Chemistry of Boranes. XXX.[1]
Carbonyl Derivatives of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$

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Abstract: Reaction of hydrated $H_2B_{12}H_{12}$ with carbon monoxide gives 1,7- and 1,12-$B_{12}H_{10}(CO)_2$ and $B_{12}H_{11}CO^-$. These carbonyls, as well as 1,10-$B_{10}H_8(CO)_2$, react with water, alcohols, and amines to form carboxylic acids, esters, and amides, respectively. Other reactions of the carbonyls result in their conversion to isocyanates, amines, urethans, nitriles, and analogous halogenated species such as 1,10-$B_{10}Cl_8(CO)_2$ and 1,10-$B_{10}I_8(NCO)_2^{2-}$.

An earlier paper in this series described 1,10-$B_{10}H_8(N_2)_2$ and its conversion to a variety of compounds including 1,10-$B_{10}H_8(CO)_2$, $C_6H_{11}B_{10}H_7(CO)_2$, and $(C_6H_{11})_2B_{10}H_6(CO)_2$.[2] This paper is concerned with the chemistry of these dicarbonyls as well as that of 1,7- and 1,12-$B_{12}H_{10}(CO)_2$ and $B_{12}H_{11}CO^-$ which was previously outlined in a communication.[3] Some similar work with 1,12-$B_{12}H_{10}(CO)_2$ and 1,10-$B_{10}H_8(CO)_2$ has since been described by others.[4] Related nonionic monocarbonyls such as 1,6-$(CH_3)_2SB_{10}H_8CO$ and $(CH_3)_3NB_{12}H_{10}CO$ have been reported separately.[5]

Preparation and Characterization. The preparation of 1,10-$B_{10}H_8(CO)_2$ was reported earlier.[2a] Reaction of hydrated $H_2B_{12}H_{12}$[6] with carbon monoxide at elevated temperatures and pressures followed by work-up in aqueous solution gives hydrated 1,7- and 1,12-$H_2B_{12}H_{10}(COOH)_2$ and $H_2B_{12}H_{11}COOH$. These acids are isolated and purified as cesium salts. The salts are reconverted to the acids by ion exchange and then to the carbonyls by removal of water.

$$H_2B_{12}H_{12}\cdot 4.5H_2O \xrightarrow{CO} \xrightarrow[Cs^+]{H_2O} Cs_2B_{12}H_{10}(COOH)_2 + Cs_2B_{12}H_{11}COOH$$

$$Cs_2B_{12}H_{10}(COOH)_2 \xrightarrow[\text{exchange}]{H^+\text{ ion}} H_2B_{12}H_{10}(COOH)_2\cdot xH_2O \xrightarrow{-H_2O} B_{12}H_{10}(CO)_2$$

$$Cs_2B_{12}H_{11}COOH \xrightarrow[\text{exchange}]{H^+\text{ ion}} H_2B_{12}H_{11}COOH\cdot xH_2O \xrightarrow{-H_2O} HB_{12}H_{11}CO\cdot 2H_2O$$

The water content of the hydrated $H_2B_{12}H_{12}$ used in the reaction with carbon monoxide should be between 4 and 5 moles of water per mole of $H_2B_{12}H_{12}$ for best yields. Dicobalt octacarbonyl is an effective catalyst. Both the mono- and the dicarboxylic acids can be obtained in its absence, but the yields are improved and are more reproducible in its presence. Additionally, dicobalt octacarbonyl affects the stereochemistry of the biscarbonylation.

The monocarboxylic acid can be obtained in 50% yield (when isolated as the cesium salt, $Cs_2B_{12}H_{11}COOH$) if the reaction is conducted at 70° (1000 atm) in the presence of 25–35% by weight of dicobalt octacarbonyl. The dicarboxylic acid is obtained primarily as the 1,12 isomer in about 40% yield as the cesium salt when the reaction is conducted as described for the monocarboxylic acid, followed by a further reaction period at 130°. Small amounts (*ca.* 5%) of the 1,7 isomer are also formed. Approximately equal yields (*ca.* 10%) of the 1,7 and 1,12 isomers are obtained by carbonylation of $HB_{12}H_{11}CO\cdot 3H_2O$ at 130° in the absence of cobalt carbonyl. The cesium salts of 1,7- and 1,12-$B_{12}H_{10}(COOH)_2^{2-}$ can be separated by fractional recrystallization.

Stereochemical characterization of the 1,7 isomer was obtained by converting it to the known 1,7-$B_{12}H_{10}(NH_3)_2$[7] by reaction with hydroxylamine-O-sulfonic acid in water. Stereochemical characterization of the 1,12 isomer was obtained by X-ray analysis.[8]

In common with 1,10-$B_{10}H_8(CO)_2$, the 1,7 and 1,12 isomers of $B_{12}H_{10}(CO)_2$ are colorless, sublimable solids with good to moderate solubility in a variety of polar and nonpolar solvents. Dissolution in protonic solvents is accompanied by reaction; this is discussed in more detail below.

Carbonyl derivatives of other boranes, such as BH_3CO[9] and B_4H_7CO,[10] tend to dissociate at relatively low temperatures. However, the thermal stabilities of the B_{10} and B_{12} carbonyls are quite good as is typical of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ and their derivatives.[2,6,11,12] All three dicarbonyls can be sublimed *in vacuo* at 100° without decomposition.

The carbonyl groups are characterized by intense absorptions in the infrared at 2140–2220 cm^{-1} as shown in Figure 1 and summarized in Table I.

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[1] Paper XXIX: W. R. Hertler, F. Klanberg, and E. L. Muetterties, *Inorg. Chem.*, 6, 1696 (1967).

[2] (a) W. H. Knoth, *J. Am. Chem. Soc.*, 88, 935 (1966). (b) For a description of the numbering convention used for polyhedral boranes, see R. Adams, *Inorg. Chem.*, 2, 1087 (1963).

[3] W. H. Knoth, J. C. Sauer, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, 86, 115 (1964).

[4] F. Haslinger, A. H. Soloway, and D. N. Butler, *J. Med. Chem.*, 9, 581 (1966).

[5] W. R. Hertler, W. H. Knoth, and E. L. Muetterties, *Inorg. Chem.*, 4, 288 (1965).

[6] E. L. Muetterties, J. H. Balthis, Y. T. Chia, W. H. Knoth, and H. C. Miller, *ibid.*, 3, 444 (1964).

[7] W. R. Hertler and M. S. Raasch, *J. Am. Chem. Soc.*, 86, 3661 (1964).

[8] K. R. Babcock, unpublished.

[9] A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, 59, 780 (1937).

[10] A. B. Burg and J. R. Spielman, *ibid.*, 81, 3479 (1959).

[11] W. H. Knoth, J. C. Sauer, D. C. England, W. R. Hertler, and E. L. Muetterties, *ibid.*, 86, 3973 (1964).

[12] W. H. Knoth, H. C. Miller, J. C. Sauer, J. H. Balthis, Y. T. Chia, and E. L. Muetterties, *Inorg. Chem.*, 3, 159 (1964).

Table I. C≡O Stretching Frequencies[a]

Compound	ν^{Nujol}, cm^{-1}	$\nu^{\text{CH}_2\text{Cl}_2}$, cm^{-1}	ν^{acetone}, cm^{-1}
2,4- and 2,7(8)-$(CH_8)_3NB_{10}H_8CO$[5]	2145[b]	...	2159
1,10-$B_{10}H_8(CO)_2$	2147[b]	2161	2143
$(CH_3)_4N$-1,10-$NCB_{10}H_8CO$	2153	...	2132
1-$(CH_8)_2SB_{10}H_8$-6-CO[5]	2157[b]	2157	2159
$(CH_8)_4NB_{12}H_{11}CO$	2178	...	2168
1,7- and 1,12-$(CH_3)_8NB_{12}H_{10}CO$ (mixt)[5]	2204[b]	...	2192, 2147
1,10-$B_{10}Cl_8(CO)_2$	2203	...	2175
1,12-$B_{12}H_{10}(CO)_2$	2210[b]	2203	2190
1,7-$B_{12}H_{10}(CO)_2$	2223[b]	2202	2180

[a] Determined on a Perkin-Elmer Model 221 grating spectrophotometer. [b] These values are slightly different from those reported earlier[2a,3,5] and are believed to be the more accurate set.

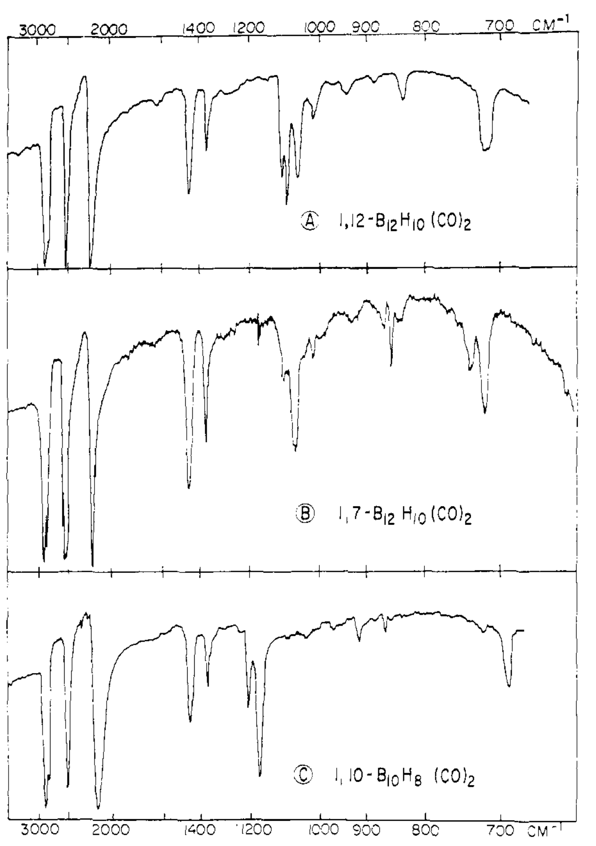
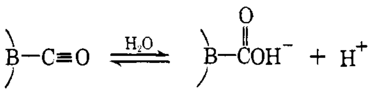


Figure 1. Infrared spectra of (A) 1,12-$B_{12}H_{10}(CO)_2$, (B) 1,7-$B_{12}H_{10}(CO)_2$, (C) 1,10-$B_{10}H_8(CO)_2$ in Nujol. Nujol bands are shown.

