3NBCl_2^+$ and Cl^-.

acid-base additions are very fast in the absence of extensive molecular rearrangements. Direct experiments concerning this point have been made with BF_3 and various amines. They showed that the addition in these cases proceeded essentially without activation energy.(66) One might reasonably expect that a three-coordinate positively charged borane should thermodynamically be even a stronger acceptor than BF_3, and therefore should react at least as rapidly as boron trifluoride. A reversible equilibirum in equation 9 is ruled out by the fact that the cations are stable at room temperature. The foregoing arguments effectively eliminate a mechanism involving ionization of the iodoborane and leave the likelihood that the boron cations are formed by a bimolecular nucleophilic substitution represented by equation 7.

Displacement of one amine by another is an alternate nucleophilic substitution which, in principle, should be a possible reaction competing with iodide displacement. Iodide being a better leaving group than amines, normally iodide displacement is the expected pattern of nucleophilic substitution reaction. Only in one case was there evidence that amine-displacement took place instead of iodide displacement. If, in general, amine exchange had occured to a significant extent, one should have isolated symmetrical 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 resulting intermediate from amine exchange, pyridine-iodoborane is more reactive in cation formation than the trimethylamine-iodoborane. The nmr spectra and other properties of the PF_6^- salts, which were isolated in almost quantitative yield and high purity, showed no evidence whatever of the presence of bis(pyridine)boronium salts. Therefore, one must conclude that the displacement of iodide 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 amines, is a slower process than iodide displacement in the three amine-iodoboranes studied here.

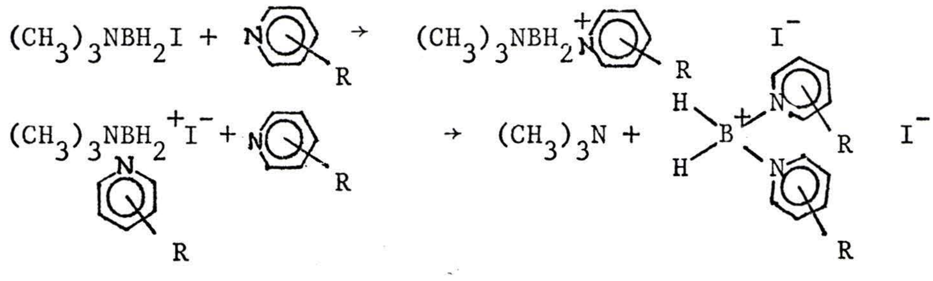
In this context it may be worth mentioning as described in one of the preceding paragraphs that when the diamine, tetramethylethylenediamine was allowed to react with trimethylamine-iodoborane at room temperature, a mixture of $TMA_2BH_2^+$ and the chelate cation, $TMEDBH_2^+$, was obtained.(7) In this particular case, the explanation given was that one of the nitrogen atoms of the diamine first displaced the iodide from a molecule of $TMABH_2I$ to give the cation $TMABH_2{}^+N(CH_3)_2\text{-}CH_2\text{-}CH_2\text{-}N(CH_3)_2$ as an intermediate. Due to the great chelating ability of the diamine to form a five-membered ring with the boron, the second nitrogen atom preferentially displaced the $(CH_3)_3N$ from the intermediate rather than an iodide from a second molecule of $TMABH_2I$, and formed the chelate cation, $TMEDBH_2^+$. The free trimethylamine reacted with the unreacted $TMABH_2I$, and formed $TMA_2BH_2^+$ and $TMEDBH_2^+$. In this particular case, it is an example of intramolecular transamination rather than a preferential amine displacement to iodide displacement.

The one example in which loss of an amine from an iodoborane adduct apparently took place in this study is the attempted synthesis of an unsymmetrical cation, with trimethylamine-iodoborane and triethylamine 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 occured 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 experiment.(10) 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. The synthesis of the unsymmetrical cation, (trimethylamine)(triethylamine)boron cation, was also demonstrated by a separate experiment as given in Chapter III. It is, of course, possible that at higher temperatures 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 iodoborane, the inverse procedure, starting with triethylamine-iodoborane and trimethylamine, cleanly gave the desired product. 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 the incoming nucleophile. Examination of molecular models reveals, however, that triethylamine coordinated to iodoborane must have the terminal CH_3 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 pairs on nitrogen. Thus there is more steric hindrance in the transition state, when free triethylamine approaches the trimethylamine-iodoborane, than the steric factors involved in the transition state when trimethylamine attacks the triethylamine-iodoborane. In the triethylamine-iodoborane the conformation of the ethyl groups is already largely fixed and offers less steric hindrance 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 ethyl groups. Iodination of triethylamine-borane indeed is visibly slower than the corresponding reaction of trimethylamine-borane.

