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Preparation of Boron Cations by Hydride Ion Abstraction[1]

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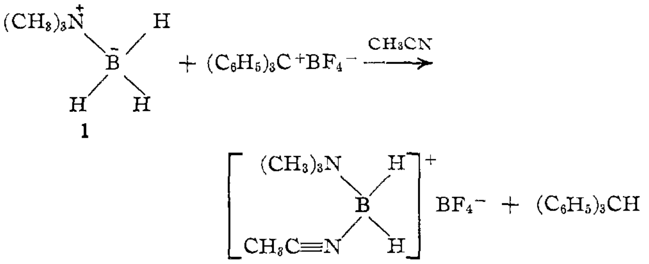
A new method for the preparation of simple boron cations is described. It involves abstraction of hydride ions from B–H-containing compounds by triphenylmethyl fluoroborate, $(C_6H_5)_3CBF_4$. Bis(base)dihydroboron(1+) cations were obtained from simple amine–boranes and from the BH_4^- anion. Some of the properties and reactions which salts containing these cations undergo are described.

During recent years, a relatively large number of papers have appeared which describe the preparation and properties of cationic boron compounds.[3–12] Such widespread interest in compounds of this type prompts us to report our own results with triphenylmethyl (trityl) fluoroborate, whose utility as a reagent for generating boron cations seems to have been overlooked. This reagent has been used extensively[13] in both organic and organometallic chemistry to prepare some remarkably stable cations. This is accomplished by hydride ion removal from the corresponding hydrocarbons and metal–hydrocarbon complexes. A similar approach to boron cations appeared to be feasible.

The compound selected to initiate this study was trimethylamine–borane (**1**) since the negative charge on the boron atom was expected to facilitate removal of the hydride ion. Indeed, it was found that this compound reacted rapidly and smoothly with trityl fluoroborate in acetonitrile solution at room temperature. Furthermore, the boronium salt so formed was easily and conveniently separated from the nonionic organic coproduct, triphenylmethane, which was isolated in quantitative yield by benzene extraction of the evaporated reaction mixture. The boron-containing salt which remained was obtained in 96% yield. In the absence of any added nucleophile, acetonitrile itself, the solvent for the reaction, stabilizes the boronium ion and becomes incorporated in the final product. The infrared spectrum and analytical results are consistent with the assigned composition, acetonitriletrimethylaminedihydroboron(1+) fluoroborate (**2**).



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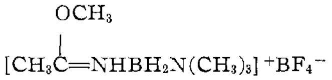
Pyridine–borane (**3**) also reacted rapidly with trityl fluoroborate in acetonitrile solution, even at −55°. In the presence of added pyridine it was converted to bis(pyridine)dihydroboron(1+) fluoroborate (**4**) in 52% yield. The analytical data, infrared spectrum, and molecular weight determination are all in agreement with the assigned structure. The salt is soluble in polar solvents like acetonitrile and methanol and insoluble in benzene and diethyl ether and can be handled in air with no special precautions.

$$\underset{\mathbf{3}}{py\cdot BH_3} + (C_6H_5)_3CBF_4 + py \xrightarrow{CH_3CN} \underset{\mathbf{4}}{(py_2BH_2)^+BF_4^-} + (C_6H_5)_3CH$$

The acetonitriletrimethylamineboron cation (**2**), in contrast, is quite susceptible to nucleophilic attack. Methanol, for example, adds across the triple bond of the acetonitrile ligand to give a new compound, (methyl acetimidate)trimethylaminedihydroboron(1+) fluoroborate (**5**). The disappearance of $-C{\equiv}N$ absorption and the appearance of new N—H and $>C{=}N-$ absorptions in its infrared spectrum indicated that the acetonitrile ligand had been converted to a methyl acetimidate ligand. This salt is an air stable, white, crystalline solid which is soluble in polar solvents.

$$\underset{\mathbf{2}}{[CH_3C{\equiv}NBH_2N(CH_3)_3]^+BF_4^-} + CH_3OH \longrightarrow$$



$$\underset{\mathbf{5}}{[CH_3\overset{\overset{\displaystyle OCH_3}{|}}{C}{=}NHBH_2N(CH_3)_3]^+BF_4^-}$$

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[2] To whom correspondence should be addressed.

