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Chemistry of Boranes. X.[1,2] Borane Cations, $H_2B(base)_2^+$

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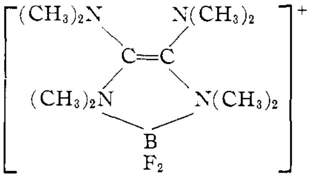
Cationic boron hydride derivatives, $H_2BD_2^+$, where D is a donor molecule of the type NR_3, PR_3, AsR_3, and SR_2, were synthesized in several ways and found to have varied chemical properties depending on the size and basicity of D. The bisamine cations, $H_2B(NR_3)_2^+$, are extremely stable to hydrolytic or oxidative attack, *e.g.*, they are not attacked by concentrated nitric acid. The cations undergo substitution reactions in which one or two B–H hydrogen atoms are replaced to give compounds of the type $Cl_2BD_2^+$, $(FSO_3)_2BD_2^+$, and $HBrBD_2^+$.

Introduction

Although there are many examples of anionic boron-containing species, it was not until Parry and coworkers[3] resolved the structural problem of the "diammoniate of diborane" that the existence of a boron cation, namely, $H_2B(NH_3)_2^+$, was completely established. Since then there have been other reports of related cationic species. Davidson and French[4] prepared $(C_6H_5)_2B(\text{bipyridine})^+ClO_4^-$ by treating a nitromethane solution of chlorodiphenylborane with silver perchlorate, filtering insoluble silver chloride, and treating the solution with 2,2′-bipyridine. More recently, Douglass,[5] in a communication, reported the preparation of $C_6H_5BH(C_5H_5N)_2^+I^-$ by the reaction of $C_6H_5BH_2C_5H_5N$ and iodine in a chloroform–pyridine solution. A similar structure, $I_2B(py)_2^+I^-$, has been suggested by Muetterties for the 2:1 adduct of pyridine and boron triiodide.[6] Nöth and Beyer[7a] have listed in brief notes a number of compounds which they claim have boron cations of the type $X_2B(NH_2R)_2^+$, $X_2B(NHR_2)_2^+$, and $X_2B(NR_3)_2^+$ where X may be H, alkyl, or Cl. However, no details are given in these notes. Nöth and Beyer[7b] also report the salts $H_2B(NH_2R)_2^+Cl^-$ and $H_2B(NC_5H_5)_2^+Cl$ from the reaction of benzoyl chloride and base–borane adducts. Addition of hydrogen chloride to tris(dimethylamino)borane gives the salt $Cl_2B[N(CH_3)_2H]_2^+Cl^-$ which is hydrolytically unstable.[7c] Another boron cation, obtained by reaction of tetrakis(dimethylamino)ethylene and boron trifluoride etherate,[8] is



This cation is sensitive to oxidation and to hydrolysis in strong acid.

We have prepared a general group of cations of formula $H_2BD_2^+$, where D is a tertiary amine, phosphine, arsine, or dialkyl sulfide. Synthesis has been effected by (1) the high temperature reaction of base–boranes with "onium" salts of large anions, (2) the displacement of the base in $H_2BD_2^+$ by a stronger base, and (3) reaction of diborane with a base–borane complex.[2] The chemical properties of the cations, as well as the effectiveness of a particular method of synthesis, are dependent on the size and basicity of the donor molecule, D. Of special interest are the bisamine cations which have remarkable hydrolytic, oxidative, and thermal stability, yet undergo facile substitution reactions at the BH site to yield mono- and disubstituted derivatives.

Discussion

Synthesis.—The most versatile preparation of $H_2BD_2^+$ cations that we have found is the reaction at elevated temperatures of base–borane adducts, $D\cdot BH_3$, with onium salts DH^+X^-. Reaction 1 may be modified

$$D\cdot BH_3 + DH^+X^- \xrightarrow{100-180^\circ} H_2BD_2^+X^- + H_2 \quad (1)$$

by changes in the anion, X^-, as well as by changes in the basicity and size of the donor molecule. The anion must be reasonably stable toward reduction and must be large so that it does not effectively compete with the donor molecule for H_2BD^+. Examples of operable anions are the iodide ion and polyhedral borane ions like $B_{12}H_{12}^{-2}$. Chloride ion successfully competes with donor molecules and reaction 2 prevails.

$$D\cdot BH_3 + DH^+Cl^- \longrightarrow D\cdot BH_2Cl + H_2 + D \quad (2)$$

The size of the donor molecule largely determines whether reaction of $D\cdot BH_3$ and DH^+X^- will yield a cationic boron species. For example, in the case of the bisamine cations, the tertiary amine must have at least one methyl group and the other hydrocarbon groups must not be branched at the α-carbon atom. Thus, diethylmethylamine and N-methylpiperidine are operable whereas N,N-dimethylcyclohexylamine and triethylamine are not. This steric limitation has been utilized to simplify synthesis procedures. It is not necessary to prepare the amineborane and the amine salt; instead, the desired amine is heated with $[(C_2H_5)_3NH]_2B_{12}H_{12}$ and triethylamineborane and the displaced triethylamine is removed by distillation.

$$[(C_2H_5)_3NH]_2B_{12}H_{12} + 2(C_2H_5)_3NBH_3 + 4R_3N \longrightarrow [H_2B(NR_3)_2]_2B_{12}H_{12} + 4(C_2H_5)_3N + 2H_2 \quad (3)$$

With weak donor molecules such as the arsines and sulfides, onium salts are not isolable, and equivalent amounts of the donor species and HX must be employed. This presents a minor complication where the acid of $B_{12}H_{12}^{-2}$ is used. Complete dehydration of $(H_3O)_2B_{12}H_{12}\cdot xH_2O$ cannot be effected, and the water present leads to a side reaction with the base–borane complex, as in reaction 4.

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[2] Synthesis of these cations directly from diborane has been described in an earlier communication: H. C. Miller, N. E. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **85**, 3885 (1963).

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[5] J. E. Douglass, *J. Am. Chem. Soc.*, **84**, 121 (1962).

