Inorg. Chem. **1980**, *19*, 887–891

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

Tris(amine) Cations of Boron[1]

MILAP A. MATHUR and GEORGE E. RYSCHKEWITSCH*

Received August 28, 1979

Divalent cations of boron of the general formula A_3BHX_2 (where A is a pyridine or a substituted pyridine and X is Br^-, I^-, or PF_6^-) were synthesized by the nucleophilic displacement on $(CH_3)_3N{\cdot}BHBr_2$ or on dihalo boron adducts of pyridine or substituted pyridine. The displacement of halide or $(CH_3)_3N$ from $(CH_3)_3N{\cdot}BHBr_2$ is controlled by favorable steric factors in the attacking amines, by the basicity of attacking amines, and by the nature of the displaced halogens. Iodo derivatives react more rapidly than the bromo derivatives. Compared with the case of the monovalent cations of boron the B–H bond in divalent cations is more resistant toward halogenation.

Introduction

Boron cations containing the BH_2^+ unit are well-characterized chemical species,[2-12] but cations with more than one positive charge are less well-known. Species with more than one positive charge per boron atom and species incorporating a boron–halogen bond have been postulated as the reaction product of boron trihalides and primary amines,[13,14] but lack of structural proof left doubt as to the identity of these materials. Subsequently salts of the brominated cation $(py)_3BBr^{2+}$ were identified and well characterized.[15]

The work reported here had as its objective to prepare species containing a BH^{2+} group and to examine the reactivity of the B–H bond when such a highly charged entity is coordinated to uncharged and otherwise unreactive bases. The general approach to the syntheses envisioned the formation of a BH unit as part of an uncharged borane adduct as an intermediate and subsequent displacement of three of the substituents on the tetrahedral boron center.

Experimental Section

Materials. Trimethylamine–borane and pyridine–borane were obtained from Callery Chemical Co. and were used without further purification. 4-Methylpyridine–borane was synthesized by using the methods reported in the literature.[12,16,17] Trimethylamine, hydrogen chloride, hydrogen bromide, and chlorine gases were purchased from Matheson Co. All other materials were standard reagent grade. The liquid amines were distilled and dried before use and were stored over calcium hydride or Molecular Sieve 3A. Ammonium hexafluorophosphate was obtained from the Ozark Mahoning Co. and was recrystallized before use. Solvents were used without purification except for drying over calcium hydride, lithium aluminum hydride, or molecular sieve when appropriate. Trimethylamine–tribromoborane[15] and bromohydro(4-methylpyridine)(trimethylamine)boron(1+) hexafluorophosphate[7,9] were previously prepared in this laboratory and were employed after purification.

Analyses. The samples for the halogen analyses were dissolved or suspended in approximately 30 mL of 1-propanol, digested for about 30 min, and then boiled for 1 h after 15 mL of 10% sodium hydroxide solution was added. Halogens were estimated in the neutralized solution either by the Vohlhard method or by potentiometric titration using Ag/AgCl and calomel electrodes. Elemental analyses for other elements were done by Peninsular Chemical Research, Inc., Gainesville, Fla., and Galbraith Laboratory, Inc., Knoxville, Tenn. Melting points of the various compounds were determined in a capillary tube (sealed in some cases) on a Thomas Hoover apparatus and were not corrected.

Instrumentation. Infrared spectra were obtained on either Beckman IR-10 or Perkin-Elmer 137 instruments. ^1H NMR spectra were taken on a Varian A-60-A instrument with tetramethylsilane as external or internal reference. ^{11}B NMR spectra were obtained at 19.3 or 32.1 MHz with trimethyl borate as the external reference.

Hydrotris(pyridine)boron(2+) Dibromide.[18a] A solution of 2.310 g (10.0 mmol) of trimethylamine–dibromoborane[18b] in 40 mL of dry pyridine was placed into a 125-mL Erlenmeyer flask equipped with reflux condenser and protected from the atmosphere by a tube filled with Drierite. The solution was brought to boiling and was refluxed for 24 h while the fine crystalline bromide salt slowly precipitated. After the solution was cooled, the solid was filtered through Whatman No. 42 paper and washed first with 100 mL of benzene and finally with 30 mL of diethyl ether. After the solid was dried under vacuum, the yield was 3.950 g (96%) of $(C_5H_5N)_3BHBr_2$, mp 215–220 °C. The product was recrystallized by slow addition of 240 mL of acetone to its water solution (0.818 g in 15 mL of water). The white precipitate, washed with acetone, yielded 0.700 g (86%) of purified salt, mp 222–224 °C. When exposed to humid atmosphere, the salt was hydrated as indicated by the bromide analysis, 35.85% Br (calcd 35.91%), for dihydrate. Both water molecules of the dihydrate could be removed by evacuating over concentrated H_2SO_4 for 40 h [1.592 g (3.6 mmol) of dihydrated salt lost 0.130 g (7.2 mmol) of water]. The infrared spectrum of the product in a KBr pellet showed peaks at 3500–3300 (b), 3020–3000 (w), 2535 (s), 1632 (s), 1520 (w), 1490 (w), 1460 (s), 1370–1350 (w, b), 1260 (w), 1160 (w), 1150 (s), 1090, 1050, 1025 (s), 970 (w), 820 (s), 770–780 (s), 745 (s), 690, 680 (s), 650, 625 (s), 590, 530 (b), 450 (b), and 420 (w) cm^{-1}.

