$[((CH_3)_3P)_4Ni(CH_3)]^{+}$ [2] and $[((CH_3)_3P)_4Co(CH_3)]$[18] and by the fact that the five-coordinate organonickel compounds which bear as coligands monodentate tertiary phosphines have low stability.[19]

Acknowledgment. Thanks are expressed to Mr. Nuzzi for microanalyses.

Registry No. $[Ni(CH_3)(np_3)]BPh_4{\cdot}CH_3COCH_3$, 62561-25-5; $[Ni(C_2H_5)(np_3)]BPh_4$, 62520-84-7; $[Ni(CH_2C_6H_5)(np_3)]BPh_4$, 62520-86-9; $[Ni(CH_3)(nas_3)]BPh_4$, 62520-88-1; $[Ni(C_2H_5)(nas_3)]BPh_4$, 62520-90-5; $[Ni(CH_2C_6H_5)(nas_3)]BPh_4$, 62520-92-7; $[Ni(CH_3)(pp_3)]BPh_4$, 62520-75-6; $[Ni(C_2H_5)(pp_3)]BPh_4$, 62520-77-8; $[Ni(CH_2C_6H_5)(pp_3)]BPh_4$, 62520-78-9.

Supplementary Material Available: Listing of structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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Trimethylamine–Isocyanoborane. Reactions and Derivatives

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The reactions of trimethylamine–isocyanoborane with Lewis acids like BCl_3 and BH_3 result in the formation of the corresponding adducts. Boronium cations are easily formed by the boryl isocyanide displacement of the iodide from $4\text{-}CH_3C_5H_4N{\cdot}BH_2I$ and $(CH_3)_3N{\cdot}BH_2NC{\cdot}B_2I$. The salts $[(CH_3)_3NBH_2NCBH_2NC_5H_5]^+X^-$ and $[(CH_3)_3NBH_2NCBH_2NC_5H_5CH_3]^+X^-$ ($X^- = I^-, PF_6^-$), as well as $[(CH_3)_3NBH_2NC]_2BH_2{}^+I^-$, have been characterized. Acid isomerization, methylation by $(CH_3)_3OBF_4$, CH_3FSO_3, and CH_3I, and the reactions of $(CH_3)_3N{\cdot}BH_2NC{\cdot}AgCN$ with B_2H_6 are also reported. The chemistry of trimethylamine–isocyanoborane is quite similar to that of alkyl isocyanides, although a distinctive behavior of boryl isocyanides is shown by some of the reported reactions.

Introduction

While little attention has been given to pseudohalogenated boranes, extensive studies of amine–haloboranes have been conducted.[1] Recently, there has been considerable interest in cyanoborohydride anion[2,3] in addition to limited studies of amine–cyanoboranes.[4-10] The feasibility of isolating boron isocyanides was implied by the existence of carbon isocyanides and the similarity between boron and carbon chemistry. The extensive chemistry of analogous isocyanide species[11] and the possibility of investigating any preference for B–CN vs. B–NC bonding prompted our interest in amine–isocyanoborane species. The synthesis of trimethylamine–isocyanoborane[12,13] and some of its reactions[14,15] showed the remarkable similarity between the chemistry of boryl and carbon isocyanides. We describe here other results obtained by studying the chemistry of the first tetrahedral isocyanoboron species reported.

Experimental Section

Details concerning the preparation of trimethylamine–isocyanoborane, solvents, products, and spectroscopic studies are similar to those reported elsewhere.[14] Analyses of the compounds isolated in this work were done by Galbraith Microanalytical Laboratories, Nashville, Tenn. All of the work was done in absence of air, either by working in a drybox or with Schlenk techniques. Proton NMR chemical shifts, δ, are reported in ppm downfield of tetramethylsilane used as standard.

Reaction of Trimethylamine–Isocyanoborane with 4-Methylpyridine–Iodoborane. A solution of 4-methylpyridine–iodoborane (0.96 g, 4.10 mmol), prepared according to Nainan,[16] in 10 mL of benzene was slowly added to a solution of trimethylamine–isocyanoborane (0.40 g, 4.08 mmol) in 10 mL of the solvent. A yellow oil was formed immediately after mixing. The solvent was decanted, and the oil was washed with fresh benzene and vacuum-dried. The product was dissolved in water and precipitated with ammonium hexafluorophosphate solution. The precipitate (1.21 g, 91% yield), mp 41–43 °C, had an elemental analysis as expected for $[(CH_3)_3NBH_2NCBH_2NC_6H_7][PF_6]$. Anal. Calcd: C, 35.87; H, 6.02; N, 8.37; B, 6.46; P, 9.25; F, 34.04. Found: C, 34.69; H, 5.79; N, 11.86; B, 6.12; P, 8.89; F, 32.44.

