Boron Cations Derived from Diamines.   Linear, Cyclic, Bicyclic 1+, and 2+ Ions and Polynuclear Species

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Diamine–bis(iodoboranes) react with diamines to yield either a five-membered ring chelate of $BH_2{}^+$ or macrocyclic ions with the general formula $[(diamine)BH_2]_n{}^{n+}$. They react with monofunctional amines to give linear ions with two $BH_2{}^+$ units. N,N'-Dimethylpiperazine gives a bicyclic norbornane homomorph.   Reaction of amine–diiodoboranes with diamines yields chelated ions of BH^{2+}.   The various types of cations diminish in their reactivity toward pyridine in the order: linear (pyridine-terminal) > bicyclo ≫ cyclo > bis(trimethylamine).   A number of new bis(borane) adducts of diamines were prepared.

Although there have been a few reports of chelated cations derived from alkyl-, aryl-, or haloboranes,[1-3] the only mention of ions derived from $BH_2{}^+$ and a diamine are found in the classic paper by Miller and Muetterties.[4] No ions derived from BH^{2+} and diamine have been reported. The present paper presents a number of syntheses of boron cations containing a diamine moiety in different structural environments. The preparations are based on a combination of halide-displacement reactions on amine–iodoboranes and transaminations on boron cations.[5-7] Principles which make these syntheses possible are outlined.

Experimental Section

Materials.—Diamines were supplied by K and K Laboratories, Inc., and Aldrich Chemical Co., Inc. N,N,N',N'-Tetramethyl-1,2-ethanediamine and 2-(2-dimethylaminoethyl)pyridine were distilled from barium oxide and stored over Molecular Sieve 3A. The other diamines were stored over Molecular Sieve only. 2,2'-Dipyridyl was recrystallized from petroleum ether and further purified by sublimation. Trimethylamine–borane and pyridine–borane were supplied by Callery Chemical Co. and used without further purification. $(4-CH_3py)_3BH^{2+}(PF_6{}^-)_2{}^{11}$ and $(4-CH_3py)_4$-$B^{3+}(PF_6{}^-)_3,{}^8$ used in molecular weight studies, were prepared as stated in references. Solvents were reagent grade and stored over Molecular Sieve 3A. Analyses were performed by Peninsular ChemResearch Inc., Gainesville, Fla.

The following abbreviations are used in this paper to denote the various amines: TMED, N,N,N',N'-tetramethyl-1,2-ethanediamine; TMPD, N,N,N',N'-tetramethyl-1,3-propanediamine; TMBD, N,N,N',N'-tetramethyl-1,4-butanediamine; DMpip, N,N'-dimethylpiperazine; py, pyridine; dipy, 2,2'-dipyridyl; 3,4-$(CH_3)_2$py, 3,4-dimethylpyridine; $(CH_3)_2NC_2H_4$py, 2-(2-dimethylaminoethyl)pyridine; and 4-CH_3py, 4-methylpyridine.

Diamine–Bis(boranes).—Diamine–bis(boranes) and 3,4-dimethylpyridine–borane were prepared in excellent yield by transamination[9] of $(CH_3)_3NBH_3$ using a small excess of diamine,

(1) (a) J. M. Davidson and C. M. French, *Chem. Ind.* (London), 750 (1959); (b) *J. Chem. Soc.*, 3364 (1962).
(2) N. Wiberg and J. W. Bucher, *Ber.*, **96**, 3000 (1963).
(3) (a) J. E. Douglass, *J. Amer. Chem. Soc.*, **84**, 121 (1962); (b) *ibid.*, **86**, 5451 (1964); (c) J. E. Douglass, G. R. Roehrig, and O. Ma, *J. Organometal. Chem.*, **8**, 421 (1967).
(4) N. E. Miller and E. L. Muetterties, *J. Amer. Chem. Soc.*, **86**, 1033 (1964).
(5) G. E. Ryschkewitsch, *ibid.*, **89**, 3145 (1967).
(6) K. C. Nainan and G. E. Ryschkewitsch, *Inorg. Chem.*, **7**, 1316 (1968).
(7) K. C. Nainan and G. E. Ryschkewitsch, *J. Amer. Chem. Soc.*, **91**, 330 (1969).
(8) G. E. Ryschkewitsch and G. L. Galloway, *Inorg. Syn.*, in press.
(9) R. A. Baldwin and R. M. Washburn, *J. Org. Chem.*, **26**, 3549 (1961).

in benzene solution. The solution was stirred and heated near reflux for about 6 hr while a stream of dry nitrogen was passed into the flask. The product was precipitated by addition of petroleum ether to the chilled solution, dried under vacuum, and recrystallized from acetone. With the exception of N,N,-N',N'-tetramethyl-1,2-ethanediamine–bis(borane), all were new compounds.

N,N,N',N'-Tetramethylpropanediamine–Bis(borane), TMPD·$2BH_3$.—$(CH_3)_3NBH_3$ (110 mmol) and TMPD (55.6 mmol) were combined in 15 ml of benzene and refluxed 24 hr; the yield was 84%. Recrystallization from acetone gave 85% recovery; mp 144–145°. *Anal.* Calcd for $C_7H_{24}B_2N_2$: C, 53.24; H, 15.32; N, 17.74. Found: C, 53.56; H, 15.47; N, 17.83.

N,N,N',N'-Tetramethylbutanediamine–Bis(borane), TMBD·$2BH_3$.—A 20-ml benzene solution of $(CH_3)_3NBH_3$ (58.0 mmol) was refluxed 6 hr with TMBD (30.0 mmol). The bis(borane) product was obtained in 87% yield; mp 147–149°. *Anal.* Calcd for $C_8H_{26}B_2N_2$: C, 55.93; H, 15.26; N, 16.30. Found: C, 56.09; H, 16.02; N, 16.53.

N,N,N',N'-Tetramethylethanediamine–Bis(borane), TMED·$2BH_3$.—$(CH_3)_3NBH_3$ (111 mmol) and TMED (55.6 mmol) were refluxed 30 ml of benzene for 6 hr. The product was obtained in 93% yield and in 80% recovery on recrystallization from acetone; mp 181–182.5°, lit.[4] mp 182.5–185°.