Conversion to Hexafluorophosphate Salt. The water-soluble tris(pyridine)boronium dibromide, 0.766 g (1.87 mmol), was dissolved in 15 mL of water. Excess saturated solution of ammonium hexafluorophosphate was added to the stirring solution. The filtered solid was washed with water (50 mL) until the washings were free of Br^- and finally washed with 30 mL of anhydrous diethyl ether. The yield of dried product was 0.973 g (96%) of $[(C_5H_5N)_3BH][(PF_6)_2]$, mp 248–250 °C. Recrystallization by letting a warm solution of the salt in 20 mL of 1:1 water–acetone evaporate slowly gave no change in the melting point. The infrared spectrum in KBr pellet showed the characteristic strong absorption for PF_6^- between 880 and 820 cm^{-1}.[19] Anal. Calcd for $C_{15}H_{16}N_3BP_2F_{12}$: C, 33.39; H, 2.97; N, 7.79; B, 2.00; P, 11.50. Found: C, 33.04; H, 2.94; N, 7.68; B, 1.79; P, 11.39.

---

(1) (a) Mathur, M. A. Doctoral Dissertation, University of Florida, 1970. (b) Presented in part at the American Chemical Society (Florida Section) Meeting in Miniature, Jacksonville, Fla., 1969.

(2) Shore, S. G.; Parry, R. W. *J. Am. Chem. Soc.* **1955**, *77*, 6084.

(3) Miller, N. E.; Muetterties, E. L. *J. Am. Chem. Soc.* **1964**, *86*, 1033.

(4) Douglass, J. E. *J. Am. Chem. Soc.* **1964**, *86*, 5431.

(5) Muetterties, E. L. *Pure Appl. Chem.* **1965**, *10*, 53.

(6) Ryschkewitsch, G. E. *J. Am. Chem. Soc.* **1967**, *89*, 3145.

(7) Ryschkewitsch, G. E.; Garrett, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 4240.

(8) Nainan, K. C.; Ryschkewitsch, G. E. *Inorg. Chem.* **1968**, *7*, 1316.

(9) Ryschkewitsch, G. E.; Garrett, J. M. *J. Am. Chem. Soc.* **1968**, *90*, 7234.

(10) Nainan, K. C. Doctoral Dissertation, University of Florida, 1969.

(11) Nainan, K. C.; Ryschkewitsch, G. E. *J. Am. Chem. Soc.* **1969**, *91*, 330.

(12) Nainan, K. C.; Ryschkewitsch, G. E. *Inorg. Chem.* **1969**, *8*, 2671.

(13) Sowa, F. V. U.S. Patent 2 655 524, 1953.

(14) Prasad, S.; Singh, N. P. *Z. Anorg. Chem.* **1966**, *346*, 217.

(15) Makosky, C. W.; Galloway, G. L.; Ryschkewitsch, G. E. *Inorg. Chem.* **1967**, *6*, 1972.

(16) Brown, H. C.; Schesinger, H. I.; Cordon, S. Z. *J. Am. Chem. Soc.* **1944**, *64*, 325.

(17) Baldwin, R. A.; Washburn, R. M. *J. Org. Chem.* **1961**, *26*, 3549.

(18) (a) Mathur, M. A.; Ryschkewitsch, G. E. *Inorg. Synth.* **1970**, *12*, 139. (b) Mathur, M. A.; Ryschkewitsch, G. E. *Ibid.* **1970**, *12*, 123.

(19) Miller, W. E.; Reznieck, D. L.; Rawatt, R. J.; Lundburg, K. R. *Inorg. Chem.* **1969**, *8*, 862.

(20) Nakomoto, K. "Infrared Spectra of Inorganic and Coordinated Compounds", 2nd ed.; Wiley-Interscience: New York, 1970.

(21) Eaton, G. E.; Lipscomb, W. N. "NMR Studies of Boron Hydrides and Related Compounds"; W. A. Benjamin: New York, 1969.

0020-1669/80/1319-0887$01.00/0

Hydrotris(pyridine)boron(2+) Dibromide from Trimethylamine–Dibromoborane and Pyridine in Benzene. Trimethylamine–dibromoborane, 1.000 g (4.32 mmol), was dissolved in 30 mL of dry benzene in an Erlenmeyer flask and was boiled with 16 mL of dry pyridine for 46 h while a fine white crystalline bromide salt slowly precipitated out, producing 1.070 g of $(C_5H_5N)_3BHBr_2$, mp 222–224 °C (61% conversion). The proton NMR and infrared spectra of this product were identical with tris(pyridine)boronium dibromide discussed in the earlier section. After unreacted $(CH_3)_3N\cdot BHBr_2$ was corrected for, the overall yield of $(C_5H_5N)_3BHBr_2$ was 86%.

Reaction of Pyridine on a Mixture of Pyridine–Bromoborane and Pyridine–Dibromoborane. Approximately 0.500 g of a mixture of $C_5H_5N\cdot BH_2Br^1$ and $C_5H_5N\cdot BHBr_2{}^1$ was dissolved in 10 mL of benzene, and to it was added 5 mL of pyridine. The solution was stirred for 1.5 h at room temperature. The solid formed was washed with benzene and ether, dissolved in water, and treated with a solution of NH_4PF_6. The washed and dried precipitate was stirred in methylene chloride for 30 min. The proton NMR spectrum and the melting point of the recovered insoluble material were identical with the data for $(C_5H_5N)_3BH(PF_6)_2$.

Synthesis of Hydrotris(4-methylpyridine)boron(2+) Bis(hexafluorophosphate) from Trimethylamine–Borane, 4-Methylpyridine, and Bromine. The synthesis of $(4\text{-}CH_3C_5H_4N)_3BH(PF_6)_2$ was carried out in four steps without isolation of intermediates. Except for the last step, all other operations were performed in an inert atmosphere of dry nitrogen. The steps were as follows:

Step 1. Trimethylamine–borane, 3.650 g (50.0 mmol), was dissolved in 100 mL of dry benzene in a three-necked flask. The necks of the flask were connected to a gas inlet and outlet through a mercury bubbler. The apparatus was flushed with nitrogen, and hydrogen bromide gas was bubbled slowly through the stirring solution of $(CH_3)_3N\cdot BH_3$ until the evolution of hydrogen ceased.