Reactions. As mentioned earlier, the carbonyls react reversibly with water to form carboxylic acids.



$$\rangle B{-}C{\equiv}O \xrightleftharpoons{H_2O} \rangle B{-}\overset{O}{\overset{\|}{C}}OH^- + H^+$$

Infrared studies show that strong C≡O absorptions are apparent for very concentrated aqueous solutions of 1,10-$B_{10}H_8(CO)_2$ but disappear rapidly with dilution. In contrast to 1,10-$B_{10}H_8(CO)_2$, which can be obtained in anhydrous form by evaporation of its aqueous solutions under ambient conditions, 1,7- and 1,12-$B_{12}H_{10}(CO)_2$ are hygroscopic and readily form crystalline hydrates of the type $(H_3O)_2B_{12}H_{10}(COOH)_2 \cdot xH_2O$ in moist air. No carbonyl groups (C≡O) are detectable in these hydrates by infrared spectroscopy. The tetramethylammonium salt of $B_{12}H_{11}CO^-$ is not hygroscopic. Ambient evaporation of aqueous solutions of 1,10-$B_{10}H_8(CO)_2$ or drying of 1,7- or 1,12-$(H_3O)_2B_{12}H_{10}(COOH)_2 \cdot xH_2O$ at elevated temperatures regenerates the corresponding dicarbonyls. Hydration of the carbonyl groups can reasonably be assumed to occur *via* nucleophilic attack by water on the carbon atoms. On this basis, the greater hydrophilicity of the $B_{12}H_{10}(CO)_2$ isomers compared to 1,10-$B_{10}H_8(CO)_2$ suggests that the B_{12} polyhedron is somewhat more electronegative than the apical positions of the B_{10} polyhedron. This could also be inferred from a comparison of the infrared stretching frequencies of unsaturated (—C≡O, >C=O, and —C≡N) substituents in analogous B_{10} and B_{12} derivatives (see Table I and Experimental Section).

Titration of aqueous solutions of the carbonyls shows the presence of the strongly and weakly acidic protons required by the formulations $(H_3O^+)_2B_{10}H_8(COOH)_2{}^{2-}$, $(H_3O^+)_2B_{12}H_{10}(COOH)_2{}^{2-}$, and $(H_3O^+)_2B_{12}H_{11}COOH^{2-}$. The thermodynamics of proton dissociation of 1,12-$B_{12}H_{10}(COOH)_2{}^{2-}$ have been reported by other workers.[13]

A variety of salts of the carboxylic acids derived from the carbonyls has been prepared. These include alkylammonium, alkali metal, alkaline earth, silver, thallium, nickel, and cobalt salts. Salts of the types $M_2B_{12}H_{10}(COOH)_2$, $M_2B_{12}H_{10}(COOM)_2$, $M_2B_{10}H_8(COOH)_2$, $M_2B_{10}H_8(COOM)_2$, $M_2B_{12}H_{11}COOH$, and $M_2B_{12}H_{11}COOM$ have been prepared. The nickel and cobalt salts of 1,12-$B_{12}H_{10}(COOH)^{2-}$ and the nickel salt of $B_{12}H_{11}COOH^{2-}$ are most readily obtained in a hydrated (>5 moles of water) form. In this form their infrared spectra resemble those of the cesium salts of the same anions. Surprisingly, as the water is removed from these hydrated transition metal salts, drastic but readily reversible changes occur throughout their infrared spectra. The changes are similar for the three salts and are interpreted similarly. The nickel salt of 1,12-$B_{12}H_{10}(COOH)_2{}^{2-}$ will serve as an example for discussion. Upon dehydration of this salt from a heptahydrate to an essentially anhydrous form, a strong sharp absorption band appears in the infrared at 2220 cm^{-1}. Concurrently the C=O stretching absorption at 1660 cm^{-1} and the carbon-oxygen single bond stretching absorption at 1280 cm^{-1} which are present in the spectra of the hydrated salt disappear. These data seem to establish the presence of carbonyl (C≡O) groups in the dehydrated product. In addition to a normal B-H absorption at 2500 cm^{-1}, the spectrum of the dehydrated product has a broad band of moderate intensity at 2380 cm^{-1} which is similar in shape to an absorption band at about 2220 cm^{-1} in the spectra of $Cu_2B_{12}H_{12}$ and $Cu_2B_{10}H_{10}$. It has been shown that the copper in the latter compound is within bonding distance of the $B_{10}H_{10}{}^{2-}$ polyhedron.[14] One interpretation

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(13) L. D. Hansen, J. N. Partridge, R. M. Izatt, and J. J. Christensen, *Inorg. Chem.*, 5, 569 (1966).

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

of the data therefore is that the dehydrated salt consists of a species of the type $(HO)_2NiB_{12}H_{10}(CO)_2$ in which there is localized interaction between the nickel and the boron cage. Free $B_{12}H_{10}(CO)_2$ is not present in the dehydrated salt; this is demonstrated both by infrared analysis and by the inability to sublime $B_{12}H_{10}(CO)_2$ from it. No gross changes have occurred in the boron polyhedron, because the dehydrated product readily re-forms the hydrated nickel salt of $1,12\text{-}B_{12}H_{10}(COOH)_2^{2-}$ in moist air.

Halogenation of the neutral dicarbonyls in nonaqueous media is extremely slow. However, halogenation in water or halogenation of carboxylic acid salts in nonaqueous media is facile, analogous to the halogenation of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$.[12] A lessened reactivity toward halogenation and deuteration of neutral derivatives of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ compared to anionic derivatives has been noted previously.[15,16]

Various halogenated derivatives of the carboxylic acids have been prepared including $1,10\text{-}B_{10}Cl_8(COOH)_2^{2-}$, $B_{12}Br_{11}COOH^{2-}$, $1,10\text{-}B_{10}Br_8(COOH)_2^{2-}$, $1,10\text{-}B_{10}I_8(COOH)_2^{2-}$, and $1,12\text{-}B_{12}I_{10}(COOH)_2^{2-}$. Dehydration of the conjugate acids of the perhalogenated B_{10} dicarboxylates has given $1,10\text{-}B_{10}Cl_8(CO)_2$, $1,10\text{-}B_{10}Br_8(CO)_2$, and $1,10\text{-}B_{10}I_8(CO)_2$.

$$H_2B_{10}H_8(COOH)_2 \xrightarrow{X_2} H_2B_{10}X_8(COOH)_2 \overset{-H_2O}{\rightleftharpoons} B_{10}X_8(CO)_2$$

In contrast to the facile dehydration of $H_2B_{10}H_8(COOH)_2$, dehydration of the halogenated B_{10} dicarboxylic acids requires elevated temperatures. The resulting carbonyls are yellow, sublimable solids which are even more thermally stable than the parent carbonyls; $B_{10}Cl_8(CO)_2$ melts at 338–340° whereas $B_{10}H_8(CO)_2$ decomposes below 250°. The halogenated carbonyls readily hydrate in moist air with regeneration of the corresponding carboxylic acids. The increased hydrophilicity of the halogenated carbonyls is attributed to electron withdrawal by the halogen atoms; this inductive effect also results in a greater acidity for $1,10\text{-}B_{10}Cl_8(COOH)_2^{2-}$ (pK_a in water $\sim$ 7.5) compared to $1,10\text{-}B_{10}H_8(COOH)_2^{2-}$ (pK_a in water $\sim$ 9.1). In contrast, $(C_6H_{11})_2B_{10}H_6(CO)_2$[2] is not significantly soluble in water. It does dissolve in aqueous sodium hydroxide to form $(C_6H_{11})_2B_{10}H_6(COO)_2^{4-}$.

Carboxyl groups are cleaved from the B_{10} and B_{12} polyhedron by halogen under free-radical conditions. This has been accomplished both thermally and with ultraviolet irradiation as shown in Table II.

Table II. Replacement of Carboxyl Groups by Halogen in Aqueous Solution

Starting material	Halogen	Conditions	Results
$1,10\text{-}B_{10}Cl_8(COOH)_2^{2-}$	Cl_2	25°	No reaction
$1,10\text{-}B_{10}Cl_8(COOH)_2^{2-}$	Cl_2	25°, $h\nu$	$B_{10}Cl_{10}^{2-}$ (100%)[12]
$1,10\text{-}B_{10}Cl_8(COOH)_2^{2-}$	Cl_2	150°	$B_{10}Cl_{10}^{2-}$ (56%)[12]
$1,10\text{-}B_{10}Cl_8(COOH)_2^{2-}$	Br_2	150°	$B_{10}Cl_8Br_2^{2-}$
$B_{12}Cl_{11}COOH^{2-}$	Cl_2	150°	$B_{12}Cl_{12}^{2-}$ (59%)[12]
$1,12\text{-}B_{12}Br_{10}(COOH)_2^{2-}$	Cl_2	150°	$B_{12}Br_{10}Cl_2^{2-}$ (46%)

The reactions of the B_{10} and B_{12} carbonyls with alcohols, ammonia, and primary and secondary amines are analogous to their reactions with water. Esters and amides are formed; typical examples are

$$1,10\text{-}B_{10}H_8(CO)_2 \overset{CH_3OH}{\rightleftharpoons} H_2\text{-}1,10\text{-}B_{10}H_8(COOCH_3)_2$$

$$1,10\text{-}B_{10}H_8(CO)_2 \xrightarrow{NH_3} (NH_4)_2\text{-}1,10\text{-}B_{10}H_8(CONH_2)_2{}^{17}$$

$$1,10\text{-}B_{10}H_8(CO)_2 \xrightarrow{C_5H_{10}NH} (C_5H_{10}NH_2)_2\text{-}1,10\text{-}B_{10}H_8(CONC_5H_{10})_2{}^{17}$$

The good thermal stabilities of the carbonyls persist in these derivatives. An excellent practical example is the dehydration of $Cs_2\text{-}1,10\text{-}B_{10}H_8(CONH_2)_2$ and $Cs_2\text{-}1,12\text{-}B_{12}H_{10}(CONH_2)_2$ at 300–375° to form $Cs_2\text{-}1,10\text{-}B_{10}H_8(CN)_2$ and $Cs_2\text{-}1,12\text{-}B_{12}H_{10}(CN)_2$. This dehydration can be effected in air without decomposition.[18]

Reaction of $1,12\text{-}B_{12}H_{10}(CONH_2)_2^{2-}$ and $1,10\text{-}B_{10}H_8(CONH_2)_2^{2-}$ with oxalyl chloride gives $1,12\text{-}B_{12}H_{10}CNCOOH^{2-}$ and $1,10\text{-}B_{10}H_8CNCOOH^{2-}$, respectively; the latter was converted to $1,10\text{-}B_{10}H_8CNCO^-$ by reaction with acid.

$$H^+ + 1,10\text{-}NCB_{10}H_8COOH^{2-} \rightleftharpoons 1,10\text{-}NCB_{10}H_8CO^- + H_2O$$

Sodium azide reacts rapidly with the B_{10} and B_{12} carbonyls. Nitrogen is evolved quantitatively and isocyanates are formed; presumably the initial products are acyl azides which undergo spontaneous Curtius rearrangements. Halogenated isocyanate derivatives can be prepared either from halogenated carbonyls and azide ion or by the halogenation of perhydroisocyanates in nonprotonic solvents.