The three synthetic methods for the preparation of bis(alkylpyridine) boron cations, given in Chapter III (syntheses #1, 2 and 3), are actually based on a common scheme of reactions, iodination of an amine-borane, followed by the displacement of iodide by excess amine to form boron cations (symmetrical cations by method #1 and unsymmetrical cations by methods #2 and 3), and, finally the displacement of the coordinated amine from the unsymmetrical cations by another amine to give symmetrical cations with C_{2v} symmetry. These reactions are illustrated in the following equations taking $(CH_3)_3NBH_3$ as the starting materials.

$$2(CH_3)_3NBH_3 + I_2 \rightarrow 2(CH_3)_3NBH_2I + H_2 \tag{10}$$



(11)

(12)

$R = CH_3$

In the first method when the starting material $NaBH_4$ reacts with I_2, BH_3 is formed which is then trapped by the alkylpyridine present in the reaction mixture to form the borane adducts. The successful syntheses of various amine- and phosphine-boranes described in Chapter III were actually based on this sequence of reaction. The alkylpyridine-boranes formed *in situ* are then iodinated to get the iodoborane adducts and hydrogen iodide which react with excess of amines to form a mixture of bis(alkylpyridine)boronium salts and alkylpyridinium salts respectively.

The other two methods do not differ very much in principle. Both the methods start with $(CH_3)NBH_3$. In method #2, $(CH_3)_3NBH_3$ is iodinated in the presence of excess of amine and therefore a mixture of unsymmetrical cations (trimethylamine)(alkylpyridine)boronium iodide, and alkylpyridinium salt, is formed. On heating with excess of amine, transamination takes place and bis(alkylpyridine)boronium iodide is the result according to equation 12. In method #3, first $(CH_3)_3NBH_3$ is iodinated in the absence of amine in the reaction mixture, as is done in the preparation of unsymmetrical boron cations. The iodoborane adduct is then reacted with excess of alkylpyridine to form the unsymmetrical cations, (trimethylamine)(alkylpyridine)boronium iodide which, without isolation, is then transaminated by heating in the presence of excess of alkylpyridines to get the bis(alkylpyridine)boronium salts according to equation 12. The unsymmetrical cations formed as an intermediate in this work have been isolated and reported.(10) In separate experiments transaminations of unsymmetrical cations to symmetrical cations have been demonstrated and details of these experiments were already given in Chapter III and IV.

The synthesis of bis-amine cations by method #3 would seem the method of choice if an iodide salt is desired, because here the compound can be obtained without the necessity of separating it from other non-volotile reaction products.

In this study iodine was the only halogen used to halogenate the borane adducts in the procedures used for the syntheses of symmetrical as well as unsymmetrical cations. The use of iodine in preference to other halogens has some justifications. First, the handling of iodine does not need any special care. Secondly, iodine being a good leaving group, nucleophilic substitution reactions take place more readily. Thirdly, diiodination of borane adducts does not take place readily at room temperature. But in the case of chlorine and bromine, dihalogenation of amine-boranes at room temperature can take place. Therefore, the use of iodine as a halogenating agent can prevent the formation of dication as a side product when $> BH_2^+$ type cations are prepared.

The results of the syntheses of borane adducts, symmetrical cations and unsymmetrical cations of this study have been reported in the literature.(5,10,37)

CHAPTER VI

SYNTHESES OF $B_3H_8^-$ AND $B_{12}H_{12}^{-2}$ IONS

It has been reported that diborane is produced in excellent yield (98%) when sodium borohydride reacts with iodine in diglyme at room temperature.(38) In the presence of donor bases like amines and phenyl-substituted phosphines, borane adducts were prepared using a reaction mixture of $NaBH_4$ and I_2 in monoglyme, and the experimental details and results of the syntheses of borane adducts were already given in the last three chapters. Experimental details and results of the attempts made to prepare $B_3H_8^-$ and $B_{12}H_{12}^{-2}$ ions from a reaction mixture of $NaBH_4$ and I_2 in diglyme at elevated temperatures are given in this chapter.