[6] E. L. Muetterties, *J. Inorg. Nucl. Chem.*, **15**, 182 (1960).

[7] (a) H. Nöth, *Angew. Chem.*, **72**, 638 (1960); H. Nöth and H. Beyer, *ibid.*, **71**, 383 (1959); (b) H. Nöth and H. Beyer, *Ber.*, **93**, 1078, 2551 (1960); (c) H. Nöth and S. Lucas, *ibid.*, **95**, 1505 (1962).

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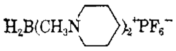
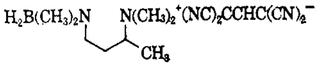
TABLE I

$H_2B(D_2)^+$ SALTS

Compound[a]		% C	% H	% B	% N	% P	% F(Cl)
$[H_2B[N(CH_3)_3]_2{}^+]_2B_{12}H_{12}{}^{-2}$, m.p. 260–270° dec.	Calcd.	35.7	13.0	37.5	13.9		
	Found	35.7	13.0	37.0	13.8		
$H_2B[N(CH_3)_3]_2{}^+PF_6{}^-$, m.p. 200–205° dec.	Calcd.	26.1	7.3	3.9	10.1	11.2	41.3
	Found	26.7	7.5	3.8	10.1	11.2	41.3
$H_2B[N(CH_3)_3]_2{}^+ICl_2{}^-$, yellow-orange crystals, m.p. 150°	Calcd.	21.9	6.1	3.3	8.5	I, 38.6	(21.6)
	Found	22.6	6.1	3.2	8.1	37.7	(21.3)
$H_2B[N(CH_3)_3]_2{}^+AuCl_4{}^-$ bright yellow needles	Calcd.	15.3	4.3	2.3	6.0		(30.2)
	Found	15.6	4.5	1.8	6.0		(33.3)
$[H_2B[N(CH_3)_2C_2H_5]_2{}^+]_2B_{12}H_{12}{}^{-2}$, m.p. 218° dec.	Calcd.	41.8	13.1	32.9	12.2		
	Found	41.4	12.8	32.8	12.2		
$H_2B[N(CH_3)_2C_2H_5]_2{}^+PF_6{}^-$, m.p. 65°	Calcd.	31.6	8.0	3.6	9.2	10.2	37.5
	Found	32.2	8.2	3.2	9.2	9.6	35.7
$H_2B[NCH_3(C_2H_5)_2]_2{}^+PF_6{}^-$, m.p. 135–136°	Calcd.	36.2	8.5	3.3	8.4	9.3	
	Found	36.8	8.7	3.3	8.5	8.6	
, m.p. 108–109°	Calcd.	40.5	7.9		7.9	8.7	
	Found	40.6	7.9		7.8	8.9	
$[H_2BTMED^+]_2B_{12}H_{12}{}^{-2}$, m.p. 340–350° dec.	Calcd.	36.1	12.1	37.8	14.0		
	Found	34.7	12.0	38.0	13.9		
$H_2BTMED^+Cl^-$	Calcd.	43.8	11.0		17.0		(21.6)
	Found	43.2	11.3		16.8		(23.8)
$H_2BTMED^+PF_6{}^-$, m.p. 240–244° dec.	Calcd.	26.3	6.6	4.0	10.2	11.3	41.6
	Found	26.8	6.6	4.4	10.1	11.0	41.8
, m.p. 240–250° dec.	Calcd.	26.5	5.9		10.3	11.4	
	Found	27.1	6.2		10.2	11.0	
	Calcd.	60.4	7.8	3.6	28.2		
	Found	60.9	8.4	3.8	28.2		
light sensitive, pale yellow needles, m.p. 95–96°							
$H_2Bbipy^+PF_6{}^-$ [b]	Calcd.	38.2	3.8	3.5		10.2	36.3
	Found	38.9	3.5	3.5		9.9	35.9
$H_2B[N(CH_3)_3]NC_2H_5(CH_3)_2{}^+PF_6{}^-$ [c]	Calcd.	28.9	7.6		9.6	10.7	
	Found	28.4	7.7		9.7	10.5	
$H_2B[P(CH_3)_3]_2{}^+PF_6{}^-$, m.p. 178°	Calcd.	23.2	6.5			30.0	
	Found	23.6	6.7			28.9	
$[H_2B[P(CH_3)_3]_2{}^+]_2B_{12}H_{12}{}^{-2}$, m.p. 169–173°	Calcd.	30.5	11.0	32.0			
	Found	30.0	11.1	34.0			
, m.p. 240–260° dec.	Calcd.	23.4	5.8	3.5		30.3	37.0
	Found	23.8	6.1	2.7		26.3	37.7
$H_2B[As(CH_3)_3]_2{}^+PF_6{}^-$	Calcd.	18.1	5.1			7.8	
	Found	18.8	5.3			8.4	
$[H_2B[S(CH_3)_2]_2{}^+]_2B_{12}H_{12}{}^{-2}$	Calcd.	23.1	9.0	36.4	S, 30.8		
	Found	21.2	9.3	36.0	21.8		

[a] Except where indicated, all are white or transparent crystalline compounds; abbreviations used are TMED = N,N,N′,N′-tetramethylethylenediamine, bipy = 2,2′-bipyridine. [b] Light sensitive (white → pink) needles, m.p. 170° dec. [c] Light sensitive (white → yellow) needles, m.p. 160–165°

$$3H_2O + (CH_3)_2SBH_3 \longrightarrow (CH_3)_2S + 3H_2 + H_3BO_3 \quad (4)$$

Reaction 1 may be used to prepare cations in which the donor molecules, D, are different. For example, trimethylamineborane and $[C_2H_5N(CH_3)_2H]_2B_{12}H_{12}$ give $H_2B[NC_2H_5(CH_3)_2N(CH_3)_3]^+$.