Reaction of Trimethylamine–Isocyanoborane with Trimethylamine–Isocyanoborane–Iodoborane. Trimethylamine–isocyanoborane–iodoborane was prepared by the reaction of trimethylamine–borane–isocyanoborane (0.26 g, 2.32 mmol) with iodine (0.23 g, 0.91 mmol) in 30 mL of benzene, with the halogen added in very small amounts at a time. Trimethylamine–isocyanoborane (0.23 g, 2.35 mmol) was added to the solution after the decoloration was complete. A finely divided solid precipitated and the mixture was stirred for another 1 h. The solid was removed by filtration, washed with fresh solvent, and vacuum-dried. The product (0.61 g, 100% yield), mp 141–143 °C, had a composition in agreement with that of $[(CH_3)_3NBH_2NC]_2BH_2I$. Anal. Calcd: C, 28.62; H, 7.21; N, 16.70; B, 9.66; I, 37.82. Found: C, 28.48; H, 7.33; N, 16.61; B, 9.69; I, 37.69.

Reaction of Trimethylamine–Isocyanoborane with Boron Trichloride. Trimethylamine–isocyanoborane (0.50 g, 5.10 mmol) was dissolved in 20 mL of benzene in a 100-mL single-neck round-bottom flask provided with a vacuum stopcock that was attached to a vacuum line. Boron trichloride (5.19 mmol) was measured in the line and condensed into the previously evacuated vessel. The brown color which developed upon contact of both reagents turned yellow overnight. Vacuum

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Table I. Proton NMR Spectra in Methylene Chloride

Compd	δ, ppm
$[((CH_3)_3NBH_2NC)BH_2NC_6H_7]PF_6$	2.70, 2.60, 7.61, 8.38^a
$(CH_3)_3N\cdot BH_2NC\cdot BH_3$	2.65
$[((CH_3)_3NBH_2NC)_2BH_2]I$	2.83
$(CH_3)_3N\cdot BH_2NC\cdot BCl_3$	2.73
$(CH_3)_3N\cdot BH_2NC\cdot AgCN\cdot BH_3$	2.66

[a] Integral ratio 2.9:1:0.66:0.66.

Table II. Infrared Spectra of Derivatives of Trimethylamine–Isocyanoborane

Compd	Freq, cm^{-1}
$[(CH_3)_3NBH_2NCBH_2NC_6H_7]PF_6$	3665, 3580, 3120, 3020, 2960, 2450, 2280, 1955, 1640, 1565, 1460, 1415, 1335, 1250, 1220, 1190, 1160, 1100, 1060, 1020, 980, 840, 745, 730
$[(CH_3)_3NBH_2NCBH_2CNBH_2N(CH_3)_3]I$	3020, 2960, 2480, 2450, 2280, 1485, 1470, 1415, 1240, 1180, 1150, 1070, 970, 855
$(CH_3)_3N\cdot BH_2NC\cdot BCl_3$	3015, 2960, 2485, 2445, 2300, 1480, 1468, 1415, 1250, 1185, 1155, 985, 970, 895, 865, 765, 735, 710
$(CH_3)_3N\cdot BH_2NC\cdot BH_3$	3025, 3015, 2980, 2450, 2350, 2240, 1485, 1470, 1415, 1245, 1190, 1160, 1105, 1015, 990, 980, 860, 640
$(CH_3)_3N\cdot BH_2N{=}C(CH_3)OSO_2F^a$	3030, 2960, 2460, 1600, 1490, 1410, 1270, 1150, 1150, 1065, 970, 945, 850, 710
$(CH_3)_3N\cdot BH_2NC(Cl)N(COCH_2)_2\cdot H_2O$	3020, 2965, 2710, 2485, 1770, 1710, 1470, 1425, 1360, 1300, 1255, 1180, 980, 910, 845, 815, 640
$(CH_3)_3N\cdot BH_2NC\cdot AgCN\cdot BH_3$	3015, 2960, 2450, 2350, 2245, 2205, 1485, 1465, 1410, 1240, 1185, 1155, 1100, 1015, 990, 975, 925, 855, 805

[a] Infrared spectrum of this species was run in KBr pellets. The rest were run in methylene chloride solutions.

evaporation of the solvent left a white-yellow residue (1.08 g), mp 105–106 °C, that had a ^{1}H NMR spectrum showing a major signal at 2.75 ppm and some impurity at 1.42 ppm. Recrystallization from benzene raised the melting point of the material to 115–116 °C, and eliminated the high-field NMR band from the ^{1}H NMR spectrum of the product (98% yield). Elemental composition is that expected for $(CH_3)_3N\cdot BH_2NC\cdot BCl_3$. Found: C, 22.05; H, 5.44; B, 9.74. Calcd: C, 22.32; H, 5.14, N, 13.03; B, 10.04; Cl, 49.43.

