of B_2H_6 reacting. If we assume that the solid residue of this reaction is initially an ammonia–borane addition compound, then we can write for the idealized stoichiometry

$$B_2H_6 + 4H_3N_3B_3H_2NH_2 \longrightarrow 2B_6N_7H_{11} + \text{addition product} \longrightarrow xH_2 + \text{polymeric substance}$$

The formation of the $NH_3 \cdot BF_3$ addition compound in the reaction with BF_3 complements evidence from the other reactions that a common feature is the elimination of ammonia from two molecules of aminoborazine to form a stable salt with the acid. These results are perhaps not surprising when considered in relation to the analogous aniline–HCl reaction which yields diphenylamine and NH_4Cl.[14]

[14] A. Contardi, *Giorn. Chim. Appl.*, **1**, 11 (1920).

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Synthesis and Properties of Some Bis(ligand)dihydroboron(n+) Salts[1]

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Salts containing bis(ligand)dihydroboron(1+) ions of the type $LL'BH_2^+$, where L and L′ are electron-donating ligands coordinated to boron through different group V or VI elements, including nitrogen, phosphorus, arsenic, and sulfur, have been prepared by displacement of halide ion from a (trialkyl donor)–haloborane adduct by the appropriate neutral ligand. Halide and hexafluorophosphate salts of the compounds have been characterized. The method is quite general for the preparation of a wide variety of boronium ions, as further illustrated by the synthesis of chelated boron(1+) ions and a dinuclear boron(2+) ion from the reaction of N,N,N′,N′-tetramethylethylenediamine with mono- and dihaloborane adducts of trimethylamine.

Introduction

Since Parry and coworkers showed the diammoniate of diborane to be the tetrahydroborate salt of the diamminedihydroboron(1+) ion,[3] numerous examples of the synthesis and characterization of salts containing four-coordinate boron cations have been reported.[4–10] Although most of these have been of the type $L_2BH_2^+$, in which two identical neutral electron donor ligands are coordinated to boron, a few examples of preparations of ions containing two different boron-bonded tertiary amines have been described.[7b,9e] The synthetic method of Nöth and Beyer,[4] involving displacement of halide from a haloamine–borane, has been found to be convenient for the preparation of both types of bis(amine)boronium salts.

We wish to relate the use of a modification of this synthesis for the preparation of a wide variety of four-coordinate boronium ions including those in which the boron atom is coordinated to two different kinds of neutral ligands wherein one (or both) of the ligands is something other than a nitrogen base. Some specific examples of the synthesis of such ions containing boron bonded to tertiary phosphines, arsines, and dimethyl sulfide as well as tertiary amines are described.[1] In each case, the reaction can be regarded as a nucleophilic displacement of halide ion from a donor–haloborane adduct by a second donor (the entering nucleophile). The study of the scope of this type of substitution has been extended to the use of N,N,N′,N′-tetramethylethylenediamine as a nucleophile in the synthesis of chelated boron(1+) ions and a dinuclear divalent boron(2+) ion.[11]

Experimental Section

Where analytical data are not provided with a preparative procedure for a salt, the composition of the cation is confirmed by analysis of the hexafluorophosphate salt reported in Table I.

Materials.—Trimethylamine–borane was obtained from Matheson Coleman and Bell and purified by sublimation *in vacuo*. Triethylphosphine (Strem Chemicals) was used without further purification. Trimethylamine–haloboranes were synthesized by methods similar to those of Nöth and Beyer[4] by allowing tri-

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[2] NDEA Research Fellow, 1966–1969.

[3] (a) S. G. Shore and R. W. Parry, *J. Am. Chem. Soc.*, **77**, 6084 (1955); (b) D. R. Schultz and R. W. Parry, *ibid.*, **80**, 4 (1958); (c) S. G. Shore and R. W. Parry, *ibid.*, **80**, 8, 12 (1958); (d) R. W. Parry and S. G. Shore, *ibid.*, **80**, 15 (1958); (e) S. G. Shore, P. R. Girardot, and R. W. Parry, *ibid.*, **80**, 20 (1958); (f) R. W. Parry, G. Kodama, and D. R. Schultz, *ibid.*, **80**, 24 (1958); (g) R. C. Taylor, D. R. Schultz, and A. R. Emery, *ibid.*, **80**, 27 (1958).

[4] (a) H. Nöth, *Angew. Chem.*, **72**, 638 (1960); (b) H. Nöth and H. Beyer, *Ber.*, **93**, 2251 (1960); (c) H. Nöth, H. Beyer, and H.-J. Vetter, *ibid.*, **97**, 110 (1964).