The second synthetic method comprises the displacement of a donor molecule, D, from a cation, $H_2BD_2{}^+$, by a stronger donor molecule or one capable of chelate function.

$$H_2BD_2{}^+ + 2D' \longrightarrow [H_2BD'_2]^+ + 2D \quad (5)$$

The experimentally observed displacement series of diamines > amines > phosphines, arsines > sulfides roughly parallels the σ donor properties of these compounds.

In the displacement method for cation synthesis, there is a more severe steric limitation than in the "onium" reaction. Trimethylamine and bipyridine displace dimethyl sulfide in $H_2B[S(CH_3)_2]_2{}^+$ but N-methylpiperidine and ethyldimethylamine do not. A congested transition state may thus be inferred for the displacement reaction.

In the third synthetic procedure, diborane is treated with base–borane adducts to give $H_2BD_2{}^+$ salts of $B_{12}H_{12}{}^{-2}$ and $B_{12}H_{11}D^-$. Details will not be described in this article. An initial communication on this subject has appeared,[2] and a full article will be published shortly.

Structure.—Most of the cations (Table I) have been characterized by n.m.r. and infrared spectra. Two active B–H stretching frequencies (symmetrical and antisymmetrical) in the infrared and a B^{11} resonance consisting of a 1 : 2 : 1 triplet, conclusively establishes two B–H bonds per boron atom which are equivalent by n.m.r. criterion. In addition, ion-exchange studies prove that both donor molecules are bound to the boron atom in a cation. Thus, the evidence clearly points to a boron cation in which two hydrogen atoms and the two donor atoms of the base molecules occupy the corners of a tetrahedron.

Optically active boron sites are present in the cations, $HXB[N(CH_3)_3]NC_2H_5(CH_3)_2^+$ and $HXB[(CH_3)_2NCH_2CH_2CHCH_3N(CH_3)_2]^+$, and we are attempting their resolution.

Stability.—The cations have a range of chemical properties depending on the nature of D. Stability to hydrolysis or oxidation, for example, increases with the base strength (from displacement series) of D. Bisaminedihydroboron (1^+) cations[9] have unusual hydrolytic and oxidative stability, and in some ways they are among the more stable boron hydride derivatives. Salts of the bisamine cations have been recovered without noticeable change from concentrated sulfuric, hydrochloric, and nitric acids and from 10% sodium hydroxide even when maintained at temperatures near 100° for prolonged periods. Strong oxidizing reagents, such as salts of gold(III) and silver(I), and 30% hydrogen peroxide are without effect at 100°. Even the potent reagent, aqua regia, does not destroy the cations but, instead, converts them to the monochloro derivatives, $HClB(NR_3)_2^+$. The cations in which D is a tertiary phosphine are stable to boiling acids and strong oxidizing reagents, such as tetrachloroauric acid, but these cations are slowly degraded in hot aqueous base, which suggests attack here may be at the phosphorus atoms. The arsine cation, $H_2B[As(CH_3)_3]_2^+$, is hydrolyzed in boiling water, although sparingly soluble salts can be recrystallized from aqueous solutions by working rapidly. Cations derived from dialkyl sulfides are rapidly destroyed in cold water

$$H_2BD_2^+ + 3H_3O \longrightarrow 2H_2 + H_3BO_3 + 2D + H^+ \quad (6)$$
$$D = SR_2, AsR_3$$

Most of the salts are quite stable thermally. For some of the bisamine salts, thermal decomposition follows a fairly simple course which is characterized by a displacement of an amine by the anion. For example, $H_2B[N(CH_3)_3]_2^+Cl^-$ at 195° yields trimethylamine and trimethylaminechloroborane

$$H_2B[N(CH_3)_3]_2^+Cl^- \longrightarrow H_2BClN(CH_3)_3 + N(CH_3)_3 \quad (7)$$

This pyrolytic route to substituted amineboranes is the subject of another paper.[10]

Properties of the Cations and Their Salts.—The cations are colorless and form crystalline, sparingly water-soluble salts with large anions such as PF_6^-, $AuCl_4^-$, Br_3^-, $B_{10}H_{10}^{-2}$, $B_{12}H_{12}^{-2}$, $Cr(NH_3)_2(SCN)_4^-$, and $(NC)_2CCHC(CN)_2^-$. These salts usually crystallize in anhydrous form. The hexafluorophosphate salts are of practical importance in isolation and characterization, since they have good temperature coefficients of solubility. The relatively light PF_6^- anion does not compress and make insensitive the analytical data pertinent to the cation. Salts of small anions, F^-, Cl^-, NO_3^-, SO_4^{2-}, etc., are very water-soluble and generally crystallize with water of hydration. These salts have been made anhydrous by recrystallization from acetonitrile or chloroform solutions. Some rather unusual solubilities of the anhydrous salts in nonaqueous solvents are of practical importance in purification. The hexafluorophosphate salts are soluble in acetonitrile, and the halide, sulfate, and tetrachloroaurate salts are soluble in halocarbons such as methylene chloride.

Conventional ion-exchange techniques and metathetical reactions have been used to prepare the various salts. In addition, since the bisamine cations are stable to strong aqueous base, the crystalline bases have been obtained by stirring aqueous solutions of the chlorides with silver oxide, filtering, and evaporating. These are strong bases and can be used to prepare salts by neutralization with acids.

Substitution Chemistry.—The bisamine cations are susceptible to substitution reactions in which the BH hydrogen atoms are replaced by atoms or groups. Chlorine and bromine yield monosubstituted derivatives, $HXB(NR_3)_2^+$. Other reagents, such as SF_5Cl, NCl_3, and aqua regia, also effect monochlorination. Iodination does not occur with iodine or iodine monochloride; the latter reagent gives dichloro derivatives at ~80°.

$$H_2B[N(CH_3)_3]_2^+ \xrightarrow{ICl} Cl_2B[N(CH_3)_3]_2^+ \quad (8)$$

By slow passage of fluorine diluted with nitrogen through an aqueous solution of $H_2B[N(CH_3)_3]_2^+$ at 0°, the disubstituted cation, $F_2B[N(CH_3)_3]_2^+$, is formed in about 40% yield. A monofluoro cation was detected but not isolated in pure form. In the presence of chloride ion, a mixed species is formed; the idealized equation is

$$^3/_2F_2 + H_2B[N(CH_3)_3]_2^+ + Cl^- \longrightarrow$$
$$ClFB[N(CH_3)_3]_2^+ + 2H^+ + 3F^- \quad (9)$$

The F^{19} n.m.r. spectrum of the fluorinated product in the latter case showed two different B–F species, probably BClF and BF_2 derivatives. The substitution derivatives exhibit stabilities similar to the parent cations.

