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Contribution from the Department of Chemistry,
University of Florida, Gainesville, Florida 32611

Mixed-Tris(amine) Cations of Boron and Formation Mechanism[1]

MILAP A. MATHUR and GEORGE E. RYSCHKEWITSCH*

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The formation of tris(substituted pyridine) cations derived from BH^{2+} starting from trimethylamine–dibromoborane can proceed through several possible intermediate steps. By synthesizing the postulated intermediate of bis(amine) adducts of $BHBr^+$ and BBr_2^+, it was possible to test their reactivities independently and to establish the following reaction sequence: $(CH_3)_3N{\cdot}BHBr_2 + R\text{-py} \rightarrow (CH_3)_3N + R\text{-py}{\cdot}BHBr_2$; $R\text{-py}{\cdot}BHBr_2 + R\text{-py} \rightarrow (R\text{-py})_2BHBr^+ + Br^-$; $(R\text{-py})_2BHBr^+ + Br^- + R\text{-py} \rightarrow (R\text{-py})_3BH^{2+} + 2Br^-$. With use of amine–diiodoboranes of suitable amines as the reaction intermediates, the mixed-tris(substituted pyridine) cations of BH^{2+} were also synthesized: $R\text{-py}{\cdot}BHI_2 + 2R'\text{-py} \rightarrow [(R\text{-py})(R'\text{-py})_2]BH^{2+} + 2I^-$. The mixed-bis(amine)halo-substituted singly charged cations were identified as the reaction intermediates.

Introduction

In a previous paper[2] we have reported the synthesis of a number of salts of cations based on the ion BH^{2+} coordinated to three like nitrogen bases. The synthesis was accomplished by the substitution on the boron atom via trimethylamine–dibromoborane and some other amine–dihaloboranes as the intermediates. In this paper we wish to extend the applicability of these methods to the formation of cations of BH^{2+} in which the remaining three coordination positions on the boron atom are occupied by three nitrogen bases which are not all alike, i.e., to form mixed-tris(amine) cations. The further objective of this work has been to throw light on the exact sequence of reactions which leads to the eventual production of the tris(amine) cations of boron.

Experimental Section

Materials. Trimethylamine and hydrogen bromide were obtained from the Matheson Co., pyridine was from Mallinckrodt, and 4-methylpyridine was from Aldrich Chemicals. The liquid amines were dried and distilled before use over an appropriate drying agent. Iodine was purchased from Fisher Scientific Co. and bromine from Baker Chemical Co. Trimethylamine–borane, $(CH_3)_3N{\cdot}BH_3$, and pyridine–borane, $C_5H_5N{\cdot}BH_3$, obtained from Callery Chemical Co., were used without further purification. 4-Methylpyridine–borane,[3-5] $4\text{-}CH_3C_5H_4N{\cdot}BH_3$, trimethylamine–bromoborane,[6] $(CH_3)_3N{\cdot}BH_2Br$, pyridine–diiodoborane,[7] $C_5H_5N{\cdot}BHI_2$, 4-methylpyridine–diiodoborane,[7] and the boron salts of the type $A_2BH_2^+$, $A'ABH_2^+$, $A'ABHBr^+$, $A''ABH_2^+$, A_3BH^{2+}, and A_4B^{3+} [where A is $4\text{-}CH_3C_5H_4N$, A′ is $(CH_3)_3N$, and A″ is C_5H_5N] with the PF_6^- or the halide anion were prepared by using the methods found in the literature.[2,8-11]

Analyses and Instrumentations. The analytical procedures and instruments employed in this study were as described by us in our previous work.[2] The ^1H NMR data of the various boron cations are reported in Table I, whereas the infrared data, the elemental analyses, and the melting points (uncorrected) are included in the text of the synthesis of each cation.

