between the two compounds. In addition, this calculated value satisfies the inequality relation $I_p(B_5H_8)_{calcd}$ = 8.4 < $I_p(I)$, $I_p(Br)$, and is lower in magnitude than those of the parent compounds $I_p(B_5H_8)_{calcd}$ = 8.4 < $I_p(B_5H_8I)$ and $I_p(B_5H_8Br)$.

The ionization efficiency curves of the I^+ and Br^+ ions from B_5H_8I and B_5H_8Br, respectively, exhibit much complex structure with $A_p(X^+) > 20$ e.v. (X = I, Br). These results are in agreement with the Stevenson principle since the X^+ ions possess ionization potentials higher than that of the B_5H_8 radical and, thus, are expected to be formed only with energies in excess of the sum of the bond dissociation energy and the ionization potential of the ions.

Dissociation Energy of the Coupling Boron–Boron Bond.

—In the fragmentation of decaborane-16 by electron impact, a process similar to that of eq. 2 is proposed as the one which leads to $B_5H_8^+$ ion formation

$$B_5H_8-B_5H_8 + e^- \longrightarrow B_5H_8^+ + B_5H_8 + 2e^-$$
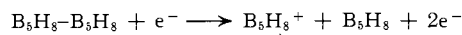
Thus

$$D(B_5H_8-B_5H_8) = A_p(B_5H_8^+) - I_p(B_5H_8)$$

Using the value of $I_p(B_5H_8)$ from eq. 6 along with the experimentally determined value of $A_p(B_5H_8)$ from Table I, we find $D(B_5H_8—B_5H_8) = 3.2 \pm 0.2$ e.v.

Although the error associated with this bond energy is subject to some uncertainty in view of the numerous assumptions that are involved in the determination of appearance potentials of large molecules,[21] the value obtained for the B–B bond energy[22] in decaborane-16 is approximately what one would expect if the bond was mainly of single bond character, i.e., a normal two-center electron pair bond. The B_5H_8 group simply replaces the apical hydrogen atom of B_5H_9 to give decaborane-16 $(B_5H_8-B_5H_8)$.

It is interesting to note here the results of an LCAO–MO calculation on decaborane-16 by Moore.[23] From

(21) H. M. Rosenstock and M. Krauss, "Advances in Mass Spectrometry," Vol. 2, Pergamon Press, New York, N. Y., 1963.

(22) Other values given for $D(B-B)$ are 3.6 e.v. by S. Gunn and L. Green, *J. Phys. Chem.*, **65**, 2173 (1961), and 3.58 e.v. by E. Prosen in a private communication quoted in ref. 12. These values, however, are for boron–boron bonds of the three-center type.

(23) E. B. Moore, *J. Am. Chem. Soc.*, **85**, 676 (1963).

an inspection of the population matrix for the decaborane-16 molecule, Moore concluded that the coupling boron–boron bond is not a multiple bond. His calculations also yielded a value of 10.2 e.v. for the ionization potential of decaborane-16.

Monoisotopic Fragmentation Patterns.

—The monoisotopic mass spectrum or electron impact fragmentation pattern of decaborane-16 was calculated from the spectrum of the compound containing 1.23% ^{10}B by subtraction of the contributions of all the ions containing ^{10}B to the spectrum. The mass spectrum of $^{11}B_{10}H_{16}$ is presented in Fig. 1 along with the spectrum of the compound of natural isotopic content. The alternation of intensities of the peaks in the parent peak region ($^{11}B_{10}H_n^+$) is characteristic of the monoisotopic spectrum of the boron hydrides. This alternation arises from the fact that hydrogen is presumably lost from the hydride upon electron impact predominantly as molecular hydrogen and, consequently, ions corresponding to the loss of an odd number of hydrogen atoms are not abundant. Also, it is to be noted that no peak in the $B_5H_n^+$ ion region occurs with $n > 8$. Thus, as expected, there are probably no $B_5H_n^+$ rearrangement ions resulting from hydrogen migration from one B_5H_8 unit to the other.

The monoisotopic spectra of 1-iodo- and 1-bromopentaborane-9 were calculated from the spectra of the compounds of natural boron isotopic content on the basis of 18.83% ^{10}B and in the B_5H_8Br case, 50.57% ^{79}Br. These calculated spectra are shown in Fig. 2 and 3 along with the observed spectra of the compounds of natural isotopic content. The monoisotopic $^{11}B_5H_8I$ spectrum is quite similar to that given by Shapiro[9] but the $^{11}B_5H_8^{79}Br$ spectrum differs in several respects. Perhaps this may be due to impurities introduced by the use of CS_2 and $AlCl_3$ which are not completely removed by the purification methods used.

[CONTRIBUTION No. 966 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON, DELAWARE]

Chemistry of Boranes. XIX.[1] Derivative Chemistry of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$

BY W. H. KNOTH, J. C. SAUER, D. C. ENGLAND, W. R. HERTLER, AND E. L. MUETTERTIES

$B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ react under acidic conditions with a number of oxygen- and sulfur-containing species and with olefins to form substitution derivatives. The substituents observed have included acyl, hydroxy, alkoxy, alkyl, mercapto, and alkylthio groups. The chemical properties of these species resemble those of organic compounds. Some of the substitution reactions are by definition electrophilic, but the majority are characterized as acid-catalyzed nucleophilic substitutions.

Introduction

This is the third of several papers[2,3] detailing the chemistry of the $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ anions[4-6] that

(1) Paper XVIII: B. L. Chamberland and E. L. Muetterties, *Inorg. Chem.*, **3**, 1450 (1964).

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

(3) W. H. Knoth, H. C. Miller, J. C. Sauer, J. H. Balthis, Y. T. Chia, and E. L. Muetterties, *ibid.*, **3**, 159 (1964).

was previously outlined in a communication.[7] The previous two papers[2,3] discussed the extreme oxidative

(4) M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, **81**, 5519 (1959).

(5) M. F. Hawthorne and A. R. Pitochelli, *ibid.*, **82**, 3228 (1960).

(6) H. C. Miller, N. E. Miller, and E. L. Muetterties, *ibid.*, **85**, 3885 (1963).

(7) W. H. Knoth, H. C. Miller, D. C. England, G. W. Parshall, J. C. Sauer, and E. L. Muetterties, *ibid.*, **84**, 1056 (1962).

and thermal stability of salts of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ and their halogenated derivatives (e.g., $B_{10}Cl_{10}^{-2}$, $B_{12}H_{10}I_2^{-2}$, $B_{12}Br_{12}^{-2}$), and their resistance to degradation by acids and bases. The acid-catalyzed thermal reactions of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ with water to give the hydroxy derivatives $B_{10}H_9OH^{-2}$[8] and $B_{12}H_{11}OH^{-2}$ was also described.[2] This paper is concerned with the related acid-catalyzed reactions of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ with a variety of other oxygen- and sulfur-containing species and with olefins. These reactions lead to new types of derivatives of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$, the properties of which continue to demonstrate the unique position held by $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ among purely inorganic species.[9] It should be emphasized that although most of the reactions reported here give analogous products for $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ this is not always true, and these species should not be regarded as completely chemically equivalent. In acid-catalyzed reactions which give different types of products for $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$, $B_{10}H_{10}^{-2}$ is more apt to parallel

This benzoyl compound is the first in which an acyl group is bonded directly to boron although others based on $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ have since been prepared.[9] $B_{10}H_9COC_6H_5^{-2}$ behaves much like an organic ketone. It can be converted to a semicarbazone using standard techniques and is oxidized to $B_{10}H_9OCOC_6H_5^{-2}$ by hydrogen peroxide in a fashion formally similar to a Baeyer–Villiger reaction. The remaining boron–hydrogen bonds in $B_{10}H_9COC_6H_5^{-2}$ can be halogenated without cleavage of the boron–carbonyl bond and in this fashion $B_{10}Cl_9COC_6H_5^{-2}$ and $B_{10}Br_9COC_6H_5^{-2}$ have been prepared. The ketonic character of the carbonyl group in $B_{10}Cl_9COC_6H_5^{-2}$ has also been demonstrated by conversion to a semicarbazone and by Baeyer–Villiger oxidation to $B_{10}Cl_9OCOC_6H_5^{-2}$. $B_{10}H_9OCOC_6H_5^{-2}$ and $B_{10}Cl_9OCOC_6H_5^{-2}$ have been hydrolyzed to the respective alcohols, $B_{10}H_9OH^{-2}$ and $B_{10}Cl_9OH^{-2}$, both of which have been prepared by other methods, as discussed below. These reactions are summarized in Scheme I.

SCHEME I
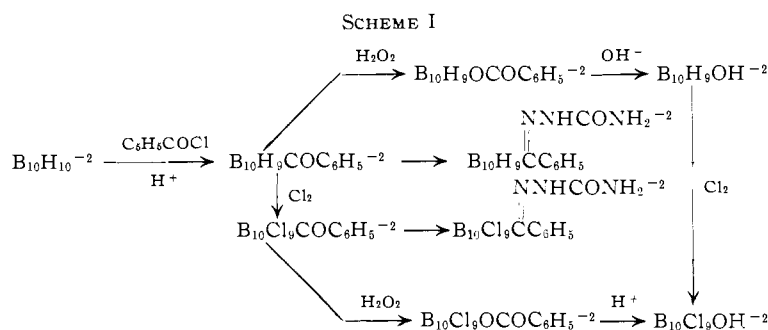
the behavior of an organic aromatic system than is $B_{12}H_{12}^{-2}$. The outstanding example of such behavior in this paper is the reaction with benzoyl chloride in which benzoylation prevails with $B_{10}H_{10}^{-2}$, whereas hydroxylation is the major reaction for $B_{12}H_{12}^{-2}$.

Reactions. $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ with Benzoylating Agents. Derived Chemistry.—Concentrated aqueous $(H_3O)_2B_{10}H_{10}^2$ reacts smoothly with benzoyl chloride in dimethoxyethane at ice-bath temperatures to give the $B_{10}H_9COC_6H_5^{-2}$ anion. In acid solution this anion is dark red and precipitates as acid salts (e.g., [CH₃-(CH₂)₂]₄N(H₃O)B₁₀H₉COC₆H₅. In basic solution, it is light yellow and precipitates as neutral salts (e.g., [(CH₃)₄N]₂B₁₀H₉COC₆H₅. The nature of the protonation of $B_{10}H_9COC_6H_5^{-2}$ is not thoroughly understood but probably involves the carbonyl group and not the boron cage. Titration of the acid form of $B_{10}H_9COC_6H_5^{-2}$ in aqueous solution gives a typical strong acid titration curve with only one inflection point which occurs at pH 7 after 2 equivalents of base have been added.

The infrared spectrum of [(CH₃)₄N]₂B₁₀H₉COC₆H₅ includes relatively sharp absorptions at 1610, 1590, and 1570 cm.$^{-1}$, the last being the most intense. The precipitation of a thallium salt by the addition of thallium nitrate to aqueous [(CH₃)₄N]₂B₁₀H₉COC₆H₅ gives a species with similar absorptions at 1610 and 1590 cm.$^{-1}$ and a relatively broad absorption at 1555 cm.$^{-1}$. From this behavior and from the infrared shifts on halogenation and/or oxidation of $B_{10}H_9COC_6H_5^{-2}$ (see below), we are assigning the 1570-cm.$^{-1}$ absorption in [(CH₃)₄N]₂B₁₀H₉COC₆H₅ as the carbonyl stretching frequency and the 1610- and 1590-cm.$^{-1}$ bands as the doublet which is characteristic of conjugated phenyl rings.[10a] This frequency (1570 cm.$^{-1}$) is quite outside the normal range for benzoyl derivatives (1670–1660 cm.$^{-1}$ for diaryl ketones[10b]) and establishes a highly polar nature for the carbonyl group in this "ketone."[11] Perhalogenation of the boron cage reduces the polarity of the carbonyl group, consistent with net inductive electron withdrawal by the halogen, as shown by a shift of the carbonyl frequency to 1615 cm.$^{-1}$ in [(CH₃)₄N]₂B₁₀Cl₉COC₆H₅. Insulation of the carbonyl group from boron by oxygen also reduces its abnormal polarity, as shown by carbonyl frequencies of 1680 and 1700 cm.$^{-1}$ for [(CH₃)₄N]₂B₁₀H₉OCOC₆H₅ and [(CH₃)₄N]₂B₁₀Cl₉OCOC₆H₅, respectively, compared to a reported[10b] range of 1730–1717 cm.$^{-1}$ for aryl esters.

