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Metalloboranes. III. Coinage Metal Derivatives of Borane Anions¹

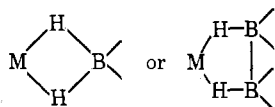
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A series of coinage metal derivatives of the borane anions $B_3H_8^-$, $B_9H_{14}^-$, $B_9H_{12}S^-$, $B_{10}H_{13}^-$, $B_{10}H_{15}^-$, and $B_{11}H_{14}^-$ has been prepared. These are of the type L_xMB where L is tri-*p*-tolylphosphine, x is 2, 3, or 4, and B is a borane ion. Solution-state structures have been probed through ³¹P and ¹¹B nmr data. Copper(I) is the most effective of this triad in binding these borane anions. This is most evident in the unique behavior of the $L_4Cu^+B^-$ salts which in solution are in equilibrium with L_3CuB and L at -100° . Furthermore, only in the copper system was $L_2MB_3H_8$ the sole isolable and solution-detectable species irrespective of L concentration. This quasi-tetrahedral complex has analogs in the $L_2CuB_{10}H_{13}$ and $Cl_2CuB_{10}H_{13}^-$ species. The most extensive range in stoichiometries was realized in the silver system. Solution species included L_2AgB , trigonal L_3Ag^+ , and tetrahedral L_4Ag^+ . Gold(I) showed no evidence of ion binding with the borane ions, and L_4Au^+ dissociation tendency was more marked than for silver or copper. In general, the tendency for the anion to enter the coordination sphere of the metal ion followed the order $Cu^+ > Ag^+ \gg Au^+$ for the metals and $B_3H_8^- > B_{10}H_{13}^- > B_9H_{12}S^- > B_9H_{14}^- \sim B_{11}H_{14}^-$ for the anions.

Results and Discussion

Introduction.—An established metalloborane class^{2a} is $(R_3P)_xMB$ where M is Cu, Ag, or Au(I) and B is a member of the borane anion set $B_3H_8^-$, $B_9H_{14}^-$, $B_9H_{12}S^-$, $B_{10}H_{13}^-$, and $B_{11}H_{14}^-$. Metal-borane interactions range from the relatively robust



type to loose ion pairs, $M^+B_x^-$.^{2b} We report herein a more definitive characterization of solution-state structures in this metalloborane class.

To enhance solubility, tri-*p*-tolylphosphine, L, was employed as the donor ligand. The reference solvent was dichloromethane, although this was modified by toluene addition to explore low-temperature ($\sim -110^\circ$) spectral regions. The ³¹P and ¹¹B nmr were the primary probes. Solution molecular weight determinations by classical cryoscopy (benzene) and vapor pressure osmometry (dichloromethane) were found relatively uninformative since both molecular and ionic dissociative phenomena were operative in these metalloborane solutions.

The most definitive structural information was obtained from ³¹P spectra at -80 to -115° where ligand exchange was slow. Molecular weight, conductivity, and ¹¹B spectral³ data were gathered at or near room temperature unless otherwise noted

$L_2CuB_3H_8$. Structure and Exchange Phenomenon.—The only isolable and detectable solution species in the $L-Cu^+-B_3H_8^-$ system was $L_2CuB_3H_8$. Quasi-tetrahedral disposition of ligands and anion was unequivocally established from the low-temperature ³¹P spec-

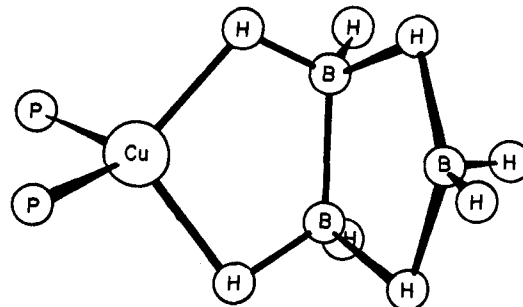
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(1) Paper II: P. A. Wegner, F. Klanberg, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.*, **7**, 2072 (1968).

(2) (a) F. Klanberg, E. L. Muetterties, and L. J. Guggenberger, *ibid.*, **7**, 2272 (1968). (b) This area of metal ion interaction with borane anion fragments is briefly reviewed in ref 2a.

(3) Reduced sensitivity with a temperature unit in our spectrometer precluded an extensive low-temperature ¹¹B exploration complementary to the ³¹P study.

trum. From -120 to -85° , the ³¹P spectrum was an AB pattern with $\delta -20.4$ and -22.4 ppm and $J_{PP} = 91$ Hz at -100° . This is fully consistent with the established⁴ solid-state structure of $[(C_6H_5)_3P]_2CuB_3H_8$.



The solution-state structure of $L_2CuB_3H_8$ at 25° is unknown; however, $Cu^+-B_3H_8^-$ binding is still substantial. The ³¹P nmr spectrum at $+20^\circ$ was a single peak ($\delta -18.7$ ppm) and the ¹¹B nmr spectrum of $L_2CuB_3H_8$ was a broad-line resonance which began to sharpen and exhibit the nonet fine structure of free $B_3H_8^-$ only after the addition of 20 equiv of free L. Furthermore, the equivalent conductance of a 0.01 M solution of $L_2CuB_3H_8$ in dichloromethane at 25° was only 0.12 mho.