Reaction of Trimethylamine–Isocyanoborane with Diborane. Trimethylamine–isocyanoborane (0.92 g, 9.7 mmol) was dissolved in 50 mL of methylene chloride and evacuated on a vacuum line. Diborane (0.50 mmol), freshly prepared and purified, was condensed into the flask and the system was warmed to room temperature. The white solid (1.00 g, 100% yield), mp 129 °C, collected by vacuum evaporation of the solvent, had ^{1}H NMR (Table I) and infrared spectra and elemental analyses as expected for $(CH_3)_3N\cdot BH_2NC\cdot BH_3$. Anal. Calcd: C, 42.96; H, 12.62; N, 25.06; B, 19.35. Found: C, 41.62; H, 12.29; N, 24.08; B, 18.74.

Reactions of Trimethylamine–Isocyanoborane with Methyl Iodide, Trimethyloxonium Tetrafluoroborate, and Methyl Fluorosulfate. Trimethylamine–isocyanoborane was dissolved in methylene chloride and methyl iodide was added to it in several molar ratios. In all of the runs a yellow-orange color appeared upon mixing and a yellow solid started to be seen 1 h later and continued precipitating for 2–5 days depending on the run. The reactions were very complex as shown by the presence of ^{1}H NMR bands at 2.87, 2.78, 2.70, 2.62, 2.50, and 2.12 ppm in 3:1.5:1:3:2:4 ratios, after 16 h of reaction. It was not possible to conclude accurately from the spectroscopic evidence the identity of the species present. The precipitate was removed by filtration, washed with benzene, and vacuum-dried. The product showed an infrared spectrum with bands at 3010, 2950, 1480, 1400, and 945 cm^{-1} and an elemental composition both in agreement with $[(CH_3)_4N]I$. Anal. Calcd: C, 23.88; H, 6.02; N, 6.99; I, 63.13. Found: C, 23.74; H, 6.07; N, 6.91; I, 63.12.

Attempts to characterize the soluble species present after 4 days of reaction, when the ^{1}H NMR signals present were at 2.98, 2.87, 2.70, 2.50, and 2.12 ppm in 1:9:9:4:3:2:7 ratios, by vacuum evaporation of the filtrate resulted in a solid, with the empirical formula $C_{27}H_{80}N_8BI_6$, which was soluble in acetonitrile and methylene chloride. The material has infrared bands at 3000, 2960, 2830, 2780, 2460, 2280, 2180, 1485, 1400, 1155, 950, 920, and 840 cm^{-1}. This solid reacted with water liberating a gas with strong amine odor and producing a solution of pH 11. This solution was a strong reductor and it was able to reduce silver ion in a fast reaction. It did not precipitate any PF_6^- salt.

The reaction with trimethyloxonium tetrafluoroborate (2.45 g, 16.56 mmol), prepared according to Curphey,[17] with trimethylamine–isocyanoborane (0.40 g, 4.08 mmol) in 10 mL of methylene chloride, showed upon mixing of the reagents the appearance of a yellow color that changed to brown in 2 h. The excess of BF_4^- salt was removed by filtration after 12 h of reaction and the filtrate was vacuum-dried. The residual solid (0.52 g), mp 93–95 °C, had bands in the infrared spectrum at 3020, 2960, 2450, 2280, 1610, 1480, 1460, 1400, 1250, 1100, 970, 920, 860, 840, and 690 cm^{-1}. The infrared spectrum was unchanged by precipitation of the solid from methylene chloride with heptane, but the melting point increased to 115–120 °C. The composition of the material suggested the empirical formula $C_7H_{11}B_4F_5$, for which we are unable to propose any structure. Anal. Found: C, 28.88; H, 7.30; N, 15.87; B, 14.73; F, 31.49. It was not possible to isolate any product from the material either by precipitation with PF_6^-, by sublimation, or by fractional crystallization.

Trimethylamine–isocyanoborane (0.40 g, 4.08 mmol) was dissolved in 20 mL of methylene chloride and methyl fluorosulfate (0.48 g, 4.21 mmol) was added dropwise to it. A yellow precipitate was formed immediately and the solution turned orange and warm with some refluxing of the solvent. The mixture was filtered 3 h and the precipitate, mp 169–170 °C, was washed with fresh solvent and dried. The elemental composition is that expected for $(CH_3)_3N\cdot BH_2N\text{-}C\cdot CH_3OSO_2F$. Anal. Calcd: C, 28.32; H, 6.65; N, 13.21; B, 5.10; S, 15.12; F, 3.96. Found: C, 26.92; H, 6.32; N, 12.18; B, 5.29; S, 14.78; F, 9.36.