3,4-Dimethylpyridine–Borane.—3,4-$(CH_3)_2$py·BH_3($CH_3)_3$-NBH$_3$ (53 mmol) and 3,4-dimethylpyridine (54 mmol) were refluxed in 20 ml of benzene for 30 hr. The yield of product was 96%; mp 111–112°. *Anal.* Calcd for $C_7H_{12}BN$: C, 69.49; H, 10.00; N, 11.58. Found: C, 69.23; H, 10.27; N, 11.44.

Chelated 1+ Ions (I). TMEDBH$_2{}^+$.—To a stirred slurry of TMED·$2BH_3$ (1.49 g, 10.3 mmol) in 20 ml of dichloromethane was added solid iodine (2.54 g, 10.0 mmol) over a 0.5-hr period. Hydrogen gas evolved from the warm solution. After an additional hour TMED (1.62 g, 14.0 mmol) was added to the dark brown solution; it decolorized rapidly. After warming for 16 hr, solvent and excess amine were evaporated to yield 5.42 g of white solid. Calculated on the basis of the equation TMED·$2BH_3 + I_2 + TMED \rightarrow H_2 + 2TMEDBH_2{}^+,I^-$, 5.12 g. The water-soluble residue was precipitated with excess NH_4PF_6 to afford the chelated $PF_6{}^-$ salt in 62% yield. This salt was recrystallized from hot water with good recovery; mp 245–247° dec, lit.[4] 240–244° dec.

The chelated cation was also obtained from trimethylamine–iodoborane. $(CH_3)_3NBH_3$ (10.0 mmol) in a 10-ml benzene solution was iodinated with 4.96 mmol of iodine. The resulting solution was then stirred for 15 hr with 11 mmol of TMED and filtered (1.94 g). The solid was converted to the $PF_6{}^-$ salt, which was completely soluble in CH_2Cl_2. The proton nmr showed this to be a mixture of 60 mol % chelate ion and 40 mol % bis(trimethylamine)boronium ion. Recrystallization from water decreased the proportion of chelated ion.

Higher ratios of $(CH_3)_3NBH_2I$ to TMED (2:1) produced a larger proportion of bis(trimethylamine)boronium ion, 44%, as

expected. No +2 ions were detected. A yet higher mole per cent of chelated ion (80%) was obtained when solid $(CH_3)_3$-NBH_2I was heated at 60° with three times the required quantity of TMED for 24 hr. The remainder of the product was $[(CH_3)_3$-$N]_2BH_2^+$, which was difficult to separate from the chelate ion.

Chelate Cation from 2-(2-Dimethylaminomethyl)pyridine.—This cation was prepared by heating $(CH_3)_3NBH_3$ (10.3 mmol) and I_2 (5.0 mmol) in benzene with 10.9 mmol of diamine for 10 hr. Iodide salt (2.72 g) was converted to 2.26 g of hexafluorophosphate representing a 73% overall reaction yield. Recrystallization from hot water gave the pure chelate salt; mp 132–133.5°. *Anal.* Calcd for $C_9H_{14}BN_2^+,PF_6^-$: C, 35.09; H, 5.24; N, 9.10. Found: C, 34.85; H, 5.00; N, 8.95.

Chelate Cation from TMPD.—In a similar reaction from TMPD·$2BH_3$ (4.00 mmol), I_2 (3.94 mmol), and TMPD (4.2 mmol) in 20 ml of CH_2Cl_2, 1.95 g of hexafluorophosphate salt was isolated. Although its weight corresponded to a 83% yield of boron cation, the product proved to be a mixture. Extraction with methylene chloride gave a 9% overall yield of the chelated cation, and an insoluble residue whose identity is discussed below, mp 241–245° dec. *Anal.* Calcd for $C_7H_{20}BN_2^+,PF_6^-$: C, 29.19; H, 7.00; N, 9.73. Found: C, 29.39; H, 7.45; N, 9.61.

This cation could also be prepared by amine displacement. $[(CH_3)_3N]_2BH_2^+I^-$ (2.52 g, 9.76 mmol) was heated with $(CH_3)_2N$-$(CH_2)_3N(CH_3)_2$ (TMPD) (4.48 g, 34.5 mmol) at reflux temperature for 34 hr. Iodide salt (2.36 g) was recovered (90% yield) and converted to 2.02 g of hexafluorophosphate salt (72% overall yield). The nmr spectrum of the PF_6 salt showed the expected pattern for diamine chelate; no methyl absorption for bis(trimethylamine)boronium ion was detected. The PF_6^- salt was recrystallized from hot water with 57% recovery; mp 276–279°, dec. *Anal.* Calcd for $C_7H_{20}BN_2^+,PF_6^-$: C, 29.19; H, 7.00; N, 9.73. Found: C, 29.28; H, 7.22; N, 9.60.

TMBDBH$_2$$^+$.—$[(CH_3)_3N]_2BH_2^+I^-$ (2.03 g, 7.85 mmol) was refluxed in $(CH_3)_2N(CH_2)_4N(CH_3)_2$ (TMBD) (3.33 g, 23.1 mmol) for 24 hr. The material recovered was converted to the PF_6^- derivative in the usual manner (1.83 g). A portion of this PF_6^- salt (0.911 g) was separated into 0.421 g of CH_2Cl_2-soluble and 0.394 g of CH_2Cl_2-insoluble components. The latter appeared to be diamineammonium salt. The CH_2Cl_2-soluble fraction represented a 36% overall reaction yield of chelate salt, which was recrystallized from hot water with 54% recovery; mp 230–231° dec. *Anal.* Calcd for $C_8H_{22}BN_2^+,PF_6^-$: C, 31.81; H, 7.34; N, 9.28. Found: C, 31.83; H, 7.41; N, 9.21.

