lutidine with triethylalane have been reported as calorimetrically determined in *n*-decane.[24] For $(C_2H_5)_3Al \cdot NC_5H_5$, $\Delta H_f = -21.2$ kcal/mole, and for $(C_2H_5)_3Al \cdot NC_5H_3(CH_3)_2$, $\Delta H_f = -18.0$ kcal/mole. These enthalpy values do not include a correction for the enthalpy of dimerization of triethylalane. This value has been reported as -16.93 ± 0.23 kcal/mole in hexadecane.[25] Since triethylalane is about 10–11% dissociated in a hydrocarbon solvent at ambient temperatures, one can only calculate the maximum enthalpy value by making the correction based on 100% dimerization of the triethylalane. Corrected in this way, these enthalpies become -29.7 kcal/mole for pyridine and -26.5 kcal/mole for 2,6-lutidine. These are surprising results since it is expected that triethylalane would have significantly larger frontal interaction than trimethylalane. The pyridines are generally weaker donors toward trimethylalane than the methylamines or ammonia but are comparable to the ethylamines.

Phosphorus Donors.—Toward trimethylalane the sequence of interaction of phosphines is: $P(C_2H_5)_3 > P(CH_3)_2 > P(C_6H_5)_3$. The enthalpy reported for the trimethylborane–trimethylphosphine adduct is much less than that observed here for trimethylalane.[20] The difference is probably due to larger steric interactions in the borane case. Steric requirements in the trimethylalane–phosphine adducts seem to be small since the greater inductive effect of the ethyl group is manifested in a larger enthalpy. The much lower enthalpy of the trimethylalane–triphenylphosphine adduct is probably due to inductive effects since the frontal strain effect is not expected to be much larger than that in the triethylphosphine adduct. The observation of little or no frontal steric interaction in trimethylalane–phosphine adducts is most likely ascribable to the comparatively long dative bond. This is to be expected in view of previous studies which indicate little or no frontal steric effects in trimethylalane–sulfide adducts.[6]

Oxygen Donors.—The donor abilities of the three tetrahydrofurans are virtually indistinguishable toward trimethylalane. Examination of molecular models reveals the methyl substituents are pinned away from the alane acceptor greatly reducing steric interaction. Diethyl ether and dimethyl ether are indistinguishable in their interaction with trimethylalane. The trimethylborane–dimethyl ether adduct does not exist for steric reasons,[26] but apparently the lower steric requirement of trimethylalane allows the quite stable adduct to form. A substantial difference is observed in the enthalpy of adduct formation of diethyl and dimethyl ethers with the acid boron trifluoride, with dimethyl ether being the stronger base.[27] Also tetrahydrofuran is a stronger base than dimethyl ether toward boron trifluoride[28] as is found in this study with trimethylalane.

The enthalpies of adduct formation of a number of aliphatic and alicyclic sulfides with trimethylalane in hexane have been reported.[6] The sulfides as a class were observed to be weaker donors toward trimethylalane than the ethers. The order of donor strengths $O > S$ and $N > P$ is found in previous work with trimethylborane and is observed in this work with trimethylalane. Over-all, the following sequence of decreasing basicity of the alkylated donors toward trimethylalane in hexane is observed: $N > P \geq O > S$.

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Transition Metal Borohydride Complexes. II.[1] The Reaction of Copper(I) Compounds with Boron Hydride Anions

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The reaction between solutions containing $(R_3Y)_nCuCl$ and $NaBH_4$, where R is an alkyl or aryl group and Y is P, As, or Sb, has been investigated. In those cases where Y is phosphorus and R an aryl group (C_6H_5, *p*-$CH_3C_6H_4$, *m*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$), stable crystalline borohydride complexes of composition $(R_3Y)_2Cu(BH_4)$ could be isolated. With trialkylphosphine, triphenylarsine, and triphenylstibine ligands under identical conditions, decomposition, rather than complex formation, occurred. Similar studies of the reaction between $[(C_6H_5)_3Y]_mCuCl$ compounds and CsB_3H_8 yielded complexes $[(C_6H_5)_3Y]_nCu(B_3H_8)$ for Y = P ($n = 2$), As ($n = 2$), and Sb ($n = 3$). The results of infrared spectral and other physical studies of the new complexes are presented and discussed in terms of their molecular structures. Possible factors influencing the course of the reaction of copper(I) compounds with the borohydride ion are set forth.

Introduction

The borohydride ion, BH_4^-, is one of the more common inorganic reducing agents. It is therefore of considerable interest to establish the stereochemical and electronic principles which are operative when

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[1] Part I: S. J. Lippard and K. M. Melmed, *J. Am. Chem. Soc.*, **89**, 3929 (1967); *Inorg. Chem.*, **6**, 2223 (1967).

