

ductivity  $90 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , color yellow; for  $A = B(C_6H_5)_4$  conductivity  $82 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , color yellow. Anal. Calcd for  $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2(CO)_3][SbF_6]$ : C, 42.9; H, 2.7; P, 5.5; Fe, 10.0; F, 10.2. Found: C, 42.9; H, 2.7; P, 5.5; Fe, 9.8; F, 10.3. Anal. Calcd for  $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2(CO)_3][B(C_6H_5)_4]$ : P, 5.2; Fe, 9.3; B, 0.9. Found: P, 5.2; Fe, 9.4; B, 1.0.

(20) **Reaction of  $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2][B(C_6H_5)_4]$  with Carbon Monoxide.** Carbon monoxide was bubbled through a chloroform suspension (ca. 10 mL) of  $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2][B(C_6H_5)_4]$  (0.5 g) until complete dissolution of this compound had been effected. The solvent was removed under reduced pressure to afford a yellow residue which was shown to contain  $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2(CO)_3][B(C_6H_5)_4]$  by means of IR spectroscopy; numerous attempts to obtain this compound analytically pure proved unsuccessful.

(21) **Reaction of  $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2][B(C_6H_5)_4]$  with Dihydrogen.** Dihydrogen was bubbled through a suspension of  $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2][B(C_6H_5)_4]$  (0.5 g) in chloroform (ca. 10 mL) for 15 min. An IR spectrum of the resultant solution revealed the absence of bridging carbonyl stretching peaks but attempts to isolate the product in crystalline form proved unsuccessful. Passage of dinitrogen through the solution led to the regeneration of  $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2][B(C_6H_5)_4]$  (see Results and Discussion for a discussion of this species).

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**Registry No.**  $FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)$ , 38816-40-9;  $FeS(C_2H_5)(CO)_2(\eta-C_5H_5)$ , 12108-34-8;  $FeS(t-C_4H_9)(CO)_2(\eta-C_5H_5)$ , 38816-45-4;  $FeS(C_6H_5)(CO)_2(\eta-C_5H_5)$ , 12110-44-0;  $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2(C_6H_5)_2][SbF_6]$ , 72228-85-4;  $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2(C_6H_5)_2][P(CH_3)_2C_6H_5][SbF_6]$ , 72228-87-6;  $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2(C_6H_5)_2][P(OC_6H_5)_3][SbF_6]$ , 72268-98-5;  $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2(C_6H_5)_2][P(OC_6H_5)_3][SbF_6]$ , 72268-98-5;

$[Rh\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2][SbF_6]$ , 72228-89-8;  $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2][PF_6]$ , 37299-51-7;  $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2][SbF_6]$ , 37299-52-8;  $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2][B(C_6H_5)_4]$ , 37299-50-6;  $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2(C_6H_5)_2][P(CH_3)_2C_6H_5][SbF_6]$ , 38903-34-3;  $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2][SbF_6]$ , 37299-53-9;  $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2][B(C_6H_5)_4]$ , 72137-99-6;  $[Rh\{FeS(t-C_4H_9)(CO)_2(\eta-C_5H_5)\}_2][SbF_6]$ , 37299-06-2;  $[Fe_2(\eta-C_5H_5)_2(CO)_3S(C_2H_5)][B(C_6H_5)_4]$ , 56953-82-3;  $[Fe_2(\eta-C_5H_5)_2(CO)_3S(t-C_4H_9)][B(C_6H_5)_4]$ , 56953-84-5;  $[Rh\{FeS(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2(C_6H_5)_2][SbF_6]$ , 72138-01-3;  $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2][P(OC_6H_5)_3][B(C_6H_5)_4]$ , 37299-55-1;  $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2][P(C_6H_5)_3][B(C_6H_5)_4]$ , 37299-60-8;  $[Rh(CO)_3\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2][PF_6]$ , 72138-03-5;  $[Rh(CO)_3\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2][SbF_6]$ , 72173-26-3;  $[Rh(CO)_3\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2][B(C_6H_5)_4]$ , 72173-27-4;  $[Ir(CO)_3\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2][B(C_6H_5)_4]$ , 72243-71-1;  $Rh(CO)\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2Cl$ , 72252-31-4;  $Rh(CO)\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2Cl$ , 72252-32-5;  $Ir(CO)\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2Cl$ , 72138-09-1;  $Ir(CO)\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2Cl$ , 72138-10-4;  $Rh(CO)\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2Br$ , 72138-11-5;  $Ir(CO)\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2Br$ , 72138-12-6;  $Rh(CO)\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2I$ , 72138-13-7;  $Rh(CO)\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2I$ , 72152-02-4;  $Ir(CO)\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2I$ , 72138-14-8;  $Rh(CO)\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2CN$ , 72138-15-9;  $Ir(CO)\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2CN$ , 72138-16-0;  $Rh\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2Cl$ , 72152-03-5;  $Rh\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2Br$ , 72252-33-6;  $Rh\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2I$ , 72138-17-1;  $Ir\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2I$ , 72138-18-2;  $Rh\{FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)\}_2CN$ , 72138-19-3;  $[Rh\{FeS(t-C_4H_9)(CO)_2(\eta-C_5H_5)\}_2][B(C_6H_5)_4]$ , 72138-20-6;  $FeP(C_6H_5)_2(CO)_2(\eta-C_5H_5)(C_6H_5)_2$ , 38816-41-0;  $[Fe(\eta-C_5H_5)(CO)_2][P(C_6H_5)_2H][B(C_6H_5)_4]$ , 72138-21-7;  $[Rh(C_8H_{12})\{P(CH_3)_2C_6H_5\}_2][SbF_6]$ , 72138-23-9;  $[Rh(C_8H_{12})(C_6H_5)_2PC_2H_4P(C_6H_5)_2][SbF_6]$ , 72138-24-0;  $Fe(\eta-C_5H_5)(CO)_2Cl$ , 12107-04-9;  $Fe(\eta-C_5H_5)(CO)_2I$ , 12078-28-3;  $[Fe(\eta-C_5H_5)(CO)_2]$ , 12154-95-9;  $[Rh(C_8H_{12})Cl]_2$ , 12092-47-6;  $[Rh\{P(OC_6H_5)_3\}_2Cl]_2$ , 25966-16-9;  $[Ir(C_8H_{12})Cl]_2$ , 12112-67-3;  $[Rh(CO)_2Cl]_2$ , 14523-22-9;  $[Rh(CO)_2SC_6H_5]_2$ , 24818-80-2.

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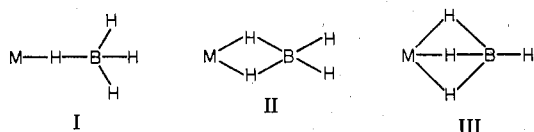
## Single Hydrogen-Boron Bridged Species: Tris(methyldiphenylphosphine) Complexes of Silver(I) and Copper(I) Containing Tetrahydroborate and (Ethoxycarbonyl)trihydroborate

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The complexes (tetrahydroborato)tris(methyldiphenylphosphine)copper(I), (tetrahydroborato)tris(methyldiphenylphosphine)silver(I), ((ethoxycarbonyl)trihydroborato)tris(methyldiphenylphosphine)copper(I), and ((ethoxycarbonyl)trihydroborato)tris(methyldiphenylphosphine)silver(I) have been synthesized and characterized. IR data and analysis support the presence of a hydrogen singly bridged to the metal in the solid species. In solution, conductivity, molecular weight, and NMR data indicate the existence of equilibrium between singly and doubly bridged species. Factors influencing the formation of a singly bridged vs. a doubly bridged species are discussed.