[5] J. E. Douglass, *J. Am. Chem. Soc.*, **86**, 5431 (1964).

[6] (a) S. G. Shore and K. W. Boddeker, *Inorg. Chem.*, **3**, 914 (1964); (b) S. G. Shore, C. W. Hickam, Jr., and D. Cowles, *J. Am. Chem. Soc.*, **87**, 2755 (1965).

[7] (a) H. C. Miller, N. E. Miller, and E. L. Muetterties, *ibid.*, **85**, 3885 (1963); (b) N. E. Miller and E. L. Muetterties, *ibid.*, **86**, 1033 (1964); (c) E. L. Muetterties, *Pure Appl. Chem.*, **10**, 53 (1965).

[8] P. C. Moews, Jr., and R. W. Parry, *Inorg. Chem.*, **5**, 1552 (1966).

[9] (a) G. E. Ryschkewitsch, *J. Am. Chem. Soc.*, **89**, 3145 (1967); (b) G. E. Ryschkewitsch and J. M. Garrett, *ibid.*, **89**, 4240 (1967); **90**, 7234 (1968); (c) C. W. Makowsky, G. L. Galloway, and G. E. Ryschkewitsch, *Inorg. Chem.*, **6**, 1972 (1967); (d) K. C. Nainan and G. E. Ryschkewitsch, *ibid.*, **7**, 1316 (1968); (e) K. C. Nainan and G. E. Ryschkewitsch, *J. Am. Chem. Soc.*, **91**, 330 (1969).

[10] M. Inoue and G. Kodama, *Inorg. Chem.*, **7**, 430 (1968).

[11] The preparation of this dinuclear ion by another method as well as the synthesis of other unsymmetrical boron(1+) and (2+) ions by similar displacement reactions has been recently reported: N. E. Miller, D. L. Reznicek, R. J. Rowatt, and K. R. Lundberg, *ibid.*, **8**, 862 (1969).

TABLE I

ANALYTICAL DATA FOR HEXAFLUOROPHOSPHATE SALTS

		Analyses, %					
		Calcd			Found		
Cation	Mp, °C	C	N	H	C	N	H
$(CH_3)_3P(CH_3)_3NBH_2^+$ (292.98)	215 dec	24.60	4.78	6.88	24.29	4.63	6.77
$(CH_3)_3As(CH_3)_3NBH_2^+$ (336.93)	142.5 dec	21.39	4.16	5.98	21.13	4.01	5.85
$(CH_3)_3As(C_2H_5)_3PBH_2^+$ (395.98)	80–81	27.30		6.62	27.12		6.68
$(CH_3)_2S(CH_3)_3NBH_2^+$ (279.03)	71–71.5	21.52	5.02	6.14	21.12	5.06	6.19
$TMED[(CH_3)_3NBH_2]_2^{2+}$ (550.01)	213 dec	26.20	10.19	6.96	25.98	10.06	7.13
$TMEDBH_2^+$ (274.00)	230–231 dec	26.30	10.22	6.62	25.99	10.13	6.93

methylamine–borane to react with stoichiometric quantities of iodine or boron tribromide. The reaction with iodine was carried out in refluxing benzene; the product was recovered by flash evaporation and subsequently purified by sublimation *in vacuo* at 50°. Trimethylamine–dibromoborane was recovered by precipitation with petroleum ether and recrystallized from ethanol. Trimethylphosphine, trimethylarsine, and trimethylstibine were synthesized from the reaction of methylmagnesium iodide with the appropriate trichloride in anhydrous ether under nitrogen[7b,12,13] and stored in a high-vacuum apparatus prior to use. Tetrahydrofuran and diethyl ether were purified by previously reported procedures,[14] and benzene was prepared by distillation over sodium. Boron trifluoride–diethyl ether complex (Baker) was distilled *in vacuo* before use. Sodium tetrahydroborate (95% purity) and trimethyl borate were obtained from Ventron Corp. The N,N,N′,N′-tetramethylethylenediamine (TMED) was obtained from Matheson Coleman and Bell and distilled (bp 120–122°).

