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Metalloboranes. I. Metal Complexes of B_3, B_9, B_9S, B_{10}, and B_{11} Borane Anions

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Triborohydride ion ($B_3H_8^-$) reacts with metal hexacarbonyls to give $M(CO)_4B_3H_8^-$ with M = Cr, Mo, W. Isolated as crystalline salts, these anions are yellow and air stable. The triborohydride moiety is attached to the metal atom in these complexes by means of two adjacent M–H–B three-center bonds as shown by the crystal structure analysis of a $Cr(CO)_4B_3H_8^-$ salt. An identical mode of structural attachment is proposed for the complexes of $[(C_6H_5)_3P]_2M'B_3H_8$ (M' = Cu, Ag) and $(C_5H_5)_2TiB_3H_8$. The fragment anions $B_9H_{14}^-$ and $B_9H_{12}S^-$ form a series of colorless tristriphenylphosphine complexes of copper, silver, and gold which appear to be simple salts in the solid state and in highly polar media. X-Ray studies of the gold derivative show a trigonal P_3Au^+ cation and a $B_9H_{12}S^-$ anion with the predicted B_9S skeleton ($B_{10}H_{14}^{2-}$ analog). In solution, particularly nonpolar media, there appears to be a significant interaction between the cation and the anion as evidenced by the perturbation of the characteristic $B_9H_{14}^-$ and $B_9H_{12}S^-$ B^{11} nmr spectra. Analogous metal complexes derived from $B_{10}H_{13}^-$ show varied behavior and in some of these, particularly the copper derivative, there may be metal–borane interactions. The properties of copper and gold phosphine derivatives of $B_{11}H_{14}^-$ are consonant with simple salts of $B_{11}H_{14}^-$.

Introduction

Metalloborane chemistry[1,2] has developed into one of the most rapidly expanding and diversified areas of inorganic chemistry. The largest and best structured class of metalloboranes comprises the icosahedral group derived from the ligands $B_9C_2H_{11}^{2-}$,[1-3] $B_{10}CH_{11}^{3-}$,[4] and $B_{10}H_{10}S^{2-}$ [5]— the paradigm is $Fe(B_9C_2H_{11})_2^{2-}$, a formal analog of ferrocene. Very recent work[6] has extended the area of closed metal carborane polyhedra to 10- and 9-atom systems derived from $B_7C_2H_9^{2-}$ and $B_6C_2H_8^{2-}$. Icosahedra with two metal atoms have also been prepared[7] as in the $Co_2B_8C_2$ skeleton of $B_9C_2H_{11}CoB_8C_2H_{10}CoB_9C_2H_{11}^{2-}$.

Another area of metalloborane chemistry is derived from the basic boron hydride fragments: borane (BH_3) and borohydride ion (BH_4^-). Borane, a strong Lewis acid, forms adducts with nucleophilic metal complexes[8] such as $Mn(CO)_5^-$ through a metal–boron bond. Borane is also capable of functioning in a more complex fashion in polynuclear systems. Exemplary is $HMn_3(CO)_{10}(BH_3)_2$ where each BH_3 group bridges three manganese atoms through multicenter Mn–H–B bonding.[9] Borohydride ion forms numerous metal complexes but structural detail has been established for only a few. The BH_4^- ligand is doubly bridging in $(H_3C)_3N \cdot Al(BH_4)_3$[10] and appears to be triply bridging in $Zr(BH_4)_4$.[11] In $[(C_6H_5)_3P]_2CuBH_4$,[12] the BH_4 moiety is, *prima facie*, a bidentate donor, but the rather long Cu–H distances (2.02 Å) and the short Cu–B distance (2.18 Å) suggest the possibility of direct Cu–B as well as Cu–H–B overlap. The 2.18-Å distance compares with Cu–B distances of 2.14–2.33 Å in $Cu_2B_{10}H_{10}$[13] and 2.20 Å in $Cu(B_9C_2H_{11})_2^{2-}$.[14]

We wish to report in this article the preparation and characterization of metal derivatives of the polyhedral fragment ions $B_3H_8^-$, $B_9H_{14}^-$, $B_9H_{12}S^-$, $B_{10}H_{13}^-$, and $B_{11}H_{14}^-$, which not only enlarge the spectrum of metalloboranes but also traverse the areas of the more compact structures of near-icosahedral geometry, the open structures derived from the very small borane fragments, and simple salts.

Results and Discussion

Complexes of $B_3H_8^-$.—Octahydrotriborotetracarbonyl derivatives of chromium, molybdenum, and tungsten have been prepared by the displacement of 2 mol of carbon monoxide from the hexacarbonyls

$$M(CO)_6 + B_3H_8^- \longrightarrow (OC)_4MB_3H_8^- + 2CO \qquad (1)$$

Crystalline, air-stable salts of the anions were obtained with tetraalkylammonium ions. These salts undergo essentially complete ionization in solvents such as acetonitrile. These solutions are not air stable.

A titanium derivative, $(C_5H_5)_2TiB_3H_8$, was obtained from $(C_5H_5)_2TiCl_2$ and CsB_3H_8.[15] This neutral triborohydride derivative is volatile and soluble in nonpolar solvents. Reactivity is pronounced as exemplified by its rapid oxidation in air but the site of reactivity is probably the metal atom, not the borane fragment. A bis(triphenylphosphine)copper derivative, $[(C_6H_5)_3P]_2CuB_3H_8$, was prepared by reduction of copper(II) sulfate with $B_3H_8^-$ in the presence of triphenylphosphine[16] and the analogous silver compound was pre-

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(1) E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, Inc., New York, N. Y., 1968.

(2) M. F. Hawthorne, *Accounts Chem. Res.*, **1**, 281 (1968).

(3) M. F. Hawthorne, D. C. Young, and P. A. Wegner, *J. Am. Chem. Soc.*, **87**, 1818 (1965).

(4) W. H. Knoth, *ibid.*, **89**, 3343 (1967).

(5) W. R. Hertler, F. Klanberg, and E. L. Muetterties, *Inorg. Chem.*, **6**, 1696 (1967).

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(7) J. N. Francis and M. F. Hawthorne, *ibid.*, **90**, 1663 (1968).

(8) G. W. Parshall, *ibid.*, **86**, 361 (1964).

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(10) N. A. Bailey, P. H. Bird, and M. G. H. Wallbridge, *Chem. Commun.*, 286 (1966).

(11) P. H. Bird and M. H. Churchill, *ibid.*, 403 (1967).

(12) S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, **6**, 2223 (1967).

(13) R. D. Dobrott and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 1779 (1962).

(14) R. M. Wing, *J. Am. Chem. Soc.*, **89**, 5599 (1967).

(15) The reaction parallels the one described by H. Nöth and R. Hartwimmer (*Chem. Ber.*, **93**, 2238 (1960)) for the preparation of $(C_5H_5)_2TiBH_4$ but requires more forcing conditions.

(16) This compound has also been made from $[(C_6H_5)_3P]_3CuCl$ and CsB_3H_8: S. J. Lippard and D. Ucko, *Chem. Commun.*, 983 (1967); *Inorg. Chem.*, **7**, 1051 (1968).

