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Borane Cations with Functionally Substituted Bases

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Monovalent and divalent borane cations derived from two amides, an amino acid ester, and several bases with group IV, V, and VI organometallic substituents have been prepared and characterized. The hydrolytic stability exhibited by these boranes was a sensitive function of structure. Only the cations with dimethylformamide and ethyl N,N-dimethylglycinate had hydrolysis rates sufficiently rapid to be measurable.

Boron cation chemistry has developed rapidly after its late start with the elucidation of the structure of the diammoniate of diborane as $H_2B(NH_3)_2^+BH_4^-$.[2] Now there are many classes of these cations known: borane cations: $H_2B(base)_2^+$,[3a,b] $HRB(base)_2^+$,[3a,b] $H_2B(base)(base')^+$,[3b,c] $HRB(base)(base')^+$,[3c] $(base)BH_2SCH_3BH_2(base)^+$,[3d] $(base)BH_2SCH_3BH_2SCH_3BH_2(base)^+$;[3d] disubstituted boron cations: $R_2B(base)_2^+$;[3b, e–g] and multivalent cations: $BrB(base)_3^{2+}$,[3h] $B(base)_4^{3+}$.[3h]

New synthetic routes to cations have also been uncovered. Probably the most significant advance is the method of iodide displacement from iodoboranes, pioneered by Douglass[4] and modified to an elegant method by Ryschkewitsch[5]

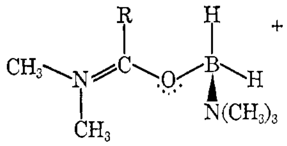
$$(base)BH_2I + base \rightarrow (base)_2BH_2^+,I^- \qquad (1)$$

The borane class of cations is worth special attention because chemistry on intact cations was first demonstrated for them.[3b] Either or both of the hydrogen atoms bonded to boron may be replaced without significantly altering the remarkable kinetic stability of borane cations toward hydrolysis. A yet unexplored area is the chemistry of replacement or transformation of groups other than hydrogen on these species. This intriguing area is being studied here, and we wish to report a number of substituted borane cations with functionality on the base site.

Discussion

Cations derived from bases with carbonyl functionality have been prepared by iodide displacement from amine iodoboranes, R_3NBH_2I. Two amides—N,N-dimethylformamide (DMF) and N,N-dimethylacetamide (DMA)—and ethyl N,N-dimethylglycinate were used to prepare cation salts **1–7** in Table I. Without exception these salts were crystalline white solids of low melting points.

A structural aspect of importance in the cations with DMF and DMA is the linkage to boron. Because of their "available" or unpaired electrons, either nitrogen or oxygen in these amides can be the ligation site. The evidence favors bonding through the oxygen atoms



The ^1H nmr spectra of the cations have two resonances in the amide methyl region near 3.0 ppm (downfield from TMS) which are more structured than those in the parent DMF and DMA but are of similar separations. The nonequivalence of the amide methyls appears to be preserved in the cations, so it is concluded that the planar NCOR configuration still obtains in the cations, implying boron–oxygen links. If the bonding was nitrogen to boron, the amide methyls would be expected to be equivalent unless there was a preferred orientation. There is no reason based on steric arguments, however, to expect such a preferred orientation, at least with cations containing DMF. The steric requirements of DMF are somewhat less than those of dimethylethylamine which is known to form a borane cation, $(CH_3)_3NBH_2N(CH_3)_2C_2H_5^+$, wherein the N-methyl protons are equivalent.[3b] Linkage of a planar amide structure to boron *via* oxygen, therefore, best explains the amide methyl proton resonances.

There are several observations, then, which require comment in view of this assignment: the carbonyl proton (CH) resonance is shifted much less by coordination than the amide methyls in the DMF cations, yet this proton is adjacent to the ligation oxygen site; the "carbonyl" absorption is not essentially shifted on coordination; and the cations are remarkably stable (toward hydrolysis). First, because the CH proton is

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(3) The references listed are not exhaustive, rather representative citations of work on cation classes: (a) H. Nöth and H. Beyer, *Ber.*, **93,** 1078, 2551 (1960); (b) N. E. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, **86,** 1033 (1964); (c) G. E. Ryschkewitsch and J. M. Garrett, *ibid.*, **89,** 5509 (1967); (d) R. J. Rowatt and N. E. Miller, *ibid.*, **89,** 5509 (1967); (e) J. M. Davidson and C. M. French, *Chem. Ind.* (London), 750 (1959); (f) N. Wiberg and J. W. Buchler, *J. Am. Chem. Soc.*, **85,** 244 (1963); (g) B. M. Mikhailov, *et al.*, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2165 (1964); (h) C. W. Makosky, G. L. Galloway, and G. E. Ryschkewitsch, *Inorg. Chem.*, **6,** 1972 (1967).