Trimethylaminetrimethylphosphinedihydroboron(1+) Iodide.—A 100-ml Pyrex tube equipped with a 24/40 standard taper joint containing a constriction was charged with 3.28 g of freshly sublimed trimethylamine–monoiodoborane (16.5 mmol), then attached to the high-vacuum apparatus, and evacuated. A total of 1.25 g of trimethylphosphine (16.4 mmol) was condensed into the tube at −196° along with sufficient argon to generate a pressure of 5 atm at room temperature. The tube was sealed at the constriction then allowed to stand at 25° overnight behind a safety shield in a hood. A white solid product was obtained. The tube was crushed in a 3-in. i.d. pipe and the solid was washed with benzene and dried *in vacuo* to give an off-white powder; yield 3.89 g (86% theory); mp 213° dec. The product becomes yellow on standing at room temperature and appears to decompose rapidly in ethanol at 25°.

Trimethylaminetrimethylarsinedihydroboron(1+) Iodide.—A 4.12-g sample of trimethylamine–monoiodoborane (20.7 mmol) was treated with 2.50 g of trimethylarsine (20.8 mmol) in a pressure tube similar to the method described for preparation of the phosphine derivative. On standing overnight, the mixture was found to contain some residual liquid. This disappeared on heating 1–2 hr at 60°. The crude solid was washed in benzene and dried *in vacuo;* yield (white powder) 6.42 g (97% theory). The compound was recrystallized from lukewarm 95% ethanol; mp 151° dec. *Anal.* Calcd for $(CH_3)_3N(CH_3)_3AsBH_2{}^+I^-$ (318.87): C, 22.60; N, 4.39; H, 6.32. Found: C, 22.33; N, 4.38; H, 6.36.

Triethylphosphine–Borane.—A suspension of 8.45 g of 95% sodium tetrahydroborate (0.212 mol) in 260 ml of tetrahydrofuran was cooled in an ice–water bath, stirred, and treated with a solution of 35 ml (0.27 mol) of boron trifluoride–diethyl ether complex in 100 ml of tetrahydrofuran by dropwise addition over a period of 45 min. After being stirred for another 30 min, this suspension was treated with a solution of 26.1 g (0.22 mol) of triethylphosphine in 70 ml of tetrahydrofuran by dropwise addition (1 hr). The suspension was warmed to room temperature and solids were collected by filtration under nitrogen and washed with fresh tetrahydrofuran. Evaporation of solvent from the filtrate *in vacuo* gave a white crystalline solid. The product was washed with about 150 ml of distilled water and dried *in vacuo;* yield 26.5 g (91.3% theory). *Anal.* Calcd for $(C_2H_5)_3PBH_3$ (131.99): H, 13.75; H (hydridic), 2.29; B, 8.20; P, 23.46. Found: H, 13.79, 13.64; H (hydridic), 2.23, 2.23; B, 8.6, 8.5; P, 23.5, 23.7; mp 50–51°.

Triethylphosphine–Monoiodoborane.—A total of 9.22 g of triethylphosphine–borane (69.9 mmol) was dissolved in anhydrous benzene under a nitrogen atmosphere and 10 g of iodine (39.4 mmol) was added to the stirred solution over a period of 15–20 min. After the mixture had stood under nitrogen overnight, solvent was removed by flash evaporation and the remaining oil was distilled *in vacuo.* The distillate was a clear oil which turned to a white waxy material when the vacuum was replaced by a nitrogen atmosphere; yield 8.47 g (47% theory). *Anal.* Calcd for $(C_2H_5)_3PBH_2I$ (257.89): H (hydridic), 0.78; B, 4.20. Found: H (hydridic), 0.76; B, 4.32. The pK_a of triethylphosphonium ion is 8.68; lit.[15] 8.69; bp 170–174° (5 mm). The product becomes yellow on standing in the atmosphere.

Trimethylarsinetriethylphosphinedihydroboron(1+) Iodide.—By a procedure similar to that described above, 5.00 g of freshly distilled triethylphosphine–monoiodoborane (19.4 mmol) was treated in a Pyrex capsule with 2.42 g of trimethylarsine (20.2 mmol). After standing overnight at room temperature, the capsule contained some liquid which disappeared on heating for 4 hr at 55°. The product was washed in benzene and dried *in vacuo* to give a yellow-white solid which slowly darkened on standing under nitrogen; yield 3.92 g (53% theory). The salt slowly evolves gas in warm water and is rapidly decomposed in 95% ethanol.