$$\begin{tikzcd}
1,10\text{-}B_{10}H_8(CO)_2 + 2N_3^- \arrow[r] \arrow[ddd, "Cl_2"'] & {[1,10\text{-}B_{10}H_8(CON_3)_2^{2-}]} \arrow[dr, "-N_2"] & \\
 & & 1,10\text{-}B_{10}H_8(NCO)_2^{2-} \arrow[d, "Cl_2"', "CH_3CN"] \\
 & & 1,10\text{-}B_{10}Cl_8(NCO)_2^{2-} \\
1,10\text{-}B_{10}Cl_8(CO)_2 + 2N_8^- \arrow[r] & {[1,10\text{-}B_{10}Cl_8(CON_8)_2^{2-}]} \arrow[ur, "-N_2"'] &
\end{tikzcd}$$

Other isocyanates that were prepared include $1,12\text{-}B_{12}H_{10}(NCO)_2^{2-}$, $1,10\text{-}B_{10}I_8(NCO)_2^{2-}$, and $1,12\text{-}B_{12}I_{10}(NCO)_2^{2-}$. Salts of the isocyanates are stable in water; they can conveniently be converted to the corresponding amines by acidic ion exchange.

$$Cs_2B_{10}Cl_8(NCO)_2 \xrightarrow[\text{exchange}]{H^+\text{ ion}} \xrightarrow{-H_2O} H_2\text{-}1,10\text{-}B_{10}Cl_8(NH_2)_2 \equiv 1,10\text{-}B_{10}Cl_8(NH_3)_2$$

This approach has also been used to prepare $1,10\text{-}B_{10}H_8(NH_3)_2$, $1,12\text{-}B_{12}H_{10}(NH_3)_2$, $1,12\text{-}B_{12}I_{10}(NH_3)_2$, and $1,10\text{-}B_{10}I_8(NH_3)_2$. The first two amines have been prepared previously by other methods.[2,7] Still another preparation of amine derivatives consists of treating

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(15) W. H. Knoth, W. R. Hertler, and E. L. Muetterties, *Inorg. Chem.*, 4, 280 (1965).

(16) H. C. Miller, W. R. Hertler, E. L. Muetterties, W. H. Knoth, and N. E. Miller, *ibid.*, 4, 1216 (1965).

(17) Similar reactions of carbon monoxide borane with ammonia and amines have been described; see J. C. Carter and R. W. Parry, *J. Am. Chem. Soc.*, 87, 2354 (1965). For recent extensions of their work, see L. J. Malone and R. W. Parry, *Inorg. Chem.*, 6, 817 (1967).

(18) W. R. Hertler, W. H. Knoth, and E. L. Muetterties, *J. Am. Chem. Soc.*, 86, 5434 (1964).

Table III

Compound	Calcd, %				Found, %			
	B	C	H	M	B	C	H	M
$Cs_2B_{12}H_{11}COOH \cdot H_2O$[a]	27.6	2.6	3.0	56.6	28.0	2.3	3.0	56.9
$Cs_2B_{12}H_{11}COOH$[b]	28.7	2.7	2.7	58.8	28.8	2.5	2.8	58.8
$H_3OB_{12}H_{11}CO \cdot H_2O$	63.0	5.8	7.8	...	62.8	5.3	8.3	...
$(CH_3)_4NB_{12}H_{11}CO$[c]	53.4	...	9.5	5.8 (N)	53.7	...	9.4	5.8 (N)
$Ag_2B_{12}H_{11}COOH \cdot 0.5H_2O$	31.6	2.9	...	52.5	31.7	2.8	...	52.8
$Cs_2B_{12}H_{11}COOCs$	22.2	2.1	1.9	68.3	22.1	2.2	2.7	67.2
$[(CH_3)_4N]_2B_{12}H_{11}COOH$[d]	38.8	32.3	10.9	...	39.5	31.7	10.8	...
$NiB_{12}H_{11}COOH \cdot 4.7H_2O$	39.4	3.6	6.6	17.8	39.9	3.5	7.0	17.4
$HONiB_{12}H_{11}CO \cdot 1.5H_2O$	47.8	4.4	...	21.6	47.6	4.3	...	21.4
$BaB_{12}H_{11}COOH \cdot H_2O$	38.0	3.5	4.1	40.2	38.8	3.1	3.9	38.8
$CoB_{12}H_{11}COOH \cdot 5H_2O$	38.8	3.6	...	17.6	38.8	3.2	...	17.6
$HOCoB_{12}H_{11}CO$	53.0	4.9	...	24.1	53.3	4.2	...	24.3

[a] Neut equiv: calcd, 470; found, 473. pK_a in water ~8.9. Infrared spectra in Nujol mulls include absorption bands at: [b] 2480 (s), 1670 (s), 1260 (s), 1060 (ms), 990 (m), 880 (w), 725 (w), and 695 cm^{-1}; [c] 2500 (s), 2178 (s), 1270 (w), 1110 (w), 1090 (w), 1075 (m), 1035 (m), 945 (ms), and 720 cm^{-1} (there was no ultraviolet maximum in acetonitrile solution); [d] 3450 (m), 2500 (s), 1670 (s), 1260 (m), 1140 (s), 1050 (s), 990 (s), 945 (s), 875 (w), and 730 (m) cm^{-1}.

the carbonyls with hydroxylamine-O-sulfonic acid in water.

$$1,10\text{-}B_{10}H_8(CO)_2 + 2H_2NOSO_3H + 2H_2O \longrightarrow 1,10\text{-}B_{10}H_8(NH_8)_2 + 2CO_2 + 2H_2SO_4$$

This method has also been used to prepare 1,12-$B_{12}H_{10}(NH_3)_2$, 1,7-$B_{12}H_{10}(NH_3)_2$, and 1,10-$B_{10}Cl_8(NH_3)_2$.

Reaction of 1,12-$B_{12}H_{10}(NCO)_2{}^{2-}$ and 1,10-$B_{10}Cl_8(NCO)_2{}^{2-}$ with ethanol–hydrogen chloride results in preparation of the urethans 1,12-$B_{12}H_{10}(NHCO_2C_2H_5)_2{}^{2-}$ and 1,10-$B_{10}Cl_8(NHCO_2C_2H_5)_2{}^{2-}$, respectively. Surprisingly, a similar reaction with 1,10-$B_{10}H_8(NCO)_2{}^{2-}$ gave 1,10-$H_3NB_{10}H_8NHCO_2C_2H_5{}^{-}$.

Ketonic derivatives can be prepared from the carbonyls and organomercury compounds. Diethylmercury reacts smoothly with 1,10-$B_{10}Cl_8(CO)_2$ in toluene–glyme at ambient temperature to give $(C_2H_5Hg)_2$-1,10-$B_{10}Cl_8(COC_2H_5)_2$. Dissolution of this salt in aqueous sodium hydroxide followed by the addition of tetramethylammonium chloride precipitates $[(CH_3)_4N]_2$-1,10-$B_{10}Cl_8(COC_2H_5)_2$. The reaction of diphenylmercury with 1,10-$B_{10}H_8(CO)_2$ followed by bromination gave 1,10-$B_{10}Br_8(COC_6H_5)_2{}^{2-}$.

Reduction of 1,10-$B_{10}H_8(CO)_2$ with lithium aluminum hydride gives 1,10-$B_{10}H_8(CH_3)_2{}^{2-}$.

Experimental Section

$B_{12}H_{11}COOH^{2-}$ and $B_{12}H_{11}CO^{-}$. Pulverized dicobalt octacarbonyl (12.5 g, 36.6 mmoles) and $(H_8O)_2B_{12}H_{12} \cdot 2.5H_2O$ (37.5 g, 0.17 mole)[6] were mixed thoroughly in an atmosphere of dry nitrogen and charged to a 400-ml silver-lined pressure vessel. The pressure vessel was chilled in Dry Ice–methanol, evacuated, and pressured to 400 atm with carbon monoxide. It was heated to 70 and 1000 atm for 30 min. The tube was cooled to room temperature, excess carbon monoxide was vented, and the tube contents were rinsed out with a small amount of water and filtered. The filtrates from two such runs were combined and treated with hydrogen sulfide to precipitate heavy metal impurities (from the pressure vessel) as the sulfides. These were removed by filtration through sintered glass; nitrogen was passed through the filtrate to remove excess hydrogen sulfide and the solution was passed through a strongly acidic ion-exchange column (450 g of resin). The effluent was adjusted to pH 6.0 with aqueous cesium hydroxide and concentrated on a steam bath to 300 ml. Crystallization of $Cs_2B_{12}H_{11}COOH \cdot H_2O$ was completed by chilling to 0°. The crude product was recrystallized twice from water (0.8 ml of water per gram of solid) to obtain 80 g (50%) of $Cs_2B_{12}H_{11}COOH \cdot H_2O$ (no melting point to 400°). Dehydration was effected by drying at 100°.

Passage of an aqueous solution of $Cs_2B_{12}H_{11}COOH$ through a strongly acidic ion-exchange resin followed by evaporation of the effluent to dryness *in vacuo* at 25° left solid $H_3OB_{12}H_{11}CO \cdot H_2O$ (decomposes at 60°). In different preparations the total water content varied from 2 to 4 moles; the infrared spectra of these products all had strong C≡O absorption bands suggesting that the water was associated with the strongly acidic protons and not with the carbonyl (C≡O) group. An aqueous solution of $Cs_2B_{12}H_{11}COOH$ (10 g, 21.3 mmoles) was passed through a strongly acidic ion-exchange column. The effluent was divided into two equal portions. One portion was brought to pH 6.0 with tetramethylammonium hydroxide. The two portions were then recombined and evaporated on a steam bath to leave crystalline $(CH_3)_4NB_{12}H_{11}CO$ (5.2 g, 100%, decomposes at 250°). This salt did not hydrate in air. The addition of aqueous (0.672 *M*) $H_2B_{12}H_{11}COOH$ (25 ml, 16.8 mmoles) to a solution of silver nitrate (33.6 mmoles) in water (50 ml) precipitated $Ag_2B_{12}H_{11}COOH$. An aqueous solution of $Cs_2B_{12}H_{11}COOH$ was brought to pH 12.15 with cesium hydroxide. Evaporation of the solution and recrystallization of the residue from water gave $Cs_2B_{12}H_{11}COOCs$. A solution of 0.72 *M* $H_2B_{12}H_{11}COOH$ (70 ml, 50.4 mmoles) was brought to pH 5.53 with tetramethylammonium hydroxide. The solution was chilled to precipitate $[(CH_8)_4N]_2B_{12}H_{11}COOH$ (13.4 g, 80%); this was separated and recrystallized from 25 ml of water. Nickel(II) carbonate (8.16 g, 69 mmoles) was dissolved in 100 ml (67 mmoles) of 0.67 *M* $H_2B_{12}H_{11}COOH$ by stirring overnight at ambient temperature. Water was removed *in vacuo* at 25°, and the residual light green solid was further dried *in vacuo* at 25° for 24 hr. The yield of light green $NiB_{12}H_{11}COOH \cdot 4.7H_2O$ was 21.9 g, 99%. This material was converted to brownish yellow $HONiB_{12}H_{11}CO \cdot 1.5H_2O$ by further drying at 50° (10–20 μ) for 26 hr. This material rapidly re-formed a green hydrated nickel salt of $B_{12}H_{11}COOH^{2-}$ on exposure to moist air. Analogous cobalt salts were similarly prepared. Infrared changes accompanying the changes in hydration of these nickel and cobalt salts were similar to those described in the Discussion for the analogous nickel salts of $B_{12}H_{10}(COOH)_2{}^{2-}$. The neutralization (to pH 5.5) of aqueous $H_2B_{12}H_{11}COOH$ with barium hydroxide followed by evaporation and drying of the residue at 25° *in vacuo* over phosphorus pentoxide gave $BaB_{12}H_{11}COOH \cdot H_2O$, a very water-soluble species. Analytical results are given in Table III.

