

Contribution from the Department of Chemistry,  
University of Florida, Gainesville, Florida 32603**Trimethylamine-Isocyanoborane. Synthesis of the First Tetrahedral Boron Isocyanide<sup>1</sup>**

JOSÉ L. VIDAL\* and G. E. RYSCHKEWITSCH

Received July 2, 1976

AIC60482X

The reaction of trimethylamine-iodoborane with silver cyanide at 0 °C has resulted in the isolation of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}\cdot\text{AgCN}$ . The reaction of this complex with hydrogen sulfide liberated  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}$ , the first known tetrahedral boron isocyanide. This novel species is able to coordinate with silver cyanide and iodide to yield  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}\cdot\text{AgCN}$  and  $2\cdot(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}\cdot\text{AgI}$ , respectively. It is also able to cleave the boron-iodine bond in its reaction with trimethylamine-iodoborane producing  $[(\text{CH}_3)_3\text{N}\cdot\text{BH}_2]_2\text{CN}^+$ ; the  $[\text{Ag}_2\text{I}_3]^-$ ,  $\text{PF}_6^-$ , and  $\text{I}^-$  salts of this cation have been characterized. A reaction mechanism is proposed explaining the presence of this cation together with a silver salt complex when the reaction of  $\text{AgCN}$  with  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{I}$  is conducted at room temperature. The assignments of a cyanide linkage to the isomers of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2(\text{CN})$  reported in the literature and of a boron-isocyanide linkage in the isomer reported in this work are made.

**Introduction**

The reactions of amine-boranes ( $\text{R}_3\text{N}\cdot\text{BH}_3$ ), with several halogenating agents have been found to give the corresponding amine-haloborane species.<sup>2-4</sup> The large number of halogenated amine-boranes known is in contrast with the few reported examples of pseudohalogenated derivatives of these adducts. Aftandilian et al.,<sup>5</sup> Wizemann et al.,<sup>6</sup> and Sowerby<sup>7</sup> described the preparation of isothiocyanato derivatives of amine-boranes, and, more recently, Bratt et al.<sup>8</sup> mentioned the synthesis of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{X}$  ( $\text{X} = \text{NCO}, \text{NCS}$ ).

Despite the fact that the chemistry of a tetrahedral cyano boron species like  $\text{BH}_3\text{CN}^-$  is well known,<sup>9</sup> there are only a few reports concerning amine-cyanoboranes. The first compound of this type,  $\text{H}_3\text{N}\cdot\text{BH}_2\text{CN}$ , was reported by Aftandilian et al.<sup>5</sup> Subsequently, Kelly et al.<sup>10</sup> prepared trimethylamine-cyanoborane and other cyanoborane species starting from  $\text{MBH}_3\text{CN}$ . Two other publications concerning the synthesis of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2(\text{CN})$  appeared while this paper was being prepared. Bratt et al.<sup>8</sup> and Beachley and Washburn<sup>11</sup> prepared a cyanoborane species similar to the one originally reported by Kelly et al.<sup>10</sup> The lack of any structural assignment to the B-(CN) linkage in this material raised a question about the nature of the compound.

We decided to study the synthesis of trimethylamine-isocyanoborane in an attempt to identify the isomer of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2(\text{CN})$  reported in the literature<sup>8,10,11</sup> and to collect information concerning the boron-cyanide linkage in amine-cyanoboranes.

The presence of a B—C≡N linkage in the isomer of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2(\text{CN})$  previously reported, and a B—N≡C linkage in the one described in this paper, is proposed on the basis of the spectroscopic and chemical<sup>11,12-13</sup> evidence collected. Other derivatives of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2(\text{CN})$  previously observed by Reznicek and Miller<sup>14</sup> to occur as side-products of the reaction of methyl isocyanide with trimethylamine-iodoborane have been obtained by us, in very satisfactory yield, by direct reaction between the components. New derivatives of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}$  have also been characterized.<sup>1,12,13</sup>

The results described in this work show some of the similarities between boryl and alkyl isocyanides.

**Experimental Section**

All the work was done inside an oxygen-free drybox, except for the isolation of the hexafluorophosphate salts. The use of Schlenk techniques<sup>15</sup> was required for the synthesis of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}\cdot\text{AgCN}$  and  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}$ . All the solvents used were dried by conventional methods,<sup>16</sup> distilled on a vacuum line, collected under vacuum, and stored in the drybox. The chemicals mentioned were used as commercially available. Trimethylamine-iodoborane was routinely

prepared in situ as described by Nainan and Ryschkewitsch.<sup>17</sup>

Infrared spectra were run on a Beckman IR-10 spectrophotometer using 0.125-mm sodium chloride cells. <sup>1</sup>H NMR spectra were obtained on a Varian A-60 with all the chemical shifts reported as downfield of tetramethylsilane used as internal standard. <sup>11</sup>B and <sup>13</sup>C NMR spectra were run on a Varian XL-100 using trimethyl borate and methylene chloride, respectively, as internal standards. Melting points were measured on a Thomas-Hoover apparatus and are not corrected. Elemental analyses were done by Galbraith Microanalytical Laboratories, Nashville, Tenn.

**Reactions of Trimethylamine-Iodoborane with Metal Cyanides. (a)**

**Potassium Cyanide.** Trimethylamine-iodoborane (2.94 g, 14.8 mmol) did not react with KCN (7.14 g, 110 mmol) in refluxing methylene chloride as concluded from the persistence of the <sup>1</sup>H NMR band of the borane at 2.82 ppm after 4 h of contact time. The addition of dibenzo-18-crown-6 (4.94 g, 13.70 mmol) resulted in the appearance of <sup>1</sup>H NMR borane bands at 2.90, 2.82, 2.70, and 2.62 ppm in 1:1:3:2 ratios. The residue collected, after filtration and drying of the solution, was sublimed at an oil bath temperature of 65 °C. A sublimate (0.52 g, 5.3 mmol, yield 36%, mp 50–51 °C, <sup>1</sup>H NMR bands at 2.70 and 2.63 ppm) was analyzed as  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2(\text{CN})$  (Table I).

**(b) Silver Cyanide at Room Temperature.** Trimethylamine-iodoborane (8.79 g, 44.21 mmol) in 40 mL of methylene chloride was added dropwise to a magnetically stirred mixture of AgCN (2.34 g, 17.52 mmol) in 30 mL of the solvent. The resulting mixture was filtered after 10 h of reaction. The yellow filtrate gave a <sup>1</sup>H NMR spectrum with bands at 2.92, 2.82, and 2.70 ppm in 1:3:1 ratio and an infrared spectrum with main bands at 2460, 2445, 2275, and 2180  $\text{cm}^{-1}$ . The slow precipitation of a solid (0.91 g, 1.2 mmol, yield 5%), characterized as  $[(\text{CH}_3)_3\text{NBH}_2]_2\text{CN}[\text{Ag}_2\text{I}_3]$ , mp 165–167 °C, was accompanied by the disappearance of the <sup>1</sup>H NMR band at 2.68 ppm.

The residue (4.34 g) resulting from the vacuum evaporation of the filtrate was divided into two fractions. One of them (2.17 g) was extracted with cold water, filtered, and precipitated with a saturated solution of ammonium hexafluorophosphate to give a solid (0.50 g, 1.6 mmol, yield 7%) characterized after recrystallization from water at 70 °C as  $[(\text{CH}_3)_3\text{NBH}_2]_2\text{CN}[\text{PF}_6]$ .

A second fraction of the reaction product soluble in methylene chloride was sublimed at an oil bath temperature of 155 °C. The solid turned yellow upon heating and a white product sublimed and was characterized as  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{CN}$  (0.03 g, 0.3 mmol, yield 1%). It had a <sup>1</sup>H NMR band at 2.70 ppm and infrared absorptions at 2430, 2420, and 2195  $\text{cm}^{-1}$ . Elemental analysis was as expected for  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2(\text{CN})$ . A fractional sublimation of this material at oil bath temperatures of 45 °C resulted in the isolation of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}$  (0.1 g, 1.0 mmol, yield 5%).

**(c) Excess of Silver Cyanide at 0 °C.** A solution of trimethylamine-iodoborane (42.80 g, 215.3 mmol), contained in a pressure-compensated addition funnel (Figure 1), was added in 30 min to a stirred mixture of silver cyanide (124.0 g, 926.0 mmol) and 180 mL of methylene chloride cooled at ice-water temperature. The mixture was filtered after 0.5 h into a previously evacuated second flask cooled with a liquid-nitrogen bath, and the filtrate was warmed to room temperature while protected from light. Treatment of the filtrate with a 1:1 mixture of diethyl ether-heptane precipitated an oil that solidified (42.10 g, 181 mmol, yield 84%) after overnight

\* To whom correspondence should be addressed at the Technical Center, Union Carbide Corp., South Charleston, W.Va. 25303.