TABLE I

B^{11} NMR DATA OF B_3H_8 AND BH_4 COMPLEXES

Compound	Solvent	Chem shift[a]	Rel intens
$[(CH_3)_4N][Cr(CO)_4B_3H_8]$	$(CH_3)_2CO$	+21.6	1
		+60.8	2
$[(CH_3)_4N][Mo(CO)_4B_3H_8]$	CH_3CN	+22.9	1
		+61.3	2
$[(CH_3)_4N][W(CO)_4B_3H_8]$	CH_3OH	+24.2	1
		+60.9	2
$[(C_6H_5)_3P]_2CuB_3H_8$	C_6H_6	+51.5	Broad peak without fine structure
$[(C_6H_5)_3P]_2CuB_3H_8$	CH_2Cl_2	+51.3	
$[(C_6H_5)_3P]_2CuBH_4$	CH_2Cl_2	+48.9	
CsB_3H_8	H_2O	+48.5	J_{B-H} = 35 cps
$NaBH_4$	H_2O	+60.3	J_{B-H} = 79 cps
$LiBH_4$	$(CH_3OCH_2)_2$	+59.4	J_{B-H} = 82 cps

[a] Chemical shifts in ppm relative to $B(OCH_3)_3$ as external standard.

pared in a similar fashion. The silver compound is photosensitive and in solution undergoes reduction to silver metal. The reduction proclivity is even more marked for the Au–B_3H_8 complex which has proved too unstable to be isolable. In this series of B_3H_8 complexes, the stability sequence is clearly Cu > Ag ≫ Au.

No dissociation of the copper complex $[(C_6H_5)_3P]_2CuB_3H_8$ occurs in benzene solution, at least to the extent detectable by measurement of colligative properties. Resonance studies, on the other hand, suggest lability of ligands. The B^{11} nmr spectrum of $[(C_6H_5)_3P]_2CuB_3H_8$ solutions consists of a broadened structureless signal, typical of exchange-controlled equilibria. There is no differentiation in the chemical shift for the two environmental sets of boron atoms as observed for the $M(CO)_4B_3H_8^-$ anions (Table I and Figure 1).[17]

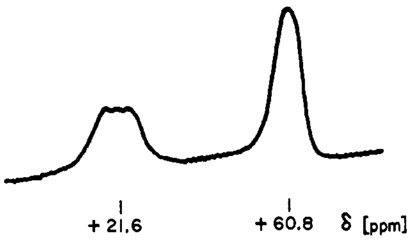

Figure 1.—B^{11} nmr spectrum of $[(CH_3)_4N][Cr(CO)_4B_3H_8]$ in acetone at 19.3 Mc. External reference, $B(OCH_3)_3$.

Ligand lability was established from P^{31} studies of mixtures of the copper complex and triphenylphosphine. A single low-field resonance was observed and the shift was a function of "free" ligand concentration. In all the other copper, silver, and gold complexes (Table II), ligand lability was established, but the shift was in the opposite direction, consonant with an averaging of free and bound ligand environments. Possibly the low-field shift in the Cu–$B_3H_8^-$ complex is explicable in terms of a fast equilibration with a new solution species such as $[(C_6H_5)_3P]_3CuB_3H_8$.

The molecular structure of the $(OC)_4CrB_3H_8^-$ ion has been elucidated from a three-dimensional X-ray structure investigation of $[(CH_3)_4N][Cr(CO)_4B_3H_8]$.[18] The structure of the anion (Figure 2) consists of an octahedrally hybridized Cr atom coordinated to four carbonyl groups and a B_3H_8 group. The plane of the three boron atoms makes an angle of 60° with the equatorial plane defined by the two bridging hydrogen atoms, the Cr atom, and the two equatorial CO groups. In this way two hydrogen atoms are pointed directly at the Cr atom permitting the B_3H_8 moiety to bond to the Cr atom through two three-center, two-electron M–H–B bonds. Some of the pertinent distances and angles involved in the B_3H_8 bonding to the Cr atom are shown in Figure 2. The positional parameters of the hydrogen atoms of the B_3H_8 group were included in the refinement of the $[(CH_3)_4N][Cr(CO)_4B_3H_8]$ structure.

TABLE II

P^{31} NMR SPECTRA AT 40.5 Mc[a]

Compound	Ppm	
	Complex	Complex + $(C_6H_5)_3P$
$(C_6H_5)_3P$ (= L)	+5.6	...
L_3CuCl	+4.4	...
$L_2CuB_3H_8$	−1.8	−3.5
$L_3CuB_9H_{12}S$	±0.0	+1.7
$L_3AuB_9H_{12}S$	−40.8	−19.8
$L_3AgB_9H_{14}$	−8.4	−3.5
$L_2CuB_{10}H_{13}$	±0.0	+3.8

[a] Solvent, CH_2Cl_2; chemical shifts relative to H_3PO_4 (external).

We believe the structure of the $(OC)_4CrB_3H_8^-$ ion is the *structural* prototype of most, if not all, B_3H_8 metal complexes presently known insofar as the mode of attachment of the B_3H_8 group to the metal is concerned. The molybdenum and tungsten complexes are isostructural with $(OC)_4CrB_3H_8^-$, and there is little difference between the infrared B–H stretching regions for $(OC)_4MB_3H_8^-$ anions and $[(C_6H_5)_3P]_2CuB_3H_8$ (Table III).

Although stoichiometry and spectral data connote a *formal* analogy between metal complexes of BH_4^- and $B_3H_8^-$, the analogy must be qualified because a close examination reveals subtleties. The cynosure is the titanium system: $(C_5H_5)_2TiBH_4$ and $(C_5H_5)_2TiB_3H_8$. The former complex displays an intense, sharp infrared band at 1942 cm^{-1}, ascribed to a Ti–H vibration,[15] to which there is no counterpart in the spectrum of $(C_5H_5)_2TiB_3H_8$. We have synthesized the deuterated

[17] The paramagnetic titanium compound $(C_5H_5)_2TiB_3H_8$ exhibits a structureless esr signal with an essentially temperature-invariant line width of ~9.85 G.

[18] F. Klanberg and L. J. Guggenberger, *Chem. Commun.*, 1293 (1967). Complete structural details will be reported separately by L. J. Guggenberger.

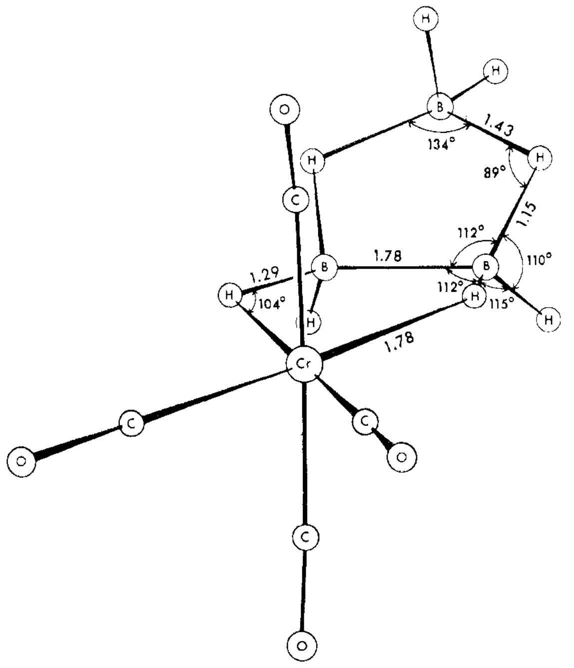

Figure 2.—The molecular configuration of $Cr(CO)_4B_3H_8^-$.