Synthesis of Dihydrobis(4-methylpyridine)boron(1+) Bromide, $(4\text{-}CH_3C_5H_4N)_2BH_2Br$. Trimethylamine–bromoborane[6] (7.75 g, 51 mmol) was heated with 20 mL of dry 4-methylpyridine for 2 h between 100 and 120 °C. Trimethylamine gas was evolved, and a white solid was formed. The solid was washed with benzene and ether and dried under vacuum. The yield of the solid was 12.3 g, 86.0% calculated for $(4\text{-}CH_3C_5H_4N)_2BH_2Br$; mp 127–129 °C. The proton NMR of this product was in excellent agreement with the formula $(4\text{-}CH_3C_5H_4N)_2BH_2Br$. A small amount of this bromide salt was dissolved in water and was treated with a saturated solution of NH_4PF_6. The white crystalline material obtained after drying had spectral and other properties identical with those of the known compound $(4\text{-}CH_3C_5H_4N)_2BH_2PF_6$.[12]

Synthesis of Bromohydrobis(4-methylpyridine)boron(1+) Bromide, $(4\text{-}CH_3C_5H_4N)_2BHBr_2$. A sample of 3.37 g (11.3 mmol) of previously prepared $(4\text{-}CH_3C_5H_4N)_2BH_2Br$ was dissolved in 75 mL of CH_2Cl_2. Two milliliters of bromine was added drop by drop into the stirring solution. The reaction was immediate with the evolution of heat and HBr gas. After all the bromine was added, the progress of the reaction was followed by monitoring the proton NMR spectrum of the reaction mixture. After 4 h of reaction time the proton NMR of the reaction mixture showed no further change. The reaction was quenched by cooling the reaction mixture to 0 °C and by removing excess bromine with cyclohexene. The solid product was precipitated from its CH_2Cl_2 solution with an excess of hexane. The yield of the dry product was 4.29 g, 99.3% calculated for $(4\text{-}CH_3C_5H_4N)_2BHBr_2$. The product had no sharp melting point. The proton NMR of the purified material showed that the peaks due to the 2,6 protons of the 4-methylpyridine were shifted by 0.41 ppm (Table I) downfield from the unbrominated salt. A peak due to boron attached hydrogen was not observed. Anal. Calcd for $C_{12}H_{15}N_2BBr_2$: C, 40.25; H, 4.22; N, 7.83; Br, 44.65. Found: C, 39.71; H, 3.54; N, 7.8; Br, 44.51. The product decomposed rapidly on dissolving, even in ice-cold water, with evolution of a neutral gas (probably H_2) and did not form a PF_6^- salt when treated with a saturated solution of NH_4PF_6 in water.

Synthesis of Dibromobis(4-methylpyridine)boron(1+) Bromide, $(4\text{-}CH_3C_5H_4N)_2BBr_3$. A sample of 6.20 g (22.3 mmol) of earlier prepared $(4\text{-}CH_3C_5H_4N)BH_2Br$ was dissolved in 100 mL of dry CH_2Cl_2 and was placed in a three-necked flask equipped with a nitrogen supply, a dropping funnel, and a septum cap. To the stirring solution of $(4\text{-}CH_3C_5H_4N)_2BH_2Br$ was added 20 mL of bromine in small aliquots through the dropping funnel. The solution was stirred magnetically, and the progress of the reaction was followed by monitoring the ^1H NMR spectra of the samples of the reaction mixture withdrawn through the septum cap. After the addition of all of the bromine the dropping funnel was replaced by a reflux condenser cooled by ice-cold water. The ^1H NMR spectrum taken after 12 h showed no starting material (no peak at −2.65 ppm) but showed a peak at −2.67 ppm and a shoulder 4 Hz downfield from the peak. In comparison of the ^1H NMR chemical shifts of the known compounds, the peak at −2.67 ppm was assigned to $(4\text{-}CH_3C_5H_4N)_2BHBr_2$ and the shoulder was assigned to $(4\text{-}CH_3C_5H_4N)_2BBr_3$. The ^1H NMR spectrum of the reaction mixture after 240 h showed that the shoulder (changed into a peak) had acquired a maximum in its peak area relative to the areas of the other peaks (at −7.98 and 9.02 ppm, respectively). In order to ensure the completion of the reaction, we refluxed the mixture further for 4 h. After the solution was cooled, the excess bromine was removed by injecting enough cyclohexene in small amounts into the reaction mixture, until the reaction mixture became almost colorless. The solvent then was removed on a rotary evaporator; the paste so obtained was washed with hexane and dried. The yield was 8.34 g, 86.0% calculated for $(4\text{-}CH_3C_5H_4N)BBr_3$. The ^1H NMR spectrum of this product had an expected pattern (Table

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Table I. Proton NMR Spectra of Boron Cations[a]