Polynuclear Cations (II). (TMBDBH$_2$)$_n$$^{n+}$.—TMBD·$2BH_3$ (3.50 mmol) was halogenated on the BH_2I adduct by reaction with an equivalent quantity of iodine and allowed to react with TMBD (3.7 mmol) as above for 4.5 hr. Conversion of the reaction product to the PF_6^- salt gave a water and methylene chloride insoluble product in 80% yield. The greater part of this material was also insoluble in acetone; mp 157–159° dec. On occasion a methylene chloride soluble component was isolated in small quantity, which was identical in its nmr spectrum with the authentic chelate cation TMBDBH$_2$$^+$. *Anal.* Calcd for $(C_8H_{22}BN_2)_n^{n+},(PF_6^-)_n$: C, 31.81; H, 7.34; N, 9.28. Found: C, 31.33; H, 7.27; N, 9.10. This salt was soluble in nitromethane, dimethyl sulfoxide, and acetonitrile.

(TMPDBH$_2$$^+$)$_n$$^{n+}$.—This cation was obtained as the major product in the synthesis of the TMPD chelate ion described above. It was separated from the chelate as the PF_6^- salt in the methylene chloride insoluble fraction, in about 70% yield. *Anal.* Calcd for $(C_7H_{20}BN_2)_n^{n+},(PF_6^-)_n$: C, 29.19; H, 7.00; N, 9.73. Found: C, 28.19; H, 6.51; N, 9.16.

Bis(BH$_2$$^+$) Chain Ions (III).—In general, these compounds were prepared from diamine-bis(iodoboranes) by addition of excess amine. In a few instances they were also isolated from the reaction of a diamine with an amine–iodoborane.

(CH$_3$)$_3$NBH$_2$TMEDBH$_2$N(CH$_3$)$_3$$^{2+}$.—A solution of TMED·$2BH_3$ (10.0 mmol) in 10 ml of CH_2Cl_2 was iodinated on both boron atoms by addition of iodine (9.65 mmol). Trimethylamine was then passed through the brown solution (10 min), producing a

white solid. After standing overnight, the solvent was evaporated, leaving a solid product which was dissolved in water and precipitated with NH_4PF_6 solution to give 4.86 g, or 87% yield, of PF_6^- salt. Poor recovery of this salt resulted when it was recrystallized from hot water; recrystallization from acetonitrile–diethyl ether gave a good yield of purified compound; mp 183–184° dec.[10] *Anal.* Calcd for $C_{12}H_{38}B_2N_4^{2+},(PF_6^-)_2$: C, 26.21; H, 6.96; N, 10.19. Found: C, 26.01; H, 6.71; N, 9.95.

(CH$_3$)$_3$NBH$_2$TMPDBH$_2$N(CH$_3$)$_3$$^{2+}$.—In a similar fashion, a preparation from TMPD·$2BH_3$ (8.7 mmol), I_2 (8.0 mmol), and excess $(CH_3)_3N$ over a 7-hr period gave eventually 2.10 g of PF_6^- salt (47% yield); mp 195–197° dec. *Anal.* Calcd for $C_{13}H_{40}B_2N_4^{2+},(PF_6^-)_2$: C, 27.69; H, 7.15; N, 9.94. Found: C, 27.56; H, 7.37; N, 9.81.

The same compound was obtained when $(CH_3)_3NBH_2I$ (9.90 mmol) and TMPD (19.8 mmol) were heated at 60° for 11 hr. The yield of iodide (1.72 g) was 65%, which was converted to 1.69 g of PF_6^- salt (92%). Extraction with CH_2Cl_2 gave 87% recovery of the 2+ ion, mp 192–195° dec., which was identical in its nmr spectrum with the analyzed sample above. Only 0.025 g of CH_2Cl_2-soluble material was recovered (13.6%), which proved to be a mixture of chelate ion and bistrimethylamine cation.

(CH$_3$)$_3$NBH$_2$TMBDBH$_2$N(CH$_3$)$_3$$^{2+}$.—The compound was prepared from 1 mmol of TMBD·$2BH_2I$ and excess $(CH_3)_3N$. The yield of final purified product was 18%; mp 185–187° dec. *Anal.* Calcd for $C_{14}H_{42}B_2N_4^{2+},(PF_6^-)_2$: C, 29.08; H, 7.33; N, 9.69. Found: C, 29.42; H, 7.96; N, 9.80.

pyBH$_2$TMEDBH$_2$py^{2+}.—The compound was prepared from the diamine–bis(borane) on a 10-mmol scale of starting materials in 20 ml of CH_2Cl_2 as above, using a small exces of pyridine. The PF_6^- salt was obtained in 68% yield; mp 143–145. *Anal.* Calcd for $C_{16}H_{30}B_2N_4^{2+},(PF_6^-)_2$: C, 32.57; H, 5.13; N, 9.50. Found: C, 32.54; H, 5.25; N, 9.59.

pyBH$_2$TMPDBH$_2$py^{2+}.—The compound was prepared as above on a 1.7-mmol scale, using benzene as solvent instead of CH_2Cl_2. The yield was 73%; mp 152–153.5. *Anal.* Calcd for $C_{17}H_{32}B_2N_4^{2+},(PF_6^-)_2$: C, 33.80; H, 5.34; N, 9.28. Found: C, 34.46; H, 5.43; N, 9.37.

pyBH$_2$TMBDBH$_2$py^{2+}.—The compound was prepared from 4.0-mmol quantities in 10 ml of CH_2Cl_2 in 83% yield; mp 168–169° dec. *Anal.* Calcd for $C_{18}H_{34}B_2N_4^{2+},(PF_6^-)_2$: C, 34.98; H, 5.55; N, 9.07. Found: C, 36.02; H, 5.73; N, 8.90.
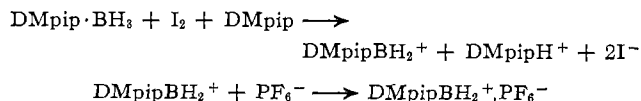
pyBH$_2$DMpipBH$_2$py^{2+}.—To pyridine–iodoborane, prepared from pyridine–borane (20.05 mmol) and I_2 (18.5 mmol) in 50 ml of CH_2Cl_2, was added DMpip (9.22 mmol). The precipitate which immediately formed was filtered off after 15 min and converted to the hexafluorophosphate derivative. Substantially pure PF_6^- salt (2.08 g), representing a 52% yield, was recrystallized from CH_3CN–CH_2Cl_2; mp 170–175° dec. *Anal.* Calcd for $C_{16}H_{28}B_2N_4^{2+},(PF_6^-)_2$: C, 32.68; H, 4.80; N, 9.53. Found: C, 32.62; H, 4.60; N, 9.40.