An exchange process which equilibrates phosphine environments in $L_2CuB_3H_8$ was evident in the temperature dependence of the ³¹P spectrum. At $\sim -70^\circ$, the AB pattern began to broaden and then merged at $\sim -60^\circ$ to a broad single peak ($\delta -20.9$) that sharpened on further temperature increase. The possible equilibration processes include (1) fluxional CuB_3 character (*e.g.*, inversion of the CuB_3 framework), (2) ion dissociation, (3) ligand dissociation, and (4) bidentate \rightleftharpoons unidentate ion coordination. The exchange is primarily unimolecular in character. With added tri-*p*-tolylphosphine (1–2 mol), the ³¹P nmr spectrum was characteristic of free L and $L_2CuB_3H_8$ up to temperatures of -20° , and the $L_2CuB_3H_8$ ³¹P nmr similarly was unperturbed in mixtures of $L_2CuB_3H_8$ and $R_4N^+B_3H_8^-$. Hence processes (2) and (3) can be unequivocally eliminated as the ma-

(4) S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, **8**, 2755 (1969).

for rearrangement mechanism(s). Although the data do not permit a distinction between (1) and (4), we tend to favor the latter. Above -20° another more highly activated process is evident in mixtures of $L_2CuB_3H_8$ and L. Around -10° the lines characteristic of $L_2CuB_3H_8$ and free L merge at a position that represents an average of the $L_2CuB_3H_8$ and the L chemical shifts. The rate of this ligand (L) exchange process is about 10^{-3} at 0° .

The $Cu-B_{10}H_{13}^-$ System.—A similar pattern to that of $L_2CuB_3H_8$ was evident in the chemistry and solution behavior of $L_2CuB_{10}H_{13}$. Nonequivalent phosphine environments were established from the AB ^{31}P nmr pattern ($\delta -21.8, -22.0$ ppm and $J_{PP} = 78$ Hz at -100°). This eliminates some modes of $Cu^+B_{10}H_{13}^-$ binding but is not structurally definitive. The AB pattern began to broaden at $\sim -90^\circ$ and a single peak emerged at $\sim -80^\circ$ ($\delta -20.7$). Rapid exchange between $L_2CuB_{10}H_{13}$ and free L occurred above -80° . A single peak was observed at the position calculated for 1 equiv of $L_2CuB_{10}H_{13}$ and 1 equiv of free L under conditions of fast exchange. The equivalent conductance in dichloromethane is 1.7 mhos at $+25^\circ$. The $L_2CuB_{10}H_{13}$ complex is more labile than $L_2CuB_3H_8$, and ligand exchange between complex and "free ligand" L is a less activated process for the former.

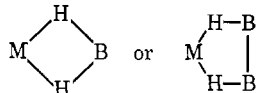
The new complex $Cl_2CuB_{10}H_{13}^{2-}$ has been isolated from the reaction of copper(II) chloride and $B_{10}H_{13}^-$. This ionic complex is probably analogous in structure to $L_2CuB_{10}H_{13}$.

L_3CuB and L_4CuB .—The only stable phosphinocopper salts isolated⁵ with $B_9H_{14}^-$, $B_9H_{12}S^-$, and $B_{11}H_{14}^-$ were the tetrakis(phosphino)copper salts, $L_4Cu^+B^-$. Solutions of these salts show a two-line ^{31}P spectrum at -115 to -100° . The major ($\sim 80\%$) resonance at -17.8 ppm is attributed to the L_4Cu^+ complex and the minor one at ~ -22 ppm to L_3CuB .⁶ Addition of 1 equiv of L essentially suppressed L_3CuB formation; the resonance at -22 ppm was only faintly discernible. The chemical shift for the $L_4Cu^+B^-$ salts agrees very well with that observed in other studies⁷ for $L_4Cu^+NO_3^-$ ($\delta \simeq -17.8$ ppm) and $L_4Cu^+PF_6^-$ ($\delta \simeq -17.6$ ppm). Above -95° , L exchange between L_4Cu^+ and L_3CuB is fast on the nmr time scale.

Silver Complexes.—Crystalline $L_4Ag^+B^-$ salts were isolated with $B_9H_{14}^-$, $B_9H_{12}S^-$, $B_{10}H_{13}^-$, and $B_{11}H_{14}^-$. Although no $L_4Ag^+B_3H_8^-$ could be isolated, the sole species observed at low temperatures in the ^{31}P nmr of a mixture of $L_2AgB_3H_8$ and 2L was $L_4Ag^+B_3H_8^-$. Below $\sim -40^\circ$ in dichloromethane-toluene solutions all these

(5) Clearly, solubility factors are operative since $[(C_6H_5)_3P]_3CuB$ with B representing $B_9H_{14}^-$, $B_9H_{12}S^-$, and $B_{11}H_{14}^-$ have been prepared.²

(6) In all complexes based on a bound $B_9H_{14}^-$, $B_9H_{12}S^-$, or $B_{10}H_{13}^-$ ion, the ^{31}P and ^{11}B spectroscopic data do not allow for structural conclusions. For the bound anion, metal-borane interaction may comprise



bridge binding or metal incorporation into a polyhedral fragment [e.g. analogous to $B_{10}H_{12}^{2-}$ (ref 1) and $B_9H_{12}S^-$ (A. R. Kane, L. J. Guggenberger, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **92**, 2571 (1970))].