	$N\text{-}CH_3$		$R\text{-}CH_3$			ring proton			
cations	δ	*M*	δ	*M*	ring proton	δ	*M*	*J*, Hz	solvent
as bromide salts									
$(4\text{-}CH_3C_5H_4N)_2BH_2^+$			2.65	1	$H_{3,5}$	7.81	2	7	CH_2Cl_2
					$H_{2,6}$	8.84	2	7	
$(4\text{-}CH_3C_5H_4N)_2BHBr^+$			2.67	1	$H_{3,5}$	7.83	2	7	CH_2Cl_2
					$H_{2,6}$	9.25	2	7	
$(4\text{-}CH_3C_5H_4)_2BBr_2^+$			2.73	1	$H_{3,5}$	7.95	2	7	CH_2Cl_2
					$H_{2,6}$	9.23	br		
as iodide salts									
$[(4\text{-}CH_3C_5H_4N)(CH_3)_3]BHI^+$	2.87	1	2.65	1	$H_{3,5}$	7.87	2	7	H_2O
					$H_{2,6}$	8.97	2	7	
$[(4\text{-}CH_3C_5H_4N)(C_5H_5N)_2]BH^{2+}$			2.00	1	other protons	7.18–8.22	8		CH_3NO_2 (impure)
as PF_6^- salts									
$(4\text{-}CH_3C_5H_4N)_2BBr_2^+$			2.03	1	$H_{3,5}$	7.21	2	7	CH_3NO_2
					$H_{2,6}$	8.25	2		
$[(4\text{-}CH_3C_5H_4N)(CH_3)_3N]BHI^+$	2.39	1	2.13	1	$H_{3,5}$	7.21	2	7	CH_3NO_2
					$H_{2,6}$	7.25	2	7	
	2.98	1	2.77	1	$H_{3,5}$	7.90	2	7	CH_2Cl_2
					$H_{2,6}$	8.95	2	7	
$[(4\text{-}CH_3C_5H_4N)_2(C_5H_5N)]BH^{2+}$			2.00	1	$H_{3,5}$ 4-$CH_3C_5H_4N$	7.23	2	7	CH_3NO_2
					other ring protons	7.42–7.95	6		
$[(4\text{-}CH_3C_5H_4N)(C_5H_5N)_2]BH^{2+}$			2.10	1	other ring protons	7.18–8.17	8		CH_3NO_2

[a] The chemical shifts are downfield from external tetramethylsilane. $N\text{-}CH_3 = CH_3$ groups from trimethylamine. $R\text{-}CH_3$ = methyl group attached to pyridine ring.

I). The bromide analysis gave 54.93% Br (calculated 54.91%). The yield of the hexafluorophosphate derivative prepared at 25 °C was only 26.2% of the amount of $(4\text{-}CH_3C_5H_4N)_2BBr_3$ taken, showing that the product decomposed in water at this temperature. The yield, however, increased to 89.2% when the derivative was prepared in ice-cold water. The melting point of the PF_6^- salt was 202–204 °C, and its ^1H NMR spectrum had a singlet, a doublet, and a multiplet (Table I) in the area ratio of 3.1:2:2 (calculated 3:2:2). The infrared spectrum in KBr pellet had absorptions at 3500–3400 (br, w), 3270 (w), 3160 (w), 3140 (w), 3080 (w), 3060 (w), 3202 (w), 2930 (w), 2860 (w), 2730 (w), 2545 (w), 1960 (w), 1860 (w), 1700 (w), 1635 (s), 1670 (w), 1520 (s), 1460 (s), 1380, 1350, 1265 (w), 1250 (s), 1105–1095 (s), 710 (s), 670 (s), 567 (s), 530 (s), 510 (w), 485, 378, 345 (w), and 270 cm^{-1}. Anal. Calcd for $C_{12}H_{14}N_2BBr_2PF_6$: C, 28.71; H, 2.82; N, 5.58; Br, 31.90. Found: C, 28.71; H, 2.72; N, 5.67; Br, 32.00.

Reaction of Bromohydrobis(4-methylpyridine)boron(1+) Bromide with 4-Methylpyridine. A mixture of $(4\text{-}CH_3C_5H_4N)_2BHBr_2$ and 4-methylpyridine in the millimolar ratio 1.7:12.0 was suspended in 15 mL of dry benzene and was refluxed in an atmosphere of dry nitrogen for 16 h. The contents were cooled, the solvent was removed, and the solid obtained was washed with benzene and dried. The weight of the solid recovered was 0.780 g or 99.7% calculated for $(4\text{-}CH_3C_5H_4N)_3BHBr_2$. The identity of the product was confirmed by comparing its melting point and ^1H NMR and infrared spectra with those of a known sample of $(4\text{-}CH_3C_5H_4N)_3BHBr_2$.[2] Further confirmation was obtained by converting a sample of this product to its hexafluorophosphate derivative and comparing its melting point (220–223 °C) with that of an authentic sample of $(4\text{-}CH_3C_5H_4N)_3BH(PF_6)_2$.[2]