Step 2. The solution then was titrated with 0.559 M solution of bromine in dry benzene under a slow and steady flow of nitrogen. A total of 89.5 mL (corresponding to 8.001 g or 50.0 mmol of Br_2) of bromine solution was used. The end of reaction was indicated by the persistent yellow color of the resulting solution which was discharged by adding a few drops of cyclohexene. While HBr was flushed out with nitrogen, benzene was removed by boiling and finally by evacuation on a rotary evaporator. The residue was a white solid.

Step 3. The solid obtained from step 2 was dissolved in 30 mL of dry 4-methylpyridine in the same three-necked flask. One of the side necks of the flask was closed by a glass stopper while the buret from the central neck was replaced by a water-cooled reflux condenser. The top of the condenser was vented through a drying tube containing calcium chloride and calcium sulfate to a hood through an absorbent for $(CH_3)_3N$. The solution was heated gently in an oil bath. At 90 °C a slow evolution of colorless gas was observed; simultaneously the solution became turbid. The evolved gas was identified by proton NMR to be $(CH_3)_3N$. Trimethylamine was therefore evolved along with the formation of precipitate. The solution was then heated to boiling and further refluxed for 6 h. The contents were cooled, and the solid was separated from unreacted 4-methylpyridine by filtration and was washed with dry benzene (100 mL) and by anhydrous diethyl ether. It was dried under vacuum. The original blackish brown color of the solid changed to a tan-white color after washing and evacuation of excess solvents.

Step 4. The solid product of step 3 was dissolved in 75 mL of ice-cold water to give a dark brown transluscent solution. A saturated solution of ammonium hexafluorophosphate solution was added into the stirring solution of the product until the supernatant liquid was free of BH^{2+} ions. The light brown precipitate collected after the contents were cooled in a refrigerator for 12 h was first washed with 60 mL of ice-cold water and then with 50 mL of anhydrous ether. It was dried under vacuum in a desiccator and weighed 19.79 g. The yield calculated for $(4\text{-}CH_3C_5H_4N)_3BH(PF_6)_2$, on the basis of the amount of $(CH_3)_3N\cdot BH_3$ taken as the starting material in step 1, was 68%. The melting point of the product was 218–221 °C. The melting point remained unchanged on recrystallization in an acetone–water mixture. The infrared spectrum of this salt in KBr pellet gave peaks at 3130, 3080, 2540 (s), 2050 (w), 1845 (w), 1635 (s), 1580 (w), 1500 (w), 1465 (s), 1400 (w), 1365, 1270, 1225, 1170–1120 (s, b), 1060, 1025 (s), 960 (w), 890–790 (s, b), 770 (w), 745 (w), 680 (s), 590, 550 (s), 460 (w), and 430 cm^{-1}. Anal. Calcd for $C_{18}H_{22}N_3BP_2F_{12}$: C, 37.18; H, 3.79; N, 7.23; B, 1.89; P, 10.67. Found: C, 37.05; H, 3.81; N, 7.25; B, 2.31; P, 10.49.

Hydrotris(3-methylpyridine)boron(2+) Salts. Trimethylamine–dibromoborane, 1.084 g (4.7 mmol), was dissolved in 15 mL of 3-picoline in a 100-mL round-botton flask. The flask was fitted with a water-cooled reflux condenser with nitrogen flowing "T" at the open end. The reaction mixture was heated at 120 °C for 6 h. After the solution was cooled, unreacted 3-picoline and $(CH_3)_3N\cdot BHBr_2$ were washed out with benzene. The yield was 1.98 g (98%) of $(3\text{-}CH_3\text{-}C_5H_4N)_3BHBr_2$. The bromide salt (0.185 g) was converted in 5 mL of water to the hexafluorophosphate. The yield was 0.180 g (76%); mp 179–181 °C. The infrared spectrum in a KBr pellet showed absorptions at 3450-3350 (b), 3020, 2820, 2540, 1730, 1630 (s), 1590, 1490, 1470–1450, 1400 (w), 1270 (w), 1250 (s), 1205 (s), 1160–1140 (s, b), 1040 (s), 890–810 (s, b), 770 (w), 750–745, 695 (s), 660 (w), 610 (w), 620 (w), 560 (s), 500 (w), and 415–430 (w) cm^{-1}. Anal. Calcd for $C_{18}H_{22}N_3BP_2F_{12}$: C, 37.18; H, 3.79; N, 7.23. Found: C, 37.14; H, 3.51; N, 7.15.

Hydrotris(3,5-dimethylpyridine)boron(2+) Dibromide. A mixture of 1.179 g (5.1 mmol) of $(CH_3)_3N\cdot BHBr_2$, 20 mL of dry toluene, and 15 mL of dry 3,5-dimethylpyridine was refluxed for 16 h in a nitrogen atmosphere. A weight of 2.320 g (92%) of $C_{12}H_{28}N_3BBr_2$ was isolated. Recrystallization was accomplished by precipitating with hexane from CH_2Cl_2 solution. The proton NMR spectra in CH_2Cl_2 and in nitromethane gave the three singlets in the ratio of 2:1:6 expected for tris(3,5-dimethylpyridine)boron(2+) ions. Anal. Calcd for $C_{21}H_{28}N_3BBr_2$: C, 51.25; H, 5.53; N, 8.58; Br, 32.47. Found: C, 48.33; H, 5.62; N, 7.55; Br, 32.00. The bromide salt is hygroscopic and contains one to three molecules water of crystallization. The presence of water was revealed by the infrared spectrum and explains the difference in the calculated and observed values of elemental analysis. Attempts to obtain anhydrous $[3,5\text{-}(CH_3)_2C_5H_3N]_3BHBr_2$ were unsuccessful.