Most of the reagents we found effective in cation substitutions are known to produce free radicals and this suggests a free radical mechanism. There is one substitution reaction that surely proceeds through free radical attack, the reaction of $H_2B[N(CH_3)_3]_2PF_6$ with peroxydisulfuryl difluoride

$$H_2B[N(CH_3)_3]_2^+ \xrightarrow{S_2O_6F_2} (FSO_3)_2B[N(CH_3)_3]_2^+ \quad (10)$$

Nuclear Magnetic Resonance Data.—The B^{11} n.m.r. spectra of the bisamine cations are 1:2:1 triplets and those of the monosubstituted derivatives are doublets due to spin coupling of the boron atom with two and one hydrogen atoms, respectively. Table II summarizes the chemical shift and coupling constant data. The B^{11} spectrum of $H_2B[P(CH_3)_3]_2^+$, however, needs some explanation since it is a 0.5/4.4/5.5/4.4/0.5 quintet. This is probably the result of BH and BP coupling constants that are nearly the same within the peak width of 30–50 c.p.s., since the expected spectrum for a AX_4 species with four equivalent atoms each with $I = {}^1/_2$ is a 1/4/6/4/1 quintet.

Experimental

Materials.—Most of the organic bases were commercial reagents and were purified by standard procedures. The amines, $N(CH_3)_2C_2H_5$, $NCH_3(C_2H_5)_2$, and N-methylpiperidine, were prepared from $NH_2C_2H_5$, $NH(C_2H_5)_2$, and piperidine using formaldehyde and formic acid.[11] Trimethylphosphine was synthesized by the reaction of CH_3MgBr and PCl_3 in ethyl ether. The product was separated as the $[(CH_3)_3P\cdot AgI]_4$ complex and regenerated by heating.[12] The vapor pressure was 159 mm. at 0°, which agreed with the literature value of 157 mm. Trimethylarsine was prepared similarly from CH_3MgI and $AsCl_3$ in ether. The trimethylarsine codistilled with ether near 38° and was separated as the $[(CH_3)_3AsAgI]_4$ complex by shaking with aqueous $KAgI_2$. The complex dissolved in the ethereal phase when sufficient ether was present. The ethereal phase was dried, and the ether removed under reduced pressure at 0° to give the white

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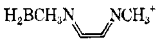
[9] We have named the cations as coordination compounds, choosing what we consider the best alternatives for naming the H^- ligand and indicating charge. See *J. Am. Chem. Soc.*, **82**, 5523 (1960), for the "1957 Report of the Commission on the Nomenclature of Inorganic Chemistry."

[10] N. E. Miller, B. L. Chamberland, and E. L. Muetterties, *Inorg. Chem.*, to be published.

[11] A. T. Clarke, H. B. Gillespie, and S. A. Weisshaus, *J. Am. Chem. Soc.*, **55**, 4571 (1933).

[12] M. Halmann, *Spectrochim. Acta*, **16**, 407 (1960).

TABLE II

Cation	B^{11} spectra[a]			Proton spectra[a]
		Chemical shift	BH coupling constant	Chemical shift
$H_2B[N(CH_3)_3]_2^+$	1:2:1 triplet	14.5 ± 0.4	120 ± 5 c.p.s.	
$H_2B[N(CH_3)_2C_2H_5]_2^+$	1:2:1 triplet	16	110	CH_2 (1/2.5/2.5/1 quartet), −3.70 NCH_3, −3.33 CH_3 (1.3/2/0.7 triplet), −1.82
$H_2B[NCH_3(C_2H_5)_2]_2^+$	Very diffuse 1:2:1 triplet	18	...	CH_2 (1/2.7/3/1.0 quartet), −3.56 NCH_3, −3.20 CH_3 (1.5/2/0.6 triplet), −1.70
$H_2B(TMED)^{+}$[b]	1:2:1 triplet	12.0	111	
 $H_2BCH_3N\quad NCH_3^+$	1:2:1 triplet	17.2	119	
$H_2B[P(CH_3)_3]_2^+$	0.5/4.4/5.5/4.4/0.5 quintet	52	90	
$HBrB[N(CH_3)_3]_2^+$	Sym. doublet	12.2	134	
$HClB[N(CH_3)_3]_2^+$	Sym. doublet	17.3	134	

[a] Of water solution of the chloride salts; proton chemical shifts are in p.p.m. from external 5% solution of tetramethylsilane in CCl_4, and B^{11} chemical shifts are in p.p.m. from external trimethyl borate. [b] TMED = N,N,N′,N′-tetramethylethylenediamine.

solid complex, which was then heated to 90° to liberate trimethylarsine in 40% yield. Purification was effected by drying over calcium hydride and then distilling. The vapor pressure of the purified product was 100 mm. at 0°.

$TMED \cdot 2BH_3$, white crystals from benzene, m.p. 182.5–184°, was prepared by allowing a 1,2-dimethoxyethane solution of $(CH_3)_3NBH_3$ and excess TMED (N,N,N′,N′-tetramethylethylenediamine) to evaporate slowly. $(C_2H_5)_3NBH_3$ was prepared by passing diborane into triethylamine at 15–25°; the resulting adduct was distilled under reduced pressure (about 20 mm.). The preparations of $[(C_2H_5)_3NH]_2B_{12}H_{12}$ and $Na_2B_{12}H_{12}$ are described in paper VIII.[13] For analytical procedures see paper I of this series.[14]

Synthesis of Cations.—Synthesis of bisbasedihydroboron cations by the "onium" salt or displacement reactions are illustrated for representative bases. Table I lists all the cations prepared.