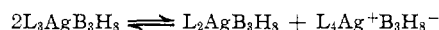
(7) E. L. Muetterties and C. W. Alegranti, *ibid.*, **92**, 4114 (1970).

salts showed two doublets of roughly equal intensity, which were due to $^{107}Ag-^{31}P$ and $^{109}Ag-^{31}P$ spin-spin coupling. The ^{107}Ag and ^{109}Ag splittings were 226 and 259 ± 3 Hz, respectively,⁸ and the chemical shifts were within the narrow range of 25.5 ± 0.2 ppm. These splittings and the observed chemical shifts are identical within experimental error for those of an extensive set of $L_4Ag^+X^-$ salts based on anions other than boranes.⁷ The equivalent conductances (0.01 M) of these salts in dichloromethane at $+25^\circ$ were high, e.g., 39.5 mhos for $L_4AgB_9H_{12}S$ as compared to 35.0 mhos for $(C_6H_5)_4AsB_9H_{12}S$.

Ligand lability was evident in the collapse of the L_4Ag^+ doublets into a single line between -60 and -50° . Ostensibly, the genesis of this is in a simple dissociative process, although there may be an anion effect.⁹

The tris complex $L_3AgB_9H_{12}S$ appears to be ionized to a trigonal L_3Ag^+ ($\delta -35.5$ ppm at -86°) cation and borane anion. Conductivity in dichloromethane at 25° is high (33 mhos) and the $J_{^{107}Ag-P}$ constant of 316 Hz is close to the calculated 303-Hz value for trigonal silver.⁷ The bis complex $L_2AgB_9H_{12}S$ ($\delta -33.9$ ppm at -86°) is relatively nonconductive in dichloromethane ($\Lambda_0 = 4.6$ mhos) at 25° and the $J_{^{107}Ag-P}$ value of 420 Hz is lower than calculated for linear⁷ L_2Ag^+ (452 Hz) and for observed⁷ L_2Ag^+ (~ 500 Hz). The molecular weight of $L_2AgB_9H_{12}S$ at 25° indicates a nonionic complex and is consistent with an anion-bound silver complex.⁶ The ^{11}B nmr of $L_2AgB_9H_{12}S$ at 25° is a broad resonance whereas the formulated salt $L_3Ag^+B_9H_{12}S^-$ shows the characteristic $B_9H_{12}S^-$ ion ^{11}B resonance.

The compound $L_2AgB_3H_8$ was isolated as a unique crystalline phase. The ^{31}P nmr spectrum of a dichloromethane solution of this borane showed a single ^{31}P environment¹⁰ ($\delta -30.8$ ppm at -80°). The $^{107}Ag-P$ splitting was 390 Hz. Additional evidence for a bound anion in $L_2AgB_3H_8$ is the solution disproportionation of the $L_3AgB_3H_8$ composition (1 equiv of $L_2AgB_3H_8$ + 1 equiv of L)



The individual $J_{^{107}Ag-^{31}P}$ and $J_{^{109}Ag-^{31}P}$ doublets characteristic for all three species were discerned in the ^{31}P spectrum of a solution of $L_2AgB_3H_8$ + L at -86° . The nmr data for $L_3AgB_3H_8$ ($\delta -26.8$ ppm and $J_{^{107}Ag-P} = 310$ Hz) are structurally inconclusive; no statement can be made concerning extent or strength of anion binding. This disproportionation of $L_3AgB_3H_8$ was not observed⁸ for $L_3Ag^+PF_6^-$ and $L_3Ag^+ClO_4^-$ where the anions are not bound in either the L_3Ag^+ or L_2Ag^+ salts. There must be a driving force in the disproportionation unique to the B_3H_8 system which we ascribe to ion binding in $L_2AgB_3H_8$.

(8) $J(109)/J(107)$: obsd, 1.15; theory, 1.15. Hereafter only the $J(107)$ values are reported since the ratio was invariably 1.15 ± 0.01 .

(9) A general study of exchange phenomena in phosphinosilver complexes is in progress.

(10) An AB pattern was not detected, precluding any comment about structural details for $L_2AgB_3H_8$ in the solution state. The anion appears less strongly bound than in $L_2CuB_3H_8$ because the broad ^{11}B resonance (25°) of $L_2AgB_3H_8$ transformed to the characteristic $B_3H_8^-$ nonet after addition of only about 6 equiv of additional L.

Gold Complexes.—No phosphinogold(I) $B_3H_3^-$ derivatives of adequate stability for isolation and full characterization were found. For the other borane anions, tetrakis(phosphino)gold salts were obtained unfailingly despite control of stoichiometry with the exception of the $B_9H_{12}S^-$ system. Failure to isolate tris or bis complexes may have been due to solubility phenomena; attempts to isolate such complexes by marked depletion of phosphine concentration often led to reaction mixtures that deposited elemental gold.

The X-ray crystal analysis established a planar L_3Au^+ species for $[(C_6H_5)_3P]_3Au^+B_9H_{12}S^-$ in the solid state.² The ^{31}P resonance for $L_3AuB_9H_{12}S$ was at a slightly higher field (-62.1 ppm at -84°) than $L_2AuB_9H_{12}S$ (64.0 ppm at -84°) and could not represent an average of $L_2AuB_9H_{12}S + \text{free } L$ (δ for free ligand is -11.8 ppm at -84°). Furthermore, the ^{31}P spectrum of a synthetic 1:1 mixture of $L_3AuB_9H_{12}S$ and $L_2AuB_9H_{12}S$ at -84° ¹¹ consisted of two resonances at ~ -62.5 and -64 ppm of equal intensities, establishing the identities of the two gold complexes in solution. The equivalent conductances of the two gold complexes at 25° were the same, ~ 40.5 mhos, consistent with ion formulation. Thus the data point to discrete L_2Au^+ and L_3Au^+ cationic complexes. The conductances were reduced to ~ 10 mhos at -78° , a decrease comparable in degree to that observed for the reference $(C_6H_5)_4As^+B_9H_{12}S^-$. Therefore, it does not appear that ion binding is significant even at lower temperatures.

