

1134 (w,  $\rho_{\text{CH}_3}$  and/or  $\delta_{\text{BH}_3}$ ), 1068 (m,  $\nu_{\text{C-N}}$  and/or  $\delta_{\text{BH}_3}$ ), 998–973 (s,  $\nu_{\text{as}}$ ,  $(\text{CH}_3)_2\text{N-P}$ ), 821 (s,  $\nu_{\text{s}}$ ,  $\text{P-F}$ ), 775 (ms,  $\rho_{\text{BH}_3}$  or  $\nu_{\text{P-F}}$ ), 750 (s), 706 (mw,  $\nu_{\text{N}_2\text{-P-F}}$ ), 685 (w,  $\nu_{\text{N}_2\text{-P-F}}$ ), 574 (w,  $\nu_{\text{P-B}}$ ). The nmr spectra give the following constants:  $^1\text{H}$  (neat),  $\delta$  2.63 ppm relative to TMS (d,  $J_{\text{HF}} = 9$  Hz,  $\text{N}(\text{CH}_3)_2$ ); member of a doublet is a doublet ( $J_{\text{HB}} = 3$  Hz);  $\delta$  0.33 ppm (q,  $J_{\text{HB}} = 100$  Hz,  $\text{H}_3\text{B}$ );  $^{19}\text{F}$  (neat),  $\delta$  12.88 ppm relative to TFA (d,  $J_{\text{F-P}} = 1070$  Hz,  $\text{FP}(\text{NR}_2)_2$ );  $^{31}\text{P}$  (neat),  $\delta$  -133 ppm relative to 85%  $\text{H}_3\text{PO}_4$  (d,  $J_{\text{P-F}} = 1075$  Hz,  $\text{PF}(\text{NR}_2)_2$ ); each member of a doublet is a quartet ( $J_{\text{PB}} = 80$  Hz);  $^{11}\text{B}$  (neat),  $\delta$  60.5 ppm relative to  $\text{B}(\text{OCH}_3)_3$  (quintet, 1:4:6:4:1,  $J_{\text{BH}} = 98$  Hz,  $J_{\text{BP}} = 86$  Hz,  $\text{H}_3\text{BP}$ ).

**The Reaction of  $\text{FP}[\text{N}(\text{CH}_3)_2]_2$  with  $\text{BF}_3$ .**—In a typical reaction  $\text{BF}_3$  (5.54 mmol) was condensed with  $\text{FP}[\text{N}(\text{CH}_3)_2]_2$  (1.74 mmol). The tube, open to a blowout manometer, was allowed to warm slowly to room temperature. After three such cycles, the volatile products were distilled from the reaction vessel at  $-23^\circ$  through a trap at  $-95^\circ$  into a trap at  $-196^\circ$ . The reaction vessel was gradually warmed from  $-23$  to  $0^\circ$ ; then the distillation was terminated. Boron trifluoride (2.44 mmol) was trapped at  $-196^\circ$  while  $\text{F}_3\text{BF}_2\text{PN}(\text{CH}_3)_2$  (1.34 mmol) was retained in the trap at  $-95^\circ$ . The ratio of  $\text{BF}_3$  to  $\text{FP}[\text{N}(\text{CH}_3)_2]_2$  was 1.78:1.00. Since the amount of  $\text{F}_3\text{BF}_2\text{PN}(\text{CH}_3)_2$  was low by 0.4 mmol, one can assume the presence of up to 0.4 mmol of  $\text{PF}_3$  in the  $\text{BF}_3$ . Such an assumption could alter the stoichiometry to give a ratio of  $\text{BF}_3$  to  $\text{FP}[\text{N}(\text{CH}_3)_2]_2$  of 2.00:1.00.

**Preparation of  $(\text{H}_3\text{C})_3\text{BFP}[\text{N}(\text{CH}_3)_2]_2$ .**—Trimethylborane (2.02 mmol) was condensed with  $\text{FP}[\text{N}(\text{CH}_3)_2]_2$  (0.87 mmol) in a reaction vessel open to a blowout manometer. The vessel was warmed stepwise from  $-196$  to  $-78^\circ$  using appropriate constant-temperature baths. After 5 hr at  $-78^\circ$  the reaction tube was first cooled to  $-196^\circ$  and then warmed to  $-126^\circ$ . Excess  $(\text{H}_3\text{C})_3\text{B}$  (1.96 mmol) was removed by distillation from the reaction vessel at  $-126^\circ$  to a trap held at  $-196^\circ$ . The ratio of  $(\text{H}_3\text{C})_3\text{B}$  consumed to  $\text{FP}[\text{N}(\text{CH}_3)_2]_2$  used was 0.99:1.00. The addition compound, retained in the reaction vessel, was a white crystalline solid melting to a colorless liquid near room temperature. It exhibited a dissociation pressure of about 9 mm at  $25^\circ$ . An infrared spectrum of the vapor showed only the absorption peaks for free  $(\text{CH}_3)_3\text{B}$  and free  $[(\text{CH}_3)_2\text{N}]_2\text{PF}$ .

Attempts to purify the new adduct by distillation *in vacuo* from the reaction vessel held at room temperature resulted in an irreversible dissociation of the addition compound into its components. Only by cooling to  $-196^\circ$  and repetition of the stepwise warming process could the adduct be re-formed. Once formed, the new compound,  $[(\text{CH}_3)_2\text{N}]_2\text{PF}(\text{CH}_3)_3$ , seemed fairly stable at room temperature as long as no distillation was attempted.