$[H_2B[N(CH_3)_3]_2^+]_2B_{12}H_{12}^{-2}$.—A mixture of 4 g. (15.3 mmoles) of $[(CH_3)_3NH]_2^+B_{12}H_{12}^{-2}$ and 3 g. (41 mmoles) of $(CH_3)_3NBH_3$ was heated in a 100-ml. stainless steel pressure vessel at 175° for 10 hr. with agitation. After cooling, the gaseous product was introduced into a vacuum line and found to be hydrogen (12 mmoles). The remaining white solid, 7.2 g., was recrystallized once from hot water and again from aqueous base to destroy trimethylammonium ion to give 1.55 g. (3.8 mmoles, yield 24%) of colorless crystals.

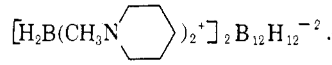
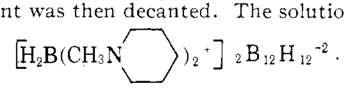
Anal. Calcd. for $[H_2B[N(CH_3)_3]_2^+]_2B_{12}H_{12}^{-2}$: C, 35.7; H, 13.0; N, 13.8; B, 37.5. Found: C, 35.7; H, 13.0; N, 13.8; B, 37.0.

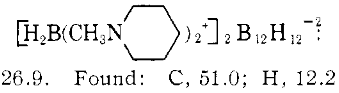
$H_2B[N(CH_3)_3]_2^+I^-$.—A 100-ml. heavy-walled glass tube was charged with 2.3 g. (31.5 mmoles) of $(CH_3)_3NBH_3$ and 6 g. (32 mmoles) of $(CH_3)_3NH^+I^-$ (prepared from $(CH_3)_3N$ and aqueous HI; recrystallized from CH_3OH) and was heated at 100° for 12 hr. and then at 175° for 8 hr. The reaction tube was connected to a vacuum line, cooled to −196°, and opened. The gases were passed through a −196° trap to a calibrated volume. The noncondensable gas, chiefly hydrogen, amounted to 29 mmoles. The tube was warmed to 50–90° and evacuated to leave 7.8 g. of white residue. This residue was recrystallized from ethanol to give colorless needles. A small amount of $(CH_3)_4NI$ was removed in an initial, less-soluble fraction.

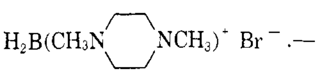
Anal. Calcd. for $H_2B[N(CH_3)_3]_2^+I^-$: C, 27.9; H, 7.8; N, 10.9; I, 49.2. Found: C, 27.5; H, 7.7; N, 10.9; I, 50.6.

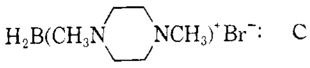
$[H_2B(TMED)^+]_2B_{12}H_{12}^{-2}$.—A 100-ml. stainless steel pressure vessel was charged with $TMED \cdot 2BH_3$ (2.2 g., 15.4 mmoles) and $TMED \cdot 2H^+B_{12}H_{12}^{-2}$ (4.0 g., 15.3 mmoles) and then evacuated. The mixture was heated with agitation for 10 hr. at 180°, cooled to room temperature, and then vented through a −196° trap into a calibrated volume. Noncondensable gases amounted to 31 mmoles. The nonvolatile, white, solid product in the reactor was recrystallized from water to give $[H_2B(TMED)]_2B_{12}H_{12}$ (4.2 g., 69% yield).

Anal. Calcd. for $[H_2B(TMED)]_2B_{12}H_{12}$: C, 36.1; H, 12.1; N, 14.0; B, 37.8. Found: C, 35.8; H, 12.0; N, 13.9; B, 38.0. The carbon values were not reproducible and varied from 34.5 to 35.8 suggesting incomplete combustion.

 $[H_2B(CH_3N\quad)_2^+]_2B_{12}H_{12}^{-2}$.—A 200-ml. flask equipped with a magnetic stirring bar was charged with 8.7 g. (0.025 mole) of $[(C_2H_5)_3NH]_2B_{12}H_{12}$, 5.8 g. (0.05 mole) of $(C_2H_5)_3NBH_3$, 10 g. (0.10 mole) of N-methylpiperidine, and about 40 ml. of *n*-decane. A 24 in. packed column (1/8 in. glass helices) was attached, and the flask was heated to 140°. The fraction boiling up to 90° was collected (6 ml.). Then 8 ml. of methylcyclohexane was added, and an additional 6-ml. fraction boiling at ~90° was obtained. The reaction temperature was raised to 174° and stirring was continued for several hours until 1.2 l. of gas had evolved. The solid in the reaction flask was separated by filtration and washed with ether. This product was dissolved in boiling water which was first acidified with HCl (to destroy R_3NBH_3) and then made basic with 20% NaOH (to destroy R_3NH^+); a small amount of insoluble oil present was then decanted. The solution on cooling yielded 2.8 g. of  $[H_2B(CH_3N\quad)_2^+]_2B_{12}H_{12}^{-2}$. The yield was 20% based on N-methylpiperidine charged. Recrystallization from hot water gave white crystals, m.p. 212–216°

Anal. Calcd. for  $[H_2B(CH_3N\quad)_2^+]_2B_{12}H_{12}^{-2}$: C, 51.2; H, 12.2; N, 9.9; B, 26.9. Found: C, 51.0; H, 12.2; N, 9.7; B, 27.3.

 $H_2B(CH_3N\quad NCH_3)^+Br^-$.—A 100-ml. flask, purged with nitrogen, was charged with $(CH_3)_2SBH_3$ (9.7 g., 0.13 mole), $(CH_3)_2S$ (10 g., 0.16 mole), and hydrogen bromide (0.13 mole). After the initial heat of reaction, the flask was evacuated to remove unreacted $(CH_3)_2SBH_3$ and $(CH_3)_2S$. The oily product was extremely water sensitive, and its infrared spectrum was poorly defined. A solution of the product in dichloromethane was treated with excess N,N′-dimethylpiperazine (heat evolved) and then the solution was evaporated. The solid was recrystallized from acetone–acetonitrile to give white crystals, 0.35 g.