The CH_2Cl_2 filtrate slowly deposited more precipitate. Solution and precipitate were extracted into two 20-ml portions of water and converted to PF_6^- salts by slow crystallization from boiling water after addition of NH_4PF_6. The product, 0.790 g, consisted of 95% $(C_5H_5N)_2BH_2^+PF_6^-$ (2.38 mmol), mp 114–116°, and 5% pyBH$_2$DMpipBH$_2$py$^{2+},(PF_6^-)_2$ (0.06 mmol). The water filtrate contained DMpip. In a separate experiment it was found that pyBH$_2$DMpipBH$_2$py^{2+} and the bicyclo cation IV hydrolyzed nearly completely under the conditions employed in the slow crystallization. In the hydrolysis of the former compound no py$_2$BH$_2$$^+$ was detected.

Bicyclic Cations (IV). DMpipBH$_2$$^+$.—Trimethylamine–borane (52.0 mmol) was transaminated with N,N'-dimethylpiperazine (52.0 mmol) by refluxing in benzene (35 ml) for 2 hr. The mixture was iodinated with 38.4 mmol of iodine in the presence of an additional 10 ml of amine and heated for 5 hr. After addition of 100 ml of petroleum ether the precipitate was dissolved in

(10) While this research was under way this compound was reported by a similar method, mp 179–180°: N. E. Miller, *et al.*, *Inorg. Chem.*, **8**, 862 (1969).

water, precipitated with excess NH_4PF_6, and then extracted twice with 50 ml of CH_2Cl_2. From the extract 7.66 g of hexafluorophosphate salt of the bicyclic compound (IV) was isolated. This corresponds to 73% of the weight calculated based on the equations

$$DMpip \cdot BH_3 + I_2 + DMpip \longrightarrow$$
$$DMpipBH_2{}^+ + DMpipH^+ + 2I^-$$

$$DMpipBH_2{}^+ + PF_6{}^- \longrightarrow DMpipBH_2{}^+,PF_6{}^-$$

The CH_2Cl_2-insoluble residue was piperazinium hexafluorophosphate. The boron cation was recrystallized from hot water (80% recovery); mp 265–267°. *Anal.* Calcd for $C_{16}H_{16}BN_2{}^+$, $PF_6{}^-$: C, 26.49; H, 5.93; N, 10.29. Found: C, 26.48; H, 6.04; N, 10.16.

DMpipBHCl$^+$.—Through a solution of $DMpipBH_2{}^+,PF_6{}^-$ (3.77 mmol) in 20 ml of CH_2Cl_2 chlorine was passed for 20 hr. After solvent evaporation the residue was dissolved in hot water, excess NH_4PF_6 was added, and the precipitate obtained on cooling was recrystallized again from hot water. The overall yield was 0.643 g (55%); mp 240–245° dec. *Anal.* Calcd for $C_6H_{15}BClN_2{}^+,PF_6{}^-$: C, 23.51; H, 4.93; N, 9.14. Found: C, 23.42; H, 4.98; N, 9.02.

Chelated Ions of BH^{2+} (V). (3,4-$(CH_3)_2$py)(TMED)BH^{2+}.— A benzene solution (5 ml) of 3,4-dimethylpyridine–borane (3.0 mmol) was converted to the diiodoborane by heating it with 3.04 mmol of iodine for 1 hr. After cooling TMED (3.1 mmol) was added. The solid which was filtered off after 7 hr stirring was dissolved in 5 ml of water, filtered, and precipitated with excess NH_4PF_6 to give 0.705 g of solid, representing a 45% crude yield. Two recrystallizations from hot water gave the purified product with low recovery; mp 228–234° dec. *Anal.* Calcd for $C_{13}H_{28}BN_3{}^{2+},(PF_6{}^-)_2$: C, 29.73; H, 4.99; N, 8.00. Found: C, 31.45; H, 5.10; N, 7.92.

(3,4-$(CH_3)_2$py)(dipy)BH^{2+}.—In a similar preparation from 3,4-dimethylpyridine–borane (10.0 mmol) and I_2 (10.0 mmol) in 50 ml of benzene, refluxed for 19.5 hr and then for 1 hr with 2,2′-dipyridyl (11.0 mmol), there was isolated the hexafluorophosphate salt in 54% yield. The $PF_6{}^-$ salt was recrystallized twice from hot water; mp 214–218° dec. *Anal.* Calcd for $C_{17}H_{18}BN_3{}^{2+},(PF_6{}^-)_2$: C, 36.13; H, 3.21; N, 7.44. Found: C, 36.74; H, 3.22; N, 7.73.

(py)(dipy)BH^{2+}.—Similarly, 5.15 mmol of pyridine–borane and 4.98 mmol of I_2 heated for 1 hr in 10 ml of benzene, and then left with 2,2′-dipyridyl (5.0 mmol) for 3 days, yielded 2.20 g of an orange solid which was converted to the $PF_6{}^-$ derivative. The infrared spectrum showed three bands in the B–H stretching region at 2540, 2460, and 2420 cm^{-1}, indicating that the product was a mixture of mono- and dications. Accordingly, the singly charged cation was extracted with acetone, and the insoluble residue was recrystallized from hot water, yielding 0.22 g of purified product; mp 244–245° dec. *Anal.* Calcd for $C_{15}H_{14}$-$BN_3{}^{2+},(PF_6{}^-)_2$: C, 33.55; H, 2.63; N, 7.82. Found: C, 33.60; H, 2.64; N, 7.86.

Molecular Weights.—Apparent molecular weights, *i.e.*, average weights per ion, were obtained with a Mechrolab Model 302 vapor pressure osmometer, equipped with a 37° nonaqueous probe, in acetonitrile solution. Data are represented in Figure 1. The instrument was calibrated using benzil in acetonitrile; a linear calibration plot was obtained for the concentration range 0.005 to 0.4 M.