Table III

Infrared Spectra of B_3H_8 Complexes[a]

Compound	BH vibrations	CO vibrations
$[(CH_3)_4N][Cr(CO)_4B_3H_8]$	2489 m	2019 m
	2435 m	1903 vs
	2134 w	1884 s
	2109 w	1848 s
$[(CH_3)_4N][Mo(CO)_4B_3H_8]$	2488 m	2028 m
	2436 m	1908 vs
	2145 w	1881 m
	2105 w	1850 s
$[(CH_3)_4N][W(CO)_4B_3H_8]$	2494 m	2021 m
	2439 m	1936 m
	2145 w	1882 vs
	2105 w	1846 s
$[(C_6H_5)_3P]_2CuB_3H_8$	2489 s	
	2400 m	
	2125 m, b	
	2100 w, sh	
$(C_5H_5)_2TiB_3H_8$	2510 vs	
	2460 vs	
	2155 m	
	2100 m	
	2055 m, sh	

[a] Infrared absorptions in tetrahydrofuran solution except for $(C_5H_5)_2TiB_3H_8$ (Nujol mull); wave numbers ± 2 cm^{-1}.

titanium complex $(C_5H_5)_2TiBD_4$ in which the "unique" band is shifted to 1440 cm^{-1} suggesting that it is primarily associated with a B–D rather than a Ti–D vibration. Structural data are critically needed here.

Formal analogs of the $(OC)_4MB_3H_8^-$ ions, *i.e.*, the hypothetical ions $(OC)_4MBH_4^-$, do not seem to be readily isolable. This may reflect the lower order of bidentate efficacy in BH_4^-. Alternatively, the kinetic pathway to the more stable hydrogen-bridged anions $HM_2(CO)_{10}^-$ [19] may simply be more accessible in the BH_4^- system. In fact, even the $(OC)_4MB_3H_8^-$ ions rearrange to $HM_2(CO)_{10}^-$ ions by treatment with cesium fluoride in methanol.

$B_9H_{14}^-$ and $B_9H_{12}S^-$ Derivatives.—Reactions of simple salts of copper(II), silver(I), and gold(III) with CsB_9H_{14} and with $CsB_9H_{12}S$ in solutions of aqueous ethanol containing excess triphenylphosphine yield a series of complexes of the general stoichiometries $[(C_6H_5)_3P]_3MB_9H_{14}$ and $[(C_6H_5)_3P]_3MB_9H_{12}S$, respectively. These colorless, crystalline complexes do not differ significantly in their thermal and oxidative stability. Decomposition on exposure to the atmosphere is slow and manifests itself only after weeks when the originally transparent crystals become cloudy. There is a suggestion that the hydrolytic and oxidative stability in the $B_9H_{12}S^-$ group is Au > Ag > Cu, but the differences between individual compounds are not pronounced. The colorless copper $B_9H_{12}S^-$ derivative yellowed slightly on prolonged exposure to the atmosphere, whereas the gold complex under the same conditions has shown no signs of photodecomposition or oxidative decomposition after an exposure of more than 1 year. The copper derivatives tend to retain solvent if separation from solvent is rapid. This phenomenon is most pronounced on recrystallization from tetrahydrofuran.

The infrared spectral data for these complexes, as well as for complexes of the related species, are given in Table IV. All of these complexes have one weak to medium absorption in the region between 2200 and 2400 cm^{-1}, except for the $L_3AuB_9H_{14}$ complexes which have two weak bands in this region. The exact position of this (these) band(s) rises in going from copper to silver to gold. We initially associated this vibration with B–H–M multicenter bonds. In general, the band contours in the spectra of gold complexes are broad and diffuse compared to the quite sharp bands for the copper and silver complexes.

Table IV

B–H Vibrations of $B_9H_{12}S^-$, $B_9H_{14}^-$, $B_{10}H_{13}^-$, and $B_{11}H_{14}^-$ Complexes[a]

Compound	B–H str, cm^{-1}	B–H–B or M–H–B str, cm^{-1}
$L_3CuB_9H_{12}S$	2535 s, 2440 sh	2220 m
$L_3AgB_9H_{12}S$	2535 s, 2425 w	2275 m
$L_3AuB_9H_{12}S$	2535 s, 2425 m	2315 w
$L_3CuB_9H_{14}$	2535 s	2220 m
$L_3AgB_9H_{14}$	2535 s, 2440 sh	2275 m
$L_3AuB_9H_{14}$	2535 s, 2440 sh	2315 w, 2250 w
$L_2CuB_{10}H_{13}\cdot CH_2Cl_2$	2538 s	2335 w
$L_3AgB_{10}H_{13}\cdot 0.5$-$CH_2Cl_2$	2520 s	2300 vw
$L_3AuB_{10}H_{13}$	2535 s	2330 m
$L_2CuB_{11}H_{14}$	2550 s	2380 w, sh
$L_3AuB_{11}H_{14}$	2505 s	. . .

[a] Spectra in KBr disks; L = $(C_6H_5)_3P$.

An X-ray crystal structure investigation of $[(C_6H_5)_3P]_3AuB_9H_{12}S$ was undertaken to determine the configuration of the thiaborane cage and to examine the nature of the interaction between the metal atom and the polyhedral cage. The gold complex was chosen

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(19) (a) U. Anders and W. A. Graham, *Chem. Commun.*, 499 (1965); (b) L. B. Handy, P. M. Treichel, L. F. Dahl, and R. G. Hayter, *J. Am. Chem. Soc.*, **88**, 366 (1966); (c) R. G. Hayter, *ibid.*, **88**, 4376 (1966).

for this study because the copper complex decomposes slowly in the X-ray beam. Crystals of $[(C_6H_5)_3P]_3Au-B_9H_{12}S$ are triclinic with two formula units per cell. Approximately 3500 pieces of data were collected on a diffractometer using Mo Kα radiation. The structure was solved by heavy-atom techniques and at this point in the refinement the R factor $(\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ is 0.08.

The structure of $[(C_6H_5)_3P]_3AuB_9H_{12}S$ is shown in Figure 3 where a' is perpendicular to the bc^* plane completing an orthogonal-coordinate system. The structure shows that this complex is a salt composed of $[(C_6H_5)_3P]_3Au^+$ cations and $B_9H_{12}S^-$ anions. The closest gold-to-boron approach distance is 4.9 Å, too long to permit any metal–cage bonding interaction. Thus the infrared absorptions in the 2200–2400-cm^{-1} region (Table III) cannot be due to M–H–B bonds. The cation consists of three triphenylphosphine groups trigonally coordinated to gold(I). We believe this is the first authenticated case of a gold(I) complex which can be unambiguously identified as a trigonally hybridized metal atom.[20,21] We believe the Cu and Au derivatives have the same structure. Both complexes crystallize in the same crystal system with the same space group and very similar cell sizes (Experimental Section). The Cu derivative has a tendency to crystallize with varying amounts of dimethoxyethane included in the crystal; this solvent appears to be merely trapped in the crystal.