Anal. Calcd. for  $H_2B(CH_3N\quad NCH_3)^+Br^-$: C, 34.8; H, 7.8; N, 13.5; B, 5.2; Br, 38.6. Found: C, 35.1; H, 7.9; N, 13.4; B, 5.3; Br, 39.6.

H_2BTMED^+ by Displacement.—A 100-ml. stainless steel pressure vessel charged with TMED (3 g., 26 mmoles) and $H_2B[N(CH_3)_3]_2B_{12}H_{12}$ (5 g., 12 mmoles) was heated with agitation for 10 hr. at 180°. The reactor was connected to a vacuum line, and the volatile gases were introduced into a calibrated volume through a −196° U-trap. The noncondensable gas was hydrogen, 19.5 mmoles. There was 5.4 g. of nonvolatile white solid remaining in the reactor. It was chiefly $(H_2BTMED)_2B_{12}H_{12}$ as judged from its infrared spectrum (which also showed some NH absorption). A portion was dissolved in hot water and passed through an Amberlite IRA-400 (chloride form) column. The effluent was concentrated and treated with NH_4PF_6. The resulting precipitate was identified as $H_2BTMED^+PF_6^-$ by analysis (Table I).

$[H_2BNC_2H_5(CH_3)_2N(CH_3)_3^+]_2B_{12}H_{12}^{-2}$.—A 2.1-g. sample of $[C_2H_5N(CH_3)_2H]_2^+B_{12}H_{12}$ (7.3 mmoles) and 1 g. of $(CH_3)_3NBH_3$

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[13] E. L. Muetterties, J. H. Balthis, Y. T. Chia, W. H. Knoth, and H. C. Miller, *Inorg. Chem.*, **3**, 444 (1964).

[14] V. D. Aftandilian, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **83**, 2471 (1961).

(14 mmoles) were charged in a small round-bottom flask with 10 ml. of *n*-decane. The mixture was stirred under nitrogen and heated by an oil bath held at 180–190°. After 2 hr., 3.7 l. of gas had evolved, and a solid phase separated. The solid product was separated by filtration, crushed, and washed with ether. A solution of the solid in water was passed through an ion-exchange column (strong base resin in the chloride form). The effluent was treated with NH_4PF_6, precipitating a crystalline solid. The solid was recrystallized from water to give 0.9 g. of colorless, light-sensitive crystals, m.p. 160–165°. The infrared spectrum was unique and distinctly different from those of $H_2B[N(CH_3)_3]_2^+PF_6^-$ and $H_2B[N(CH_3)_2C_2H_5]_2^+PF_6^-$. Analysis is given in Table I.

$[H_2B[P(CH_3)_3]_2^+]_2B_{12}H_{12}^{-2}$.—Trimethylphosphine (2.9 g., 38 mmoles) was condensed in a 100-ml. stainless steel pressure vessel and then a reservoir containing 38.5 mmoles of diborane was opened to the vessel which was cooled to −78°. The reactor was brought to 0° and evacuated to remove excess diborane. After filling with dry argon, the reactor was charged with $[(CH_3)_3NH]_2B_{12}H_{12}$ (5 g., 19.1 mmoles) and then evacuated at −78°. The vessel was heated at 180° with agitation for 10 hr. The volatile product was removed by distillation at reduced pressure. The nonvolatile solid was recrystallized from water to yield 1.4 g. of solid A and a clear filtrate. The filtrate was made basic, treated with NH_4PF_6, and the precipitate was recrystallized from hot water.

Anal. Calcd. for $H_2B[P(CH_3)_3]_2^+PF_6^-$: C, 23.3; H, 6.5; P, 30.0; B, 3.5. Found: C, 23.7; H, 6.8; P, 26.5; B, 3.3.

The sparingly water-soluble product A was recrystallized from dilute base to yield crystalline $[H_2B[P(CH_3)_3]_2^+]_2B_{12}H_{12}^{-2}$ (Table I). The poor agreement of the phosphorus and boron analyses is believed to result from the mutual interference of these two elements in the analyses. Changes in the methods of decomposition of the samples gave scattered data in poor agreement with the theoretical values.

$H_2B[As(CH_3)_3]_2^+PF_6^-$.—A 50-ml. heavy-walled glass tube was charged with trimethylarsine (1.7 g., 14 mmoles) and diborane (2.05 g., 7.4 mmoles). On warming to room temperature, the crystalline adduct $(CH_3)_3AsBH_3$ formed. Excess diborane was removed by evacuation at −78°. Then, hydrogen iodide (13.6 mmoles) and trimethylarsine (12.7 mmoles) were condensed in the tube. The tube was sealed, and the mixture was allowed to stand overnight and then was heated for 1 hr. at 180°. After cooling to −196°, the tube was opened, and the volatile product was removed. The gray, nonvolatile solid product was extracted with benzene to remove unreacted $(CH_3)_3AsBH_3$, and the insoluble fraction was then vacuum dried. This solid was chiefly $H_2B[As(CH_3)_3]_2^+I^-$ with a small amount of $(CH_3)_4As^+I^-$ impurity as judged from the infrared spectrum. An aqueous solution of this salt was passed through an IRA-400 ion-exchange column, in chloride form, and NH_4PF_6 was added to precipitate $H_2B[As(CH_3)_3]_2^+PF_6^-$ which was recrystallized from hot water. Analysis is given in Table I.

Anhydrous Halides.—Dehydration of halide salts was accomplished by suspending the salt in chloroform, adding a little acetone to remove water as an azeotrope, and boiling the suspension. The solid soon completely dissolved, and boiling was continued until most of the water was removed. Then, on cooling, the salt with chloroform of crystallization separated. The chloroform was removed by evacuation under mild heating to leave a fluffy powder which was very hygroscopic.