The irreversible decomposition occurring upon distillation prevented obtaining any significant infrared data using the low-temperature cell. The nmr spectra can be summarized as follows:  $^1\text{H}$  (neat),  $\delta$  2.67 ppm (d,  $J_{\text{H-P}} = 7$  Hz,  $(\text{H}_3\text{C})_2\text{NP}$ ); each member of the doublet was also a doublet ( $J_{\text{H-F}} = 3$  Hz,  $(\text{H}_3\text{C})_2\text{NPF}$ );  $\delta$  -0.18 ppm (s,  $\text{H}_3\text{C})_3\text{B}$ );  $^{19}\text{F}$  (neat),  $\delta$  30.2 ppm relative to TFA (d,  $J_{\text{PF}} = 1133$  Hz,  $\text{FP}(\text{NR}_2)_2$ ); each member of a doublet is a septet (1:2:2:3:6:4:0:3:6:2:2:1,  $J_{\text{FP}[\text{N}(\text{CH}_3)_2]_2} = 2$ -3 Hz);  $^{11}\text{B}$  (neat),  $\delta$  24.3 ppm relative to  $\text{B}(\text{OCH}_3)_3$ .

**Preparation of  $\text{H}_7\text{B}_3\text{F}_2\text{PN}(\text{CH}_3)_3$ .**—A 4.97-mmol sample of  $\text{B}_4\text{H}_{10}$  was frozen into a reaction tube with  $(\text{CH}_3)_2\text{NPF}_2$  (9.35 mmol). The reactants were alternately warmed to room temperature and chilled with liquid nitrogen over a period of 0.5 hr while the reactants were being stirred with a magnetic jump stirrer. The reaction system was then held at  $25^\circ$  for 1 hr and finally fractionated ( $0^\circ$  for reaction vessel,  $-45$ ,  $-78$ ,  $-196^\circ$ ) while stirring was continued. The compound  $(\text{CH}_3)_2\text{NPF}_2\text{BH}_3$  was retained at  $-78^\circ$  while the product in the reaction vessel was identified as  $(\text{CH}_3)_2\text{NPF}_2\text{B}_3\text{H}_7$ . It has a vapor pressure of about 1 mm at  $26^\circ$ . *Anal.* Calcd for  $(\text{CH}_3)_2\text{NPF}_2\text{B}_3\text{H}_7$ : C, 15.74; H, 8.59; N, 9.18. Found: C, 16.04, 16.11; H, 8.67, 8.74; N, 8.92. The infrared spectrum is compared to that of  $(\text{CH}_3)_2\text{NPF}_2\text{B}_4\text{H}_8$  in Table I. The similarity between the two is striking and confirms the B-P bond.

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## Transition Metal Hydroborate Complexes. IV.<sup>1</sup> Cyanotrihydroborate Complexes of the Group Ib Metals

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The synthesis of several copper(I) and silver(I) compounds containing tertiary group V donor ligands and a coordinated cyanotrihydroborate or cyanotriphenylborate anion is reported. Complexes of general formula  $\text{L}_3\text{M}(\text{NCBR}_3)$  are shown by physical measurements to contain metal-nitrogen bonds, both in the solid state and in chlorinated hydrocarbon solvents. In acetonitrile solution  $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{Cu}(\text{NCBH}_3)$  is a weak electrolyte, as determined from conductivity studies. The relative extent of dissociation of hydroborate and chloride ligands from triphenylphosphine-coordinated copper(I) ions in acetonitrile is found to be  $\text{B}_3\text{H}_8^- \sim \text{H}_3\text{BCN}^- > \text{BH}_4^- \sim \text{Cl}^-$ . The cyanotrihydroboratotrakis(triphenylphosphine)silver(I) compound is more highly ionized. From its infrared spectrum, the complex of empirical formula  $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Cu}(\text{NCBH}_3)$  is concluded to be a dimer, with bridging cyanotrihydroborate ligands coordinated to form both Cu-NCBH<sub>3</sub> and Cu-HBH<sub>2</sub>CN type linkages.

### Introduction

As discussed previously,<sup>2</sup> the chemical reactivity of small, reducing hydroborate anions toward copper(I) complexes depends upon the stereochemical environment of the copper atom and the choice of hydroborate ligand. Thus sodium borohydride will decompose a

solution containing a 3:1 triphenylarsine:copper(I) ratio, but borohydride-tris(triphenylphosphine)-copper(I) solutions are stable,<sup>2,3</sup> and cesium octahydrotriborate forms the crystalline complex  $[(\text{C}_6\text{H}_5)_3\text{As}]_2\text{Cu}(\text{B}_3\text{H}_8)$ .<sup>2</sup> The preparation and characterization of coinage metal derivatives of the larger borane anions have also been reported.<sup>4,5</sup>

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TABLE I  
 ANALYTICAL RESULTS FOR CYANOTRIHYDROBORATE COMPLEXES OF COPPER(I) AND SILVER(I)

Complex	% C		% H		% N		% Cl		Mp, °C
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
$[(C_6H_5)_3P]_3Cu(NCBH_3)$	74.20	74.95	5.43	5.56	1.57	1.15	...	...	157-158
$[(C_6H_5)_3P]_3Cu(NCBH_3) \cdot CHCl_3$	66.62	66.59	4.89	5.12	1.39	1.28	10.54	10.04 <sup>a</sup>	<i>b</i>
$[(C_6H_5)_3As]_3Cu(NCBH_3) \cdot CHCl_3$	58.92	58.42	4.33	4.38	1.23	1.24	9.32	9.17	126-127
$[(C_6H_5)_3Sb]_3Cu(NCBH_3) \cdot CHCl_3$	52.47	52.67	3.85	3.84	1.09	0.99	8.32	10.85	118-119
$[(C_6H_5)_3P]_3Cu(NCBH_3)$	70.77	70.71	5.29	5.23	2.23	2.17	...	...	179-180
$[(C_6H_5)_3P]_3Ag(NCBH_3) \cdot CHCl_3$	63.82	63.05	4.69	4.57	1.33	1.27	10.09	9.92	202-205 (dec)
$\{[(p-CH_3C_6H_4)_3P]_4Ag\}(NCBH_3)$	74.78	74.13	6.42	6.27	1.03	<i>b</i>	...	...	184-185
$[(C_6H_5)_3P]_3Cu[NCB(C_6H_5)_3] \cdot CHCl_3$	71.80	72.59	4.97	4.92	1.13	<i>b</i>	8.59	8.22	230-245

<sup>a</sup> By difference. Calcd: B, 1.07; P, 9.20; Cu, 6.29. Found: B, 1.62; P, 9.27; Cu, 6.08. <sup>b</sup> Not determined.