Recent communications have reported the existence of a single-hydrogen bridge attachment of tetrahydroborate to copper(I).<sup>2,3</sup> Of the three possible orientations I-III these



(1) Eloise Gerry Fellow, 1977-1978.

are the only reports of type I with  $M = \text{copper}$ . In this paper, we report in detail the synthesis and characterization of four methyldiphenylphosphine complexes, the evidence for which suggests that a single-hydrogen bridge attachment of the boron-containing moiety to the metal is present. The complexes are (tetrahydroborato)tris(methyldiphenylphosphine)copper(I)

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[(MePh<sub>2</sub>P)<sub>3</sub>CuBH<sub>4</sub>], (tetrahydroborato)tris(methyldiphenylphosphine)silver(I) [(MePh<sub>2</sub>P)<sub>3</sub>AgBH<sub>4</sub>], ((ethoxycarbonyl)trihydroborato)tris(methyldiphenylphosphine)copper(I) [(MePh<sub>2</sub>P)<sub>3</sub>CuH<sub>3</sub>BCO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>], and ((ethoxycarbonyl)trihydroborato)tris(methyldiphenylphosphine)silver(I) [(MePh<sub>2</sub>P)<sub>3</sub>AgH<sub>3</sub>BCO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>]. Comparison of these complexes to the analogous triphenylphosphine complexes and rationale for the differences in mode of the BH<sub>4</sub> attachment are presented.

### Experimental Section

**General Techniques.** Infrared spectra were taken on a Beckman IR-20A. <sup>1</sup>H NMR spectra were obtained from Varian XL-100, A-60, or EM-360 spectrometers. Chemical shifts were based upon internal references (Me<sub>4</sub>Si or known solvent). Low-temperature <sup>1</sup>H and <sup>11</sup>B spectra were obtained from the XL-100 system with the temperature control device calibrated by using an independent thermocouple placed within the NMR tube situated in the probe. <sup>31</sup>P NMR spectra were run at The Ohio State University in the laboratory of Dr. Sheldon G. Shore. Vapor pressure osmometry was performed on a Mechrolab, Inc., Model 301A osmometer at 37 °C with chloroform solvent. Conductivity of the complex solutions was measured with a General Radio Co. Type 1608-A impedance bridge and a submersible conductivity cell with cylindrical plates and a cell constant of 1.1626 cm<sup>-1</sup>. Spectral grade acetonitrile and nitromethane were used for the conductance measurements. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, unless indicated otherwise. Percent yields in the synthesis of the complexes were comparable to those of triphenylphosphine complexes<sup>4</sup> and ranged from 80 to 90%.

**Materials.** Diborane,<sup>5</sup> borane carbonyl,<sup>6</sup> potassium (ethoxycarbonyl)trihydroborate,<sup>7</sup> and methyldiphenylphosphine<sup>8</sup> (bp 93–96 °C (0.4 mm)) were prepared by previously published procedures. All other chemicals were obtained commercially and used without further purification.

**Complex Preparation. (Tetrahydroborato)tris(methyldiphenylphosphine)copper(I) and (Tetrahydroborato)tris(methyldiphenylphosphine)silver(I).** Essentially the same procedure was used for the two complexes. A 3.00-g (15-mmol) sample of CH<sub>3</sub>Ph<sub>2</sub>P and 0.40 g (4 mmol) of CuCl were stirred in 30 mL of chloroform for about 6 h. The remaining solid was filtered out, and 0.190 g (5 mmol) of NaBH<sub>4</sub> dissolved in 10 mL of absolute ethanol was added to the filtrate. The solution was stirred for 15 min, filtered, and flash evaporated to dryness. The solid was dissolved in 15 mL of methylene dichloride, and the solution was filtered to remove remaining inorganic salts. Pentane (15–20 mL) was added to the filtrate slowly until crystallization began. The solution was then cooled to –20 °C for several hours; the crystals were filtered, washed with pentane, and dried under high vacuum at ambient temperature. A qualitative chloride test of the white crystalline product proved to be negative: mp 119–121 °C (decomposes slowly); <sup>1</sup>H NMR δ<sub>Ph</sub> 7.3, δ<sub>CH<sub>3</sub></sub> 1.7 ppm, (J<sub>P-H</sub> = 4.5 Hz); <sup>11</sup>B NMR δ<sub>B-H</sub> 0.90. Anal. Calcd for C<sub>39</sub>H<sub>43</sub>P<sub>3</sub>BCu: C, 69.52; H, 6.27; B, 1.56; Cu, 9.20. Found: C, 69.40; H, 6.31; B, 1.40; Cu, 9.04.

For the silver tetrahydroborate complex, 0.225 g (1.5 mmol) of AgNO<sub>3</sub>, 2.0 g (10 mmol) of CH<sub>3</sub>Ph<sub>2</sub>P, and 0.076 g (2 mmol) of NaBH<sub>4</sub> were used. After flash evaporation, 4 mL of methylene dichloride dissolved the complex, and 20 mL of pentane was added with cooling. Although the product initially oiled out, subsequent stirring and cooling resulted in crystallization taking place over about a 3-min period. Reduction becomes a problem if further recrystallization is attempted without a large excess of phosphine. Satisfactory analytical results were obtained without further purification: mp 90–93 °C dec; <sup>1</sup>H NMR δ<sub>Ph</sub> 7.3, δ<sub>CH<sub>3</sub></sub> 1.7 (J<sub>P-H</sub> = 4.5 Hz); <sup>11</sup>B NMR δ<sub>B-H</sub> +1.0. Anal. Calcd for C<sub>39</sub>H<sub>43</sub>P<sub>3</sub>BAG: C, 64.75; H, 5.99; B, 1.49; Ag, 14.91. Found: C, 64.59; H, 5.96; B, 1.60; Ag, 14.80.