A sample of 0.727 g (1.50 mmol) of this bromide salt gave 0.646 g (1.04 mmol) of water-insoluble hexafluorophosphate salt when treated with NH_4PF_6 solution (70% yield); mp 219–221 °C. The melting point remained unchanged on recrystallization in acetone–water mixture. The proton NMR spectrum, of this product in nitromethane gave only two singlets in the ratio 2:1 at 1.91 and 7.68 ppm, respectively, downfield from external tetramethylsilane. The infrared spectrum of the product in a KBr pellet gave absorption at 3690 (w), 3675 (w), 3120–3080 (d), 2942, 2540 (s), 1835, 1735, 1630–1610 (s, d), 1500 (w), 1490–1450 (s, b), 1400 (s), 1340 (w), 1300 (s), 1210–1110 (s, b), 1060 (w), 1050 (s), 1020 (w), 930 (s), 910–800 (s, b), 790, 765, 760 (s), 710 (s), 690 (s), 660, 570 (s), 510 (s), 475 (w), 450 (s), 428, and 275 cm^{-1}. Anal. Calcd for $C_{21}H_{28}N_3BP_2F_{12}$: C, 40.46; H, 4.50; N, 6.74. Found (I): C, 40.53; H, 4.64; N, 6.69. Found (II): C, 40.76; H, 4.64; N, 6.64.

A Study of the Reactivity of Different Pyridines toward Trimethylamine–Dibromoborane in Benzene. Five 250-mL Erlenmeyer flasks were charged separately, each with 1.155 g (5.0 mmol) of $(CH_3)_3N\cdot BHBr_2$ dissolved in 40 mL of dry benzene. The flasks were fitted with water-cooled reflux condensers, on top of which was maintained a flow of dry nitrogen through a T connection. To each of these flasks was added 10 mL of one of the amines in the following order: 4-methylpyridine, pyridine 2,6-dimethylpyridine, 2-methylpyridine, and 2-fluoropyridine. Thus the final composition in each flask was 5 mmol of $(CH_3)_3N\cdot BHBr_2$, in 20% amine and 80% benzene by volume, making a 0.1 M solution of $(CH_3)_3N\cdot BHBr_2$. All the solutions were heated to boiling and were refluxed for 36 h. The precipitated salts were washed first with benzene and then with diethyl ether inside a drybox. The filtrate and washing were collected and treated separately to recover unreacted $(CH_3)_3N\cdot BHBr_2$. Adhering benzene and ether were removed by pumping in a desiccator. Results are summarized in Table I.

Alternate Methods for the Synthesis of $(4\text{-}CH_3C_5H_4N)_3BH^{2+}$ Cation. (A) From 4-Methylpyridine–Borane.[1] A sample of 1.123 g of 4-methylpyridine–borane was dissolved in 30 mL of dry toluene and was treated with 41 mL of 0.259 M iodine in the same solvent. Half of the iodine solution was added into the stirring solution of $4\text{-}CH_3C_5H_4N\cdot BH_3$ at room temperature. The remaining half was added all at one time, and the solution was kept at 60 °C for 20 h. To half of the cooled solution was added 10 mL of dry 4-methylpyridine. The light yellow solid which precipitated was filtered, washed with benzene, and then washed with ether. Excess solvent was removed under vacuum. The yield was 2.429 g (85%) of $(4\text{-}CH_3C_5H_4N)_3BHI_2$. A portion of the salt was converted to the PF_6^- derivative. The ^1H NMR and infrared spectra of this product were identical with those of

Table I. Data Showing % Recovery of Unreacted $(CH_3)_3N{\cdot}BHBr_2$ after Refluxing It with Different Pyridines in Benzene Solution for 36 h

						B mass balance	
1 amines used	2 wt of $(CH_3)_3N{\cdot}BHBr_2$ taken, g	3 wt[b] of solid obtained after evaporating the solvents, g	4 wt of pure unreacted $(CH_3)_3N{\cdot}BHBr_2$ recovered, g	5 % of $(CH_3)_3N{\cdot}BHBr_2$ recovered	6 % product formed as A_3BHBr_2[a]	7 % accounted for	8 % loss
4-methylpyridine	1.155	0.868	0.692	59.9	30.5 39.8[c]	99.7	0.3
pyridine	1.155	0.900	0.860	74.5	21.1 23.8[c]	98.3	1.7
2,6-dimethylpyridine	1.155	1.093	1.081	93.8	[0.8] [1.3[c]]	95.1	4.9
2-methylpyridine	1.155	1.095	1.092	94.8	[1.2] [1.3[c]]	96.1	3.9
2-fluoropyridine	1.155	1.100	1.100	95.3	[0.0]	95.3	4.7

[a] A = amine. [b] These weights were due to unreacted $(CH_3)_3N{\cdot}BHBr_2$ and some of A_3BHBr_2; the water extract in case of pyridine did give a precipitate with PF_6^-. [c] These yields were calculated by adding the difference of weight of column numbers 3 and 4 to the weight of A_3BHBr_2 obtained by assuming that the loss in weight was because of the solubility of A_3BHBr_2 in water. The values given in brackets under column 6 show uncertainty about the nature of the product.

authentic $(4\text{-}CH_3C_5H_4N)_3BH(PF_6)_2$; mp 234–236 °C.