(8) The reaction of $B_{20}H_{18}^{-2}$ with hydroxide ion was initially reported [A. Kaczmarczyk, R. D. Dobrott, and W. N. Lipscomb, Proc. Natl. Acad. Sci. U. S., 48, 729 (1962)], erroneously, to give $B_{10}H_9OH^{-2}$. More recently the product has been identified [M. F. Hawthorne, R. L. Pilling, P. F. Stokely, and P. M. Garrett, J. Am. Chem. Soc., 85, 3704 (1963)] as $B_{20}H_{17}$-OH^{-4}. As a result of the accompanying confusion, there is a statement on p. 200 of a book by W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, that the compound labeled in the text "$B_{10}H_9$-OH^{-2} (?)" is most probably $B_{20}H_{17}OH^{-4}$. Unfortunately the "$B_{10}H_9OH^{-2}$ (?)" notation was used throughout the book for $B_{10}H_9OH^{-2}$ regardless of context. The correction should apply only in cases where the $B_{20}H_{18}^{-2}$-hydroxide product is referred to and not, as was apparently also intended, to those instances referring to "$B_{10}H_9OH^{-2}$ (?)" as prepared by methods outlined in our communication[7] and detailed in this paper.
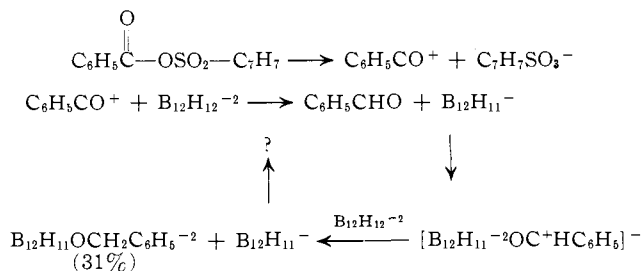
(9) Further work along these lines has recently been described by W. H. Knoth, J. C. Sauer, H. C. Miller, and E. L. Muetterties, J. Am. Chem. Soc., 86, 115 (1964).

(10) (a) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 71, 72; (b) Correlation Chart No. 3, p. 7, also pp. 137, 179.

(11) There are relatively few acyl derivatives of metalloids reported and no other for boron. Perhaps the closest comparison is with a series of benzoylsilanes [A. G. Brook, et al., J. Am. Chem. Soc., 82, 5102 (1960)] which are reported to have a carbonyl stretching frequency at 6.18 μ (1620 cm.$^{-1}$) and a doublet at 6.28 (1592) and 6.32–6.34 μ (~1580 cm.$^{-1}$).

The reaction of $B_{12}H_{12}^{-2}$ with benzoyl chloride is more typical of normal B–H carbonyl reactions in that the major products are boron-oxygen-bonded species. Bromination of the reaction product of benzoyl chloride with $(H_3O)_2B_{12}H_{12}\cdot3H_2O$ in dimethoxyethane has given $B_{12}Br_{10}(OH)_2^{-2}$; a similar reaction in which a catalytic amount of aluminum chloride was present also gave $B_{12}Br_{10}(OH)_2^{-2}$ plus small amounts of possible carbonyl-containing fractions. Reaction of $Na_2B_{12}H_{12}$ with benzoyl p-toluenesulfonate gave $B_{12}H_{11}OCH_2C_6H_5^{-2}$. When this reaction was conducted in the presence of p-chlorobenzaldehyde in acetonitrile solution, a substantial part of the product was $B_{12}H_{11}OCH_2C_6H_4Cl^{-2}$. These results are consistent with the mechanism shown in the following equations.

$$C_6H_5\overset{\overset{O}{\|}}{C}\!-\!OSO_2\!-\!C_7H_7 \longrightarrow C_6H_5CO^+ + C_7H_7SO_3^-$$

$$C_6H_5CO^+ + B_{12}H_{12}^{-2} \longrightarrow C_6H_5CHO + B_{12}H_{11}^-$$

$$B_{12}H_{11}OCH_2C_6H_5^{-2} + B_{12}H_{11}^- \xleftarrow{\quad B_{12}H_{12}^{-2}\quad} [B_{12}H_{11}^{-2}OC^+HC_6H_5]^-$$
$$(31\%)$$

Thus, the benzoylcarbonium ion formed from the ionization of benzoyl p-toluenesulfonate may abstract a hydride ion from $B_{12}H_{12}^{-2}$ to give benzaldehyde and $B_{12}H_{11}^-$, which react to give the species in brackets which can then abstract a hydride ion from $B_{12}H_{12}^{-2}$ to give $B_{12}H_{11}OCH_2C_6H_5^{-2}$. In criticism of this mechanism, it is not obvious why the intermediate benzaldehyde should compete so effectively with the acetonitrile solvent for $B_{12}H_{11}^-$.

$B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ with Amides.—The course of the reaction of dimethylformamide (DMF) with $B_{10}H_{10}^{-2}$ under acidic conditions depends on the amount of water present. If aqueous $(H_3O)_2B_{10}H_{10}$ or aqueous hydrochloric acid is used as the source of acid, two products can be isolated. The major product is $B_{10}H_9$-$OCHO^{-2}$, a formate of $B_{10}H_9OH^{-2}$, and the minor product is $B_{10}H_9N(CH_3)_2H^-$. The latter anion is monovalent because of the quaternary nitrogen present, and it might be expected that base would generate $B_{10}H_9N(CH_3)_2^{-2}$. However, precipitation of a thallium salt from solutions of $B_{10}H_9N(CH_3)_2H^-$ in aqueous sodium hydroxide gives $TlB_{10}H_9N(CH_3)_2H$. Thus, it appears that $B_{10}H_9NMe_2^{-2}$ is a stronger base than OH^-. Exchange of NH proton with solvent does occur as shown by facile exchange with deuterium oxide to give $B_{10}H_9N(CH_3)_2D^-$.

If $(NH_4)_2B_{10}H_{10}$ and anhydrous hydrogen chloride are treated with dimethylformamide, thus excluding gross amounts of water, the major product is $B_{10}H_9OCH{=}N(CH_3)_2^-$. The boron-oxygen bonding in this dimethylformamide complex has been demonstrated by proton magnetic resonance studies which show the presence of two nonequivalent methyl groups[12] at τ 6.9 (doublet, $J = 0.8$ c.p.s.) and 7.1 (doublet, $J = 1.2$ c.p.s.), respectively. The boron-amide bond is moderately stable to acid but is rapidly cleaved by hydroxide to give $B_{10}H_9OH^{-2}$. N-Methylpyrrolidone (NMP) re-

acts with $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$, using aqueous hydrochloric acid as the acid source, to give $B_{10}H_9\cdot NMP^-$ and $B_{12}H_{11}\cdot NMP^-$ or $B_{10}H_8(NMP)_2$ and $B_{12}H_{10}(NMP)_2$, depending on reaction temperature. This varies from 180 to 220° and, considering the acid nature of the reaction mixture, offers another example of the surprising stability of these B_{10} and B_{12} "cages." The neutral bis-amide complexes are insoluble in water and so can be readily separated from the monovalent mono-amide complexes. Subsequent treatment of these amide complexes with sodium hydroxide gives the corresponding hydroxy derivatives, $B_{10}H_9OH^{-2}$ and $B_{12}H_{11}OH^{-2}$ or $B_{10}H_8(OH)_2^{-2}$ and $B_{12}H_{10}(OH)_2^{-2}$. The composition of these species has been further established by perhalogenation and esterification. The presence of boron-oxygen bonds in the B_{10} and B_{12} cages diminishes their oxidative stability as shown by the formation of some boric acid in the aqueous chlorination of these hydroxyl derivatives (no degradation, however, upon chlorination in anhydrous acetonitrile) and by polarographic studies, discussed separately below. These reactions are summarized in Scheme II.

$B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ with Ethers.—$B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ react with ethers under acidic conditions although the course of reaction is not always clean. The simplest reaction is

$$ROR + B_{12}H_{12}^{-2} \xrightarrow{H^+} B_{12}H_{11}OR^{-2} + RH$$
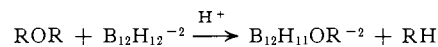
This is observed for $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ with 1,2-dimethoxyethane which gives $B_{10}H_9OCH_2CH_2OCH_3^{-2}$ and $B_{12}H_{10}(OCH_2CH_2OCH_3)_2^{-2}$. There are some experimental difficulties with the B_{12} reaction because mixtures of anions of varying degrees of substitution can be obtained. These anions, however, are quite stable and are not readily cleaved by base or dilute acid; they undergo aqueous halogenation without cleavage of the alkoxy groups, and thus $B_{10}Br_9OCH_2$-$CH_2OCH_3^{-2}$ and $B_{12}Br_{10}(OCH_2CH_2OCH_3)_2^{-2}$ have been prepared. The alkoxy groups can be cleaved from either the perhydro or the halogenated derivatives by refluxing them with concentrated hydrobromic or hydriodic acids and the corresponding hydroxy derivatives are obtained. Methyl ether reacts fairly cleanly with $B_{12}H_{12}^{-2}$ under acidic conditions to give $B_{12}H_{10}$-$(OCH_3)_2^{-2}$, but higher ethers appear to give mixtures of hydroxy and alkoxy derivatives.
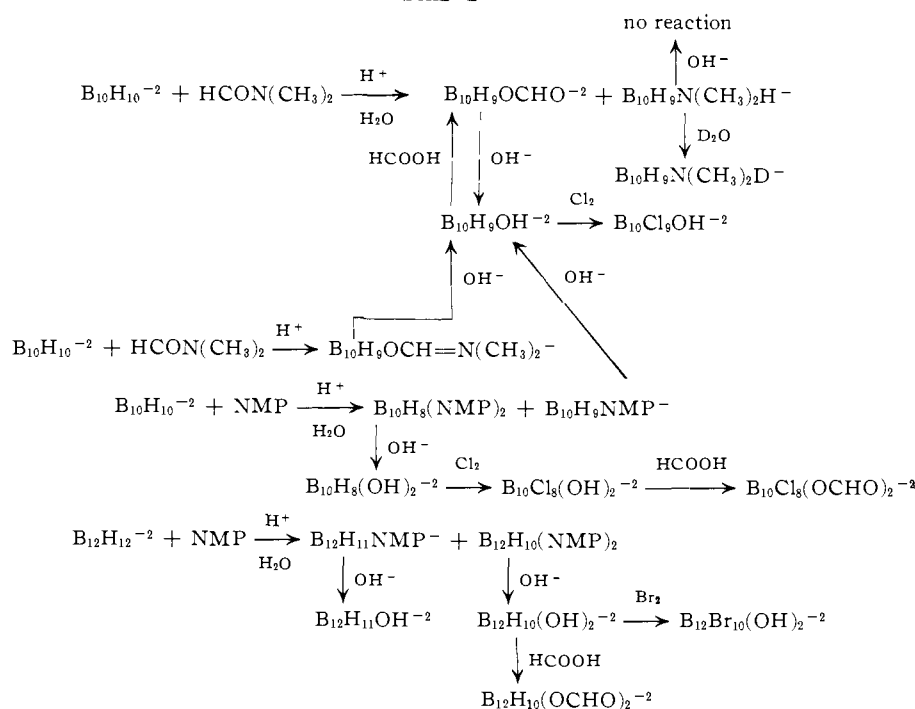
$B_{12}H_{12}^{-2}$ with Acids, Alcohols, Formaldehyde, and Ketones.—The reactions of $B_{12}H_{12}^{-2}$ with acids, alcohols, formaldehyde, and ketones under acidic conditions all give rise to boron-oxygen-bonded species. Oxalic acid yields $B_{12}H_{11}OH^{-2}$ directly while formic and acetic acids appear, from infrared and elemental analyses of the crude products, to give mixtures of hydroxy, alkoxy, and ester derivatives. These have not been satisfactorily separated. Chlorination of the product from formic acid has allowed the isolation of $B_{12}HCl_{10}OCH_3^{-2}$ as a cesium salt.[13] Chlorination of the crude acetic acid product apparently completely hydrolyzed any ester or alkoxy linkages and only salts of $B_{12}HCl_{10}OH^{-2}$ have been isolated.

Primary alcohols give mainly alkoxy derivatives, pure monoalkoxy derivatives being obtained from 1-

(12) Oxygen has been demonstrated to be the bonding element in other amide complexes: see, for example, W. D. Bull, S. K. Madan, and J. E. Willis, *Inorg. Chem.*, **2**, 302 (1963).