Reaction of 4-Methylpyridine with Bromohydro(4-methylpyridine)(trimethylamine)boron(1+) Bromide. The compound $[(4\text{-}CH_3C_5H_4N)(CH_3)_3N]BHBr_2$ used for this study was prepared and purified by the procedure reported by Ryschkewitsch and Garrett.[9] A sample of 0.168 g (0.52 mmol) of the salt was refluxed for 24 h with 4.8-mL solution of 4-methylpyridine in benzene (7.5 mmol of $4\text{-}CH_3C_5H_4N$ in 4 mL of C_6H_6). The weight of the solid obtained after removal of excess 4-benzene was 0.214 g. The ^1H NMR spectrum of this product in CH_2Cl_2 revealed that it was a mixture of starting material and the expected reaction product $(4\text{-}CH_3C_5H_4N)_3BHBr_2$.[2]

A portion of this mixture was converted into the hexafluorophosphate derivatives in aqueous solution. The PF_6^- derivative was separated from water and washed with diethyl ether. A sample of 0.099 g of this PF_6^- derivative was suspended in 10 mL of CH_2Cl_2 and stirred for 30 min. Undissolved solid was collected and washed with 5 mL of CH_2Cl_2. The ^1H NMR spectrum of this solid in nitromethane and the melting point were identical with those of $(4\text{-}CH_3C_5H_4N)_3BH(PF_6)_2$. It weighed 0.056 g (0.096 mmol). Solvent was removed from the filtrate and washings by evaporation. The ^1H NMR and infrared spectra of the resulting solid product were identified with those of the PF_6^- derivative of the starting cation. It weighed 0.036 g (0.10 mmol). The loss in weight was 0.005 g during this separation. No other product was detected.

Synthesis of Hydroiodo(4-methylpyridine)(trimethylpyridine)boron(1+) Iodide, $[(4\text{-}CH_3C_5H_4N)(CH_3)_3N]BHI_2$. A sample of 1.06 g (9.9 mmol) of 4-methylpyridine–borane was reacted with 2.54 g (10.0 mmol) of iodine for 5 h at 90 °C in 30 mL of toluene. After the reaction mixture was cooled to 35 °C, trimethylamine gas was bubbled through it until no more precipitate formation was observed. The yellow precipitate obtained was washed with benzene and was dried. The yield was 2.93 g, 96.0% calculated for $[(4\text{-}(CH_3C_5H_4N)(CH_3)_3N]BHI_2$; mp 198–202 °C. The ^1H NMR spectrum in water solution gave the expected two singlets and two doublets (Table I) with an area ratio of 3:8.1:2:1.8 (calculated 3:9:2:2). Iodide analysis gave 60.17% I (calculated 60.84%). A 0.452-g sample of this iodide salt was converted to the hexafluorophosphate derivative. The yield was 91%; mp 145–148 °C. The ^1H NMR spectrum of this product in nitromethane gave expected two singlets and two doublets (Table I) in the area ratio of 3:9:2:2, as calculated for $[(4\text{-}CH_3C_5H_4N)(CH_3)_3N]BHIPF_6$. The infrared spectrum of the PF_6^- salt in KBr pellet showed absorptions at 3135, 3075 (w), 3050 (s), 2970 (w), 2925 (w), 2860 (w), 2510 (w), 1855 (w), 1640 (s), 1565 (w), 1510 (w), 1490–1450 (br, s), 1420 (s), 1320 (w), 1340, 1280 (w), 1245 (s), 1230 (w), 1220, 1200 (w), 1155–1114 (d, s), 1035 (s), 970 (s), 900–800 (br, s), 750, 740 (s), 705 (s), 680 (s), 650, 635 (s), 560 (s), 510, 495, 430 (w), 400 (w), 370 (w), and 220 (w) cm^{-1}. Anal. Calcd $C_9H_{18}N_2BIPF_6$: C, 24.77; H, 3.90; N, 6:42;, I, 29.12. Found: C, 26.34; H, 4.16; N, 6.66; I, 27.97. The lower percent of I and the higher percent of C and H were attributed to the probable impurity of the $[(4\text{-}CH_3C_5H_4N)(CH_3)_3N]BH_2PF_6$ salt.