Table I. Elemental Analysis of the Amine-Cyanoborane Species Isolated and Characterized in This Work

Compounds	% calcd										% found									
	C	H	B	Cu	F	I	N	P	Ag	C	H	B	Cu	F	I	N	P			
$(\text{CH}_3)_3\text{N}\cdot\text{BH}_2(\text{CN})^a$	49.04	11.32	11.03				28.60		48.50	11.22	11.04				28.30					
$(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}$	49.04	11.32	11.03				28.60		48.10	11.30	11.07				28.59					
$[(\text{CH}_3)_3\text{NBH}_2]_2\text{CN}[\text{Ag}_2\text{I}_2]$	10.97	5.49	2.82			49.70	5.34	28.14	10.93	2.94	2.91			47.70	5.33	9.70				
$[(\text{CH}_3)_3\text{NBH}_2]_2\text{CN}[\text{PF}_6]$	26.70	7.04	6.87		36.21		13.34		26.79	7.11	6.84			36.24	13.56					
$(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}\cdot\text{AgCN}$	25.91	4.78	4.66			42.76	18.13	46.51	26.02	4.85	4.67				18.21					
$(\text{CH}_3)_3\text{NBH}_2\cdot\text{CN}$	28.32	7.42	7.28			27.47	14.16	25.03	28.34	7.40	7.47			42.44	14.30					
$2[(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}]\cdot\text{AgI}$	22.31	5.15	5.02			37.63	13.01		21.67	5.00	5.37			26.54	14.19					
$3[(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}]\cdot 2\text{CuI}$	21.35	4.93	4.80	18.82			12.45		21.17	4.82	4.49	21.30		35.85	12.30					
$(\text{BH}_2\text{CN})_n$	30.93	5.22	27.83				36.08		31.10	5.11	27.67				35.79					

<sup>a</sup> Isomeric mixture of trimethylamine-cyano- and -isocyanoboranes.

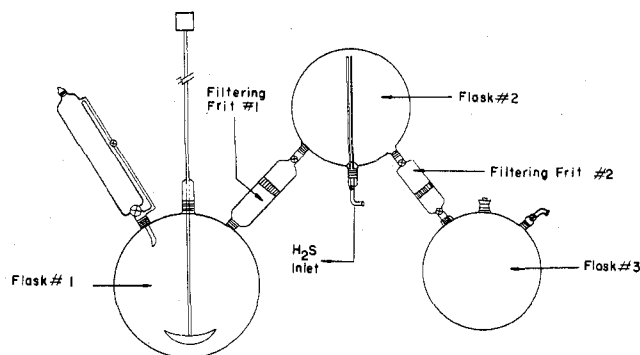


Figure 1. Schlenk system used in the synthesis of trimethylamine-isocyanoborane.

Table II. Infrared Spectra of Derivatives of Trimethylamine-Isocyanoborane

Compound	IR spectrum, $\text{cm}^{-1}$
$(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{CN}$	3010, 2980, 2420, 2230, 2195, 1475, 1460, 1410, 1400, 1250, 1170, 1140, 1095, 1010, 985, 965, 860
$(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}$	3010, 2970, 2430, 2135, 1470, 1410, 1400, 1250, 1190, 1150, 1100, 975, 845, 805, 700, 625
$[(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}\cdot\text{BH}_2\text{N}(\text{CH}_3)_2]\text{I}$	3020, 2010, 2960, 2465, 2440, 2420, 2275, 1475, 1465, 1455, 1405, 1400, 1250, 1180, 1150, 1090, 1010, 970, 955, 870, 730, 665
$[(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}\cdot\text{BH}_2\text{N}(\text{CH}_3)_2]\text{PF}_6$	3040, 2970, 2450, 2275, 1485, 1470, 1410, 1245, 1180, 1150, 1085, 1005, 970, 825, 665
$[(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}\cdot\text{BH}_2\text{N}(\text{CH}_3)_2]\text{Ag}_2\text{I}_2$	3010, 2940, 2465, 2440, 2270, 1475, 1460, 1400, 1240, 1175, 1145, 1135, 1085, 1005, 965, 945, 860
$(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}\cdot\text{AgCN}$	3005, 2945, 2845, 2805, 2430, 2170, 2135, 1485, 1465, 1410, 1385, 1255, 1185, 1160, 1110, 985, 865, 805, 715
$2[(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}]\cdot\text{AgI}$	3010, 2955, 2450, 2200, 2180, 2135, 1480, 1460, 1410, 1380, 1250, 1185, 1155, 1105, 1020, 980, 860, 795

Table III. Proton NMR Spectra in Methylene Chloride

Compound	$\delta$ , ppm	Integral ratio
$(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}$	2.63	
$(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{CN}$	2.70	
$[(\text{CH}_3)_3\text{NBH}_2]_2\text{CN}[\text{I}]$	2.90, 2.82	1:1
$[(\text{CH}_3)_3\text{NBH}_2]_2\text{CN}[\text{PF}_6]$	2.80, 2.73	1:1
$(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}\cdot\text{AgCN}$	2.68	
$2[(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}]\cdot\text{AgI}$	2.68	

<sup>a</sup> Shifts are downfield of  $\text{Me}_4\text{Si}$  used as internal standard.

cooling at 5 °C. The product, characterized as  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{N}\cdot\text{C}\cdot\text{AgCN}$ , mp 60–63 °C, was prepared usually with a yield greater than 87% based on the initial borane. Reactions of this filtrate with gaseous hydrogen sulfide resulted in the precipitation of silver sulfide; the filtering step described above was repeated once more. The white creamy solid (16.0 g, 163 mmol, yield 76%), mp 42–45 °C, collected after evaporation of solvent from the filtrate, was characterized as trimethylamine-isocyanoborane. Sublimation of the crude product at an oil bath temperature of 44 °C gave an uncharacterized yellow oil and a white material (11.5 g, 117 mmol, yield 55%), mp 45–46

**Table IV.** Boron-11 Spectra of the Cyanide Derivatives of Trimethylamine-Borane

Compound	$^{11}\text{B}$ shift, <sup>a</sup> ppm	Multiplicity	$J(^{11}\text{B}-\text{H})$ Hz
$(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}$	25.8	1:2:1 triplet	118
$(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{CN}$	33.3	1:2:1 triplet	108
$(\text{CH}_3)_3\text{N}\cdot\text{BH}_2(\text{CN})^b$	25.9, 33.3	Mult	
$[(\text{CH}_3)_3\text{NBH}_2)_2\text{CN}]_1$	29.0	Broad mult	
$[(\text{CH}_3)_3\text{NBH}_2)_2\text{CN}]\text{PF}_6$	28.5	Broad mult	
$(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}\cdot\text{AgCN}$	25.7	Unresolved signal	

<sup>a</sup> All shifts are upfield of  $\text{B}(\text{OCH}_3)_3$  (external reference). Spectra run at 32.1 MHz. <sup>b</sup> Isomeric mixture of trimethylamine-cyanoborane.

$^\circ\text{C}$ , with infrared (Figure 2, Table II) and  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra (Tables III and IV) and elemental analysis corresponding to  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}$ . Yields were usually in the range 55–60 and 70–80% for large- and small-scale synthesis, respectively. They were affected by the excess of hydrogen sulfide employed, as were also the properties of the crude product upon storage. Crystals of sublimed trimethylamine-isocyanoborane were kept in a closed vial stored inside a desiccator for 6 months without any change.

**(d) Reactions of Trimethylamine-Iodoborane with Potassium Dicyanoargentate.** Trimethylamine-iodoborane, prepared as described before, was reacted with  $\text{K}[\text{Ag}(\text{CN})_2]$  in several molar ratios with the results shown in Table V. The procedure followed in these runs (1–3, 5) is similar to the one described for the reactions with  $\text{AgCN}$ , except that the reactions are conducted at room temperature.  $^1\text{H}$  NMR spectra of the final solutions showed resonance bands at 2.70, 2.79, 2.82, and 2.87 ppm, assigned to a silver salt complex of trimethylamine-isocyanoborane (2.70), to trimethylamine-iodoborane (2.82), and to  $[(\text{CH}_3)_3\text{NBH}_2)_2\text{CN}^+$  (2.79 and 2.87).

It was observed by monitoring the progress of the reaction with  $^1\text{H}$  NMR (runs 1 and 2) that the band at 2.70 ppm disappeared at the same time as a precipitate characterized as  $[(\text{CH}_3)_3\text{NBH}_2)_2\text{CN}[\text{Ag}_2\text{I}_3]$  was formed in low yields. This precipitate was formed in runs 1–4 but it was absent in run 6.

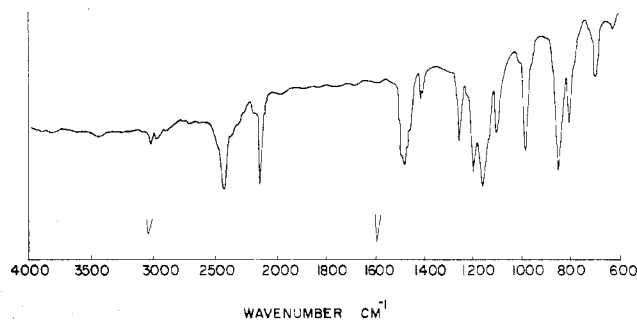
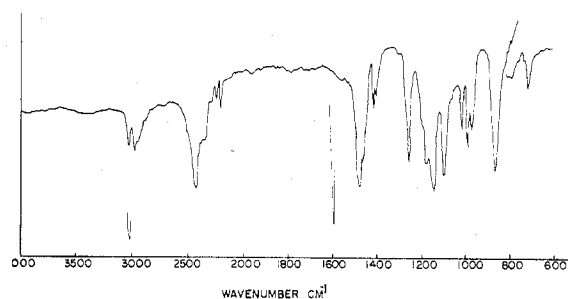
An attempt to prevent the formation of the bis(trimethylamine-borane) cyanide cation by conducting the reaction at water-ice temperatures led to no reaction. Nevertheless, this system reacted as any other run (run 4) upon increasing the temperature to  $25^\circ\text{C}$ .

Products were isolated by division of the reaction product in two portions, one of which was extracted with warm water. Precipitation of the filtrate with ammonium hexafluorophosphate solution resulted in the precipitation and characterization of  $[(\text{CH}_3)_3\text{NBH}_2)_2\text{CN}[\text{PF}_6]$ . Sublimation of the other fraction of the reaction product ( $60\text{--}120^\circ\text{C}$ ) gave a yellow residue and a white sublimate, characterized as  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}$ , in low yields ( $\sim 10\%$ ).