Infrared Spectra.—Infrared spectra were recorded on a Beckman IR 10 instrument using KBr wafers. Boron cations of the type $(CH_3)_2N(CH_2)_nN(CH_3)_2(H_2Bamine)_2{}^{2+}$ showed stretching vibrations for the BH_2 group in the 2300–2500-cm^{-1} region. In certain cases they appeared as four peaks, the two smaller peaks occurring at lower wave number. The spectra were complex in the region 1100–1250 cm^{-1} and no assignments could be made. A strong band near 1630 cm^{-1} is found in pyridine coordinated salts and attributed to a pyridine ring deformation. Dications of the type (amine)(diamine)BH^{2+} showed a single B–H stretching frequency at 2540 cm^{-1}
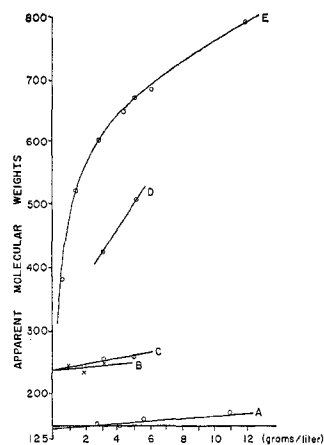

Figure 1.—Apparent molecular weights of various boron cations: A, $TMEDBH_2{}^+PF_6{}^-$; B, $(4\text{-}CH_3py)_3BH^{2+}(PF_6{}^-)_2$; C, $(CH_3)_3NBH_2TMEDBH_2N(CH_3)_3{}^{2+}(PF_6{}^-)_2$; D, $(4\text{-}CH_3py)_4$-$B^{3+}(PF_6{}^-)_3$; E, $[TMBDBH_2]_n{}^{n+}(PF_6{}^-)_n$.

Nmr Spectra.—Proton nmr spectra of the hexafluorophosphate salts were run on a Varian A-60A spectrometer. Values of δ are given using tetramethylsilane as the internal reference. There is a downfield shift of $\delta \sim 0.4$ for $(CH_3)_2N$ protons upon coordinating diamine to two BH_3 groups and a further downfield shift of $\delta \sim 0.1$ and 0.3 when pyridine or trimethylamine is bonded to the diamine–$(H_2B)_2{}^{2+}$ moiety. Tetramethylethanediamine shows two sharp peaks for $(CH_3)_2N$ and CH_2 protons, the separation between them increasing δ 0.4–0.7 upon coordinating the free diamine to BH_3 or $BH_2{}^+$. Tetramethylpropane- and tetramethylbutanediamines, whether coordinated or uncoordinated, show methylene absorptions, upfield from that of the methyl protons, which were determined by peak integrations to be due to carbon–carbon-bonded CH_2 group(s). A downfield shift of about δ 1, relative to the above-mentioned methylene protons, was found for methylene groups bonded to the more electronegative nitrogen atom. There is no evidence for a preferred conformation (chair or boat) in these five-, six-, and seven-membered rings at ambient temperatures. The methyl proton absorptions are all symmetrical singlets as is the CH_2 peak in $TMEDBH_2{}^+$. The methylene resonances in $TMPDBH_2{}^+$ show the expected first-order pattern, the four downfield protons being split into a triplet by the unique CH_2 group, which in turn is split into a quintet by the other four methylene protons. The spectrum of $TMBDBH_2{}^+$, a seven-membered ring, was similar to the aforementioned cation, but the spin coupling appeared to give a higher order pattern not amenable to simple interpretation. If conformers were actually present there would be nonequivalence of axial–equatorial hydrogen atoms and methyl groups and one should find more complicated spectra than observed. The compound (3,4-$(CH_3)_2$py)(TMED)$BH^{2+},(PF_6{}^-)_2$ exhibits two methyl absorptions of equal area associated with the TMED grouping. The peak at higher field is thought to be due to shielding of two nearby CH_3 groups by the lutidine ring current. The integrated intensities in all cases agreed well with those expected from the assigned structures. Chemical shift data are given in Table I.

Transamination.—Samples of several salts were placed in nmr tubes, pyridine was added, and nmr spectra of these solutions were periodically examined after standing at room temperature (23–25°) or after heating in boiling water. $pyBH_2DMpip$-$BH_2py^{2+},(PF_6{}^-)_2$ was almost completely destroyed within 5 min after dissolution. The bicyclic chelate cation slowly developed two new bands corresponding to N,N′-dimethylpiperazine dissolved in pyridine. The disappearance of the cation followed a first-order rate law with a specific rate constant of approximately 6×10^{-5} sec^{-1}. The chlorinated derivative of the bicyclic ion did not react under those conditions over a 5-day period, nor did the bis(trimethylamine) cation. At 100° the bis(trimethyl-

<div align="center">

Table I

Proton Nmr Data of Boron Cations and Boranes[a]