With the counter anions $B_9H_{14}^-$ and $B_{11}H_{14}^-$, only $L_4Au^+B^-$ complexes were isolated. No unequivocal solution evidence was obtained for an L_4Au^+ cation from spectral studies. The ^{31}P chemical shifts at -84° for all the L_4AuB species were approximately -49 ppm which is close to the value of -47 ppm calculated for a mixture of L and L_3Au^+ , assuming fast ligand exchange. The chemical shifts decreased slightly (~ 1.3 ppm) in the temperature range of ~ -110 to -80° and then increased (~ 1 ppm) between -80 and 20° . This might be indicative of an equilibrium between L_4Au^+ and $L_3Au^+ + L$; the ^{31}P shift for all the other metal-phosphine complexes progressively increased in the temperature range -110 – 20° .

The $L_4Au^+B_{10}H_{13}^-$ previously reported² has now been identified as $L_4Au^+B_{10}H_{15}^-$ based on ^{11}B nmr.

Experimental Section

Reagents and Procedures.—Reagent grade metal salts were employed without further purification. All solvents were dried over metal hydrides or molecular sieve and distilled prior to use. Decaborane was purchased from the Callery Chemical Co. and was recrystallized from petroleum ether (bp 30 – 60°).

Proton nuclear magnetic resonance spectra were obtained on the Varian Associates Model HA-100 with a Varian V4343 temperature controller and HR-220 with a variable-temperature unit. The ^{31}P spectra were obtained at 40.5 MHz with the HA-100 instrument. The ^{11}B nmr data were obtained at 19.2 MHz with a Varian Associates Model HR-60 and also at 32 MHz on a Varian HA-100 through the courtesy of Professor M. F. Hawthorne and Mr. G. Dunks. Reference materials were tetramethylsilane

for proton spectra, trimethyl borate for boron, and triethylphosphine for phosphorus.

The conductivity measurements were done on dichloromethane solutions at concentrations of 10^{-2} and 10^{-3} *M*. All results reported in the text are for 10^{-2} *M* solutions. The conductivity bridge used was an Industrial Instruments Inc. Model RC 16 B2. The measurements were done at ambient temperature, -30 and -78° . Low-temperature determinations were carried out in a dry nitrogen atmosphere. The equivalent conductance ($\text{ohm}^{-1} \text{cm}^2 \text{equiv}^{-1}$) of some reference compounds (at room temperature unless noted) was found to be as follows: $(n-C_3H_7)_4NCl$, 9.2 (10^{-2} equiv/l.), 19 (10^{-3} equiv/l.); $(n-C_3H_7)_4NS_2PF_2$, 14.6 (10^{-2} equiv/l.), 28 (10^{-3} equiv/l.); $(C_6H_5)_4AsCl$, 35 (10^{-2} equiv/l.), 52 (10^{-3} equiv/l.); $(C_6H_5)_4AsB_9H_{12}S$, 40 (10^{-2} equiv/l.), 60 (10^{-3} equiv/l.); $(C_6H_5)_4AsB_9H_{12}S$, 35 (10^{-2} equiv/l.), 54 (10^{-3} equiv/l.), at -78° , 10 (10^{-2} equiv/l.), 14 (10^{-3} equiv/l.); $(C_6H_5)_4AsB_9H_{14}$, 35 (10^{-2} equiv/l.), 52 (10^{-3} equiv/l.), at -78° , 11 (10^{-2} equiv/l.), 16 (10^{-3} equiv/l.).

$[(p\text{-}CH_3C_6H_4)_3P]_2CuB_9H_3$.—To a hot ethanol solution (300 ml) containing tri-*p*-tolylphosphine (20.0 g, 0.066 mol) was added a solution of copper(II) sulfate pentahydrate (4.0 g, 0.02 mol) in 75 ml of water. To this was added a solution of cesium triborohydride (6.8 g, 0.04 mol) in 100 ml of ethanol and 50 ml of water. Considerable gas and heat were evolved on addition and the reaction mixture was quickly cooled to 0° and held at that temperature for 90 min. The reaction mixture was filtered; the solid was washed with 1 l. of ethanol. The crude product was recrystallized twice by dissolution in acetonitrile warmed to 50° followed by addition of water to the point of incipient precipitation. Slow cooling to 0° yielded white crystals. These were vacuum dried at 25° for 24 hr at 0.001 mm. The crystals are modestly stable in air for short periods of time but for long storage they must be protected from the atmosphere; mp 165 – 166° dec. *Anal.* Calcd for $C_{42}H_{50}B_9CuP_2$: C, 70.8; H, 7.07; B, 4.55; Cu, 8.92; P, 8.69. Found: C, 69.9; H, 7.14; B, 5.06; Cu, 8.80; P, 8.56. Equivalent conductance (CH_2Cl_2 , $+25^\circ$) was 0.12 at 10^{-2} equiv/l.