**((Ethoxycarbonyl)trihydroborato)tris(methyldiphenylphosphine)copper(I) and ((Ethoxycarbonyl)trihydroborato)tris(methyldiphenylphosphine)silver(I).** A 2.0-g (10-mmol) sample of CH<sub>3</sub>Ph<sub>2</sub>P

and 0.30 g (3 mmol) of CuCl were stirred together in 30 mL of chloroform for 2 h. The solution was filtered to remove any remaining CuCl. A 0.415-g (3.3-mmol) sample of K<sub>2</sub>H<sub>3</sub>BCOOC<sub>2</sub>H<sub>5</sub> dissolved in 5 mL of absolute ethanol was added to the filtrate and stirred for 15 min. The mixture was filtered and flash evaporated to dryness. The complex and excess ligand were dissolved in 10 mL of dry methylene dichloride, and the solution was filtered to remove excess KH<sub>3</sub>BCOOC<sub>2</sub>H<sub>5</sub> and KCl. Dry pentane (40 mL) was added to the filtrate, and the solution was cooled to –20 °C for several hours in a tightly stoppered container. The white crystals that formed were filtered, washed with pentane, and dried under high vacuum. A second crop of crystals was recovered from the filtrate by addition of another 40 mL of pentane: mp 110–111.5 °C; dec pt 116–118 °C; <sup>1</sup>H NMR δ<sub>Ph</sub> 7.3, δ<sub>PCH<sub>3</sub></sub> 1.68, δ<sub>CH<sub>3</sub></sub> 1.16, δ<sub>CH<sub>2</sub></sub> 4.04. Anal. Calcd for C<sub>42</sub>H<sub>47</sub>P<sub>3</sub>O<sub>2</sub>BCu: C, 67.16; H, 6.31; B, 1.44; Cu, 8.46. Found: C, 66.93; H, 6.40; B, 1.50; Cu, 8.43.

In the preparation of the silver salt, 3.6 g (18 mmol) of CH<sub>3</sub>Ph<sub>2</sub>P and 0.595 g (3.5 mmol) of AgNO<sub>3</sub> were used. After flash evaporation to remove solvent, 15 mL of dry methylene dichloride was added and the solution filtered. The volume of solution was reduced to approximately 8 mL, and 15 mL of dry pentane was added, whereupon some KH<sub>3</sub>BCOOC<sub>2</sub>H<sub>5</sub> precipitated. The solution was filtered, and another 30 mL of dry pentane was added. The solution was cooled to –20 °C for several hours during which time the complex was deposited as an oil. The supernatant was decanted, and the oil was washed with 15 mL of pentane. The oil was then placed under high vacuum for 0.5 h at ambient temperature to remove all solvent. The product was a clear, highly viscous oil which decomposed rapidly upon being heated: <sup>1</sup>H NMR δ<sub>Ph</sub> 7.3, δ<sub>PCH<sub>3</sub></sub> 1.65, δ<sub>CH<sub>3</sub></sub> 1.12, δ<sub>CH<sub>2</sub></sub> 4.01. Anal. Calcd for C<sub>42</sub>H<sub>47</sub>P<sub>3</sub>O<sub>2</sub>BAG: C, 63.42; H, 5.96; B, 1.36; Ag, 13.56. Found (Chemalytics, Inc., Tempe, AZ): C, 63.31; H, 6.03; B, 1.60; Ag, 13.29. This oil slowly crystallized over a period of several months of being stored at about –20 °C with infrequent temperature variation and agitation.

### Results and Discussions

Halotris(methyldiphenylphosphine)copper(I) complexes have been prepared by Lippard and Mayerle.<sup>9</sup> They reported that these complexes were stable in solution in the presence of the tetrahydroborate ion, BH<sub>4</sub><sup>-</sup>, with no apparent reaction after several days. It was suggested that since these halo complexes dissociate to a lesser extent in solution than the halotris(triphenylphosphine)copper(I) complexes, complexation by the tetrahydroborate would involve displacement of both the halide and a phosphine ligand. The intimation is that this type of replacement is a thermodynamically unfavorable process. In light of our recent studies in which the monodentate coordination mode was exhibited by the (carboxylato)trihydroborate derivatives,<sup>4,10</sup> we surmised that it would not appear necessary for one of the phosphine ligands to be displaced in order for coordination by tetrahydroborate or a (carboxylato)trihydroborate derivative to occur. Our investigation shows that this is so, and the relative factors affecting the mode of coordination, both steric and electronic, have now been clarified.

Although no reaction was observed upon allowing either iodotris(methyldiphenylphosphine)copper(I) or iodotris(dimethylphenylphosphine)copper(I) to interact with tetrahydroborate, when chloride was substituted for iodide, the reaction with tetrahydroborate and (ethoxycarbonyl)trihydroborate proceeded immediately with essentially 100% displacement of chloride as shown by qualitative chloride analysis of the product. Nitrate was also displaced by tetrahydroborate and (ethoxycarbonyl)trihydroborate in the complex (nitrate)bis(methyldiphenylphosphine)silver(I) in the presence of excess phosphine. Full characterization of only the methyldiphenylphosphine complexes was pursued, since studies by other investigators have shown the dimethylphenylphosphine complexes to behave very similarly in solu-

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Table I. Infrared Absorptions Assigned to B-H<sub>n</sub> moieties in BH<sub>4</sub><sup>-</sup> and H<sub>3</sub>BCO<sub>2</sub>C<sub>2</sub>H<sub>5</sub><sup>-</sup> Methylidiphenylphosphine-Copper Complexes

compd	absorption range, cm <sup>-1</sup>					
	2500-2200	2200-1900	1700-1500	1500-1300	1300-1000	1000...
(MePh <sub>2</sub> P) <sub>3</sub> CuBH <sub>4</sub>	2335 sh <sup>d</sup> 2315 s BH <sub>t</sub> str	2045 s BH <sub>b</sub> str		c	1060 s BH <sub>3</sub> def	
(MePh <sub>2</sub> P) <sub>3</sub> AgBH <sub>4</sub>	2300 s BH <sub>t</sub>	2050 s BH <sub>b</sub>		c	1070 s BH <sub>3</sub> def	
(MePh <sub>2</sub> P) <sub>3</sub> CuBD <sub>4</sub>			1735 s 1690 s BD <sub>t</sub> str ν <sub>H</sub> /ν <sub>D</sub> = 1.35	1510 s BD <sub>b</sub> str ν <sub>H</sub> /ν <sub>D</sub> = 1.35	c	805 s BH <sub>3</sub> def ν <sub>H</sub> /ν <sub>D</sub> = 1.32
(MePh <sub>2</sub> P) <sub>3</sub> CuH <sub>3</sub> BCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	2330 s BH <sub>t</sub> str 2260 sh	2090 s, br BH <sub>b</sub> str	1660 s C=O	1400 sh?	1130-1140 s 1045 vs	
(MePh <sub>2</sub> P) <sub>3</sub> AgH <sub>3</sub> BCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	2320 s BH <sub>t</sub> str 2270	2130 s, br 2130 s, br	1660 s C=O str		1230 m 1120-1130 s 1045 vs	805 m
(MePh <sub>2</sub> P) <sub>3</sub> CuBH <sub>4</sub> (CHCl <sub>3</sub> ; 0.04 g/mL)	2345 s 2370 sh 2280 sh BH <sub>t</sub> str 2240 w <sup>a</sup>	2010 s 1970 sh BH <sub>b</sub> str		1370 m bridge str	1125 s BH <sub>3</sub> def 1060 vw	
(MePh <sub>2</sub> P) <sub>3</sub> CuBH <sub>4</sub> (CHCl <sub>3</sub> ; 0.7 g/mL)	2370 sh 2300 s BH <sub>t</sub> str	2035 s BH <sub>b</sub> str		1380 vw	1125 m 1060 s	
(MePh <sub>2</sub> P) <sub>3</sub> CuH <sub>3</sub> BCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (CHCl <sub>3</sub> ; 0.04 g/mL)	2340 s BH <sub>t</sub> str	2050 s BH <sub>b</sub> str				
(MePh <sub>2</sub> P) <sub>3</sub> CuH <sub>3</sub> BCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (CHCl <sub>3</sub> ; 0.6 g/mL)	2320 s BH <sub>t</sub> str	2090 s BH <sub>b</sub> str				
(Ph <sub>3</sub> P) <sub>2</sub> CuBH <sub>4</sub> <sup>b</sup>	2395 s 2340 sh BH <sub>t</sub> str	1985 s 1935 s BH <sub>b</sub> str	1370 m bridge str	1135 s BH <sub>2</sub> def		
(Ph <sub>3</sub> P) <sub>2</sub> AgBH <sub>4</sub> <sup>b</sup>	2355 s BH <sub>t</sub> str 2260 w <sup>a</sup> 2210 w	2000 s 1965 s BH <sub>b</sub> str	1380 m bridge	1110 s BH <sub>2</sub> def		