(13) The introduction of only ten chlorine atoms into a $B_{12}H_{11}X^{-2}$ anion under the conditions used is not surprising. It has been shown[3] that $B_{12}H_{12}^{-2}$ readily chlorinates only to about the decachloro stage even at 100° in water.

SCHEME II

$$B_{10}H_{10}^{-2} + HCON(CH_3)_2 \xrightarrow[H_2O]{H^+} B_{10}H_9OCHO^{-2} + B_{10}H_9N(CH_3)_2H^- \xrightarrow{OH^-} \text{no reaction}$$

$$B_{10}H_9N(CH_3)_2H^- \xrightarrow{D_2O} B_{10}H_9N(CH_3)_2D^-$$

$$B_{10}H_9OH^{-2} \xrightarrow{Cl_2} B_{10}Cl_9OH^{-2}$$

(with HCOOH and OH⁻ pathways to $B_{10}H_9OH^{-2}$)

$$B_{10}H_{10}^{-2} + HCON(CH_3)_2 \xrightarrow{H^+} B_{10}H_9OCH=N(CH_3)_2^-$$

$$B_{10}H_{10}^{-2} + NMP \xrightarrow[H_2O]{H^+} B_{10}H_8(NMP)_2 + B_{10}H_9NMP^-$$

$$B_{10}H_8(OH)_2^{-2} \xrightarrow{Cl_2} B_{10}Cl_8(OH)_2^{-2} \xrightarrow{HCOOH} B_{10}Cl_8(OCHO)_2^{-2}$$

(OH⁻ pathway)

$$B_{12}H_{12}^{-2} + NMP \xrightarrow[H_2O]{H^+} B_{12}H_{11}NMP^- + B_{12}H_{10}(NMP)_2$$

$$B_{12}H_{11}OH^{-2}$$

$$B_{12}H_{10}(OH)_2^{-2} \xrightarrow{Br_2} B_{12}Br_{10}(OH)_2^{-2}$$

$$B_{12}H_{10}(OCHO)_2^{-2}$$

(OH⁻ and HCOOH pathways)

propanol, 1-butanol, β,β,β-trifluoroethanol, and ethylene chlorohydrin. 2-Propanol reacts to give $B_{12}H_{11}$-$OCH(CH_3)_2^{-2}$. Interestingly, as shown in Table I,

TABLE I

GASEOUS BY-PRODUCTS FORMED IN REACTIONS OF
$(H_3O)_2B_{12}H_{12}\cdot 9H_2O$ WITH ALCOHOLS[a]

Alcohol	RH (mole equiv.)	H₂ (mole equiv.)
MeOH	1.9	0.10
	2.0	0.10
EtOH	1.0	0.40
	1.1	0.50
PrOH	0.62	0.58
	0.66	0.61
n-BuOH	0.26	0.71
	0.40	0.82
i-PrOH	0.70	0.62
	0.65	0.50
sec-BuOH	0.74	0.50
t-BuOH	3.9	0.0
t-C₅H₁₁OH	2.0	0.0

[a] In these experiments, 10 ml. of the alcohol and 5.75 mmoles of $(H_3O)_2B_{12}H_{12}\cdot 9H_2O$ were heated in sealed tubes at 100° for 15 hr.

analysis of by-products formed in the reactions with 1-propanol and 1-butanol showed that the first reaction evolves approximately equimolar amounts of hydrogen and propane, and the second reaction, while mainly giving hydrogen, also gives significant amounts of butane. Similar reactions with methanol and ethanol give impure alkoxy derivatives, and in these reactions more alkane than hydrogen was formed. This could result from condensation of some of the alcohol to form an ether under the highly acidic reaction conditions. The $B_{12}H_{12}^{-2}$ could then react directly with alcohol to give alkoxy derivatives plus hydrogen or with the ether to give alkoxy derivatives plus alkane. That this may not be the reaction path is demonstrated by the reaction of $B_{12}H_{12}^{-2}$, acid, and t-butyl alcohol. This gives polyhydroxy derivatives of B_{12}-H_{12}^{-2} and isobutane, no hydrogen and very little iso-

butene being formed. Salts of the polyhydroxy derivatives were too soluble to purify readily; bromination gave $B_{12}Br_6(OH)_6^{-2}$. The formation of isobutane appears anomalous. The formation of di-t-butyl ether from t-butyl alcohol under the highly acidic conditions is most unlikely, and it would appear that an acid-catalyzed concerted exchange of OH⁻ and H⁻ between $B_{12}H_{12}^{-2}$ and t-butyl alcohol must be involved.

Formaldehyde reacts with $B_{12}H_{12}^{-2}$ to give $B_{12}H_{11}$-OCH_3^{-2} under acidic and also under neutral conditions.

Acetone does not react with $Na_2B_{12}H_{12}$ during 4 hr. at 100° but reacts readily at 20-25° with $(H_3O)_2B_{12}H_{12}$ to give a mixture of $B_{12}H_{11}OCH(CH_3)_2^{-2}$, $B_{12}H_{11}OH^{-2}$, and 2-propanol. Diethyl ketone and cyclohexanone behave similarly.

$B_{12}H_{12}^{-2}$ with Sulfur-Containing Species.—Dimethyl disulfide reacts with $(H_3O)_2B_{12}H_{12}$ to give $B_{12}H_{11}SCH_3^{-2}$ or $B_{12}H_{10}(SCH_3)_2^{-2}$ and $B_{12}H_9(SCH_3)_3^{-2}$ depending on reaction conditions. Transmethylation of trimethylsulfonium iodide with $B_{12}H_{11}SCH_3^{-2}$ and $B_{12}H_{10}$-$(SCH_3)_2^{-2}$ gives the inner sulfonium salts $B_{12}H_{11}S$-$(CH_3)_2^-$ and $B_{12}H_{10}[S(CH_3)_2]_2$, identical by infrared analysis with those species as prepared from diborane and methyl sulfide.[6] $B_{12}H_{11}S(CH_3)_2^-$ can also be obtained by methylation of $B_{12}H_{11}SH^{-2}$, prepared from $(H_3O)_2B_{12}H_{12}$ and hydrogen sulfide.
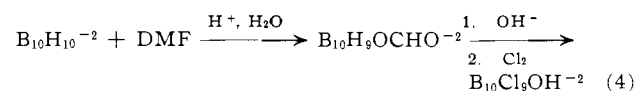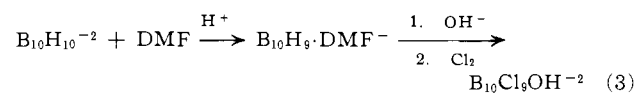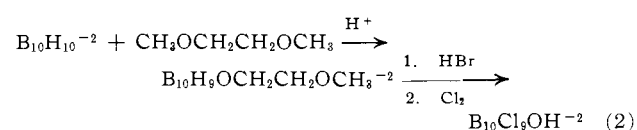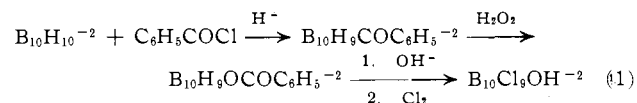
Sulfur dioxide reacts with $(H_3O)_2B_{12}H_{12}$ to give B_{12}-$H_{11}OH^{-2}$.

$B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ with Olefins.—$(H_3O)_2B_{10}H_{10}$ and$(H_3O)_2B_{12}H_{12}$ react readily with olefins to give alkyl and polyalkyl derivatives. The extent of reaction is difficult to control, and mixtures of anions of different degrees of substitution which are difficult·to separate are frequently obtained. Nonetheless reactions with styrene and propylene have led, though not readily reproducibly, to products which analyze for integral adducts. Styrene and propylene with $(H_3O)_2B_{12}H_{12}$ have given $B_{12}H_{10}(C_8H_9)_2^{-2}$ and $B_{12}H_{11}C_3H_7^{-2}$, respectively. Proton magnetic resonance spectra suggest that
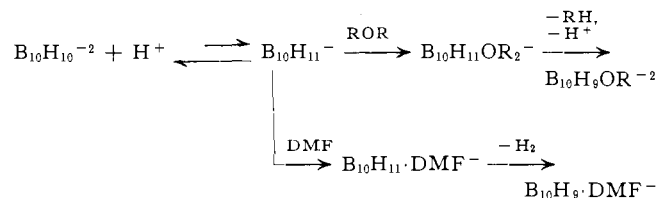
both of the possible modes of addition of B–H to these nonsymmetrical olefins occurred so that the products are mixtures of position isomers. Chlorination of these anions has given $B_{12}Cl_{10}(C_8H_9)_2^{-2}$ and $B_{12}Cl_7$-$H_4C_3H_7^{-2}$, respectively. Refluxing a $B_{12}H_{12}^{-2}$-styrene adduct with hydrobromic acid·resulted in slow cleavage of the boron–carbon bond and concurrent formation of ethylbenzene. $(H_3O)_2B_{10}H_{10}$ and styrene reacted similarly to give $B_{10}H_8(C_8H_9)_2^{-2}$.

Stereochemistry.—Early work on the stereochemistry of substitution in $B_{10}H_{10}^{-2}$ suggested that electrophilic sustitution occurs preferentially at the 1,10 (apical) boron atoms. Thus, preferential apical substitution occurs in the acid-catalyzed hydrogen–deuterium exchange reactions of $B_{10}H_{10}^{-2}$,[2,7] in the reaction of $B_{10}H_{10}^{-2}$ with dimethyl sulfoxide under acid conditions to give $B_{10}H_8[S(CH_3)_2]_2$,[7] and in the formation of $B_{10}H_8$-$(N_2)_2$ which involves as a first step the reaction of $B_{10}H_{10}^{-2}$ with nitrous acid.[9] Preferential electrophilic substitution at the $B_{10}H_{10}^{-2}$ apices was also predicted by Hoffmann and Lipscomb on the basis of LCAO–MO calculations.[14] More recently, however, studies in these laboratories have demonstrated predominant equatorial substitution for a number of other electrophilic substitutions of $B_{10}H_{10}^{-2}$.[15-17]

In addition, preliminary results of structure determinations on a number of the $B_{10}H_{10}^{-2}$ derivatives discussed in this paper suggest that they are also predominantly equatorially substituted. Thus, B_{10}-Cl_9OH^{-2} has been prepared in four ways.

$$B_{10}H_{10}^{-2} + C_6H_5COCl \xrightarrow{H^-} B_{10}H_9COC_6H_5^{-2} \xrightarrow{H_2O_2}$$
$$B_{10}H_9OCOC_6H_5^{-2} \xrightarrow[2.\ Cl_2]{1.\ OH^-} B_{10}Cl_9OH^{-2} \quad (1)$$

$$B_{10}H_{10}^{-2} + CH_3OCH_2CH_2OCH_3 \xrightarrow{H^+}$$
$$B_{10}H_9OCH_2CH_2OCH_3^{-2} \xrightarrow[2.\ Cl_2]{1.\ HBr} B_{10}Cl_9OH^{-2} \quad (2)$$

$$B_{10}H_{10}^{-2} + DMF \xrightarrow{H^+} B_{10}H_9 \cdot DMF^- \xrightarrow[2.\ Cl_2]{1.\ OH^-} B_{10}Cl_9OH^{-2} \quad (3)$$

$$B_{10}H_{10}^{-2} + DMF \xrightarrow{H^+,\ H_2O} B_{10}H_9OCHO^{-2} \xrightarrow[2.\ Cl_2]{1.\ OH^-} B_{10}Cl_9OH^{-2} \quad (4)$$

In each case, the $B_{10}Cl_9OH^{-2}$ was isolated as a tetramethylammonium salt, and the four samples obtained have been shown to be identical by powder X-ray comparison. Furthermore, the hydroxyl group has been demonstrated to be in an equatorial position indicating equatorial substitution for a significant portion of the product in the first step of each of the above four reaction sequences.[18] The reaction of benzoyl chloride with $B_{10}H_{10}^{-2}$ in reaction sequence 1, above, must be electrophilic, but the substitution reactions in sequences 2, 3, and 4 are probably best classified as acid-catalyzed nucleophilic substitutions.[3] A possible reaction path would be

(14) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 520 (1962).
(15) W. R. Hertler and M. S. Raasch, *J. Am. Chem. Soc.*, **86**, 3661 (1964).
(16) W. R. Hertler, *Inorg. Chem.*, **3**, 1195 (1964).
(17) W. R. Hertler, *J. Am. Chem. Soc.*, **86**, 2949 (1964).
(18) A reported facile rearrangement of apically substituted $B_{10}H_9OH^{-2}$ [A. Kaczmarczyk, R. Dobrott, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **48**, 729 (1962)] has been since shown to be erroneous [M. F. Hawthorne, R. L. Pilling, P. F. Stokely, and P. M. Garrett, *J. Am. Chem. Soc.*, **85**, 3704 (1963)].

$$B_{10}H_{10}^{-2} + H^+ \underset{\longleftarrow}{\overset{\longrightarrow}{}} B_{10}H_{11}^- \xrightarrow{ROR} B_{10}H_{11}OR_2^- \xrightarrow[-H^+]{-RH,} B_{10}H_9OR^{-2}$$
$$\downarrow DMF$$
$$\longrightarrow B_{10}H_{11}\cdot DMF^- \xrightarrow{-H_2} B_{10}H_9\cdot DMF^-$$

The fact that the same stereochemistry is observed in all four preparations further demonstrates that the mechanism of substitution in $B_{10}H_{10}^{-2}$ is more complex than cursory inspection would suggest.