TABLE I

ANALYTICAL RESULTS FOR COPPER(I) BORON HYDRIDE COMPLEXES

	% C		% H		% X		
Complex	Calcd	Found	Calcd	Found	Calcd	Found	Mp (dec), °C
$[(C_6H_5)_3P]_2Cu(BH_4)$[a]	71.6	71.9	5.63	5.85	1.79	1.13[b]	165–166
$[(p\text{-}CH_3C_6H_4)_3P]_2Cu(BH_4)$	73.4	72.4	6.70	6.90	9.02	9.38[c]	169–172
$[(m\text{-}CH_3C_6H_4)_3P]_2Cu(BH_4)$	73.4	72.6	6.70	6.58	9.02	9.18[c]	147–151
$[(p\text{-}CH_3OC_6H_4)_3P]_2Cu(BH_4)$	64.4	63.9	5.88	6.49	7.91	7.64[c]	165–168
$[(C_6H_5)_3P]_2Cu(B_3H_8)$[d]	68.9	68.5	6.05	6.23	9.87 5.16	9.82[c] 5.19[b]	159–161
$[(C_6H_5)_3As]_2Cu(B_3H_8)$	60.3	59.8	5.36	5.56	...	...	145–151
$[(C_6H_5)_3Sb]_3Cu(B_3H_8)$	55.8	55.3	4.60	4.18	...	...	130–135

[a] This compound has been previously prepared by other workers.[7,8] [b] X = boron. [c] X = phosphorus. [d] The preparation of this compound was reported in a preliminary communication.[19]

BH_4^- interacts with other chemical species. Although occasional attempts to investigate these factors have appeared in the literature,[2] surprisingly little is known. A number of workers have succeeded in isolating stable transition metal borohydride complexes.[3–16] Because of the potential utility of these complexes as models for understanding the detailed manner in which BH_4^- acts as a reducing agent, we have been studying their chemical and structural properties.

Of the various known transition metal borohydride complexes, $L_2Cu(BH_4)$ compounds are among the simplest to prepare.[7,8] Previously, we have described[1] the crystal and molecular structure of one such compound, $[(C_6H_5)_3P]_2Cu(BH_4)$, in which the borohydride group is bonded to the copper atom through two hydrogen atoms. The present work was carried out in order to examine the effects of modifying the stereochemical and electronic properties of the ligands L on the chemical stability of the copper–borohydride attachment. Similarly, we were interested to discover whether modifications of the BH_4^- group itself, as described below, would lead to any significant changes in the chemical behavior of this system. The results have provided new information concerning the factors which determine the course of the reaction of Cu(I) complexes with the borohydride ion.

Experimental Section

All compounds were prepared from the highest purity chemicals available. Sodium borohydride and sodium borodeuteride were obtained from Metal Hydrides and Alfa Inorganics, respectively, and stored in a desiccator when not in use. Cesium octahydrotriborate was generously provided by Dr. Klanberg of Du Pont. Tri-*p*-anisylphosphine was prepared according to a modification of the method of Mann and Chaplin,[17] isolated as suggested by Senear, Valient, and Wirth,[18] and recrystallized from methanol. Tricyclohexylphosphine was kindly donated by Dr. Steven Roman of Columbia University. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Melting points reported are uncorrected. Molecular weights were determined at 37° using a Mechrolab vapor pressure osmometer calibrated with benzil.

Copper–Borohydride Complexes, $L_2Cu(BH_4)$.—All copper–borohydride complexes reported in Table I were prepared at room temperature by a modification of the method devised by Cariati and Naldini[8] for $[(C_6H_5)_3P]_2Cu(BH_4)$. In each case, 4 mmol of ligand (L) was dissolved in 50 ml of chloroform. To this solution was then added 1 mmol (0.099 g) of anhydrous copper(I) chloride. After being stirred for 30 min, most of the cuprous chloride had dissolved. The solution was filtered and 2 mmol (0.076 g) of sodium borohydride in ~10 ml of ethanol was stirred with the filtrate for 1 hr. Addition of 200 ml of ethanol followed by cooling gave a precipitate which was recrystallized from chloroform–ethanol. Yields ranged from 50 to 80%. The products are white, crystalline materials, soluble in chloroform, benzene, and acetone and insoluble in ethanol, water, ether, and hexane. The deuterated complex, $[(C_6H_5)_3P]_2Cu(BD_4)$, was obtained by the method of Cariati and Naldini[8] in which sodium borodeuteride was substituted for sodium borohydride.