The reaction is slow, as shown by monitoring its  $^1\text{H}$  NMR spectrum. It did not proceed after 7 h at  $0^\circ\text{C}$ , but it started upon increasing the temperature and was complete after 25 h of contact time, Table VI.

**(e) Reactions of Trimethylamine-Iodoborane with Transition Metal Cyanides.** These reactions have been studied by use of an experimental procedure similar to the one described for the silver cyanide system; only additional relevant details are mentioned here.

**(1) Attempted Reaction with Anhydrous Nickel Cyanide and Zinc Cyanide.** Trimethylamine-iodoborane (3.41 g, 17.15 mmol) dissolved in 25 mL of methylene chloride was added to a mixture of anhydrous nickel cyanide (8.05 g, 72.71 mmol) and 50 mL of methylene chloride or to zinc cyanide (15.05 g, 128.4 mmol) in the same amount of this

**Figure 2.** Infrared spectra of trimethylamine-isocyanoborane (bottom) and of trimethylamine-cyanoborane (top).

solvent. The  $^1\text{H}$  NMR spectra of the systems, after 4 h at  $0^\circ\text{C}$  and 20 h at  $25^\circ\text{C}$ , showed only the band at 2.82 ppm assigned to trimethylamine-iodoborane. Recovery of the reactants by filtration of the mixture and vacuum drying of the filtrate resulted in practically quantitative recovery in both cases.

**(2) Reaction of Trimethylamine-Iodoborane with Copper Cyanide.** Anhydrous copper cyanide was prepared by heating copper cyanide at  $130^\circ\text{C}$  for 20 h in a continuously evacuated sublimator. Trimethylamine-iodoborane (2.72 g, 13.68 mmol) was reacted with copper cyanide (21.0 g, 234.5 mmol) in 100 mL of methylene chloride.

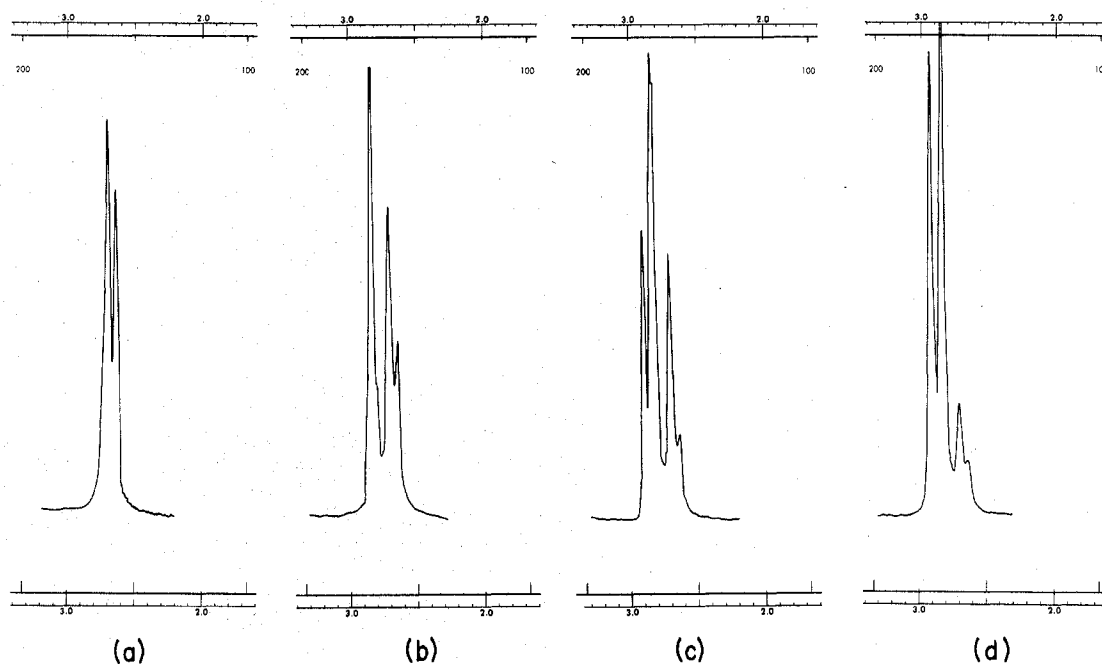
A 3-h mixing period at room temperature was followed by a 24-h reaction time. The mixture was filtered as in the silver cyanide case and the filtrate was transferred to the drybox. Its proton NMR spectrum showed a sharp band at 2.68 ppm. The solvent was vacuum evaporated to one-third of the volume and the solution was treated with petroleum ether, to obtain a mixture of white and yellow oils which solidified upon freezing overnight. The solid (0.91 g), mp  $125\text{--}128^\circ\text{C}$ , had the same proton NMR spectrum reported above and an infrared spectrum which resembled that of trimethylamine-isocyanoborane silver cyanide, except for the presence of three cyanide stretching vibrations at 2160, 2140, and  $2120\text{ cm}^{-1}$ . Elemental analysis of this product was in agreement with that expected for  $3[(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}]\cdot\text{Cu}_2\text{I}_2$ . This reaction did not occur at  $0^\circ\text{C}$ . It was noted that a methylene chloride solution of the material did not react with gaseous hydrogen sulfide as concluded from the persistence of the infrared and  $^1\text{H}$  NMR spectra of the original solution and the absence of any visible indication of change.

**Reactions of Trimethylamine-Isocyanoborane.** The following reactions have been studied in an attempt to establish the probability of their occurrence in our system.

**(a) Reaction of Trimethylamine-Isocyanoborane with Trimethylamine-Iodoborane.** Trimethylamine-iodoborane (1.00 g, 5.07

**Table V.** Reaction of Trimethylamine-Iodoborane with Potassium Dicyanoargentate

Run no.	Molar ratio B:Ag	$T, ^\circ\text{C}$	Time, h	$^1\text{H}$ NMR ppm	Integral ratio	Characterized products		
						Bis(borane) cation salts	Sublimed materials	$T, ^\circ\text{C}$
1	1:1	25	10	2.90, 2.82, 2.70	2:2:1	$\text{PF}_6^-, \text{Ag}_2\text{I}_3^-$	$(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}$ $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}$ $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{CN}$	60 120
2	2:1	25	12	2.93, 2.82, 2.70	2:2:1	$\text{PF}_6^-, \text{Ag}_2\text{I}_3^-$	As above	
3	1:8:1	25	20	2.90, 2.82, 2.69	4:4:1	$\text{PF}_6^-, \text{Ag}_2\text{I}_3^-$	As above	
4	1:5	0	7	2.82		Not checked		
		25	25	2.90, 2.82, 2.69	1:5:1	$\text{PF}_6^-, \text{Ag}_2\text{I}_3^-$	As above	
5	8:1	25	25	2.85, 2.79	1:1	$\text{PF}_6^-$	Not sublimed	120



**Figure 3.** Proton NMR spectra of the isomeric mixture of (a)  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2(\text{CN})$  and of its reaction with  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{I}$  after (b) 15 min, (c) 45 min, and (d) 120 min of reaction time in methylene chloride. (Chemical shifts were obtained in methylene chloride with  $\text{Me}_4\text{Si}$  as internal standard.)

**Table VI**

$T, ^\circ\text{C}$	Reaction time, h	$^1\text{H}$ NMR, ppm	Integral ratio
0	8	2.82	
Room temp	15	2.90, 2.82, 2.68	1.38:1.54:1.00
Room temp	22	2.91, 2.82, 2.68	1.43:1.50:1.00
Room temp	41	2.90, 2.82, 2.67	1.48:1.49:1.00

mmol), dissolved in 20 mL of methylene chloride, was added to a solution of trimethylamine-isocyanoborane (0.50 g, 5.10 mmol) in 20 mL of the same solvent and the system was stirred overnight. The solid collected after vacuum evaporation of the solvent was thoroughly washed with benzene and dried. The product (1.42 g, 4.78 mmol, yield 94%), mp 173–175  $^\circ\text{C}$ , had a  $^1\text{H}$  NMR spectrum consisting of a doublet at 2.90 and 2.82 ppm in 1:1 ratio and an infrared spectrum (Tables II–IV) with characteristic bands at 2440 and 2280  $\text{cm}^{-1}$ , as expected for  $[(\text{CH}_3)_3\text{NBH}_2]_2\text{CNI}$ .

This reaction was also studied by mixing trimethylamine-iodoborane (1.10 g, 5.08 mmol) dissolved in 12 mL of methylene chloride with trimethylamine-isocyanoborane (0.50 g, 5.10 mmol), also dissolved in 12 mL of the solvent, and monitoring by use of  $^1\text{H}$  NMR spectroscopy a sample of this system sealed in an NMR tube at 35  $^\circ\text{C}$ , with the results below. Resonance bands were present at 2.90, 2.82, and 2.63 ppm in the following respective integral ratios (reaction time (min), integral ratio): 20, 1.0:2.1:1.3; 50, 1.0:1.4:0.5; 95, 1.0:1.3:0.3; 155, 1.0:1.1:0.1; 300, 1.0:1.1:0.1.