Trimethylamine(dimethyl sulfide)dihydroboron(1+) Iodide.—Using a similar procedure, 3.81 g (19.2 mmol) of trimethylamine–monoiodoborane was treated with 1.40 ml (19.2 mmol) of dimethyl sulfide, and the tube sealed and allowed to stand at 25° for 10–12 hr. A small amount of $(CH_3)_2S$ was removed from the mixture and the crude solid product was washed with benzene and dried *in vacuo;* yield 4.45 g (89.0% theory). On standing, the white product turned yellow and the odor of dimethyl sulfide was observed.

Triphenylphosphinetrimethylaminedihydroboron(1+) Iodide.—A total of 4.32 (21.7 mmol) of trimethylamine–monoiodoborane was dissolved in 150 ml of dry benzene and the stirred solution was treated dropwise with 30 ml of a benzene solution containing 5.68 g (21.7 mmol) of triphenylphosphine. The mixture was heated under reflux for 10–12 hr, producing a solid material which subsequently was removed by filtration. Solvent was removed from the filtrate by flash evaporation to give a white solid product; yield 9.53 g (95.3% theory). Recrystallization from ethanol gave white needles. Analysis indicates approximately 1 mol of ethanol per mole of salt; mp 150° dec. *Anal.* Calcd for $(C_6H_5)_3P(CH_3)_3NBH_2I \cdot C_2H_5OH$ (507.20): C, 54.46; N, 2.76; H, 6.36. Found: C, 54.30; N, 2.71; H, 6.29. The salt undergoes decomposition in hot water.

Bis(trimethylaminedihydro)-μ-N,N′-(N,N,N′,N′-tetramethylethylenediamine)diboron(2+) Iodide.—A total of 3.59 g (18.0

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(12) (a) F. G. Mann, A. F. Wells, and D. Purdie, *J. Chem. Soc.*, 1828 (1937); (b) F. G. Mann and A. F. Wells, *ibid.*, 702 (1938).

(13) (a) M. Halman, *Spectrochim. Acta*, **16**, 407 (1960); (b) H. Hibbert, *Ber.*, **39**, 160 (1906).

(14) Tetrahydrofuran should be peroxide free. Explosions on heating tetrahydrofuran with potassium hydroxide have been reported. A warning on the purification of this solvent has been published: *Org. Syn.*, **46**, 105 (1966).

(15) C. A. Streuli, *Anal. Chem.*, **32**, 985 (1960).

Table II

Proton Nmr Spectra

		Rel	Chem shift (δ), ppm			J, cps	
Salt	Signal	intens	DMSO-d_6	CD_3CN	D_2O	DMSO-d_6	CD_3CN
$(CH_3)_3P(CH_3)_3NBH_2{}^+PF_6{}^-$	Sym doublet, $(CH_3)_3P$	1.0	−1.9	−1.9		J_{HP} = 12	14
	Sym doublet, $(CH_3)_3N$	1.0	−3.2	−3.4		J_{PBNCH} = 2	
$(CH_3)_3As(CH_3)_3NBH_2{}^+I^-$	Singlet, $(CH_3)_3As$	1.0			−2.0		
	Singlet, $(CH_3)_3N$	1.0			−3.3		
$(CH_3)_3As(CH_3)_3NBH_2{}^+PF_6{}^-$	Singlet, $(CH_3)_3As$		−1.9	−1.8			
	Singlet, $(CH_3)_3N$		−3.2	−3.1			
$(CH_3)_3As(C_2H_5)_3PBH_2{}^+PF_6{}^-$	Group, $(C_2H_5)_3P$		−1.1 to −1.8	−1.0 to −1.5			
	Singlet, $(CH_3)_3As$		−1.9	−1.7			
	Group, $(C_2H_5)_3P$		−2.0 to −2.4	−1.7 to −2.2			
$(CH_3)_2S(CH_3)_3NBH_2{}^+PF_6{}^-$	Singlet, $(CH_3)_2S$	2.0	−2.4	−2.6			
	Singlet, $(CH_3)_3N$	3.0	−2.9	−2.9			
$(C_6H_5)_3P(CH_3)_3NBH_2{}^+I^-\cdot C_2H_5OH$	Sym triplet, C_2H_5		−1.4			J_{HCCH} = 7	
	Singlet, OH		−2.4				
	Sym doublet, $(CH_3)_3N$	3.0	−3.1			J_{PBNCH} = 2	
	Group, C_2H_5		−3.4 to −3.9				
	Group, $(C_6H_5)_3P$	5.0	−8.0 to −8.4				
$(C_6H_5)_3P(CH_3)_3NBH_2{}^+PF_6{}^-$	Sym doublet, $(CH_3)_2N$	3.0		−2.7		J_{PBNCH}	2
	Group, $(C_6H_5)_3P$	5.2		−7.7 to −8.0			
$TMED[(CH_3)_3NBH_2]_2{}^+(PF_6{}^-)_2$	Singlet, $(CH_3)_3N$	17.2		−2.9			
	Singlet, $(CH_3)_2N$	11.0		−3.0			
	Singlet, CH_2	4.0		−3.6			
$TMEDBH_2{}^+I^-$	Singlet, $(CH_3)_2N$	3.1			−3.4		
	Singlet, CH_2	1.0			−4.0		
$TMEDBH_2{}^+PF_6{}^-$	Singlet, $(CH_3)_2N$	3.1	−3.2				
	Singlet, CH_2	1.0	−3.9				
$TMEDBBrH^+Br^-$	Singlet, $(CH_3)_2N$	3.0			−3.4		
	Singlet, CH_2	1.0			−4.1		