$H_2B[N(CH_3)_3]_2^+OH^-$.—A 2.0-g. sample of $H_2B[N(CH_3)_3]_2^+Cl\cdot0.44H_2O$ was slurried with 6 g. of silver oxide in water. After filtering and treating the filtrate with a fresh portion of silver oxide, a strongly basic solution was obtained which, on standing, became clear. An aliquot was titrated with standard 0.1 *N* H_2SO_4 to give an equiv. wt. of 174 (calcd., 174). The titration curve was typical of a strong base.

The crystalline base was obtained as colorless prisms by vacuum evaporation of an aqueous solution. The infrared spectrum showed very broad, strong OH stretching and bending absorptions at 3400 and 1550 cm.$^{-1}$, in addition to the characteristic absorptions of $H_2B[N(CH_3)_3]_2^+$.

Fluoride and sulfate salts were obtained by neutralization of the base with the corresponding aqueous acids. The bicarbonate salt was obtained by saturation of the base with carbon dioxide. The carbonate was made by dividing a solution of the base into two equal parts, saturating one with carbon dioxide, and then adding the other half to convert the bicarbonate to the carbonate and evaporating to a white crystalline solid.

Monochlorination.—A solution of $H_2B[N(CH_3)_3]_2^+Cl^-$ (1 g., 6 mmoles) in concentrated nitric acid was boiled until evolution of nitrogen dioxide ceased. About 3 ml. of 5 *M* HCl was then added, and the mixture was boiled again until evolution of nitrogen dioxide ceased. The mixture was cooled, made slightly basic, and treated with concentrated aqueous NH_4PF_6. The precipitate was collected and recrystallized from hot water to yield colorless flakes (1.15 g., 70% yield).

Anal. Calcd. for $HClB[N(CH_3)_3]_2^+PF_6^-$: C, 23.2; H, 6.2; N, 9.0; B, 3.5; P, 10.0; F, 36.7; Cl, 11.4. Found: C, 23.5; H, 6.4; N, 9.0; B, 3.1; P, 9.9; F, 36.3; Cl, 10.7.

Thirteen grams of a 19% solution of nitrogen trichloride in heptane was added slowly to a water–ethanol solution of $H_2B[N(CH_3)_3]_2^+Cl^-$ (2 g., 12 mmoles). Heat was evolved, and the small amount of NH_4Cl which formed was removed by filtration. The filtrate was treated with concentrated aqueous NH_4PF_6. The precipitate was recrystallized twice from hot water to give white crystals (1.89 g., 50% yield) of $HClB[N(CH_3)_3]_2^+PF_6^-$.

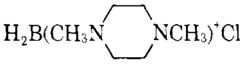
A solution of $H_2B[N(CH_3)_3]_2^+Cl^-$ (1 g., 6 mmoles) in chloroform was irradiated in a quartz vessel with a low-pressure mercury discharge lamp, and SF_5Cl (1 g., 6 mmoles) was slowly introduced through an immersed gas inlet tube. Water was added, and the chloroform was removed by boiling. Addition of concentrated aqueous NH_4PF_6 precipitated $HClB[N(CH_3)_3]_2^+PF_6^-$ (0.6 g., 2 mmoles) which was identified by its infrared spectrum.

Dichlorination.—Three grams (18 mmoles) of $H_2B[N(CH_3)_3]_2^+Cl^-$ was slowly added to 15 ml. of iodine monochloride. After the initial exothermic reaction subsided, the mixture was heated at 85° for 1 hr. The mixture was extracted with CS_2, leaving a solid product which was dissolved in water and converted to the PF_6^- salt by addition of aqueous NH_4PF_6. The slightly soluble, crystalline product was separated by filtration and recrystallized twice from hot water to give white crystals whose infrared spectrum had no B–H absorption.

Anal. Calcd. for $Cl_2B[N(CH_3)_3]_2^+PF_6^-$: C, 20.9; H, 5.4; P, 9.0; Cl, 20.5. Found: C, 21.9; H, 5.5; P, 9.1; Cl, 20.8.

Monobromination.—An aqueous solution of $H_2B[N(CH_3)_3]_2^+Cl^-$ (2 g., 12 mmoles) was treated with liquid bromine until there was an obvious excess of bromine present. An oily scum appeared on addition of bromine, probably due to a poorly soluble salt of $H_2B[N(CH_3)_3]_2^+$ and an interhalogen anion. The mixture was boiled to expel excess bromine, and the resulting solution was passed through an ion-exchange column in the chloride form. The effluent was treated with a solution of NH_4PF_6, and the resulting precipitate was collected and twice recrystallized from hot water to yield 1.70 g. (40%) of white crystals, m.p. 192°.

Anal. Calcd. for $HBrB[N(CH_3)_3]_2^+PF_6^-$: C, 20.3; H, 5.4; B, 3.0; N, 7.9; P, 8.7; Br, 22.5; F, 32.1. Found: C, 20.5; H, 5.8; B, 2.6; N, 7.9; P, 8.8; Br, 22.7; F, 32.0.

A 5.7-mmole sample of  $H_2B(CH_3N(CH_2CH_2)_2NCH_3)^+Cl^-$ was dissolved in water and treated with bromine until the solution was slightly colored. Concentrated aqueous NH_4PF_6 was added, and the resulting precipitate was collected and recrystallized from hot water to give 1.1 g. (55%) of white crystals, m.p. 245–248° dec.

Anal. Calcd. for $HBrBCH_3N(CH_2CH_2)_2NCH_3^+PF_6^-$: C, 20.5; H, 4.3; P, 8.8; Br, 22.8. Found: C, 21.3; H, 4.7; P, 8.8; Br, 22.1.