In an extension of these studies, the synthetic and structural chemistry of the cyanotrihydroborate anion,  $H_3BCN^-$ , with group Ib metal complexes has been investigated. This ion was first isolated as the lithium salt by Wittig<sup>6</sup> and has been shown to be a versatile organic reducing agent.<sup>7</sup> Recently, Purcell and coworkers have described the spectroscopic and certain chemical properties of the cyanotrihydroborate anion,<sup>8</sup> developed a new and convenient synthetic procedure for  $NaH_3BCN$ ,<sup>9,10</sup> and suggested the potential of the ion as a ligand in transition metal chemistry.<sup>8</sup> Preliminary studies in our laboratory had confirmed this suggestion and demonstrated that the cyanotrihydroborate ion coordinates to transition metals through the nitrogen atom.<sup>11</sup> A cationic, N-bonded cyanotrihydroborate-ruthenium-ammine complex was subsequently reported.<sup>12</sup> The isocyanotrihydroborate ligand is also known to exist in the compound (*o*-phen)<sub>2</sub>Fe(CNBH<sub>3</sub>)<sub>2</sub>, prepared from the corresponding iron(II) cyanide complex and diborane.<sup>13</sup>

In the present paper, the preparation of several N-bonded copper(I) and silver(I) cyanotrihydroborate complexes containing tertiary group V donor ligands is described. As will be shown, the ability of the  $H_3BCN^-$  ligand to coordinate through the hydrogen end of the molecule to form multicenter B-H-Cu bonds has been conclusively demonstrated. A preliminary study of the closely related  $(C_6H_5)_3BCN^-$  ion as a ligand is also reported.

### Experimental Section

All compounds were prepared from the highest purity chemicals available. Sodium cyanotrihydroborate was obtained from Alfa Inorganics and sodium cyanotriphenylborate from K & K Laboratories, Inc. Tris(triphenylphosphine)copper(I) chloride was prepared according to ref 2. Microchemical analyses were performed by Galbraith Laboratories, Knoxville, Tenn. The results are presented in Table I. Melting points were determined using a Nalge Co. hot-stage microscope and are uncorrected. The molecular weight determination was carried out at 37° in chloroform using a Mechrolab vapor pressure osmometer calibrated with benzil. Infrared spectra were obtained with a Perkin-Elmer 621 grating instrument in the range 4000-600  $cm^{-1}$ . Samples were either milled in Nujol and spread between NaCl plates or dissolved in chloroform. Polystyrene was used as the

calibrant, and the resulting frequencies are estimated to be accurate to  $\pm 2 \text{ cm}^{-1}$ . Electrolytic conductance measurements were carried out over a concentration range using an Industrial Instruments conductivity bridge with a 30-cm<sup>3</sup> cell equipped with 1-cm<sup>2</sup> platinum electrodes at  $25 \pm 2^\circ$ . Spectrograde acetonitrile, distilled over calcium hydride, was used as the solvent.

**Cyanotrihydroboratotris(triphenylphosphine)copper(I)**,  $[(C_6H_5)_3P]_3Cu(NCBH_3)$ .—Sodium cyanotrihydroborate (0.100 g, 1.59 mmol) was dissolved in 30 ml of ethanol and the solution was filtered. This solution was added to 1.17 g (1.32 mmol) of chlorotris(triphenylphosphine)copper(I) in 20 ml of chloroform. Colorless crystals developed from the reaction mixture and were filtered out. If crystallization was slow, further addition of ethanol speeded the process. The yield was 1.06 g (90%) of colorless crystals. The osmometric molecular weight indicates dissociation: calcd for  $C_{55}H_{48}NP_3Cu$ , 890; found, 645 and 628, at concentrations of 0.0355 and 0.0105 *M*, respectively. Further recrystallization from chloroform-ethanol resulted in a chloroform molecule of crystallization as shown by analysis.

**Cyanotrihydroboratotris(triphenylarsine)copper(I)**—Chloroform,  $[(C_6H_5)_3As]_3Cu(NCBH_3) \cdot CHCl_3$ .—Triphenylarsine (1.23 g, 4.1 mmol) was dissolved in 50 ml of chloroform. Copper(I) chloride (0.100 g, 1 mmol) was added and the mixture was stirred for 1 hr. The reaction mixture was then filtered and a slight excess of sodium cyanotrihydroborate in ethanol was added. Further ethanol was added and the reaction was allowed to stand until clear crystals formed.

**Cyanotrihydroboratotris(triphenylstibine)copper(I)**—Chloroform,  $[(C_6H_5)_3Sb]_3Cu(NCBH_3) \cdot CHCl_3$ .—Triphenylstibine (1.41 g, 3.99 mmol) was dissolved in 50 ml of chloroform and copper(I) chloride (0.104 g, 1 mmol) was added. The reaction mixture was stirred for 1 hr, and filtered. A slight excess of sodium cyanotrihydroborate was dissolved in ethanol and filtered. The filtrate was added to the chloroform solution. The reaction was allowed to stand for 12 hr after which the white crystalline product was filtered out. A second crop of crystals was obtained by addition of 150 ml of ethanol. The total yield was 36%, based on copper.