<sup>a</sup> Weak peaks at this frequency have been assigned to an overtone of a BH<sub>2</sub> deformation. <sup>b</sup> Our spectra. <sup>c</sup> Only neutral ligand peaks are observed. <sup>d</sup> Key: vs, very strong; s, strong; m, medium; w, weak; str, stretch; def, deformation; H<sub>t</sub>, terminal H; H<sub>b</sub>, bridging H.

Table II. Conductivity of Copper and Silver Complexes in Acetonitrile

complex	concn × 10 <sup>3</sup> , M	(concn) <sup>1/2</sup> , M <sup>1/2</sup>	[added ligand], M	sp conductance, Ω <sup>-1</sup>	equiv conductance, Ω <sup>-1</sup> cm <sup>2</sup> equiv <sup>-1</sup>
(MePh <sub>2</sub> P) <sub>3</sub> CuBH <sub>4</sub>	3.60	0.060		5.30 × 10 <sup>-5</sup>	14.7
	1.80	0.0424		3.28 × 10 <sup>-5</sup>	18.1
	0.720	0.0268		1.92 × 10 <sup>-5</sup>	26.6
	0.360	0.01895		1.18 × 10 <sup>-5</sup>	32.7
	0.180	0.0134		9.95 × 10 <sup>-6</sup>	55.3
	3.60	0.060	0.40	1.88 × 10 <sup>-4</sup>	52.2
(MePh <sub>2</sub> P) <sub>3</sub> AgBH <sub>4</sub>	20.0	0.141		3.52 × 10 <sup>-4</sup>	17.6
	2.0	0.0447		4.26 × 10 <sup>-5</sup>	21.3
	0.40	0.020		1.63 × 10 <sup>-5</sup>	40.8
(MePh <sub>2</sub> P) <sub>3</sub> CuH <sub>3</sub> BCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	3.60	0.060		2.95 × 10 <sup>-4</sup>	82.0
	1.80	0.0424		1.61 × 10 <sup>-4</sup>	89.2
	0.720	0.0268		7.54 × 10 <sup>-5</sup>	105.0
	0.360	0.01895		4.10 × 10 <sup>-5</sup>	114.0
	0.180	0.0134		2.21 × 10 <sup>-5</sup>	123.0
	3.60	0.060	0.40	3.18 × 10 <sup>-4</sup>	88.5
(MePh <sub>2</sub> P) <sub>3</sub> AgH <sub>3</sub> BCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	15.25	0.123		8.82 × 10 <sup>-4</sup>	57.8
	1.525	0.0390		1.24 × 10 <sup>-4</sup>	81.2
	0.610	0.0247		5.74 × 10 <sup>-5</sup>	94.1

tion.<sup>9</sup> The analytical and spectral data support monodentate attachment as the prototype for all of the (methylidiphenylphosphine)copper(I) and -silver(I) tetrahydroborate and (ethoxycarbonyl)trihydroborate complexes prepared.

Elemental analyses support monodentate coordination by BH<sub>4</sub><sup>-</sup> and H<sub>3</sub>BCO<sub>2</sub>C<sub>2</sub>H<sub>5</sub><sup>-</sup> in the solid-state complexes. Infrared absorptions attributed to the complexed ions are tabulated in Table I. Since Nujol mulls or KBr samples gave the same results as neat samples, only the neat results are reported. Solution data are included for ease of comparison.<sup>2</sup> Absorp-

tions due to neutral ligands are excluded. NMR data for the complexes are presented in the Experimental Section, conductivity in acetonitrile is given in Table II, and molecular weight (osmometric) data may be found in Table III.

**Infrared Spectra.** The IR spectrum of (tetrahydroborato)tris(methylidiphenylphosphine)copper(I) has been reported,<sup>2</sup> and absorption values in Table I are included for ease of comparison. Pertinent features supporting monodentate coordination are the position and number of peaks in the terminal and stretching region, in particular the presence of

Table III. Molecular Weight (Osmometric) Data for Complexes in Chloroform at 37 °C

complex	[complex], g/mL	[free L, added], M	$M_{\text{calcd}}^a$ , M	$M_{\text{obsd}}^b$ , M	$M_{\text{obsd}}/M_{\text{calcd}}$	[L], M	$[L_2M]_M^c$ , M	$[L_3M]_M^d$ , M	$K_{\text{diss}}^e$ , M	fwf	mol wtg	% diss of L <sup>f</sup>
(MePh <sub>2</sub> P) <sub>3</sub> CuBH <sub>4</sub>	0.0190	0.0715	0.0274	0.0497	1.81	0.0938	0.0223	0.0051	0.41	691.0	381	81
	0.0199	0.0537	0.0288	0.0538	1.87	0.0787	0.0250	0.0038	0.53	691.0	370	87
	0.0199	0.0284	0.0288	0.0551	1.91	0.0547	0.0263	0.0025	0.57	691.0	361	91
	0.0330	0	0.0478	0.0906	1.90	0.0428	0.0428	0.0050	0.37	691.0	364	90
	0.0208	0.0980	0.0288	0.0410	1.42	0.1102	0.0122	0.0166	0.081	723.4	508	42
(MePh <sub>2</sub> P) <sub>3</sub> AgBH <sub>4</sub>	0.0208	0.0735	0.0288	0.0448	1.56	0.0895	0.0160	0.0128	0.11	723.4	464	56
	0.0216	0.0735	0.0288	0.0355	1.23	0.0802	0.0067	0.0221	0.024	751.1	608	23
	0.0221	0.0500	0.0295	0.0390	1.33	0.0595	0.0095	0.0200	0.028	751.1	566	33
	0.0220	0.0295	0.0293	0.0440	1.50	0.0442	0.0147	0.0146	0.044	751.1	500	50
	0.0376	0	0.0501	0.0736	1.47	0.0235	0.0235	0.0266	0.021	751.1	511	47
(MePh <sub>2</sub> P) <sub>3</sub> AgH <sub>3</sub> BCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	0.0229	0.1011	0.0288	0.0401	1.39	0.1124	0.0113	0.0175	0.073	795.3	571	39
	0.0229	0.0735	0.0288	0.0425	1.48	0.0872	0.0137	0.0151	0.0791	795.3	539	48
	0.0229	0.0396	0.0288	0.0463	1.61	0.0571	0.0175	0.0113	0.088	795.3	495	61
									∞	909.6	647	100
									0.33	981.7	573	71
								0.15	953.6	592	61	
										602.9	578	
										674.7	643	