Proof of the equatorial position of the hydroxyl group in the products isolated from the above reactions rests on chemical studies which will be described in a later paper and on B^{11} n.m.r. spectroscopy. The B^{11} n.m.r. spectra of $B_{12}H_{11}OH^{-2}$ and $B_{12}H_{10}(OH)_2^{-2}$ (*vide infra*) show that hydroxyl substitution in these cage anions results in a low-field shift of the resonance due to the substituted boron atom. The B^{11} n.m.r. spectrum of $B_{10}H_9OH^{-2}$ has no resonance at lower field than that due to the unsubstituted apical boron atoms and has a low-field doublet (relative intensity 3.1) and a high-field triplet (relative intensity 6.9). Clearly, the low-field doublet includes both unsubstituted apical boron atoms and an equatorial boron atom shifted to low field by attachment to hydroxyl. In addition, predominant equatorial substitution is indicated by the B^{11} n.m.r. spectrum of $B_{10}H_9COC_6H_5^{-2}$. This spectrum has a low-field doublet and a very broad high-field peak. The relative intensities are 2.8 to 7.2, consistent with predominant equatorial substitution causing a low-field shift of one equatorial boron atom into the doublet of the two unsubstituted boron atoms.

Predominant equatorial substitution also occurs in the formation of $B_{10}H_9NH(CH_3)_2^-$ from dimethylformamide, $B_{10}H_{10}^{-2}$, and aqueous acid. The stereochemistry of this and related B_{10} amine derivatives has been discussed elsewhere.[15]

Polarographic Studies.—Polarographic oxidation studies were conducted on $B_{10}H_9OH^{-2}$, $B_{10}H_8(OH)_2^{-2}$, $B_{10}Cl_9OH^{-2}$, $B_{10}Cl_8(OH)_2^{-2}$, $B_{12}H_{11}OH^{-2}$, $B_{12}H_{10}$-$(OH)_2^{-2}$, and $B_{12}Br_{10}(OH)_2^{-2}$. A comparison of these values with those previously reported for $B_{10}H_{10}^{-2}$,[2] $B_{12}H_{12}^{-2}$,[2] and $B_{10}Cl_{10}^{-2}$ [3] gives the following relationships in order of decreasing oxidative stability: (1) $B_{12}H_{12}^{-2} > B_{12}H_{11}OH^{-2} > B_{12}H_{10}(OH)_2^{-2}$; (2) B_{12}-$Br_{10}(OH)_2^{-2} > B_{12}H_{10}(OH)_2^{-2}$; (3) $B_{10}Cl_{10}^{-2} > B_{10}$-$Cl_9OH^{-2} > B_{10}H_{10}^{-2} > B_{10}Cl_8(OH)_2^{-2} > B_{10}H_9OH^{-2} > B_{10}H_8(OH)_2^{-2}$. Thus, introduction of hydroxyl tends to decrease oxidative stability while introduction of halogen tends to increase it.

Experimental

Preparations of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ have been described previously.[2,4-6] Except where indicated, the other reagents used are commercially available and were used without purification. Infrared spectra were obtained on a Model 21 Perkin-Elmer spectrophotometer. In most of the spectra reported below, only relatively major absorptions are listed, omitting carbon–hydrogen stretching and deformation frequencies. Ultraviolet and visible spectra were examined on a Cary Model 14 spectrometer. Nuclear magnetic resonance spectra were obtained on a Varian spectrometer, Model V4300. Double irradiation was effected with an NMR Specialties Model SD60 spin decoupler (H¹ saturation by 60-Mc. irradiation while examining B^{11} at 19 Mc.). All B^{11} spectra are referred to methyl borate.

$B_{10}H_9COC_6H_5^{-2}$.—A solution of $(H_3O)_2B_{10}H_{10}$ (22.5 g., 145 mmoles) in 40 ml. of water was chilled in an ice bath. 1,2-Di-

methoxyethane (100 ml.) was added with stirring followed by benzoyl chloride (19 ml., 165 mmoles). Stirring was continued overnight at room temperature, and the resulting blood-red solution was poured into 200 ml. of methanol containing 45 g. of tetramethylammonium chloride to precipitate 16.5 g. (43%) of [(CH$_3$)$_4$N]$_2$B$_{10}$H$_{10}$. This was filtered and tetramethylammonium hydroxide was added to the still blood-red filtrate until the color suddenly lightened considerably; a 10-g. excess of the hydroxide was then added and the solution was stirred into 700 ml. of ethanol whereupon [(CH$_3$)$_4$N]$_2$B$_{10}$H$_9$COC$_6$H$_5$ (19 g., 35%) precipitated as a cream-colored solid, dec. pt. 285–290°.

Anal. Calcd. for [(CH$_3$)$_4$N]$_2$B$_{10}$H$_9$COC$_6$H$_5$: B, 29.2; C, 48.6; H, 10.3; N, 7.6. Found: B, 29.8; C, 46.3; H, 10.6; N, 7.4. Ultraviolet: $\lambda_{max}^{CH_3CN}$ 319 mμ (ϵ 3550) and 232 (11,000). The infrared spectrum in KBr includes absorptions at 2470, 1610, 1590, 1570, 1220, 1070, 1000, 950, 826, 785, and 700 cm.$^{-1}$.

A solution of [(CH$_3$)$_4$N]$_2$B$_{10}$H$_9$COC$_6$H$_5$ (0.2566 g.) that had been recrystallized from dilute aqueous tetramethylammonium hydroxide was passed through Amberlite IR 120(H) resin. The effluent was titrated with 0.1 N sodium hydroxide. A typical smooth strong-acid titration curve with one inflection point was obtained. The neutral equivalent found was 185 (calcd. 185).

An aqueous solution of [(CH$_3$)$_4$N]$_2$B$_{10}$H$_9$COC$_6$H$_5$ was mixed with aqueous tetrapropylammonium hydroxide to precipitate [(CH$_3$CH$_2$CH$_2$)$_4$N]$_2$B$_{10}$H$_9$COC$_6$H$_5$. This was recrystallized from 10% aqueous tetrapropylammonium hydroxide and obtained as glistening yellow crystals which did not melt to 400°.

Anal. Calcd. for [(CH$_3$CH$_2$CH$_2$)$_4$N]$_2$B$_{10}$H$_9$COC$_6$H$_5$: B, 18.2; C, 62.6; H, 11.9; N, 4.7. Found: B, 18.6; C, 62.7; H, 12.0; N, 4.7.

Concentrated hydrochloric acid (10 ml.) was added to a solution of [(CH$_3$)$_4$N]$_2$B$_{10}$H$_9$COC$_6$H$_5$ in 150 ml. of water. A small amount of red solid precipitated and was removed. The solution was passed through an ion-exchange column filled with Amberlite IR 120(H) resin. The addition of tetrapropylammonium bromide to the effluent precipitated 1.2 g. (28 mmoles) of [CH$_3$(CH$_2$)$_2$]$_4$N$^+$, H$_3$O$^+$, B$_{10}$H$_9$COC$_6$H$_5$$^{-2}$ as a brick-red solid.

Anal. Calcd. for [CH$_3$(CH$_2$)$_2$]$_4$N$^-$, H$_3$O$^+$, B$_{10}$H$_9$COC$_6$H$_5$$^{-2}$: B, 25.3; C, 53.4; H, 10.5; N, 3.3. Found: B, 24.4; C, 54.3; H, 10.8; N, 3.5. Ultraviolet: $\lambda_{max}^{CH_3CN}$ 435 mμ (ϵ 7700), 306 (5300), and 264 (9300). The infrared spectrum in KBr includes absorptions at 2470, 1600, 1580, 1280, 1220, 1180, 1100, 1040, 980, 970, 820, 785, 740, and 690 cm.$^{-1}$. There is also broad absorption in the 1330–1430-cm.$^{-1}$ region, more than can be due to C–H deformation alone.

[(CH$_3$)$_4$N]$_2$B$_{10}$H$_9$COC$_6$H$_5$ was stirred in methanol, and water was added until it dissolved. After filtration, aqueous cesium hydroxide was added to precipitate Cs(CH$_3$)$_4$NB$_{10}$H$_9$COC$_6$H$_5$. This was recrystallized from water and washed with ice water.

Anal. Calcd. for Cs(CH$_3$)$_4$NB$_{10}$H$_9$COC$_6$H$_5$: B, 25.2; C, 30.8; H, 6.1. Found: B, 24.8; C, 30.4; H, 6.4.

The tetramethylammonium salt was converted to Na$_2$B$_{10}$H$_9$COC$_6$H$_5$ by passage of an aqueous solution of the former through Amberlite IR 120(Na) resin and evaporation of the effluent. The B^{11} spectrum of Na$_2$B$_{10}$H$_9$COC$_6$H$_5$ in water consists of a doublet, which can be decoupled, at 17.8 p.p.m. (*J* = 144 c.p.s.) with a high-field shoulder plus a stronger broad, unsymmetrical peak at about 46 p.p.m. The area ratio of the doublet and its shoulder to the 44.5 p.p.m. peak is 2.8:7.2.

Reaction of Na$_2$B$_{10}$H$_9$COC$_6$H$_5$ with semicarbazide hydrochloride gave a semicarbazone which was precipitated from aqueous solution with tetramethylammonium hydroxide and recrystallized from water.

Anal. Calcd. for [(CH$_3$)$_4$N]$_2$B$_{10}$H$_9$C(C$_6$H$_5$)=NNHCONH$_2$·H$_2$O: B, 24.2; C, 43.0; H, 9.7; N, 15.7. Found: B, 23.5; C, 43.6; H, 9.7; N, 15.3. The infrared spectrum in KBr includes absorptions at 3450, 3330, 2470, 1670, 1580, 1080, 1000, 985, 780, 765, and 705 cm.$^{-1}$. The semicarbazone absorptions in this spectrum are similar to those in the spectrum of cyclohexanone semicarbazone.

B$_{10}$Br$_9$COC$_6$H$_5$$^{-2}$.—Bromine (2.5 ml., 46 mmoles) in 10 ml. of methanol was added with stirring to a solution of [(CH$_3$)$_4$N]$_2$-B$_{10}$H$_9$COC$_6$H$_5$ (0.5 g., 1.4 mmoles) in 20 ml. of 50% aqueous methanol with cooling to keep the temperature below 40°. The solution was filtered and the filtrate was chilled briefly in liquid nitrogen to precipitate [(CH$_3$)$_4$N]$_2$B$_{10}$Br$_9$COC$_6$H$_5$. This was filtered cold and then recrystallized from water.

Anal. Calcd. for [(CH$_3$)$_4$N]$_2$B$_{10}$Br$_9$COC$_6$H$_5$: B, 10.0; C, 16.6; H, 2.7; Br, 66.6. Found: B, 10.1; C, 16.6; H, 3.0; Br, 68.3.