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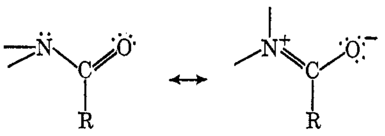
TABLE I

ANALYSES

			% calcd				% found			
		Mp, °C	C	H	N	B (E)	C	H	N	B (E)
1	$(CH_3)_3NBH_2OCHN(CH_3)_2^+,PF_6^-$	107–108	24.8	6.3	9.7	3.7	24.8	6.4	9.6	2.2
2	$(CH_3)_3NBH_2OC(CH_3)N(CH_3)_2^+,PF_6^-$	128–129	27.7	6.6	9.2	3.6	27.7	6.4	9.3	3.6
3	$(CH_3)_3NBH_2N(CH_3)_2CH_2CO_2C_2H_5^+,PF_6^-$	98–99	31.1	6.9	8.0	3.1	31.5	7.3	7.4	1.9
4	$(CH_3)_3SiCH_2(CH_3)_2NBH_2OCHN(CH_3)_2^+,PF_6^-$	62–66	29.8	7.2	7.7		30.1	7.0	7.8	
5	$(CH_3)_3SiCH_2(CH_3)_2NBH_2OC(CH_3)N(CH_3)_2^+,PF_6^-$	88–90	31.9	7.5	7.5	2.9	32.2	8.1	7.9	4.0
6	$(CH_3)_2NCHOBH_2N(CH_3)_2C_2H_4N(CH_3)_2BH_2OCHN(CH_3)_2^{2+},2PF_6^-$	107–109	24.9	5.9	9.7	3.8	25.7	6.1	9.8	5.5
7	$(CH_3)_2NC(CH_3)OBH_2N(CH_3)_2C_2H_4N(CH_3)_2BH_2OC(CH_3)N(CH_3)_2^{2+},2PF_6^-$	151–152	27.7	6.3	9.2	3.6	28.5	6.5	9.2	5.9
8	$(CH_3)_3SiCH_2N(CH_3)_2BH_2N(CH_3)_2C_2H_4N(CH_3)_2BH_2N(CH_3)_2CH_2Si(CH_3)_3^{2+},2PF_6^-$	150–151	31.1	7.8	8.1	3.1	31.7	8.1	8.0	4.7
9	$(CH_3)_3NBH_2N(CH_3)_2C_2H_4N(CH_3)_2BH_2N(CH_3)_3^{2+},2PF_6^-$	179–180°	26.2	7.0	10.2	3.9	26.4	6.7	10.5	3.7
10	$(CH_3)_3NBH_2N(CH_3)_2CH_2SCH_3^+,PF_6^-$	60–62	26.1	6.9	8.7	10.0 (S)	26.6	6.8	9.1	10.7
11	$(CH_3)_3NBH_2P(CH_3)_2CH_2SCH_3^+,PF_6^-$	54–57	24.8	6.5	4.1		24.4	6.4	4.3	
12	$(CH_3)_3NBH_2P(CH_3)_2CH_2Si(CH_3)_3^+,PF_6^-$		29.6	7.8	3.8		29.6	7.1	3.6	
13	$(CH_3)_3NBH_2CH[Si(CH_3)_3]P(CH_3)_3^+,PF_6^-$	155 dec	33.0	8.3		3.0 8.5 (P)	33.1	8.2		3.2 9.9 (P)
14	$(CH_3)_3NBH_2CH[Si(CH_3)_3]As(CH_3)_3^+,PF_6^-$	152–154 dec	28.5	7.1	3.3	14.7 (P) 17.7 (As)	29.2	6.9	3.6	9.6 (P) 15.7 (As)
15	$(CH_3)_3NBH_2N(CH_3)_2CH_2Si(CH_3)_3^+,PF_6^-$	93–94	31.1	8.1	8.1	3.1 8.9 (P)	31.4	7.8	9.1	3.4 10.1 (P)
16	$(CH_3)_3PBH_2N(CH_3)_2CH_2Si(CH_3)_3^+,PF_6^-$	118–123	29.6	7.7	2.8	3.0 17.0 (P)	29.6	7.8	3.7	2.8 16.9 (P)
17	$(CH_3)_3NBH_2CH_2P(C_6H_5)_3^+,PF_6^-$	196–198	53.7	5.7	2.8	2.2 12.5 (P)	52.7	5.7	3.7	3.0 12.4 (P)

already so electron poor, it would not be a sensitive measure of further electron loss at the carbonyl site. In the DMA cations, however, the C–CH_3 is shifted about as much downfield as the amide methyls. The downfield shift of amide methyl peaks of course would be expected from the drift of π-electron density from nitrogen to oxygen upon coordination. After coordination, the amide would be represented as predominantly the b form of resonance structure rather than the a form favored originally. Second, the "carbonyl" absorption may go to predominantly $C{=}N^+$ absorption at a similar frequency in these cations. Finally, since kinetic stability of the cations is dependent on a host of structural parameters, not many of which are now sorted out, it is premature to cite this chemical evidence in confirming or negating a structure hypothesis.