A qualitative study of the reaction of an isomeric mixture of trimethylamine-cyanoborane and trimethylamine-iodoborane was done on an NMR tube scale by monitoring the  $^1\text{H}$  NMR spectrum of the system (Figure 3). A methylene chloride solution of the mixture of isomers (Figure 3a) showed the  $^1\text{H}$  NMR resonances of  $(\text{C}_6\text{H}_5)_3\text{N}\cdot\text{BH}_2\text{CN}$  and  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}$  at 2.63 and 2.70 ppm, respectively. Addition of an excess of trimethylamine-iodoborane solution resulted, after 20 min of contact time, in bands assigned to  $[(\text{CH}_3)_3\text{NBH}_2]_2\text{CN}^+$ ,  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{I}$ , and both isomers of cyanoborane at 2.90, 2.82 and 2.63 and 2.70 ppm, respectively. The presence of cyanide stretching infrared bands at 2280, 2180–2190, and 2135  $\text{cm}^{-1}$  confirmed the presence of the proposed species. The decrease of the intensities of the bands assigned to both cyanoboranes and to the iodide adducts and the increase in the intensity of the cation resonances (Figure 3c) after 30 min of reaction, indicate the partial and slow consumption of the adducts. Another spectrum taken 2 h later (Figure 3d) showed further decrease of both of the cyanoborane bands and the corresponding increase in the cation resonances. The

faster decrease in the intensity of the trimethylamine-isocyanoborane band indicates a more favorable reaction in this case.

**(b) Reaction of Trimethylamine-Isocyanoborane with Silver Iodide and Silver Cyanide.** Trimethylamine-isocyanoborane (1.00 g, 10.21 mmol) was dissolved in 20 mL of methylene chloride and mixed with silver iodide (12.0 g, 51.13 mmol), and the solution was stirred overnight and filtered. Vacuum evaporation of the solvent left a white residue (1.52 g, 3.5 mmol, yield 69%) mp 110–111  $^\circ\text{C}$ , characterized as  $2[(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}]\cdot\text{AgI}$ .

The silver cyanide complex was prepared by adding trimethylamine-isocyanoborane (1.00 g, 10.21 mmol) dissolved in 40 mL of methylene chloride to a mixture of silver cyanide (6.00 g, 44.81 mmol) in 30 mL of the solvent. The resulting mixture was stirred overnight and filtered. The filtrate was precipitated with a 1:1 mixture of diethyl ether-heptane and frozen overnight. A solid (1.85 g) was collected after strong shaking and drying. The product, mp 60–63  $^\circ\text{C}$ , was characterized as  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}\cdot\text{AgCN}$  (8.1 mmol, yield 78%).

**Reactions of Trimethylamine-Isocyanoborane-Silver Salt Complexes.** The precipitation in our systems of the complex anion  $[\text{Ag}_2\text{I}_3]^-$  indicated the presence of methylene chloride soluble species containing or being able to form silver iodide. The reactions below have been studied in an attempt to understand the formation of this anion.

**(a) Reaction of Trimethylamine-Isocyanoborane-Silver Cyanide with Hydrogen Sulfide.** Trimethylamine-isocyanoborane-silver cyanide (6.05 g, 26.07 mmol) was dissolved in 40 mL of methylene chloride and gaseous hydrogen sulfide was bubbled into the system, precipitating immediately a black solid (7.2 g, 91% of the weight expected for silver sulfide). Filtration of the mixture gave a clear filtrate which gave a cream white solid (2.6 g or 100% of the expected amount of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}$  after vacuum evaporation of the solvent. Sublimation of this material at an oil bath temperature of 45  $^\circ\text{C}$  gave 2.1 g (84%) of pure  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}$ .

**(b) Reaction of Bis(trimethylamine-isocyanoborane)-Silver Iodide with Silver Cyanide.** Bis(trimethylamine-isocyanoborane)-silver iodide (0.27 g, 0.63 mmol) was dissolved in 25 mL of methylene chloride and mixed with silver cyanide (3.00 g, 27.39 mmol). The mixture was stirred overnight and filtered. The filtrate was concentrated to half volume and precipitated with petroleum ether. The white solid (0.17 g, 0.73 mmol, yield 58%) collected after freezing the mixture overnight and shaking was characterized as  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}\cdot\text{AgCN}$ .

**(c) Reactions of Trimethylamine-Isocyanoborane-Silver Cyanide and of Bis(trimethylamine-isocyanoborane)-Silver Iodide with Trimethylamine-Iodoborane.** Trimethylamine-isocyanoborane-silver cyanide (0.97 g, 4.18 mmol) was dissolved in 5 mL of methylene chloride and mixed with trimethylamine-iodoborane (1.54 g, 7.7

Table VII. Thermal Stability

Solvent	T, °C	Time, h	<sup>1</sup> H NMR, <sup>a</sup> ppm	Observations
CH <sub>2</sub> Cl <sub>2</sub>	65	12	2.62 (2.70)	Soln yellow; no solid visible
	95	10	2.75, 2.70, 2.62	Soln yellow; yellow solid present
C <sub>6</sub> H <sub>6</sub>	65	12	2.47, 2.25, 2.17, (2.20), 2.12	As above
	65	16	2.47, 2.25, 2.17, 2.12, 1.93	As above
	95	5	2.47, 2.25, 2.17, (2.20), 2.12	As above

<sup>a</sup> Bands in parentheses were low-intensity, unresolved, not integrable signals.

mmol) in 10 mL of the solvent. There was precipitate present and the solvent was vacuum evaporated to obtain a residue (2.43 g) that was washed with benzene and dried. The solid, mp 143–144 °C, had <sup>1</sup>H NMR and infrared spectra characteristic of the bis(trimethylaminoboryl) cyanide cation. The composition of the material is that corresponding to a mixture of 3 mol of [(CH<sub>3</sub>)<sub>3</sub>NBH<sub>2</sub>]<sub>2</sub>CNI and 1 of [(CH<sub>3</sub>)<sub>3</sub>NBH<sub>2</sub>]<sub>2</sub>CN[AgI<sub>2</sub>]. Anal. Calcd: C, 23.83; H, 6.28; B, 5.36; I, 44.20; N, 11.91; Ag, 7.64. Found: C, 23.31; H, 6.02; B, 5.87; I, 44.55; N, 11.41; Ag, 8.75.

Bis(trimethylamine-isocyanoborane)-silver iodide (0.33 g, 0.76 mmol) was dissolved in 25 mL of methylene chloride and mixed with trimethylamine-iodoborane (0.81 g, 4.10 mmol) in 20 mL of the solvent. The reaction is faster than that of the silver cyanide complex. The solution was stirred overnight and the precipitate present was removed and characterized as [(CH<sub>3</sub>)<sub>3</sub>NBH<sub>2</sub>]<sub>2</sub>CN[Ag<sub>2</sub>I<sub>3</sub>]. The filtrate was vacuum dried and the residue collected was washed with benzene. The insoluble material (0.14 g) was dried and shown by elemental analysis to have a composition corresponding to 3 mol of [(CH<sub>3</sub>)<sub>3</sub>NBH<sub>2</sub>]<sub>2</sub>CNI to 1 of [(CH<sub>3</sub>)<sub>3</sub>NBH<sub>2</sub>]<sub>2</sub>CN[AgI<sub>2</sub>]. Anal. Found: C, 23.30; H, 6.03; N, 11.42; B, 5.80; Ag, 7.80.

**Stability of Trimethylamine-Isocyanoborane.** The thermal stability of the boryl isocyanide was studied by sealing an NMR tube containing a solution of trimethylamine-isocyanoborane and warming it for a specified length of time in an oil bath, with the results shown in Table VII. The thermal stability in the absence of solvents was tested by warming a sealed thick-walled tube containing trimethylamine-isocyanoborane at several oil bath temperatures. The orange oil present in the tube at the end of the warming period was dissolved in methylene chloride.<sup>1</sup> The <sup>1</sup>H NMR of these solutions is given in Table VIII.

A strong odor of amine suggested the decomposition of (CH<sub>3</sub>)<sub>3</sub>N·BH<sub>2</sub>NC. This was confirmed by heating molten trimethylamine-isocyanoborane (0.62 g, 6.33 mmol) at 100 °C in an evacuated reaction flask connected to a vacuum line. The orange oil formed bubbled strongly for about 20 min and turned into a white cream solid. Trimethylamine (5.97 mmol) was characterized by its infrared spectrum as the volatile material trapped at liquid nitrogen temperatures in the line. The residual solid (0.27 g) was washed with benzene and vacuum dried. This solid, decomposition temperature 165–168 °C, had an elemental analysis as expected for (BH<sub>2</sub>CN)<sub>n</sub>.

## Results and Discussion

The reactions of trimethylamine-haloboranes with potassium and silver cyanides were selected as potential ways of preparing trimethylamine-cyano- and -isocyanoboranes, because of the selectivity of the reactions of these salts with alkyl halides.<sup>18–20</sup> The strength of the boron-halogen bond is perhaps responsible for the inertness shown by trimethylamine-chloro- and -bromoboranes toward these salts and for the smooth reactions of the iodine adduct with the same reagents under milder conditions. We decided that the study of this last reaction was more convenient for our purposes.

**Study of [(CH<sub>3</sub>)<sub>3</sub>NBH<sub>2</sub>]<sub>2</sub>CN<sup>+</sup>: Formation, Properties, and Salts.** The presence of this cation in some of our systems was indicated by its isolation as the PF<sub>6</sub><sup>-</sup> salt, a species already

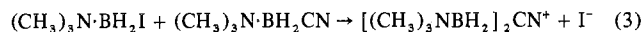
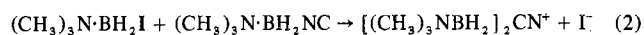
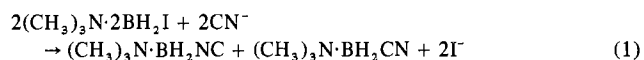
Table VIII. <sup>1</sup>H NMR Data

Run no.	T, °C	Time, h	<sup>1</sup> H NMR, ppm	Observations
1	60	16	2.70, 2.63, 2.13	2.62 major signal
2	110	2.5	2.88, 2.85, 2.77, 2.70, 2.62, 2.13	2.70 major signal
3	95	2	2.88, 2.85, 2.77, 2.70, 2.62, 2.13	2.62 major signal
4	95	5	2.88, 2.85, 2.77, 2.70, 2.62, 2.13	2.70 major signal
5	95	17	2.88, 2.85, 2.77, 2.70, 2.13	2.70 major signal

reported in the literature.<sup>14</sup> The study of the cation was found fundamental for the optimization of the synthesis of (C-H<sub>3</sub>)<sub>3</sub>N·BH<sub>2</sub>NC.