**Cyanotrihydroboratobis(triphenylphosphine)copper(I)**,  $[(C_6H_5)_3P]_2Cu(NCBH_3)$ .—“Chlorobis(triphenylphosphine)copper(I)”<sup>14</sup> (1.186 g, 1.89 mmol) was dissolved in 20 ml of chloroform, and sodium cyanotrihydroborate (0.115 g, 1.83 mmol) in 15 ml of ethanol was added. A white precipitate formed immediately. The reaction mixture was allowed to stand for 24 hr. Then it was filtered to obtain 0.941 g of white solid. Some of this white solid was dissolved in hot chloroform, and ethanol was added to the filtered solution. Colorless crystals developed on standing.

**Cyanotrihydroboratotris(triphenylphosphine)silver(I)**—Chloroform,  $[(C_6H_5)_3P]_3Ag(NCBH_3) \cdot CHCl_3$ .—Chlorotris(triphenylphosphine)silver(I) was made by stirring 1.43 g (10 mmol) of silver chloride with 9.49 g (36.2 mmol) of triphenylphosphine in chloroform. This solution was filtered and to it was added a filtered ethanol solution containing a slight excess of sodium cyanotrihydroborate. The reaction was allowed to stand for 24 hr and then the large crystals of product were separated by filtration.

**Tetrakis(tri-*p*-tolylphosphine)silver(I) Cyanotrihydroborate**,  $\{[(p-CH_3C_6H_4)_3P]_4Ag\}(NCBH_3)$ .—Silver chloride (0.243 g, 1.70 mmol) and tri-*p*-tolylphosphine (1.97 g, 6.48 mmol) were stirred together in 50 ml of chloroform for 3 hr and then filtered to give a clear filtrate. Sodium cyanotrihydroborate (0.150 g, 2.38 mmol) was dissolved in 100 ml of ethanol, filtered, and added to the chloroform solution. A cloudy solution resulted. Further

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(14) We thank Dr. Walter T. Reichle, Union Carbide Corp., for a sample of the compound having this composition.

TABLE II  
SUMMARY OF SELECTED INFRARED SPECTRAL BANDS FOR  
CYANOTRIHYDROBORATE AND CYANOTRIPHENYLBORATE COMPOUNDS<sup>a, b</sup>

$(R_3P)_3Cu(NCBH_3)$		$(R_3As)_3Cu(NCBH_3)$		$(R_3Sb)_3Cu(NCBH_3)$	$(R_3P)_3Ag(NCBH_3)$		$NaH_3BCN$	Assignment <sup>c</sup>
Solid	Solution	Solid	Solution	Solid	Solid	Solution	Solid	
2358 sh	2355 sh	2360 sh <sup>d</sup>	2360 sh	2360 sh <sup>d</sup>	2350 sh	2350 br	2350 sh	$\nu_5(^{10}B)$ , $\nu^e_{BH}$
2330 s <sup>d</sup>	2332 s <sup>d</sup>	2325 s <sup>d</sup>	2335 s <sup>d</sup>	2331 s <sup>d</sup>	2321 s <sup>d</sup>	2330 s <sup>d</sup>	2325 s <sup>d</sup>	$\nu_5(^{11}B)$ , $\nu^e_{BH}$
2280 m <sup>d</sup>	2290 sh	2280 m <sup>d</sup>	2280 w <sup>d</sup>	2285 m <sup>d</sup>	2280 m	2250 w <sup>d</sup>	2282 m	c
2228 sh	...	2222 sh	...	2222 sh	2220 sh	...	2230 sh	$\nu_1(^{10}B)$ , $\nu^{a1}_{BH}$
2212 w	2210 sh	2202 w	2212 m	2208 w	2207 w	2210 sh	2220 m	$\nu_1(^{11}B)$ , $\nu^{a1}_{BH}$
2192 s <sup>e</sup>	2191 s	2187 s	2188 s	2191 s	2180 s	2180 m	2179 s	$\nu_2$ , $\nu^{a1}_{CN}$
1125 sh	...	1123 sh	1125 sh	1127 sh	1126 sh	1122 sh	1145 sh	$\nu_3(^{10}B)$ , $\delta^{a1}_{BH}$
1115 s	1112 s	1113 s	1115 s	1115 s	1113 s	1115 m	1130 s	$\nu_3(^{11}B)$ , $\delta^{a1}_{BH}$

$(R_3P)_2Cu(NCBH_3)$		$(R_3P)_2Cu(NCBr_3)$	$NaR_3BCN$
Solid		Solid	Solid
2409 sh	2207 s	2206 s ( $\nu_{CN}$ )	2168 s <sup>f</sup> ( $\nu_{CN}$ )
2388 sh	2200 br	2200 sh <sup>g</sup>	
2376 s	2190 s		
2350 m	1100 vs <sup>h</sup>		

<sup>a</sup> Solid samples were milled in Nujol; solution spectra were run in chloroform. <sup>b</sup> Abbreviations: R, C<sub>6</sub>H<sub>5</sub>; s, strong; m, medium; w, weak; br, broad; v, very; sh, shoulder; ... means no band observed. <sup>c</sup> Taken from ref 8. More recent work by these authors (K. F. Purcell, private communication) assigns the  $\nu_1$  absorptions to frequencies of 2285 and 2290 cm<sup>-1</sup>, after a -20-cm<sup>-1</sup> correction for Fermi resonance. The ca. 2280-cm<sup>-1</sup> band therefore probably corresponds to the B-H stretching mode of a<sub>1</sub> symmetry, and the bands at ca. 2220 cm<sup>-1</sup> to  $\nu_3$ . <sup>d</sup> Broad or very broad absorption. <sup>e</sup> This band has a shoulder ~2188 cm<sup>-1</sup> in the solid mull spectrum but not in solution. <sup>f</sup> Occasionally two bands appeared in the infrared spectrum of Nujol mulls of this compound, the second occurring at 2182 cm<sup>-1</sup>. <sup>g</sup> Compare footnote e. <sup>h</sup> Since the triphenylphosphine absorption at this frequency has been greatly intensified, the BH<sub>2</sub> deformation mode is assumed to be hidden under the R<sub>3</sub>P band.

addition of ethanol gave a clear solution. Evaporation of this clear solution gave a white solid. Recrystallization from acetone-water or acetonitrile-water gave colorless crystals.