Synthesis of Hydrobis(4-methylpyridine)(pyridine)boron(2+) Bis(hexafluorophosphate), $[(4\text{-}CH_3C_5H_4N)_2(C_5H_5N)]BH(PF_6)_2$. Pyridine–borane, 1.638 g (17.6 mmol), was diiodinated by reaction with 4.578 g (17.5 mmol) of solid iodine in 30 mL of toluene. Reaction was completed by heating the reaction mixture to 75 °C for 12 h. The products of the reaction were a light yellow solution and a dark solid deposited on the sides of the flask. The solid was rejected after filtration. Trimethylamine gas was bubbled through the remaining solution, and a light yellow solid was obtained. The solid was collected and washed with benzene and ether, and the solid was dried, the yield was 1.529 g, 21.5% (calculated for $[(C_5H_5N)(CH_3)_3N]BHI_2$). The ^1H NMR spectrum of the product in nitromethane gave two singlets at 2.12 and 2.28 ppm and three unresolved doublets at 7.47, 7.97, and 8.50 ppm, respectively, downfield from external tetramethylsilane.

The appearance of two peaks at 2.12 and 2.28 ppm suggested that the product could have been a mixture of dihydro(pyridine)(trimethylamino)boron(1+) iodide, $[(C_5H_5N)(CH_3)_3N]BH_2I$,[8] hydrobis(trimethylamine)(pyridine)boron(2+) iodide, $[\{(CH_3)_3N\}_2(C_5H_5N)]BHI_2$, and hydroiodo(trimethylamine)(pyridine)boron(1+) iodide, $[(C_5H_5N)_2(CH_3)_3N]BHI_2$. All these compounds contain a $(CH_3)_3N$ group and could be the products in this reaction.

A sample of 1.04 g of product was dissolved in 30 mL of nitromethane, and 2 mL of 4-methylpyridine was added to it. The solution was heated for 2 h between 45 and 50 °C. A basic gas was evolved, and the solid collected after evaporation of excess nitromethane weighed 1.41 g. In order to identify the components of the mixture, we converted the product into the PF_6^- salt. The yield was 1.17 g. The PF_6^- salt was suspended in 20 mL of CH_2Cl_2 and was stirred for 1 h. A solid was separated, dried, and weighed (1.11 g). The melting point was 209–212 °C. The ^1H NMR spectrum of this solid in nitromethane gave a singlet, a doublet, and six more peaks (Table I). The ratio of the sum of areas under all the peaks downfield to that of the singlet was 2.18:1 which was close to the calculated ratio for $[(4\text{-}CH_3C_5H_4N)_2(C_5H_5N)]BH(PF_6)_2$ of 2.17:1. The infrared spectrum of the product in KBr pellet showed absorptions at 3660 (s), 3600, 3460–3420 (br), 3140 (s), 3080, 3060 (w), 2860 (w), 2540 (s), 1960–1940 (d, w), 1690 (w), 1640 (s), 1630 (w), 1565, 1518, 1498, 1470–1460 (d, s), 1080 (w), 1060 (s), 1030 (s), 970 (w), 890–830 (br, s), 800 (w), 765 (w), 760 (s), 720 (w), 695 (s), 670 (w), 650 (w), 625, 560 (s), 530 (w), 500–490 (d), 450–440 (w), and 220 (w) cm^{-1}. Anal. Calcd for $C_{17}H_{20}N_3BP_2F_{12}$: C, 36.01; H, 3.55; N, 7.4. Found: (i) C, 35.30; H, 3.73; N, 7.25. Found: (ii) C, 35.75; H, 3.68; N, 7.29. The filtrate obtained above was evaporated to dryness and weighed (0.06 g). The melting point of (66–68 °C) was close to the melting point (67–68 °C) of the reported compound $[(C_5H_5N)(4\text{-}CH_3C_5H_4N)]BH_2PF_6$.[10]