Reactions of Trimethylamine–Isocyanoborane with *N*-Haloamines. Commercial *N*-chlorosuccinimide was dissolved in warm water and recrystallized by cooling with ice water. The crystals were washed thoroughly with water and vacuum-dried at 40 °C for 10 days. Trimethylamine–isocyanoborane (1.25 g, 12.76 mmol) was dissolved in 20 mL of benzene contained in a 250-mL two-neck round-bottom flask cooled to 7 °C with an ice-water bath. *N*-Chlorosuccinimide (1.75 g, 13.11 mmol) was dissolved in 150 mL of benzene and added dropwise to the other solution. The appearance of a brown color and the formation of a precipitate of the same color was noted. It was not possible to identify any free trimethylamine upon pumping of the system on the vacuum line 4 h after mixing. The mixture was filtered and the residue (2.70 g) was washed with benzene (9 × 10 mL) and vacuum-dried. The filtrate did not show any ^{1}H NMR absorption and it was discarded. The solid product had an infrared spectrum with bands at 3005, 2960, 2700, 2440, 1710, 1480, 1370, 1250, 1170, 1100, 990, 840, and 810 cm^{-1} in which there is no band assignable to a cyanide absorption. The product was soluble in methylene chloride, but the yellow solution turned brown-black several minutes after preparation and a ^{1}H NMR spectrum of it showed bands at 2.77 ppm and a broad signal at 2.63 ppm in 2.3:1 ratio. The solution's infrared spectrum showed bands at 3040, 2970, 2430, 2300, 2260, 1730, 1680, 1610, 1485, 1410, 1360, 1240, 1160, 1100, 1000, 830, and 670 cm^{-1}. Addition of heptane gave a yellow solid (2.1 g), dec pt 209 °C, with a ^{1}H NMR spectrum similar to the one above but with an infrared spectrum (Table II) which differed from that of the solution by the presence of bands at 2710 and 2485 cm^{-1} and the absence of those at 2430, 2300, 2260, and 1610 cm^{-1}. The elemental analysis of the material is in good agreement with that expected for $C_8H_{17}N_3B_1O_3Cl$. Anal. Calcd: C, 38.50; H, 6.87; N, 16.84; B, 4.33; Cl, 14.21. Found: C, 28.57; H, 7.02; N, 16.92; B, 4.60; Cl, 14.40.

Table III

Solvent	Time, h	^{1}H NMR, ppm	Assignment of bands
C_6H_6	0	2.25, 2.18	$(CH_3)_3N{\cdot}BH_2CN$, $(CH_3)_3N{\cdot}BH_2NC$
	0	1.90	CH_3COOH
	0.10	2.55, 2.50, 2.38, 2.25, 2.18, (2.03), 1.90	
	0.50	2.55, 2.50, 2.38, 2.25, (2.18), 2.03, 1.90	
	4.50	2.55, 2.50, 2.38, 2.25, 2.03, 1.90	
CH_2Cl_2	0	2.70, 2.63	$(CH_3)_3N{\cdot}BH_2CN$, $(CH_3)_3N{\cdot}BH_2NC$
	0	2.05	CH_3COOH
	0.10	2.70, 2.63, (2.48, 2.15), 2.05	
	0.50	2.78, 2.70, 2.63, 2.48, 2.20, 2.05	
	12.50	(2.78), 2.70, (2.63), 2.48, 2.20, 2.05	

Table IV

Reacn time, h	^{1}H NMR, ppm
0.25	(2.78, 2.63, (2.50, 2.20), 2.05
3.00	2.78, (2.70), 2.63, (2.50), 2.47, 2.18, 2.02
9.80	(2.78), 2.70, 2.63, 2.50, 2.47, 2.18, 2.02
22.0	2.70, (2.63), 2.47, 2.18, 2.08, 1.96, 1.93
48.0	2.70, 2.50, 2.47, 2.10, 2.00, 1.96

Studies of Proton-Induced Isomerization. The reactions of $(CH_3)_3N{\cdot}BH_2CN$ with glacial acetic acid have been studied in methylene chloride, THF, and benzene, by monitoring the progress of the reaction by use of proton NMR spectroscopy. Solutions of the mixture of isomers $(CH_3)_3N{\cdot}BH_2CN$–$(CH_3)_3N{\cdot}BH_2NC$ or of pure $(CH_3)_3N{\cdot}BH_2NC$ and glacial acetic acid in the mentioned solvents have been prepared in concentrations of 0.01 and 0.1 M, respectively. The mixing of the solutions was done in an NMR tube, which was sealed at liquid nitrogen temperature afterward.

The appearance of new bands in the spectra, in addition to those of the reagents, was noted immediately after contact, both with the pure isocyanoborane and with the mixture of isomers. The disappearance of the resonance band assigned to $(CH_3)_3N{\cdot}BH_2NC$ was observed in all cases with the unequivocal appearance of the signal corresponding to the other isomer in the experiment in which pure trimethylamine–isocyanoborane was initially present. The results obtained with the mixture of $(CH_3)_3N{\cdot}BH_2CN$ isomers are given in Table III. The results obtained with pure $(CH_3)_3NBH_2NC$ and glacial acetic acid in methylene chloride are given in Table IV. The complexity of the spectral pattern precluded obtaining reliable integrals. Bands in parentheses were of low intensity or were unresolved unintegrable signals. The results in tetrahydrofuran parallel those above.