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Compound	Solvent	Aliphatic δ	Aromatic δ
TMED·2BH$_3$	CH$_3$CN	(CH$_3$)$_2$N, 2.58; CH$_2$, 3.14	
TMPD·2BH$_3$	CH$_3$CN	(CH$_3$)$_2$N, 2.53	
TMBD·2BH$_3$	CH$_3$CN	(CH$_3$)$_2$N, 2.50	
3,4-(CH$_3$)$_2$py·BH$_3$	CH$_3$CN	3-CH$_3$, 2.26; 4-CH$_3$, 2.35	H$_5$, 7.30; H$_{2,6}$, 8.20
pyBH$_2$TMEDBH$_2$(py)$^{2+}$(PF$_6^-$)$_2$	CD$_3$CN	(CH$_3$)$_2$N, 2.68; CH$_2$, 3.40	H$_{3,5}$, 7.98; H$_4$, 8.45; H$_{2,6}$, 8.74
(CH$_3$)$_3$NBH$_2$TMEDBH$_2$N(CH$_3$)$_3^{2+}$(PF$_6^-$)$_2$	CF$_3$CN	(CH$_3$)$_3$N, 2.84; (CH$_3$)$_2$N, 2.89; CH$_2$, 3.37	
pyBH$_2$TMPDBH$_2$(py)$^{2+}$(PF$_6^-$)$_2^b$	CH$_3$NO$_2$	(CH$_3$)$_2$N, 2.10	H$_{3,5}$, 7.37; H$_4$, 7.81; H$_{2,6}$, 8.15
(CH$_3$)$_3$NBH$_2$TMPDBH$_2$N(CH$_3$)$_3^{2+}$(PF$_6^-$)$_2$	CD$_3$CN	(CH$_3$)$_3$N, 2.81; (CH$_3$)$_2$N, 2.80^c	
pyBH$_2$TMBDBH$_2$(py)$^{2+}$(PF$_6^-$)$_2$	CD$_3$CN	(CH$_3$)$_2$N, 2.58	H$_{3,5}$, 7.98; H$_4$, 8.47;H$_{2,6}$, 8.75
(CH$_3$)$_3$NBH$_2$TMBDBH$_2$N(CH$_3$)$_3^{2+}$(PF$_6^-$)$_2^b$	CH$_3$NO$_2$	(CH$_3$)$_3$N, 2.25; (CH$_3$)$_2$N, 2.20	
TMEDBH$_2^+$PF$_6^-$	CH$_2$Cl$_2$	(CH$_3$)$_2$N, 2.90; CH$_2$, 3.55	
TMPDBH$_2^+$PF$_6^-$	CH$_2$Cl$_2$	(CH$_3$)$_2$N, 2.80; CH$_2$, 2.20, 3.10	
TMBDBH$_2^+$PF$_6^-$	CH$_2$Cl$_2$	(CH$_3$)$_2$N, 2.80; CH$_2$, 2.02, 3.20	
[TMBDBH$_2$]$_n^{n+}$(PF$_6^-$)$_n$	CD$_3$CN	(CH$_3$)$_2$N, 2.78; CH$_2$, 1.77, 3.03	
[(CH$_3$)$_2$NC$_2$H$_4$py]BH$_2^+$PF$_6^-$	CH$_2$Cl$_2$	(CH$_3$)$_2$N, 2.77; CH$_2$, 3.43	H$_{3,5}$, 7.63; H$_4$, 8.03; H$_6$, 8.18
DMpipBH$_2^+$PF$_6^-$	CH$_2$Cl$_2$	CH$_3$, 2.93; CH$_2$, 3.44	
DMpipBHCl$^+$PF$_6^-$	CH$_2$Cl$_2$	CH$_3$, 2.88; CH$_2$, 3.58	
DMpipBHBr$^+$PF$_6^-$	CH$_2$Cl$_2$	CH$_3$, 2.91; CH$_2$, 3.61	
pyBH$_2$DMpipBH$_2$(py)$^{2+}$(PF$_6^-$)$_2$	CD$_3$CN	CH$_3$, 2.72; CH$_2$, 3.25	H$_{3,5}$, 8.00; H$_4$, 8.4; H$_{2,6}$; 8.77
(3,4-(CH$_3$)$_2$py)(TMED)BH^{2+}(PF$_6^-$)$_2$	CD$_3$CN	3-CH$_3$, 2.50; 4-CH$_3$, 2.62; (CH$_3$)$_2$N, 2.88; 3.08; CH$_2$, 3.82	H$_5$, 7.90; H$_{2,6}$, 8.47
(py)(dipy)BH^{2+}(PF$_6^-$)$_2^d$	CD$_3$CN		H$_{3,5}$, H$_{5,5'}$, 8.17 H$_4$,H$_{4,4'}$, 8.66 H$_{2,6}$, H$_{3,3'}$, H$_{6,6'}$, 8.83
(3,4-(CH$_3$)$_2$py)(dipy)BH^{2+}(PF$_6^-$)$_2^d$	CD$_3$CN	3-CH$_3$, 2.35; 4-CH$_3$, 2.55	H$_5$, 7.80; H$_{4,4'}$, H$_{5,5'}$, 8.22 H$_{2,6}$, H$_{3,3'}$, H$_{6,6'}$, 8.83

[a] δ values are in ppm downfield from internal tetramethylsilane and represent the centers of resolvable or complex multiplets. Symbols used have the meanings previously given in the Experimental Section. [b] Referenced with external TMS. [c] Shoulder. [d] These spectra were complex and assignments are tentative. Primed pairs of subscripts refer to dipyridyl H, unprimed to those on lutidine or pyridine.
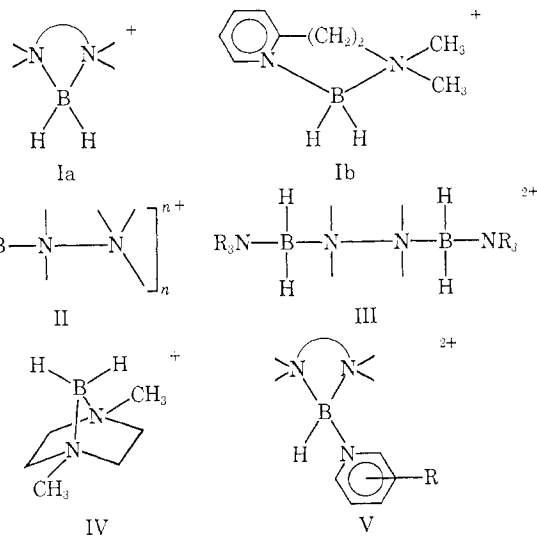
amine) cation reacted slowly (6% in 45 min), while the chelate cation from TMED gave 24% reaction in this time.

Hydrolytic Stability.—The divalent salts (amine)(diamine)-BH^{2+}(PF$_6^-$)$_2$ showed good hydrolytic stability and generally low solubility in common organic solvents. The chelated ion TMED-BH$_2^+$PF$_6^-$ also was stable toward hydrolysis in boiling water. The bicyclic ion IV was slowly hydrolyzed in boiling water.