The structure of the thiaborane anions is essentially a decaborane cage with the sulfur atom occupying one of the positions on the periphery of the cage as shown in Figure 3. The back side of the cage closest to the Au atom is depicted in Figure 3. The structure found for the thiaborane cage had been predicted earlier[5] by analogy to $B_{10}H_{14}^{2-}$.

The solution behaviors of these $B_9H_{14}^-$ and $B_9H_{12}S^-$ derivatives are to a degree consistent with electrolyte behavior. Conductivities in acetonitrile are comparable to standard 1:1 electrolytes. Solution molecular weight determinations indicate an essential two-fragment dissociation, but these include solvents such as benzene where an alternative dissociative behavior

$$[(C_6H_5)_3P]_3M^+B_9H_{12}S^- \underset{\text{solvent}}{\overset{\text{nonpolar}}{\rightleftarrows}} [(C_6H_5)_3]_2MB_9H_{12}S + P(C_6H_5)_3 \quad (2)$$

cannot be excluded from consideration. "Dissociative" tendency is a function of the polarity and nucleophilicity of the solvent with dimethyl sulfoxide promoting three-particle fragmentation. A P^{31} nmr study of these boranes is consistent with phosphine dissociation. Each complex has a characteristic single P^{31} signal. When triphenylphosphine is added to a solution of the complex, a new broader peak appears at a position between that of the complex and free triphenylphosphine. These observations do establish the lability of the triphenylphosphine ligands but do not confirm nor negate the possibility of an equilibrium like (2). There are many plausible alternatives for the exchange process. Solution B^{11} nmr spectra of the $B_9H_{14}^-$ and $B_9H_{12}S^-$ derivatives were not those characteristic of these ions but consisted of relatively broad unstructural peaks suggesting an interaction of the cation and anion to a degree sufficient significantly to alter the relaxation times of the boron nuclei.

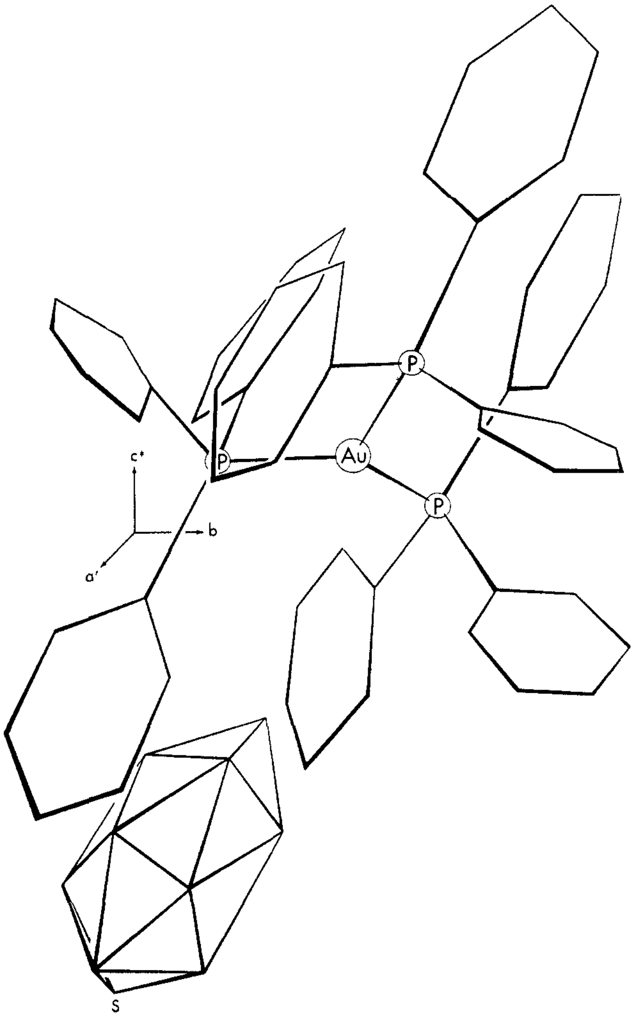

Figure 3.—The structure of $[(C_6H_5)_3P]_3AuB_9H_{12}S$.

In the hope of obtaining covalent complexes with metal–boron or metal–hydrogen–boron bonding, attempts were made to prepare complexes of the stoichiometry $[(C_6H_5)_3P]_2MB_9H_{12}S$. Mixtures were obtained and a separation was effected only in the case of silver. This bisphosphine complex behaves as a 1:1 electrolyte (conductivity and molecular weight data) in acetonitrile but appears to be largely undissociated in dichloromethane. Definitive structural studies are in progress and will be reported with those of the $B_{10}H_{13}^-$ derivatives.

Complexes of $B_{10}H_{13}^-$.—The reaction of triphenylphosphine complexes of copper and silver chloride with

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[20] The descriptive and structural chemistry of poly(triphenylphosphine) complexes of copper, silver, and gold(I) salts is far from definitive. Structurally established is the salt $[(C_6H_5)_3P]_2Au^+I^-$ with the ubiquitous linear gold coordination for PAuP: J. W. Collier, A. R. Fox, I. G Hinton, and F. G. Mann, *J. Chem. Soc.*, 1819 (1964).

[21] Since the structural demonstration of the trigonal gold cation, we have made analogous PF_6^- salts of the $(C_6H_5)_3M^+$ (Ag and Au) cations: E. L. Muetterties and C. W. Alegranti, to be submitted for publication.

alkali metal salts of $B_{10}H_{13}^-$ or $B_{10}H_{14}^{2-}$ yields $[(C_6H_5)_3P]_2CuB_{10}H_{13}$, $[(C_6H_5)_3P]_2AgB_{10}H_{13}$, and $[(C_6H_5)_3P]_3AgB_{10}H_{13}$. From chlorinated solvents, these compounds crystallize with at least one solvent molecule. In the initial reaction with the $B_{10}H_{14}^{2-}$ ion, the resulting copper complex is colorless and may be a $B_{10}H_{14}^{2-}$ salt. However, this Cu–$B_{10}H_{14}^{2-}$ species, too unstable for isolation, is converted with loss of hydrogen to the stable yellow complex of $B_{10}H_{13}^-$. The yellow color is associated with a relatively weak absorption in the visible region at 3500 Å (ϵ 2060). The color has persisted through many purification steps but may nevertheless be caused by an analytically undetectable impurity. Purified samples of $[(C_6H_5)_3P]_3AgB_{10}H_{13}$ and $[(C_6H_5)_3P]_3AuB_{10}H_{13}$ are nearly colorless although samples of lesser purity usually show yellow hues of varying intensity.