Reactions of Trimethylamine–Isocyanoborane with Donor Molecules. The reactions of trimethylamine–isocyanoborane with trimethylamine, triethylamine, hexamethylphosphoramide, and triphenylphosphine were all studied in a similar way. A typical reaction is the one with trimethylamine. In this case trimethylamine–isocyanoborane (0.17 g, 1.74 mmol) was dissolved in 20 mL of benzene and trimethylamine (4.106 mmol) was condensed into the flask. The system was warmed to room temperature. After a reaction time of about 12 h the solution was studied. No change was noted in the infrared and ^{1}H NMR spectra with respect to those of the original borane.

The reaction with 4-methylpyridine (4.0 g, 40.4 mmol) was conducted by dissolving trimethylamine–isocyanoborane (0.70 g, 7.1 mmol) in the amine. The solution was stirred for 24 h at room temperature in a closed, partially evacuated flask. At this point, the flask was attached to the vacuum line and its contents pumped through a series of traps at −25, −95, and −195 °C. The condensable material trapped at liquid nitrogen temperatures was shown, by its gas infrared spectrum, to be trimethylamine (1.42 mmol, 20% of the initial amount). The remaining solution was treated with heptane to give a yellow oil in which some white solid was clearly visible. An attempt to precipitate this material from its aqueous solution as a PF_6^- salt was unsuccessful. The proton NMR spectrum of the product in methylene chloride solution showed bands at 2.63 and 2.55 ppm in 6:1 ratio and two nonintegrated doublets in the aromatic region. The neat infrared spectrum taken on sodium chloride plates had bands at 3000, 2940, 2420, 2350, 2160, 2135, 1640, 1485, 1465, 1445, 1255, 1200, 1160, 1110, 990, 860, and 820 cm^{-1}. Similar results were obtained after 48-h reaction time.

Reaction with Hydrogen Chloride. Trimethylamine–isocyanoborane (0.25 g, 2.55 mmol) was dissolved in 40 mL of methylene chloride and an excess of hydrogen chloride was bubbled into the solution. An orange-gold color appeared upon mixing and the solution remained unchanged for several hours. The ^{1}H NMR spectrum showed the disappearance of the characteristic isocyanoborane resonance at 2.63 ppm downfield of TMS. Instead, signals at 2.97, 2.92, 2.82, and 2.80 ppm were present. The infrared spectrum of the solution showed the absence of cyanide infrared absorptions. Attempts to isolate any product from this system, either by vacuum-drying of the solution or by precipitation with hexane followed in both cases by extraction of the resulting solids with benzene and by treatment of their aqueous solution with PF_6^- salts, resulted always in failure.

Reaction of Trimethylamine–Isocyanoborane–Silver Cyanide with Diborane. $(CH_3)_3N{\cdot}BH_2NC{\cdot}AgCN$[13] (0.51 g, 2.20 mmol) was dissolved in 50 mL of CH_2Cl_2 and B_2H_6 (1.20 mmol) was condensed into the previously evacuated reaction vessel. Vacuum evaporation of the filtrate resulted in a brown solid, mp 102 °C, characterized as $(CH_3)_3N{\cdot}BH_2NC{\cdot}AgCN{\cdot}BH_3$ (0.42 g, 1.7 mmol, 78% yield) based on its ^{1}H NMR and IR spectra and elemental analyses. Anal. Calcd: C, 24.45; H, 5.70; N, 17.11; B, 8.80; Ag, 43.92. Found: C, 24.47; H, 5.81; N, 16.95; B, 8.91; Ag, 43.85.

Results and Discussion

Trimethylamine–isocyanoborane has been characterized as a Lewis base able to coordinate with a wide number of compounds.[13–15] This new ligand has also been found to have a chemistry similar to that of carbon isocyanides.[13–15] The extensions of the studies of the donor ability of $(CH_3)_3N{\cdot}BH_2NC$ and the comparison of its chemistry with carbon isocyanides led to the study of the reactions described below.

Trimethylamine–isocyanoborane has been shown to be able to cleave the boron–iodine bond of trimethylamine–iodoborane resulting in the formation of the boronium cation $[(CH_3)_3NBH_2]_2CN^+$, confirming previous suggestions regarding the formation of this cation in other systems.[10] The general nature of this reactivity is shown by the isolation of two other boronium cations (PF_6^- and I^- salts) in the reactions of $(CH_3)_3N{\cdot}BH_2NC$ with 4-methylpyridine–iodoborane and $(CH_3)_3N{\cdot}BH_2NC{\cdot}BH_2I$. The species $[(CH_3)_3NBH_2NCBH_2NC_5H_4CH_3]^+$ has not been previously reported, but the tris(borane) cation $[(CH_3)_3NBH_2NC]_2BH_2^+$ has been obtained before in low yields.[10] The synthesis of this cation from $(CH_3)_3N{\cdot}BH_2NC$ and $(CH_3)_3N{\cdot}BH_2NC{\cdot}BH_2I$ confirms previous predictions.[10]