a b

It is reassuring to find that DMA and DMF are interpreted as oxygen-site donors toward various other acids including boron trihalide.[6]

Assuming boron–oxygen bonding in the DMA- and DMF-containing cations, it is possible to assign the N-methyl proton resonances as *cis* and *trans* to the carbonyl. In each of the DMA-cation spectra, the upfield N-methyl resonance is split into an apparent unsymmetrical quartet, coupling constant 1 cps. Similarly, in each of the DMF-cation spectra the upfield N-methyl resonance is split into an unsymmetrical doublet of 1-cps separation. Using the argument[7] of stronger *trans* coupling through the double bond, the upfield peaks are assigned to *cis* amide methyl hydrogens.

The larger coupling constants of N-methyl proton resonances in the cations compared to that of uncomplexed amides ($J \sim 0.6$ cps) are consistent with the structure assignment. The boron–oxygen linkage forces greater planarity in the amide–carbonyl moiety and subsequent larger coupling. Similar increases of coupling with forced planarity of amides in sulfuric acid solution have been observed.[8]

Surprisingly, the cations with oxygen bonds to so weak a base as N,N-dimethylformamide have considerable aqueous stability. There was no observable decomposition in neutral solutions at 60° or in 5 *M* hydrochloric acid to 45° for about 1 hr. In alkaline aqueous solution hydrolysis proceeded at a measurable rate even at room temperature. Third-order kinetics, second order in hydroxide, was determined by following hydrogen evolution. However, the cations derived from the similar base N,N-dimethylacetamide were more stable. $(CH_3)_3NBH_2OC(CH_3)N(CH_3)_2^+$, for example, was degraded less than 5%, based on hydrogen evolution, in 0.9 *N* sodium hydroxide at 38° for 1 hr, and less than 2% in 1 *N* hydrochloric acid at 38° for 1 hr. The marked chemical difference in basic solution with a subtle change in structure was unexpected. A detailed consideration of the difference will be presented along with an evaluation of the hydrolysis kinetic data in a subsequent publication.[9]

Another new variety of borane cations has also been established having a novel combination of structural features: divalency, two boron sites, functionally substituted base, and a four-atomed N,N,N′,N′-

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[7] R. C. Newman and L. B. Young, *J. Phys. Chem.*, **69**, 1777 (1965).

[8] L. LaPlanche and M. T. Rogers, *J. Am. Chem. Soc.*, **86**, 337 (1964).

[9] We thank Mr. D. Herold for these stability observations made in the course of a study supported by a National Science Foundation Undergraduate Research Project grant.