The trisphosphine derivatives are undoubtedly salts analogous to $[(C_6H_5)_3P]_3Au^+B_9H_{12}S^-$ with respect to the solid and polar solution state. However, this preliminary account of $B_{10}H_{13}^-$ metal derivatives is necessarily adumbrative in that available spectral, solution, and hydrolytic stability data are not wholly consistent in a structural context. Covalent interactions are presumed for the bis(phosphino)silver and copper complexes. However, confirmation cannot be derived from spectral studies and single-crystal X-ray studies appear necessary now. There is also evidence for the existence of $(C_6H_5)_3PAuB_{10}H_{13}$, which, if confirmed, would surely be a metalloborane with either Au–B or Au–H–B interactions. Formation of transition metal complexes of $B_{10}H_{12}^{2-}$ from $B_{10}H_{13}^-$ are presented in paper II of this series[22] and a complete account of $B_{10}H_{13}^-$ metalloboranes will be reported when the structural studies are completed. Note that P^{31} nmr studies establish that these B_{10} derivatives are not based on the $B_{10}H_{13}P(C_6H_5)_3^-$ anion.

Complexes of $B_{11}H_{14}^-$.–The cesium salt of $B_{11}H_{14}^-$ reacts with Cu(II) and Au(III) salts in the presence of triphenylphosphine to give complexes of composition $[(C_6H_5)_3P]_3MB_{11}H_{14}$. Both the copper and the gold complexes do not undergo thermal degradation below 200°. In solution, the B^{11} nmr spectra of these complexes are essentially that of the $B_{11}H_{14}^-$ ion, and perhaps in such nonpolar solutions the aggregates are primarily ion pairs.

Experimental Section

Salts of $M(CO)_4B_3H_8^-$.—Metal hexacarbonyl (0.040 mol for Cr, Mo, and W) and CsB_3H_8 (6.8 g, 0.040 mol) were dissolved in a mixture of 1,2-dimethoxyethane (150 ml) and 2,2′-dimethoxyethyl ether (250 ml). The solution was heated to reflux under nitrogen for 1–3 hr. The color of the mixture after this time was dark yellow to red. The solution was allowed to cool to room temperature and filtered, and the filtrate was poured into a large volume of water (1–2 l.) containing a molar excess of tetramethylammonium chloride. The resulting precipitate was collected, recrystallized from methanol (100–175 ml), and dried at 60° (0.001 mm). Small amounts of unreacted metal hexacarbonyl sublimed under these conditions. The yield was uniformly about 70%.

Anal. Calcd for $[(CH_3)_4N][Cr(CO)_4B_3H_8]$: C, 34.5; H, 7.2; N, 5.0; B, 11.7; Cr, 18.7. Found: C, 34.4; H, 6.9; N, 5.2; B, 11.7; Cr, 18.3; mp 167–172° dec. Calcd for $[(CH_3)_4N][Mo(CO)_4B_3H_8]$: C, 29.8; H, 6.3; N, 4.3; B, 10.1; Mo, 29.7. Found: C, 29.7; H, 6.1; N, 4.4; B, 9.9; Mo, 29.3; mp 161–164° dec. Calcd for $[(CH_3)_4N][W(CO)_4B_3H_8]$: C, 23.4; H, 4.9; N, 3.4; B, 7.9; W, 44.8. Found: C, 23.5; H, 4.6; N, 3.1; B, 7.9; W, 44.1; mp 167–169° dec.

Electronic spectral data are given in Table V.

TABLE V

ELECTRONIC SPECTRA OF $M(CO)_4B_3H_8^-$ SALTS

Salt	$\lambda(CH_3CN)_{max}$, Å	Molar extinction coeff
$[(CH_3)_4N][Cr(CO)_4B_3H_8]$	3980	1,450
	3150	3,150
	2400	26,700
	2240	28,200
$[(CH_3)_4N][Mo(CO)_4B_3H_8]$	3780	2,080
	2950	11,060
	2280	46,400
$[(CH_3)_4N][W(CO)_4B_3H_8]$	3720	1,650
	2890	7,030
	2470	29,300
	2220	37,800

$HW_2(CO)_{10}^-$ from $W(CO)_4B_3H_8^-$.—A solution of $[(CH_3)_4N][W(CO)_4B_3H_8]$ (2.2 g, 0.005 mol) in acetonitrile (100 ml) was passed through a sodium ion exchange column. The column was eluted with 200 ml of acetonitrile–water (1:1), and the effluent was evaporated to dryness to give 1.8 g of yellow, hygroscopic $[Na][W(CO)_4B_3H_8]$. The sodium salt was dissolved in a minimum amount of methanol and treated with a methanolic solution of cesium fluoride. The mixture was filtered, and 200 ml of water was added to the filtrate. The resulting pale yellow precipitate (0.8 g) was recovered by filtration and recrystallized from 10 ml of methanol. The infrared and ultraviolet spectra of the precipitate were identical with those of an authentic sample of $Cs[HW_2(CO)_{10}]$.[19] Treatment with tetraethylammonium chloride in aqueous methanol converted the cesium salt to $[(C_2H_5)_4N][HW_2(CO)_{10}]$.

Anal. Calcd for $[(C_2H_5)_4N][HW_2(CO)_{10}]$: C, 27.8; H, 2.7; N, 1.8. Found: C, 28.0; H, 3.1; N, 1.8.

$(C_5H_5)_2TiB_3H_8$.—A mixture of $(C_5H_5)_2TiCl_2$ (2.5 g, 0.010 mol) and CsB_3H_8 (3.4 g, 0.020 mol) in 200 ml of 1,2-dimethoxyethane was refluxed for 3 hr. After a series of transient color changes, the solution finally remained azure blue. The mixture was filtered, the filtrate evaporated to dryness, and the residue sublimed at 120–150° (0.001 mm) (rigorous exclusion of air). The yield was 1.5 g of a dark blue, crystalline solid, mp 117–120° in a sealed tube under N_2.

Anal. Calcd for $(C_5H_5)_2TiB_3H_8$: C, 54.9; H, 8.3; Ti, 21.9; B, 14.9. Found: C, 54.8; H, 8.3; Ti, 22.0; B, 15.0.

The mass spectrum was consistent with the formula showing a parent peak at m/e 219 and other fragments at 178 ($(C_5H_5)_2Ti^+$), 113 ($C_5H_5Ti^+$), 48 (Ti^+), and 41–30 ($B_3H_{8-x}^+$ fragments).

$[(C_6H_5)_3P]_2CuB_3H_8$.—A solution of CsB_3H_8 (3.4 g, 0.02 mol) in 50 ml of ethanol and 25 ml of water was gradually added to a filtered solution of triphenylphosphine (8 g, 0.03 mol) and copper sulfate (2 g, 0.013 mol) in a mixture of 105 ml of warm ethanol and 30 ml of water. A vigorous, exothermic reaction ensued with precipitation of a white solid. This solid was dissolved in 50 ml of tetrahydrofuran; the solution was filtered and then evaporated to dryness. The residue was recrystallized from 50 ml of acetone and cyclohexane (1:1) to give $[(C_6H_5)_3P]_2CuB_3H_8$ as large colorless crystals (2.1 g). Another crop (0.6 g) was obtained from the mother liquor, mp 156–158° dec.

Anal. Calcd for $[(C_6H_5)_3P]_2CuB_3H_8$: C, 68.8; H, 6.1; P, 9.9; B, 5.2; Cu, 10.1. Found: C, 68.6; H, 6.1; P, 9.5; B, 5.3; Cu, 10.2.