The formation of this cation in the reactions of trimethylamine-iodoborane with KCN, AgCN, and K[Ag(CN)<sub>2</sub>] is caused by reaction of the haloborane with either one or both isomers of (CH<sub>3</sub>)<sub>3</sub>N·BH<sub>2</sub>(CN), as shown below.

The cleavage of the boron-iodine bond by the cyanide group occurs under mild conditions, either with a weak base such as methyl isocyanide<sup>14</sup> or with a strong one such as the cyanide ion.<sup>8</sup> We have found that both ends of the cyanide ion are able to cleave the mentioned bond as concluded from the formation of both isomers of (CH<sub>3</sub>)<sub>3</sub>N·BH<sub>2</sub>(CN) in the reaction of trimethylamine-iodoborane with KCN. Moreover, this bond is also cleaved by the two isomers of trimethylamine-cyanoborane resulting in the formation of [(CH<sub>3</sub>)<sub>3</sub>NBH<sub>2</sub>]<sub>2</sub>CN<sup>+</sup>, as observed in the reactions of trimethylamine-iodoborane with trimethylamine-isocyanoborane and with the mixture of isomers. These reactions are concurrent with the reaction with KCN.



The exchange reaction of trimethylamine-iodoborane with alkali pseudohalides has been reported<sup>8</sup> although the only product isolated in the case of the cyanide was trimethylamine-cyanoborane. In our case, the reaction of cyanide ion with trimethylamine-iodoborane gave as products the bridged cyanide cation and the isomeric cyanoborane mixture. This was concluded from the presence of the characteristic resonance bands and cyanide frequencies of these species in the <sup>1</sup>H NMR and infrared spectra of the solution and confirmed by isolation of the products.

<sup>1</sup>H NMR studies of the reaction of both isomers of trimethylamine-cyanoborane with the iodoborane adduct have shown both reactions to be slow, trimethylamine-isocyanoborane reacting faster than the other isomer (Figure 3). The slowness of the reactions is a probable consequence of the bulk of both reagent molecules as indicated by the faster reactions observed with less-hindered amine-iodoboranes, e.g., 4-methylpyridine-iodoborane.<sup>12</sup> The inability of (CH<sub>3</sub>)<sub>3</sub>N·BH<sub>2</sub>NC to cleave the boron-iodine bond in trimethylamine-iodoborane at 0 °C is a consequence of the mentioned steric effect, as suggested by the ability of cyanide ion to cleave this bond under similar conditions.

The preference for a boron-carbon over a boron-nitrogen bond is shown by these results. Since both trimethylamine-cyanoboranes should have similar steric requirements, the differences in their reactivity toward (CH<sub>3</sub>)<sub>3</sub>N·BH<sub>2</sub>I could be caused by the greater basicity of the carbon electron pair

over that of the nitrogen one, and by the larger energy of activation of  $CN \rightarrow B$  attack over that of  $NC \rightarrow B$ , as proposed for the reaction of  $CN^-$  with  $THF \cdot BH_3$ .<sup>9</sup>

The formation of  $[(CH_3)_3NBH_2]_2CN^+$  in the reaction of trimethylamine–iodoborane with  $(CH_3)_3N \cdot BH_2NC$  led to the preparation of the  $I^-$  and  $PF_6^-$  salts of the cation in addition to the  $[Ag_2I_3]^-$  salts. The hexafluorophosphate salt has been previously isolated in very low yields in the reaction  $(CH_3)_3N \cdot BH_2I$  with methyl isocyanide.<sup>14</sup> We were able to prepare the iodide and  $PF_6^-$  salts in 100 and 60% yields, respectively. The iodide salt is inert to trimethylamine as already observed,<sup>14</sup> to glacial acetic acid, and to methyl iodide. It could be heated under high vacuum up to 150 °C without decomposition. The  $PF_6^-$  salt did not react with an excess of  $Ag(CN)$  or  $K[Ag(CN)_2]$ . The diargentate anion has been reported before in salts with other large inorganic anions such as cesium.<sup>21</sup>

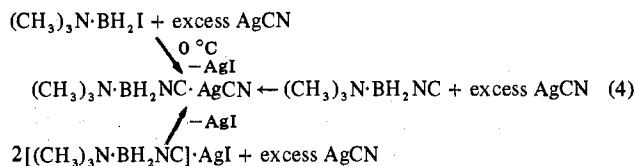
The infrared spectra of the salts of this cation (Table II) show two boron–hydrogen infrared active bands at 2465 and 2440  $cm^{-1}$  and a bridging cyanide band at 2275–2280  $cm^{-1}$ , as would correspond to the coordination of either of the isomers. The  $^1H$  NMR spectra of the several salts are in agreement with that expected for the cation (Table III) with the differences in chemical shifts possibly being caused by the different anions. The reported assignment<sup>14</sup> of the proton resonances of the cation at 2.87 ppm to  $(CH_3)_3N \cdot BH_2N$  and at 2.80 ppm to  $(CH_3)_3N \cdot BH_2C$  does not seem correct on the basis of the chemical shifts found by us for the two isomers (Table III). We found that the formation of the cation shifts the proton resonance of the methyl groups of both amine–cyanoborane species as expected from the deshielding caused by the positive charge. Unless an inversion of shifts could be caused by the electronegativity of the nitrogen end of the bridging  $CN^-$ , there is no apparent reason for us to expect the downfield band to be other than that of  $(CH_3)_3N \cdot BH_2C$ , and the other one that of  $(CH_3)_3N \cdot BH_2N$ .

**Silver Salt Complexes of Trimethylamine–Isocyanoborane.** The formation of the  $[Ag_2I_3]^-$  anion strongly indicated the presence of silver-containing species soluble in  $CH_2Cl_2$ . The reactions of  $(CH_3)_3N \cdot BH_2NC$  with  $AgI$  and  $AgCN$  were studied in this respect in an attempt to explain the formation of those species.

Trimethylamine–isocyanoborane reacted with silver iodide producing a methylene chloride soluble material of empirical formula  $2[(CH_3)_3N \cdot BH_2NC] \cdot AgI$ . This complex is weak as shown by the precipitation of silver iodide upon redissolution during attempts to measure its conductivity. The presence of three cyanide stretches at 2200, 2180, and 2135  $cm^{-1}$  in the infrared spectrum of the material indicates the presence of several cyanoborane moieties (Table II). The cyanide stretch at 2135  $cm^{-1}$  could indicate free trimethylamine–isocyanoborane while the one at 2180  $cm^{-1}$  is assigned to the bridging cyanide group of a trimethylamine–isocyanoborane moiety, like in  $(CH_3)_3N \cdot BH_2NC \cdot AgI$ , by analogy with a similar assignment in trimethylamine–isocyanoborane–silver cyanide. These assignments are also suggested by the expected increase generally observed for this frequency upon coordination of nitrile<sup>18</sup> and isocyanide<sup>20</sup> ligands and the relative positions of the cyanide stretching frequency in the two isomers of  $(CH_3)_3N \cdot BH_2(CN)$ . Finally, the absorption at 2200  $cm^{-1}$  could indicate the presence of  $[(CH_3)_3N \cdot BH_2NC]_2Ag^+$  by analogy with  $[p-CH_3C_6H_4NC]_2Ag^+$ .<sup>22</sup> The comparison between the two complexes is supported by the similarity of the ligands. Both free isocyanide species show a cyanide stretching band at around 2135  $cm^{-1}$  and both of them are expected to show a similar increase in this frequency upon coordination to silver. *p*-Tolyl isocyanide has been concluded to be unable to accept electronic charge by  $\pi$  back-bonding from silver in

this complex<sup>22</sup> and a similar behavior is expected for  $(CH_3)_3N \cdot BH_2NC$  as a result of the nature of the boryl moiety. Since  $(CH_3)_3N \cdot BH_2NC \cdot AgI$  is expected to show a larger amount of  $\pi$  back-bonding from the silver to the isocyanide ligand than  $[(CH_3)_3N \cdot BH_2NC]_2Ag^+$ , the assignment above seems correct.

The greater stability of the silver cyanide complex with trimethylamine–isocyanoborane over that of the corresponding silver iodide species results in the displacement of this salt from its complex under very mild conditions. The resulting silver cyanide complex has also been prepared in two other ways.

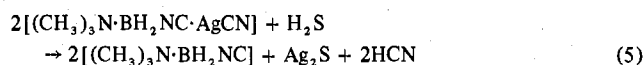


The easy exchange of salts observed by us in the boron case is in contrast with the more drastic conditions required in the carbon isocyanide case.<sup>23</sup>

The structure of this complex has been proposed based on infrared and conductometric evidence. The two cyanide infrared stretching bands at 2170 and 2135  $cm^{-1}$  (Table I) shown by the products of all three reactions above are assigned to bridge and terminal cyanide groups,<sup>24,25</sup> respectively. Although  $\{2[(CH_3)_3N \cdot BH_2NC] \cdot AgI\} \cdot AgCN$  and  $[(CH_3)_3N \cdot BH_2]_2CN[Ag(CN)_2]$  could be responsible for the presence of both cyanide infrared bands, the absence of the  $^1H$  NMR and characteristic cyanide infrared bands for the cation at 2.90 and 2.82 ppm and at 2280  $cm^{-1}$ , respectively, are indications of the absence of  $[(CH_3)_3NBH_2]_2CN^+$  from the product. Further evidence against ionic structures is based on the low electrical conductivity of the material.<sup>26</sup>

The presence in this complex of a  $BN \equiv CAg$  moiety instead of a  $BC \equiv NAg$  one is also concluded from infrared evidence. It is highly unlikely that the band at 2170  $cm^{-1}$  would result from the second type of bonding because coordination of cyanide ligands results invariably in an increase of the cyanide frequency over that of the free ligand<sup>27–30</sup> and back-bonding from silver to cyanide ligands is not large enough to account for a decrease of  $\sim 25$   $cm^{-1}$  in the cyanide stretching frequency of the coordinated cyanoborane. Thus, the presence of a moiety like  $BC \equiv NAg$  should result in a cyanide band at higher frequency than that present in the free ligand at 2195  $cm^{-1}$ . That is not consistent with our observations.