Synthesis of Hydrobis(pyridine)(4-methylpyridine)boron(2+) Diiodide, $[(C_5H_5N)_2(4\text{-}CH_3C_5H_4N)]BHI_2$. 4-Methylpyridine–borane, 1.10 g (10.3 mmol), was dissolved in 30 mL of dry benzene and was reacted with 2.89 g (11.4 mmol) of solid iodine between 25 and 60 °C. The resulting solution was cooled to room temperature and was treated with 20 mL of dry pyridine. Immediately a light yellow precipitate was formed. The precipitate was washed with benzene followed by ether and was dried in a desiccator. The yield was 4.15 g, 77.5% (calculated for $[(C_5H_5N)_2(4\text{-}CH_3C_5H_4N)]BHI_2$). The ^1H NMR spectrum of the product in nitromethane gave a singlet and eight peaks in groups of four spread between regions of 7.18–7.55 ppm and 7.85–8.22 ppm downfield from external tetramethylsilane, respectively. The ratio of the total area under the eight peaks to that of singlet was 5.45:1.00 (calculated 4.66:1.00), indicating that the iodide salt was impure. A known weight (0.622 g) of the iodide salt on conversion to the PF_6^- salt gave 0.466 g of the PF_6^- salt: yield 70.5%; mp 216–218 °C. The ^1H NMR spectrum of the PF_6^- salt in nitromethane showed a singlet and eight peaks spread between 7.18 and 8.17 ppm (Table I). The ratio of the total peak area under the eight peaks to that of singlet was as the calculated value (4.66:1.00). The infrared spectrum in a KBr pellet showed absorptions at 3440 (br), 3140, 3080 (w), 2920, 2860 (w), 2550, 1620 (s), 1635 (s), 1580 (w), 1498, 1465 (s), 1245 (w), 1220 (s), 1160–1135 (d, br, s), 765 (w), 750 (w), 690 (s), 630 (w), 590 (w), 560 (s), and 495 (w) cm^{-1}. Anal. Calcd for $C_{16}H_{18}N_3BP_2F_{12}$: C, 34.71; H, 3.29; N, 7.59. Found: C, 34.52; H, 3.52; N, 7.46.

Discussion

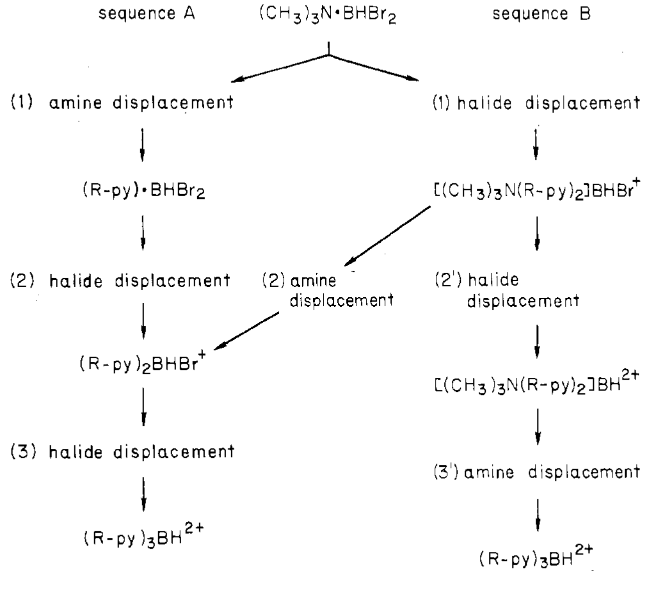
Stoichiometric Mechanism. The net reaction between trimethylamine–dibromoborane and pyridine bases, R-py, is

$$(CH_3)_3N{\cdot}BHBr_2 + 3\text{R-py} \rightarrow (\text{R-py})_3BH^{2+} + 2Br^- + (CH_3)_3N$$

Since there are three substituents on boron which are replaced, the reaction must involve a number of separate steps and therefore a number of intermediates.

Several substituted pyridines were allowed to react with $(CH_3)_3N{\cdot}BHBr_2$ at elevated temperatures. The examination of the end products in each of the experiments gave either the bromides of doubly charged boron dications or the starting material or both.[2] In none of the experiments were there detected intermediates between $(CH_3)_3N{\cdot}BHBr_2$ and $(\text{R-py})_3BHBr_2$. The mass balance of the product and the starting material was between 95.1 and 99.7% which again indicated that there were no intermediates which were stable and persistent under the conditions of reactions. It is therefore necessary to assume that all steps except the first step must have been fast and that the first step was the rate-determining step.