TABLE II

SYNTHESIS DATA

Compd[a]	Method[b]	Solvent	Reagents	Recrystallization conditions for PF_6^- salt, yield[c]
1	A	$CHCl_3$	36 mmol of $(CH_3)_3NBH_2I$, 3.87 mmol of $(CH_3)_2NCHO$	CH_2Cl_2–hexane
2	A	38 ml of $CHCl_3$	11.9 mmol of $(CH_3)_3NBH_2I$, 12.5 mmol of $(CH_3)_2NCOCH_3$	65° water, 54 (R)
3	A	160 ml of $CHCl_3$	4 g of $(CH_3)_3NBH_3$, 7.5 g of I_2, 3.4 g of $(CH_3)_2NCH_2CO_2C_2H_5$	80° water, 10 (C)
4	A	$CHCl_3$	0.435 g of $(CH_3)_3SiCH_2N(CH_3)_2BH_3$, 0.382 g of I_2, 0.23 ml of $(CH_3)_2NCHO$	CH_2Cl_2–hexane
5	A	28 ml of $CHCl_3$	0.463 g of $(CH_3)_3SiCH_2N(CH_3)_2BH_3$, 0.365 g of I_2, 0.35 ml of $(CH_3)_2NCOCH_3$	65° water, 72 (C)
6	A	35 ml of $CHCl_3$	0.508 g of $H_3BN(CH_3)_2C_2H_4N(CH_3)_2BH_3$, 0.897 g of I_2, 0.64 ml of $(CH_3)_2NCHO$	75° water
7	A	28 ml of $CHCl_3$	0.372 g of $H_3BN(CH_3)_2C_2H_4N(CH_3)_2BH_3$, 0.658 g of I_2, 0.2 ml of $(CH_3)_2NCOCH_3$	65° water, 78 (C)
8	A	35 ml of $CHCl_3$	0.485 g of $H_3BN(CH_3)_2C_2H_4N(CH_3)_2BH_3$, 0.858 g of I_2, 1.010 g of $(CH_3)_3SiCH_2N(CH_3)_2$	60° water, 33 (C)
9	A	40 ml of $CHCl_3$	0.663 g of $H_3BN(CH_3)_2C_2H_4N(CH_3)_2BH_3$, 1.188 g of I_2, 10.4 mmol of $(CH_3)_3N$	75° water, 82 (R)
10	A	$CHCl_3$	2.64 mmol of $(CH_3)_3NBH_2I$, 0.277 g of $CH_3SCH_2N(CH_3)_2$	Boiling water, 40 (R)
11	A	15 ml of $CHCl_3$	2.2 mmol of $(CH_3)_3NBH_2I$, 0.32 g of $CH_3SCH_2P(CH_3)_2$	Water wash, 48 (C)
12	A	$CHCl_3$	1.3 mmol of $(CH_3)_3NBH_2I$, 0.39 g of $(CH_3)_3SiCH_2P(CH_3)_2$	Boiling water, 10 (C)
13	B	100 ml of $CHCl_3$	1.866 g of $(CH_3)_3SiCHBH_3P(CH_3)_3$, 2.77 g of I_2, 20 mmol of $N(CH_3)_3$	Boiling water, 96 (C), 44 (R)
14	B	55 ml of $CHCl_3$	5 mmol of $(CH_3)_3SiCHBH_3As(CH_3)_3$, 1.27 g of I_2, 10 mmol of $N(CH_3)_3$	Boiling water, 38 (C)
15	C		0.412 g of $(CH_3)_3NBH_3$, 1.471 g of $(CH_3)_3SiCH_2N(CH_3)_2H^+$, I^-; heated in ampoule 13 hr at 146°	60° water, 20 (R)
16	A	$CHCl_3$	0.332 g of $(CH_3)_3SiCH_2N(CH_3)_2BH_3$, 0.291 g of I_2, 2.27 mmol of $P(CH_3)_3$	60° acidified water, 58 (C)
17	B	50 ml of $CHCl_3$	7.1 mmol of $PH_3PCH_2BH_3$, 6.2 mmol of I_2, 7 mmol of $N(CH_3)_3$	Boiling water, 54 (C)

[a] Compounds numbered **1–17** are identical with those in Table I. [b] Abbreviations for synthesis method are: A, iodide displacement; B, Douglass reaction; C, pyrolysis of oniom salt. [c] Yields are reported in per cent crude (C) or recrystallized (R) product.

TABLE III

^1H NMR DATA[a]