Attempts to prepare stable copper–borohydride complexes by the above method for L = $(n\text{-}C_4H_9)_3P$, $(n\text{-}C_8H_{17})_3P$, $(c\text{-}C_6H_{11})_3P$, $(o\text{-}CH_3C_6H_4)_3P$, $(C_6H_5)_3As$, and $(C_6H_5)_3Sb$ were unsuccessful. In each case hydrogen was evolved and a black solid formed immediately.

$Cu\text{-}B_3H_8^-$ Complexes, $L_nCu(B_3H_8)$.[19]—Stable crystalline complexes (Table I) were prepared by mixing 50 ml of an acetone solution containing 2 mmol of L_nCuCl (prepared as described below) with 4 mmol (0.69 g) of CsB_3H_8 in 50 ml of acetone, stirring for 30 min at room temperature, and then adding water until the white precipitate formed did not redissolve when the solution is swirled. After cooling the solution to 0°, filtration gave white crystals which were washed with ethanol. The complex $[(C_6H_5)_3P]_2Cu(B_3H_8)$ could be recrystallized from chloroform–ethanol, but the arsine analog slowly decomposed in these media. A chloroform solution of the crude stibine product, which was slightly yellow, was decolorized with Norit and recrystallized by adding ethanol and cooling. Analysis of this material showed it to be the $[(C_6H_5)_3Sb]_3Cu(B_3H_8)$ complex. Yields ranged from 70 to 90%. The compounds are soluble in chloroform, acetone, DMF, and acetonitrile and insoluble in ethanol and water.

Molecular weight measurements were performed for the phosphine and arsine complexes dissolved in benzene (the stibine analog was insufficiently soluble for such a determination) with

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(2) See, for example, K. M. Mochalov and V. S. Khain, *Zh. Fiz. Khim.*, **39**, 1960 (1965).

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the results: Calcd for $[(C_6H_5)_3P]_2Cu(B_3H_8)$: 629. Found: 624. Calcd for $[(C_6H_5)_3As]_2Cu(B_3H_8)$: 714. Found: 730.

$[(C_6H_5)_3Y]_mCuCl$ Compounds, Y = P, As, Sb.—These compounds were used to prepare the $B_3H_8^-$ complexes, as previously indicated. Cariati and Naldini describe the preparation of $[(C_6H_5)_3P]_3CuCl$,[8] which we were able to reproduce. A detailed procedure for obtaining this compound, not available in the original literature, follows. A solution containing 0.05 mol (13.1 g) of triphenylphosphine in 100 ml of chloroform is stirred for 30 min with 0.013 mol (1.23 g) of CuCl. Addition of 400 ml of ethanol to the filtered solution yields, upon standing, 7 g (80%) of tris(triphenylphosphine)copper(I) chloride.

Anal. Calcd for $C_{54}H_{45}P_3CuCl$: C, 73.2; H, 5.12; P, 10.49. Found: C, 72.4; H, 5.31; P, 10.75. As reported by the original workers,[8] solutions of this material have low molecular weights, which is probably indicative of ligand dissociation. Accordingly, attempts to recrystallize the product yielded materials which were analytically unsatisfactory. Found for product recrystallized from chloroform–ethanol: C, 65.3; H, 4.50; P, 9.25. The unrecrystallized product was used in the preparation of the $B_3H_8^-$ complex. A similar procedure in which triphenylstibine is used in place of triphenylphosphine yielded tris(triphenylstibine)copper(I) chloride. *Anal.* Calcd for $C_{54}H_{45}Sb_3CuCl$: C, 56.0; H, 3.92. Found: C, 55.1; H, 3.70 (for the crude product); C, 56.1; H, 4.12 (for the product recrystallized once from chloroform–ethanol). An attempt to prepare the arsine analog by the same procedure gave, after recrystallization, a product which analyzed as $[(C_6H_5)_3As]CuCl$. *Anal.* Calcd for $C_{18}H_{15}AsCuCl$: C, 53.4; H, 3.73. Found: C, 53.4; H, 3.77. The crude product from the reaction mixture analyzed, before recrystallization, as something best approximated by the formula $[(C_6H_5)_3As]_2CuCl$. *Anal.* Calcd for $C_{36}H_{30}As_2CuCl$: C, 60.8; H, 4.21. Found: C, 59.3; H, 4.16. However, this may well have been a mixture of tris- and mono(triphenylarsine)copper(I) chloride compounds. As with the phosphine the crude arsine and stibine products were used to prepare the $B_3H_8^-$ complexes.