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

[4] G. E. Ryschkewitsch, *J. Amer. Chem. Soc.*, **89**, 3145 (1967).

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

[6] J. E. Douglass, *J. Amer. Chem. Soc.*, **86**, 5431 (1964); **84**, 121 (1962).

[7] N. E. Miller and E. L. Muetterties, *ibid.*, **86**, 1033 (1964); H. C. Miller, N. E. Miller, and E. L. Muetterties, *ibid.*, **85**, 3885 (1963).

[8] H. Nöth and H. Beyer, *Chem. Ber.*, **93**, 1078, 2551 (1960); H. Nöth and S. Lucas, *ibid.*, **95**, 1505 (1962).

[9] J. H. Davidson and C. H. French, *Chem. Ind.* (*London*), 750 (1959).

[10] B. H. Mikhailov and T. K. Kosminskaya, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1703 (1963), and earlier papers.

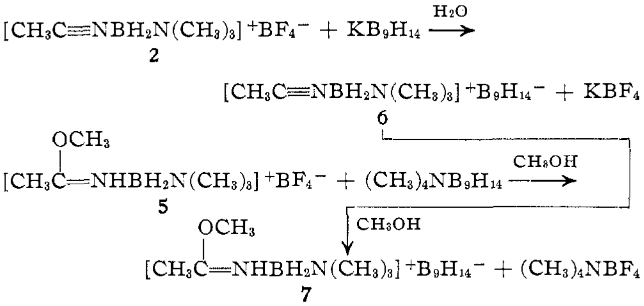
[11] D. R. Schultz and R. W. Parry, *J. Amer. Chem. Soc.*, **80**, 4 (1958); S. G. Shore and R. W. Parry, *ibid.*, **80**, 8, 12, 15 (1958); S. G. Shore, P. R. Girardot, and R. W. Parry, *ibid.*, **80**, 20 (1958); R. W. Parry, G. Kodama, and D. R. Schultz, *ibid.*, **80**, 24 (1958); R. C. Taylor, D. R. Schultz, and A. R. Emery, *ibid.*, **80**, 27 (1958).

[12] G. L. Smith and H. C. Kelly, *Inorg. Chem.*, **8**, 2000 (1969).

[13] H. J. Dauben, Jr., and D. L. Pearson, Abstracts, 126th National Meeting of the American Chemical Society, New York, N. Y., Sept 13, 1954, p 18-O; H. J. Dauben, F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *J. Amer. Chem. Soc.*, **79**, 4557 (1957); H. J. Dauben and L. R. Hannen, *ibid.*, **80**, 5570 (1958); H. J. Dauben and D. J. Bartelli, *ibid.*, **83**, 497, 4657 (1961); J. E. Mahler and R. Pettit, *ibid.*, **85**, 3955 (1963); J. F. Emerson, J. E. Mahler, R. Pettit, and R. Collins, *ibid.*, **86**, 3590 (1964); E. O. Fischer and R. D. Fischer, *Angew. Chem.*, **72**, 919 (1960).

Trityl fluoroborate is easily hydrolyzed and acetonitrile, when bound to boron as a ligand, is susceptible to nucleophilic attack. For these reasons, preparative reactions should be carried out under anhydrous conditions.

The exchange of the fluoroborate anion in these salts was readily accomplished by metathesis. The reaction of **2** with potassium tetradecahydrononaborate(1−),[14] KB_9H_{14}, in water led to the precipitation of acetonitriletrimethylaminedihydroboron(1+) tetradecahydrononaborate(1−) (**6**) as a white, crystalline solid. Recrystallization from methanol converted this salt to the methylacetimidate derivative (**7**). This compound was also obtained directly from the acetimidate fluoroborate (**5**) and tetramethylammonium tetradecahydrononaborate(1−) in methanol solution.



$$\underset{\mathbf{2}}{[CH_3C{\equiv}NBH_2N(CH_3)_3]^+BF_4^-} + KB_9H_{14} \xrightarrow{H_2O} \underset{\mathbf{6}}{[CH_3C{\equiv}NBH_2N(CH_3)_3]^+B_9H_{14}^-} + KBF_4$$

$$\underset{\mathbf{5}}{[CH_3\overset{OCH_3}{\overset{|}{C}}{=}NHBH_2N(CH_3)_3]^+BF_4^-} + (CH_3)_4NB_9H_{14} \xrightarrow{CH_3OH}$$