1,12-$B_{12}H_{10}(COOH)_2{}^{2-}$ and 1,12-$B_{12}H_{10}(CO)_2$. Pulverized dicobalt octacarbonyl (16.67 g, 49 mmoles) and $(H_8O)_2B_{12}H_{12} \cdot 2.5H_2O$ (50 g, 0.22 mole) were mixed thoroughly under nitrogen and charged to a 400-ml silver-lined pressure vessel. This was chilled in Dry Ice–methanol, evacuated, and pressured to 400 atm with carbon monoxide. The pressure vessel was then heated to 70° and 800 atm for 3 hr and then to 130° and 1000 atm for 3 hr. The vessel was cooled and vented, and the contents were rinsed out with a little water and filtered. The filtrates from three such runs were combined and treated with hydrogen sulfide. The mixture was filtered, and nitrogen was passed through the filtrate to remove

Table IV

Compound	Calcd, %				Found, %			
	B	C	H	M	B	C	C	M
Cs_2-1,12-$B_{12}H_{10}(COOH)_2 \cdot H_2O$	25.3	4.6	2.8	51.7	25.3	5.2	3.0	50.3
Cs_2-1,12-$B_{12}H_{10}(COOH)_2$[a]	26.2	4.8	2.4	53.6	26.2	4.6	2.4	52.3
Cs_2-1,12-$B_{12}H_{10}(COOCs)_2$	17.1	3.2	1.3	70.0	16.8	3.4	2.3	68.2
1,12-$B_{12}H_{10}(CO)_2$,[b]								
$[(CH_3)_4N]_2$-1,12-$B_{12}H_{10}$-$(COOH)_2$[c]	34.3	31.8	9.6	...	34.4	30.7	9.7	...
Ni-1,12-$B_{12}H_{10}(COOH)_2 \cdot 7H_2O$	31.3	5.8	6.3	14.2	31.6	6.0	6.3	14.1
$(HO)_2$Ni-1,12-$B_{12}H_{10}(CO)_2$	45.0	8.3	4.2	20.3	45.0	8.5	4.5	20.6

Infrared spectra in Nujol mulls include absorption bands at: [a] 3570 (m), 2500 (s), 1680 (s), 1260 (s), 1080 (w), 1045 (m), 930 (ms), 720 (w), and 690 (w) cm^{-1}; [b] see Figure 1a; [c] 3500 (m), 2480 (s), 1680 (s), 1250 (s), 1180 (w), 1150 (w), 1050 (w), 1040 (m), 1010 (m), 945 (ms), 920 (ms), 845 (w), 725 (mw), 710 (mw), and 685 (ms) cm^{-1}.

Table V

Compound	Calcd, %				Found, %			
	B	C	H	Cs	B	C	H	Cs
Cs_2-1,7-$B_{12}H_{10}(COOH)_2$[a]	26.2	4.8	2.4	53.6	26.3	4.4	1.7	53.6
1,7-$B_{12}H_{10}(CO)_2$[b]	66.3	12.3	5.1	...	66.4	12.6	5.3	...

Infrared spectra in Nujol mulls include absorption bands at: [a] 3570 (m), 3220 (m), 2500 (s), 1650 (s), 1255 (m), 1180 (s), 1060 (mw), 1000 (ms), 850 (w), 725 (mw), 690 (m), and 680 (m) cm^{-1}; [b] see Figure 1b.

hydrogen sulfide. The solution was passed through a strongly acidic ion-exchange column (450 g of resin). The effluent was brought to pH 5.4 with 50% aqueous cesium hydroxide and concentrated on a steam bath to 1300 ml. Crystallization of Cs_2-1,12-$B_{12}H_{10}(COOH)_2 \cdot H_2O$ was completed by chilling the mixture in a water–ice bath. The product was recrystallized from water (1.6 ml of water per gram of solid) to obtain 130 g (38%) of Cs_2-1,12-$B_{12}H_{10}(COOH)_2 \cdot H_2O$ (no melting point to 400°). Dehydration could be accomplished by vacuum drying at 100°.

A solution of Cs_2-1,12-$B_{12}H_{10}(COOH)_2 \cdot H_2O$ (130 g, 0.25 mole) in 1300 ml of water was prepared at 85–90° and passed through a preheated ion-exchange column which was packed with 450 g of a strongly acidic ion-exchange resin. The acidic effluent was concentrated to a small volume in a rotary evaporator at 25–30° *in vacuo*. The residue was taken to dryness on a steam bath and then sublimed at 135–150° (0.05 mm) to obtain 1,12-$B_{12}H_{10}(CO)_2$ (45 g, 92%), a hygroscopic, colorless solid (no melting point to 400°). In a preparation which began with 90 g (0.39 mole) of $(H_3O)_2B_{12}H_{12} \cdot 2.7H_2O$, the filtrate from isolation of the crude Cs_2-1,12-$B_{12}H_{10}(COOH)_2$ was passed through an acidic ion-exchange column. Evaporation of the effluent followed by sublimation of the residue gave 3.6 g (4.5%) of 1,7-$B_{12}H_{10}(CO)_2$. Various salts of 1,12-$B_{12}H_{10}(COOH)_2{}^{2-}$ were prepared essentially as described above for the corresponding salts of $B_{12}H_{11}COOH^{2-}$. Analytical results are given in Table IV.

The B^{11} nmr spectrum of 1,12-$B_{12}H_{10}(CO)_2$ in acetonitrile consists of a symmetrical doublet (relative intensity 5) at 30.0 ppm (J = 150 cps) and a broad singlet (relative intensity 1) at 41.2 ppm (referred to methyl borate). In water [1,12-$H_2B_{12}H_{10}(COOH)_2$] the B^{11} nmr spectrum consists of a doublet at 32.9 ppm (J = 121 cps) which is unsymmetrical at 19.2 Mc due to coincidence of the low-field member of the doublet with a singlet at 30 ppm. Studies on the acidity of aqueous solutions of 1,12-$B_{12}H_{10}(CO)_2$ have been reported by other workers.[18]

1,7-$B_{12}H_{10}(COOH)_2{}^{2-}$. $H_3OB_{12}H_{11}CO \cdot 2.9H_2O$ (40 g, 0.17 mole) was carbonylated at 130° and a cesium salt was prepared from the product as described above for the biscarbonylation of the $B_{12}H_{12}{}^{2-}$ acid, except for omission of the cobalt carbonyl. Fractional recrystallization of the cesium salt gave 9.55 g (10.9%) of 1,12-$Cs_2B_{12}H_{10}(COOH) \cdot H_2O$ as the least soluble species, 1.87 g of a mixture of salts, and 9.03 g (10.3%) of 1,7-$Cs_2B_{12}H_{10}(COOH)_2$. The 1,7 isomer was also obtained directly from the analogous carbonylation of $(H_3O)_2B_{12}H_{12} \cdot 2.5H_2O$ in the absence of cobalt carbonyl in extremely erratic yield. The cesium salt was converted to 1,7-$B_{12}H_{10}(CO)_2$ (softens at 155–160°, mp 215–225°) as described above for the 1,12 isomer. Analytical results are given in Table V.

The B^{11} nmr spectrum of 1,7-$B_{12}H_{10}(CO)_2$ in acetonitrile consists of a doublet at 29.2 ppm (J = 145 cps) representing eight hydrogen-substituted boron atoms, a doublet which represents two hydrogen-substituted boron atoms, whose low-field member is at 356 cps at 19.2 Mc and whose high-field member is obscured by the low-field member of the larger doublet, and a singlet at 45.7 ppm (referred to methyl borate) which represents the two carbonyl-substituted boron atoms. In water [1,7-$H_2B_{12}H_{10}(COOH)_2$], the B^{11} nmr spectrum consists of a doublet at 33.0 ppm (J = 124 cps) which is unsymmetrical at 19.2 Mc because of coincidence of the low-field component with the singlet which represents the carboxyl-substituted boron atoms.

1,10-$B_{10}H_8(COOH)_2{}^{2-}$, $C_6H_{11}B_{10}H_7(COOH)_2{}^{2-}$, and $C_6H_{11}B_{10}H_6$-$(COOH)^{2-}$. Examination of a solution of 1,10-$B_{10}H_8(CO)_2$[2a] in water (hydrated H_2-1,10-$B_{10}H_8(COOH)_2$) revealed a neutral equivalent as strong dibasic acid of 85.5 (calculated 86.0). Ultraviolet: $\lambda_{\max}^{H_2O}$ 257 mμ (ϵ 7300) and 223 mμ (ϵ 19,000). The titration curve suggested a pK_a of about 9.1 for 1,10-$B_{10}H_8(COOH)_2{}^{2-}$. The B^{11} nmr spectrum has already been described.[2]

A solution of cesium chloride (20 g, 112 mmoles) in water (20 ml) was mixed with 1,10-$B_{10}H_8(CO)_2$ (8 g, 46.5 mmoles) in water (55 ml). The mixture was chilled in an ice-water bath and filtered cold to obtain 21.1 g (96%) of Cs_2-1,10-$B_{10}H_8(COOH)_2$ which was recrystallized from water (no melting point to 400°, darkens at 200°). A thallium salt was prepared similarly using thallium nitrate but was not recrystallized. Precipitation of a thallium salt from strongly basic (sodium hydroxide) solution gave Tl_2-1,10-$B_{10}H_8(COOTl)_2$. The addition of aqueous cesium chloride to aqueous $C_6H_{11}B_{10}H_7(CO)_2$[2] precipitated $Cs_2C_6H_{11}B_{10}H_7(COOH)_2$ which was recrystallized from water. The biscyclohexylated compound, $(C_6H_{11})_2B_{10}H_6(CO)_2$,[2] was insoluble in water. It was dissolved in aqueous sodium hydroxide solution and treated with thallium nitrate to precipitate $Tl_2(C_6H_{11})_2B_{10}H_6(COOTl)_2$. Analytical results are given in Table VI.