mmol) of trimethylamine–monoiodoborane was mixed with about 2 ml of dry benzene. An approximately equal volume of a benzene solution containing 0.71 g (6.11 mmol) of TMED was added dropwise to the stirred solution of monoiodoborane, resulting in the formation of a white precipitate. The mixture was stirred for 2 hr at 25° and filtered under nitrogen pressure. The crystals were washed in benzene and dried *in vacuo;* yield 2.82 g (89.8% theory); mp 275° dec. The product decomposes in warm ethanol.

N,N,N′,N′-Tetramethylethylenediaminedihydroboron(1+) Iodide.—A total of 3.76 g (18.9 mmol) of trimethylamine–monoiodoborane was added in small portions with stirring to 65 ml of TMED at 60°, resulting in gradual precipitation of a white solid. After standing 18 hr at 60°, the solid was collected by filtration and dried *in vacuo;* yield 3.51 g (72.4% theory). This material was recrystallized from a mixture of dichloromethane, methanol, and benzene to obtain white crystals. No melting was observed up to 360°. *Anal.* Calcd for $TMEDBH_2{}^+I^-$ (255.94): C, 28.16; N, 10.94; H, 7.09. Found: C, 27.88; N, 10.72; H, 7.00.

N,N,N′,N′-Tetramethylethylenediaminebromohydroboron(1+) Bromide.—By a similar procedure, 2.20 g (9.53 mmol) of trimethylamine–dibromoborane was added with stirring to 15 ml of TMED. The mixture was heated to 60–70° for 12 hr, after which a yellow-white solid was collected by filtration. Recrystallization from ethanol gave white crystals; yield 2.15 g (78.5% theory); mp 265–270° dec. *Anal.* Calcd for $TMEDBBrH^+Br^-$ (287.85): C, 25.04; N, 9.73; H, 5.95; Br, 55.52; Br^- (ionic), 27.76. Found: C, 24.86; N, 9.63; H, 5.95; Br, 55.19; Br^- (ionic), 27.00.

Syntheses of trimethylaminetrimethylstibenedihydroboron(1+) iodide and (di-*n*-propyl sulfide)trimethylaminedihydroboron(1+) iodide were attempted by reaction of the appropriate ligand with trimethylamine–monoiodoborane in a glass tube, but proved unsuccessful. In the stibine reaction, both starting materials were recovered unchanged (quantitative recovery of iodoborane by weight). In the sulfide reaction, decomposition was observed on attempted recovery of product. The synthesis of trimethylaminetrimethylphosphinebromohydroboron(1+) bromide was attempted by combining trimethylphosphine and trimethylamine–dibromoborane in a sealed tube. After standing at 50° for 2 days, starting materials were reclaimed.

Synthesis of N-methylmorpholinetriphenylphosphinedihydroboron(1+) iodide by addition of N-methylmorpholine to a benzene solution of triphenylphosphine–monoiodoborane proved unsuccessful even after refluxing for 10–12 hr and triphenylphosphine–monoiodoborane was recovered without change.

Hexafluorophosphate Salts.—Several $PF_6{}^-$ salts were obtained by a method similar to that described by Muetterties and coworkers.[7b] The corresponding halide salts were dissolved in water to give approximately 2–3% aqueous solutions which subsequently were treated with ammonium hexafluorophosphate to precipitate the respective $PF_6{}^-$ salts. These were collected by filtration, washed with water, and dried *in vacuo.* Analytical data are given in Table I.