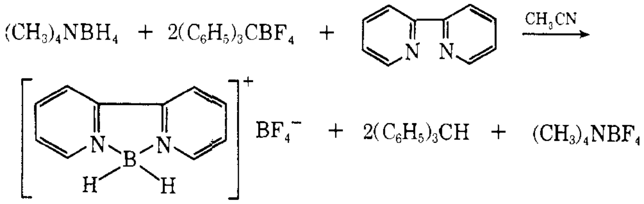
$$\xrightarrow{CH_3OH} \underset{\mathbf{7}}{[CH_3\overset{OCH_3}{\overset{|}{C}}{=}NHBH_2N(CH_3)_3]^+B_9H_{14}^-} + (CH_3)_4NBF_4$$

The behavior of boron hydride anions toward trityl fluoroborate was also of interest since stepwise removal of two hydride ions would convert them into cations. Because of its similarity to trimethylamine–borane, the borohydride ion was selected for study. Steric and electronic factors suggested that the BH_4 anion might be even more reactive toward trityl fluoroborate than the amine–boranes. In this regard, Ryschkewitsch has recently observed[4] a great difference in reactivity between BH_4^- and $pyBH_3$ toward electrophilic attack which results in hydride-transfer reactions.

Tetramethylammonium borohyride was a convenient salt to use for this purpose because it was easily recrystallized and handled. When treated at low temperature (*ca.* −50°) with an acetonitrile solution containing 1 equiv each of trityl fluoroborate and pyridine, it was converted into the liquid pyridine–borane, isolated in somewhat less than 50% yield. Unexpectedly, some gas (presumably hydrogen) was evolved during the course of this reaction. When 2 equiv each of pyridine and trityl fluoroborate were used, tetramethylammonium borohyride was converted into bis(pyridine)dihydroboron(1+) fluoroborate (**4**) in 59% yield. This compound was identical with the one previously prepared from pyridine–borane. When 2,2′-bipyridine was used as the ligand in place of pyridine, the heterocyclic salt **8** was obtained, but in very low yield. Analytical data and the infrared spectrum are in agreement with the assigned structure.

$$(CH_3)_4NBH_4 + (C_6H_5)_3CBF_4 + py \xrightarrow{CH_3CN} py\cdot BH_3 + (C_6H_5)_3CH + (CH_3)_4NBF_4$$

$$(CH_3)_4NBH_4 + 2(C_6H_5)_3CBF_4 + 2py \xrightarrow{CH_3CN} \underset{\mathbf{4}}{(py_2BH_2)^+BF_4^-} + 2(C_6H_5)_3CH + (CH_3)_4NBF_4$$



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Diborane and the $B_3H_8^-$ anion were also found to react readily with triphenylmethyl fluoroborate. Triphenylmethane was obtained in quantitative yields, but pure, stable boron products were not isolated. Although hydride abstraction reactions may be possible routes to multiboron cations, the utility of triphenylmethyl salts for this purpose has not been explored beyond what is reported here.

Experimental Section

Acetonitriletrimethylaminedihydroboron(1+) Fluoroborate (2).—Trityl fluoroborate (9.9 g; 0.03 mol) in dry acetonitrile (50 ml) was added dropwise over a 30-min period to a solution of trimethylamine–borane (2.19 g; 0.03 mol) in dry acetonitrile (10 ml). The colorless reaction mixture was stirred for an additional 10 min after the addition was completed and was then evaporated to dryness under reduced pressure. Triphenylmethane was separated from the solid residue by three extractions with benzene (70 ml total). The crude product, which is benzene insoluble, weighed 5.74 g (96% yield). It was purified by dissolving it at room temperature in 5 ml of acetonitrile and then slowly adding 20 ml of benzene to precipitate the product. In this manner, 3.64 g of white, crystalline product was collected, mp 107.5–109°. An additional 0.6 g of material with an identical melting point was isolated from the filtrate; total, 4.24 g (71% yield). Two additional recrystallizations of a portion of this material raised the melting point to 109–110°. *Anal.* Calcd for $C_5H_{14}N_2B_2F_4$: C, 30.05; H, 7.06; N, 14.02; B, 10.83. Found: C, 29.63; H, 6.86; N, 14.33; B, 10.30.