<sup>a</sup> The concentration of complex added based upon the theoretical formula weight and the amount added. <sup>b</sup> The observed molarity based upon vapor pressure osmometer readings. <sup>c</sup>  $M_{\text{obsd}} - M_{\text{calcd}}$ . <sup>d</sup>  $M_{\text{calcd}} - [L_2M]_M$ . <sup>e</sup>  $[L]_M/[L_2M]_M$ . <sup>f</sup> Formula weight based upon stoichiometry shown. <sup>g</sup> Molecular weight calculated from osmometric data. <sup>h</sup>  $([L_2M]_M/M_{\text{calcd}}) \times 100$ . <sup>i</sup> Actually  $(Ph_3P)_2AgBH_4 + Ph_3P$ . <sup>j</sup> Included for comparison; complex solution data presented elsewhere.<sup>4</sup>

the strong 1060-cm<sup>-1</sup> absorption assignable to the BH<sub>3</sub> deformation.<sup>11</sup> Deuteration studies and solution IR measurements<sup>2</sup> further support the presence of a complex which shows other than bidentate complexation. The IR absorptions of (CH<sub>3</sub>Ph<sub>2</sub>P)<sub>3</sub>CuBD<sub>4</sub> appear as a doublet at 1735 and 1510 cm<sup>-1</sup> assignable to the BD<sub>2</sub> stretch ( $\nu_H/\nu_D = 1.35$ ) and as a singlet at 1510 cm<sup>-1</sup> which is assigned to the bridge stretch ( $\nu_H/\nu_D = 1.35$ ); both absorptions occur in the regions expected upon deuteration.

The infrared spectrum of the silver tetrahydroborate complex is very similar to that of its copper analogue. The decrease in the B-H<sub>i</sub> stretching frequency from 2315 cm<sup>-1</sup> in the copper to 2300 cm<sup>-1</sup> in the silver complex, along with the slight increase in the B-H<sub>b</sub> stretching frequency from 2045 cm<sup>-1</sup> in the copper to 2050 cm<sup>-1</sup> in the silver complex, parallels the trend which is observed in the bidentate (triphenylphosphine)copper and -silver tetrahydroborate complexes. Since the bidentate efficiency of the anion relative to the size of the metal is not a factor in the unidentate case, the variance in stretching frequency between the two complexes can best be attributed to decreased covalency in the silver complex due to the weaker polarizing ability of the metal. Decreased covalency is further suggested by the fact that the higher BH<sub>3</sub> deformation frequency exhibited by the silver complex (1070 vs. 1060 cm<sup>-1</sup>) is closer to the deformation frequency for the ionic tetrahydroborates (for KBH<sub>4</sub>: 1110 cm<sup>-1</sup>).

The B-H stretching frequencies for the solid-state spectrum of the copper (ethoxycarbonyl)trihydroborate complex are somewhat higher than the corresponding frequencies for the analogous tetrahydroborate complex. This is the same trend encountered with the triphenylphosphine complexes and it was attributed to the less negative character of the borane group in the (ethoxycarbonyl)trihydroborate.<sup>4</sup> Also attributable to the latter is a decrease in covalent interaction resulting in the decrease in frequency separation between terminal and bridging modes for the (ethoxycarbonyl)trihydroborate complex compared to the case for the tetrahydroborate analogue (270 vs. 240 cm<sup>-1</sup>). The relatively small separation of the terminal and bridging bands along with their absolute frequencies of absorption supports a single-hydrogen bridge mode of coordination.

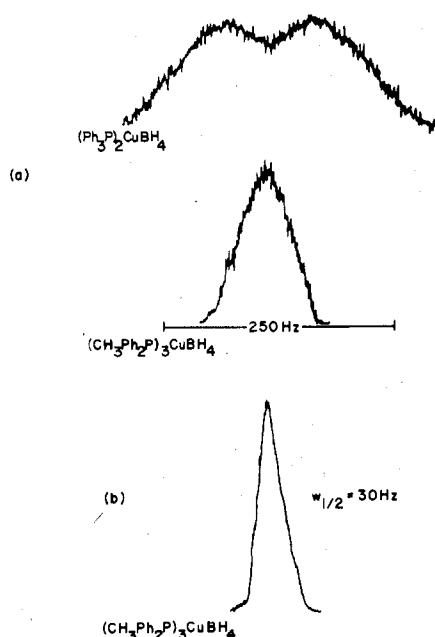
The separation between terminal and bridging B-H stretching modes for the (ethoxycarbonyl)trihydroborate-silver complex is 190 cm<sup>-1</sup>, the smallest yet noted for this type of copper or silver complex. This separation is 50 cm<sup>-1</sup> less than for the corresponding copper complex, indicating that it is also a monodentate complex with somewhat less covalency between the metal and the borane hydrogens.

Assignments for the (ethoxycarbonyl)trihydroborate complexes in the B-H deformation region of 1000–1200 cm<sup>-1</sup> are difficult to make with confidence because of other (ethoxycarbonyl)trihydroborate absorptions in the region. The carbonyl absorption appears at 1660 cm<sup>-1</sup>, which it does in practically all of the (alkoxycarbonyl)trihydroborate complexes whether bidentate or monodentate, and, as previously noted, is consistent with lack of coordination by the oxygen sites.<sup>4,10</sup>

Solution IR data for the tetrahydroborate complex are presented elsewhere<sup>2</sup> and for the (ethoxycarbonyl)trihydroborate complex are presented in the discussion of neutral ligand dissociation.

**NMR Spectra.** Only the proton resonances due to the phosphine ligands are observed under normal instrument power settings, and these occur in the expected regions ( $\delta_{\text{Ph}} \sim 7.3$  and  $\delta_{\text{PCH}_3} \sim 1.7$ ). Borane <sup>1</sup>H resonances in the tetrahydroborate complexes consist of a broad, featureless absorption or a very broad doublet depending upon the extent of "thermal" de-

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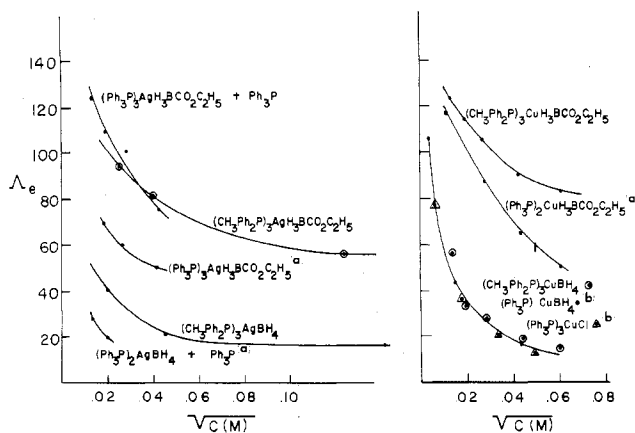