<u>Synthesis of triborohydride ion, $B_3H_8^-$</u>.--The apparatus used in this experiment was similar to the one used for the preparation of borane adducts (Figure 1). Sodium borohydride, 6.935 g (183.5 mmoles), was taken with 160 ml of dry diglyme (distilled from lithium aluminum hydride) in a 500 ml two-necked flask as shown in Figure I. Iodine solution, prepared by dissolving 9.012 g (35.5 mmoles) of iodine in 80 ml of dry diglyme, was taken in a pressure-compensated-dropping funnel which was fixed in one of the outlets of the flask. A bubbler containing a benzene-4-picoline mixture was connected to the other outlet of the reaction flask in order to prevent the diborane gas from escaping into the atmosphere.

The reaction flask was placed in an oil bath whose temperature was kept constant near 99° throughout the addition of iodine solution. The reaction mixture in the flask was kept stirred constantly and vigorously by a magnetic stirrer when iodine was added. Before the addition of iodine, the apparatus was flushed with nitrogen for 5 minutes. It took 40 minutes to add the iodine solution. During the addition of iodine solution the reaction was vigorous and hydrogen gas was evolved and escaped through the bubbler. Now the color of the reaction mixture was pale yellow.

After the addition of iodine the reaction mixture was stirred for 30 minutes at 93°. Then the solvent was evaporated off by vacuum-pumping while the flask was kept in the oil bath at 55°. After evaporation the residue was treated with an excess saturated solution of tetra-n-butylammonium iodide to precipitate the polyhedral ions. Due to the vigorous bubbling in the reaction flask, the ammonium salt was added slowly and carefully. The precipitate which was nearly white was filtered, washed with some ether, dried and weighed 3.870 g. The reaction was expected to proceed according to the following equation and the yield

$$3NaBH_4 + I_2 \rightarrow NaB_3H_8 + 2NaI + H_2 \qquad (1)$$

of tetra-n-butylammonium triborohydride salt was calculated based on the iodine used for the reaction (39%).

The triborohydride was characterized by B^{11} nmr and infrared data. The B^{11} nmr spectrum of the tetra-n-butylammonium triborohydride in methylene chloride was taken at 32.1 Mc spectrometer against a trimethylborate external standard. The spectrum consisted of a symmetrical septet (Figure IX) with $J = 33$ cps and $\delta = 47.9$ ppm. The values reported in literature are $J = 32$ cps, $\delta = 47.5$ ppm,(41) and $J = 33$ cps, $\delta = 47.9 \pm 0.5$ ppm.(42) The B^{11} nmr spectrum did not show any additional peaks.

The infrared spectrum of the tetra-n-butylammonium triborohydride was taken in a KBr pellet and showed B-H stretching bands at 2450 cm^{-1}

and 2400 cm^{-1} and also absorptions at 2300 cm^{-1}, 2240 cm^{-1}, 1140 cm^{-1}, 1015 cm^{-1} and 950 cm^{-1}. These assignments are in agreement with the previously published data.(41,42) Tetra-n-butylammonium triborohydride melted at 208-210° with decomposition.

Attempt to prepare $B_{12}H_{12}^{-2}$.--Another experiment was performed to prepare a higher polyhedral borane, $B_{12}H_{12}^{-2}$. The general procedure and the apparatus were exactly the same as used for the preparation of $B_3H_8^{-1}$. Sodium borohydride, 5.160 g (136.5 mmoles),were taken in 175 ml of dry diglyme. Iodine solution was prepared by dissolving 11.198 g (44.0 mmoles) of iodine in 80 ml of diglyme. In this reaction the oil bath temperature was about 158° while iodine solution was added to the borohydride in the flask. It took 3 hours to add the iodine solution. After the iodine addition, the diglyme was evaporated off and the unreacted borohydride was destroyed by adding water. The total volume of the solution was 93.5 ml.