B$_{10}$Cl$_9$COC$_6$H$_5$$^{-2}$.—Chlorine was passed into a solution of [(CH$_3$)$_4$N]$_2$B$_{10}$H$_9$COC$_6$H$_5$ (7.5 g., 20.2 mmoles) in 170 ml. of acetonitrile at a moderate rate, and the temperature was maintained below 35° by use of an ice bath. As the reaction progressed, a clear, dark red solution formed. After the exothermic phase was over, the ice bath was removed and chlorination was continued briefly at ambient temperature. The solution was concentrated to one-third of its original volume and stirred into excess alcoholic tetramethylammonium hydroxide. [(CH$_3$)$_4$N]$_2$-B$_{10}$Cl$_9$COC$_6$H$_5$ separated as a light tan solid (12.0 g., 87%) which was recrystallized from aqueous alcohol.

Anal. Calcd. for [(CH$_3$)$_4$N]$_2$B$_{10}$Cl$_9$COC$_6$H$_5$: B, 15.8; C, 26.4; H, 4.3; Cl, 46.9; N, 4.1. Found: B, 16.1; C, 25.9; H, 4.6; Cl, 45.8; N, 4.3. Ultraviolet: $\lambda_{max}^{CH_3CN}$ 278 mμ (ϵ 3160) and 244 (9400). The infrared spectrum in KBr includes absorptions at 1615, 1600, 1575, 1235, 1150, 995, 845, and 790 cm.$^{-1}$.

A similar chlorination of Na$_2$B$_{10}$H$_9$COC$_6$H$_5$ *in water* followed by precipitation of a cesium salt resulted in partial chlorination of the phenyl ring.

Anal. Calcd. for Cs$_2$B$_{10}$Cl$_9$COC$_6$H$_3$Cl$_2$·H$_2$O: Cs, 30.0; B, 12.2; C, 9.5; H, 0.6; Cl, 44.0. Found: Cs, 29.2; B, 12.2; C, 10.6; H, 0.9; Cl, 44.1.

[(CH$_3$)$_4$N]$_2$B$_{10}$Cl$_9$COC$_6$H$_5$ (2.5 g., 3.7 mmoles) was converted to the corresponding sodium salt by passage in hot aqueous solution through Amberlite IR 120(H) resin and neutralization of the effluent with sodium hydroxide. The volume of the solution was adjusted to 10 ml., and this was mixed with a solution of sodium acetate (3 g., 37 mmoles) and semicarbazide hydrochloride (2 g., 118 mmoles) in 20 ml. of water and heated on a steam bath for 2 hr. The addition of aqueous trimethylsulfonium iodide precipitated [(CH$_3$)$_3$S]$_2$B$_{10}$Cl$_9$C(C$_6$H$_5$)=NNHCONH$_2$ which was recrystallized from water (1.2 g., 44%), dec. pt. 197–198°.

Anal. Calcd. for [(CH$_3$)$_3$S]$_2$B$_{10}$Cl$_9$C(C$_6$H$_5$)=NNHCONH$_2$: B, 14.5; C, 22.5; H, 3.5; N, 5.6; Cl, 43.0. Found: B, 15.0; C, 21.7; H, 3.4; N, 4.9; Cl, 44.2. The infrared spectrum was in agreement with the semicarbazone formulation.

B$_{10}$H$_9$OCOC$_6$H$_5$$^{-2}$.—A solution of [(CH$_3$)$_4$N]$_2B_{10}H_9COC_6H_5$ (5.0 g., 13.5 mmoles) in 65 ml. of water was mixed with 25 ml. of 30% hydrogen peroxide. The solution was allowed to stand for 3 days during which time 2.1 g. (40%) of [(CH$_3$)$_4$N]$_2$B$_{10}$H$_9$OCO-C$_6$H$_5$ separated as a light tan crystalline solid, which was recrystallized from water. The product decomposed at 360–365°.

Anal. Calcd. for [(CH$_3$)$_4$N]$_2$B$_{10}$H$_9$OCOC$_6$H$_5$: B, 28.0; C, 46.6; H, 9.8; N, 7.2. Found: B, 27.8; C, 47.0; H, 10.0; N, 7.2. Ultraviolet: $\lambda_{max}^{CH_3CN}$ 270 mμ (ϵ 3600) and 288 (12,000). The infrared spectrum in KBr includes absorptions at 2470, 1680, 1605, 1590, 1325, 1310, 1170, 1145, 1075, 980, 950, and 745 cm.$^{-1}$.

B$_{10}$Cl$_9$OCOC$_6$H$_5$$^{-2}$.—Hydrogen peroxide (30%, 40 ml.) was added to a solution of 23 mmoles of (H$_3$O)$_2$B$_{10}$Cl$_9$COC$_6$H$_5$ in 95 ml. of water (prepared by passage of [(CH$_3$)$_4$N]$_2$B$_{10}$Cl$_9$COC$_6$H$_5$ through Amberlite IR 120(H) resin) and allowed to stand for 3 days. The solution was made alkaline with sodium hydroxide, and tetramethylammonium chloride was added to precipitate [(CH$_3$)$_4$N]$_2$B$_{10}$Cl$_9$OCOC$_6$H$_5$ which was recrystallized from water (0.8 g., 58%).

Anal. Calcd. for [(CH$_3$)$_4$N]$_2$B$_{10}$Cl$_9$OCOC$_6$H$_5$: B, 15.5; C, 25.8; H, 4.2; Cl, 45.8. Found: B, 15.9; C, 25.8; H, 4.4; Cl, 46.0. Ultraviolet: $\lambda_{max}^{CH_3CN}$ 225 mμ (ϵ 19,000), 270 (3000), and 279 (2500). The infrared spectrum in KBr includes absorptions at 1700, 1600, 1580, 1310, 1290, 1190, 1150, 1125, 1100, 950, 835, and 715 cm.$^{-1}$.

B$_{10}$H$_9$OCHO^{-2} and B$_{10}$H$_9$N(CH$_3$)$_2$H$^-$.—A solution of dimethylformamide (500 ml.) and aqueous (H$_3$O)$_2$B$_{10}$H$_{10}$ (150 ml. containing 0.47 mole) was distilled through a short Vigreux column at atmospheric pressure until the head temperature reached 145°. At this point 215 ml. of distillate had been collected. The residue was refluxed for 5 hr., and then 240 ml. of liquid was removed by distillation at 16 mm. and a temperature of about 60°. The residue, a clear, colorless, viscous liquid, was added to a solution of cesium hydroxide (150 g., 1 mole) in 30 ml. of water and 500 ml. of ethanol. A white solid precipitated. This was filtered and recrystallized from water to obtain 108 g. (54%) of Cs$_2$B$_{10}$H$_9$-OCHO, dec. pt. 330–332°.

Anal. Calcd. for Cs$_2$B$_{10}$H$_9$OCHO: Cs, 62.1; B, 25.0; C, 2.8; H, 2.3. Found: Cs, 62.0; B, 25.4; C, 2.7; H, 2.6. Ultraviolet: no maximum. The infrared spectrum in KBr includes absorptions at 2470, 1690, 1240, 1035, 1110, 1060, 995, 750, and 720 cm.$^{-1}$.

The filtrate from the crude $Cs_2B_{10}H_9OCHO$ was concentrated on a steam bath to leave a viscous oil which crystallized after several days. This solid, which was crude $CsB_{10}H_9NH(CH_3)_2$, was stirred for 20 min. with 150 ml. of water and filtered. The soluble portion was recrystallized from 55 ml. of water to obtain 11.4 g. (8.2%) of $CsB_{10}H_9NH(CH_3)_2$. The analytical sample was recrystallized a second time and dried at 100° under vacuum.

Anal. Calcd. for $CsB_{10}H_9NH(CH_3)_2$: Cs, 45.1; B, 36.6; C, 8.1; H, 5.4; N, 4.8. Found: Cs, 44.5; B, 36.0; C, 8.0; H, 5.5; N, 4.8.

The aqueous extract of the crude $CsB_{10}H_9NH(CH_3)_2$ was split into two equal portions. To one was added 15 g. of tetramethylammonium chloride and to the other was added 10 g. of trimethylsulfonium iodide. In this fashion, 1.4 g. (1.3%) of $(CH_3)_4NB_{10}H_9NH(CH_3)_2$ and 1.5 g. (1.3%) of $(CH_3)_3SB_{10}H_9NH(CH_3)_2$ were obtained. Infrared analysis suggested slight contamination with the corresponding $B_{10}H_9OCHO^{-2}$ salts, but this was removed by recrystallization from water.

Anal. Calcd. for $(CH_3)_4NB_{10}H_9NH(CH_3)_2$: B, 45.7; C, 30.5; H, 11.9; N, 11.9. Found: B, 45.1; C, 30.8; H, 12.1; N, 11.9.

The B^{11} spectrum of $(CH_3)_4NB_{10}H_9NH(CH_3)_2$ in aqueous acetonitrile consists of three peaks appearing as an indistinct triplet at 15.6, 21.3, and 26.8 p.p.m. and of a triplet at 40.8, 46.7, and 51.9 p.p.m. The three low-field peaks decouple to one fairly sharp peak; the 40.8, 46.7, and 51.9 peaks decouple at different irradiating frequencies. The intensity ratio of the three low-field peaks to the high-field triplet is 2.9:7.1.

Anal. Calcd. for $(CH_3)_3SB_{10}H_9NH(CH_3)_2$: B, 45.2; C, 25.1; H, 10.5; N, 5.8; S, 13.4. Found: B, 45.1; C, 25.3; H, 10.3; N, 5.6; S, 13.3. The infrared spectrum of $(CH_3)_3SB_{10}H_9$-$NH(CH_3)_2$ includes absorptions at 3210, 2470, 1135, 1075, 1055, 1020, 970, and 910 cm.$^{-1}$.

Recrystallization of $(CH_3)_3SB_{10}H_9NH(CH_3)_2$ from D_2O gave a salt whose infrared spectrum had no N–H absorption but did have N–D absorption at 2400 cm.$^{-1}$. Recrystallization of $(CH_3)_4NB_{10}H_9NH(CH_3)_2$ from aqueous potassium hydroxide containing excess tetramethylammonium hydroxide gave unchanged $(CH_3)_4NB_{10}H_9NH(CH_3)_2$. The addition of aqueous thallium nitrate to a solution of $(CH_3)_4NB_{10}H_9NH(CH_3)_2$ in hot 10% aqueous sodium hydroxide precipitated $TlB_{10}H_9NH(CH_3)_2$ as shown by infrared and thallium analysis.

Anal. Calcd. for $TlB_{10}H_9NH(CH_3)_2$: Tl, 55.7. Found: Tl, 54.5.

$B_{10}H_9OCH=N(CH_3)_2^-$.—Hydrogen chloride was bubbled rapidly through a solution of $(NH_4)_2B_{10}H_{10}$ (30 g., 195 mmoles) in dimethylformamide (100 ml.). The temperature rose quickly to 155° with much fuming. After 2.5 hr. the temperature had fallen to 90° and the reaction was discontinued and filtered. The filtrate was concentrated under vacuum until it was a thick sirup. This was stirred into a solution of 100 g. of cesium fluoride in 500 ml. of water; 42 g. (63%) of $CsB_{10}H_9OCH=N(CH_3)_2$ (no m.p. to 400°) separated slowly. This was recrystallized rapidly from water; prolonged boiling caused hydrolysis to $B_{10}H_9OH^{-2}$.

Anal. Calcd. for $CsB_{10}H_9OCH=N(CH_3)_2$: Cs, 41.0; B, 33.4; C, 11.1; H, 5.0; N, 4.3. Found: Cs, 39.4; B, 32.7; C, 11.3; H, 5.1; N, 4.4. Ultraviolet: no maximum; shoulder on end absorption at 216 mμ (ε 8400). The infrared spectrum in KBr includes absorptions at 2470, 1680, 1335, 1240, 1090, 1045, 990, and 860 cm.$^{-1}$.

The B^{11} spectrum of $CsB_{10}H_9OCH=N(CH_3)_2$ in aqueous dimethylformamide has four peaks appearing as an indistinct quadruplet at 18.2, 21.6, 25.8, and 29.7 p.p.m. plus a strong broad unsymmetrical peak at 49.9 p.p.m. with a low-field shoulder. The quadruplet can be decoupled to a somewhat broad peak. The low-field shoulder on the 49.9 p.p.m. peak also decouples.

In a similar experiment, the anion was precipitated as a tetramethylammonium salt and recrystallized twice from water to obtain $(CH_3)_4NB_{10}H_9OCH=N(CH_3)_2$, dec. pt. 301–302°.

Anal. Calcd. for $(CH_3)_4NB_{10}H_9OCH=N(CH_3)_2$: B, 41.0; C, 31.8; H, 10.6; N, 10.6. Found: B, 40.5; C, 32.7; H, 10.4; N, 10.5.