$[(p\text{-}CH_3C_6H_4)_3P]_2AgB_9H_3$.—Silver nitrate (1.7 g, 0.01 mol) in 10 ml of water was added to a slurry of tri-*p*-tolylphosphine (6.08 g, 0.02 mol) in 100 ml of acetonitrile and 100 ml of methanol. The reaction mixture was cooled with ice and a solution of cesium triborohydride (1.7 g, 0.01 mol) in 100 ml of ethanol was added. Reaction was evidenced by gas and heat evolution and the separation of a light brown precipitate. The solid was recovered by filtration. Recrystallization of the crude product was (and must be) effected with minimum exposure to light. The recrystallization procedure repeated twice consisted of dissolution in acetonitrile at room temperature followed by addition of water to the point of incipient precipitation and then cooling to 0° . The product was collected and dried for 24 hr at 25° (0.001 mm) and protected from exposure to light; yield 1.2 g. *Anal.* Calcd for $C_{42}H_{50}P_2AgB_9$: C, 66.6; H, 6.66; P, 8.18; Ag, 14.3; B, 4.28. Found: C, 66.2; H, 6.39; P, 7.92; Ag, 14.0; B, 4.42.

$[(p\text{-}CH_3C_6H_4)_3P]_4CuB_9H_{14}$.—A solution of copper(II) sulfate pentahydrate (3.2 g, 0.013 mol) in 100 ml of water was added to a solution of tri-*p*-tolylphosphine (12.0 g, 0.04 mol) in 300 ml of ethanol warmed to 80° . To this green solution was added CsB_9H_{14} (4.8 g, 0.02 mol) dissolved in 100 ml of aqueous ethanol. A gummy yellow solid immediately separated. The reaction mixture was cooled to 0° and stirred for a period of 2 hr. The yellow solid was collected by filtration and washed with 1 l. of petroleum ether and then with 200 ml of ethanol. The crude product was recrystallized twice by dissolution in hot benzene and *n*-heptane was added to the point of incipient precipitation and then cooled slowly to room temperature. At this point the recrystallization flask was placed in ice for 4 hr (nitrogen atmosphere). After this time the yellow crystals were collected and vacuum dried for 24 hr at 25° (0.001 mm); yield 6.0 g; mp 125° slight decomposition, 187° softening, 230 – 232° melting with decomposition. The crystals are subject to slow degradation on extended exposure to the atmosphere. *Anal.* Calcd for $C_{34}H_{38}B_9CuP_4$: C, 72.5; H, 7.09; B, 6.99; Cu, 4.66; P,

(11) Above -70° , L exchange between L_2Au^+ and L_3Au^+ is fast on the nmr time scale.

8.90. Found: C, 72.0; H, 7.04; B, 7.44; Cu, 4.49; P, 8.76. Equivalent conductance (CH_2Cl_2 , $+25^\circ$) was 18 at 10^{-2} equiv/l. and 15 at 10^{-3} equiv/l.

$[(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}]_4\text{AgB}_9\text{H}_{14}$.—Silver nitrate (3.4 g, 0.02 mol) in 40 ml of water was added to a refluxing solution of tri-*p*-tolylphosphine (36.0 g, 0.12 mol) in 800 ml of ethanol. A solution of $\text{CsB}_9\text{H}_{14}$ (5.4 g, 0.02 mol) in 100 ml of ethanol and 20 ml of water was added to the warm reaction mixture. A white solid separated and this was collected by filtration after the reaction mixture had been cooled to 0° for 2 hr. The solid was washed with 200 ml of ethanol, 1 l. of petroleum ether, and finally 400 ml of cyclohexane. After vacuum drying at 25° the solid was recrystallized twice from hot benzene. The recrystallization was effected in a nitrogen atmosphere. The crystals were vacuum dried at 25° (0.001 mm); mp 205° slight decomposition, 220° brown, 305° dec. The compound decomposes slowly on exposure to the atmosphere. *Anal.* Calcd for $\text{C}_{84}\text{H}_{98}\text{AgB}_9\text{P}_4$: C, 70.2; H, 6.87; Ag, 7.51; B, 6.77; P, 8.62. Found: C, 69.4; H, 7.01; Ag, 7.24; B, 7.15; P, 9.14. Equivalent conductance (CH_2Cl_2 , $+25^\circ$) was 26 at 10^{-2} equiv/l. and 33 at 10^{-3} equiv/l.

$[(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}]_4\text{AuB}_9\text{H}_{14}$.—A solution of $\text{AuCl}_3 \cdot \text{H}_2\text{O}$ (6.0 g, 0.02 mol) in 80 ml of aqueous ethanol was added dropwise to a mixture of tri-*p*-tolylphosphine (28.0 g, 0.09 mol) and $\text{CsB}_9\text{H}_{14}$ (4.0 g, 0.016 mol) in 450 ml of a 10:1 ethanol-water solution maintained at 0° . There was an immediate precipitate accompanied by heat and gas evolution. After the addition was completed, the reaction was filtered and stirred for a period of 30 min maintaining an average temperature of about 0° . The crude product was collected by filtration and washed with 1.5 l. of petroleum ether. The crude brown product was then dissolved in 300 ml of acetonitrile warmed to 50° . After addition of 5 g of Darco, the mixture was filtered and maintained at 50° while water was added to the point of incipient precipitation. On cooling to 0° , yellow crystals separated out. These were collected and the recrystallization procedure was repeated. The crystals were dried for 24 hr at 50° (0.001 mm); yield 9.5 g; mp $176\text{--}178^\circ$ with slight decomposition. The complex decomposes slowly on exposure to air. *Anal.* Calcd for $\text{C}_{84}\text{H}_{98}\text{AuB}_9\text{P}_4$: C, 66.1; H, 6.47; Au, 12.9; B, 6.38; P, 8.12. Found: C, 66.1; H, 6.40; Au, 13.0; B, 6.69; P, 8.14. Equivalent conductance (CH_2Cl_2 , $+25^\circ$) was 40 at 10^{-2} equiv/l. and 48 at 10^{-3} equiv/l.