Five milliliters of the solution was treated with 10 ml of tetra-n-butylammonium iodide solution. The precipitate formed was washed with 2 ml of water, dried and weighed 0.150 g. The B^{11} nmr and infrared spectra of this ammonium salt showed that it was a mixture of $B_{12}H_{12}^{-2}$ and $B_3H_8^{-}$ ions. The B^{11} nmr spectra of the tetra-n-butylammonium salt in methylene chloride taken at 32.1 Mc spectrometer gave a doublet, δ = 33.51 ppm, H = 132 cps (literature values, δ = 32.7, J = 126 cps(39); δ = 35 ppm, J = 130 cps(67)) for $B_{12}H_{12}^{-2}$ and a septet for $B_3H_8^{-}$ ion with chemical shifts and coupling constants similar to those given previously. The B^{11} spectrum of $B_{12}H_{12}^{-2}$ and $B_3H_8^{-}$ is reproduced in Figure X. The infrared spectrum of the ammonium salt showed the characteristic absorptions both for $B_{12}H_{12}^{-2}$ and $B_3H_8^{-}$ ions.(42,67)

Another 5 ml of the solution (from 93.5 ml) was acidified by 2.5 ml of 0.72N HCl to destroy $B_3H_8^-$ ions. $B_{12}H_{12}^{-2}$ is not decomposed by dilute hydrochloric acid.(67) A saturated solution of tetra-n-butylammonium iodide, 10 ml, was added to precipitate $B_{12}H_{12}^{-2}$ ion. The precipitate was washed with 5 ml of acidified water, dried and weighed 0.075 g. The B^{11} spectrum of the salt showed only a doublet characteristic to the isosahedral polyhedral borane, $B_{12}H_{12}^{-2}$. The spectral values obtained were $\delta = 33.4$ ppm and $J = 127$ cps. The infrared spectrum showed absorptions of the $B_{12}H_{12}^{-2}$ ion, a sharp absorption at 2480 cm^{-1} for B-H stretching, a strong absorption near 1060 cm^{-1} for cage frequency, and weaker absorptions near 715 cm^{-1}, 745 cm^{-1} and 1115 cm^{-1}. These values are in agreement with the published data.(67) The tetra-n-butylammonium salt of $B_{12}H_{12}^{-2}$ was recrystallized from methylene chloride-ether mixture and analyzed. Analysis calculated for $[(C_4H_9)_4N]_2B_{12}H_{12}$: C, 61.26%; H, 4.47%; B, 20.71%; Found: C, 61.62%; H, 4.06%; B, 20.51%.