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[22] F. Klanberg, P. A. Wegner, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.*, **6**, 2072 (1968).

The ultraviolet absorption maxima are 2750 (ϵ 14,000) and 2630 Å (ϵ 15,450).

$[(C_6H_5)_3P]_2AgB_3H_8$.—A solution of CsB_3H_8 (1.7, 0.01 mol) in 40 ml of a 1:1 mixture of water and ethanol was added to a warm solution of 15 g of triphenylphosphine and 1.7 g of $AgNO_3$ in 200 ml of ethanol and 10 ml of water. The resulting white precipitate was treated with 250 ml of warm tetrahydrofuran, and insoluble material ($CsNO_3$) was removed by filtration. Evaporation of the filtrate left 12 g of white solid. This solid proved very difficult to purify by recrystallization because degradation occurred in warm solvents. Small crystals (3 g) were obtained by isothermal concentration of a solution (140 ml of a 4:2:1 mixture of dimethoxyethane, tetrahydrofuran, chloroform, and 12 g of crude product). The crystals remained colorless while covered with solvent but became beige and nontransparent when dry. They yellowed gradually above 100° and decomposed to a gray-black liquid at 165°.

Anal. Calcd for $[(C_6H_5)_3P]_2AgB_3H_8$: C, 69.4; H, 5.7; B, 3.5; Ag, 11.5. Found: C, 69.0; H, 5.3; B, 2.4; Ag, 9.0.

$[(C_6H_5)_3P]_3CuB_9H_{12}S$.—A solution of $CsB_9H_{12}S$ (3 g, 0.01 mol) in 30 ml of ethanol was added to a mixture of triphenylphosphine (8 g, 0.03 mol) and $CuSO_4$ (1.6 g, 0.01 mol) in 150 ml of ethanol and 50 ml of water to give a white precipitate. This was recrystallized first from 100 ml of tetrahydrofuran and then from 90 ml of dimethoxyethane; yield, 3.0 g of colorless crystals, mp 166–167° dec.

Anal. Calcd for $[(C_6H_5)_3P]_3CuB_9H_{12}S$: C, 65.4; H, 5.8; P, 9.4; B, 9.8; S, 3.2; Cu, 6.4. Found: C, 65.2; H, 6.4; P, 8.8; B, 9.8; S, 3.1; Cu, 6.2.

The compound absorbed ultraviolet radiation in CH_3CN solution at 2750 (ϵ 19,230) and 2620 Å (ϵ 21,950).

$[(C_6H_5)_3P]_3AgB_9H_{12}S$.—A solution of $CsB_9H_{12}S$ (2.7 g, 0.01 mol) in 40 ml of ethanol–water (1:1) was added to a solution containing 15 g of triphenylphosphine and 1.7 g of $AgNO_3$ with precipitation of a solid. The solid was extracted with 300 ml of warm tetrahydrofuran, the mixture was filtered, and the filtrate was concentrated until crystals precipitated. This crystalline solid was dissolved in 300 ml of warm chloroform. Reduction of the volume to 50 ml with chilling gave 5.6 g of small white crystals which darkened above 180° and melted with decomposition at 190–192°.

Anal. Calcd for $[(C_6H_5)_3P]_3AgB_9H_{12}S$: C, 62.6; H, 5.5; P, 9.0; B, 9.4; S, 3.1; Ag, 10.4. Found: C, 62.5; H, 5.8; P, 8.7; B, 9.5; S, 3.2; Ag, 10.6.

$[(C_6H_5)_3P]_3AuB_9H_{12}S$.—An ethanolic solution (100 ml) of triphenylphosphine (6.0 g, 0.023 mol) was added to a solution of $NaAuCl_4 \cdot 2H_2O$ (3.0 g, 0.008 mol) in 40 ml of aqueous ethanol. The slightly turbid reaction mixture was filtered. To the filtrate, there was added $CsB_9H_{12}S$ (2 g, 0.008 mol) in 30 ml of aqueous ethanol. A white solid precipitated which was collected and recrystallized from 40 ml of 1,2-dimethoxyethane to give 2.7 g of colorless crystals, mp 181–183° dec.

Anal. Calcd for $[(C_6H_5)_3P]_3AuB_9H_{12}S$: C, 57.6; H, 5.1; P, 8.3; B, 8.7; S, 2.9; Au, 17.5. Found: C, 57.9; H, 5.1; P, 7.9; B, 8.6; S, 2.9; Au, 17.5.

In attempts to prepare an analogous complex, $[(C_6H_5)_3As]_3AuB_9H_{12}S$, multiphase products proved inseparable by several conventional procedures.

$[(C_6H_5)_3P]_3CuB_9H_{14}$.—Copper sulfate (1.6 g, 0.01 mol) in 50 ml of water was mixed with triphenylphosphine (5.2 g, 0.02 mol) in 150 ml of ethanol, and CsB_9H_{14} (2.4 g, 0.01 mol) was added to the mixture. The resulting white precipitate was extracted with 75 ml of warm tetrahydrofuran, and the solution thus obtained was concentrated until a solid precipitated. This solid was purified by recrystallization from an acetone–cyclohexane (2:1) mixture; the recovered material (2 g) was recrystallized again from 3 ml of warm 1,2-dimethoxyethane to give colorless crystals (0.7 g). Another crop (0.6 g) of lower purity was obtained from the mother liquor. The pure crystals melted with decomposition at 154–156°.

Anal. Calcd for $[(C_6H_5)_3P]_3CuB_9H_{14}$: C, 67.4; H, 6.2; P, 9.7; B, 10.1; Cu, 6.6. Found: C, 67.7; H, 6.2; P, 9.3; B, 10.2; Cu, 6.7.

The ultraviolet spectrum in acetonitrile showed a peak at 2670 Å (ϵ 24,500). The B^{11} nmr spectrum displayed a broad peak centered at 41.4 ppm.

$[(C_6H_5)_3P]_3AgB_9H_{14}$.—A solution of CsB_9H_{14} (2.7 g, 0.01 mol) in 50 ml of ethanol and 10 ml of water was rapidly added to a mixture of triphenylphosphine (15 g, 0.06 mol) and $AgNO_3$ (1.7 g, 0.01 mol) in 160 ml of ethanol and 10 ml of water. The resulting white precipitate was dissolved in 220 ml of warm tetrahydrofuran and filtered. The tetrahydrofuran filtrate was concentrated to about one-third of the original volume, where small crystals started to precipitate. These crystals were recrystallized from 175 ml of chloroform and subsequently from 100 ml of tetrahydrofuran. The yield was 7.0 g (two crops) of colorless crystals, mp 187–189° dec. The compound is light sensitive.

Anal. Calcd for $[(C_6H_5)_3P]_3AgB_9H_{14}$: C, 64.5; H, 5.9; P, 9.2; B, 9.7; Ag, 10.7. Found: C, 64.9; H, 6.4; P, 8.4; B, 9.1; Ag, 10.2.

The B^{11} nmr spectrum consisted of a broad peak at 40 ppm.