Compd[f]	Solvent	Resonances	Peak intensities	
			Obsd	Calcd
1	CH_2Cl_2	$(CH_3)_3N$, 2.63; $(CH_3)_2CO$, 3.20,[e] 3.32; CHO, 7.95	9:3:2.8:1	9:3:3:1
2	CH_2Cl_2	$(CH_3)_3N$, 2.68; $(CH_3)_2NCO$, 3.22,[b] 3.28; CH_3CO, 2.38	3:2:1	3:2:1
3	CH_2Cl_2	$(CH_3)_3N$, 2.85; $(CH_3)_2N$, 3.05; CH_2, 3.75; $C_2H_5CH_3$, 1.30 (J = 7.5 cps); $C_2H_5CH_2$, 4.24 (J = 7.5 cps)	9.1:5.8:2:3:2	9:6:2:3:2
4	CH_2Cl_2	$(CH_3)_3Si$, 0.28; $SiCH_2$, 2.59; $(CH_3)_2NCSi$, 2.75; $(CH_3)_2NCO$, 3.28,[e] 3.32	9:1.9:6.3:3.0:3.0	9:2:6:3:3
5	CH_2Cl_2	$(CH_3)_3Si$, 0.19; $SiCH_2$, 2.56; $(CH_3)_2NCSi$, 2.72; $(CH_3)_2NCO$, 3.23,[b] 3.32; CH_3CO, 2.39	9:2:6:3:3:3	9:2:6:3:3:3
6	CD_3CN	$(CH_3)_2N$tmen, 2.65; $(CH_3)_2NCO$, 3.13,[e] 3.25;[b] CHO, 8.00; CH_2 probably at 3.25	6:8:1	6:8:1
7	CD_3CN	$(CH_3)_2N$tmen, 2.69; $(CH_3)_2NCO$, 3.07,[b] 3.26;[b] $COCH_3$, 2.32; CH_2, probably at 3.26	6:8:3	6:8:3
8	CD_3CN	$(CH_3)_2N$,[d] 2.88; CH_2CH_2, 3.34; CH_2Si, 2.79; $(CH_3)_3Si$, 0.21	12:2:2:9	12:2:2:9
9	CD_3CN	$(CH_3)_2N$, 2.87; $(CH_3)_3N$, 2.81; CH_2, 3.35	7.5:8:2	6:9:2
10	CH_2Cl_2	$(CH_3)_3N$, 2.85; $(CH_3)_2N$, 2.82; CH_2, 4.15; CH_3S, 2.35		
11	CD_3CN	$(CH_3)_3N$, 2.82; $(CH_3)_2P$, 1.60[c] (J_{PCH} = 11 cps); CH_3S, 2.26[e] (J_{PCSCH} = 1 cps); CH_2, 3.03	9:6.1:2.9:2	9:6:3:2
12	CD_3CN	$(CH_3)_3N$, 2.79; $(CH_3)_2P$,[c] 1.56 (J_{PCH} = 11 cps); CH_2, 1.18 (J_{PCH} = 7 cps); $(CH_3)_3Si$, 0.19		
13	CH_2Cl_2	$(CH_3)_3N$, 2.51; $(CH_3)_3P$[c] (J_{PCH} = 11 cps), 1.72; $(CH_3)_3Si$, 0.20	1:1:1	1:1:1
14	$CHCl_3$	$(CH_3)_3N$, 2.54;[e] $(CH_3)_3As$, 1.70;[e] $(CH_3)_3Si$, 0.13[e]		
15	$CHCl_3$	$(CH_3)_3Si$, 0.20;[e] $(CH_3)_3N$, 2.83;[e] $(CH_3)_2N$, 2.90;[e] CH_2, 2.65[e]	9:7.5:5.2:2	9:9:6:2
16	CH_2Cl_2	$(CH_3)_3Si$, 0.20; $(CH_3)_2N$, 2.85; $(CH_3)_3P$, 1.53[c] (J_{PCH} = 11 cps); CH_2, 2.69[c] (J_{PCH} = 3 cps)	9:6:9:2	9:6:9:2
17	CH_2Cl_2	$(CH_3)_3N$, 2.59; $P(C_6H_5)_3$, 7.68[b,c]	9:13.8	9:15

[a] In ppm downfield from internal tetramethylsilane. Spectra were run on a Varian A-60A nmr spectrometer. [b] Multiplet-structured resonance. [c] Doublet. [d] Two kinds of $(CH_3)_2N$ appear as one peak. [e] Referenced with external 5% TMS. [f] Compound numbering corresponds with that of Table I.

tetramethylethylenediamine (tmen) bridge. Compounds **6–9** have cations of this type. The cation of **9** would be the parent, having two $(CH_3)_3NBH_2-$ moieties separated by a tmen bridge. As expected from their divalency, these cations form salts of rather low or no solubility in moderately polar solvents. Whereas most borane cation salts dissolve readily in methylene chloride and/or chloroform, the divalent cation salts are insoluble in these solvents, but they are soluble in acetonitrile and hot water. In hydrolytic behavior these bis-borane divalent cations resemble their structurally similar monovalent ions. For example, the pseudo-first-order rate for $(CH_3)_2NCHOBH_2N(CH_3)_2C_2H_4N(CH_3)_2BH_2OCHN(CH_3)_2^{2+}$ was almost twice that of $(CH_3)_3NBH_2OCH(CH_3)_2^+$ as expected from collision theory for two active sites on one substrate.

The only cation derived from an amino acid was $(CH_3)_3NBH_2N(CH_3)_2CH_2CO_2C_2H_5^+$. It is much more sensitive to alkaline hydrolysis than the amide-derived cations. Furthermore the hydrolysis rate is independent of hydroxide ion concentration above about 0.3 M, implicating a catalytic role for OH^-.

Another functional substitution of consequence effected on the base portion of cations is that of methylthio groups. Several cations have been made, but only two have been sufficiently purified to report at this time, namely, those in compounds **10** and **11** of Table I. Attempts to transform or replace the thiomethyl group by reaction, for example with hydrogen iodide, led only to $[(CH_3)_3N]_2BH_2^+$.