1,10-$B_{10}Cl_8(COOH)_2{}^{2-}$ and 1,10-$B_{10}Cl_8(CO)_2$. Chlorine was passed into a solution of $B_{10}H_8(CO)_2$ (5 g, 29 mmoles) in water (150 ml) in an ice-water bath for 30 min, then at ambient temperature for 2 hr, and finally at 60° for 2 hr. The solution was evaporated *in vacuo* and the residue was dried at 40° (1 mm) to obtain 15 g of hydrated $(H_3O)_2B_{10}Cl_8(COOH)_2$ as a colorless crystalline solid. This was recrystallized by dissolution in water (25 ml) followed by filtration and slow partial concentration of the filtrate. After drying at ambient temperature *in vacuo* for 2 hr the product had the composition $(H_3O)_2B_{10}Cl_8(COOH)_2 \cdot 5H_2O$. Other degrees of hydration were obtained from different preparations. Dissolution of the acid in water followed by the addition of tetramethylammonium

Table VI

Compound	Calcd, %				Found, %			
	B	C	H	M	B	C	H	M
$Cs_2B_{10}H_8(COOH)_2$[a]	22.9	5.1	2.1	56.4	22.7	5.2	2.4	56.3
$Tl_2B_{10}H_8(COOH)_2$	17.6	3.9	1.6	66.5	17.3	4.1	2.0	63.5
$Tl_2B_{10}H_8(COOTl)_2$	10.6	2.3	0.8	79.9	11.1	2.7	1.0	78.4
$Cs_2C_6H_{11}B_{10}H_7(COOH)_2$	19.5	17.5	3.6	48.0	18.9	17.0	3.8	47.0
$Tl_2(C_6H_{11})_2B_{10}H_6(COOTl)_2$	9.1	14.2	2.4	69.0	9.9	13.3	2.5	66.4

[a] The infrared spectrum in a potassium bromide wafer includes absorptions at 2480 (s), 2490 (s), 1640 (s), 1290 (m), 1130 (m), 1010 (m), 745 (w), and 720 (m) cm^{-1}.

Table VII

Compound	Calcd, %				Found, %			
	B	C	H	Cl	B	C	H	Cl
$(H_3O)_2B_{10}Cl_8(COOH)_2 \cdot 5H_2O$[a]	17.7	...	...	46.6	18.4	...	...	46.9
$[(CH_3)_4N]_2B_{10}Cl_8(COOH)_2 \cdot H_2O$	16.7	18.5	4.3	43.7	17.0	18.6	4.7	43.8
$[(CH_3)_4N]_2B_{10}Cl_8(COOH)_2$[b]	17.1	19.1	4.1	45.1	16.5	19.2	4.4	45.1
$B_{10}Cl_8(CO)_2$[c]	24.1	5.3	0.0	63.3	24.2	6.3	0.9	63.3

[a] Neut equiv calculated as strong acid to be 305 (found 303). The titration curve of $Na_2B_{10}Cl_8(COOH)_2$ indicated a pK_a of about 7.5. [b] Ultraviolet $\lambda_{max}^{CH_3CN}$ 230 mμ (ϵ 15,200), shoulder 265 mμ (ϵ 2370). The infrared spectrum in a potassium bromide wafer includes absorption bands at 3300–2600 (broad multiplet, O–H and C–H), 1650 (s), 1495 (s), 1380 (w), 1288 (m), 1140 (ms), 1010 (s), 950 (ms) 845 (m), and 735 (w) cm^{-1}. [c] The infrared spectrum in a Nujol mull includes absorption bands at 2203 (s), 1230 (w), 1175 (m), 1010 (s), 945 (m), and 810 (m) cm^{-1}.

chloride precipitated $[(CH_3)_4N]_2$-1,10-$B_{10}Cl_8(COOH)_2$ which crystallized from water as a monohydrate. Anhydrous $[(CH_3)_4N]_2$-1,10-$B_{10}Cl_8(COOH)_2$ was obtained from the monohydrate at 135° *in vacuo.* The anhydrous salt (no melting point to 400°) was not hygroscopic. Heating hydrated $(H_3O)_2$-1,10-$B_{10}Cl_8(COOH)_2$ to 200° *in vacuo* resulted in dehydration to 1,10-$B_{10}Cl_8(CO)_2$ which then sublimed as a bright yellow hygroscopic solid. The over-all yield of twice-sublimed 1,10-$B_{10}Cl_8(CO)_2$ (mp 338–340°) from 1,10-$B_{10}H_8(CO)_2$ was 72%. Analytical results are given in Table VII.

1,10-$B_{10}Br_8(COOH)_2^{2-}$ and 1,10-$B_{10}Br_8(CO)_2$. Bromine was added to a solution of 1,10-$B_{10}H_8(CO)_2$ (3 g, 17.5 mmoles) in 100 ml of water until the bromine color persisted. Water and excess bromine were removed *in vacuo;* the residual solid was dissolved in 100 ml of water and mixed with a solution of tetramethylammonium chloride (10 g, 91 mmoles) in 100 ml of water to precipitate 13 g (44%) of $[(CH_3)_4N]_2$-1,10-$B_{10}Br_8(COOH)_2$. The analytical sample (no melting point to 400°, darkens at 290°) was recrystallized from water. *Anal.* Calcd for $[(CH_3)_4N_2B_{10}Br_8(COOH)_2$: C, 12.2; H, 2.6; B, 11.0; Br, 64.9. Found: C, 11.7; H, 2.6; B, 11.0; Br, 63.4. Ultraviolet: $\lambda_{max}^{CH_3CN}$ 263 mμ (ϵ 2030) and 239 mμ (ϵ 8900).

The infrared spectrum in a potassium bromide wafer strongly resembled that of $[(CH_3)_4N]_2$-1,10-$B_{10}Cl_8(COOH)_2$. The band at 1010 cm^{-1} in the latter species was shifted to 980 cm^{-1}.

Passage of a hot aqueous solution of $[(CH_3)_4N]_2$-1,10-$B_{10}Br_8$-$(COOH)_2$ through an acidic ion-exchange column followed by evaporation of the effluent and sublimation of the residue at 200° *in vacuo* gave 1,10-$B_{10}Br_8(CO)_2$ (mp 378–385°) as a hygroscopic yellow crystalline solid (14 g, 83% yield). *Anal.* Calcd for $B_{10}Br_8$-$(CO)_2$: C, 3.0; H, 0.0; B, 13.4; Br, 79.5. Found: C, 3.1; H, 0.3; B, 13.2; Br, 78.2. Ultraviolet: $\lambda_{max}^{(C_2H_5)_2O}$ 274 mμ (ϵ 2800) and 241 mμ (ϵ 7800).

$B_{12}Br_{11}COOH^{2-}$ **and 1,12-$B_{12}Br_{10}(COOH)_2^{2-}$.** Bromine (125 g, 0.780 mole) was added to a solution of $H_2B_{12}H_{11}COOH$ in water (300 ml) which had been prepared by acid ion exchange of $Cs_2B_{12}H_{11}$-$COOH \cdot H_2O$ (20 g, 53 mmoles). After the bromine addition, chlorine was passed through the solution until the bromine color was almost discharged. Tetramethylammonium chloride (20 g, 180 mmoles) was added to precipitate $[(CH_3)_4N]_2B_{12}Br_{11}COOH$ which was solvated with 1 equiv of acetonitrile after two recrystallizations from aqueous acetonitrile (29.8 g, 56% yield, no melting point to 400°). *Anal.* Calcd for $[(CH_3)_4N]_2B_{12}Br_{11}COOH \cdot CH_3CN$: C, 10.6; H, 2.2; B, 10.4; Br, 70.5; N, 3.4. Found: C, 11.0; H, 2.6; B, 10.7; Br, 70.2; N, 3.4. Ultraviolet: $\lambda_{max}^{CH_3CN}$ 255 mμ (ϵ 216). Recrystallization from water (3.2 g, from 200 ml of water, 2.3-g recovery) followed by vacuum drying at 100° for 3 hr gave a nonsolvated product. *Anal.* Calcd for $[(CH_3)_4N]_2$-$B_{12}Br_{11}COOH$: C, 9.0; H, 2.1; B, 10.8; Br, 73.0; N, 2.3. Found: C, 9.4; H, 2.6; B, 10.8; Br, 72.4; N, 2.4.

The infrared spectrum in a Nujol mull included bands at 3640 (w), 3390 (w), 1710 (m), 1660 (ms), 1280 (m), 1000 (s), 980 (s), and 945 (ms) cm^{-1}.

Similar bromination of a solution of 1,12-$B_{12}H_{10}(CO)_2$ (2.0 g, 10.2 mmoles) in 80 ml of water gave the corresponding solvated (86% yield) and unsolvated salts. *Anal.* Calcd for $[(CH_3)_4N]_2$-$B_{12}Br_{10}(COOH)_2 \cdot 2CH_3CN$: C, 13.5; H, 2.6; B, 10.4; Br, 64.0; N, 4.5. Found: C, 13.0; H, 2.7; B, 10.6; Br, 63.9; N, 3.8. Ultraviolet: $\lambda_{max}^{CH_3CN}$ 238 mμ (ϵ 815). *Anal.* Calcd for $[(CH_3)_4]_2$-$B_{12}Br_{10}(COOH)_2$: C, 10.4; H, 2.2; B, 11.1; Br, 68.5; N, 2.4. Found: C, 10.6; H, 2.3; B, 10.9; Br, 68.0; N, 2.8.

The infrared spectrum in a Nujol mull included bands at 3640 (w), 3390 (w), 1720 (m), 1695 (m), 1660 (s), 1280 (ms), 995 (s), 980 (s), 945 (ms), and 925 (m) cm^{-1}.

1,10-$B_{10}I_8(COOH)_2^{2-}$ and 1,10-$B_{10}I_8(CO)_2$. A mixture of Cs_2-1,10-$B_{10}H_8(COOH)_2$ (21.1 g, 44.7 mmoles), iodine (30 g, 112 mmoles), and tetrachloroethane (250 ml.) was stirred for 1 hr. Iodine monochloride (80 ml, 0.5 mole) was added; the mixture was refluxed for 18 hr, cooled, and filtered. The filter cake was washed with methylene chloride and then dissolved in 100 ml of boiling water. Small portions of zinc dust were added periodically until the solution was colorless. It was then filtered and cooled to obtain 32.6 g of Cs_2-1,10-$B_{10}I_8(COOH)_2$. Partial concentration of the mother liquors gave an additional 9.6 g for a total yield of 42.2 g (61%). The analytical sample (darkens at 260°, no melting point to 400°) was recrystallized twice from water and dried at 135° *in vacuo* for 18 hr. *Anal.* Calcd for $Cs_2B_{10}I_8(COOH)_2$: C, 1.6; H, 0.1; B, 7.3; I, 68.5; Cs, 18.0. Found: C, 1.9; H, 0.7; B, 7.3; I, 68.3; Cs, 17.9. Ultraviolet: no maximum, shoulder at 310 mμ (CH_3CN).