$[(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}]_4\text{CuB}_9\text{H}_{14}\text{S}$.—A solution of copper(II) sulfate pentahydrate (3.2 g, 0.013 mol) in 100 ml of water was added to a solution of tri-*p*-tolylphosphine (20.0 g, 0.07 mol) in 700 ml of ethanol warmed to 70° . To this reaction mixture was added $\text{CsB}_9\text{H}_{14}\text{S}$ (6.0 g, 0.02 mol) in 75 ml of aqueous ethanol. The reaction mixture was quickly cooled to 0° and held there for 30 min. The insoluble, crude product, collected by filtration, was washed with 1 l. of cyclohexane and 500 ml of diethyl ether. The crude product was recrystallized twice from benzene in a nitrogen atmosphere. The crystals were dried for 24 hr at 25° (0.001 mm); yield 5.0 g; mp $240\text{--}242^\circ$ dec. *Anal.* Calcd for $\text{C}_{84}\text{H}_{98}\text{B}_9\text{CuP}_4\text{S}$: C, 70.9; H, 6.80; B, 6.84; Cu, 4.47; P, 8.71; S, 2.25. Found: C, 70.3; H, 6.83; B, 6.84; Cu, 4.41; P, 8.34; S, 2.65. Equivalent conductance (CH_2Cl_2 , $+25^\circ$) was 30 at 10^{-2} equiv/l. and 29 at 10^{-3} equiv/l.

$[(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}]_4\text{AgB}_{10}\text{H}_{13}\text{S}$.—Silver nitrate (1.69 g, 0.01 mol) in about 10 ml of water was added to a solution of tri-*p*-tolylphosphine (6.08 g, 0.02 mol) in 500 ml of methanol and 110 ml of acetonitrile. While cooling the reaction mixture to 0° , a solution of $\text{CsB}_9\text{H}_{14}\text{S}$ (2.74 g, 0.01 mol) in 20 ml of ethanol and 20 ml of acetonitrile was added. The resulting white precipitate, collected by filtration, was washed with 100 ml of ethanol and 1 l. of petroleum ether. The product was recrystallized twice from acetonitrile warmed to 35° with water addition to the point of incipient precipitation and resultant cooling of the system to 0° . This procedure was (and must be) effected in essentially complete darkness. The crystals were dried for 24 hr at 25° (0.001 mm); yield, 5.0 g of gray needles; mp $176\text{--}192^\circ$ softening and darkening; no melting below 300° . *Anal.* Calcd for $\text{C}_{42}\text{H}_{54}$

$\text{AgB}_9\text{P}_2\text{S}$: C, 58.8; H, 6.34; Ag, 12.6; B, 11.3; P, 7.22; S, 3.74. Found: C, 58.6; H, 6.40; Ag, 12.4; B, 11.1; P, 7.60; S, 3.41. Equivalent conductance (CH_2Cl_2 , $+25^\circ$) was 5.2 at 10^{-2} equiv/l. and 10 at 10^{-3} equiv/l.

$[(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}]_4\text{AgB}_9\text{H}_{12}\text{S}$.—To a reaction mixture of tri-*p*-tolylphosphine (35.0 g, 0.12 mol) and silver nitrate (3.4 g, 0.02 mol) in 50 ml of water and 800 ml of ethanol at 70° was added a solution of $\text{CsB}_9\text{H}_{14}\text{S}$ (5.4 g, 0.02 mol) in 80 ml of a 1:1 ethanol-water mixture. The reaction mixture was immediately cooled to 0° and held there for a period of 1 hr under a nitrogen atmosphere. The reaction mixture was then evaporated to dryness under vacuum and the solid was washed with 1 l. of petroleum ether. The crude solid was then recrystallized twice by dissolution in warm benzene followed by slow cooling to room temperature and then to 10° for 16 hr. The recrystallization procedure was done in a nitrogen atmosphere. The off-white crystals were dried for 24 hr at 50° (0.001 mm); yield 2.0 g; mp $223\text{--}224^\circ$ dec. *Anal.* Calcd for $\text{C}_{84}\text{H}_{98}\text{AgB}_9\text{P}_4\text{S}$: C, 68.8; H, 6.60; Ag, 7.35; B, 6.63; P, 8.45; S, 2.19. Found: C, 68.2; H, 6.56; Ag, 6.41; B, 7.14; P, 8.30; S, 2.59. Equivalent conductance (CH_2Cl_2 , $+25^\circ$) was 40 at 10^{-2} equiv/l. and 48 at 10^{-3} equiv/l.