(B) From Trimethylamine–Borane, Iodine, and 4-Methylpyridine. Trimethylamine–borane, 1.450 g (19.9 mmol), in 50 mL of dry toluene was mixed with 5.680 g (22.4 mmol) of solid iodine (added in small portions). The solution was then boiled for 19 h. The iodine color still remained. The solution was cooled to room temperature, and trimethylamine gas was bubbled through it to remove trimethylamine–iodoborane $[(CH_3)_3N{\cdot}BH_2I]$ as insoluble $[(CH_3)_3N]_2BH_2I$. After filtration, 7.0 mL (71.4 mmol) of dry 4-methylpyridine was added. There was no immediate reaction; when the reaction mixture was refluxed a light yellow precipitate weighing 3.690 g was obtained. A portion of this solid was treated with the saturated solution of NH_4PF_6 as described earlier, and a light yellow solid, mp 234–236 °C, was obtained. The proton NMR and the infrared spectra of this solid were identical with those of authentic $(4\text{-}CH_3C_5H_4N)_3BH(PF_6)_2$. Anal. Calcd for $C_{18}H_{22}N_3BP_2F_{12}$: C, 37.12; H, 3.79; N, 7.23. Found: C, 36.70; H, 4.30; N, 7.20.

Synthesis of Hydrotris(2-methylpyridine)boron(2+). The 2-methylpyridine–borane needed for this synthesis was prepared by the methods reported in the literature.[12,16,17] A 1.07-g (10 mmol) sample of this borane was dissolved in 20 mL of dry benzene and mixed first with 1.279 g of I_2 in 45 mL of benzene at room temperature. The temperature was raised to 60 °C, and an additional 1.330 g of I_2 in 45 mL benzene was added. The solution was then refluxed for 8 h until no more HI evolution was observed. To the reaction solution was added 10 mL of 2-methylpyridine. A thick oily liquid gradually formed which solidified to a paste after some time. The mixture was further refluxed for 2 h. After the solution was cooled, the solvent and excess 2-methylpyridine were removed by filtration, and the remaining solid was washed with benzene. The yield of dry product was 4.559 g (83.2%) of the weight calculated for $(2\text{-}CH_3C_5H_4N)_3BHI_2$. The hexafluorophosphate salt prepared from the iodide was impure and contained about 11% impurity. This impurity was removed by extraction with CH_2Cl_2 (0.644 g of salt, 20 mL of solvent, 14 h of stirring) and identified by its NMR and infrared spectra and melting point as $(2\text{-}CH_3C_5H_4N)_2BH_2PF_6$.[10]

The proton NMR spectrum of the remaining purified product in nitromethane showed a sharp singlet at 2.01 ppm ($-CH_3$) and a complex pattern for the ring protons of a doublet (7.21 ppm), broad singlet (7.45 ppm), and a complex multiplet in the region 7.69–7.97 ppm. The area ratios in the ^1H NMR pattern were in agreement with that calculated for $2\text{-}CH_3C_5H_4N$. The infrared spectrum in a KBr pellet showed absorption at 3650 (w), 3600 (w), 3400 (b), 3150–3080 (t); 2940 (w), 2540, 2340 (w), 2040 (w), 1950 (w), 1890 (w), 1725 (w), 1630 (s), 1572 (s), 1490–1460 (d); 1385, 1320 (s), 1265 (w), 1245 (w), 1180–1130 (b d, s); 1100 (s), 1065 (s), 1030, 910–800 (b, s); 780–770 (s), 740 (w), 720 (s), 620 (s), 555 (s), 480 (s), 455 (w), 415 (w), and 270 (w) cm^{-1}. Anal. Calcd for $C_{18}H_{22}N_3BP_2F_{12}$: C, 37.12; H, 3.79; N, 7.23. Found (I): C, 36.93; H, 4.01; N, 7.34. Found (II): C, 36.52; H, 3.54; N, 7.12. The melting point was 239.5–240.5 °C.

Results and Discussion

Doubly charged boron cations can be prepared simply by the reaction of trimethylamine–dibromoborane with pyridine and substituted pyridines in refluxing inert solvents such as benzene or toluene or in the amine itself

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

where R = H or CH_3.

The anhydrous bromide salt normally precipitates from the solution in yields approaching 100%. The bromides tend to be hygroscopic and easily water soluble. Hexafluorophosphate salts are readily obtained by precipitation from aqueous solution.

Bromides are soluble in acetone, nitromethane, and methylene chloride whereas the hexafluorophosphate salts dissolved in the former two solvents but not in CH_2Cl_2. Both series of salts were stable at room temperature, but only the PF_6^- salts gave sharp melting points; the bromides apparently decomposed before melting.

Reactivity. Oxidizing agents such as Ag^+, Cu^{2+}, $Cr_2O_7^{2-}$, or 30% H_2O_2 were without effect on $(4\text{-}CH_3C_5H_4N)_3BH^{2+}$ after 24 h exposure. Acidic permanganate, however, was decolorized rapidly. Since the unsubstituted pyridine derivative reacted even more rapidly with MnO_4^-, oxidation at the methyl group can be excluded as a primary step.

A number of reactivity studies were made with the ion derived from 4-methylpyridine. There was no change in the NMR spectrum after 8 h in boiling water or in 0.5 M HCl, but there was evidence of slow decomposition in boiling 0.5 M NaOH. Hot alcoholic NaOH gave rapid decomposition.

While the positive ions are stable to decomposition in boiling acid, they are attacked, albeit slowly, in hot base. The reverse is true for borohydride ion and amine–borane. Apparently, there is a complete change in the mechanism by which hydrolysis occurs in these two groups of tetrahedral B–H compounds.