The infrared spectrum in a potassium bromide wafer included bands at 3600–3300 (w), 1695 (s), 1670 (s), 1310 (s), 1180 (w), 1105 (ms), 965 (ms), 950 (s), 880 (m), and 825 (ms) cm^{-1}.

Passage of an aqueous solution of Cs_2-1,10-$B_{10}I_8(COOH)_2$ through an acidic ion-exchange column followed by evaporation of the effluent and sublimation of the solid residue at 200° *in vacuo* gave 1,10-$B_{10}I_8(CO)_2$, a hygroscopic yellow-orange solid. *Anal.* Calcd for $B_{10}I_8(CO)_2$: B, 9.2; I, 86.0. Found: B, 9.2; I, 84.8.

1,12-$B_{12}I_{10}(COOH)_2$. Iodination of Cs_2-1,12-$B_{12}H_{10}(COOH)_2 \cdot H_2O$ (35.5 g, 68 mmoles) by a procedure analogous to that used above gave Cs_2-1,12-$B_{12}I_{10}(COOH)_2$ in 81% yield (no melting point to 400°). *Anal.* Calcd for $Cs_2B_{12}I_{10}(COOH)_2$: C, 1.4; H, 0.1;

Table VIII

	Calcd, %					Found, %				
Compound	C	H	B	N	Cs	C	H	B	N	Cs
$(C_5H_{12}N)_2B_{10}H_8(CONC_5H_{10})_2$	51.5	10.2	21.1	10.9	...	52.0	10.2	21.0	11.2	...
$Cs_2B_{10}H_8(CONH(CH_2)_3CH_3)_2$	20.6	4.8	18.6	4.8	...	21.1	4.9	18.5	5.0	...
$Cs_2B_{10}H_8(CONH_2)_2$[a]	5.1	2.6	23.0	6.0	56.5	4.8	2.8	20.1	5.2	57.6
$Cs_2B_{12}H_{10}(CONH_2)_2$[b]	4.9	2.9	26.9	5.7	53.9	5.0	3.3	26.7	5.7	52.9

[a] The infrared spectrum in a potassium bromide wafer included bands at 2450 (s), 1590 (s), 1555 (s), 1350 (s), 1150 (m), and 1010 (m) cm^{-1}. [b] The infrared spectrum in a Nujol mull included bands at 2500 (s), 1610 (s), 1550 (s), 1045 (m), 940 (m), and 800 (w) cm^{-1}.

B, 7.4; I, 72.3; Cs, 15.2. Found: C, 1.6; H, 0.5; B, 7.0; I, 72.0; Cs, 14.6. Ultraviolet: $\lambda_{max}^{H_2O}$ 258 mμ (ε 4580).

The infrared spectrum in a Nujol mull includes bands at 1695 (s), 1685 (s), 1290 (s), 1140 (m), 940 (s), 935 (s), and 880 (m) cm^{-1}.

$B_{10}H_3I_5(COOH)_2{}^{2-}$. A mixture of 1,10-$B_{10}H_8(CO)_2$ (1.0 g, 5.8 mmoles), iodine (13 g, 51 mmoles), and water (100 ml) was refluxed for 3 hr. Zinc dust was added and the mixture was stirred to remove residual iodine. Filtration of the mixture followed by the addition of tetramethylammonium chloride precipitated $[(CH_3)_4N]_2B_{10}H_3I_5(COOH)_2$ which was recrystallized from water. *Anal.* Calcd for $[(CH_3)_4N]_2B_{10}H_3I_5(COOH)_2$: C, 12.3; H, 3.0; B, 11.0; I, 64.5. Found: C, 12.1; H, 3.0; B, 1.7; I, 63.0.

Replacement of Carboxyl by Halogen. A mixture of 1,10-$B_{10}Cl_8(CO)_2$ (0.5 g, 1.1 mmoles), bromine (5 g, 31 mmoles), and water (15 ml) was heated to 145–150° for 4 hr in a sealed glass tube. The reaction mixture was removed from the tube and heated on a steam bath to remove excess bromine. The addition of tetramethylammonium chloride precipitated $[(CH_3)_4N]_2$-1,10-$B_{10}Cl_8Br_2$ (darkens at 340°, no melting point to 400°) which was recrystallized from aqueous alcohol. *Anal.* Calcd for $[(CH_8)_4N]_2B_{10}Cl_8Br_2$: C, 13.7; H, 3.4; B, 15.4; Br, 22.8; Cl, 40.0. Found: C, 13.9; H, 3.4; B, 16.0; Br, 22.7; Cl, 40.3. Ultraviolet: $\lambda_{max}^{CH_3CN}$ 273 mμ (ε 245) and 225 mμ (ε 12,250). In another run, the corresponding cesium salt was isolated and obtained as a hydrate (A). This was heated to 500° for 2.5 hr *in vacuo*. The infrared spectrum was essentially unchanged except that the salt was now anhydrous (B). Recrystallization of B from water gave a hydrate (C). The X-ray powder patterns of B and C were identical but were different from that of A, suggesting that polyhedral rearrangement[18] had occurred. *Anal.* Calcd for $Cs_2B_{10}Cl_8Br_2 \cdot H_2O$: B, 12.9; Br, 19.1; Cl, 34.0. Found (A): B, 13.0; Br, 19.1; Cl, 34.6. Found (C): B, 13.3. Calcd for $Cs_2B_{10}Cl_8Br_2$: B, 13.2; Br, 19.6; Cl, 34.7. Found (B): B, 13.2; Br, 19.4; Cl, 34.7.

A solution containing 1,10-$B_{10}Cl_8(CO)_2$ (2.9 g, 6.5 mmoles), chlorine (15 g., 210 mmoles), and water (40 ml) was heated to 150° for 3.5 hr in a silver-lined pressure vessel. The addition of tetramethylammonium chloride precipitated 2.3 g (56%) of $[(CH_8)_4N]_2B_{10}Cl_{10}$,[12] identified by infrared analysis. Chlorine was passed through a solution of 1,10-$B_{10}Cl_8(CO)_2$ (0.5 g, 1.1 mmoles) in water (20 ml) for 70 min at ambient temperature with concomitant ultraviolet irradiation. The addition of tetramethylammonium chloride precipitated 0.7 g (100%) of $[(CH_8)_4N]_2B_{10}Cl_{10}$. No reaction occurred in the absence of ultraviolet irradiation.

An aqueous solution of $Cs_2B_{12}H_{11}COOH \cdot H_2O$ (45 g, 0.96 mole) was passed through an acidic ion-exchange column. The effluent was chlorinated first with cooling in an ice bath, then at ambient temperature, and then at reflux. The infrared spectrum of a tetramethylammonium salt prepared from an aliquot of the reaction solution was consistent with that expected for $[(CH_3)_4N]_2B_{12}Cl_{11}COOH$ except for a very slight amount of B–H absorption. The reaction solution was then heated to 150° for 3.5 hr with chlorine (30 g) in a silver-lined pressure vessel. The addition of tetramethylammonium chloride precipitated a solid which was recrystallized from aqueous acetonitrile to obtain a 59% yield of $[(CH_8)_4N]_2B_{12}Cl_{12}$,[12] identified by infrared analysis. Treating $[(CH_8)_4N]_2$-1,12-$B_{12}Br_{10}(COOH)_2$ with chlorine in similar fashion gave $[(CH_3)_4N]_2$-1,12-$B_{12}Br_{10}Cl_2$ (no melting point to 400°) in 46% yield. This was converted to the corresponding cesium salt (no melting point to 400°). There was no change in the X-ray powder pattern of this salt after 2.5 hr at 500°. *Anal.* Calcd for $[(CH_3)_4N]_2B_{12}Br_{10}Cl_2$: B, 11.6; Cl, 6.3. Found: B, 10.7; Cl, 6.9. Calcd for $Cs_2B_{12}Br_{10}Cl_2 \cdot H_2O$: B, 10.0; Br, 62.2; Cl, 5.5. Found: B, 10.1; Br, 61.6; Cl, 5.7.

Amides. A mixture of 1,10-$B_{10}H_8(CO)_2$ (0.5 g, 2.9 mmoles) and piperidine (12 ml) was heated on a steam bath until the carbonyl dissolved. The solution was cooled; crystals of $(C_5H_{10}NH_2)_2$-1,10-$B_{10}H_8(CONC_5H_{10})_2$ (0.8 g, 54%, mp 250–254°) separated. A mixture of 1,10-$B_{10}H_8(CO)_2$ (0.5 g, 2.9 mmoles) and *n*-butylamine (4 ml) was warmed slightly on a steam bath to dissolve the carbonyl. Water (5 ml) and excess aqueous potassium hydroxide were added. The butylamine was removed by extraction with ether. The addition of cesium fluoride to the aqueous solution precipitated Cs_2-1,10-$B_{10}H_8[CONH(CH_2)_8CH_8]_2$ (decomposes at 295–200°) which was recrystallized from water. A solution of 1,10-$B_{10}H_8(CO)_2$ (1.0 g, 5.8 mmoles) in liquid ammonia was allowed to evaporate. The residue was dissolved in water; the addition of aqueous cesium fluoride precipitated Cs_2-1,10-$B_{10}H_8(CONH_2)_2$. This was recrystallized from a small amount of water. In similar fashion, except that the precipitant was cesium hydroxide, Cs_2-1,12-$B_{12}H_{10}(CONH_2)_2$ was prepared from 1,12-$B_{12}H_{10}(CO)_2$ in 53% yield. The thermal dehydration of the last two amides to the corresponding nitriles was described earlier.[16] Analytical results are given in Table VIII.