**Cyanotriphenylboratotrakis(triphenylphosphine)copper(I)-Chloroform**, [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>3</sub>Cu[NCB(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]·CHCl<sub>3</sub>.—Chlorotris(triphenylphosphine)copper(I) (0.802 g, 0.907 mmol) was dissolved in 10 ml of CHCl<sub>3</sub>. To this solution was added a solution of 0.257 g (0.882 mmol) of sodium cyanotriphenylborate in 10 ml of ethanol. A white precipitate formed immediately, which was washed with ethanol and weighed. The yield after drying was 1.06 g or 107% assuming no chloroform of crystallization. This material was then heated under vacuum to 70° for several hours and was analyzed. The analysis indicated approximately one chloroform molecule of crystallization (Table I). Analytical results for the initial precipitate showed several molecules of lattice chloroform. This material was observed to lose weight upon heating *in vacuo* to yield the monochloroform adduct.

## Results and Discussion

**Synthesis and Solid-State Structure of L<sub>3</sub>M(NCBr<sub>3</sub>) Complexes.**—The preparation of L<sub>3</sub>M(NCBr<sub>3</sub>) complexes, where L = (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P (M = Cu, R = H, C<sub>6</sub>H<sub>5</sub>; M = Ag, R = H), L = (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>As (M = Cu, R = H), and L = (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Sb (M = Cu, R = H), was carried out in a manner analogous to that employed previously for the tetrahydroborate derivatives.<sup>2,3</sup> The presence of chloroform molecules of crystallization, a common occurrence when tris(triarylphosphine)metal(I) compounds are precipitated from chlorinated hydrocarbon solvent mixtures,<sup>15</sup> was directly confirmed by analysis (Table I). As in the tetrahydroborate system,<sup>16</sup> solutions of the cyanotrihydroborate silver complex tend to be less stable than the copper analogs and slowly deposit a silver mirror during attempts to recrystallize the compound from chloroform-ethanol mixtures. In order to improve the solubility of the silver cyanotrihydroborate complex for low-temperature <sup>31</sup>P nmr studies, an effort was made to synthesize L<sub>3</sub>Ag(NCBH<sub>3</sub>) for L = tri-*p*-tolylphosphine. The tetrakis(tri-*p*-

tolylphosphine)silver(I) cyanotrihydroborate salt (Table I) was isolated, however.

The stoichiometries of the solid products, L<sub>3</sub>M(NCBH<sub>3</sub>), may be compared with the composition of the L<sub>2</sub>MX compounds (X = *bidentate* BH<sub>4</sub>, B<sub>3</sub>H<sub>3</sub>) isolated from chloroform solutions containing L:M ratios of 3:1 or greater.<sup>1-3</sup> This result alone suggests bonding of the NCBH<sub>3</sub><sup>-</sup> anion to the metal through the nitrogen atom. To substantiate this suggestion, the compound [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>3</sub>Cu[NCB(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>] was synthesized. Here the cyanotriphenylborate ligand can only coordinate to the copper atom in a monodentate fashion using the nitrogen atom. Further chemical and structural studies of transition metal complexes of this ligand are in progress.

Additional evidence for metal-nitrogen bonding in the solid L<sub>3</sub>M(NCBr<sub>3</sub>) complexes is provided by their infrared spectra, selected features of which are summarized in Table II. Considering first the cyanotriphenylborate compound, the C-N stretching frequency is seen to be 38 cm<sup>-1</sup> (or 24 cm<sup>-1</sup>, see Table II, footnote f) higher in energy for the complex than for the sodium salt of the ligand. Such frequency shifts are common for coordinated nitrile ligands<sup>17</sup> and have been attributed to increased C-N  $\sigma$  bonding upon complexation.<sup>18,19</sup> In the cyanotrihydroborate complexes, similar frequency shifts are observed for the C-N stretching modes. Although these are considerably smaller (1-13 cm<sup>-1</sup>) than for the cyanotriphenylborate derivative, weaker binding of the NCBH<sub>3</sub><sup>-</sup> anion to the metal atom is not necessarily to be inferred, since the normal mode referred to as a C-N stretching frequency may differ significantly in character for the two ligands. Comparison of the frequency shifts for the copper and silver cyanotrihydroborate compounds (Table II) is more valid, however, and suggests<sup>18</sup> weaker coordina-

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tion of the anion for the silver complex. This behavior parallels the results of solution conductivity studies (*vide infra*) and is consistent with results for coinage metal derivatives of the larger borane anions.<sup>4</sup>

In  $\text{LiH}_3\text{BCN} \cdot \text{diox}$ , the C-N stretching band occurs at  $2198 \text{ cm}^{-1}$ , which has been attributed to a Li-N interaction.<sup>8</sup> An increased C-N stretching frequency (to  $2206 \text{ cm}^{-1}$ ) has also been reported for the  $[\text{Ru}(\text{NH}_3)_5(\text{NCBH}_3)]^{2+}$  cation, in which ruthenium-nitrogen bonding occurs.<sup>12</sup> In the ruthenium(II) cation  $[\text{Ru}(\text{NH}_3)_5(\text{NCBH}_3)]^+$ , however, the C-N band is at  $2170 \text{ cm}^{-1}$ , demonstrating the ability of the cyanotrihydroborate ligand to accept  $\pi$ -electron density when coordinated to a strong  $\pi$ -donor metal atom.<sup>12</sup> Since the N-C stretching frequency in sodium isocyanotrihydroborate is  $2070 \text{ cm}^{-1}$ ,<sup>9</sup> it seems unlikely that the ligand has isomerized in the  $\text{L}_3\text{M}(\text{NCBH}_3)$  compounds. The possibility of isomerization cannot be completely eliminated, however, since in  $(o\text{-phen})_2\text{Fe}(\text{CNBH}_3)_2$ , the C-N absorptions occur at  $2165$  and  $2154 \text{ cm}^{-1}$ .<sup>13</sup>