There is a fair amount of evidence that the reactions of BH_4^- or amine–boranes with acids occur by electrophilic attack of a proton on the electron density in the B–H bond.[22,23] This mode of reaction would thus be disfavored by a decrease in the electron density around boron. Although the formal charge on boron remains constant upon successive isoelectronic substitution of hydride ion in BH_4^- by a nitrogen base, the downfield shifts in the boron-11 spectra[21] clearly reflect continuous and substantial decreases in electron density and thus foreshadow decreased hydridic reactivity in the B–H bond.

In spite of the increase in net positive charge of the boron species, however, the boron-attached protons are not ex-

---

(22) Mesmer, R. E.; Jolly, W. L. *Inorg. Chem.* **1962**, *1*, 600.
(23) Wiggins, J. W.; Ryschkewitsch, G. E. *Inorg. Chim. Acta* **1970**, *4*, 33.

Table II. Infrared Data (cm^{-1}) of Compounds Having BH Bonds

	B–H str	ring str	ref
BH_4^-	2244, 2270	...	20
$4\text{-}CH_3C_5H_4N$	...	1605	8
$4\text{-}CH_3C_5H_4N\cdot BH_3$	2240, 2390	1624	8
$(4\text{-}CH_3C_5H_4N)_2BH_2^+$	2460, 2480	1632	8
$(4\text{-}CH_3C_5H_4N)_3BH^{2+}$	2540	1635	

Table III. Proton NMR Data of BH^{2+} Cations[a]

cations	CH_3 δ	CH_3 M	ring protons	δ	M	J_{H-H}, Hz
			A. PF_6^- Salts			
$[C_5H_5N]_3BH^{2+}$	...		$H_{2,6}$	7.99	2	7
			$H_{3,4,5}$	7.50	3	7
$[4\text{-}CH_3C_5H_4N]_3BH^{2+}$	1.95	1	$H_{2,6}$	7.55	2	7
			$H_{3,5}$	7.07	2	7
$[3\text{-}CH_3C_5H_4N]_3BH^{2+}$	1.83	1	$H_{2,4,6}$	7.77	3	...
			H_5	7.31	3	...
$[2\text{-}CH_3C_5H_4N]_3BH^{2+}$	2.02	1	$H_{3,4,5,6}$	6.76–7.83	6	...
$[3,5\text{-}(CH_3)_2C_5H_3N]_3BH^{2+}$	1.92	...	$H_{2,4,6}$	7.68	1	...
			B. Br^- Salts			
$[C_5H_5N]_3BH^{2+}$				8.07–8.79	9	...
$[4\text{-}CH_3C_5H_4N]_3BH^{2+}$	2.70		$H_{2,6}$	9.46	2	7
			$H_{3,5}$	7.93	2	7
$[3,5\text{-}(CH_3)_2C_5H_3N]_3BH^{2+}$	2.77		H_4	8.27		
			C. I^- Salts			
$[4\text{-}CH_3C_5H_4N]_3BH^{2+}$	2.63	1	$H_{2,6}$	8.60	2	7
			$H_{3,5}$	7.65	2	7

[a] The spectra for the PF_6^- salts were run in nitromethane and for Br^- and I^- salts were run in dichloromethane. The chemical shifts are measured relative to tetramethylsilane as internal reference. M = multiplicity.

changeable in 0.2 M NaOD in D_2O in the cold. C–H protons in doubly charged $(py)_2CH_2^+$ ions exchange.

Unlike the bis(amine) BH_2^+ ions,[8,11] $(4\text{-}CH_3C_5H_4N)_3BH(PF_6)_2$ was inert to refluxing bromine over 30 h and to chlorine in nitromethane at 85 °C over 20 h. Only at 115 °C was there evidence of slow reaction to yield unidentified products.

The remarkable inertness of the BH^{2+} structure toward halogenation correlates well with the increase in the stretching frequency of the B–H bond as the net positive charge increases (Table II). Borohydride ion and neutral borane adducts react with chlorine and bromine very rapidly, with bis(amine) BH_2^+ ions at a more moderate rate,[8] and with BH^{2+} ions only under forcing conditions, if at all. In a free-radical halogenation on the B–H bond[24] hydrogen abstraction by atomic halogen would require increasing activation energy as the homolytic bond energy of the B–H bond increases. Inasmuch as the stretching frequencies are a measure of the bond strength, the correlation is not unexpected.

Displacement of one pyridine substituent by another occurs slowly at 90 °C in nitromethane and apparently reaches an equilibrium governed in the absence of steric factors by relative base strengths. For example, displacment of one of the three 4-methylpyridine substituents by the weaker base pyridine can be followed in the proton NMR. An equilibrium constant of about 4×10^{-2} (90 °C, CH_3NO_2 solvent) was calculated for the displacement.

Characterization. The new cations were characterized fully by their composition and by their infrared and their ^{11}B and ^1H magnetic resonance spectra. The vibrational spectra show, besides the absorptions attributable to the pyridine substituent, a strong singlet near 2540 cm^{-1} which is assigned to the B–H stretching mode. As is evident from Table II, progressive substitution of hydride by pyridines in the sequence BH_4^-, $pyBH_3$, $(py)_2BH_2^+$, and $(py)_3BH^{2+}$ leads to systematic shifts of the B–H stretching vibrations to higher frequencies.