$[(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}]_2\text{AuB}_9\text{H}_{12}\text{S}$.—To a mixture of $\text{AuCl}_3 \cdot \text{H}_2\text{O}$ (6.0 g, 0.02 mol) and tri-*p*-tolylphosphine (13.8 g, 0.045 mol) in 350 ml of aqueous ethanol warmed to about 60° was added a solution of $\text{CsB}_9\text{H}_{14}\text{S}$ (4.0 g, 0.015 mol) in 50 ml of aqueous ethanol. The reaction mixture was quickly cooled to 0° and held there for a period of 1 hr. The slurry was filtered and the brown solids were washed with 200 ml of ethanol and 1 l. of petroleum ether. The product was recrystallized twice by dissolution of the material in acetonitrile warmed to 50° , addition of Darco, filtration, and then water addition to the point of incipient precipitation. After cooling to 0° for 1 hr, the off-white crystals were collected by filtration. The crystals were dried for 24 hr at 25° (0.001 mm); mp $188\text{--}189^\circ$ dec. *Anal.* Calcd for $\text{C}_{42}\text{H}_{54}\text{AuB}_9\text{P}_2\text{S}$: C, 53.3; H, 5.75; Au, 20.8; B, 10.3; P, 6.54; S, 3.39. Found: C, 53.0; H, 5.65; Au, 20.9; B, 10.0; P, 6.70; S, 3.36. Equivalent conductance (CH_2Cl_2 , $+25^\circ$) was 39 at 10^{-2} equiv/l., 55 at 10^{-3} equiv/l.; (CH_2Cl_2 , -78°) 10 at 10^{-2} equiv/l., 14 at 10^{-3} equiv/l.

$[(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}]_3\text{AuB}_9\text{H}_{12}\text{S}$.—The above procedure was followed but with 20.0 g (0.06 mol) of tri-*p*-tolylphosphine and 550 ml of ethanol. The work-up and recrystallization procedure was as above; mp $192\text{--}193^\circ$. *Anal.* Calcd for $\text{C}_{63}\text{H}_{75}\text{AuB}_9\text{P}_3\text{S}$: C, 60.5; H, 6.04; P, 7.42; Au, 15.7; B, 7.77; S, 2.56. Found: C, 60.1; H, 5.72; P, 7.42; Au, 15.7; B, 7.86; S, 3.15. Equivalent conductance (CH_2Cl_2 , $+25^\circ$) was 42 at 10^{-2} equiv/l., 52 at 10^{-3} equiv/l.; (CH_2Cl_2 , -78°) 11 at 10^{-2} equiv/l., 15 at 10^{-3} equiv/l.

$[(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}]_4\text{AuB}_9\text{H}_{12}\text{S}$.—The procedure described above for the bis(phosphino)gold complex was followed except that 40 g (0.13 mol) of tri-*p*-tolylphosphine and 850 ml of ethanol were employed. Essentially the same work-up and recrystallization procedure described above was followed; yield, 15.8 g of white crystals; mp $184\text{--}186^\circ$ dec (red melt). *Anal.* Calcd for $\text{C}_{84}\text{H}_{98}\text{AuB}_9\text{P}_4\text{S}$: C, 64.8; H, 6.22; Au, 12.7; B, 6.25; P, 7.96; S, 2.06. Found: C, 64.9; H, 6.24; Au, 12.6; B, 6.22; P, 7.76; S, 2.12. Equivalent conductance (CH_2Cl_2 , $+25^\circ$) was 43 at 10^{-2} equiv/l., 52 at 10^{-3} equiv/l.; (CH_2Cl_2 , -78°) 11 at 10^{-2} equiv/l., 15 at 10^{-3} equiv/l.

$[(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}]_4\text{AgB}_{10}\text{H}_{13}$.—Decaborane (1.8 g, 0.01 mol) in 50 ml of diethyl ether was added slowly to a slurry of 2.5 g of sodium hydride in 50 ml of diethyl ether. The slurry was stirred for 2 hr and was filtered (nitrogen atmosphere) into a solution of $[(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}]_3\text{AgCl}$ (12.0 g, 0.011 mol) in 100 ml of methylene chloride. The reaction mixture was cooled to 0° for 2 hr and maintained in a nitrogen atmosphere. The solids were filtered and the filtrate was stripped to dryness in a drybox. The yellow residue was then twice recrystallized by dissolution in 500 ml of 50:50 methylene chloride-diethyl ether at room temperature, followed by evaporation of 50% of the solvent and final cooling to -50° for 16 hr. The yellow crystals, which proved to be air

sensitive, were collected and vacuum dried for 24 hr at 50° (0.001 mm); yield 6.6 g; mp 195° slight decomposition, 205–206° dec. *Anal.* Calcd for $C_{84}H_{97}AgB_{10}P_4$: C, 69.8; H, 6.75; Ag, 7.46; B, 7.47; P, 8.56. Found: C, 69.3; H, 7.00; Ag, 7.27; B, 7.44; P, 8.30. Equivalent conductance (CH_2Cl_2 , +25°) was 17 at 10^{-2} equiv/l. and 24 at 10^{-3} equiv/l.