1,10-$NCB_{10}H_8CO^-$, 1,10-$NCB_{10}H_8COOH^{2-}$, and 1,12-$NCB_{12}H_{10}COOH^{2-}$. Oxalyl chloride (10 ml) was added to a mixture of Cs_2-1,10-$B_{10}H_8(CONH_2)_2$ (9.8 g, 20.8 mmoles) and acetonitrile. After reaction ceased, the mixture was filtered and water (5 ml) was added to the filtrate which was then evaporated on a steam bath. The viscous orange residue was taken up in water (30 ml) and filtered to obtain 0.5 g (5%) of Cs_2-1,10-$B_{10}H_8(COOH)_2$. The addition of tetramethylammonium chloride to the filtrate precipitated $[(CH_3)_4N]_2$-1,10-$NCB_{10}H_8COOH$ which was recrystallized from water (2.3 g, 37% yield, decomposes at 310–320°). *Anal.* Calcd for $[(CH_8)_4N]_2NCB_{10}H_8COOH$: C, 35.8; H, 9.9; B, 32.3; N, 12.5. Found: C, 35.1; H, 9.9; B, 31.6; N, 12.1. Ultraviolet: $\lambda_{max}^{H_2O}$ 254 mμ (ε 4950) and 218 (ε 33,500).

The infrared spectrum included CN absorption at 2170 cm^{-1} and C=O absorption at 1640 cm^{-1}.

The addition of hydrochloric acid to an aqueous solution of $[(CH_8)_4N]_2$-1,10-$NCB_{10}H_8COOH$ precipitated $(CH_3)_4N$-1,10-$NCB_{10}H_8CO$ as a crystalline solid, mp 294–297°. *Anal.* Calcd for $(CH_3)_4NNCB_{10}H_8CO$: C, 29.5; H, 8.2; B, 44.3. Found: C, 28.9; H, 8.0; B, 44.0. Ultraviolet: $\lambda_{max}^{CH_3CN}$ 248 mμ (ε 25,200) and 305 mμ (ε 860).

In a fashion similar to the preparation of 1,10-$NCB_{10}H_8COOH^{2-}$, 1,12-$NCB_{12}H_{10}COOH^{2-}$ was prepared from Cs_2-1,12-$B_{12}H_{10}(CONH_2)_2$ and isolated as a cesium salt in 21% yield. The product did not melt to 400°. *Anal.* Calcd for $Cs_2NCB_{12}H_{10}COOH$: C, 5.0; H, 2.3; B, 27.6; N, 2.9. Found: C, 4.5; H, 2.5; B, 28.3; N, 2.8. Ultraviolet: no maximum.

The infrared spectrum had CN absorption at 2200 cm^{-1} and C=O absorption at 1660 cm^{-1}.

1,7-$B_{12}H_{10}(COOCH_8)_2{}^{2-}$. Methanol (10 ml) was mixed with 1,7-$B_{12}H_{10}(CO)_2$ (0.5 g, 2.7 mmoles). An exothermic reaction occurred; the resulting solution was refluxed gently for 30 min. The addition of a solution of tetramethylammonium chloride (1.0 g, 9.1 mmoles) in methanol (20 ml) precipitated $[(CH_3)_4N]_2$-1,7-$B_{12}H_{10}(COOCH_8)_2$, (0.9 g, 87%, decomposes at 300–302°). *Anal.* Calcd for $[(CH_3)_4N]_2B_{12}H_{10}(COOCH_3)_2$: C, 35.5; H, 9.9; B, 32.0; N, 6.9. Found: C, 35.1; H, 10.0; B, 31.9; N, 7.0.

1,10-$B_{10}H_8(COOC_2H_5)_2{}^{2-}$. Sodium (0.5 g, 22 mg-atoms) was dissolved in anhydrous ethanol (50 ml). One gram (5.8 mmoles) of 1,10-$B_{10}H_8(CO)_2$ was added. The addition of anhydrous tetramethylammonium chloride (3 g, 27 mmoles) in ethanol (40 ml) precipitated $[(CH_8)_4N]_2$-1,10-$B_{10}H_8(COOC_2H_5)_2$ which was recrystallized twice from aqueous ethanol. *Anal.* Calcd for $[(CH_3)_4N]_2B_{10}H_8(COOC_2H_5)_2$: B, 26.4; H, 10.3; N, 6.9. Found: B, 26.0; H, 10.3; N, 6.8.

The infrared spectrum had C=O absorption at 1650 cm^{-1}.

Isocyanates. A solution of 1,10-$B_{10}H_8(CO)_2$ (6.0 g, 35 mmoles) in acetonitrile (60 ml) was added to a slurry of sodium azide in

Table IX

Compound	Calcd, % C	H	B	N	X	Found, % C	H	B	N	X
$[(CH_3)_4N]_2B_{10}H_8(NCO)_2$[a]	34.5	9.2	31.0	16.1	...	34.7	9.2	31.0	16.2	...
$[(CH_3)_4N]_2B_{10}Cl_8(NCO)_2$[b]	19.2	3.8	17.3	9.0	45.4	19.5	3.9	16.6	9.0	46.0
$[(CH_3)_4N]_2B_{12}H_{10}(NCO)_2$[c]	32.3	9.2	34.9	15.0	...	32.2	9.1	34.8	15.2	...
$Cs_2B_{10}I_8(NCO)_2$[d]	1.6	0.0	7.3	1.9	68.8	1.5	0.2	7.4	1.9	68.4

Ultraviolet, $\lambda_{max}^{CH_3CN}$, data and ν_{NCO} are as follows: [a] 217 mμ (ε 22,800), 2300 cm^{-1}. [b] 229 mμ (ε 14,900), 2280 cm^{-1}. [c] No maximum 2300 cm^{-1}. [d] 321 mμ (ε 900) and 260 (sh, 6700), 215 (sh, 11,800); 2250 cm^{-1}.

Table X

Compound	Calcd, % C	H	B	N	Found, % C	H	B	N
$(CH_3)_4N$-1,10-$H_3NB_{10}H_8NHCO_2C_2H_5$	28.5	9.9	36.7	14.2	28.5	10.0	36.0	14.0
$[(CH_3)_4N]_2B_{10}Cl_8(NHCO_2C_2H_5)_2$	23.4	5.0	15.1	7.8	23.5	5.1	15.2	7.8
$[(CH_3)_4N]_2B_{12}H_{10}(NHCO_2C_2H_5)_2$	36.2	10.1	27.9	12.1	36.3	10.4	28.2	12.3

acetonitrile (60 ml). The temperature rose to 64° and nitrogen (69.5 mmoles, 99%) was evolved smoothly. The mixture was filtered and the filtrate was concentrated until it became a viscous oil. This was diluted with water (80 ml); the addition of excess tetramethylammonium chloride precipitated $[(CH_3)_4N]_2$-1,10-$B_{10}H_8(NCO)_2$ which was recrystallized from water (8 g, 66% yield, decomposes at 334–336°). Chlorine was passed through a mixture of $[(CH_3)_4N]_2$-1,10-$B_{10}H_8(NCO)_2$ (4.0 g, 11.5 mmoles) and acetonitrile (125 ml) for 4.5 hr at 5–10°. The acetonitrile was evaporated. The residual viscous liquid was added to ethanol, precipitating $[(CH_3)_4N]_2$-1,10-$B_{10}Cl_8(NCO)_2$ (5.0 g, 78%, no melting point to 400°). This was also prepared from $B_{10}Cl_8(CO)_2$ and sodium azide. In similar fashion, reaction of sodium azide with the appropriate carbonyls gave $[CH_3)_4N]_2$-1,12-$B_{12}H_{10}(NCO)_2$ (87% yield, decomposes at 280–282°), Cs_2-1,10-$B_{10}I_8(NCO)_2$ (40%), $[(CH_3)_4N]_2$-1,7-$B_{12}H_{10}(NCO)_2$, and Cs_2-1,12-$B_{12}I_{10}(NCO)_2$. The latter two were characterized by infrared analysis only. Analytical results are given in Table IX.

Urethans. Hydrogen chloride was passed into a mixture of $[(CH_3)_4N]_2$-1,10-$B_{10}H_8(NCO)_2$ (2.0 g, 7.5 mmoles) and ethanol (50 ml). The temperature rose to 78° and the isocyanate dissolved. The hydrogen chloride flow was discontinued when the temperature dropped to 30°. The solution was concentrated to 7 ml to partially remove excess hydrogen chloride; the concentrate was diluted with 25 ml of ethanol and then with 150 ml of propanol. The precipitated solid was extracted three times with boiling ethanol and then recrystallized from water to obtain 1.1 g (50%) of $(CH_3)_4N$-1,10-$H_3NB_{10}H_8NHCO_2C_2H_5$ (mp 268–270°). Similar reactions with $[(CH_3)_4N]_2$-1,10-$B_{10}Cl_8(NCO)_2$ and $[(CH_3)_4N]_2$-1,7-$B_{12}H_{10}(NCO)_2$ gave $[(CH_3)_4N]_2$-1,10-$B_{10}Cl_8(NHCOOC_2H_5)_2$ (no melting point to 400°, darkens at 205°) and $[(CH_3)_4N]_2$-1,7-$B_{12}H_{10}(NHCOOC_2H_5)_2$ (decomposes at 231°), respectively. Analytical results are given in Table X.

Amines. A solution of hydroxylamine-O-sulfonic acid (1.5 g, 13.3 mmoles) in water (10 ml) was added to a solution of 1,10-$B_{10}H_8(CO)_2$ (0.52 g, 3 mmoles) in water (5 ml). Carbon dioxide (5.7 mmoles, 94%) was evolved rapidly and 1,10-$B_{10}H_8(NH_3)_2$ (0.32 g, 70%) precipitated and was identified by infrared analysis.[2] Similar treatment of the 1,12 and 1,7 isomers of $B_{12}H_{10}(CO)_2$ gave the corresponding isomers of $B_{12}H_{10}(NH_3)_2$[7] in good yield. A mixture of hydroxylamine-O-sulfonic acid (36 g, 0.32 mole) and 1,10-$B_{10}Cl_8(CO)_2$ (23.5 g, 52.5 mmoles) in water (80 ml) was heated to 100° for several hours. The mixture was cooled, additional hydroxylamine-O-sulfonic acid (20 g, 0.18 mole) was added, and the mixture was reheated to a slow reflux for 3 hr. It was then allowed to stand for 2.5 days at ambient temperature. Some 1,10-$B_{10}Cl_8(NH_3)_2$ crystallized during this time. This was removed by filtration; the filtrate was treated with water (25 ml) and an additional 20 g (0.18 mole) of hydroxylamine-O-sulfonic acid was added; the mixture was refluxed for 21 hr, cooled, and filtered. The combined filter cakes were recrystallized from water (18 ml) to obtain 1,10-$B_{10}Cl_8(NH_3)_2$ (6.8 g). Partial concentration of the mother liquor gave additional 1,10-$B_{10}Cl_8(NH_3)_2$ (8.6 g) for a total yield of 60%. The analytical sample was recrystallized again from water and dried *in vacuo* at 60° (no melting point to 360°). *Anal.* Calcd for $B_{10}Cl_8(NH_3)_2$: B, 25.4; Cl, 66.6; N, 6.6. Found: B, 25.1; Cl, 65.7; N, 6.6.