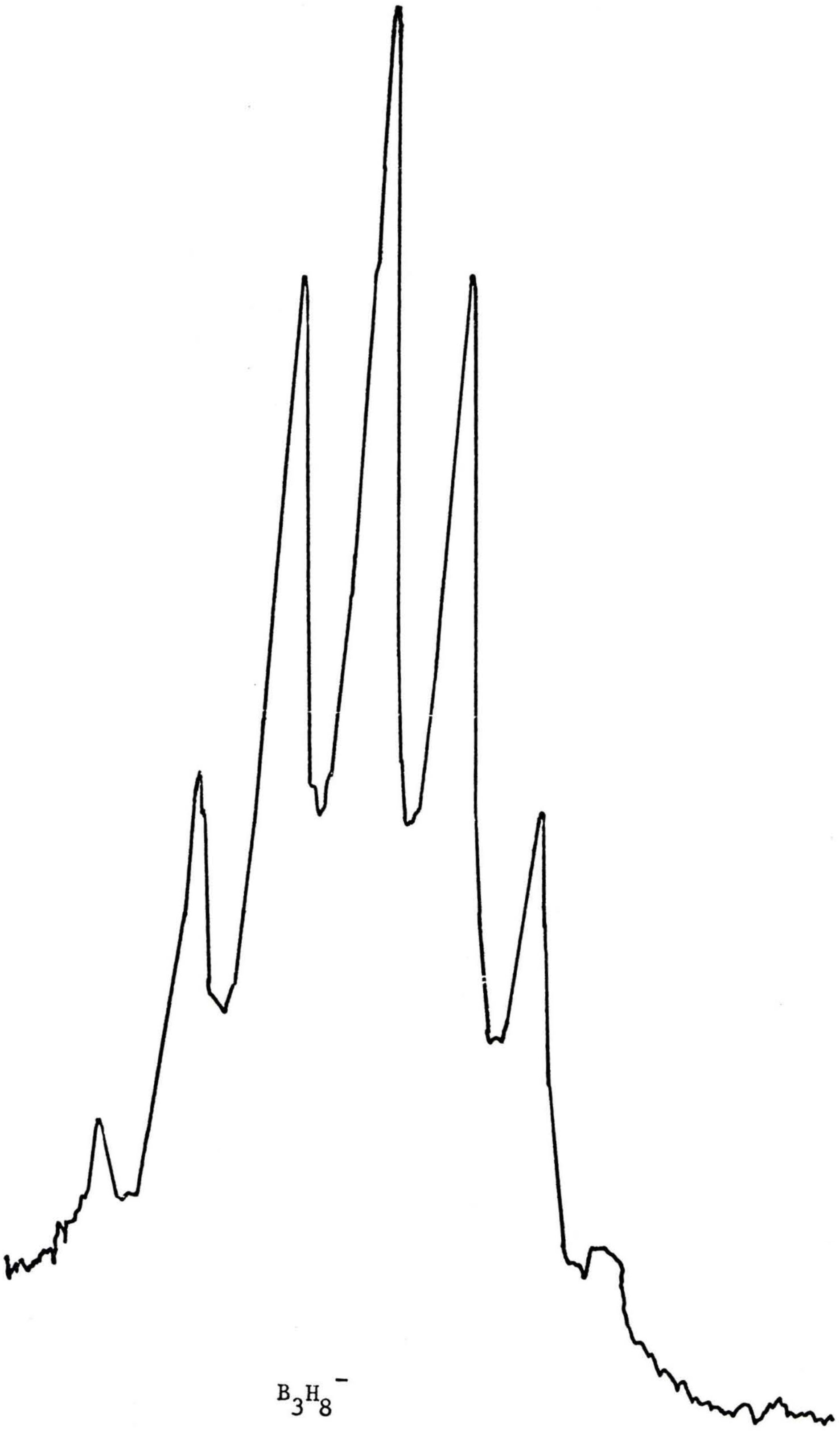
$[(CH_3)_4N]_2B_{12}H_{12}$ and $Cs_2B_{12}H_{12}$ were also prepared and their spectral data were compared with the reported values(67) and thus the formation of $B_{12}H_{12}^{-2}$ was confirmed.

The decomposition of $B_3H_8^-$ ion to $B_{12}H_{12}^{-2}$ at higher temperatures has been reported.(39)

$$5B_3H_8^- \rightarrow B_{12}H_{12}^{-2} + 3BH_4^- + 8H_2 \qquad (2)$$

Therefore, one could consider the formation of $B_{12}H_{12}^{-2}$ in the present reaction as a decomposition product of $B_3H_8^-$ ion which was formed according to equation 1. In that case, the total yield of $B_3H_8^-$ ion, as tetra-n-butylammonium triborohydride, would be 4.565 g from the 93.5 ml of solution. This yield includes the undecomposed $B_3H_8^-$ ion and the ion decomposed according to equation 2. Based on iodine used in this reaction according to equation 1, the yield would be 37% as tetra-n-butylammonium triborohydride.

Even though the yields are not very high, this method of producing $B_3H_8^-$ and $B_{12}H_{12}^{-2}$ ions is a convenient one. The apparatus is simple; the starting materials are readily available and the experimental procedure is not difficult. Since the diborane is produced *in situ*, there is no special technique involved in this method. Probably other polyhedral boranes may be prepared by this method with some modifications.