Stability of $B_3H_8^-$ Complexes in Solution.—The following qualitative observations were noted. A mixture of cuprous chloride and CsB_3H_8 in 1:1 acetone–chloroform slowly decomposes on standing at room temperature, whereas immediate decomposition occurs when $NaBH_4$ is added to the solution. The complexes $[(C_6H_5)_3Y]_nCu(B_3H_8)$ were dissolved in 1:1 chloroform–acetone solutions (0.01 *M*), and for Y = As and Sb, there was slow decomposition at 24°, whereas for Y = P, no decomposition could be observed, even at 60°. Aliquots of the phosphine-containing solutions left at 24° were observed to be unchanged upon standing for 24 hr. In each case described above, decomposition was characterized by the release of hydrogen gas and the precipitation of a black metallic solid, presumably Cu(0).[7]

Physical Measurements.—Infrared spectra were obtained with a Perkin-Elmer 621 grating instrument in the range 4000–250 cm^{-1} for all compounds. Samples were either mulled in Nujol, pressed into KBr disks, or dissolved in chloroform. Each spectrum was run at least twice and the frequencies reported are considered to be accurate to better than ±4 cm^{-1}. Electrolytic conductance measurements were carried out over a concentration range using an Industrial Instruments conductivity bridge with a 30-cc cell equipped with platinum electrodes at 25 ± 2°.

Results and Discussion

The L–Cu–(BH_4) System.—When an ethanol solution of sodium borohydride is added to the solution obtained by mixing ligand (L) and copper(I) chloride (4:1) in chloroform at 25°, one of two reaction pathways is observed, depending upon the nature of L. When L is a triarylphosphine, in particular triphenylphosphine, tri-*p*-tolylphosphine, tri-*m*-tolylphosphine, or tri-*p*-anisylphosphine, a stable copper(I) borohydride complex of composition $L_2Cu(BH_4)$ forms, which can be precipitated from the solution upon addition of ethanol. When L is a trialkylphosphine (*e.g.*, tri-*n*-butylphosphine, tricyclohexylphosphine, or tri-*n*-octylphosphine), triphenylarsine, triphenylstibine, or the sterically hindered tri-*o*-tolylphosphine, addition of borohydride causes a rapid darkening of the solution which is accompanied by the evolution of hydrogen and, eventually, precipitation of a dark, metallic solid, presumably copper.[7] Apart from the four compounds described above, the only other known copper(I) borohydride complex is $(dpe)Cu(BH_4)$,[20] which can apparently be prepared in an ethanol–benzene reaction mixture,[8] although we have had to modify the published procedure to obtain this compound. Attempts to extend the number of copper(I) borohydride complexes with the ligands mentioned previously by working in different solvent media and by trying ligand-exchange reactions have thus far been unsuccessful. Discussion of the factors influencing the course of the reaction will be taken up later.

The complexes $L_2Cu(BH_4)$ dissolve in various solvents to form nonconducting solutions from which they may be recrystallized. The solid-state structure of borohydridobis(triphenylphosphine)copper(I) has been determined by X-ray diffraction.[1] Noteworthy is the mode of attachment of the borohydride ion to the copper atom through two protons (Figure 1a). In Table II we summarize the solid-state and chloroform solution infrared spectral bands for various $L_2Cu(BH_4)$ complexes in the B–H stretching frequency region. Typical spectra are displayed in Figure 2 for L = triphenylphosphine. From the table it is apparent that the spectra are all qualitatively very similar. This result strongly suggests that the compounds tabulated have

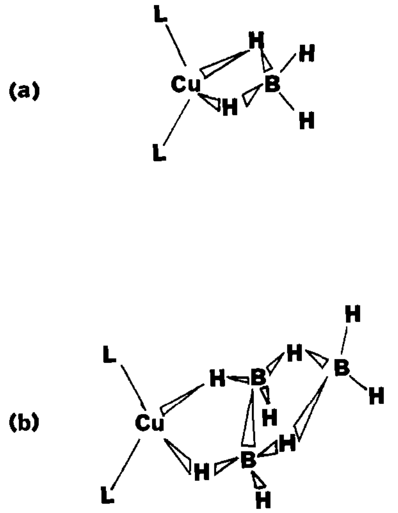

Figure 1.—(a) Sketch of the structure[1] of borohydridobis(triphenylphosphine)copper(I) showing the mode of attachment of the borohydride ion to the copper atom. (b) Sketch of the structure (S. J. Lippard and K. M. Melmed, to be submitted for publication) of octahydrotriboratobis(triphenylphosphine)copper(I) showing the mode of attachment of the octahydrotriborate ion to the copper atom. In both drawings, L represents triphenylphosphine.

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(20) dpe = 1,2-bis(diphenylphosphino)ethane.