$B_{10}H_9 \cdot NMP^-$ and $B_{10}H_8(NMP)_2$.—N-Methylpyrrolidone (150 ml.), $(NH_4)_2B_{10}H_{10}$ (20 g., 130 mmoles), and hydrochloric acid (22 ml.) were mixed. The mixture was distilled until the flask temperature reached 180° (20 ml. of distillate) when heating was discontinued. The mixture was filtered and the filtrate was stirred into 800 ml. of water to precipitate $B_{10}H_8(NMP)_2$ (3 g., 7.3%) which was filtered, washed with water, and dried. A higher yield of $B_{10}H_8(NMP)_2$ was obtained, with corresponding

decrease in the yield of $B_{10}H_9NMP^-$, by holding the reaction temperature at 180° for several hours (25 g., 61%, after 2 hr.).

Anal. Calcd. for $B_{10}H_8(NMP)_2$: B, 34.4; C, 38.2; H, 8.3; N, 8.9. Found: B, 33.0; C, 38.8; H, 8.6; N, 8.8.

The filtrate from the isolation of the $B_{10}H_8(NMP)_2$ was mixed with excess tetrapropylammonium hydroxide to precipitate $(C_3H_7)_4NB_{10}H_9NMP$ which was recrystallized from aqueous alcohol (21 g., 40%).

Anal. Calcd. for $(C_3H_7)_4NB_{10}H_9NMP$: B, 27.0; C, 49.6; H, 11.1. Found: B, 26.7; C, 49.8; H, 11.7.

$B_{10}H_9OCH_2CH_2OCH_3^{-2}$.—A solution of $(H_3O)_2B_{10}H_{10}$ (18.0 g., 117 mmoles) in 40 ml. of water was added to 100 ml. of 1,2-dimethoxyethane and heated on a steam bath for 40 min. The reaction solution was then added to a solution of 40 g. of tetramethylammonium hydroxide in 100 ml. of ethanol and 200 ml. of 2-propanol, and the resulting precipitate was isolated. Fractional recrystallization from aqueous methanol and ethanol separated this crude product into $[(CH_3)_4N]_2B_{10}H_{10}$ and 8.9 g. (22%) of the more soluble $[(CH_3)_4N]_2B_{10}H_9OCH_2CH_2OCH_3$.

Anal. Calcd. for $[(CH_3)_4N]_2B_{10}H_9OCH_2CH_2OCH_3$: B, 31.9; C, 38.6; H, 11.9; N, 8.3. Found: B, 31.4; C, 38.6; H, 11.8; N, 8.3. The infrared spectrum of $[(CH_3)_4N]_2B_{10}H_9OCH_2CH_2$-$OCH_3$ in a Nujol mull includes absorptions at 2470, 1190, 1180, 1160, 1110, 1090, 1075, 1065, 1050, 1030, 985, 945, 855, and 845 cm.$^{-1}$.

$B_{10}Br_9OCH_2CH_2OCH_3^{-2}$.—Bromine (6 g., 37.5 mmoles) in 20 ml. of methanol was added to a solution of $[(CH_3)_4N]_2B_{10}H_9$-$OCH_2CH_2OCH_3$ (1 g., 2.9 mmoles) in 30 ml. of methanol and 10 ml. of water. The solution was stirred until reaction ceased. The addition of tetramethylammonium hydroxide and recrystallization of the resulting white solid from water gave 1.3 g. (41%) of $[(CH_3)_4N]_2B_{10}Br_9OCH_2CH_2OCH_3$.

Anal. Calcd. for $[(CH_3)_4N]_2B_{10}Br_9OCH_2CH_2OCH_3$: B, 10.3; C, 12.4; H, 2.9; Br, 68.4. Found: B, 10.0; C, 12.4; H, 3.2; Br, 68.0.

$B_{10}H_9OH^{-2}$.—Sodium hydroxide (2.3 g., 56 mmoles), CsB_{10}-$H_9 \cdot HCON(CH_3)_2$ (17 g., 53 mmoles) and 50 ml. of water were mixed and refluxed for 6 hr. The solution was passed through excess Amberlite IR 120(H), and the effluent was neutralized with tetramethylammonium hydroxide and evaporated. The residue was recrystallized from aqueous alcohol to obtain 4 g. (25%) of $[(CH_3)_4N]_2B_{10}H_9OH$. This darkened at 280° but did not melt to 400°.

Anal. Calcd. for $[(CH_3)_4N]_2B_{10}H_9OH$: B, 38.2; C, 34.0; H, 12.0; N, 9.9. Found: B, 38.0; C, 34.0; H, 12.3; N, 9.4. Ultraviolet: no maximum. The infrared spectrum of $[(CH_3)_4$-$N]_2B_{10}H_9OH$ in KBr include absorptions at 3570, 2470, 1290, 1155, 1080, 1050, 985, and 945 cm.$^{-1}$.

Sodium borohydride (1 g., 26 mmoles) and $Cs_2B_{10}H_9OCHO$ (4 g., 9.3 mmoles) were mixed in 6 ml. of of water and allowed to stand overnight. The solution was heated on a steam bath to decompose the remaining borohydride and then poured into 200 ml. of ethanol containing 3 g. of cesium hydroxide. The precipitated solid was recrystallized from water to obtain $Cs_2B_{10}H_9OH$ (1.8 g., 48%) as long rod-shaped crystals. Sodium hydroxide can be used in place of sodium borohydride in this reaction.

Anal. Calcd. for $Cs_2B_{10}H_9OH$: Cs, 66.5; B, 27.0; H, 2.5. Found: Cs, 63.9; B, 26.4; H, 2.7. Ultraviolet: no maximum. The infrared spectrum of $Cs_2B_{10}H_9OH$ in KBr includes absorptions at 3570, 2460, 1140, 1110 (broad), 1050, 995, and 835 cm.$^{-1}$.

The B^{11} spectrum of $Cs_2B_{10}H_9OH$ in water consists of a doublet at 21.5 p.p.m. ($J = 109$ c.p.s.) and of an apparent weak-strong-weak triplet at 38.6, 44.6, and 50.6 p.p.m. with a shoulder at 57.0 p.p.m. The intensity ratio of the doublet to the triplet and its shoulder is 3.1:6.9.

A small amount of $Cs_2B_{10}H_9OH$ was dissolved in glacial formic acid and heated on a steam bath for 2 min. The solution was diluted with water; the addition of thallium nitrate solution precipitated $Tl_2B_{10}H_9OCHO$, identical by infrared analysis with the $Cs_2B_{10}H_9OCHO$ prepared above.

$B_{10}Cl_9OH^{-2}$. **A. From $B_{10}H_9 \cdot DMF^-$.—**An aqueous solution of $Cs_2B_{10}H_9OH$, prepared by hydrolysis of $CsB_{10}H_9 \cdot DMF$ (17 g., 52.3 mmoles) as described above, was converted to an aqueous solution of the corresponding acid by passage through an acidic ion-exchange column. Chlorine was passed through the solution for 3 hr. at 50–52° and then discontinued because of the formation of a small amount (2.0 g.) of boric acid. The addition of tetramethylammonium chloride precipitated 6.4 g. (20%) of $[(CH_3)_4$-$N]_2B_{10}Cl_9OH$ which was recrystallized from 50% aqueous ethanol. It did not melt to 400°.

B. From $B_{10}H_9OCH_2CH_2OCH_3^{-2}$.—Chlorine was passed through a slurry of $[(CH_3)_4N]_2B_{10}H_9OCH_2CH_2OCH_3$ (14.4 g.) in 150 ml. of anhydrous acetonitrile for 1 hr. using ice-bath cooling to maintain the temperature at 20–25°. The resulting clear dark-colored solution was evaporated to leave a thick sirup which gave a white solid on stirring with aqueous tetramethylammonium chloride. Five grams of this product was refluxed for 1.5 hr. in 30 ml. of 48% hydrobromic acid. Fifteen milliliters of liquid was removed by distillation; the residue was cooled, filtered, and recrystallized from 50% aqueous alcohol to obtain 1.1 g. of $[(CH_3)_4N]_2B_{10}Cl_9OH$.

C. From $B_{10}H_9OCHO^{-2}$.—$B_{10}H_9OH^{-2}$, prepared from $B_{10}H_9OCHO^{-2}$ prepared in turn from $B_{10}H_{10}^{-2}$, aqueous hydrochloric acid, and dimethylformamide, as described above, was perchlorinated in aqueous solution as described in A above. The $B_{10}Cl_9OH^{-2}$ was precipitated as a tetramethylammonium salt which was recrystallized from 50% aqueous ethanol.

D. From $B_{10}H_9COC_6H_5^{-2}$.—$[(CH_3)_4N]_2B_{10}H_9OCOC_6H_5$ (7.0 g., 20 mmoles), prepared by oxidation of $B_{10}H_9COC_6H_5^{-2}$ as above, was refluxed for 6 hr. in 150 ml. of 50% aqueous alcohol containing 5 g. of sodium hydroxide. Filtration gave 3.7 g. of unsaponified ester. The filtrate was concentrated to a sirup under vacuum and stirred into a solution of tetramethylammonium hydroxide in propanol. The resulting precipitate of $[(CH_3)_4N]_2B_{10}H_9OH$ was isolated and chlorinated in acetonitrile at 20–25° and identified by infrared analysis.

Anal. Calcd. for $[(CH_3)_4N]_2B_{10}Cl_9OH$: B, 18.3; C, 16.2; H, 4.2; Cl, 53.9. Found (A): B, 18.3; C, 16.8; H, 4.7; Cl, 53.6. Found (B): B, 18.3; C, 16.8; H, 4.7; Cl, 53.4. Found (C): B, 17.4; C, 17.1; H, 4.6; Cl, 53.6.

| | Ultraviolet | |
Route	$\lambda_{max}^{CH_3CN}$ (ϵ)	$\lambda_{shoulder}^{CH_3CN}$ (ϵ)
A	221 (9180	250 (766)
B	221 (9340)	250 (770)
C	220 (10,780)	250 (835)
D	221 (9300)	250 (800)

The infrared spectrum of $[(CH_3)_4N]_2B_{10}Cl_9OH$ as a Nujol mull includes absorptions at 3570, 1155, 1080, 1005, 940, and 845 cm.$^{-1}$. The powder X-ray patterns of $[(CH_3)_4N]_2B_{10}Cl_9OH$ prepared by each of the above four routes were identical.

$B_{10}H_8(OH)_2^{-2}$.—A solution of $B_{10}H_8(NMP)_2$ (13.5 g., 43 mmoles) and sodium hydroxide (4.0 g., 100 mmoles) in 100 ml. of water was refluxed for 5 hr. and then stirred into a solution of 21 g. of tetramethylammonium hydroxide pentahydrate in 400 ml. of 1-propanol. An oil separated. This was dissolved in methanol, filtered, and diluted with three times its volume of ethanol. The resulting milky solution precipitated crystalline $[(CH_3)_4N]_2B_{10}H_8(OH)_2$ (2.9 g., 23%) when warmed on a steam bath. The product darkened at 310° but did not melt to 400°.

Anal. Calcd. for $[(CH_3)_4N]_2B_{10}H_8(OH)_2$: B, 36.2; C, 32.2; H, 11.4; N, 9.4. Found: B, 36.0; C, 32.0; H, 11.6; N, 8.6. The infrared spectrum in KBr includes absorptions at 3570, 2470, 1290, 1149–1090 (broad), 955, and 950 cm.$^{-1}$.

$B_{10}Cl_8(OH)_2^{-2}$.—A solution of $B_{10}H_8(NMP)_2$ (20.5 g., 65 mmoles) and sodium hydroxide (7 g.) in 100 ml. of water was refluxed for 4 hr. The solution was acidified with hydrochloric acid and chlorine was passed into it. The temperature rose to 96° and fell to 55° in the first hour. Chlorination was continued for an additional 30 min. at 50°. Addition of 25 g. of tetramethylammonium chloride precipitated $[(CH_3)_4N]_2B_{10}Cl_8(OH)_2$ (10.5 g., 28%) which was recrystallized from water. It darkened at 355° but did not melt to 400°.