The B-H stretching and  $\text{BH}_2$  deformation frequencies in the free and coordinated cyanotrihydroborate ligand are very similar (Table II). It therefore appears that the  $\text{C}_{3v}$  symmetry of the anion is closely approximated in the  $\text{L}_3\text{M}(\text{NCBH}_3)$  complexes. More important, coordination of the ligand to the metal through multicenter B-H-M bonding may be ruled out. Presumably because of the interference from the  $(\text{C}_6\text{H}_5)_3\text{Y}$  ligands, infrared bands assigned to  $\nu_6$ ,  $\delta^{\text{BH}}$  ( $1195 \text{ cm}^{-1}$  (m)),  $\nu_7$ ,  $\rho^{\text{BH}}$  ( $890 \text{ cm}^{-1}$  (w)), and  $\nu_4$ ,  $\nu^{\text{a1}}_{\text{BC}}$  ( $865 \text{ cm}^{-1}$  (w)) in the free ligand<sup>8</sup> could not be identified in the complexes.

The infrared spectrum of a Nujol mull of the tetrakis(tri-*p*-tolylphosphine)silver(I) cyanotrihydroborate salt resembled those of the  $\text{L}_3\text{Cu}(\text{NCBH}_3)$  compounds in all respects, except that the C-N stretching frequency region had a broad band with some structure extending from  $2155$  to  $2175 \text{ cm}^{-1}$ . At present we have no interpretation of this result. As discussed below, the  $[(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}]_4\text{Ag}^+$  cation has been positively identified in solutions of this compound.

**Solution Studies of  $\text{L}_3\text{M}(\text{NCBH}_3)$  and  $[\text{L}_4\text{Ag}](\text{NCBH}_3)$  Compounds.**—The behavior of coinage metal phosphine and related complexes in solution has been a subject of recent interest. Using  $^{31}\text{P}$  nmr spectroscopy at low temperatures ( $-100^\circ < T < -50^\circ$ ), the structures of a number of copper(I), silver(I), and gold(I) compounds in methylene chloride-toluene solvent mixtures have been established.<sup>20</sup> Vapor pressure osmometric studies of a large number of  $\text{L}_n(\text{CuX})_m$  compounds, moreover, have produced considerable information concerning the equilibria that exist at  $37^\circ$  in chloroform solutions of these compounds.<sup>21</sup> In the present instance, the concern has been to determine whether the cyanotrihydroborate anion is a sufficiently good donor ligand to remain coordinated in solutions prepared using both weakly coordinating ( $\text{CH}_3\text{-CN}$ ) and noncoordinating ( $\text{CHCl}_3$ ) solvents.

From the close resemblance (Table II) between the infrared spectral results for the solid state mulls and chloroform solutions of the  $\text{L}_3\text{M}(\text{NCBH}_3)$  complexes, especially the C-N stretching frequency, the cyano-

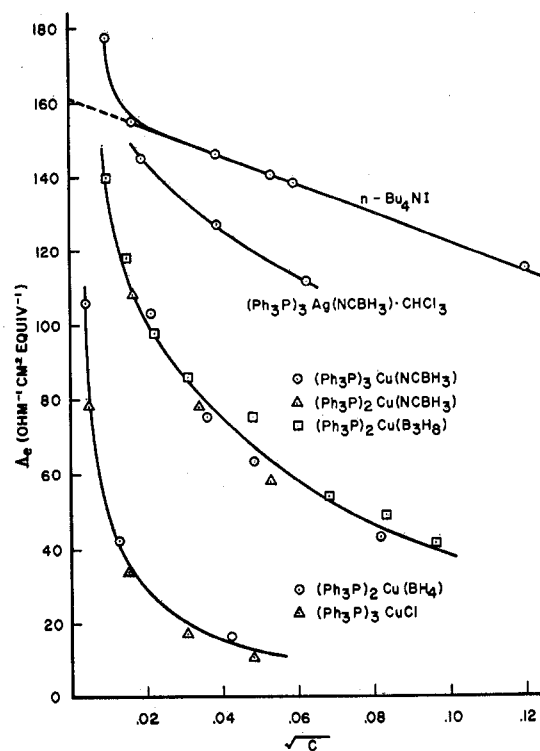


Figure 1.—Plots of equivalent conductance ( $\Lambda_e$ ) against the square root of concentration for cyanotrihydroborate and related complexes in acetonitrile solution.

trihydroborate ligand is seen to be essentially completely coordinated in the chlorinated hydrocarbon solvent. No evidence of splitting of the C-N band was observed in any of the spectra. Dissociation of the anion therefore does not appear to be responsible for the low molecular weight results obtained by vapor pressure osmometry for  $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{Cu}(\text{NCBH}_3)$  in chloroform. Instead, dissociation of the triphenylphosphine ligand is assumed to occur, as observed for chloroform solutions of chlorotris(triphenylphosphine)-copper(I).<sup>21</sup>

Evidence for the coordination of the cyanotrihydroborate ligand in  $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{Ag}(\text{NCBH}_3)$ , dissolved in a mixture of dichloromethane and toluene, was obtained by  $^{31}\text{P}$  nmr spectroscopy.<sup>22</sup> Working in the temperature interval  $-85$  to  $-95^\circ$  where ligand exchange is slow, the average  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$  splitting of the  $^{31}\text{P}$  resonance came out to be  $283 \text{ Hz}$ , which agrees quite well with values obtained for other pseudotetrahedral  $\text{L}_3\text{AgX}$  aggregates.<sup>4,23</sup> The  $^{31}\text{P}$  nmr spectrum of the more soluble  $[(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}]_4\text{Ag}^+(\text{BH}_3\text{CN}^-)$  salt exhibited  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$  splittings of  $224$  and  $258 \text{ Hz}$ , respectively, which agree within experimental error with values obtained for a large range of  $\text{L}_4\text{Ag}^+$  salts.<sup>4,20</sup>

The results of conductivity studies of a number of cyanotrihydroborate and related complexes over a concentration range in acetonitrile solutions are summarized in Figure 1. Included for comparison are data for an "ideal" 1:1 electrolyte in that solvent, tetra-*n*-butylammonium iodide. The values for the slope,  $-385$ , and  $\Lambda_0$ ,  $161 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$ , for this reference compound compare favorably with data for

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(22) We are grateful to Dr. Earl L. Muetterties of Du Pont for having these spectra run for us. Experimental details may be found by consulting ref 4 and 20.