Some cations with bases bearing trimethylsilyl groups were also prepared, as in compounds **12–16**. The trimethylsilyl groups had little noticeable effect on the thermal and hydrolytic properties of the cations. When α to a tetravalent phosphorus, as in

12 and **13**, the trimethylsilyl group was readily cleaved by alkali. However trimethylsilyl α to tetravalent nitrogen was not attacked even in hot alkali. Thus in their reactivity toward hydroxide, the cations exactly parallel simple quaternary onium salts.[10]

Finally, we report a new type of borane cation having a boron–carbon linkage—which might alternately be viewed as a borane cation with one base site interposed by a methylene bridge. The original Douglass reaction (eq 2) was employed for synthesis, but there is every reason to believe that the Ryschkewitsch modification would also be applicable and probably cleaner.

$$2N(CH_3)_3 + I_2 + (base)BH_3 \rightarrow (base)BH_2N(CH_3)_3^+,I^- + (CH_3)_3NH^+,I^- \quad (2)$$

Again, the general properties of these cations, solubility and thermal and aqueous stability, are similar to those of $H_2B(NR_3)_2^+$ cations. Consistently higher melting points are recorded for salts of the B–C bonded cations than for related cations without the methylene bridge, but it is premature to speculate more on this trend in melting points than to note that it appears to reflect structural parameters of the cations. Compounds **13**, **14**, and **17** have cations with methylene bridges.

For the few functional groups studied so far there is total absence of any kind of interaction between the BH_2 moiety and the substituent. This supports the hope that the range of substitution on the base portion will be limited only by the strength of the boron–base bond. Substitution with very bulky or potent electron-withdrawing substituents close to the B–base bonds would therefore constitute the limiting situation. A narrowly defined maximum value of pK_a for a base which will still give good aqueous stability, say to 60°, is yet unattained, but its determination would be worthwhile.

Experimental Section

Reagent grade solvents were employed. Chloroform and methylene chloride were purified by distillation from phosphorus oxide (P_4O_{10}).

Metathesis of a salt to the hexafluorophosphate was accomplished by adding aqueous saturated ammonium hexafluorophosphate solution to a solution of the salt until precipitation was complete. The precipitated hexafluorophosphate was collected by filtration and recrystallized.

Synthesis details for selected compounds follow. Quantitative data for the preparation of the other compounds of Table I are summarized in Table II. Infrared and ^1H data are collected in Tables III and IV.

Iodide-Displacement Synthesis.—The experimental details for two typical preparations are given below, one for a monovalent and the other for a divalent cation.

TABLE IV

INFRARED DATA[a]

Compd[b]	Absorbance,[c] cm^{-1}
1	2460 m, 2400 w, 2330 w, 1700 s, b, 1350 s, 1260 m, 1210 m, 1170 s, 1145 w, 1120 w, 1070 w, 1025 w, 1000 m, 800 s
2	2450 m, doublet, 2380 w, 2315 w, 1645 s, 1485 m, 1408 m, 1250 w, 1200 m, 1175 s, 1120 m, 990 m, 850 s, b
3	2470 (several shoulders) w, 1735 s, 1420 w, 1390 w, 1230 w, 1200 m, 1100 w, 1030 m, 970 doublet, w, 950 w, 850 s
4	2350 m, 2300 w, 2220 w, 1640 s, b, 1400 m, multiplet, 1330 w, 1300 m, 1270 w, 1220 w, 1200 m, 1185 m, 1160 m, 1120 m, 1100 w, 1085 w, 1015 w, 985 w, 960 m, 940 w, 870 m, doublet, 800 s, b, 700 w, 735 w
5	2460 w, 2430 w, 1640 s, 1420 w, 1315 w, 1250 m, doublet, 1235 w, 1200 m, doublet, 1170 s, 1145 m, 1025 w, doublet, 1000 w, 910 w, 800 s, b
6	2470 w, 2400 w, 1690 s, 1485 m, 1375 m, 1340 s, 1320 m, 1250 w, 1225 w, 1205 w, 1180 m, 1170 s, 1135 m, 1115 w, 1060 w, 1030 w, 1005 w, 990 m, 920 m, 850 s, 800 m
7	2460 m, 1650 s, 1415 m, 1320 w, 1270 w, 1245 w, 1230 w, 1195 m, 1170 s, 1135 m, 1050 w, 1030 w, 1005 m, 980 m, 850 s, b, 800 w
8	2510 w, 1485 m, 1420 w, 1325 w, 1305 w, 1265–1250 m, doublet, 1225 w, 1205 w, 1185 w, 1170 w, 1035 w, 1015–1000 w, doublet, 970 w, 850 s, b
9	2500 w, multiplet, 1500 m, 1480 s, 1425 w, 1410 w, 1290 m, doublet, 1205 m, doublet, 1150 w, 1135 w, 1000 m, 985 m, 940 w, 800 s, b
10	2500 w, b, 2360 w, 1320 w, 1300 w, 1250 s, 1210 s, 1190 w, 1150 w, 1090 s, 1000 m, multiplet, 830 s, b, 750 m
11	2440 m, doublet, 1440 m, doublet, 1310 m, 1260 w, 1170 m, 1140 m, 1090 m, 1030 m, 960 m, 940 m, 850 s
12	2440 w, 2405 w, 1310 m, doublet, 1255 m, 1140 m, b, 1070 m, 1020 m, 955 m, 930 m, 830 s, b
13	2450 w, 2380 m, 2310 w, 2275 w, 1490 m, 1325 w, 1305 m, doublet, 1305 m, triplet, 1215 m, 1175 m, 1125 w, 1110 m, 995 m, doublet, 980 s, 965 m, 840 s, b
14	2360 w, 2300 w, 1490 m, 1255 m, 1210 m, 1175 m, 1100 w, 1020 w, 980 m, 930 m, 850 s, b
15	2475 m, 2350 w, 1450 s, multiplet, 1420 m, 1310 w, 1250 s, multiplet, 1205 m, 1175 m, doublet, 1150 w, 1130 w, 1110 w, 1000 m, 980 m, 850 s, b, 780 w, 765 w, 700 w
16	2450 w, 2400 w, 1475 s, 1435 m, doublet, 1315 w, doublet, 1300 m, 1250 s, 1200 w, 1160 w, 1150 w, 1105 s, 1030 w, 985 m, 965 s, doublet, 850 s, b, 780 w, 770 w
17	2400 m, 2330 w, 1485 m, 1440 s, 1250 w, 1180 s, 1110 s, 980 m, 850 s, 750 m, 725 m, 700 m