Anal. Calcd. for $[(CH_3)_4N]_2B_{10}Cl_8(OH)_2$: B, 18.8; C, 16.8; H, 4.5; Cl, 49.4; N, 4.8. Found: B, 19.1; Cl, 17.1; H, 4.9; Cl, 49.3; N, 3.7. Ultraviolet: $\lambda_{max}^{CH_3CN}$ 216 mμ (ϵ 3700) and shoulder 248 (116). The infrared spectrum in KBr includes absorptions at 3570, 3450, 1240, 1140, 1080, 1010, 970, 950, and 850 cm.$^{-1}$.

$B_{10}Cl_8(OCHO)_2^{-2}$.—A solution of $[(CH_3)_4N]_2B_{10}Cl_8(OH)_2$ (4.0 g., 7 mmoles) in 50 ml. of glacial formic acid was distilled until 15 ml. of distillate was obtained. The residue was poured into excess ethanol, precipitating $[(CH_3)_4N]_2B_{10}Cl_8(OCHO)_2$, a colorless solid which was recrystallized rapidly from water. It did not melt to 400°.

Anal. Calcd. for $[(CH_3)_4N]_2B_{10}Cl_8(OCHO)_2$: B, 17.1; C, 19.0; H, 4.1; Cl, 45.0; N, 4.4. Found: B, 17.5; Cl, 18.4; H, 4.6; Cl, 45.9; N, 4.6.

$B_{10}H_8(C_8H_9)_2^{-2}$.—A viscous aqueous solution of $(H_3O)_2B_{10}H_{10}$ (9 g.) was carefully mixed with 2-propanol (7 ml.) at 0°. Styrene (5 g.) was added with stirring at 0–10°. The mixture was stirred in an ice bath for 2 hr. and at room temperature for 2 hr. It was then neutralized with 10% aqueous sodium hydroxide, steam distilled for 20 min., and concentrated to a mush in a rotary evaporator. This residue was mixed with excess aqueous 50% cesium fluoride, giving a cesium salt which was extracted with 200 ml. of boiling water. $Cs_2B_{10}H_8(C_8H_9)_2$ separated from this extract on cooling.

Anal. Calcd. for $Cs_2B_{10}H_8(C_8H_9)_2$: B, 18.2; C, 32.4; H, 4.4. Found: B, 18.0; C, 30.5; H, 4.3.

$B_{12}H_{11}OCH_3^{-2}$.—A solution of $Na_2B_{12}H_{12}\cdot H_2O$ (12 g., 58 mmoles) in 45 ml. of 37% aqueous formaldehyde was refluxed overnight. The addition of aqueous cesium fluoride precipitated $Cs_2B_{12}H_{11}OCH_3$.

Anal. Calcd. for $Cs_2B_{12}H_{11}OCH_3$: B, 29.6; C, 2.7; H, 3.2. Found: B, 29.9; C, 3.6; H, 3.6.

$B_{12}HCl_{10}OCH_3^{-2}$.—A solution of $(H_3O)_2B_{12}H_{12}\cdot 5H_2O$ (5 g., 18.5 mmoles) in 25 ml. of glacial formic acid was heated on a steam bath for 24 hr. Excess 50% aqueous cesium fluoride was added; recrystallization of the resulting solid from water with digestion for 15 min. gave $Cs_2B_{12}H_{11}OCH_3$, identical by infrared analysis with that prepared from $B_{12}H_{12}^{-2}$ and formaldehyde, above. Aqueous chlorination at 90° gave $Cs_2B_{12}HCl_{10}OCH_3\cdot H_2O$.

Anal. Calcd. for $Cs_2B_{12}HCl_{10}OCH_3\cdot H_2O$: Cs, 33.2; B, 16.2; C, 1.5; H, 0.8; Cl, 44.4. Found: Cs, 32.9; B, 16.4; C, 1.3; H, 1.0; Cl, 44.1.

$B_{12}H_{10}(OCH_3)_2^{-2}$.—A mixture of $(H_3O)_2B_{12}H_{12}\cdot 5H_2O$ (15 g., 55 mmoles) and dimethyl ether (50 g., 1100 mmoles) was heated to 110° for 1 hr. under autogenous pressure. The volatile materials (shown by infrared analysis to contain methane) were removed and the residue neutralized with aqueous cesium hydroxide. Recrystallization of the resulting solid from water gave 9 g. (35%) of $Cs_2B_{12}H_{10}(OCH_3)_2$.

Anal. Calcd. for $Cs_2B_{12}H_{10}(OCH_3)_2$: B, 27.7; C, 5.1; H, 3.4. Found: B, 27.1; C, 4.8; H, 3.5.

$B_{12}H_{10}(OCH_2CH_2OCH_3)_2^{-2}$.—A solution of $(H_3O)_2B_{12}H_{12}\cdot 5H_2O$ (5 g., 18 mmoles) in 1,2-dimethoxyethane (100 ml.) was refluxed for 2 hr. and then allowed to stand at room temperature 15 hr. Concentration under vacuum in a rotary evaporator gave a crystalline mush which was dissolved in 10% aqueous sodium hydroxide and steam distilled for 30 min. It was then concentrated again, to about 40 ml., and excess 50% aqueous cesium fluoride was added. The precipitated salt was recrystallized from water to obtain 6 g. (60%) of $Cs_2B_{12}H_{10}(OCH_2CH_2OCH_3)_2$.

Anal. Calcd. for $Cs_2B_{12}H_{10}(OCH_2CH_2OCH_3)_2$: Cs, 47.7; B, 23.2; C, 12.9; H, 4.4. Found: Cs, 47.2; B, 23.2; C, 12.9; H, 5.0.

$B_{12}Br_{10}(OCH_2CH_2OCH_3)_2^{-2}$.—Bromine was added to a solution of $Cs_2B_{12}H_{10}(OCH_2CH_2OCH_3)_2$ in water until the color was no longer discharged. The solution was refluxed, excess bromine was added, and chlorine was passed through to complete the bromination. Recovery of the cesium salt followed by recrystallization from water gave $Cs_2B_{12}Br_{10}(OCH_2CH_2OCH_3)_2$.

Anal. Calcd. for $Cs_2B_{12}Br_{10}(OCH_2CH_2OCH_3)_2$: Cs, 19.8; B, 9.7; C, 5.4; H, 1.0; Br, 59.4. Found: Cs, 19.5; B, 9.9; C, 5.4; H, 1.5; Br, 60.6.

$B_{12}H_{11}OCH_2C_6H_5^{-2}$.—A mixture of $Na_2B_{12}H_{12}$ (1 g., 5.3 mmoles), benzoyl p-toluenesulfonate[19] (3 g., 11 mmoles), and anhydrous acetonitrile (40 ml.) was stirred for 15 min. at room temperature. Water (5 ml.) was added and the acetonitrile was removed under reduced pressure. The yellow residue was made alkaline with dilute sodium hydroxide. The addition of tetramethylammonium chloride precipitated 615 mg. (29%) of $[(CH_3)_4N]_2B_{12}H_{11}OCH_2C_6H_5$ which was recrystallized from water.

Anal. Calcd. for $[(CH_3)_4N]_2B_{12}H_{11}OCH_2C_6H_5$: B, 32.8; H, 10.7; C, 45.5; N, 7.06. Found: B, 33.3; H, 10.9; C, 45.5; N, 6.91.

The 60-Mc. n.m.r. spectrum of the product in $(CD_3)_2SO$ shows a singlet at τ 2.74 (external tetramethylsilane reference) and a singlet at τ 5.57 in the ratio of 5:2 corresponding, respectively, to five aromatic hydrogens and two methylene hydrogens. A strong peak at τ 6.9 corresponds to the methyl hydrogens of $(CH_3)_4N^+$. The infrared spectrum of the product shows absorption at 1140 cm.$^{-1}$ consistent with an ether.

A mixture of 2 g. of $Na_2B_{12}H_{12}$, 6 g. of benzoyl p-toluenesulfonate,[19] 4.2 g. of p-chlorobenzaldehyde, and 80 ml. of aceto-

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nitrile was stirred for 15 min. at room temperature. Water (10 ml.) was added and acetonitrile was removed under reduced pressure. The residue was made alkaline by addition of dilute aqueous sodium hydroxide and the resulting suspension was washed twice with ether. The aqueous solution was mixed with tetramethylammonium chloride and the resulting precipitate collected and washed with ether and water, leaving 2 g. of solid which was recrystallized from water to give 590 mg. of a mixture of $[(CH_3)_4N]_2B_{12}H_{11}OCH_2C_6H_4Cl$ and $[(CH_3)_4N]_2B_{12}H_{11}OCH_2$-$C_6H_5$.

Anal. Calcd. for $[(CH_3)_4N]_2B_{12}H_{11}OCH_2C_6H_5$: B, 32.8; H, 10.7; C, 45.5; N, 7.06; Cl, 0.0. Calcd. for $[(CH_3)_4N]_2B_{12}H_{11}$-$OCH_2C_6H_4Cl$: B, 30.1; H, 9.57; C, 41.8; N, 6.50; Cl, 8.23. Found: B, 29.4; H, 9.22; C, 43.1; N, 6.47; Cl, 6.49.

$B_{12}H_{11}OCH(CH_3)_2^{-2}$.—A solution of $(H_3O)_2B_{12}H_{12}\cdot 8H_2O$ (28 g., 88 mmoles) in 2-propanol (110 ml.) was refluxed on a steam bath. Aliquots were removed at intervals and cesium salts were precipitated from them using aqueous cesium fluoride. After 100 hr., the infrared spectrum became constant and did not change on heating an additional 100 hr. The solution was neutralized with 50% aqueous sodium hydroxide and 60 g. of 50% aqueous cesium fluoride was added. The resulting precipitate was filtered and recrystallized from water to give 33.6 g. (81%) of $Cs_2B_{12}H_{11}OCH(CH_3)_2$.

Anal. Calcd. for $Cs_2B_{12}H_{11}OCH(CH_3)_2$: Cs, 57.0; B, 27.8; C, 7.7; H, 3.9. Found: Cs, 55.4; B, 29.0; C, 7.1; H, 3.6.

A solution of $Cs_2B_{12}H_{11}OCH(CH_3)_2$ (5 g., 10.7 mmoles) in 48% hydrobromic acid (25 ml.) was refluxed for 30 min. and then cooled. Most of the hydrogen bromide was removed by blowing air through the mixture, and the residue was made basic with 50% aqueous sodium hydroxide. Recovery of the cesium salt and recrystallization from water gave 3.5 g. (77%) of the double salt, $Cs_2B_{12}H_{11}OH\cdot CsBr$, identified by infrared comparison with an authentic sample (see below).

$B_{12}H_{11}OCH_2CH_2CH_3^{-2}$.—A solution of $(H_3O)_2B_{12}H_{12}$ (2 g., 6 mmoles) in 10 ml. of 1-propanol was sealed in a Carius tube which was then heated in a steam bath for 15 hr. The tube was cooled in liquid nitrogen and opened. The reaction mixture was mixed with 5 ml. of 50% cesium fluoride, chilled, and filtered. Recrystallization of the precipitate gave 2.4 g., (86%) of $Cs_2B_{12}H_{11}$-$OCH_2CH_2CH_3$.

Anal. Calcd. for $Cs_2B_{12}H_{11}OCH_2CH_2CH_3$: B, 27.8; C, 7.7; H, 3.9. Found: B, 27.5; C, 7.8; H, 4.1.

$B_{12}H_{11}O(CH_2)_3CH_3^{-2}$.—The above procedure was repeated with 1-butanol in place of the 1-propanol. $Cs_2B_{12}H_{11}O(CH_2)_3CH_3$ (2.1 g., 73%) was obtained.

Anal. Calcd. for $Cs_2B_{12}H_{11}O(CH_2)_3CH_3$: B, 27.1; C, 10.0; H, 4.2. Found: B, 26.9; C, 9.8; H, 4.3.

$B_{12}H_{11}OCH_2CF_3^{-2}$.—A solution of $(H_3O)_2B_{12}H_{12}\cdot 5H_2O$ (25 g., 93 mmoles) in β,β,β-trifluoroethanol (100 ml.) was refluxed for 12 hr., cooled, and neutralized with cesium hydroxide. The precipitated cesium salt was filtered and recrystallized from water (25 g., 53% yield). Concentration of the filtrate gave an additional 10 g. of $Cs_2B_{12}H_{11}OCH_2CF_3$ (75% total yield).

Anal. Calcd. for $Cs_2B_{12}H_{11}OCH_2CF_3$: B, 25.8; C, 4.8; H, 2.6; F, 11.2. Found: B, 26.1; C, 4.9; H, 3.0; F, 10.9.