The chemical stability of  $(CH_3)_3N \cdot BH_2NC \cdot AgCN$  is shown by the inertness of this compound toward triphenylphosphine and trimethylamine and the slight reaction observed with tetrabutylammonium iodide. It reacts quantitatively with hydrogen sulfide with the immediate precipitation of silver sulfide.

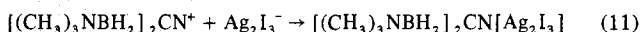
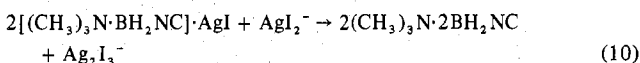
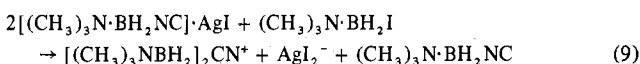
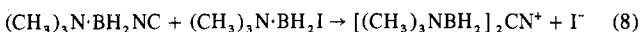
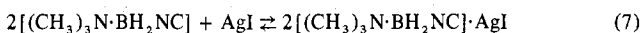
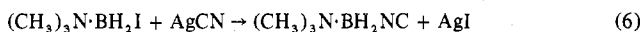


The reactions of trimethylamine–iodoborane with the silver iodide and cyanide complexes of trimethylamine–isocyanoborane result in the precipitation of  $[(CH_3)_3NBH_2]_2C \cdot N[Ag_2I_3]$  and in a soluble product characterized as a 3:1 mixture of the  $I^-$  and  $AgI_2^-$  salts of the bridge cyanide cation. The diiodo argentate salt has also been generated in low yields by the reaction of  $[(C_4H_{11})_4N]I$  with the silver iodide complex.

The reaction of trimethylamine–iodoborane with  $(CH_3)_3N \cdot BH_2NC \cdot AgCN$  was expected to yield  $[(CH_3)_3NBH_2NC]_2AgI$ . The influence of the high silver–iodide affinity could be the reason for the decomposition of this cation, initiating in this way the series of reactions leading to the formation of  $[Ag_2I_3]^-$ . The isolation of the same products from the reactions of trimethylamine–iodoborane with the silver iodide and

cyanide complexes of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}$  seems to be in agreement with these ideas. Evidence has been also found for a fast exchange, outside of the  $^1\text{H}$  NMR 60-MHz time scale, between the free and coordinated trimethylamine-isocyanoborane for  $2[(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}]\cdot\text{AgI}$  and  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}\cdot\text{AgCN}$  by observing the presence and position of only one resonance band in the  $^1\text{H}$  NMR spectra of mixtures of these complexes with variable amounts of ligands.

**Synthesis of Trimethylamine-Isocyanoborane.** The formation of  $[(\text{CH}_3)_3\text{NBH}_2]_2\text{CN}[\text{Ag}_2\text{I}_3]$  in our systems is explained by means of the mechanism shown in the set of equations below:



The metathetical reaction between trimethylamine-iodoborane and silver cyanide (eq 6) is supported by the isolation of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}\cdot\text{AgCN}$  while the formation of the silver iodide complex of this ligand (eq 7) indicates formation of this species as the reason for the solubilization of silver iodide in our solutions, in the absence of an excess of silver cyanide.

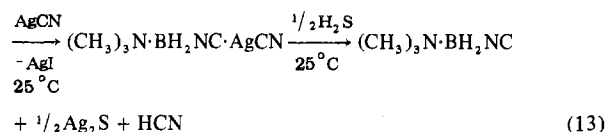
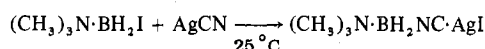
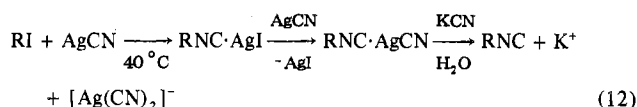
Formation of  $[(\text{CH}_3)_3\text{NBH}_2]_2\text{CN}^+$  in these systems could be explained in various ways. The reaction of trimethylamine-isocyanoborane with trimethylamine-iodoborane (eq 8) has been shown to yield this cation. Moreover, it has been also shown that the reaction of bis(trimethylamine-isocyanoborane)-silver iodide with trimethylamine-iodoborane (eq 9) provides another pathway to the formation of the cation and to the formation of the  $[\text{AgI}_2]^-$  anion.

The disappearance of the  $^1\text{H}$  NMR resonance at 2.68 ppm, associated with  $2[(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}]\cdot\text{AgI}$ , upon precipitation of the  $[\text{Ag}_2\text{I}_3]^-$  salt is a strong indication of the consumption of the former complex during the formation of the anion. The presence of the diiodoargentate anion in the product of the reaction of trimethylamine-iodoborane with  $2[(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}]\cdot\text{AgI}$  suggests that further reaction of this anion with the silver iodide complex (eq 10) is the most probable way of forming  $[\text{Ag}_2\text{I}_3]^-$  in our case.

The presence of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}$  in these cases is concluded from the cyanide infrared absorption at  $2135\text{ cm}^{-1}$  present in the spectra of the reaction solution and from the presence in the sublimate of both isomers of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2(\text{CN})$ . The last conclusion is based on the observations that  $[(\text{CH}_3)_3\text{NBH}_2]_2\text{CNI}$  is stable under vacuum at  $150^\circ\text{C}$ , while  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}\cdot\text{AgCN}$  is not able to give up any ligand, and that  $2[(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}]\cdot\text{AgI}$  produced only trimethylamine-isocyanoborane. Thus, the only cyanoborane species which is present and known to produce  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{CN}$  under our experimental conditions is  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}$ . Nevertheless the above cyanide absorption could also indicate the presence of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}\cdot\text{AgCN}$ . The similar NMR chemical shifts of this species and of the silver iodide complex, and the fast exchange shown to exist between these complexes and the free ligand, indicate that the presence of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}$  and its silver cyanide complex could not be ruled out on the basis of the  $^1\text{H}$  NMR data obtained. In any case, the presence of trimethylamine-isocyanoborane-silver cyanide in addition to the silver iodide complex will result in the same mechanism for the formation of the  $[\text{Ag}_2\text{I}_3]^-$  anion, as indicated by the reaction between  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}\cdot\text{AgCN}$  and  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{I}$ .

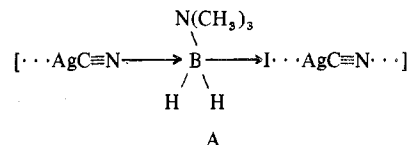
The formation of  $2[(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}]\cdot\text{AgI}$  and the subsequent series of side-reactions leading to the formation of  $[(\text{CH}_3)_3\text{NBH}_2]_2\text{CN}^+$  and to the precipitation of its  $[\text{Ag}_2\text{I}_3]^-$  salt have been prevented by working with a fivefold excess of silver cyanide at ice-water temperature. The low temperature is needed to prevent the occurrence of the reactions leading to the formation of the bis(trimethylamine-borane)cyanide cation, while the excess of silver cyanide is required for an efficient conversion of the initially present trimethylamine-iodoborane and for the transformation of any silver iodide complex of trimethylamine-isocyanoborane formed into the stable silver cyanide complex.

The synthesis of trimethylamine-isocyanoborane by means of the reaction of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{I}$  with silver cyanide is shown by us to be remarkably similar to the preparation of alkyl isocyanides,<sup>31</sup> although the formation of  $[(\text{CH}_3)_3\text{NBH}_2]_2\text{CN}^+$  in the boron case is distinctly different. This is a consequence of the strength of the boron-iodine bond being less than that of the carbon-iodine bond.



The similarities found between alkyl and boryl isocyanides are also present in the reactions with metal cyanides. Nickel and zinc cyanides are inert toward alkyl<sup>20</sup> and boryl iodides. Reactions with copper(II) and mercury(II) are found to be complex in both cases.<sup>30-35</sup> The empirical formula, molar conductivity ( $6.90 \times 10^{-4}\text{ M}$ ,  $\Lambda = 0.62 \times 10^{-4}\ \Omega^{-1}\text{ cm}^2\text{ equiv}^{-1}$ ), and the cyanide stretches present in the infrared spectrum of the product are consistent with a complex such as  $[(\text{CH}_3)_3\text{NBH}_2(\text{CN})]_2\text{Cu}(\mu\text{-I})_2\text{Cu}(\text{CH}_3)_3\text{NBH}_2(\text{CN})$ . Complexes of a similar type are known for carbon isocyanides, e.g.,  $2\text{C}_2\text{H}_5\text{NC}\cdot\text{CuCN}$ ,  $3\text{C}_2\text{H}_5\text{NC}\cdot\text{CuCN}$ , and  $3\text{CuCN}\cdot\text{CH}_3\text{I}$ .<sup>20</sup> It was not possible to isolate any product from the mercury cyanide reactions.