TABLE II

SUMMARY OF INFRARED SPECTRAL BANDS FOR $L_2Cu(BH_4)$ COMPLEXES IN THE B–H STRETCHING FREQUENCY REGION

Complex	Frequency, cm^{-1}					Ref
			Nujol Mulls[a]			
$[(C_6H_5)_3P]_2Cu(BH_4)$	2392 s	2350 sh	2262 w	1984	1924	*b*
	2420 vs	2400 s	2290 w	2010	1932	*f*
	2385	2353	. . .	2001	1959	*g*
$[(p\text{-}CH_3OC_6H_4)_3P]_2Cu(BH_4)$	2385 s	2350 sh	2270 w, sh	2005	1961	*b*
$[(p\text{-}CH_3C_6H_4)_3P]_2Cu(BH_4)$	2382 s	2343	2245 w	1990	1930	*b*
$[(m\text{-}CH_3C_6H_4)_3P]_2Cu(BH_4)$	2380 s	2343 sh	2240 w	2018	1944	*b*
$(dpe)Cu(BH_4)$[c]	2380 vs	2360 s	. . .	2010	. . .	*f*
$[(C_6H_5)_3P]_2Cu(BD_4)$	1821 w[d]	1805 s[e]	1760 w, sh[d]	1745[e]	1682 vw	*b*
			Chloroform Solutions			
$[(C_6H_5)_3P]_2Cu(BH_4)$	2385 s	2350 sh	2250 w	2008	1955	*b*
	2385	2353	. . .	2001	1959	*g*
$[(p\text{-}CH_3OC_6H_4)_3P]_2Cu(BH_4)$	2385 s	2350 sh	2250 w	2010	1950 w, sh	*b*
$[(p\text{-}CH_3C_6H_4)_3P]_2Cu(BH_4)$	2386 s	2351	. . .	2005	. . .	*b*
$[(m\text{-}CH_3C_6H_4)_3P]_2Cu(BH_4)$	2382 s	2350	2250 w	2009	1947	*b*

[a] s, strong; w, weak; v, very; sh, shoulder; . . . means not reported or, if referenced to this work, unobserved. [b] This work. [c] dpe = 1,2-bis(diphenylphosphino)ethane. [d] ^{10}B–H. [e] ^{11}B–H. [f] See ref 8. [g] See ref 7.

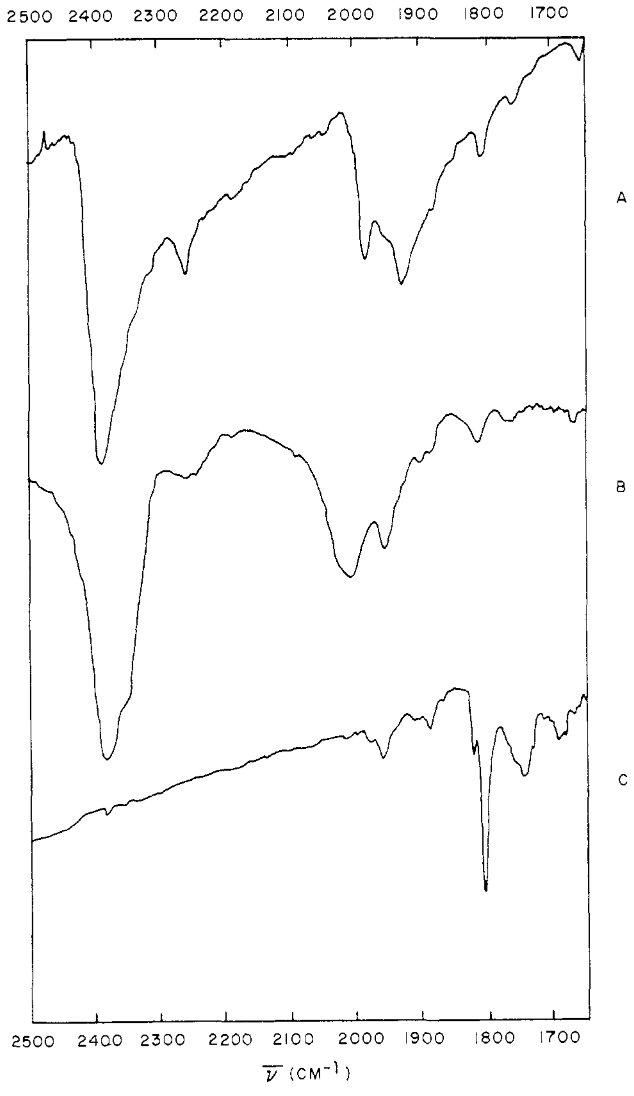

Figure 2.—Infrared spectra in the B–H stretching frequency region of (A) $[(C_6H_5)_3P]_2Cu(BH_4)$ mulled in Nujol, (B) $[(C_6H_5)_3P]_2Cu(BH_4)$ dissolved in chloroform, and (C) $[(C_6H_5)_3P]_2Cu(BD_4)$ mulled in Nujol.

the same type of metal–borohydride attachment as displayed in Figure 1a for $[(C_6H_5)_3P]_2Cu(BH_4)$. Conclusions about the latter compound may therefore be assumed to apply to the others as well.