**Figure 1.** 100.1-MHz  $^1\text{H}$  NMR spectra of borane hydrogens for phosphine complexes at comparable concentration in (a)  $\text{CDCl}_3$  at ambient temperature and (b) 2/1  $\text{CH}_2\text{CHCl}/\text{CH}_2\text{CHF}$  at  $-120^\circ\text{C}$ .

coupling<sup>12</sup> and are not observed unless very high rf power and signal amplification are employed. The borane resonances in the (ethoxycarbonyl)trihydroborate complexes are obscured by the methyl peaks of the  $\text{C}_2\text{H}_5$  moiety. The difference in the borane hydrogen absorptions of  $(\text{Ph}_3\text{P})_2\text{CuBH}_4$  and  $(\text{CH}_3\text{Ph}_2\text{P})_3\text{CuBH}_4$  (Figure 1a) shows the variance in extent of "thermal" decoupling at ambient temperature of the two complexes and has been related to the magnitude of the nuclear quadrupole coupling constant, which is proportional to the field gradient at boron in the particular molecule and to differences in correlation times, which are likely the result of a change in the rate of molecular reorientation due to the differing sizes of the molecules.<sup>12b-d</sup> At  $-120^\circ\text{C}$  in 2/1  $\text{CH}_2\text{CHCl}/\text{CH}_2\text{CHF}$  a reasonably sharp ( $W_{1/2} = 30$  Hz, where  $W_{1/2}$  is the width of the absorption at half the peak height) borane hydrogen singlet (Figure 1b) can be observed for  $(\text{CH}_3\text{Ph}_2\text{P})_3\text{CuBH}_4$  and is the behavior expected compared to the case of similar complexes.<sup>4,12</sup>

The  $^{11}\text{B}$  NMR spectra of the complexes substantiate the presence of  $\text{BH}_3$  as indicated by the somewhat broadened quartet or quintet, depending upon whether (ethoxycarbonyl)trihydroborate or tetrahydroborate is the ligand.

The  $^{31}\text{P}$  NMR spectrum of the tetrahydroborate-copper complex at room temperature confirms that a rapid exchange of free and coordinated phosphine occurs.<sup>3</sup> The  $^{31}\text{P}$  NMR spectra in  $\text{CD}_2\text{Cl}_2$  exhibit one sharp singlet over the temperature range  $-110$  to  $-70^\circ\text{C}$  with proton decoupling. This suggests equivalence of the phosphine groups on the NMR time scale as well as rapid exchange of the phosphine on existing structures even at low temperature. The lowering of the temperature did not result in the appearance of signals for different compounds, which is in direct contrast to work reported by Muetterties and Alegranti,<sup>13</sup> in which complexes of the type  $\text{L}_m\text{CuX}$  ( $\text{L} = \text{tri-}p\text{-tolylphosphine}$ ) at  $-70$  to  $-100^\circ\text{C}$  occurred as several different species. At higher temperatures the absorptions in  $^{31}\text{P}$  NMR spectrum for their com-



**Figure 2.** Plots of equivalent conductance ( $\Lambda_e$ ) against the square root of concentration for copper and silver complexes in acetonitrile: (a) ref 4; (b) ref 14.

plexes collapsed to a single peak because of rapid ligand exchange. As the temperature is increased from  $-110$  to  $-70^\circ\text{C}$  in the (methyldiphenylphosphine)copper tetrahydroborate complex, the resonance remains as a singlet and moves slightly upfield (from 15.7 to 16.6 ppm upfield from 85%  $\text{H}_3\text{PO}_4$ ).

**Conductivity Data.** Conductivity data have been reported on similar complexes,<sup>4,14</sup> and one may compare our data (Table II, Figure 2) with them. The larger values of the (ethoxycarbonyl)trihydroborate complexes compared to those for the tetrahydroborate complexes at comparable concentrations are consistent with the previously observed phenomenon that the (ethoxycarbonyl)trihydroborate ion is less strongly coordinated to the metals than is tetrahydroborate.<sup>4</sup> Infrared and dissociation data also support the latter. The exception to the observation that the equivalent conductance for the singly bridging complexes is higher than for the doubly bridging complexes is the complex designated as  $(\text{CH}_3\text{Ph}_2\text{P})_3\text{CuBH}_4$ , which has about the same conductivity as the doubly bridging triphenylphosphine complex. Molecular weight and IR studies in  $\text{CHCl}_3$  show that at comparable concentrations this complex actually exists as nearly completely the bis(phosphine) species. Dissociation of phosphine in acetonitrile would account for the lower than expected conductivity. All of the tris singly bridging complexes dissociate in this manner but to a lesser extent. Therefore the conductivity data for them are a function of the actual concentration of the species as well as their ionic character. In conjunction with this, it is noted that the equivalent conductance is increased substantially by addition of excess phosphine ligand to the tris complexes (Figure 2). This is nicely rationalized by the argument that addition of excess phosphine increases the concentration of tris(phosphine)monodentate species, for which the conductivity is higher. In fact, even for those complexes which crystallize with the bidentate mode of anion coordination, an increase in conductivity is observed upon addition of excess phosphine, thereby suggesting formation of some tris complex.<sup>4</sup>

**Neutral Ligand Dissociation.** Studies on transition-metal phosphine complexes have shown phosphine dissociation to be dependent on steric and electronic properties.<sup>4,9,5-17</sup> Results of vapor pressure osmometric studies in  $\text{CHCl}_3$  at  $37^\circ\text{C}$  are given in Table III.  $K_{\text{diss}} = [\text{L}][\text{L}_2\text{MH}_2\text{BH}_2]/[\text{L}_3\text{MHBH}_3]$  and is a measure of the dissociation of the tris complex to give the

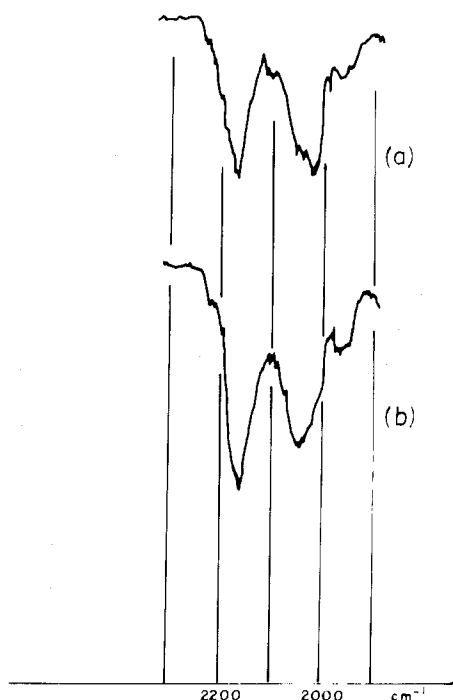
(12) (a) Beall, H.; Bushweller, C. H.; Dewkett, W. J.; Grace, M. *J. Am. Chem. Soc.* **1970**, *92*, 3484. (b) Marks, T. J.; Shimp, L. A. *Ibid.* **1972**, *94*, 1542. (c) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263. (d) Beall, H.; Bushweller, C. H. *Ibid.* **1973**, *73*, 465.  
(13) Muetterties, E. L.; Alegranti, C. W. *J. Am. Chem. Soc.* **1970**, *92*, 4114.