The formation of boronium cations of the type $[(CH_3)_3NBH_2NCBH_2(\text{amine})]^+$ has been found to depend upon the bulk of the amine. Qualitatively, the cation formation is less favorable with bulky amines: $(CH_3)_3N < 4\text{-}CH_3C_5H_4N < (CH_3)_3N{\cdot}BH_2NC$. The facile boronium cation formation in these systems could result from the preference for carbon-coordinated amine–isocyanoborane such as $(CH_3)_3N{\cdot}BH_2NCR$, as mentioned already for the formation of amine$\cdot BH_2NC{\cdot}BH_3$ from ammonium salts and $H_3B\text{–}NC\text{–}BH_3^-$ [4,6,8] and also suggested by the coordination of $(CH_3)_3N{\cdot}BH_2NC$ to weak Lewis acids such as silver halides.[13,14] The ability of methyl isocyanide to form $[(CH_3)_3NBH_2NCCH_3]^+$ in reaction with trimethylamine–iodoborane provides additional evidence for the close analogy previously reported to exist[13,14] between carbon and boryl isocyanides.

The adducts of $(CH_3)_3N{\cdot}BH_2NC$ with diborane and boron trichloride are characteristic of boryl isocyanides while similar species have not been reported with carbon isocyanides.[11,18] The latter adduct is now reported for the first time, but the former has been prepared before from the reaction of $Na[H_3BNCBH_3]$ with iodine and $(CH_3)_3N$.[6,10] The quan-

Table V. Boron-11 Spectra of the Cyanide Derivatives of Trimethylamine-Borane[a]

Compd	^{11}B shift, ppm	Multiplicity	$J(^{11}$B-H), Hz
$[((CH_3)_3NBH_2NC)_2BH_2]I$	25.9, 60.8	Two broad unresolved signals	
$(CH_3)_3N{\cdot}BH_2NC{\cdot}BH_3$	26.3, 63.6	Triplet and quartet	110, 95

[a] All shifts are upfield of $B(OCH_3)_3$ (external reference). Spectra run at 32.1 MHz.

titative addition of trimethylamine–isocyanoborane to diborane results from the ability of this ligand to cleave the B_2H_6 molecule. Carbon isocyanides have been reported to add to diborane at low temperature but the adducts undergo a rearrangement into heterocyclic boron species at room temperature.[19,20] The increased stability of the bis(borane) adduct could result from the basicity of the $(CH_3)_3NBH_2$ moiety precluding any transfer of a hydride from the BH_3 to the –NC group. Similar arguments could explain the stability of $(CH_3)_3N{\cdot}BH_2NC{\cdot}BCl_3$.

The presence of a boron-coordinated isocyanoborane group, $N—B—N{\equiv}C—B$, in the adducts and boronium cations reported is based on spectroscopic evidence. The characteristic cyanide frequency in the infrared spectra of the compounds at 2280, 2300, and 2240 cm^{-1} for the cations and the BCl_3 and BH_3 adducts, respectively, is expected from the position of this frequency in free $(CH_3)_3N{\cdot}BH_2NC$[12-14] and the effect of coordination of isocyanides on this band.[18] The changes in the frequency of that band in these compounds follow the Lewis acid strength in the series $BCl_3 > (amine)BH_2^+ > BH_3$, as expected from the major increase in the contributions of the triple-bond isocyanide resonance form.[21]

Proton NMR spectra of the cations and the adducts are in agreement with those expected for these compounds. The single band in the spectra of $(CH_3)_3N{\cdot}BH_2NC{\cdot}BCl_3$ and $(CH_3)_3N{\cdot}BH_2NC{\cdot}BH_3$ indicates the absence of mixtures of isomers $(CH_3)_3N{\cdot}BH_2CN$,[14] while the single resonance of $[(CH_3)_3NBH_2NC]_2BH_2^+$ results from the equivalence of both cyanoborane ligands. The slight difference in chemical shifts observed for the cation in the present work from those reported in the literature[10] could result from the effect of dissimilar anions. The four bands in the spectrum of $[(CH_3)_3NBH_2NCBH_2NC_5H_4CH_3]^+$ at 2.70, 2.00, 7.61, and 8.38 ppm are in the expected ratio for the protons in the $(CH_3)_3N$, CH_3–, and C_5H_4 moieties. The deshielding of the protons of $(CH_3)_3N{\cdot}BH_2NC$ caused by coordination to a cation results in a further downfield shift of the $(CH_3)_3N$ signal in the boronium cations from that of the adducts, possibly caused by the positive charge. Although proton NMR evidence by itself cannot be used for structural assignment in this type of compound, it is possible to conclude from the original resonances for free $(CH_3)_3N{\cdot}BH_2NC$ and $(CH_3)_3N{\cdot}BH_2CN$ at 2.63 and 2.70 ppm, respectively, and the fact that both signals are shifted further downfield upon coordination[14] that the bands of the BH_3 and BCl_3 adducts very probably result from coordinated trimethylamine–isocyanoborane.