Davidson[7] has assigned the infrared absorption bands at 2385 and 2353 cm^{-1} to terminal B–H stretching modes and the bands at 2001 and 1959 cm^{-1} to the bridging modes for borohydridobis(triphenylphosphine)-copper(I) (Table II). An alternative assignment[8] of the infrared spectrum of this molecule identifies only one of the two bands in the 1900–2150-cm^{-1} region with a B–H bridging mode, the other being attributed to a combination band, not further defined. The second B–H bridging band is suggested[8] to occur at ~1400–1500 cm^{-1}, a region obscured by ligand vibrations. Although this possibility cannot at present be completely ruled out, the intensity of the two bands at 1900–2150 cm^{-1} (Figure 2) and the failure on our part to detect any new bands in $[(C_6H_5)_3P]_2Cu(BD_4)$ at 1000–1200 cm^{-1} make it less credible than the original[7] assignment. In the infrared spectrum of the deuterated analog, $[(C_6H_5)_3P]_2Cu(BD_4)$ (Table II and Figure 2), the terminal B–D modes may be identified at 1821 (^{10}B–D), 1805 (^{11}B–D), 1760 (^{10}B–D), and 1745 (^{11}B–D) cm^{-1}, whereas the bridging bands are now presumably obscured by triphenylphosphine absorptions. The magnitudes of these shifts are in satisfactory agreement with the values expected on the basis of the change in reduced mass of the oscillators, the calculated and observed (^{11}B–D)/(^{11}B–H) frequency ratios being 0.736 and 0.749 ± 0.005 (average of two values), respectively. The calculated (^{10}B–D)/(^{11}B–D) frequency ratio is 1.008; the average value obtained from the above assignments is 1.009. In Table II may be noted the presence of a weak band in all of the L_2Cu-BH_4 complexes around 2260 cm^{-1}. This may be attributed to an overtone of the BH_2-deformation band occurring for all compounds investigated at ~1130 cm^{-1}. In the deuterated compound the overtone shifts to 1682 cm^{-1} (Table II), a value corresponding to a (^{11}B–D)/(^{11}B–H) frequency ratio of 0.743.

The L–Cu–B_3H_8 System.—In order to define better the stereochemical and electronic effects which determine the course of the interaction of the borohydride ion with copper(I) complexes, we are interested in modifying BH_4^- itself. As has been discussed, the use of BD_4^- in place of BH_4^- represents one such modification. Among other possibilities, we decided[19,21–23] to try $B_3H_8^-$ because of the presence of certain stereochemical[24] and electronic factors which will be outlined in greater detail later.

From chloroform–acetone solutions containing dissolved $[(C_6H_5)_3Y]_mCuCl$ and CsB_3H_8, white crystalline products, $[(C_6H_5)_3Y]_nCu(B_3H_8)$, were isolated upon the addition of water for Y = P (n = 2), As (n = 2), and Sb (n = 3). The presence of acetone and water in the reaction mixture is a variation of the procedure used in the corresponding borohydride reactions since CsB_3H_8 and $NaBH_4$ have somewhat different solubility properties. The difference in composition between the bis-phosphine and -arsine complexes and the tris-stibine complex is not surprising, since the materials used to prepare the first two compounds are apparently much more labile in solution than tris(triphenylstibine)-copper(I) chloride (see the Experimental Section).

Molecular weight measurements of the new octahydrotriborate complexes, $[(C_6H_5)_3P]_2Cu(B_3H_8)$ and $[(C_6H_5)_3As]_2Cu(B_3H_8)$, show them to be monomeric in benzene solution. Conductivity studies of the phosphine complex in chloroform indicate the absence of $B_3H_8^-$ dissociation in this solvent as well. As reported previously,[19] conductivity measurements on acetonitrile solutions of $[(C_6H_5)_3P]_2Cu(B_3H_8)$ over a limited range of concentrations (0.007–0.003 M) seemed consistent with a 2:1 electrolyte, a result which could be rationalized by the trinuclear formulation, $\{[(C_6H_5)_3P]_6Cu_3(B_3H_8)\}(B_3H_8)_2$. Attempts to isolate such a compound from acetonitrile solutions yielded only the starting material. Subsequent extension of the conductivity measurements to higher dilutions (0.003–0.001 M) revealed more complicated behavior, as evidenced by the nonlinearity of plots of Λ_e *vs.* $\sqrt{C}$. These results probably indicate partial dissociation of the $B_3H_8^-$ ion from the complex. The behavior of this octahydrotriborate complex as a weak electrolyte may be contrasted with the corresponding borohydride complex, which is a nonconductor in acetonitrile.