$[(p-CH_3C_6H_4)_3P]_4AuB_{10}H_{14}$.—A solution of $Cs_2B_{10}H_{14}$ (6.0 g, 0.0155 mol) in 100 ml of ethanol and 75 ml of water was added to a hot solution of $AuCl_3 \cdot H_2O$ (6.0 g, 0.02 mol) and *p*-tolylphosphine (54.0 g, 0.18 mol) in 600 ml of ethanol. A white precipitate formed immediately on the addition. After cooling the reaction mixture to 0° for 2 hr the solid was collected by filtration and washed with 300 ml of ethanol, 400 ml of cyclohexane, and 400 ml of petroleum ether. The product was twice recrystallized by dissolution in acetonitrile at 50° followed by addition of water to incipient precipitation and then cooling to room temperature. The yellow crystals were vacuum dried for 24 hr at 25° (0.001 mm); mp 125° slight decomposition, 150° melting to a red liquid. *Anal.* Calcd for $C_{84}H_{99}AuB_{10}P_4$: C, 65.7; H, 6.46; Au, 12.8; B, 7.03; P, 8.06. Found: C, 65.4; H, 6.40; Au, 12.8; B, 6.95; P, 7.55.

$(C_2H_5)_4N](Cl_2CuB_{10}H_{13})$.—Decaborane (5 g, 0.02 mol) was dissolved in 250 ml of ether and 3 g of sodium hydride was added. The slurry was cooled and stirred for 1 hr. The filtrate was filtered and chilled to –10°. To this filtrate was added a solution of copper(II) chloride dihydrate (3.4 g, 0.02 mol) in 30 ml of cold tetrahydrofuran. The reaction mixture was stirred at –10° for 10 min and then a solution of tetraethylammonium chloride in 15 ml of water was added to give a yellow precipitate. After stirring for 5 min the slurry was filtered and the solid was washed with two 25-ml portions of cold water. The solid was vacuum dried at 25° for 24 hr. The crude product was recrystallized three times from tetrahydrofuran to give a bright yellow solid; mp 145° darkening, 155–167° dark brown, no melting below 400°. *Anal.* Calcd for $C_{16}H_{53}N_2CuB_{10}Cl_2$: C, 37.2; H, 10.4; N, 5.46; Cu, 12.3; B, 20.9; Cl, 13.7. Found: C, 37.0; H, 10.4; N, 5.96; Cu, 11.9; B, 21.1; Cl, 14.8.

$(p-CH_3C_6H_4)_3P]_4AuB_{11}H_{14}$.—A solution of $AuCl_3 \cdot H_2O$ (1.1 g, 0.003 mol) in 20 ml of aqueous ethanol was added to a solution of tri-*p*-tolylphosphine (8.1 g, 0.026 mol) in 250 ml of hot ethanol. While cooling the mixture to 0°, a solution of $CsB_{11}H_{14}$ (1.0 g, 0.0037 mol) in aqueous ethanol was quickly added. The resulting brown precipitate was collected by filtration and washed with

500 ml of petroleum ether and 1 l. of cyclohexane. The crude product was twice recrystallized by dissolution in acetonitrile at 50° followed by addition of water to incipient precipitation and then cooled slowly to 0°. The yellow crystals were vacuum dried for 24 hr at 25° (0.001 mm). *Anal.* Calcd for $C_{84}H_{98}AuB_{11}P_4$: C, 65.2; H, 6.38; Au, 12.7; B, 7.68; P, 8.01. Found: C, 64.7; H, 6.45; Au, 12.5; B, 7.59; P, 7.63. Equivalent conductance (CH_2Cl_2 , +25°) was 36 at 10^{-2} equiv/l. and 46 at 10^{-3} equiv/l.

$[(p-CH_3C_6H_4)_3P]_4AgB_{11}H_{14}$.—The above procedure for gold was followed but with 0.51 g (0.003 mol) of $AgNO_3$ in 20 ml of water. The work-up and recrystallization were as above. *Anal.* Calcd for $C_{84}H_{98}AgB_{11}P_4$: C, 69.2; H, 6.77; Ag, 7.40; B, 8.15; P, 8.49. Found: C, 69.3; H, 6.83; Ag, 6.97; B, 8.06; P, 8.41.

$[(p-CH_3C_6H_4)_3P]_2CuB_{10}H_{13}$.—Decaborane (2.4 g, 0.02 mol) in 50 ml of diethyl ether was added slowly to a slurry of 2.5 g of sodium hydride in 50 ml of diethyl ether. The slurry was stirred for 2 hr and was filtered, under nitrogen, into a solution of $[(p-CH_3C_6H_4)_3P]_2CuCl$ (12 g, 0.012 mol) in 125 ml of methylene chloride. The reaction mixture was cooled to 0° for 2 hr and maintained in a nitrogen atmosphere. The solids were filtered and the filtrate was stripped to dryness in a drybox. The yellow residue was then recrystallized by dissolution in 400 ml of 50:50 methylene chloride–diethyl ether at room temperature, followed by evaporation of 80% of the solvent and final cooling to –50° for 2 hr. The yellow crystals were then recrystallized by dissolution in 125 ml of benzene. Slow evaporation of the benzene solution over a period of 1 week yielded yellow crystals. The yellow crystals, which proved to be air sensitive, were collected and vacuum dried for 48 hr at 25° (0.001 mm); yield 2.0 g; mp 272–273°. The reproducibility of this procedure is poor. *Anal.* Calcd for $C_{42}H_{55}CuB_{10}P_2$: C, 63.6; H, 6.99; Cu, 8.01; B, 13.6; P, 7.77. Found: C, 63.8; H, 6.77; Cu, 7.25; B, 13.4; P, 7.45. Equivalent conductance (CH_2Cl_2 , +25°) was 1.7 at 10^{-2} equiv/l. and 2.4 at 10^{-3} equiv/l.

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