Results and Discussion

The work reported here substantiates the syntheses of a series of cations containing BH$_2^+$ or BH^{2+} coordinated to diamines. These cations belong to five distinct structural types: I, cations in which (a) a symmetrical or (b) an unsymmetrical diamine acts as a chelating agent and completes a cyclic structure; II, polynuclear species containing BH$_2^+$ groups joined by a diamine in a large ring or linear structure; III, doubly charged species in which two amine-coordinated BH$_2^+$ groups are joined by a diamine to form a chain structure; IV, bicyclic ions where a BH$_2^+$ group serves as the bridge and common member of two five-membered rings in a structure similar to bicyclo[2.2.1]heptane, but carrying a positive charge; V, doubly charged ions containing a chelated BH^{2+} ion, with the fourth coordination position occupied by another amine.

All of these cations could be obtained by displacement of iodide from an iodinated borane adduct by a nitrogen base, a reaction which has recently been demonstrated to be generally applicable to the synthesis of 1+ or 2+ boron cations derived from monofunctional nitrogen bases.[7,11] In the present work, however, the type of

(11) G. E. Ryschkewitsch and M. A. Mathur, *Chem. Commun.*, in press.

product which was isolated depended very much on the proper choice of starting materials and on the nature of the ring system which could potentially form.

The reactions with tetramethylethane-, propane-, and butanediamine derivatives illustrate this point. The diamine–bis(monoiodoborane) was prepared *in situ* by iodination of the bis(boranes) and then allowed to react with the equimolar amount of diamine required for complete conversion to the derivative chelated cation I. Only tetramethylethanediamine gave this product in substantial yield; the tetramethylpropanediamine compound produced the expected six-membered ring in only about 10% yield, whereas with the corresponding

tetramethylbutanediamine no chelate compound could be isolated by this method. In the latter two reactions the predominant product was a cation to which structure II was assigned.

When trimethylamine–monoiodoborane was treated with saturated diamines, again different products were obtained, depending on the number of atoms in the diamine chain. The tetramethylethanediamine structure gave a mixture of chelate and bis(trimethylamine)-BH_2^+ ions, whereas the tetramethylpropanediamine structure gave the 2+ chain ion with structure III as the major product. These results can be explained in a straightforward way as the consequence of the following reaction sequence.

(1) Displacement of iodide from the amine–iodoborane, giving a bis(amine) boron cation with a free amine function pendant on one of the substituents. We were not able to isolate such an intermediate, nor

$$R_3NBH_2I \; + \; :N\!\!-\!\!-\!\!-\!\!N: \; \longrightarrow \; R_3N\overset{H}{\underset{H}{\overset{|}{\underset{|}{B}}}}N\!\!-\!\!-\!\!-\!\!N:^+,I^-$$
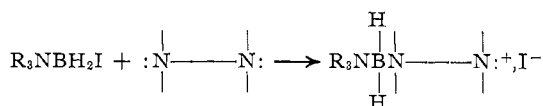
did we find clear-cut evidence for its existence in the spectra of incompletely reacted mixtures. Nevertheless, its formation is the only reasonable choice on the basis of analogy to the reactivity of monofunctional amines. The possibility that the diamine displaced the tertiary amine before halide was displaced is ruled out by our previous observation that such a process is extremely slow at room temperature[7] and by the evidence presented below.

(2) Because there is still a donor site available in the product, there are now two possible reaction paths for the intermediate: (a) intramolecular ring closure to give structure I, or (b) intermolecular reaction with another amine–iodoborane function.
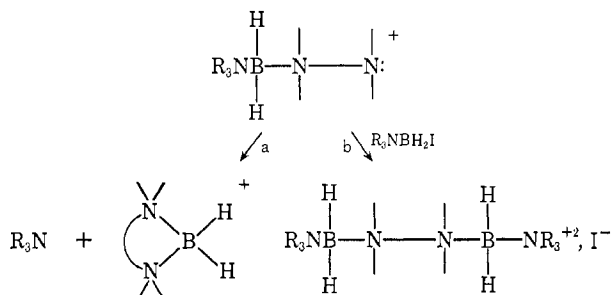
(3) Any amine liberated in step 2a then can compete for unreacted iodoborane to give a bis-amine cation: $R_3N + R_3NBH_2I \rightarrow (R_3N)_2BH_2^+,I^-$.

In terms of this reaction scheme the results of the experiments with $(CH_3)_3NBH_2I$ and TMED lead to two conclusions. First, because significant quantities of $[(CH_3)_3N]_2BH_2^+$ were formed even with excess TMED, $(CH_3)_3N$ can compete effectively with TMED for the iodoborane in step 3. This is perhaps not surprising in the light of previous experiments where trimethylamine reacted very much faster than triethylamine for steric and conformational reasons.[7] Second, because

only chelate (I) and no chain ion (III) was found even when $(CH_3)_3NBH_2I$ was in excess, ring closure (step 2a) must be considerably faster in this system than intermolecular reaction with amine–iodoborane (step 2b). It is noteworthy that bimolecular iodide displacement on iodoboranes is generally much faster than bimolecular transamination.[7] In the present instance however, the transamination in step 2a is a unimolecular reaction and for this reason should be accelerated relative to bimolecular step 2b.

The reaction of trimethylamine–iodoborane with TMPD took an entirely different course. Even with excess TMPD essentially no chelate compound was produced; instead, the chain compound was formed. This is a clear indication that the six-membered ring is more difficult to form than the five-membered one. The alternate interpretation that the free amine function of singly coordinated TMPD has substantially enhanced reactivity toward $(CH_3)_3NBH_2I$ is rejected on the basis that singly coordinated TMED has the same functionality as TMPD on the free amine end of the molecule, and therfore both should have similar reactivity. The relative ease of formation of the five-membered ring system is also illustrated by the reaction of equimolar amounts of N,N'-dimethylpiperazine with $(CH_3)_3NBH_2I$, which gave on heating in benzene an approximately equimolar mixture of $[(CH_3)_3N]BH_2^+$ and the bicyclic cation IV and no evidence for a structure corresponding to III.