Selected features of the molecular structure of octahydrotriboratobis(triphenylphosphine)copper(I), as determined by an X-ray crystallographic investigation,[25] are set forth in Figure 1b. Of interest is the mode of attachment of the $B_3H_8^-$ group to the copper atom through terminal protons on two different boron atoms. This structure, rather than the one suggested[19] earlier, is apparently the preferred one for $B_3H_8^-$ complexes and has also been found[23] to occur in $[(CO)_4Cr(B_3H_8)]^-$.

Table III contains a summary of both solution and solid-state infrared spectral bands in the B–H stretching frequency region for the copper–octahydrotriborate complexes reported here. Some actual spectra are shown in Figure 3. Comparison of the qualitative features of the spectra (Table III) indicates that the solid phosphine and arsine complexes are structurally similar but different from the stibine complex. This result is consistent with the different chemical composition of the compounds. Of interest are the changes in the complexity of the terminal B–H stretching frequency (2200–2500 cm^{-1}) and bridging B–H stretching frequency (2000–2200 cm^{-1}) regions that occur in going from CsB_3H_8 to $[(C_6H_5)_3P]_2Cu(B_3H_8)$ (Figure 3). These changes are qualitatively consistent with the conversion of two terminal B–H bonds in the salt into bridging B–H bonds in the complex.

TABLE III

INFRARED SPECTRAL RESULTS FOR $[(C_6H_5)_3Y]_nCu(B_3H_8)$ COMPLEXES IN THE B–H STRETCHING FREQUENCY REGION

Y	n	Medium	Frequency, cm^{-1} [a]
P	2	Nujol mull	2495 s, 2462 s, 2418 s, 2370 w, 2100 br, 2045 br
		Chloroform solution	2495 s, 2445 s, . . ., . . ., 2120 br, 2035 br
As	2	Nujol mull	2495 s, 2462 s, 2418 s, . . ., 2100 w, 2000 br
		Chloroform solution	2495 s, 2442, . . ., 2360 vw, 2125 br, 2010 br
Sb[b]	3	Nujol mull	2475 s, 2420, . . ., 2380 sh, 2120 w, . . .

[a] s, strong; w, weak; br, broad; sh, shoulder; v very. [b] Insufficiently soluble for a solution spectrum to be recorded.

Possible Factors Influencing the Reaction Pathway.—The ability of triarylphosphines to stabilize copper(I) borohydride complexes may be attributed to a combination of steric and electronic effects. From the geometric features[1] of borohydridobis(triphenylphosphine)copper(I) it may be argued[25] that the copper atom has suitable orbitals available for back-bonding[26] with the phosphorus d_π orbitals. Further delocalization of charge onto the phenyl rings is also possible, which would account for the different behavior of the aryl- and alkylphosphine copper(I) complexes toward borohydride. The inability of triphenylarsine and triphenylstibine to stabilize copper(I) with respect to reduction to the metal cannot be rationalized solely on the basis of the π-acceptor properties of these ligands compared to triphenylphosphine, however, since phosphorus, arsenic, and antimony are commonly thought[26,27] to be about equally good π-acceptor ligands. One alternative explanation, suggested by the steric interaction between the borohydride and triphenylphosphine ring protons found[1] to occur in the solid-state structure of $[(C_6H_5)_3P]_2Cu(BH_4)$, is that a specific stereochemical attachment of the borohydride

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[21] The potential utility of the octahydrotriborate ion as a ligand for transition metal complexes was first drawn to our attention by a formal proposal of Mr. Peter Stokely (MIT, 1966). Nonionic $B_3H_8^-$ compounds appear to have been $Mg(B_3H_8)_2(THF)_n$ and $Mg(BH_4)(B_3H_8)\cdot5THF$.[22] $B_3H_8^-$ complexes of certain metal carbonyls have also been reported.[23]

[22] S. Heřmánek and J. Plešek, *Collection Czech. Chem. Commun.*, **31**, 177 (1966).

[23] F. Klanberg and L. J. Guggenberger, *Chem. Commun.*, 1293 (1967).

[24] C. R. Peters and C. E. Nordman, *J. Am. Chem. Soc.*, **82**, 5758 (1960).

[25] S. J. Lippard and K. M. Melmed, to be submitted for publication.