The displacement of halides from alkyl halides in the presence of silver salts has been shown to occur by a "silver assisted mechanism" which could result in a "push-pull mechanism" when a concerted attack by the anion of the silver salt occurs.<sup>36</sup> A similar mechanism could be operative in the heterogeneous reaction of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{I}$  with silver cyanide if one silver atom acts as an iodine scavenger after insertion of the iodoborane into an isocyanide-silver bond (A). This

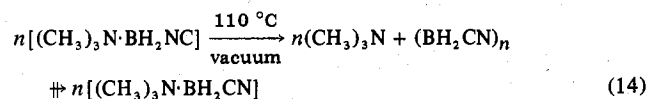


interaction should increase the boronium ion character, resulting in a high selectivity toward isocyanide coordination. Similar reactivity is not possible with  $\text{K}[\text{Ag}(\text{CN})_2]$ . The absence of a "push-pull mechanism" in this case, and its probable presence in the silver cyanide case, could explain the slow and fast reactions of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{I}$  with  $\text{K}[\text{Ag}(\text{CN})_2]$  and  $\text{AgCN}$ , respectively.

**Thermal Stability of Trimethylamine-Isocyanoborane.** Trimethylamine-isocyanoborane undergoes an easy thermal isomerization accompanied by decomposition upon warming



to 60 °C under vacuum, as shown by the sublimation and isolation of a mixture of both isomers of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2(\text{CN})$  and the formation of an uncharacterized yellow oil left as residue. These results are in close analogy with those noted for carbon isocyanides.<sup>37,38</sup> Proton NMR studies showed that isomerization and decomposition occurred upon heating solutions of molten trimethylamine–isocyanoborane. The characterization of the stoichiometrically expected amount of free trimethylamine and the identification of the residue as  $(\text{BH}_2\text{CN})_n$  prompt proposal of the following equation for the thermal degradation of molten  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}$ .



Further reaction of  $(\text{BH}_2\text{CN})_n$  with trimethylamine could result in the cleavage of the boron–nitrogen bond and the formation of trimethylamine–cyanoborane. Although possible, this is highly unlikely because of the inability of trimethylamine to cleave the same bond in reaction with trimethylamine–isocyanoborane at 40 °C.

**Structures of Trimethylamine–Cyanoboranes.** The assignment of a boron–nitrogen bond to the linkage of the cyanide to the trimethylamine–boryl moieties in the isomer of trimethylamine–cyanoborane prepared in this work rests on the chemical<sup>11,12,13</sup> and spectroscopic evidence gathered in the course of our study.

An initial chemical and simple indication of the structure of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}$  was the observation that the reaction of transition metal cyanides with alkyl iodides leads almost exclusively to the isocyanide derivative and the fact that similar reactions with silver cyanide give only the isocyanide species.<sup>20</sup> The presence of only a single cyanoborane in the product of the reaction of silver cyanide with trimethylamine–iodoborane suggests it to be an isocyanide species. This conclusion is supported by the structural assignment of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}\cdot\text{AgCN}$ , the species from which  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}$  was liberated under such mild conditions that the possibility of isomerization seems to be reasonably discountable.

A reinforcement of the identification of our isomer as trimethylamine–isocyanoborane is offered by the <sup>11</sup>B NMR spectrum of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}\cdot\text{BH}_3$ , prepared by us by direct reaction of diborane with trimethylamine–isocyanoborane.<sup>1,12,13</sup> The larger broadening of the triplet corresponding to the  $\text{BH}_2$  moiety results from nuclear quadrupolar interaction of the two nitrogens bonded to the same boron atom.<sup>14</sup> If the cyanide structure were the one present in the original cyanoborane species, a similar breadth should be expected for the triplet and the quartet present in the <sup>11</sup>B NMR spectrum of the diborane adduct.

Other spectroscopic evidence collected in this work also confirms the mentioned assignment of structure (Table IX). A comparison of the cyanide infrared frequencies of the two isomers of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2(\text{CN})$  with the well-known fact that such frequencies are observed for carbon isocyanides at about 100  $\text{cm}^{-1}$  lower than the same absorption for a carbon cyanide, it being also more intense than for the latter,<sup>20</sup> could indicate the presence of an isocyanide–boron bond in our material and a boron–cyanide linkage in the compound reported by Kelly et al.,<sup>10</sup> because of its cyanide frequency in the range of 2185–2280  $\text{cm}^{-1}$ .

The comparison of the <sup>11</sup>B NMR spectra of  $\text{BH}_3\text{CN}^-$  and  $\text{BH}_3\text{NC}^-$  with those of the two isomers of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2(\text{CN})$  provides further evidence of the structure of both isomers. It is observed that cyanoborohydride and the isomer reported in the literature and proposed by us to be  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{CN}$  both have a larger upfield shift and a smaller boron–hydrogen coupling constant than do  $\text{BH}_3\text{NC}^-$  and the isomer isolated

Table IX. Spectroscopic Data for the Corresponding Cyanide and Isocyanide Species of Trimethylamine–Cyanoborane and the Cyanoborohydride Anion

	$(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{CN}$ <i>a</i>	$(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}$ <i>c</i>	$\text{H}_3\text{B}^-$ $\text{BCN}^-$ <i>b</i>	$\text{H}_3\text{B}^-$ $\text{BNC}^-$ <i>b</i>
$\delta(^1\text{H})$ , ppm	2.70	2.25 <sup>d</sup>	+2.63	
$\delta(^{11}\text{B})$ , ppm	+32.1	+33.2	+25.8	+6.62 +45.5
$J(^{11}\text{B}-\text{H})$ , Hz	105	108	115	90 94
$\delta(^{13}\text{C})$ , <sup>e</sup> ppm			-119	
$\nu(\text{CN})$ , $\text{cm}^{-1}$	2280, 2195	2185– 2280	2135	
$\nu(\text{BH})$ , $\text{cm}^{-1}$	2420	2410		

<sup>a</sup> Data obtained in this work. <sup>b</sup> Data obtained by Wade et al.<sup>9</sup> <sup>c</sup> Data obtained by Kelly et al.<sup>10</sup> <sup>d</sup> Determined in benzene as a solvent. <sup>e</sup> <sup>13</sup>C shifts are reported with respect to methylene chloride as internal standard, and <sup>11</sup>B shifts with respect to trimethyl borate.

in this work and identified as  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}$ . Furthermore, the position of the resonance bands could also be used for structural assignment as done by two other groups.<sup>5,9</sup> The band further downfield has been usually assigned to the N–B–N moiety, usually in these compounds at 25–28 ppm, and the other at higher shifts than this to the B–CN moiety. This pattern is also followed by the two  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2(\text{CN})$  species and the linkage assigned before is confirmed further.

A direct and desirable confirmation of these structural assignments would be the x-ray determination of the crystal and molecular structure of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}$ , as recently reported for  $\text{H}_3\text{N}\cdot\text{BH}_2\text{NCS}$ .<sup>39</sup>

**Linkage Preference in the Boron Bond to the Cyanide Moiety in Amine–Boranes.** Any thermodynamic preference for a boron–carbon over a boron–nitrogen bond in amine–boranes is expected to result in the migration of the boron bonded to the cyanide moiety in  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}$ .

The easy isomerization of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}$  into  $(\text{C}-\text{H}_3)_3\text{N}\cdot\text{BH}_2\text{CN}$  is conclusive evidence of the thermodynamic preference for a boron–carbon bond. The seemingly faster reaction of  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{I}$  with  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}$  than with  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{CN}$  provides another indication of this, although the kinetic preference for a  $\text{NC} \rightarrow \text{B}$  over a  $\text{CN} \rightarrow \text{B}$  transition state, mentioned for the reaction of  $\text{CN}^-$  with  $\text{THF}\cdot\text{BH}_3$ , complicates the latter argument.

We have shown in this work that the boron–carbon bond is preferred over a boron–nitrogen bond in amine–boranes, although the inverse was expected based on reports that the coordination of two nitrogens to a boryl group represented the most stable situation in amine–boranes.<sup>9</sup> Our results indicate that the most stable case, in amine–cyanoborane compounds, at least, is N–B–C and not N–B–N.

**Registry No.**  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{CN}$ , 30353-61-8;  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}$ , 60045-36-5;  $[(\text{CH}_3)_3\text{NBH}_2]_2\text{CN}[\text{Ag}_2\text{I}_2]$ , 60165-99-3;  $[(\text{CH}_3)_3\text{NBH}_2]_2\text{CN}[\text{PF}_6]$ , 36510-02-8;  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}\cdot\text{AgCN}$ , 62906-24-5;  $[(\text{CH}_3)_3\text{NBH}_2]_2\text{CNI}$ , 62906-23-4;  $2[(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}]\cdot\text{AgI}$ , 62906-22-3;  $3[(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{NC}]\cdot 2\text{CuI}$ , 62906-20-1;  $(\text{BH}_2\text{CN})_2$ , 60633-76-3;  $[(\text{CH}_3)_3\text{NBH}_2]_2\text{CN}[\text{AgI}_2]$ , 62906-18-7;  $(\text{CH}_3)_3\text{N}\cdot\text{BH}_2\text{I}$ , 25741-81-5; KCN, 151-50-8; AgCN, 506-64-9; CuCN, 544-92-3; AgI, 7783-96-2;  $\text{K}[\text{Ag}(\text{CN})_2]$ , 506-61-6.