$[(C_6H_5)_3P]_3AuB_9H_{14}$.—A solution of $NaAuCl_4 \cdot 2H_2O$ (3.0 g, 0.008 mol) in 40 ml of aqueous ethanol was added dropwise to a mixture of triphenylphosphine (12 g, 0.046 mol) and CsB_9H_{14} (2 g, 0.008 mol) in 220 ml of ethanol–water (10:1). A crude brown solid precipitated with simultaneous gas evolution and some formation of metallic gold. The crude solid (6.2 g) was recrystallized twice from 30–60 ml of 1,2-dimethoxyethane. The final yield was 3.5 g of nearly colorless, transparent crystals of $[(C_6H_5)_3P]_3AuB_9H_{14}$, mp 177–179° dec.

Anal. Calcd for $[(C_6H_5)_3P]_3AuB_9H_{14}$: C, 59.2; H, 5.4; P, 8.5; B, 8.9; Au, 18.0. Found: C, 59.4; H, 5.8; P, 8.0; B, 8.8; Au, 18.0.

The B^{11} nmr spectrum in CH_3CN showed a broad peak centered at 39.5 ppm.

$[(C_6H_5)_3P]_2CuB_{10}H_{13} \cdot CH_2Cl_2$.—To a freshly filtered ethereal solution of $NaB_{10}H_{13}$ prepared from $B_{10}H_{14}$ (2.4 g, 0.020 mol) and excess sodium hydride was added $[(C_6H_5)_3P]_3CuCl$ (8.9 g, 0.010 mol) in 125 ml of CH_2Cl_2. The mixture was stirred for 1 hr and then filtered. The yellow filtrate was concentrated on a rotating evaporator to a volume of 25 ml whereupon a yellow crystalline solid separated. The crude solid (5 g) was purified by recrystallization from 100 ml of CH_2Cl_2 to give 3.0 g of small, platelike, yellow crystals, mp 147–150°.

Anal. Calcd for $[(C_6H_5)_3P]_2CuB_{10}H_{13} \cdot CH_2Cl_2$: C, 56.0; H, 5.7; P, 7.8; B, 13.6; Cu, 8.0; Cl, 8.9. Found: C, 56.3; H, 5.9; P, 7.8; B, 14.0; Cu, 7.8; Cl, 7.6.

The ultraviolet spectrum in CH_2Cl_2 showed absorption at 3500 (ϵ 2060) and at 2520 Å (ϵ 25,000).

$[(C_6H_5)_3P]_3AgB_{10}H_3 \cdot {}^1/_2CH_2Cl_2$.—A solution of $[(C_6H_5)_3P]_3AgCl \cdot {}^5/_3CHCl_3$[23] (10 g, 0.009 mol) in 100 ml of CH_2Cl_2 was stirred for 30 min with an ethereal solution of $NaB_{10}H_{13}$ prepared from $B_{10}H_{14}$ (1.8 g, 0.015 mol) and NaH as above. A thick yellowish precipitate formed from which the desired complex was separated from the accompanying NaCl by extraction with dichloromethane in a Soxhlet apparatus. The dichloromethane extract was evaporated to dryness, and the resultant solid residue was recrystallized from 400 ml of ether–dichloromethane (1:1). Slow cooling to −20° was necessary to obtain crystals (4.5 g), mp 100° dec.

Anal. Calcd for $[(C_6H_5)_3P]_3AgB_{10}H_{13} \cdot {}^1/_2CH_2Cl_2$: C, 61.8; H, 5.6; P, 8.8; B, 10.2; Ag, 10.2; Cl, 3.4. Found: C, 62.5; H, 5.6; P· 8.0; B, 10.7; Ag, 9.6; Cl, 2.7.

The ultraviolet spectrum in CH_2Cl_2 showed a weak inflection at 3500 Å and a peak at 2530 Å (ϵ 37,300). The B^{11} nmr spectrum

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(23) This solvate, mp 178–180°, was invariably obtained when the synthesis of $[(C_6H_5)_3P]_3AgCl$ was attempted according to the procedure reported by F. Cariati and L. Naldini, *Gazz. Chim. Ital.*, **95**, 3, 201 (1965). *Anal.* Calcd for $[(C_6H_5)_3P]_3AgCl \cdot {}^5/_3CHCl_3$: C, 59.3; H, 4.2; P, 8.2; Ag, 9.5; Cl, 18.8. Found: C, 59.6; H, 4.3; P, 7.8; Ag, 9.3; Cl, 18.9. Similarly, the reaction of CuCl with triphenylphosphine in $CHCl_3$ leads to $[(C_6H_5)_3P]_3CuCl \cdot xCHCl_3$, where $x \approx 1$. These crystals cannot be desolvated by heating to 60° (0.0001 mm). A nearly chloroform-free product was obtained by recrystallization from acetone–1,2-dimethoxyethane.

showed a broad peak at +18.2 ppm (from external $B(OCH_3)_3$) and a high-field doublet at +53.7 ppm with $J_{B-H} = 138$ cps. The relative intensities of these two areas of absorption was 8:2.

Preparation of $[(C_6H_5)_3P]_2AgB_9H_{12}S$.—A solution of $CsB_9H_{12}S$ (2.74 g, 0.01 mol) in 20 ml of ethanol and 20 ml acetonitrile was added to a solution of silver nitrate (1.69 g, 0.01 mol) and triphenylphosphine (5.24 g, 0.02 mol) in about 3 ml of water, 150 ml of methanol, and 110 ml of acetonitrile. On mixing, a white solid immediately separated, which, after being stirred for about 10 min, turned slightly pinkish. The solid was recovered by filtration and then dissolved in a cold mixture of acetonitrile (80%), toluene (10%), and dimethoxyethane (10%). The solution was filtered, slightly concentrated under vacuum, and then cooled. On cooling, large white crystals separated and these were collected by filtration and vacuum dried at room temperature, mp 178–184° dec.

Anal. Calcd for $[(C_6H_5)_3P]_2AgB_9H_{12}S$: C, 55.9; H, 5.47; Ag, 14.0; B, 12.6; S, 4.14 (mol wt 773.7). Found: C, 56.5; H, 5.48; Ag, 14.4; B, 12.4; S, 4.77 (mol wt 372 (CH_3CN), 743 (CH_2Cl_2); vapor pressure osmometer).

$[(C_6H_5)_3P]_3AuB_{10}H_{13}$.—A solution of $Cs_2B_{10}H_{14}$ (2 g, 0.005 mol) in 25 ml of ethanol and 15 ml of water was added to the warm mixture of triphenylphosphine (15 g, 0.006 mol) and $NaAuCl_4 \cdot 2H_2O$ (2 g, 0.005 mol) in 200 ml of ethanol. A precipitate formed which was separated by filtration and then extracted with 50 ml of tetrahydrofuran. The extract was evaporated on a rotating evaporator to a yellowish solid. The crude product (12 g) was purified by recrystallization from 25 ml of dimethoxyethane to give, in several crops, a total of 4.1 g of platelike crystals. The purest fraction melted at 125–127° into a dark red liquid. The compound decomposed in refluxing benzene producing a gold mirror but was stable in refluxing chloroform.

Anal. Calcd for $[(C_6H_5)_3P]_3AuB_{10}H_{13}$: C, 58.7; H, 5.4; P, 8.4; B, 9.8; Au, 17.8. Found: C, 58.6; H, 6.0; P, 8.1; B, 9.6; Au, 17.6.