The ^{11}B NMR data (Table V) are valuable in assigning structure not only to the adducts but also, by inference, to the original ligand. The 1:2:1 triplet located at 26.3 ppm in the spectrum of $(CH_3)_3N{\cdot}BH_2NC{\cdot}BH_3$ is assigned to the boron atom in the BH_2 moiety because of the known boron–hydrogen coupling[22] and the usual positions of this resonance in the 25.7–29.0-ppm range in $(CH_3)_3N{\cdot}BH_2NC$ and its derivatives.[14] The 1:3:3:1 quartet present in the same spectrum corresponds to the expected hydrogen splitting of the boron resonance for the BH_3 group. This chemical shift is practically identical with that reported for the boron linked to carbon in $H_3BCNBH_3^-$.[4] The greater quadrupolar relaxation of boron bonded to nitrogen has been shown to result in broader signals in situations in which two nitrogen atoms are bonded to a single boron as compared to those when only one nitrogen is bonded. This argument has been used to establish cyanide linkage in amine $BH_2NC{\cdot}BH_3$[4] and in the previous report concerning $(CH_3)_3N{\cdot}BH_2NC{\cdot}BH_3$.[10] Since our spectrum for the latter species is identical with that reported previously,[10] we have considered this to be indicative of the presence of a B–NC linkage in the free ligand. Finally, the two boron signals of the tris(borane) cation at 25.9 and 60.8 ppm could be assigned to the boron atoms in the $N–BH_2–N$ and $C–BH_2C$ moieties based on the above arguments.

The methylation of $(CH_3)_3N{\cdot}BH_2NC$ was initially attempted in the belief that the isolation of $(CH_3)_3NBH_2NCCH_3^+$ [23] would provide further evidence for the boron–cyanide linkage in trimethylamine–isocyanoborane. This was based on analogy with $(CH_3)_3NBH_2CNCH_3^+$.[10] Instead, it was found that such reactions were very complex. The occurrence of the α-addition reactions reported for carbon isocyanides[24,26] could explain our results.[27]

The formation of $(CH_3)_4NI$ in the reaction of trimethylamine–isocyanoborane with methyl iodide strongly indicates the presence of free trimethylamine. The nature of our systems as well as known carbon isocyanide chemistry[11,26] indicates that an α-addition reaction of methyl iodide could be responsible for these results, since a free nitrogen–electron pair bonded to boron is known to cause the displacement of trimethylamine from tetrahedral boron compounds.[1] Similar arguments certainly explain the disappearance of the characteristic cyanide absorption of $(CH_3)_3N{\cdot}BH_2NC$ in its reactions with hydrogen chloride, $(CH_3)_3OBF_4$, *N*-chlorosuccinimide, and CH_3FSO_3.[27]

The composition of the products of the reactions of $(CH_3)_3N{\cdot}BH_2NC$ with *N*-chlorosuccinimide and CH_3FSO_3 is consistent with the expectation for an addition reaction. The absence of any infrared cyanide absorption in the reaction solutions or products for all of these cases is also in agreement with an α-addition reaction. Further support for the presence of this type of reactivity is offered by the structure proposed for $(CH_3)_2NBH_2N{=}C(CH_3)FSO_3$ based on analysis of the product's infrared spectrum which possesses characteristic bands for CH, BH, C–N, and FSO–C groups at 3030 and 2960, 2460, 1600, and 1490 cm^{-1}, respectively, and at 1270, 1065, 945, and 710 cm^{-1} for SO–C and F–S bonds.[25]

The occurrence of the reported α-addition reaction of carboxylic acids to carbon isocyanides[24] in our system explains the results obtained in our attempt to isomerize $(CH_3)N{\cdot}BH_2NC$ with glacial acetic acid. The analysis of this reaction was prompted by the reported isomerization of H_3BNC^- by this acid, without any other sign of reaction.[2] The immediate formation of products in the $(CH_3)_3N{\cdot}BH_2NC$ case was shown by the appearance of several unidentified bands in the proton NMR spectrum of the solutions together with the characteristic resonance of $(CH_3)_3N{\cdot}BH_2CN$. Conceivably, the different behavior of the two isocyano–boron species could result from their difference in charge.

Attempts to prepare other adducts of BH_2NC by the displacement of trimethylamine by hexamethylphosphoramide, triethylamine, and triphenylphosphine were thwarted by the lack of reactivity of trimethylamine–isocyanoborane under these conditions, as was an attempt to cleave the boron–isocyanide bond with trimethylamine. By contrast, 4-methylpyridine is able to displace trimethylamine as expected from the known transamination reaction of amine–boranes.[1] Although it was not possible to isolate any product from this reaction, the inability to precipitate with PF_6^- indicates the absence of either $[(CH_3)_3N]_2BH_2^+$ or $[(CH_3)_3NBH_2NC_6H_7]^+$. Furthermore, the presence of more than one $R_3N{\cdot}BH_2CN$ species is indicated by two characteristic cyanide absorptions at 2135 and 2165 cm^{-1}. The assignment of the first one to unreacted $(CH_3)_3N{\cdot}BH_2NC$ suggests that the other band could belong to $C_6H_7N{\cdot}BH_2CN$.