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(15) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956.

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(17) Muetterties, E. L.; Peet, W. G.; Wegner, P. A.; Alegranti, C. W. *Inorg. Chem.* **1970**, *9*, 2447.



**Figure 3.** Infrared spectrum of  $(\text{MePh}_2\text{P})_3\text{CuH}_3\text{BCOOC}_2\text{H}_5$  in  $\text{CHCl}_3$ : (a) 0.04 g/mL of solvent, 0.3-mm sample thickness and matching reference cell; (b) 0.6 g/mL of solvent, 0.05-mm sample thickness and matching reference cell.

bis complex. The small difference in degree of ligand dissociation as indicated by the observed molecular weight compared to the calculated formula weight for bis(triphenylphosphine) complexes<sup>4</sup> is in direct contrast to the values obtained for the tris(diphenylmethylphosphine) complexes. For triphenylphosphine complexes steric interaction is the dominant consideration in ligand dissociation to give essentially only the bis attachment. The assumption that steric forces lessen as the cone angles become smaller is supported by studies conducted by Lippard and Mayerle,<sup>9</sup> which showed that ligand dissociation was greatly affected for the complexes  $\text{L}_3\text{CuX}$  upon going from triphenylphosphine to methyl-diphenylphosphine but not significantly changed by substitution of dimethylphosphine for methyl-diphenylphosphine.

That the ligand dissociative process is the major process occurring in solution is supported not only by the IR data presented for the tetrahydroborate-copper complex<sup>2</sup> but also by the IR data for the (ethoxycarbonyl)tri-hydroborate-copper complex. As with the tetrahydroborate complex, absorptions of the (ethoxycarbonyl)tri-hydroborate complex change with increasing dilution. A gradual shift of the terminal B-H stretching mode to higher frequency and the bridging B-H mode to lower frequency occurs. For  $(\text{MePh}_2\text{P})_3\text{CuH}_3\text{BCOOC}_2\text{H}_5$ , the frequencies at a concentration of 0.6 g/mL of solvent in chloroform are  $\nu(\text{B-H}_t)$  2320 and  $\nu(\text{B-H}_b)$  2090  $\text{cm}^{-1}$ , and at 0.04 g/mL of solvent they are 2340 and 2050  $\text{cm}^{-1}$ , respectively (see Figure 3 for comparison of the two spectra). For  $(\text{MePh}_2\text{P})_3\text{CuBH}_4$  the frequencies at 0.7 g/mL of solvent in chloroform are  $\nu(\text{B-H}_t)$  2300 (with a shoulder) and  $\nu(\text{B-H}_b)$  2035  $\text{cm}^{-1}$  (singlet), and at 0.04 g/mL of solvent they are 2345 (with a shoulder) and 2010  $\text{cm}^{-1}$  (with a shoulder), respectively. These shifts in the absorption maxima as well as the number of peaks can logically be attributed to a change in the relative concentration of the monodentate and bidentate species in solution. Group-theoretical calculations by Marks et al.<sup>11</sup> predict such changes for  $\text{BH}_4^-$ , and many of these predictions can be extended to  $\text{H}_3\text{BCOOC}_2\text{H}_5^-$  with little difficulty. The B-H absorptions are broad enough and close enough together that the individual absorptions are not

resolved, but the position of the composite maximum is dependent upon their relative intensities. The direction of the resultant shifts with dilutions is consistent with increased neutral ligand dissociation and the subsequent increase in concentration of the doubly bridging species.

Also supporting the ligand dissociative process are the  $K_{\text{diss}}$  values obtained within the precision capabilities of the technique. Thus the major equilibrium for systems in which the tris(phosphine) single-hydrogen bridge complex is a major constituent is dissociation of the phosphine ligand from the tris complex with subsequent formation of the doubly bridged hydrogen complex and the reverse process involving formation of the singly bridged species by addition of a phosphine.

Relative  $K_{\text{diss}}$  values may be rationalized by contributions from both steric and electronic factors. From a comparison of the  $K_{\text{diss}}$  of the  $\text{Ph}_3\text{P}$  to the  $\text{CH}_3\text{Ph}_2\text{P}$  complexes it is obvious that the  $\text{Ph}_3\text{P}$  tends to dissociate from a given tris complex to a greater extent that does  $\text{CH}_3\text{Ph}_2\text{P}$  as would be predicted if the degree of steric interaction is the predominant factor differentiating ligand-metal bond strength for these two ligands. Tolman has found this to be true for Ni(0) complexes as well.<sup>16</sup> Also consistent with steric interactions being predominant for  $\text{Ph}_3\text{P}$  complexes is that there is a large difference in the dissociation constant of  $(\text{Ph}_3\text{P})_3\text{AgBH}_4$  and  $(\text{Ph}_3\text{P})_3\text{AgH}_3\text{BCO}_2\text{C}_2\text{H}_5$ , whereas the difference in the value of  $(\text{CH}_3\text{Ph}_2\text{P})_3\text{AgBH}_4$  and  $(\text{CH}_3\text{Ph}_2\text{P})_3\text{AgH}_3\text{BCO}_2\text{C}_2\text{H}_5$  is small. The greater difference in  $K_{\text{diss}}$  for  $(\text{CH}_3\text{Ph}_2\text{P})_3\text{CuBH}_4$  and  $(\text{CH}_3\text{Ph}_2\text{P})_3\text{CuH}_3\text{BCO}_2\text{C}_2\text{H}_5$  as compared to the difference for the corresponding silver complexes may be ascribed to the ability of the larger silver to more easily accommodate the phosphines. The results for the copper triphenylphosphine (existing essentially as bidentates) compared to the diphenylmethylphosphine complexes are reasonable since a similar effect is observed for the tris(phosphine)copper(I) halides:<sup>9</sup> dissociation decreases in the order  $\text{Cl} > \text{Br} > \text{I}$  with the differences being most pronounced for  $(\text{Ph}_3\text{P})_3\text{CuX}$  complexes and being of smaller magnitude as methyl-substituted phosphines replace  $\text{Ph}_3\text{P}$ . To summarize: the data from Table III show that for the tetrahydroborate and (ethoxycarbonyl)tri-hydroborate complexes, dissociation decreases in the order  $\text{BH}_4^- > \text{H}_3\text{BCOOC}_2\text{H}_5^- > \text{H}_3\text{BCOOH}^-$  for the  $\text{Ph}_3\text{P}$  silver complexes and  $\text{BH}_4^- > \text{H}_3\text{BCOOC}_2\text{H}_5^-$  for the (methyl-diphenylphosphine)silver and -copper complexes with greater differences observed for triphenylphosphine complexes compared to methyl-diphenylphosphine complexes and for methyl-diphenylphosphine complexes of copper compared to those of silver. Thus it appears that for complexes in which the metal-phosphine bond strengths are significantly affected by steric repulsions, small differences in the coordinating anion also have a large effect upon the phosphine-metal interaction. This could be viewed as the result of perturbations of the metal-complexing orbitals by the anion. The effect of these perturbations upon phosphine dissociation would be greater in the highly strained complexes where the factors that determine bond stability are at a critical level. Comparison of phosphine dissociation of other  $\text{BH}_4^-$  and  $\text{H}_3\text{BCOOC}_2\text{H}_5^-$  as well as halide complexes suggests that the higher the electron density on the coordinating portion of the anion, the more neutral ligand dissociation will occur.<sup>4,18</sup>