$B_3H_8^-$

Figure IX. B^{11} nmr spectrum of $[CH_3(CH_2)_3]_4NB_3H_8$

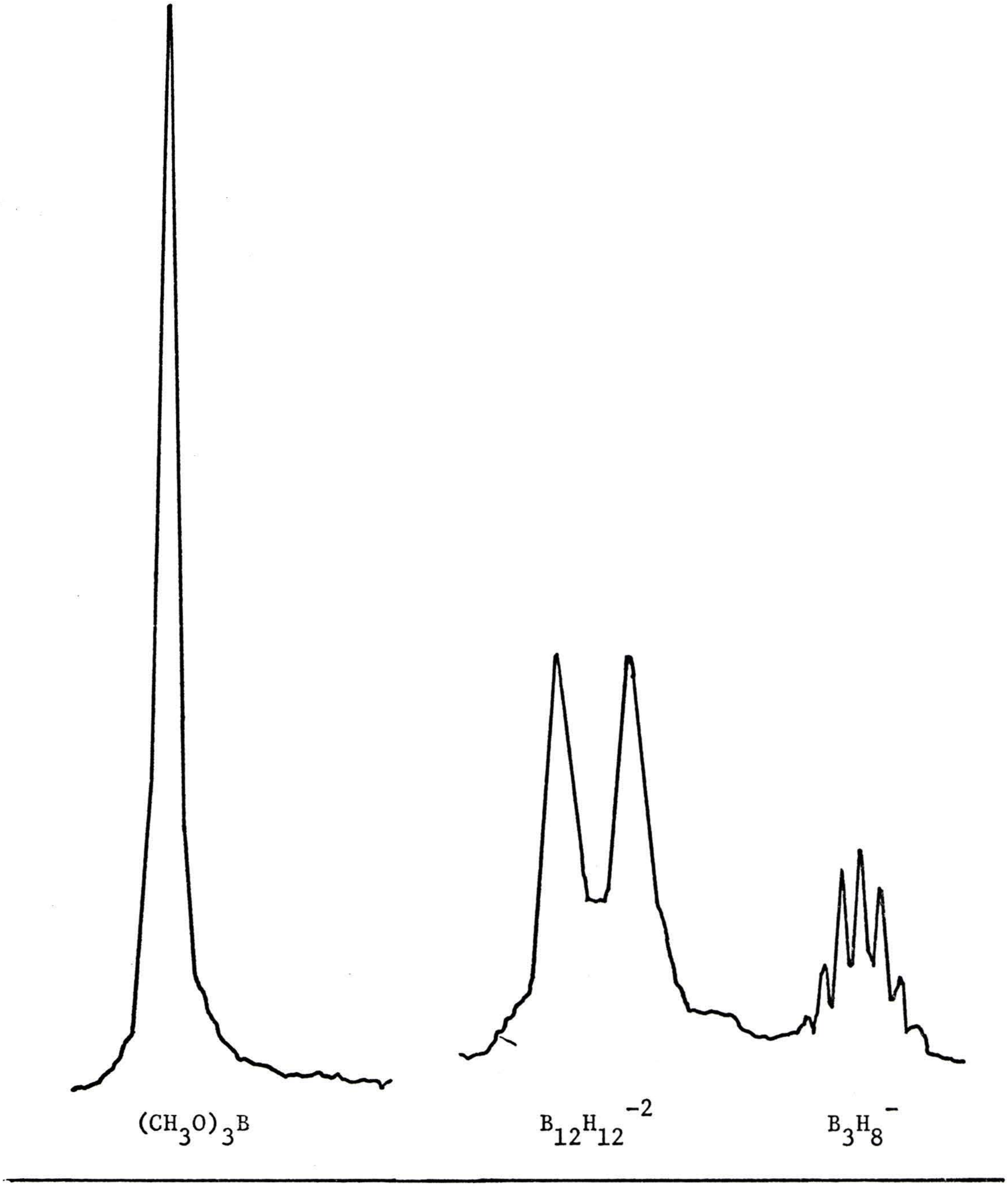


Figure X. B^{11} nmr spectrum of a mixture of tetra-n-butylammonium salt of $B_3H_8^-$ and $B_{12}H_{12}^{-2}$.

CHAPTER VII

SUMMARY

A number of boron cations of the type $(\text{amine})_2BH_2^+$, $(\text{amine}_1)(\text{amine}_2)BH_2^+$, and $(\text{amine})(\text{phenyl-substituted phosphine})BH_2^+$, borane adducts of amines and phenyl-substituted phosphines, and salts of the borane anions, $B_3H_8^-$ and $B_{12}H_{12}^{-2}$, were prepared in this study by synthetically simple and new methods.