[a] Spectra run on a Perkin-Elmer 237B spectrophotometer. [b] Compound numbering corresponds to that of Table I. [c] Samples run as mineral oil mulls. Absorbances masked by mineral oil peaks are not listed. Abbreviations used are: s, strong; m, moderate; w, weak; b, broad.

Preparation of $(CH_3)_3NBH_2OCHN(CH_3)_2^+$.—To a solution of 3.6 mmol of $(CH_3)_3NBH_2I$ in 10 ml of chloroform was added dropwise 0.3 ml (3.87 mmol) of N,N-dimethylformamide with stirring. After 3 hr at room temperature, the solvent was removed under vacuum, leaving a tacky white residue. This residue was dissolved in water, and the water solution was separated from trace amounts of occluded chloroform. The hexafluorophosphate salt was prepared from the water solution and recrystallized from methylene chloride-hexane, giving $(CH_3)_3NBH_2OCHN(CH_3)_2^+,PF_6^-$.

A small sample of the hexafluorophosphate when heated in water to 60° for 20 min was recovered having the same infrared spectrum. Similarly, after treatment in 5 *M* hydrochloric acid at 45°, the salt had almost the same infrared spectrum as initially.

Preparation of $(CH_3)_3NBH_2N(CH_3)_2CH_2CH_2N(CH_3)_2BH_2N(CH_3)^{2+}$.—The iodoborane, $IBH_2N(CH_3)_2CH_2CH_2N(CH_3)_2BH_2I$,

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(10) N. E. Miller, *Inorg. Chem.*, **4**, 1458 (1965).

TABLE V

HYDROLYSIS OF CATIONS[a]

Compd	Conditions[b]	ml of hydrogen mg of compound	Time, sec
$(CH_3)_3NBH_2CH[Si(CH_3)_3]P(CH_3)_3^+,PF_6^-$	$[H_3O^+] = 1.0\ M$	0.02/2.9	3900
	$[OH^-] = 1.0\ M$	0.03/2.8	3900
$(CH_3)_3NBH_2CH[Si(CH_3)_3]As(CH_3)_3^+,PF_6^-$	$[H_3O^+] = 1.0\ M$	0.02/2.9	2000
	$[OH^-] = 1.0\ M$	0.02/2.9	(24 hr)
$(CH_3)_3NBH_2N(CH_3)_2CH_2Si(CH_3)_3^+,PF_6^-$	$[H_3O^+] = 1.0\ M$	0.02/2.4	2800
	$[OH^-] = 1.0\ M$	0.01/3.4	4700
$(CH_3)_3NBH_2CH_2P(C_6H_5)_3^+,PF_6^-$	$[H_3O^+] = 1.0\ M$	0.03/3.9	2000
	$[OH^-] = 1.0\ M$	0.03/3.2	3000

[a] Hydrolyses conducted so that evolved hydrogen was collected and measured in a well-calibrated buret of 5-mm i.d. [b] Temperature for each experiment is 40.0°.

was prepared from 0.6628 g (4.62 mmol) of tmen$(BH_3)_2$ in 10 ml of chloroform by addition of 30 ml of a chloroform solution containing 1.1879 g (4.68 mmol) of iodine. The addition of iodine solution was carried out in three portions interrupted by 1-hr periods of stirring. After the final portion was added, the mixture was stirred overnight, whereupon a two-phased system of a gold-colored liquid and a yellow solid was produced. The solid was only slightly soluble in chloroform and methylene chloride and had a unique infrared spectrum. It was considered to be $IBH_2N(CH_3)_2CH_2CH_2N(CH_3)_2BH_2I$ and was used without further purification or characterization.