Table IV. ^1H NMR Data of Amine, Amine-Borane, and Boronium Cations[a]

compd	chem shifts, δ: CH_3 protons	2,6 protons	3,5 protons	ref
$4\text{-}CH_3C_5H_4N$	2.32	8.41	7.08	
$4\text{-}CH_3C_5H_4N\cdot BH_3$	2.48	8.40	7.33	12
$(4\text{-}CH_3C_5H_4N)_2BH_2^+$ [b]	2.58	8.53	7.67	8
$(4\text{-}CH_3C_5H_4N)_3BH^{2+}$ [c]	2.70	9.46	7.93	

[a] ^1H spectra were run in dichloromethane at 60 MHz. The chemical shifts are repeated downfield from internal tetramethylsilane. [b] PF_6^- salt. [c] Bromide salt.

Table V. ^{11}B NMR Data of Amine–Borane and Boronium Cations[a]

compd	chem shift, δ	M	J_{B-H}, Hz	ref
BH_4^-	56			21
$4\text{-}CH_3C_5H_4N\cdot BH_3$	30.6	4	100	12
$(4\text{-}CH_3C_5H_4N)_2BH_2^+$	19.2 ± 1.1	b	...	8
$(4\text{-}CH_3C_5H_4N)_3BH^{2+}$	11 ± 2	b	...	
$(C_5H_5N)_3BH^{2+}$	13.3	2	115 ± 10	
$(2\text{-}CH_3C_5H_4N)_3BH^{2+}$	b	b		
$(3\text{-}CH_3C_5H_4N)_3BH^{2+}$	b	b		
$[3,5\text{-}(CH_3)_2C_5H_3N]_3B^{2+}$	b	b		

[a] ^{11}Br NMR of $4\text{-}CH_3C_5H_4NBH_3$ and $(4\text{-}CH_3C_5H_4N)_2BH_2^+$ were run in dichloromethane, and others were run in nitromethane. The chemical shifts are upfield from trimethyl borate external reference. Spectra were run at 32.1 Mz. b = broad.

Similar correlations can be observed in the proton magnetic resonance spectra (Table III). The frequencies of the hydrogens in the pyridine rings and of methyl substituents are progressively shifted downfield as the number of pyridine substituents on boron and therefore the positive charge increase (Table IV). Boron-11 resonances (Table V), although rather broad, also show a trend of a downfield shift with increasing charge.

Formation Mechanism. The formation of the doubly charged cations undoubtedly involves a direct nucleophilic attack by the pyridine base on a tetrahedral boron center rather than a rate-determining dissociation of one of the substituents on the starting material, $(CH_3)_3N\cdot BHBr_2$, followed by subsequent fast addition of the nitrogen base to a trigonal borane fragment. Rate-determining dissociation appears exceedingly unlikely if one considers the following arguments. First, trimethylamine–dibromoborane is stable under the conditions of cation formation with reactive amines such as 4-methylpyridine. This is shown in Table I by nearly quantitative recovery of the borane after 36 h in refluxing benzene. Had there been cleavage of the B–N bond, loss of $(CH_3)_3N$ to the gas phase and/or the known rapid redistribution of the uncoordinated $BHBr_2$ thus formed should have prevented reisolation of starting material. Second, alternate cleavage of a B–Br bond to yield a trigonal cation $(CH_3)_3NBHBr^+$ surely is not likely in view of the low ionizing power of the solvent and of previous difficulties in preparing trigonal boron cations in the absence of stabilizing substituents and coordinating solvents.[25] Third, the fact that there are substantial differences in the rate of cation formation with unhindered pyridines would preclude a common prior rate-determining step. Last, the failure of 2-methylpyridine to react under conditions when unhindered pyridines gave products implies a kinetic barrier involving the nitrogen base. There is certainly no thermodynamic reason preventing the formation of either one of the two

---

(24) Ryschkewitsch, G. E.; Miller, V. R. *J. Am. Chem. Soc.* **1972**, *94*, 2836.

(25) Ryschkewitsch, G. E.; Wiggins, J. W. *J. Am. Chem. Soc.* **1970**, *92*, 1970.

possible first intermediates a neutral borane, 2-$CH_3py{\cdot}BHBr_2$, obtained by amine loss, or a cation, $(CH_3)_3N(2\text{-}CH_3py)BHBr^+$, obtained by bromide loss. The preparation of the adduct 2-$CH_3py{\cdot}BHI_2$ as an intermediate, and the final isolation of stable $(2\text{-}CH_3py)_3BH^{2+}$ shows that sterically even more encumbered structures are capable of existence.

The reactivity order with trimethylamine–dibromoborane established in Table I, 4-methylpyridine > pyridine ≫ 2-methylpyridine > 2,6-dimethylpyridine > 2-fluoropyridine, thus is to be interpreted as reflecting decreasing nucleophilicity in the attacking amine, caused by progressively greater electron withdrawal away from the nitrogen atom or by steric inhibition of the attack on boron by substituents in the 2-position of the pyridine ring.

The observed enhanced reactivity of diiodoboranes when compared to dibromoboranes would then be a consequence of iodide being a much better leaving group than bromide, while the accelerations of cation formation when pyridine boranes are used as starting materials, rather than trimethylamine borane, are reminiscent of similar reactivity enhancement when the organic isosteric benzyl and neopentyl systems are compared.

Acknowledgment. M.A.M. wishes to thank the University of Rajasthan, Jaipur, India, for allowing him the study leave for this period and the Chemistry Department, University of Florida, and NIH for the financial support.