(23) E. L. Muetterties, private communication, 1970.

other 1:1 electrolytes in acetonitrile.<sup>24,25</sup> From the data presented in Figure 1 it is apparent that the cyanotrihydroborate anion is substantially coordinated to the tris(triphenylphosphine)copper(I) ion and, to a lesser extent, to the silver analog. The nonlinearity of the plots of equivalent conductance *vs.*  $C^{1/2}$  is characteristic behavior for a weak electrolyte and was previously observed for the octahydrotriborate complex.<sup>2</sup> Using the information contained in Figure 1, the relative extent of dissociation of anions from triphenylphosphine-coordinated cuprous ions is seen to be  $B_3H_8^- \sim H_3BCN^- > BH_4^- \sim Cl^-$ . This result may reflect the basicities of the anions, their differing free energies of solvation in acetonitrile, or both. As mentioned above, the lesser affinity of the cyanotrihydroborate ion for the triphenylphosphine-silver ion (Figure 1) is not unexpected in view of results for compounds containing larger borane anions.<sup>4</sup>

**Cyanotrihydroborate as a Bridging Ligand.**—Since hydroborate ions are well known to coordinate to transition metals by forming multicenter, hydrogen-bridged bonds,<sup>26</sup> it was of interest to investigate the possibility that the  $NCBH_3^-$  ion might act as a bridging ligand. The tetrahydroborate ion, for example, is known to bridge two copper atoms in the  $\{[(C_6H_5)_3P]_2Cu(BH_4)Cu[P(C_6H_5)_3]_2\}^+$  cation.<sup>27</sup> From a chloroform solution containing triphenylphosphine-copper(I) in a 2:1 ratio, the compound of empirical formula  $[(C_6H_5)_3P]_2Cu(NCBH_3)$  was isolated. Although numerous  $L_2CuX$  compounds ( $L = R_3P, R_3As; X$  nonchelating) have been previously synthesized and thought to contain three-coordinate copper,<sup>28</sup> structural studies of the solids often reveal dimerization with bridging X ligands, increasing the coordination number of the copper atom to 4.<sup>29,30</sup>

As indicated in Figure 2 and Table II, the infrared spectra of  $L_3Cu(NCBH_3)$  and  $L_2Cu(NCBH_3)$  are substantially different, suggesting different structures. In particular, the band at  $2330\text{ cm}^{-1}$  (s, br), assigned to the terminal B-H stretching mode ( $\nu_{BH}^e$ ) in both the free ligand and  $L_3Cu(NCBH_3)$  complex (Table II), has shifted to higher frequency and split into several components (centered about  $2376\text{ cm}^{-1}$ , Figure 2) in the  $L_2Cu(NCBH_3)$  complex. The  $2376\text{-cm}^{-1}$  absorptions in  $L_2Cu(NCBH_3)$  are comparable in frequency to the terminal  $BH_2$  stretching modes observed in  $L_2Cu(BH_4)$  and related complexes.<sup>2,33</sup> The terminal  $BH_2$  deformation mode ( $\delta_{BH}^{a1}$ ) also shifts in energy from  $1115\text{ cm}^{-1}$  in  $L_3Cu(NCBH_3)$  to *ca.*  $1100\text{ cm}^{-1}$  in  $L_2Cu-$

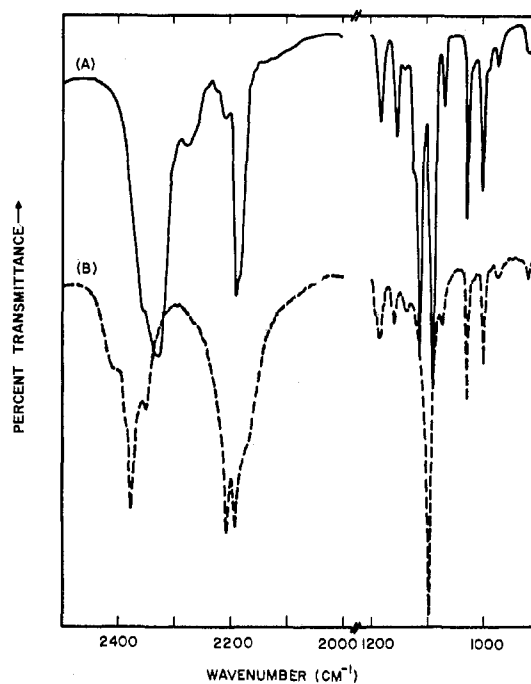


Figure 2.—Comparison of infrared spectra for (A)  $[(C_6H_5)_3P]_3Cu(NCBH_3)$  and (B)  $[(C_6H_5)_3P]_2Cu(NCBH_3)$ , both mullied in Nujol.

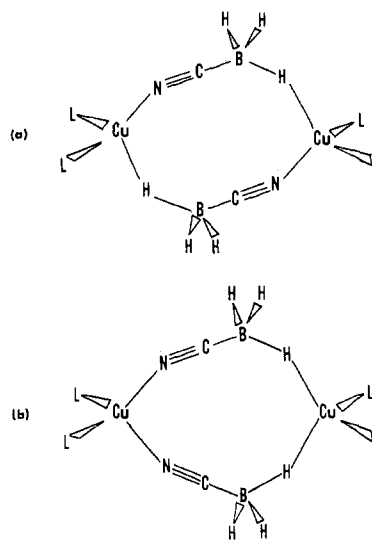


Figure 3.—Possible structures for cyanotrihydroboratobis(triphenylphosphine)copper(I); L in the drawing represents the triphenylphosphine ligand.