Spectra.—Infrared spectra were obtained for all compounds on KBr wafers of the respective salts using a Perkin-Elmer Model 237 or a Beckman IR-10 infrared spectrophotometer. A strong singlet was present in the spectrum of $TMEDBBrH^+Br^-$ at 2500 cm^{-1}; all other compounds exhibited a strong doublet in this region. A strong, broad band at 850 cm^{-1} was present in the spectra of all $PF_6{}^-$ derivatives. A strong B–N and/or P–F deformation band appears around 550 cm^{-1}.

Proton (Table II) and ^{11}B (Table III) nmr spectra were obtained using, respectively, a Varian A60-A and a Varian HA-100 nuclear magnetic resonance spectrometer. Proton spectra were taken in acetonitrile-d_3, dimethyl sulfoxide-d_6, or D_2O as a solvent with tetramethylsilane as external standard. The ^{11}B spectra were obtained in acetonitrile with trimethyl borate as external standard.

Conductivity studies on salts containing the TMED ligand were carried out in acetonitrile and water at 25° using an impedance bridge from John Fluke Manufacturing Co., Inc. The cell constant was determined by use of KCl in water and NH_4PF_6 in acetonitrile. Results are given in Table IV.

Discussion

Structural characteristics appear established on the basis of analytical and spectral data and, in the case of

TABLE III

BORON-11 NMR SPECTRA

Salt	Signal	δ, ppm	J, cps
$(CH_3)_3P(CH_3)_3NBH_2{}^+PF_6{}^-$	Overlapping sym triplets	+27.0	$J_{BH} = 110 \pm 2$ $J_{PB} = 86 \pm 2$
$(CH_3)_3As(CH_3)_3NBH_2{}^+PF_6{}^-$	Sym triplet	+25.0	$J_{BH} = 108 \pm 2$
$(CH_3)_3As(C_2H_5)_3PBH_2{}^+PF_6{}^-$	Overlapping sym triplets	+53.0	$J_{BH} = 107 \pm 2$ $J_{PB} = 108 \pm 2$

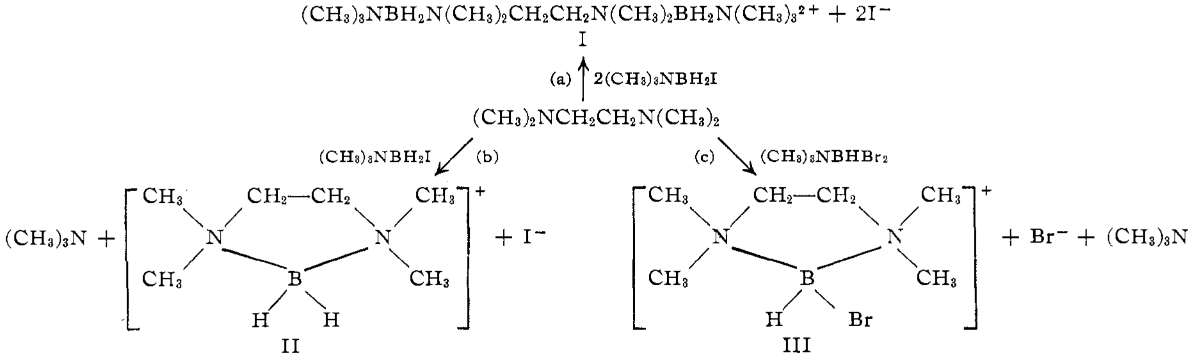
TABLE IV

MOLAR CONDUCTANCE DATA

Salt	Solvent	Molar conductance, ohm^{-1}	Charge type indicated
$[(CH_3)_3NBH_2N(CH_3)_2CH_2CH_2N(CH_3)_2BH_2N(CH_3)_3]^{2+}(PF_6{}^-)_2$	CH_3CN	270	2:1
$[(CH_3)_3NBH_2N(CH_3)_2CH_2CH_2N(CH_3)_2BH_2N(CH_3)_3]^{2+}(I^-)_2$	H_2O	218	2:1
$[(CH_3)_2NCH_2CH_2N(CH_3)_2]BH_2{}^+PF_6{}^-$	CH_3CN	164	1:1
$[(CH_3)_2NCH_2CH_2N(CH_3)_2]BHBr^+Br^-$	H_2O	118	1:1