The procedure for the preparation of the unsymmetrical boron cations basically involves iodination of an appropriate amine-borane and nucleophilic substitution of the iodide group of the iodoborane adduct by a second amine or a phenyl-substituted phosphine, whereas the synthesis of the symmetrical cation involves the additional reaction step of transamination.

$$2A_1BH_3 + I_2 \rightarrow 2A_1BH_2I + H_2 \qquad A_1 = \text{amine}$$

$$A_1BH_2I + A_2 \rightarrow A_1A_2BH_2^+I^- \qquad A_2 = \text{amine or phosphine}$$

$$A_1A_2BH_2^+I + A_2 \rightarrow (A_2)_2BH_2^+I + A_1 \qquad A_2 = \text{amine}$$

The starting materials used for the preparations of various boron cations were borane adducts of pyridine, trimethylamine, triethylamine, dimethylamine and 4-picoline, sodium borohydride, iodine, various tertiary amines and phenyl-substituted phosphines. In general, reactions were done either at room temperature or at elevated temperatures (65 - 100° range). Benzene was the medium for halogenation of amine-boranes and nucleophilic substitution reactions.

Steric and electronic factors of the substrates and the nucleophiles play an important part in cation formation. Bulky groups around the substitution sites of the substrates and nucleophiles retard the rate of the reactions whereas the basicity of the nucleophiles facilitates the reactions. In spite of the low basicity of phenyl-substituted phosphines, they behave as good nucleophiles; triphenylphosphine is a better nucleophile than triphenylamine under the same experimental conditions.

Physical, chemical and spectral properties of the cations, namely the color of the iodide salts due to charge-transfer, thermal and hydrolytic stability, stability towards oxidizing agents, derivative and transamination chemistry, infrared, uv and nmr spectra, were described in detail.

The new method of syntheses of borane adducts involves an abstraction of hydride from BH_4^- by iodine in the presence of donor bases, amines or phosphines, and this leads to the formation of borane adducts.

$$2BH_4^- + I_2 + 2\text{ base} \rightarrow 2\text{ base}\cdot BH_3 + H_2$$

In the absence of donor bases, the abstraction of hydride from BH_4^- by iodine produces diborane, and when this diborane reacts with excess BH_4^- at 100°, $B_3H_8^-$ is formed.

$$3BH_4^- + I_2 \rightarrow B_3H_8^- + 2H_2 + 2I^-$$

When the reaction is carried out above 100° $B_3H_8^-$ slowly decomposes to give $B_{12}H_{12}^{-2}$.

$$5B_3H_8^- \rightarrow B_{12}H_{12}^{-2} + 3BH_4 + 8H_2$$

Thus, starting with sodium borohydride, iodine and amines or phosphines, a number of borane adducts of amines and phosphines, a number of symmetrical and unsymmetrical dihydroboronium salts, or $B_3H_8^-$ and $B_{12}H_{12}^=$ could be readily prepared by changing the stoichiometry of reactants and the experimental conditions.

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BIOGRAPHICAL SKETCH

Kappakkamannil Chackos Nainan was born April 22, 1936, at Thumpamon, Kerala State, India. In June, 1952, he was graduated from Mar Gregorios High School, Thumpamon. In August, 1956, he received the degree of Bachelor of Science (First Class with Honours) with a major in Chemistry from Bombay University. From the same University, in August, 1958, he received the degree of Master of Science (Second Class) with a major in Inorganic Chemistry. From 1957 until 1958 he was a teaching assistant in the Department of Chemistry, Khalsa College.

In December, 1958, he was employed in Ethiopia (East Africa) to teach science in the Government Secondary School, Debra Berhan. In July, 1961, he left Ethiopia to go to Ghana (West Africa) to teach Chemistry in Ghana National College, Cape Coast, Ghana. After staying for four years in Ghana, in September, 1965, he enrolled in the Graduate School of the University of Florida. From September, 1965, until the present time he has pursued his graduate work toward the degree of Doctor of Philosophy. He worked as a teaching assistant in the Department of Chemistry from September, 1965, to September, 1966, and since then he has held a research assistantship from the National Institutes of Health.

K. C. Nainan is married to the former Omanakutty Verghese and is the father of two children, Charlie Nainan and Meena Mary Nainan.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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