[26] See, for example, F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1966, p 745 ff and references cited therein.

[27] E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 2325 (1959).

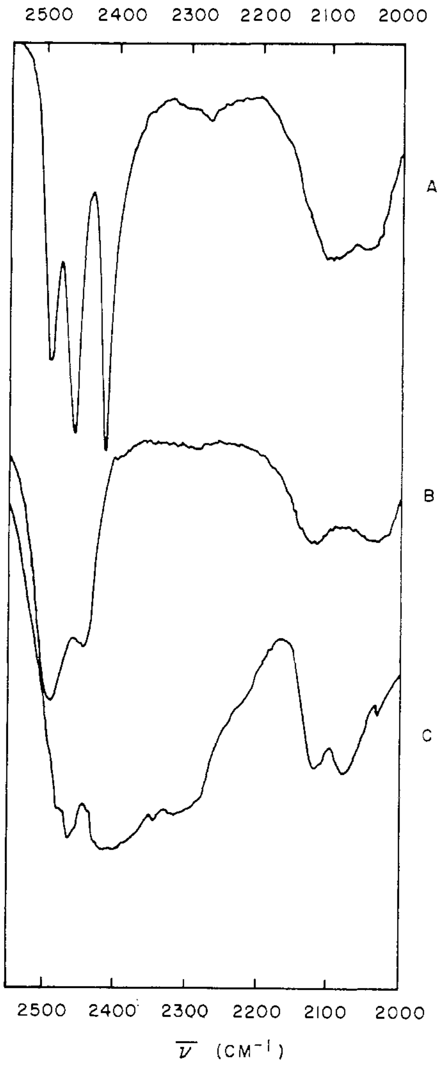

Figure 3.—Infrared spectra in the B–H stretching frequency region of (A) $[(C_6H_5)_3P]_2Cu(B_3H_8)$ mulled in Nujol, (B) $[(C_6H_5)_3P]_2Cu(B_3H_8)$ dissolved in chloroform, and (C) CsB_3H_8 mulled in Nujol.

ion to the copper atom is required for reduction.[28] In the phosphine complex, this attachment might be sterically inhibited by the *ortho* protons on the phenyl rings. Such an interaction would be less likely in the corresponding (hypothetical) arsine and stibine complexes because of the longer Cu–Y and Y–C bond distances.

As one experimental approach (others are currently in progress) to sorting out the above factors, we have investigated the reactivity of solutions containing $[(C_6H_5)_3Y]_mCuCl$ toward CsB_3H_8. The substitution of $B_3H_8^-$ for BH_4^- has the effect of (1) reducing the amount of negative charge on the boron atoms[31] and (2) limiting the number of terminal B–H bonds per boron atom to two.[24] Despite the less negative character of the borons in $B_3H_8^-$, we have demonstrated that it is capable of reducing Cu(I) in solution. For example, when a solution of cuprous chloride and cesium octahydrotriborate is warmed slightly or allowed to stand at room temperature, hydrogen is evolved and a black metallic solid forms. The rate of reactivity of $B_3H_8^-$ with Cu(I) is much slower than the analogous BH_4^- reduction, however, which occurs instantaneously at room temperature. This may indicate that, as suggested above, a specific stereochemical attachment is required for reduction which takes longer to achieve for $B_3H_8^-$ than for BH_4^-.[32,33] Consistent with this suggestion are the facts that stable crystalline $B_3H_8^-$ (but not BH_4^-) triphenylarsine and triphenylstibine copper complexes have been isolated and that solutions of these complexes are notably less stable than solutions of $[(C_6H_5)_3P]_2Cu(B_3H_8)$. Further experimental work is necessary, however, before the details of the reaction of copper(I) complexes with boron hydride anions can be fully elucidated.

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[28] One possible geometry through which reduction might occur would be to have the BH_4^- group attached to the copper atom through three protons. Such an attachment has been found[29] to occur in $Zr(BH_4)_4$ and has the advantage of placing more negative charge on the metal (each proton in BH_4^- having -0.261 charge[30]) than the two-point attachment found[1] in the phosphine complex.

[29] P. H. Bird and M. R. Churchill, *Chem. Commun.*, 403 (1967).

[30] R. A. Hegstrom, W. E. Palke, and W. N. Lipscomb, *J. Chem. Phys.*, **46**, 921 (1967).

[31] W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, Table 3-16, p 110.

[32] The $B_3H_8^-$ ion is thought[33] to undergo intramolecular rearrangement in solution, a feature which could provide the appropriate geometry[28] for reduction.

[33] W. N. Lipscomb, *Advan. Inorg. Chem. Radiochem.*, **1**, 132 (1959).