ions containing the TMED ligand, molar conductance data. For ions of the type $LL'BH_2{}^+$ containing phosphine and amine ligands, long-range coupling (~2 cps) between phosphorus and the protons of the amine-bonded methyl groups was observed in the proton nmr. This interaction was substantiated in the $(CH_3)_3N(CH_3)_3PBH_2{}^+$ ion by phosphorus decoupling. Chemical shifts observed in the ^{11}B spectra of the $(CH_3)_3N(CH_3)_3PBH_2{}^+$ (+27.0) and $(CH_3)_3N(CH_3)_3AsBH_2{}^+$ (+25.0) ions are, as might be expected, intermediate between those reported by Miller and Muetterties[7b] for the bis(trimethylamine)- and bis(trimethylphosphine)dihydroboron(1+) ions (14.5 and 52, respectively, determined using aqueous solutions of chloride salts). Also, the chemical shift observed for the $(CH_3)_3As(CH_3CH_2)_2PBH_2{}^+$ ion (+53) is nearly identical with that of the bis-phosphine derivative.[7b]

The reaction of TMED with excess trimethylamine–monoiodoborane (path a) gives the dinuclear ion (I), whereas the chelated mononuclear complex (II) is obtained by inverse addition with TMED in large excess (path b). This product distribution suggests that in both (a) and (b) the first step may be the nucleophilic displacement of iodide ion by one end of the diamine, following which a second nucleophilic substitution occurs, intermolecular displacement of iodide being favored in the presence of excess iodoborane and intramolecular transamination in excess TMED. In a previous study,[9d] the reaction of substituted pyridines with trimethylamine–monoiodoborane to produce bis(pyridine)dihydroboron(1+) iodide salts had been proposed to proceed by successive displacements of iodide and trimethylamine by pyridine.



If formation of III proceeds by displacement of bromide ion followed by transamination, it represents an interesting case of the reversal in the tendency of bromide ion and trimethylamine to serve as leaving groups from the substrates $(CH_3)_3NBHBr_2$ and $(CH_3)_3NBHBrN(CH_3)_2CH_2CH_2N(CH_3)_2{}^+$. It suggests that bromide ion is the better leaving group in the neutral dibromoborane with trimethylamine the preferred leaving group in the cation where loss of bromide would involve the relatively unfavorable process of removing a negative ion from a positively charged substrate.

Results obtained with the dibromoborane adduct suggest the use of this type of substrate as a convenient route to the synthesis of B-haloboron($n+$) ions. The preparation of a complex containing asymmetric boron has been reported previously.[9b] Displacement in a dihaloborane by an unsymmetrical diamine also may provide a useful means for the preparation of asymmetric boronium ion salts. Further use of this type of displacement reaction also should provide opportunity for wider study of the properties and reactivity of such ions as a function of the nature of boron-bonded ligands.

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Notes

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Preparation and Properties of Pentafluorosulfanyliminosulfur Dichloride, $SF_5N{=}SCl_2$

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Pentafluorosulfanylamine, SF_5NH_2, reacts with active halides such as SF_4 splitting out hydrogen halide.[1] It was of interest to see whether the reaction with sulfur dichloride would yield the simple substitution product $SF_5N{=}S$ or some more complex compound.

Experimental Section

Materials and Equipment.—Sulfur dichloride, obtained from Hooker Chemical Co., was used without further purification. Technical grade silver difluoride and silver oxide were used as obtained from Harshaw Chemical Co. Pentafluorosulfanylamine, SF_5NH_2, was prepared as described by Clifford and Duncan.[2]

Reactions were carried out in Hoke stainless steel cylinders equipped with Model Y327A series needle valves. A copper high-vacuum system equipped with Whitey Model KS41 series control valves and Kel-F traps was used for preparing pentafluorosulfanylamine. A Pyrex glass high-vacuum system was used for handling the reactants and products. Stopcocks and joints were greased with Kel-F No. 90 grease. Swagelok unions afforded vacuum-tight glass-to-metal connections.

Preparation and Properties of Pentafluorosulfanyliminosulfur Dichloride.—Pentafluorosulfanylamine (0.935 g) and SCl_2 in a mole ratio of slightly less than 1:2 were allowed to react in a 30-ml stainless steel cylinder with no solvent at room temperature for 2 days. The principal volatile reaction products were HCl and a pale yellow liquid (1.45 g, 90%) subsequently identified as SF_5NSCl_2. Traces of SiF_4, NSF_3, SOF_2, and some unreacted SCl_2 were recovered, but no unreacted SF_5NH_2. The inside of the reaction cylinder was found to be coated with a yellow solid containing 4.26% sulfur with traces of fluorine.