## References and Notes

- (1) This work is part of the Ph.D. Dissertation of José L. Vidal, University of Florida, 1974.
- (2) G. E. Ryschkewitsch and J. W. Wiggins, *Inorg. Synth.*, **12**, 116, 118 (1970).
- (3) G. E. Ryschkewitsch, "Progress in Coordination Chemistry", M. Caes, Ed., Elsevier, New York, N.Y., 1968; "Boron Cations, The Chemistry



- of Boron Hydrides", Marcel Dekker, New York, N.Y., 1973.
- (4) T. E. Sullivan, Ph.D. Dissertation, The University of Florida, Gainesville, 1970.
  - (5) V. D. Aftandilian, H. C. Miller, and E. L. Muettterties, *J. Am. Chem. Soc.*, **83**, 2471 (1961).
  - (6) T. Wizemann, H. Muller, D. Seybold, and K. Dehnicke, *J. Organomet. Chem.*, **20**, 211 (1969).
  - (7) D. Sowerby, *J. Am. Chem. Soc.*, **84**, 1831 (1962).
  - (8) P. J. Bratt, M. P. Brown, and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 2161 (1974).
  - (9) R. C. Wade, E. A. Sullivan, J. R. Bershied, and K. F. Purcell, *Inorg. Chem.*, **9**, 2146 (1970); K. F. Purcell and J. R. Bershied, *ibid.*, **9**, 624 (1970).
  - (10) (a) S. S. Uppal and H. C. Kelly, *Chem. Commun.*, 1619 (1970); (b) C. Weidig, S. S. Uppal, and H. C. Kelly, *Inorg. Chem.*, **13**, 1763 (1974).
  - (11) O. T. Beachley and B. Washburn, *Inorg. Chem.*, **14**, 120 (1975).
  - (12) Some other reactions of trimethylamine-isocyanoborane will be described in future publications.
  - (13) J. L. Vidal and G. E. Ryschkewitsch, *J. Chem. Soc., Chem. Commun.*, 192 (1976).
  - (14) D. L. Reznicek and N. E. Miller, *Inorg. Chem.*, **11**, 858 (1972).
  - (15) S. Herzog, J. Dehnert, and K. Lühder, *Tech. Inorg. Chem.*, **7**, 119 (1968).
  - (16) W. L. Jolly, "The Synthesis and Characterization of Inorganic Compounds", Prentice-Hall, Englewood Cliffs, N.J., 1970.
  - (17) K. C. Nainan and G. E. Ryschkewitsch, *Inorg. Chem.*, **7**, 1316 (1968); **8**, 2671 (1969).
  - (18) K. Friedrich and K. Wallenfels, "The Chemistry of the Cyano Group", Z. Rappoport, Ed., Interscience, New York, N.Y., 1970, Chapter 2.
  - (19) H. L. Jackson and R. C. McKusick, *Org. Synth.*, **9**, 438 (1929).
  - (20) L. Malatesta and F. Bonati, "Isocyanide Complexes of Metals", Wiley-Interscience, New York, N.Y., 1969.
  - (21) (a) H. J. Meyer, *Acta Crystallogr.*, **16**, 788 (1963); (b) C. Brink, N. F. Binnendijk, and J. Van De Linde, *ibid.*, **7**, 176 (1954).
  - (22) F. A. Cotton and F. Zingales, *J. Am. Chem. Soc.*, **83**, 351 (1961).
  - (23) (a) E. G. J. Hartley, *J. Chem. Soc.*, **109**, 1296 (1916); (b) *ibid.*, 780 (1928).
  - (24) L. H. Jones, *J. Chem. Phys.*, **26**, 1578 (1957).
  - (25) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley-Interscience, New York, N.Y., 1970, p 181.
  - (26) The molar conductivity of a  $7.61 \times 10^{-4}$  M methylene chloride solution of this complex is  $\Lambda = 0.21 \times 10^{-4} \Omega^{-1} \text{cm}^2 \text{equiv}^{-1}$ , while an  $[(\text{C}_4\text{Hg})_4\text{N}]\text{I}$   $6.26 \times 10^{-4}$  M solution has a  $\Lambda$  of  $4.34 \times 10^{-4} \Omega^{-1} \text{cm}^2 \text{equiv}^{-1}$ .
  - (27) S. Bresadola, G. Carraro, C. Pecile, and A. Turco, *Tetrahedron Lett.*, 3185 (1964).
  - (28) D. F. Schriver, *J. Am. Chem. Soc.*, **84**, 4610 (1962); **85**, 1405 (1963); **88**, 1672 (1966).
  - (29) A. Haim and W. K. Wilmarth, *J. Am. Chem. Soc.*, **83**, 509 (1961).
  - (30) R. A. Walton, *Q. Rev., Chem. Soc.*, 126 (1971).
  - (31) E. G. J. Hartley, *J. Chem. Soc.*, **109**, 1308 (1916); 780 (1928).
  - (32) K. A. Hofman and G. Bugge, *Chem. Ber.*, **40**, 1772 (1907).
  - (33) L. Malatesta, *Gazz. Chim. Ital.*, **77**, 340 (1951).
  - (34) A. Chwala, *Agnew. Chem.*, **20**, 1366 (1907).
  - (35) G. Camels, *C. R. Hebd. Seances Acad. Sci.*, **99**, 239 (1884).
  - (36) N. Kornblun, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *J. Am. Chem. Soc.*, **77**, 6269 (1955).
  - (37) F. W. Schneider and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **84**, 4215 (1962).
  - (38) J. Casanova, "Isonitrile Chemistry", I. Ugi, Ed., Academic Press, New York, N.Y., 1971, Chapter 6.
  - (39) D. S. Kendall and W. N. Lipscomb, *Inorg. Chem.*, **12**, 2920 (1973).

Contribution from the Departments of Chemistry, McMurry College, Abilene, Texas 79605, and the University of North Carolina, Chapel Hill, North Carolina 27514

## Low-Symmetry Copper(II) Complexes. Spectral Properties of Dihalo[2,6-di(2'-quinolyl)pyridine]copper(II) Complexes

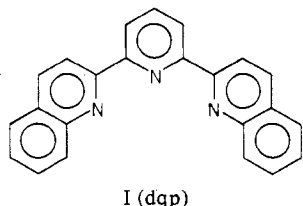
JOHN R. WASSON,<sup>1a</sup> DAVID M. KLASSEN,<sup>\*1b</sup> H. WAYNE RICHARDSON,<sup>1a</sup> and WILLIAM E. HATFIELD<sup>\*1a</sup>

Received July 26, 1976

AIC605363

The new compounds  $\text{Cu}(\text{dqp})\text{Cl}_2$  and  $\text{Cu}(\text{dqp})\text{Br}_2$  ( $\text{dqp} = 2,6\text{-di}(2'\text{-quinolyl})\text{pyridine}$ ) have been synthesized and characterized by electronic and EPR spectroscopy. A  $C_{2v}$  five-coordinate structure has been assigned to the complexes. The electronic spectra have been interpreted in terms of crystal field calculations. The complete  $g$  anisotropy is resolved for the pure compounds, the corresponding doped zinc complexes, and frozen solutions, but no nuclear hyperfine splitting was resolved. The EPR spectra of solutions of the complexes in dichloromethane and chlorobenzene are novel in that only one line is observed. An upper limit of about  $20 \times 10^{-4} \text{cm}^{-1}$  is estimated for the electron spin-nuclear spin hyperfine coupling constants.

The syntheses of 2,6-di(2'-quinolyl)pyridine, I (dqp), and



its high-spin iron(II) bis chelate have been described<sup>2</sup> as have the preparation and spectroscopic characterization of dqp complexes of ruthenium(II) and osmium(II).<sup>3</sup> The related ligand 2,2',2''-terpyridine forms a 1:1 complex<sup>4,5</sup> with copper(II) chloride which has five-coordinate distorted trigonal-bipyramidal geometry.<sup>5</sup> It was expected that dqp complexes with copper(II) chloride and bromide give rise to complexes with a related stereochemistry. In view of the current interest in the electronic structure of low-symmetry copper compounds,<sup>4-9</sup> it was important to investigate the spectral (EPR and electronic) properties of the compounds  $\text{Cu}(\text{dqp})\text{Cl}_2$  and  $\text{Cu}(\text{dqp})\text{Br}_2$ .

It was anticipated that  $\text{Cu}(\text{dqp})\text{X}_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ) complexes would adopt a geometry closely related to the pseudotetra-

hedral ( $C_{2v}$ ) geometry found for  $\text{Cu}(\text{o-phen})\text{Cl}_2$ .<sup>10</sup> If this is obtained, small values of the copper-63 and -65 electron spin-nuclear spin hyperfine coupling constants in the electron paramagnetic resonance (EPR) spectra would be expected and the dqp compounds would then be somewhat analogous to the "blue" copper proteins. Pseudotetrahedral copper(II) complexes have been suggested as possible models for the "blue" copper proteins. Five-coordinate geometries have also been proposed<sup>11-13</sup> for copper in the "blue" proteins, and studies on a variety of such low-symmetry complexes have been undertaken.

### Experimental Section

2,6-Di(2'-quinolyl)pyridine (dqp) was prepared as described by Harris, Patil, and Sinn.<sup>2</sup> Recrystallization from benzene yielded dqp in 60% yield; mp 227–228 °C. All other chemicals were of the best reagent or spectroscopic grades. Carbon, hydrogen, and nitrogen analyses were performed by Chemalytics, Inc., Tempe, Ariz. Copper was determined by EDTA titrations.<sup>14</sup>

The copper complexes were prepared by the method described previously for the related biquinoline compounds.<sup>15</sup> Yields of 91–94% were obtained. Anal. Calcd for  $\text{Cu}(\text{dqp})\text{Cl}_2$ : C, 59.05; H, 3.23; N, 8.98; Cu, 13.58. Found: C, 59.67; H, 3.37; N, 8.12; Cu, 13.39. Calcd for  $\text{Cu}(\text{dqp})\text{Br}_2$ : C, 49.62; H, 2.72; N, 7.55; Cu, 11.41. Found: C, 50.07; H, 2.69; N, 7.54; Cu, 11.47. Copper-doped zinc complexes