Bis(pyridine)dihydroboron(1+) Fluoroborate (4). a. From $(CH_3)_4NBH_4$.—The colorless homogeneous solution obtained by adding pyridine (1.62 ml; 0.02 mol) to trityl fluoroborate (6.6 g; 0.02 mol) dissolved in 50 ml of dry acetonitrile was added to solid $(CH_3)_4NBH_4$ (0.89 g; 0.01 mol) which was cooled to −55°. As the reaction mixture was allowed to warm to room temperature, gas evolution began. A total of 200 cm^3 of gas was collected during a 90-min reaction period. Tetramethylammonium fluoroborate which had precipitated from solution was collected by filtration in 75% yield. The filtrate was evaporated to dryness and extracted with benzene. A quantitative yield of triphenylmethane was recovered from the benzene solution. The benzene-insoluble solid, which was a mixture of the product and $(CH_3)_4NBF_4$, was recrystallized from methanol–ether to give a 59% yield of white, crystalline $(py)_2BH_2BF_4$. Further recrystallization from the same solvent pair gave the analytical sample which had a melting point of 95–96°. *Anal.* Calcd for $C_{10}H_{12}N_2F_4B_2$: C, 46.58; H, 4.69; N, 10.87; F, 29.47; B, 8.39. Found: C, 46.42; H, 4.86; N, 10.80; F, 29.66; B, 8.73. The molecular weight was determined by X-ray diffraction of a single crystal with a density of 1.346 g/cm^3: calcd, 257.8; found, 259.

b. From $py\cdot BH_3$.—A solution of trityl fluoroborate (1.65 g; 5 mmol) and pyridine (0.4 ml; 5 mmol) in 10 ml of dry acetonitrile was added to pyridine–borane (0.51 ml; 5 mmol) held in a flask cooled to −55°. In contrast to the previous experiment,

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[14] L. E. Benjamin, S. F. Stafiej, and E. A. Takacs, *J. Amer. Chem. Soc.*, **85**, 2674 (1963).

only 15 cm^3 of gas was evolved while the reaction mixture was being warmed to room temperature during a 1-hr period. The homogeneous solution was evaporated to dryness under reduced pressure, and from the residue, triphenylmethane was extracted with benzene. Recrystallization of the benzene-insoluble solid from methanol-ether gave a 52% yield of $(py)_2BH_2BF_4$ which was identical with the product obtained in the previous experiment.

(Methyl acetimidate)trimethylaminedihydroboron(1+) Fluoroborate (5).—The acetonitrile fluoroborate salt (**2**) (0.6 g; 3 mmol) was dissolved in 25 ml of absolute methanol and the solution was cooled to −78°. The white crystalline solid which precipitated from solution was collected by filtration and washed with two 10-ml portions of dry benzene; weight, 0.3 g (43% yield), mp 128–130°. Two crystallizations from methanol furnished an analytical sample. *Anal.* Calcd for $C_6H_{18}N_2B_2F_4O$: C, 31.08; H, 7.82; N, 12.08. Found: C, 31.23; H, 7.43; N, 12.01.

(Methyl acetimidate)trimethylaminedihydroboron(1+) Tetradecahydrononaborate(1−) (7). a. From Compound 5.—A solution of $(CH_3)_4NB_9H_{14}$ (186 mg; 1 mmol) in 10 ml of methanol was added to a solution of **5** (232 mg; 1 mmol) in 10 ml of methanol. After a short induction period, crystalline tetramethylammonium fluoroborate (120 mg; 75% yield) precipitated from solution and was collected by filtration. Evaporation of the filtrate gave 220 mg (86%) of light yellow product, mp 85–96°. Three recrystallizations from methanol–water raised the melting point to 97°. *Anal.* Calcd for $C_6H_{32}N_2B_{10}O$: C, 28.09; H, 12.57; N, 10.92; B, 42.18. Found: C, 28.48; H, 12.24; N, 11.10; B, 46.78.

b. From Compound 2.—A solution of **2** (400 mg; 2 mmol) in 5 ml of water was added to a solution of KB_9H_{14} $(dioxane)_3$ (820 mg; 2 mmol) in 10 ml of water. A precipitate of $[(CH_3)_3NBH_2NCCH_3]B_9H_{14}$ (470 mg) immediately separated from solution (calcd, 449 mg). This material softened at 64° but did not melt completely up to 175°. Its infrared spectrum showed only weak NH (or OH) stretch but very intense B–H stretch. This acetonitrile ligand salt (**6**) was converted to the methyl acetimidate compound (**7**) by recrystallization from methanol–water. From 440 mg, 140 mg of crystalline solid, mp 87–90°, was obtained, the infrared spectrum of which was identical with that of the sample obtained in part a above.