( $NCBH_3$ ). Moreover, a new intense absorption appears at  $2207\text{ cm}^{-1}$  in the bis(triphenylphosphine)copper(I) complex, as does a broad, underlying band at  $\sim 2200\text{ cm}^{-1}$  (Figure 2). From the apparent breadth of this latter absorption, it is tentatively assigned to a Cu-H-B stretching vibration. The C-N stretching frequency remains essentially unaltered at  $2190\text{ cm}^{-1}$ .

From the infrared spectral results and in view of the proclivity of  $L_2CuX$  compounds to dimerize,<sup>29</sup> the binuclear structure shown in Figure 3a is proposed for solid  $[(C_6H_5)_3P]_2Cu(NCBH_3)$ . The structure shown in Figure 3b is also a possibility and would require that two of the absorptions in the  $2200\text{-cm}^{-1}$  region of the infrared spectrum (Figure 2) be assigned to the

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(30) This tendency may be avoided by using very bulky ligands such as tricyclohexylphosphine.<sup>31</sup> For a discussion of factors influencing the stereochemistry of tetracoordinate  $L_2CuX$  copper(I) complexes with bidentate X ligands, see ref 32.

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symmetric and asymmetric CN stretching vibrations. An X-ray diffraction study of the complex, currently in progress, should clarify this point.<sup>34</sup>

Solution conductivity studies in acetonitrile reveal nearly identical results for L<sub>3</sub>Cu(NCBH<sub>3</sub>) and L<sub>2</sub>Cu(NCBH<sub>3</sub>) (Figure 1). Equilibria 1 and 2 are postulated for L<sub>3</sub>Cu(NCBH<sub>3</sub>) + CH<sub>3</sub>CN = L<sub>3</sub>Cu(NCCH<sub>3</sub>)<sup>+</sup> + H<sub>3</sub>BCN<sup>-</sup> (1)

$$[L_2Cu(NCBH_3)]_2 + 4CH_3CN = 2L_2Cu(NCCH_3)_2^+ + 2H_3BCN^- \quad (2)$$

(34) NOTE ADDED IN PROOF.—A structure similar to that shown in Figure 3a has been found by X-ray crystallography (S. J. Lippard and K. M. Melmed, to be submitted for publication), but the site symmetries of the two cyanide groups are distinctly different. The deuterated analog {[C<sub>6</sub>H<sub>5</sub>]<sub>2</sub>P]<sub>2</sub>Cu(NCBD<sub>2</sub>)<sub>2</sub>}<sub>2</sub> has also been prepared (J. J. Mayerle, unpublished results) and found to contain two sharp ir bands at 2189 and 2206 cm<sup>-1</sup>. We thank Dr. K. F. Purcell for a sample of NaD<sub>3</sub>BCN.

lated for the solution behavior of the monomeric and dimeric compounds, respectively. Because of the known tendency of triphenylphosphine-copper(I) complexes to dissociate phosphine ligands in solution,<sup>21</sup> no attempt was made to determine the molecular weight of the sparingly soluble cyanotrihydroboratobis(triphenylphosphine)copper(I) compound in chloroform or other noncoordinating solvents.

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## A Direct Proton and Fluorine-19 Nuclear Magnetic Resonance Study of Boron Trihalide Complexes with Pyrazine, Pyridazine, Pyrimidine, 4-Cyclopropylpyridine, 4-Ethylpyridine, Imidazole, 1-Methylimidazole, Pyrazole, and 1-Methylpyrazole

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A direct proton and fluorine-19 nuclear magnetic resonance chemical shift and integration study of boron trifluoride and boron trichloride complexes with pyrazine, pyridazine, pyrimidine, 4-cyclopropylpyridine, 4-ethylpyridine, imidazole, pyrazole, 1-methylimidazole, and 1-methylpyrazole has been completed. In these systems ligand exchange is slow enough to permit the direct observation of pmr signals for bulk ligand and molecules bound to the boron trihalide. The chemical shift differences between the bound and bulk ligand signals were interpreted in terms of an electrostatic effect and possible π-electron participation in the complexing process. Area measurements of the pmr and <sup>19</sup>F nmr signals provided an unambiguous determination of the stoichiometry of the complex, along with an estimate of the relative basic strengths of these species. The trends in basic strengths were as follows: pyridazine > pyrimidine > pyrazine; 4-cyclopropylpyridine ≈ 4-ethylpyridine; and 1-methylimidazole > imidazole > pyrazole > 1-methylpyrazole.

### Introduction

The utility of nuclear magnetic resonance (nmr) methods for studying a variety of Lewis acid-base systems has been demonstrated recently.<sup>1–18</sup> When samples containing an excess of base are cooled to reduce

the rate of proton and molecular exchange, it frequently is possible to observe separate resonance signals for bound and bulk ligand molecules. This has been accomplished for electrolyte solutions, leading to quantitative determinations of cation hydration numbers,<sup>1–3</sup> competitive solvation,<sup>4–6</sup> and contact ion pairing,<sup>7–12</sup> for possible hydrogen-bonding interactions,<sup>13</sup> for Co<sup>2+</sup> complexes with several bases,<sup>14</sup> and for boron trihalide interactions with organic bases.<sup>15–18</sup> The latter systems included oxygen-containing molecules,<sup>15,18</sup> substituted pyridines,<sup>17</sup> and compounds of biological relevance.<sup>18</sup>

Studies of similar systems have been attempted by calorimetric<sup>19–22</sup> and room-temperature ir and nmr techniques<sup>23–29</sup> and structural information has been ob-

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