High yields of 1,10-$B_{10}H_8(NH_3)_2$, 1,12-$B_{12}H_{10}(NH_3)_2$, 1,10-$B_{10}Cl_8(NH_3)_2$, 1,12-$B_{12}I_{10}(NH_3)_2$ (no melting point to 400°), and 1,10-$B_{10}I_8(NH_3)_2$ (no melting point to 400°) were obtained by passage of aqueous solutions of salts of the corresponding diisocyanates through acidic ion-exchange columns followed by evaporation of the effluents to dryness. *Anal.* Calcd for $B_{10}I_8(NH_3)_2$: B, 9.4; I, 87.7; N, 2.4. Found: B, 9.4; I, 87.7; N, 2.3. Calcd for $B_{12}I_{10}(NH_3)_2$: B, 9.0; I, 88.5; N, 2.0. Found: B, 17; I, 84.2; N, 1.8.

1,10-$B_{10}Cl_8(COC_2H_5)_2^{2-}$. A solution of 1,10-$B_{10}Cl_8(CO)_2$ (10 g, 22 mmoles) in a mixture of toluene (200 ml) and glyme (25 ml) was added to diethylmercury (15 g, 58 mmoles) in toluene (100 ml). The temperature spontaneously rose to 35°. The solution was refluxed for 2 hr during which time 10.3 g of a white solid separated. Analysis suggested the formula $(C_2H_5Hg)_2$-1,10-$B_{10}Cl_8(COC_2H_5)_2$. The infrared spectrum had a sharp absorption band at 1550 cm^{-1} for a carbonyl group. This solid was insoluble in water; it dissolved readily in aqueous sodium hydroxide. The addition of tetramethylammonium chloride to such a solution precipitated $[(CH_3)_4N]_2$-1,10-$B_{10}Cl_8(COC_2H_5)_2$ which was recrystallized from water. The infrared spectrum of this ketone had a sharp absorption band at 1630 cm^{-1} for a carbonyl group. *Anal.* Calcd for $(C_2H_5Hg)_2B_{10}Cl_8(COC_2H_5)_2$: C, 12.4; H, 2.1; B, 11.5; Cl, 29.4. Found: C, 12.9; H, 2.4; B, 11.1; Cl, 30.7. Ultraviolet: $\lambda_{max}^{dioxane}$ 312 mμ (ε 8800) and 277 mμ (ε 9900). Calcd for $[(CH_3)_4N]_2$-$B_{10}Cl_8(COC_2H_5)_2$: C, 25.7; H, 5.2; B, 16.5; N, 4.3; Cl, 43.5. Found: C, 26.5; H, 5.4; B, 16.5; N, 4.3; Cl, 42.4. Ultraviolet: $\lambda_{max}^{CH_3CN}$ 242 mμ (ε 7800), 219 (8200), 270 (sh 4600).

1,10-$B_{10}Br_8(COC_6H_5)_2^{2-}$. A solution of 1,10-$B_{10}H_8(CO)_2$ (4.0 g, 46.5 mmoles) and diphenylmercury (25 g, 70 mmoles) in xylene (150 ml) was heated at 60° for 2 hr. An orange solid (19 g) precipitated and was separated by filtration. The filter cake was washed with petroleum ether and dried. Three grams of this solid was dissolved in 5% aqueous sodium hydroxide (100 ml) and the solution was filtered. Excess tetramethylammonium chloride solution was added, resulting in the separation of an oil. The oil was removed and dissolved in water. Acidification with ammonium chloride caused the precipitation of a solid. Three grams of this solid was mixed with ethanol (75 ml) and bromine (120 g, 0.75 mole). The resulting solution was refluxed until a tetramethylammonium salt precipitated from an aliquot with aqueous tetramethylammonium chloride had no B–H absorption at approximately 2500 cm^{-1} in the infrared. The solution was then concentrated to 50 ml, poured into water (200 ml), and filtered. The filtrate was passed through a strongly acidic ion-exchange column; the addition of excess tetramethylammonium chloride to the effluent precipitated a solid. This was fractionally recrystallized from water. The first fractions obviously contained at least two species; tests shows the presence of mercury. The later fractions were

$[(CH_3)_4N]_2$-1,10-$B_{10}Br_8(COC_6H_5)_2$ (decomposes at 342–344°). *Anal.* Calcd for $[(CH_3)_4N]_2B_{10}Br_8(COC_6H_5)_2$: C, 23.9; H, 3.1; B, 9.8; Br, 57.8; N, 2.5. Found: C, 23.2; H, 3.2; B, 9.4; Br, 58.5; N, 2.9.

The infrared spectrum in a potassium bromide wafer included absorptions at 3030 (w), 1610 (m, C=O), 1590 (w), 1575 (w), 1480 (ms), 1260 (m), 1150 (w), 950 (s), 835 (m), 780 (m), 700 (m), and 665 (w) cm^{-1}.

1,10-$B_{10}H_8(CH_3)_2{}^{2-}$. A solution of 1,10-$B_{10}H_8(CO)_2$ (3 g, 17 mmoles) in 50 ml of ether was added slowly to ether (50 ml) containing lithium aluminum hydride (2 g, 53 mmoles). The mixture was refluxed for 2 hr and then hydrolyzed with wet ether followed by 10 ml of water. The ether was decanted from the coagulated solid and the solid was washed with water until the washing gave no precipitate with cesium fluoride. The addition of cesium fluoride to the washings precipitated Cs_2-1,10-$B_{10}H_8(CH_3)_2$ (1.8 g, 26%, no melting point to 400°). *Anal.* Calcd for $Cs_2B_{10}H_8(CH_3)_2$: C, 5.8; H, 3.4; B, 26.3. Found: C, 5.8; H, 3.4; B, 25.8. Ultraviolet: no maximum.

The infrared spectrum in a potassium bromide wafer included absorptions at 2900 (w), 2830 (w), 2440 (s), 1440 (w), 1390 (w), 1210 (m), 1175 (m), 1025 (m), and 930 (m) cm^{-1}. The B^{11} mnr spectrum of the corresponding sodium salt in water consisted of a symmetrical doublet at 43 ppm (J = 112 cps) and a singlet at 14 ppm, referred to methyl borate. The proton spectrum of a similar solution consisted of a single peak at +3.1 ppm from internal water.

Chemistry of Boranes. XXXI.[1]
1,10-Bis(hydroxymethyl)octachlorodecaborate(2−)

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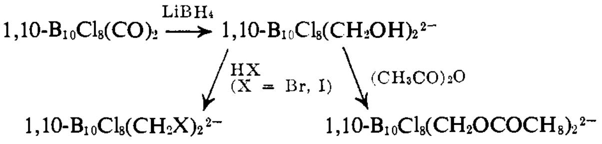
Abstract: Reduction of 1,10-$B_{10}Cl_8(CO)_2$ with lithium borohydride gives 1,10-$B_{10}Cl_8(CH_2OH)_2{}^{2-}$. This anion is readily acylated and reacts with halogen acids to form the corresponding bis(halomethyl) anions. The latter have been converted to cyanomethyl, carboxymethyl, aminomethyl, and other derivatives of $B_{10}H_{10}{}^{2-}$.

Previous work[1-3] has shown that carbonyl derivatives of $B_{10}H_{10}{}^{2-}$ and $B_{12}H_{12}{}^{2-}$ are versatile intermediates. Conversions of the carbonyl groups to amine, isocyanate, carboxyl, nitrile, alkyl, and other groups have been described. The scope of $B_{10}H_{10}{}^{2-}$ derivative chemistry has now been further extended by the reduction of 1,10-$B_{10}Cl_8(CO)_2$ to 1,10-$B_{10}Cl_8(CH_2OH)_2{}^{2-}$ (Figure 1) and the demonstration of preparative utility for this species.

The reduction to 1,10-$B_{10}Cl_8(CH_2OH)_2{}^{2-}$ is accomplished in good (60–90%) yield with lithium borohydride in glyme. The hydroxy groups are readily acylated by acetic anhydride and are easily replaced by bromine or iodine upon reaction with the corresponding halogen acid.



$$\begin{tikzcd}
1,10\text{-}B_{10}Cl_8(CO)_2 \arrow[r, "LiBH_4"] & 1,10\text{-}B_{10}Cl_8(CH_2OH)_2{}^{2-} \arrow[dl, "HX\ (X = Br,\ I)"'] \arrow[d, "(CH_3CO)_2O"] \\
1,10\text{-}B_{10}Cl_8(CH_2X)_2{}^{2-} & 1,10\text{-}B_{10}Cl_8(CH_2OCOCH_3)_2{}^{2-}
\end{tikzcd}$$

The halogen atoms bonded to carbon in 1,10-$B_{10}Cl_8(CH_2X)_2{}^{2-}$ are readily replaced by nucleophiles. In contrast, the chlorine atoms bonded to boron are quite inert, which is consistent with earlier observations on the lack of reactivity of B-halogenated derivatives of $B_{10}H_{10}{}^{2-}$.[4] This difference in halogen reactivity is similar to that which exists between phenyl and benzyl halides. This similarity is noteworthy because of other parallels[5,6] between $B_{10}H_{10}{}^{2-}$ chemistry and the chemistry of organic aromatic systems. It is emphasized, however, that no kinetic or other mechanistic studies on the reactions reported here have been made; extension of the observed parallels in reactivity to speculative parallels in causative factors, though inviting, would be premature.

The bromine atoms in 1,10-$B_{10}Cl_8(CH_2Br)_2{}^{2-}$ are hydrolyzed easily to regenerate 1,10-$B_{10}Cl_8(CH_2OH)_2{}^{2-}$. They are readily replaced by $CH_2SOCH_3{}^-$ in dimethyl sulfoxide and by cyanide in refluxing aqueous sodium cyanide. The nitrile groups in the product from the latter reaction have been hydrolyzed to form the corresponding dicarboxylic acid.

$$1,10\text{-}B_{10}Cl_8(CH_2Br)_2{}^{2-} \xrightarrow[(CH_3)_2SO]{CH_2SOCH_3{}^-} 1,10\text{-}B_{10}Cl_8(CH_2CH_2SOCH_3)_2{}^{2-}$$

$$1,10\text{-}B_{10}Cl_8(CH_2Br)_2{}^{2-} \xrightarrow[H_2O,\ reflux]{CN^-}$$

$$1,10\text{-}B_{10}Cl_8(CH_2CN)_2{}^{2-} \xrightarrow[(3)\ H^+]{(1)\ H^+\ (2)\ OH^-} 1,10\text{-}B_{10}Cl_8(CH_2COOH)_2{}^{2-}$$

Titration in aqueous solution indicates a pK_a of approximately 6.9 for $Na_2B_{10}Cl_8(CH_2COOH)_2$, compared to approximately 7.5 for $Na_2B_{10}Cl_8(COOH)_2$.[1]

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