Fluorination.—A 20-ml. sample of 0.8 *M* $H_2B[N(CH_3)_3]_2^+OH^-$ was neutralized with aqueous hydrogen fluoride in a polyethylene beaker cooled to 0°. A 1:1 mixture of fluorine and nitrogen was passed into the solution (*ca* 3 l./hr.). Aliquots were removed at intervals, treated with NH_4PF_6, and the infrared spectrum of the salt was checked. Fluorination was continued for a total of 98 min., at which time the B–H absorption in the infrared spectrum had disappeared. The solution was neutralized and treated with NH_4PF_6. The precipitate was recrystallized from hot water to give 2.0 g. (37%) of white needles, m.p. 174–176°.

Anal. Calcd. for $F_2B[N(CH_3)_3]_2^+PF_6^-$: C, 23.1; H, 5.8; N, 9.0; P, 9.9; F, 48.7. Found: C, 23.5; H, 6.4; N, 9.0; P, 9.8; F, 47.7.

The F^{19} n.m.r. spectrum of the PF_6^- salt in acetonitrile consists of a quadruplet due to the cation (δ_{BF} = 37 c.p.s.) and a doublet due to PF_6^-.

A 10-ml. portion of 0.8 *M* aqueous $H_2B[N(CH_3)_3]_2^+OH^-$ was neutralized with aqueous hydrogen fluoride and the solution was fluorinated as described. Fluorination was continued for 40 min., at which time the infrared spectra of aliquots had reached a transition point and remained constant for 10 min. The most instructive changes in the infrared were the collapse of the B–H doublet to a weak singlet (with shoulder), complete disappearance of the 1000 cm.$^{-1}$ band, and the appearance of a more or less symmetrical triplet centered at 1180 cm.$^{-1}$. The reaction solution was then neutralized with 20% NaOH and filtered, and the filtrate was treated with concentrated aqueous NH_4PF_6. The precipitate was recrystallized from hot water to yield white crystals, m.p. 159–160°.

Anal. Calcd. for $HFB[N(CH_3)_3]_2^+PF_6^-$: C, 24.5; H, 6.5; N, 9.5; F, 45.2; P, 10.5. Found: C, 24.3; H, 6.5; N, 9.3; F, 45.6; P, 10.1.

This product was a mixture as shown by its F^{19} n.m.r. spectrum which consisted of a quartet due to $F_2B[N(CH_3)_3]_2^+$ and an unresolved multiplet centered at 117 p.p.m. which was probably due to $HBF[N(CH_3)_3]_2^+$ in which both BF and HF splitting are to be expected.

Fluorination–Chlorination.—An aqueous solution of $H_2B[N(CH_3)_3]_2^+Cl^-$ (1.5 g., 9 mmole) was stirred and a 1:3 mixture of F_2 and N_2 was passed through the solution for 1.5 hr. A solution of NH_4PF_6 was added, and the precipitate was twice recrystallized from water to yield white needles, which analyzed as a 9:1 mixture of $FClB[N(CH_3)_3]_2^+PF_6^-$ and $F_2B[N(CH_3)_3]_2^+PF_6^-$.

Anal. Calcd. for $0.9FClB[N(CH_3)_3]_2^+PF_6^-$–$0.1F_2B[N(CH_3)_3]_2^+PF_6^-$: C, 22.0; H, 5.6; B, 3.2; P, 9.5; F, 41.3; Cl, 9.8. Found: C, 22.8; H, 5.8; B, 3.5; P, 9.5; F, 41.4; Cl, 9.4.

Reaction with $S_2O_6F_2$.—A 1-g. portion (3.6 mmoles) of $H_2B[N(CH_3)_3]_2^+PF_6^-$ was suspended in hexafluoropropene cyclic dimer containing excess $S_2O_6F_2$. The slurry was stirred at room temperature for 3 hr. The mixture turned dark, and a gummy material appeared which gradually formed a crystalline slurry. This mixture was added to water and filtered. The filtrate was treated with NH_4PF_6 which precipitated 450 mg. of a crystalline solid which was recrystallized from water to give transparent rectangular prisms, m.p. 222–223°.

Anal. Calcd. for $(FSO_3)_2B[N(CH_3)_3]_2^+PF_6^-$: C, 15.3; H, 3.8; N, 5.9; P, 6.6; S, 13.6; F, 32.2. Found: C, 15.7; H, 4.0; N, 5.9; P, 6.7; S, 13.7; F, 31.6.

Infrared Spectra.—The infrared spectra of Nujol mulls of the dihydrobisbase boron (1+) salts all have doublet B–H absorption near 2500 cm.$^{-1}$, which collapses to a lower intensity singlet on monosubstitution. The B–H doublet is nearly symmetrical for bisarsine or biphosphine cations, but is asymmetrical with a less intense longer wave length peak for bisamine cations. The shape and position of the doublet is not changed greatly when obtained for solutions of the cations. Two B–H stretching vibrations, symmetrical and antisymmetrical, as well as a symmetrical deformation vibration are expected for a BH_2 grouping. The bending mode of the BH_2 group usually is found in the 1100–1200 cm.$^{-1}$ region,[15] but the spectra of the bisamine cations are complex in this region, and no assignments can be made. Bands at 1110, 1100, and a doublet at 1110–1095 cm.$^{-1}$ for $H_2B[As(CH_3)_3]_2^+$, $H_2B[P(CH_3)_3]_2^+$, and $H_2BP(CH_3)_2CH_2CH_2P(CH_3)_2^+$ respectively, may be the BH_2 bending deformations. Rather strong, somewhat broad bands in the 725 to 900 cm.$^{-1}$ region observed for most bisamine cations may be due to B–N stretching or a combination of it with another mode.

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(15) R. C. Taylor, D. R. Schutz, and A. R. Emery, ref. 3, observe the bending at 1210 cm.$^{-1}$ in $H_2B(NH_3)_2^+$; J. Douglass, ref. 5, reports the bending mode of $H_2B(C_6H_5)(C_5H_5N)^+$ at 1160 cm.$^{-1}$; and W. C. Price, *J. Chem. Phys.*, **17**, 1044 (1949), determined the in-phase bending for B_2H_6 and $Al(BH_4)_3$ to be at 1180 and 1156 cm.$^{-1}$, respectively.