Registry No. $(C_5H_5N)_3BHBr_2$, 25397-28-8; $(C_5H_5N)_3BH(PF_6)_2$, 25447-31-8; $(4\text{-}CH_3C_5H_4N)_3BH(PF_6)_2$, 25338-40-3; $(3\text{-}CH_3C_5H_4N)_3BHBr_2$, 72541-38-9; $(3\text{-}CH_3C_5H_4N)_3BH(PF_6)_2$, 72541-40-3; $[3,5\text{-}(CH_3)_2C_5H_3N]_3BHBr_2$, 72541-41-4; $[3,5\text{-}(CH_3)_2C_5H_3N]_3BH(PF_6)_2$, 72541-43-6; $(4\text{-}CH_3C_5H_4N)_3BHI_2$, 25397-29-9; $(2\text{-}CH_3C_5H_4N)_3BHI_2$, 72541-44-7; $(2\text{-}CH_3C_5H_9N)_3BH(PF_6)_2$, 72541-46-9; $(4\text{-}CH_3C_5H_4N)_3BHBr_2$, 72541-47-0; $(CH_3)_3N{\cdot}BHBr_2$, 32805-31-5; $C_5H_5N{\cdot}BH_2Br$, 60228-77-5; $C_5H_5N{\cdot}BHBr_2$, 72541-88-9; $(CH_3)_3N{\cdot}BH_3$, 75-22-9; 4-$CH_3C_5H_4N{\cdot}BH_3$, 3999-39-1; 2-$CH_3C_5H_4N{\cdot}BH_3$, 3999-38-0; 4-$CH_3C_5H_4N$, 1003-67-4; C_5H_5N, 110-86-1; 2,6-$(CH_3)_2C_5H_3N$, 108-48-5; 2-$CH_3C_5H_4N$, 109-06-8; 3-$CH_3C_5H_4N$, 108-99-6; 3,5-$(CH_3)_2C_5H_3N$, 591-22-0.

Contribution from the Institut für Chemie der Universität Regensburg,
D-8400 Regensburg, Germany

Optically Active Transition-Metal Complexes. 65.[1] Conformational Analysis in Diastereoisomer Equilibria of Square-Pyramidal Dicarbonylcyclopentadienylmolybdenum–Pyridine-2-carbaldimine Complexes Using the Ruch/Ugi Rules

HENRI BRUNNER* and DEVENDRA K. RASTOGI

Received June 28, 1979

Ten chiral amines and amino acids $H_2NCH(R^1)(R^2)$ were used to prepare the corresponding pyridine-2-carbaldimines, abbreviated NN*. The unsymmetrical chelate ligands NN* were introduced into the complexes $[C_5H_5Mo(CO)_2NN^*]PF_6$, chiral at the Mo atom. Because racemic amines were used and the optically active amino acids racemized during the reaction, mixtures of two diastereoisomeric pairs of enantiomers were obtained. The diastereoisomers differ in their ^1H NMR spectra and were separated by fractional crystallization. On heating in acetone-d_6 at 80 °C the diastereoisomers interconvert. In this epimerization the labile Mo configuration changes under the influence of the stable asymmetric carbon atom in the ligand NN*. A gauge for the asymmetric induction in this equilibration is the equilibrium ratio of the diastereoisomers, obtained by ^1H NMR integration. The asymmetric inductions, ranging from 8 to 62%, can be interpreted on the basis of the stereochemical model of Ruch and Ugi, by using λ values distinctly different from those found for organic systems. The negative phenyl value indicates a weak attraction between the phenyl substituent at the asymmetric carbon atom and the MC_5H_5 group which accounts for the high optical inductions observed and the high chemical shift differences of the diastereoisomers.

Introduction

One of the challenging problems in conformational analysis is to find the preferred conformations which a substituent can adopt with respect to a ring system. Since the work of Corey and Bailar,[2] chelate rings in coordination chemistry also have been taken into consideration. The effects change with ring size, ring type, and ring structure (planar or not) and with nature, number, and position of the substituents.[3] In the present paper a conformational analysis for chiral substituents at the nitrogen atom in a planar five-membered ring is carried out. The chelate ligands used are the Schiff bases NN* derived from pyridine-2-carbaldehyde and chiral primary amines $H_2NCH(R^1)(R^2)$. The chelate ring includes the Mo atom of a $C_5H_5(CO)_2Mo$ group in the square-pyramidal complexes $[C_5H_5Mo(CO)_2NN^*]PF_6$. Chelate ligands with optically active substituents are frequently used in asymmetric catalysis.[4-7] As the orientation of the substituents at the asymmetric center affects the various other coordination positions of the metal atom, it controls the addition of a prochiral substrate with either its *re* or its *si* face which may determine the stereochemistry of its conversion to optically active products.[8,9] Thus, an understanding of the preferred conformations of a chiral substituent with respect to a chelate ring and a neighboring metal atom should provide a basis for the estimation

---

(1) Part 64: H. Brunner and H. Vogt, submitted for publication in *J. Organomet. Chem.*

(2) E. J. Corey and J. C. Bailar, *J. Am. Chem. Soc.*, **81**, 2620 (1959).

(3) C. J. Hawkins, "Absolute Configuration of Metal Complexes", Wiley-Interscience, New York, 1971.

(4) H. B. Kagan and T. P. Dang, *J. Am. Chem. Soc.*, **94**, 6429 (1972).

(5) W. S. Knowles, M. J. Sabacky, B. D. Vineyard, and D. J. Weinkauf, *J. Am. Chem. Soc.*, **97**, 2567 (1975).

(6) M. D. Fryzuk and B. Bosnich, *J. Am. Chem. Soc.*, **99**, 6262 (1977).

(7) M. D. Fryzuk and B. Bosnich, *J. Am. Chem. Soc.*, **100**, 5491 (1978).

(8) D. Valentine, Jr., and J. W. Scott, *Synthesis*, **5**, 329 (1978).

(9) H. B. Kagan, *Pure Appl. Chem.*, **43**, 401 (1975).