When equimolar quantities (5.82 mmol) were allowed to react under the same conditions, much NSF_3 was recovered along with SiF_4. Some SF_5NH_2 was also recovered and smaller yields of SF_5NSCl_2 were obtained than with the 1:2 ratio of reactants. The SF_5NSCl_2 was collected in a −45° trap, which allowed the more volatile by-products to pass through. Repeated trap-to-trap distillation was necessary to free the product from SF_5NH_2.

Elemental analysis was difficult because of the great susceptibility of the compound to hydrolysis but yielded the following results. *Anal.* Calcd for SF_5NSCl_2: S, 26.2; N, 5.73; Cl, 29.1. Found: S, 28.1; N, 6.75; Cl, 28.95. Although the liquid reacted very rapidly with mercury making vapor-pressure measurements difficult in the equipment in use, it was determined that the vapor pressure was about 1 cm at room temperature. Vapor density studies indicated the molecular weight to be about 229 whereas SF_5NSCl_2 requires 244. However, mass spectral peaks at *m/e* 210 and 208, in an approximate ratio of 3:1, which are attributable to $S_2F_5NCl^+$ support the assignment of the formula as $S_2F_5NCl_2$. No freezing point was determined but the product remained liquid at −78°.

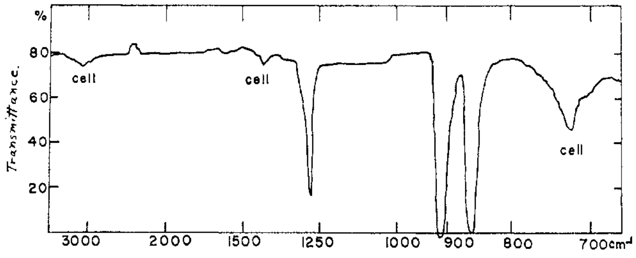

Figure 1.—Infrared absorption curve for SF_5NSCl_2.

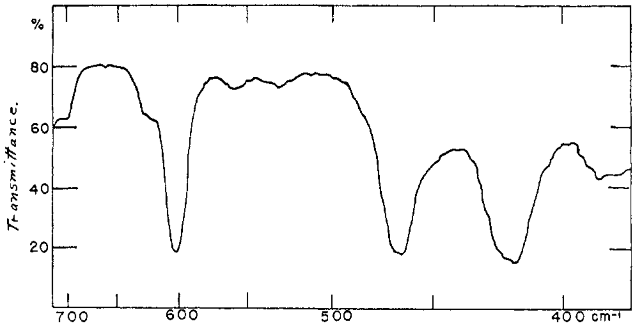

Figure 2.—Infrared absorption curve for SF_5NSCl_2.

The infrared spectrum of SF_5NSCl_2 in the 3000–700-cm^{-1} region was obtained on a Model 137 Perkin-Elmer Infracord spectrophotometer using a 10-cm gas cell with NaCl windows. The spectrum in the 700–375-cm^{-1} region was obtained with a Beckman IR5A spectrophotometer with CsBr optics using a 10-cm cell with KBr windows. Neither the NaCl nor the KBr windows were etched by the sample. The spectrum was found to bear a remarkable similarity to that of SF_5NSF_2 with the characteristic absorption bands at 760 and 714 cm^{-1} for $=SF_2$ being replaced by bands at 475 and 415 cm^{-1}, presumably for $=SCl_2$ group stretching frequencies.

When equimolar amounts of SF_5NH_2 and SCl_2 (6.28 mmol) were allowed to react at room temperature for 3 days in a 75-ml cylinder containing 10 ml of anhydrous diethyl ether, no SF_5NSCl_2 was found. About half of the SF_5NH_2 had separated into NSF_3 and HF. The remainder could not be separated from the ether by trap-to-trap distillation.

Reaction with AgF_2.—When 0.5 g of SF_5NSCl_2 was heated with AgF_2 in a steel cylinder at 100° for 1 hr and then kept at 50° for 24 hr, the principal volatile product was found to be SF_5NSF_2, identified by its infrared spectrum.[1] The yield was nearly quantitative and the reaction is presumed to be

$$SF_5NSCl_2 + AgF_2 \longrightarrow SF_5NSF_2 + AgCl + 0.5Cl_2$$

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[1] A. F. Clifford and J. W. Thompson, *Inorg. Chem.*, **5**, 1424 (1966).

[2] A. F. Clifford and L. C. Duncan, *ibid.*, **5**, 692 (1966).