Nevertheless, a six-membered ring was formed preferentially when 2-(2-dimethylaminoethyl)pyridine was used in place of TMPD. This apparent contradiction is readily resolved when one considers the established chemistry of boron cation syntheses: pyridine bases react with $(CH_3)_3NBH_2I$ much faster than do tertiary aliphatic amines,[7] and the presence of a pyridine ring on a trimethylamine–BH_2^+ unit activates the cation with respect to transamination.[7] On this basis, the expected reaction in step 1 would be cation formation with the pyridine end of the diamine, and subsequent internal transamination to give chelate (step 2a) should be faster than the corresponding reaction in the intermediate derived from TMPD.

The results from the reactions of the various diamines with diamine–bis(monoiodoboranes) can be interpreted in terms of similar considerations. Saturated rings were formed effectively only for five-membered systems (TMED or DMpip). Instead of closing the ring, pendant TMPD or TMBD apparently preferred to react at an iodoborane function. This reaction would give linear chains of polynuclear boron cations, and cyclization to large rings could also eventually occur, thus terminating the growth of the chain. In general terms, the proclivity of these systems to form five- or, to a lesser extent, six-membered rings, and to avoid seven-membered ones, parallels the situation in transition metal chelates.

Six- or seven-membered chelates were, however, readily formed by transamination of bis(trimethyl-amine)boronium iodide in refluxing diamine. The

first step in this reaction would form the species proposed as the intermediate in the reaction of diamines with an amine–iodoborane, *i.e.*, a cation in which trimethylamine and one end of the diamine are coordinated to BH_2^+ (step 1 above). Ring closure (step 2a) should be relatively more favorable since the competing reaction, leading to polynuclear species, is now another transamination rather than iodide displacement from amine–iodoborane as in step 2b. Transaminations on bis(trimethylamine)boronium ion are indeed very slow reactions as was shown in separate experiments here and elsewhere.[12]

Ebullioscopic experiments in acetonitrile solution were made for a number of salts and confirmed the structure assignments (Figure 1). Comparison with known compounds showed that 1+ ions gave nearly the expected apparent molecular weights in this solvent.[13] An increase in charge produced progressively larger deviations from the expected values in the direction expected for association of ions. The data for the polynuclear species derived from tetramethylbutane-

diamine suggest that extensive association exists in these materials and that the charge on the species is 3+ or larger. It is probable that the charge is not very great because the polynuclear species showed similar deviation from ideality as did an authentic 3+ ion. If this is true, then the elemental analysis which agrees with the formula $(diamineBH_2PF_6)_n$ suggests that the product contains large rings, rather than linear structures which would require additional terminal groups. There is little doubt, however, that the basic structural units have been correctly assigned, since, except for the generally broader appearance of absorption bands, the ir and nmr spectra closely correspond to those for the low molecular weight chelated species. These characteristics were invariant in materials obtained from reactions under different conditions. However, since solubilities in various solvents and exact elemental composition differed somewhat depending upon reaction conditions, it is likely that mixtures of polymers had been produced.

(12) T. E. Sullivan, M.S. Thesis, University of Florida, 1967.
(13) E. L. Muetterties, *J. Inorg. Nucl. Chem.*, **15**, 182 (1960); $(py)_2BI_2^+I^-$ gave an apparent molecular weight of 312 g; calcd 275 g.

Photochemistry of Borazine. B-Halogenation Reactions

By MARY OERTEL and RICHARD F. PORTER

B-Monobromoborazine has been obtained by the photolysis of a borazine–methyl bromide mixture in the gas phase with 1849-Å radiation. B-Monochloroborazine may be obtained by the photolysis of low-pressure mixtures of borazine and HCl, CH_3Cl, $CHCl_3$, CCl_4, or HSO_3Cl. Infrared spectra were obtained for monochloro- and monobromoborazine and the B-dideuterated derivatives. Aspects of the photochemical mechanism are discussed.

Introduction

Several monosubstituted borazines, including B-amino, B-hydroxy, and B-alkoxy derivatives, have been prepared by a photochemical procedure. We have now extended this procedure to halogenation reactions and in this paper we focus special attention on the reactions of borazine with methyl chloride and methyl bromide.

Experimental Section

Mixtures of borazine and halogenating reagent in the gas phase were irradiated with 1849-Å radiation in a procedure described earlier.[1] The initial ratio of borazine to reactant was about 5:1 with a total pressure between 10 and 15 mm. The series of halogenating reagents included CHF_3, HCl, CH_3Cl, $CHCl_3$, CCl_4, HSO_3Cl, CH_3Br, and CH_3I. B-Trideuterioborazine, prepared by the photochemical exchange of borazine and deuterium,[2] was also allowed to react with CH_3Cl and CH_3Br. Experiments

designed to aid in establishing mechanisms included irradiation of borazine with CH_3Br and a fivefold excess of argon and irradiation of borazine–Br_2 mixtures with radiation of wavelengths above 3000 Å. After irradiation, the reaction mixture was opened to a −130° trap, allowing the most volatile products to pass through for sampling for mass spectral analysis. The portion of the reaction mixture frozen in the −130° trap was then warmed and pumped through traps at −65 and −196°. The −65° trap was then warmed to −45° and residual borazine was removed. Mass spectral analysis showed that the material remaining in the −45° trap was the monohaloborazine. Infrared spectra of the products were obtained on a Perkin-Elmer Model 521 spectrophotometer using a 9-cm gas cell equipped with CsI windows. Far-infrared spectra were obtained on a Beckman IR-11 spectrophotometer in cells with polyethylene windows. Borazine was prepared by the reaction of $LiBH_4$ and NH_4Cl[3] and was purified by addition of ammonia to precipitate diborane and aminodiborane which are obtained as by-products.

Results

Photochemical reactions of borazine with HCl,

(1) G. H. Lee, II, and R. F. Porter, *Inorg. Chem.*, **6**, 648 (1967).
(2) R. F. Porter and E. S. Yeung, *ibid.*, **7**, 1306 (1968).
(3) G. W. Shaeffer, R. Schaeffer, and H. J. Schlesinger, *J. Amer. Chem. Soc.*, **73**, 1612 (1951).