A slurry of the above-prepared $IBH_2N(CH_3)_2CH_2CH_2N(CH_3)_2BH_2I$ in chloroform was treated with 10.4 mmol (measured as a gas) of trimethylamine. The yellow liquid phase decolorized immediately upon addition of trimethylamine. The mixture was stirred for about 12 hr at room temperature, during the first 3 hr of which there appeared a large quantity of white precipitate in the mixture. After 4 hr there was no visible change. The white solid was collected by filtration and dried under vacuum. It was considered to be the iodide salt of the divalent bis-borane cation because, on metathesis to the hexafluorophosphate salt, $(CH_3)_3NBH_2N(CH_3)_2CH_2CH_2N(CH_3)_2BH_2N(CH_2)_3^{2+},2PF_6^-$ was obtained in 82% yield (after recrystallization from 75° water). This latter salt was not soluble enough in chloroform or methylene chloride to obtain its nmr spectrum. However, it was soluble in acetonitrile.

The assignment of divalence to the cation was based upon spectral data and the insolubility of its salts in chloroform. Any mixture of monovalent cations, formed by disproportionation, for example, would be apparent in the infrared spectrum since the monovalent species $H_2B(tmen)^+$ and $H_2B[N(CH_3)_3]_2^+$ have well-differentiated spectra. Further support for the divalency was a measured conductivity of 196 mho cm^2/mol for a $10^{-3}\ M$ solution at 25.0°. This is very close to the 200 mho cm^2/mol reported for $BrB(py)_3^{2+},2PF_6^-$.[11] Conductance was measured with a Yellow Springs Instrument Co. Model 31 conductivity bridge using a cell with 0.50 constant. Deionized distilled water was used for preparing the solution.

Douglass Synthesis.—Compounds **13**, **14**, and **17** in Table I were prepared by the method of Douglass.[4] A typical preparation is given in detail below. Data for the other two compounds are in Table II.

Preparation of $(CH_3)_3NBH_2CH[Si(CH_3)_3]As(CH_3)_3^+$.—The ylide $(CH_3)_3AsCHSi(CH_3)_3$ was prepared from 1.223 g (5 mmol) of $(CH_3)_3AsCH_2Si(CH_3)_3^+,Cl^-$ and 2.90 ml (5 mmol) of *n*-butyllithium.[10] A solution of the ylide in pentane was treated with 2.52 mmol of diborane, whereupon a white solid adduct formed. Volatile materials at room temperature were removed under vacuum, and 5 ml of chloroform and 10.8 mmol of trimethylamine were added. On warming, a homogeneous solution resulted, to which was added dropwise a solution of 1.27 g (10.0 mmol) of iodine in 50 ml of chloroform. A white precipitate formed. The mixture was concentrated to half its original volume and filtered; the filtrate was diluted with 2–5 volumes of hexane, whereupon 0.827 g of crude $(CH_3)_3NBH_2CH[Si(CH_3)_3]As(CH_3)_3^+,I^-$ precipitated. A 0.133-g portion of the iodide salt was metathesized to the hexafluorophosphate salt, 0.112 g. Recrystallization from hot water gave 0.106 g of purified material.

Ligand Synthesis. N,N-Dimethyl-N-trimethylsilylmethylamine.—This was prepared from chloromethyltrimethylsilane and dimethylamine by a published method.[12] Because it was difficult to obtain a pure material following the described workup, a different procedure was used. The poorly volatile product from the reaction was dissolved in excess acid and the acidic solution was freed of neutral organic material by ether extraction. The free base was then liberated and purified by distillation.

N,N-Dimethyl-N-methylthiomethylamine, Dimethylaminomethyldimethylphosphine, and P-(Trimethylsilylmethyl)dimethylphosphine.—These ligands were prepared by addition of dimethylamine to chloromethyl methyl sulfide and by reaction of chloromethyldimethylamine and chloromethyl methyl sulfide with lithiodimethylphosphine in tetrahydrofuran. All three are colorless liquids; the sulfide amine boils at 65° (100 mm); the phosphine sulfide boils at 45° (8 mm); and the silyl phosphine has a 25° vapor pressure of 9 mm. Complete characterization data and chemical properties of these ligands are to be given elsewhere.

Hydrolysis Measurements.—The hydrolysis of the cations was followed by monitoring hydrogen evolution of solutions of the cation hexafluorophosphates in potassium chloride solutions adjusted to constant ionic strength ($I = 0.90$). A solution of a 2–10-mg sample in 10.0 ml of medium was stirred at constant temperature, and the evolved hydrogen was measured in a small buret attached to the top of the reaction vessel. Stability data are collected in Table V.

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