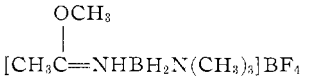
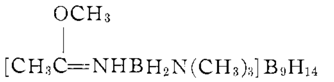
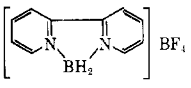
2,2′-Bipyridinedihydroboron(1+) Fluoroborate (8).—2,2′-Bipyridine (3.12 g; 0.02 mol) was added to a solution of trityl fluoroborate (6.60 g; 0.02 mol) in 50 ml of acetonitrile causing a dark red color to develop in the solution. This mixture was then added dropwise to $(CH_3)_4NBH_4$ (0.89 g; 0.01 mol) which was cooled to −60°. The reaction mixture was warmed up to room temperature during the addition and gas was evolved. After an elapsed time of 90 min, approximately 200 cm^3 of gas was collected. No precipitate of $(CH_3)_4NBF_4$ had formed. Consequently, the salmon pink solution was evaporated to dryness and the residue was extracted with benzene. From the benzene solution, there was obtained an orange viscous liquid, which was not characterized. Benzene-insoluble material (4.5 g) remained which was extracted with methanol to give 2.83 g of soluble material and 1.53 g of CH_3OH-insoluble $(CH_3)_4NBF_4$.

The 2.83 g of CH_3OH-soluble material was then recrystallized from ethanol–ether. The first two recrystallizations furnished material of mp 122–126° which showed BH and BF_4 absorption in the infrared region. On the third recrystallization, the melting point increased to 191–192° (180 mg). An additional recrystallization of this material gave the analytical sample, mp 191–193°. Yield of high-melting material was 7%. The low-melting material has not been identified. *Anal.* Calcd for $C_{10}H_{10}B_2N_2F_4$: C, 46.95; H, 3.94; N, 10.95; B, 8.45; F, 29.71. Found: C, 46.97; H, 4.39; N, 11.23; B, 8.53; F, 29.85.

Infrared Spectra.—Infrared spectra were recorded on a Beckman IR 5 spectrophotometer, using samples prepared as Nujol mulls. The data are shown in Table I.

TABLE I

INFRARED SPECTRAL DATA (CM^{-1})

$[CH_3C{\equiv}NBH_2N(CH_3)_3]BF_4$	2500 m, 2440 m, 2350 m, 1410 m, 1280 w, 1250 m, 1177 s, 1150 s, 1110–1010 vs, 982 s, 970 s, 870 s
$[(py)_2BH_2]BF_4$	3080 m, 3030 m, 2460 m, 2410 m, 1610 s, 1350 m, 1280 m, 1255 m, 1210 m, 1160 s, 1150 s, 1110–1010 vs, 990 m, 960 m, 890 w, 800 m, 775 m, 765 w, 750 m, 740 m, 735 s, 700 s, 688 s
 $[CH_3C(OCH_3){=}NHBH_2N(CH_3)_3]BF_4$	3350 m, 2450 m, 1640 s, 1540 m, 1420 m, 1280 s, 1190 m, 1165 s, 1100–1020 vs, 990 m, 930 w, 880 w, 850 s, 770 w, 760 w, 720 w, 705 w
 $[CH_3C(OCH_3){=}NHBH_2N(CH_3)_3]B_9H_{14}$	3330 m, 2550 s, 2470 s, 2360 m, 1640 m, 1535 m, 1420 w, 1290 s, 1250 w, 1190 m, 1160 s, 1110 w, 1100 m, 1050 m, 1040 m, 1020 m, 985 m, 970 m, 950 m, 925 m, 875 w, 850 m, 815 w, 775 w
	3030 m, 2440 m, 2390 m, 1620 s, 1565 m, 1490 m, 1330 m, 1280 w, 1255 w, 1160 s, 1080–1010 vs, 910 w, 810 w, 770 s, 710 w