Scheme I



There are two possible ways in which an amine can react initially with $(CH_3)_3N{\cdot}BHBr_2$: the incoming amine either may displace trimethylamine to form a new amine–dibromoborane

$$(CH_3)_3N{\cdot}BHBr_2 + \text{R-py} \rightarrow (CH_3)_3N + \text{R-py}{\cdot}BHBr_2$$

or may displace a bromide ion to give an unsymmetrical singly charged cation

$$(CH_3)_3N{\cdot}BHBr_2 + \text{R-py} \rightarrow [(CH_3)_3N(\text{R-py})]BHBr^+ + Br^-$$

Either of these intermediate products may then react further with more base until the final ion $(\text{R-py})_3BH^{2+}$ is obtained.

Essentially, the overall reaction must encompass three steps, two displacements of halide ion and one displacement of trimethylamine. Various possibilities are created which differ in the sequencing of these steps. These are outlined in Scheme I, each step representing reaction with 1 mol of pyridine base.

In order to shed light on which sequence was in fact followed by the system, we considered potential individual steps separately. One of the potential intermediates, the mixed cation bromohydro(4-methylpyridine)(trimethylamine)boron(1+), was only half converted to hydrotris(4-methylpyridine)boron(2+) over a 24-h reflux period with a large excess of the pyridine base in benzene, and no other components except the starting material were found. The reaction conditions here were comparable to those previously published,[2] in which trimethylamine–dibromoborane gave a 40% yield of hydrotris(4-methylpyridine)boron(2+) bromide on refluxing in benzene with a somewhat lesser excess of 4-methylpyridine in benzene. Thus, the first step in the 2+ cation synthesis proceeded at a rate which was very similar to the rate of conversion of a potential intermediate to 2+ cation (steps B2 and B3). If sequence B were followed, a substantial steady-state concentration of $[(CH_3)_3N(4\text{-}CH_3py)]BHBr^+$ would have to accumulate at the midpoint of reaction. This was not found, in spite of excellent analytical techniques.

In contrast, the second step in sequence A was found independently[2] to occur at a very rapid rate even at room temperature, a fact which would preclude the isolation of the first intermediate. The last step in sequence A was also shown here and elsewhere[2] to proceed to completion under much milder conditions than did the overall reaction. Neither of the two intermediates in sequence A could therefore reach significant concentrations during reaction and therefore would escape detection.

The experimental data thus were fully consistent with sequence A, in which there was a primary and slow substitution of trimethylamine–borane by 4-methylpyridine–borane. This was followed by a very rapid conversion of the neutral 4-methylpyridine–dibromoborane to the bromohydrobis(4-methylpyridine)boron(1+) ion which in turn yields the final 2+ ion at a relatively fast rate.

Relative Reactivities. The facts presented here and in previous work[1-3] allow one to make the following generalizations regarding the reactivities of haloboranes and haloborane cations toward eventual substitution by nitrogen bases.

When diiodoboranes are used in place of bromoboranes, a general increase of reactivity with respect to halide loss results,[1,2] as is the case for halide loss from monohaloboranes.[3] There is a further enhancement of reactivity when one compares trimethylamine adducts with adducts of pyridine bases. Although cations tend to be less reactive than neutral boranes, the latter relationship is maintained also for cationic species, since $(4\text{-}CH_3py)_2BHBr^+$ appeared to be more reactive than the dissymmetric $[(4\text{-}CH_3py)(CH_3)_3N]BHBr^+$.

These facts allow one to formulate strategies for the synthesis of unsymmetrically substituted boron cations via nucleophilic displacements. For example, the racemate of the dissymmetric $[(4\text{-}CH_3py)(CH_3)_3N]BHX^+$ ion, though capable of existence,[9] is not obtainable for X = Br by simple displacements, because trimethylamine–dibromoborane is too unreactive toward halide loss and instead loses trimethylamine when exposed to 4-methylpyridine. Optimal reactivity is achieved in 4-methylpyridine–diiodoborane, which allows displacement of iodide even by trimethylamine. Similarly, the enhancement of reactivity by the presence of iodide and a pyridine ring made possible the synthesis of the mixed-tris(amine) cation $(4\text{-}CH_3py)BH^{2+}$ via pyridine–diiodoborane.