The addition of diborane to the silver cyanide complex of $(CH_3)_3N{\cdot}BH_2NC$ has resulted in the characterization of $(CH_3)_3N{\cdot}BH_2NC{\cdot}AgCN{\cdot}BH_3$. This species could be formally considered to be a complex of the silver cation with the neutral ligand $(CH_3)_3N{\cdot}BH_2NC$ and the anion H_3BNC^-. The ability of H_3BCN^- to form complexes with metal ions,[3] together with the arguments above, suggest that similar complexes for the less stable isomer of the cyanoborohydride, H_3BNC^-, could be prepared by diborane coordination to the corresponding cyano species.

Registry No. $[(CH_3)_3NBH_2NCBH_2NC_6H_7]PF_6$, 62126-26-5; $[(CH_3)_3NBH_2NC)_2BH_2]I$, 62126-27-6; $(CH_3)_3N{\cdot}BH_2NC{\cdot}BCl_3$, 62126-29-8; $(CH_3)_3N{\cdot}BH_2NC{\cdot}BH_3$, 62126-07-2; $(CH_3)_3N{\cdot}BH_2N{=}C(CH_3)OSO_2F$, 62125-79-5; $(CH_3)_3N{\cdot}BH_2N{=}C(Cl)N(COCH_2)_2$, 62125-81-9; $(CH_3)_3N{\cdot}BH_2NC{\cdot}AgCN{\cdot}BH_3$, 62126-24-3; 4-methylpyridine–iodoborane, 59499-23-9; trimethylamine–isocyanoborane, 60045-36-5; trimethylamine–isocyanoborane–iodoborane, 62126-22-1; boron trichloride, 10294-34-5; diborane, 19287-45-7; methyl iodide, 74-88-4; $[(CH_3)_4N]I$, 75-58-1; methyl fluorosulfate, 421-20-5; *N*-chlorosuccinimide, 128-09-6; $(CH_3)_3N{\cdot}BH_2CN$, 30353-61-8; $(CH_3)_3OBF_4$, 420-37-1; 4-methylpyridine, 108-89-4.

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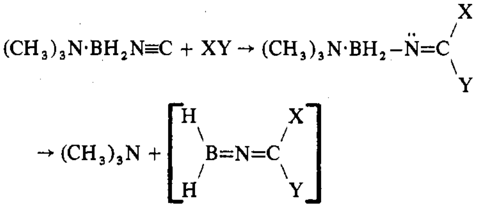
(27) The α-addition reaction of any of these reagents to $(CH_3)_3N{\cdot}BH_2NC$ and the subsequent liberation of trimethylamine could be seen as



$$(CH_3)_3N{\cdot}BH_2N{\equiv}C + XY \rightarrow (CH_3)_3N{\cdot}BH_2{-}\ddot{N}{=}C(X)(Y) \rightarrow (CH_3)_3N + [H_2B{=}N{=}C(X)(Y)]$$

The isolation of the intermediate species in the fluorosulfonate case could be caused by the inductive effect of this anion being able to prevent the displacement of trimethylamine by the nitrogen electron pair. Less electronegative anions such as chloride and iodide should be less able to do so.

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Mechanism of the Complexation of Boron Acids with Catechol and Substituted Catechols[1]

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Boron acids form only 1:1 complexes with catechol and catechol derivatives according to the equation $RB(OH)_2 + H_2L \rightleftarrows RB(OH)L^- + H_3O^+$. Both $B(OH)_3$ and phenylboronic acid, $PhB(OH)_2$, were studied with 4-nitrocatechol, catechol, and 4-methylcatechol. Stability constants for the reactions were determined by pH titration methods and kinetics were done by temperature jump at $\mu = 0.1$ M (KNO_3) and 25 °C. The stability constants increase with increasing ligand acidity. Kinetically, this is reflected in both an increased forward rate constant and a decreased reverse rate constant for the more acidic ligands. This is discussed in terms of a mechanism which emphasizes the importance of proton transfer. Complexes of $B(OH)_3$ have smaller stability constants than the analogous $PhB(OH)_2$ complexes; this, too, is reflected in both the forward and reverse processes. 4-Nitrocatechol is sufficiently acidic such that rate constants for the reactions of the 4-nitrocatecholate anion could be determined with both $B(OH)_3$ and $PhB(OH)_2$. The rate constant for this reaction is much greater than previously determined rate constants for reactions of less basic ligand anions. Possible reasons for this are discussed. The reaction of $PhB(OH)_2$ with mannitol was also investigated by pH titration and stopped flow under the same experimental conditions. These results are consistent with those for more acidic ligands and indicate that even weakly acidic ligands can react with trigonal boron acids.

Many kinetics studies involving catechol (1,2-dihydroxybenzene) and substituted catechols have recently appeared in the literature. These have included studies of substitution processes with both transition metal ions[2] and oxy anions.[3,4] Oxidation of catechol or substituted catechols by metal ions,[5] metalloproteins,[6] and molecular oxygen[7] has also been widely investigated. The last process is catalyzed by transition metal ions.[8]