$[(C_6H_5)_3P]_3CuB_{11}H_{14}$.—A mixture of triphenylphosphine (7.8 g, 0.03 mol) and copper sulfate (1.6 g, 0.01 mol) in 180 ml of ethanol and 50 ml of water was stirred with a solution of $CsB_{11}H_{14}$ (3 g, 0.01 mol) in 70 ml of water–ethanol (1:1). A cream-colored precipitate formed which was collected and dissolved in 150 ml of warm tetrahydrofuran. Concentration of this yellow solution gave 5.5 g of beige solid. Because of a very small solubility temperature coefficient in a variety of solvents, crystallization of the solid proved difficult. The best solvent found was a 1:1 mixture of benzene and dimethoxyethane. A reasonably pure sample (1 g) was obtained after three recrystallizations. The solid decomposed in the range 205–220°.

Anal. Calcd for $[(C_6H_5)_3P]_2CuB_{11}H_{14}$: C, 66.0; H, 6.1; B, 12.1; Cu, 6.5. Found: C, 65.1; H, 6.4; B, 12.3; Cu, 6.3.

$[(C_6H_5)_3P]_3AuB_{11}H_{14}$.—A solution of $NaAuCl_4 \cdot 2H_2O$ (3.3 g, 0.008 mol) in 40 ml of ethanol was added to a mixture of triphenylphosphine (6.5 g, 0.025 mol) and $CsB_{11}H_{14}$ (2.6 g, 0.01 mol) in 160 ml of warm ethanol and 10 ml of water. A pure white precipitate appeared which turned pink after standing for a short while. The crude solid was isolated by filtration and recrystallized three times from hot 1,2-dimethoxyethane (10–30 ml). The final product consisted of white crystals which yellowed at 195° and melted to a black liquid 217–218°.

Anal. Calcd for $[(C_6H_5)_3P]_3AuB_{11}H_{14}$: C, 58.1; H, 5.3; P, 8.3; B, 10.7; Au, 17.6. Found: C, 57.7; H, 5.7; P, 7.7; B, 10.2; Au, 17.1.

$(C_5H_5)_2TiBD_4$.—This compound was made analogously[15] to $(C_5H_5)_2TiBH_4$ by adding excess $LiBD_4$ to a suspension of $(C_5H_5)_2TiCl_2$ in ether. Salient infrared absorptions occur at 1850 (s), 1770 (vs), 1720 (s), 1640 (w), 1560 (sh), 1440 (vs), and 861 cm^{-1}. The corresponding absorptions in $(C_5H_5)_2TiBH_4$ are at 2470 (s), 2405 (vs), 2305 (m), 2220 (vw), 2105 (m), 1950 (vs), and 1150 (vs) cm^{-1}. There is generally good agreement between the observed values and those calculated for an isotopic ratio $\sqrt{(B-H)}/\sqrt{(B-D)} = 1.36$.

Lattice Constants.—The lattice parameters for the first three compounds were obtained from powder diffraction data recorded on a Hägg–Guinier camera using a KCl internal standard while the parameters for the last two compounds were measured from photographs taken on a precesion camera: $[(CH_3)_4N][Cr(CO)_4B_3H_8]$: monoclinic, $a = 11.074$ Å, $b = 8.938$ Å, $c = 7.784$ Å, $\beta = 98.12°$, $\rho_x = 1.216$ g/cm^3, $\rho_E = 1.216$ g/cm^3. $[(CH_3)_4N][Mo(CO)_4B_3H_8]$: monoclinic, $a = 11.249$ Å, $b = 8.896$ Å, $c = 7.812$ Å, $\beta = 98.20°$, $\rho_x = 1.385$ g/cm^3, $\rho_E = 1.374$ g/cm^3. $[(CH_3)_4N][W(CO)_4B_3H_8]$: monoclinic, $a = 11.214$ Å, $b = 8.896$ Å, $c = 7.799$ Å, $\beta = 98.33°$, $\rho_x = 1.771$ g/cm^3, $\rho_E = 1.835$ g/cm^3. $[(C_6H_5)_3P]_3AuB_9H_{12}S$: triclinic, $a = 13.07$ Å, $b = 19.58$ Å, $c = 11.19$ Å; $\alpha = 103.1°$, $\beta = 107.8°$, $\gamma = 86.6°$, $\rho_x = 1.41$ g/cm^3, $\rho_E = 1.42$ g/cm^3. $[(C_6H_5)_3P]_3CuB_9H_{12}S$: triclinic, $a = 12.78$ Å, $b = 19.91$ Å, $c = 11.73$ Å, $\alpha = 93.0°$, $\beta = 109.1°$, $\gamma = 94.9°$, $\rho_x = 1.18$ g/cm^3, $\rho_E = 1.21$ g/cm^3. In this tabulation ρ_x denotes calculated density derived from the X-ray parameters and ρ_E is the experimentally determined density obtained by the flotation method.

Susceptibility Measurements.—Diamagnetic susceptibilities determined at 8 kG and 297° K agree within experimental error with those calculated from Pascal's constants for representative complexes. (See Table VI.)

TABLE VI

Compound	$10^3\chi_M$ Obsd	$10^3\chi_M$ Calcd
$[(C_6H_5)_3P]_2CuB_3H_8$	-0.40 ± 0.02	-0.38 ± 0.01
$[(C_6H_5)_3P]_3CuB_9H_{12}S$	-0.55 ± 0.03	-0.61 ± 0.02
$[(C_6H_5)_3P]_3AuB_9H_{12}S$	-0.68 ± 0.03	-0.64 ± 0.02
$[(C_6H_5)_3P]_3AuB_{10}H_{13}$	-0.60 ± 0.03	-0.63 ± 0.02

Molecular Weight Data.—Molecular weights in C_6H_6 and $(CH_3)_2SO$ were obtained cryoscopically, in CH_2Cl_2 and CH_3CN by vapor pressure osmometer at 37° (Table VII).

TABLE VII

MOLECULAR WEIGHT DATA FOR METALLOBORANES

Compound	Solvent	Mol wt Calcd	Mol wt Found
$[(CH_3)_4N][Cr(CO)_4B_3H_8]$	$(CH_3)_2SO$	279	137
$[(CH_3)_4N][Mo(CO)_4B_3H_8]$	$(CH_3)_2SO$	323	128
$[(CH_3)_4N][W(CO)_4B_3H_8]$	$(CH_3)_2SO$	411	193
$L_2CuB_3H_8$	C_6H_6	629	618
$L_3CuB_9H_{12}S$	C_6H_6	992	426
	CH_2Cl_2		496
$L_3AuB_9H_{12}S$	CH_2Cl_2	1126	546
	$(CH_3)_2SO$		495
$L_3CuB_9H_{14}$	C_6H_6	962	557
$L_3AgB_9H_{14}$	CH_2Cl_2	1006	562
	$(CH_3)_2SO$		369
$L_2CuB_{10}H_{13} \cdot CH_2Cl_2$	CH_2Cl_2	794	623
	CH_3CN		207
$Cu_2B_{10}H_{10} \cdot 4CH_3CN$	CH_3CN	410	283

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