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Registry No. $(4\text{-}CH_3C_5H_7N)_2BH_2Br$, 74081-68-8; $(4\text{-}CH_3C_5H_4N)_2BHBr_2$, 74081-69-9; $(4\text{-}CH_3C_5H_4N)_2BBr_3$, 74081-70-2; $[(4\text{-}CH_3C_5H_4N)(CH_3)_3N]BHI_2$, 74081-71-3; $[(C_5H_5N)_2(4\text{-}CH_3C_5H_5N)]BHI_2$, 74081-72-4; $(4\text{-}CH_3C_5H_4N)_2BBr_2(PF_6)$, 27882-74-2; $[(4\text{-}CH_3C_5H_4N)(CH_3)_3N]BHI(PF_6)$,74081-74-6; $[(4\text{-}CH_3C_5H_4N)_2(C_5H_4N)]BH(PF_6)_2$, 74081-76-8; $[(C_5H_5N)_2(4\text{-}CH_3C_5H_4N)]BH(PF_6)_2$, 74112-68-8; $(4\text{-}CH_3C_5H_4N)_3BHBr_2$, 72541-47-0; $(4\text{-}CH_3C_5H_4N)_3BH(PF_6)_2$, 25338-40-3; $[(4\text{-}CH_3C_5H_4N)(CH_3)_3N]BHBr_2$, 74081-77-9; $[(C_5H_5N)(4\text{-}CH_3C_5H_4N)]BH_2PF_6$, 22638-66-0; $[(C_5H_5N)(CH_3)_3N]BHI_2$, 74081-78-0; $(CH_3)_3N{\cdot}BH_2Br$, 5275-42-3; $4\text{-}CH_3C_5H_4N{\cdot}BH_3$, 3999-39-1; $C_5H_5N{\cdot}BH_3$, 110-51-0.

Contribution from the Department of Chemistry,
University of Illinois, Chicago, Chicago, Illinois 60680

Boron Subhalide Chemistry. Formation of Octabromomethylnonaborane, $CH_3B_9Br_8$, and Other Alkylated Nonaboranes from Triethylammonium Decabromodecaborate

D. SAULYS and J. A. MORRISON*

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The thermal decomposition of $[(C_2H_5)_3NH]_2B_{10}Br_{10}$ has been investigated to determine if the oxidative-decomposition reaction of perhalogenated borane anion salts other than $(H_3O)_2B_{10}Cl_{10}$ might prove to be a viable synthetic route for the preparation of substituted boron subhalides. At temperatures near 430 °C the trialkylammonium salt is found to decompose to yield predominantly the new compound $CH_3B_9Br_8$. The decomposition appears to be radical in nature. By varying the reaction conditions we can also isolate other previously unknown alkylated boron subbromides, $C_2H_5B_9Br_8$, $(CH_3)_2B_9Br_7$, and $CH_3(C_2H_5)B_9Br_7$, along with B_9Br_9, but in smaller amounts. The boron chemical shifts of B_9Br_9 (−60.4 ppm) and $CH_3B_9Br_8$ (−62.2 ppm) are shown to be very deshielded relative to the chemical shifts of similar nine-atom frameworks that contain $2n + 2$ framework electrons.

Introduction

Little is known about the boron subhalides, e.g., B_4Cl_4, B_8Cl_8, or B_9Cl_9, and less about their derivatives. These compounds are of interest because they have two fewer framework electrons than are usually required by the well-known framework electron–structural correlation.[1] In part, the subhalides have been little studied because there are few convenient syntheses available.

The earliest preparation of these compounds involved the formation, in discharge reactions, of B_2Cl_4 which was then thermally decomposed to yield the very unusual radical species $B_{12}Cl_{11}$ along with a number of polyhedral boron subchlorides, B_nCl_n (n = 4, 7–12).[2] Diboron tetrabromide is similarly reported, primarily on the basis of mass spectral results, to yield a number of polyhedral boron subbromides, B_nBr_n (n = 7–10), when heated.[3] The yields of the boron subhalides obtainable from these decompositions are not known.

Two other preparations each of which yields only one polyhedral product have been reported. The first is the oxidation of the borane anion $B_9H_9^{2-}$ which, when reacted with 20 equiv of SO_2Cl_2, forms B_9Cl_9 in 30% yield.[4] The second is the thermal decomposition of the hydronium salt of the perchlorinated borane anion $(H_3O)_2B_{10}Cl_{10}$. From the latter reaction one of the very few known derivatives of the boron subhalides, B_9Cl_8H, has been isolated.[5] Aside from its synthetic aspects the second reaction is of particular interest because several events must occur contemporaneously: oxidation of the anion to the subhalide; substitution of one of the ligands; and reduction in cage size. Since the original publication, however, there have been no further studies to indicate

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