Upon comparison of  $K_{\text{diss}}$  for  $\text{CH}_3\text{Ph}_2\text{P}$  complexes only it is found that the extent of ligand dissociation is  $\text{L}_3\text{CuBH}_4 > \text{L}_3\text{AgBH}_4 \approx \text{L}_3\text{AgH}_3\text{BCOOC}_2\text{H}_5 > \text{L}_3\text{CuH}_3\text{BCOOC}_2\text{H}_5$ . This trend cannot be explained by steric interaction among the phosphines in conjunction with strength of interaction between the metal and the anions, since  $\text{L}_3\text{AgH}_3\text{BCOOC}_2\text{H}_5 > \text{L}_3\text{CuH}_3\text{BCOOC}_2\text{H}_5$ . If, however, the Ag-P bond is in-

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herently weaker than the Cu-P bond, which is consistent with the expected relative polarizing capability of the two metals, one might expect the trend to be  $L_3AgBH_4 > L_3AgH_3BCOOC_2H_5 > L_3CuBH_4 > L_3CuH_3BCOOC_2H_5$ . Transposition of the  $L_3CuBH_4$  to the position of greatest dissociation to give the observed trend is reasonable if  $BH_4^-$  interacts much more strongly with copper(I) than with silver(I) and thus forms a significantly more stable bidentate complex with copper than with silver. The results are that the (ethoxycarbonyl)tri-hydroborate interaction is sufficiently weaker that it does not affect dissociation to the extent that  $BH_4^-$  does and the difference in stability between bidentate copper and silver (ethoxycarbonyl)tri-hydroborate complexes is not great enough to

be the determining factor in ligand dissociation for these two complexes.

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**Registry No.**  $(MePh_2P)_3CuBH_4$ , 63371-86-8;  $(MePh_2P)_3AgBH_4$ , 72347-03-6;  $(MePh_2P)_3CuBD_4$ , 72347-04-7;  $(MePh_2P)_3-CuH_3BCO_2C_2H_5$ , 72347-05-8;  $(MePh_2P)_3AgH_3BCO_2C_2H_5$ , 72347-06-9;  $(Ph_3P)_2CuBH_4$ , 16903-61-0;  $(Ph_3P)_2AgBH_4$ , 16902-95-7.

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## Relative Proton Affinities of 1,6- $C_2B_4H_6$ and 2,4- $C_2B_3H_7$

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The ion-molecule reactions of the *closo*-carboranes 1,6- $C_2B_4H_6$  and 2,4- $C_2B_3H_7$  have been investigated by using pulsed ion cyclotron resonance (ICR) methods. Condensation reactions of the parent ion with itself are observed with loss of  $H_2$  for both molecules. Condensation of 1,6- $C_2B_4H_6$  with protonated acetone is observed again with loss of  $H_2$ . Proton affinities (PA) of the two carboranes were determined by bracketing techniques giving  $PA(1,6-C_2B_4H_6) = 208 \pm 4$  kcal/mol and  $PA(2,4-C_2B_3H_7) = 173 \pm 1$  kcal/mol. The large difference in proton affinities is attributed to the fact that the molecule  $CB_3H_7$  which is isoelectronic to  $C_2B_4H_7^+$  is known while the molecule  $CB_6H_8$  which is isoelectronic to  $C_2B_3H_8^+$  is not known.

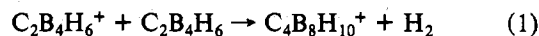
The chemistry of electron-deficient compounds has provided many insights into systems that contain novel bonding features.<sup>1</sup> The best characterized compounds of this type are the boranes and the carboranes.<sup>2</sup> The *closo*-dicarboranes belong to this class of compounds and form neutral closed polyhedra. A variety of experimental<sup>2</sup> and theoretical studies<sup>3</sup> have been made on these systems including mass spectral studies on both the positive<sup>4</sup> and negative ions<sup>5</sup> created by electron impact. The positive ion spectra for the carboranes have been compared to the spectra obtained for similar boranes.<sup>4</sup> We present in this paper a study of some of the gas-phase ion chemistry of the *closo*-carboranes 1,6- $C_2B_4H_6$  and 2,4- $C_2B_3H_7$ . A number of ion cyclotron resonance (ICR) studies<sup>6</sup> and chemical ionization mass spectral studies<sup>7</sup> of small boranes have previously been carried out but this study represents the first study of closed polyhedral systems.

The ICR studies were carried out on the trapped ion ICR apparatus at the California Institute of Technology by using experimental techniques that have previously been discussed in detail.<sup>8</sup> The carboranes were obtained in purified form from Professor T. Onak (California State College at Los Angeles). The carboranes and the other chemicals which were readily available reagent grade materials were subjected to freeze-pump-thaw cycles to remove noncondensable impurities.

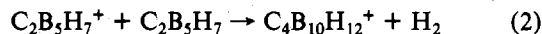
The mass spectra for the carboranes are in good agreement with those published in the literature.<sup>4</sup> Complications due to the presence of two boron isotopes ( $^{11}B/^{10}B = 4.0$ ) have previously been discussed.<sup>4</sup> For compounds with four borons, the peaks containing the  $^{11}B_4$  and  $^{11}B_3^{10}B$  moieties are the most intense and are of comparable height while, for compounds with five borons, the peak containing the  $^{11}B_4^{10}B$  moiety is the most intense with the peak containing the  $^{11}B_5$  moiety having the second highest intensity. Thus, it is relatively straight-

forward to observe the  $P + 1$  peaks associated with the  $^{11}B_4$  and  $^{11}B_5$  parent ion peaks. The previous positive ion mass spectra have been analyzed in terms of the isotopic content of the ion and it was shown that the dominant ion in the 2,4- $C_2B_3H_7$  spectrum is the parent ion while the  $P - 1$  ion is the dominant ion for the 1,6- $C_2B_4H_6$  spectrum; the parent ion for this latter compound still has considerable intensity.

A general feature of the mass spectrum taken at long reaction time is the observation of condensation reactions. The isotopic patterns for eight borons make it more difficult to unravel the data but the general reaction for the 1,6- $C_2B_4H_6$  system is condensation with loss of  $H_2$



This reaction has been confirmed by double resonance studies. For the 2,4- $C_2B_3H_7$  system a similar condensation reaction, again with loss of  $H_2$ , is also observed



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