$B_{12}H_{11}OCH_2CH_2Cl^{-2}$.—A solution of $(H_3O)_2B_{12}H_{12}\cdot 5H_2O$ (10 g., 37 mmoles) in ethylene chlorohydrin (40 ml.) was heated on a steam bath for 20 hr. The reaction mixture was cooled to room temperature and concentrated in a rotary evaporator to a mush. The residue was neutralized with cesium hydroxide. The precipitate was isolated and recrystallized from water (17.0 g., 94% yield).

Anal. Calcd. for $Cs_2B_{12}H_{11}OCH_2CH_2Cl$: C, 4.9; H, 3.1; Cl, 7.8. Found: C, 4.5; H, 3.1; Cl, 8.1.

$B_{12}H_{11}\cdot NMP^{-}$.—Concentrated hydrochloric acid (25 ml.) was added to a solution of $Na_2B_{12}H_{12}\cdot 2H_2O$ (20 g., 90 mmoles) in 200 ml. of N-methylpyrrolidone. The mixture was filtered. The filtrate was distilled until the flask temperature reached 180°. This temperature was maintained for 4 hr., and the solution was stirred into 400 ml. of ethanol and filtered. The filtrate was added to a solution of 15 g. of cesium hydroxide in 200 ml. of ethanol, precipitating $CsB_{12}H_{11}\cdot NMP$. Recrystallization from water gave 7.9 g. (24%). The product darkened at 360° but did not melt to 400°.

Anal. Calcd. for $CsB_{12}H_{11}(NMP)$: B, 33.4; C, 16.1; H, 5.0; N, 3.8. Found: B, 34.4; C, 15.3; H, 5.8; N, 3.9.

$B_{12}H_{10}\cdot 2NMP$.—Concentrated hydrochloric acid (25 ml.) was added to a solution of $Na_2B_{12}H_{12}\cdot 2H_2O$ (20 g., 90 mmoles) in 200 ml. of N-methylpyrrolidone. The mixture was filtered and the

filtrate was distilled until the flask temperature reached 205°. This temperature was maintained for 4 hr. and the solution was then added to 600 ml. of ethanol with stirring to precipitate 6.2 g. (20%) of $B_{12}H_{10}\cdot 2NMP$. Purification was achieved by dissolution in acetonitrile and reprecipitation in ethanol (dec. pt. 295–298°).

Anal. Calcd. for $B_{12}H_{10}(NMP)_2$: B, 38.4; C, 35.5; H, 8.3; N, 8.3. Found: B, 37.8; C, 35.5; H, 8.9; N, 8.3.

The B^{11} spectrum of $B_{12}H_{10}\cdot 2NMP$ in acetonitrile consists of a weak moderately broad peak at 15.7 p.p.m. plus a strong doublet at 36.6 p.p.m. ($J = 128$ c.p.s.) which decouples to a single sharp peak.

$B_{12}H_{11}OH^{-2}$.—A solution of $CsB_{12}H_{11}\cdot NMP$ (7.9 g., 21 mmoles) in 30 ml. of 10% sodium hydroxide was refluxed for 4 hr. The solution was chilled and 5 g. of cesium hydroxide was added. Filtration gave $Cs_2B_{12}H_{11}OH$ which was recrystallized twice from water. It did not melt to 400°.

Anal. Calcd. for $Cs_2B_{12}H_{11}OH$: Cs, 62.8; B, 30.6; H, 2.8. Found: Cs, 61.8; B, 30.1; H, 2.8. The infrared spectrum of $Cs_2B_{12}H_{11}OH$ in KBr includes absorptions at 3570, 2500, 2470, 1205, 1170, 1150, 1090, 1075, 1050, 1035, 910, and 740 cm.$^{-1}$. The B^{11} n.m.r. spectrum in water consists of a singlet at 11.3 p.p.m. and a doublet at 29.1 p.p.m. ($J = 108$ c.p.s.).

Recrystallization of $Cs_2B_{12}H_{11}OH$ from aqueous cesium bromide gave the double salt $Cs_2B_{12}H_{11}OH\cdot CsBr$, identical by infrared analysis with an authentic sample (*vide infra*).

Sulfur dioxide (30 g., 470 mmoles) and $(H_3O)_2B_{12}H_{12}\cdot 5H_2O$ (10 g., 37 mmoles) were heated in a Hastelloy-lined shaker tube under autogenous pressure at 60° for 4 hr. The tube was cooled to room temperature, the volatiles were vented, and nitrogen was blown through the reaction mixture briefly to remove some of the residual sulfur dioxide. The reaction product was neutralized with cesium hydroxide. The resulting precipitate was isolated and recrystallized from water two times. The infrared spectrum was unchanged by the second recrystallization.

Anal. Calcd. for $Cs_2B_{12}H_{11}OH$: B, 30.6; S, 0.0. Found: B, 30.0; S, 0.3.

The infrared spectrum was the same as that of $Cs_2B_{12}H_{11}OH$ prepared by other routes. Recrystallization from aqueous cesium bromide gave the double salt $Cs_2B_{12}H_{11}OH\cdot CsBr$, identified by infrared analysis (*vide infra*).

$(H_3O)_2B_{12}H_{12}\cdot 12H_2O$ (29 g., 73 mmoles) was added slowly with stirring to acetone (100 ml.) with cooling to maintain the temperature at 20–25°. The solution was stirred for 15 min. at 25° and then 15 ml. of 50% sodium hydroxide was added, followed by 60 g. of 50% aqueous cesium fluoride. Two aqueous recrystallizations of the resulting precipitate gave 31 g. (17%) of $Cs_2B_{12}H_{11}OH$ and 7 g. (20%) of $Cs_2B_{12}H_{11}OCH(CH_3)_2$, identified by infrared comparison with authentic samples. In another run, all the product was converted to $B_{12}H_{11}OH^{-2}$ by removing the acetone under vacuum after addition of the sodium hydroxide and refluxing the residue for 15 min. in 50 ml. of 48% hydrobromic acid. Most of the hydrogen bromide was removed in a stream of air, the residue was made basic with 50% sodium hydroxide solution, and a cesium salt was precipitated by the addition of excess 50% aqueous cesium fluoride. The salt isolated under these conditions was a double salt, $Cs_2B_{12}H_{11}OH\cdot CsBr$.

Anal. Calcd. for $Cs_2B_{12}H_{11}OH\cdot CsBr$: Cs, 62.6; B, 20.4; C, 0.0; H, 1.9; O, 2.5; Br, 12.5. Found: Cs, 62.4; B, 20.6; C, 0.5; H, 1.9; O, 3.5; Br, 12.5.

Aqueous chlorination at 90° of the crude cesium salt isolated directly from the acetone reaction also hydrolyzed the ether linkages present and gave $Cs_2B_{12}HCl_{10}OH\cdot H_2O$.

Anal. Calcd. for $Cs_2B_{12}HCl_{10}OH\cdot H_2O$: Cs, 33.8; B, 16.5; C, 0.0; H, 0.5; Cl, 45.1. Found: Cs, 32.5; B, 16.5; C, 0.2; H, 0.7; Cl, 45.3.

$(H_3O)_2B_{12}H_{12}\cdot 12H_2O$ (95 g., 12.5 mmoles) was treated with 25 ml. of acetone as described above. The mixture was neutralized with sodium hydroxide and distilled. Isopropyl alcohol, 1 ml., b.p. 83° (reported 82.3°), was collected. A phenylurethan, prepared from it, had m.p. 84–85° (reported 86–87°, mixture melting point unchanged).

Repeating this reaction with diethyl ketone and with cyclohexanone in place of the acetone gave similar results. The initial products appeared to be mixtures of alkoxy and hydroxy species. Chlorination of these initial products followed by isolation of a cesium salt as above gave $Cs_2B_{12}HCl_{10}OH\cdot H_2O$. Acetone did not react with $Na_2B_{12}H_{12}$ during a 4-hr. period at 100° in a sealed tube in the absence of acid.

A mixture of oxalic acid (1.75 g., 19.5 mmoles) and $(H_3O)_2$-$B_{12}H_{12} \cdot 7H_2O$ (3.0 g., 9.8 mmoles) was stirred and heated for 5 min. in a boiling water bath. An initial vigorous exothermic reaction occurred which soon subsided. Water (5 ml.) was added and the solution was neutralized to phenolphthalein with cesium hydroxide. The resulting solid was recrystallized from water to obtain 1.6 g. (39%) of $Cs_2B_{12}H_{11}OH$.

Anal. Calcd. for $Cs_2B_{12}H_{11}OH$: Cs, 62.6; B, 30.7; C, 0.0; H, 2.8. Found: Cs, 62.8; B, 30.1; C, 0.7; H, 2.9.

$B_{12}Br_{11}OH^{-2}$.—Bromine was added dropwise with stirring to $Cs_2B_{12}H_{11}OCH(CH_3)_2$ (1 g., 2.1 mmoles) in 20 ml. of water, additional water being added as needed to maintain solution. When bromine was no longer absorbed at ambient conditions, the solution was heated to reflux and chlorine was bubbled through with simultaneous addition of bromine for 5 min. Partial concentration of the solution then gave 1.7 g. (62%) of $Cs_2B_{12}Br_{11}OH$ which was washed with water and dried at 100° under vacuum.

Anal. Calcd. for $Cs_2B_{12}Br_{11}OH$: Cs, 20.6; B, 10.1; Br, 68.0. Found: Cs, 20.3; B, 9.8; Br, 68.4.

Similar bromination of the corresponding tetramethylammonium salt (1.0 g., 2.9 mmoles) gave 2.2 g. (65%) of $[(CH_3)_4N]_2B_{12}Br_{11}OH$.

Anal. Calcd. for $[(CH_3)_4N]_2B_{12}Br_{11}OH$: B, 11.0; C, 8.2; H, 2.1; Br, 74.8. Found: B, 10.9; C, 8.5; H, 2.2; Br, 74.9.

$B_{12}HCl_{10}OH^{-2}$.—A solution of $(H_3O)_2B_{12}H_{12} \cdot 5H_2O$ (5 g., 18.5 mmoles) in 25 ml. of glacial acetic acid was stirred for 3 hr. and then heated on a steam bath for 24 hr. Excess 50% aqueous cesium fluoride was added to precipitate a solid which was recrystallized from water to give 6.4 g. of a product. Infrared and elemental analyses suggested this was a mixture of hydroxy, ester, and ether derivatives of $B_{12}H_{12}^{-2}$. Aqueous chlorination at 90° of 1.0 g. of this product gave 1.3 g. (37%) of $Cs_2B_{12}HCl_{10}$-$OH \cdot H_2O$, the ester and ether functions present in the initial product apparently having been hydrolyzed.

Anal. Calcd. for $Cs_2B_{12}HCl_{10}OH \cdot H_2O$: Cs, 33.8; B, 16.5; C, 0.0; H, 0.5; Cl, 45.1. Found: Cs, 33.2; B, 16.4; C, 0.2; H, 0.7; Cl, 44.4.

$B_{12}H_{10}(OH)_2^{-2}$.—A solution of $B_{12}H_{10} \cdot 2NMP$ (27.5 g., 81 mmoles) and sodium hydroxide (10 g., 0.25 mole) in 150 ml. of water was refluxed for 2.5 hr. Four-fifths of this solution was then mixed with a concentrated aqueous solution of cesium hydroxide (26 g.), and 150 ml. of methanol was added. Filtration then gave $Cs_2B_{12}H_{10}(OH)_2$ which was recrystallized twice from water and dried for 15 hr. at 56° under vacuum (dec. pt. 229–230°).

Anal. Calcd. for $Cs_2B_{12}H_{10}(OH)_2 \cdot H_2O$: Cs, 58.1; B, 28.4; H, 3.1. Found: Cs, 58.3; B, 28.2; H, 3.4. The infrared spectrum of $Cs_2B_{12}H_{10}(OH)_2$ in KBr includes absorptions at 3570, 2470, 1050, 1100, 1025, 890, 765, and 725 cm.$^{-1}$. The B^{11} n.m.r. has a singlet at 14.6 p.p.m. and a doublet at 29.1 p.p.m. ($J = 108$ c.p.s.).

$B_{12}Br_{10}(OH)_2^{-2}$.—The remaining one-fifth of the reaction solution from the above preparation of $B_{12}H_{10}(OH)_2^{-2}$ was diluted with 20 ml. of water. Bromine was added slowly with stirring until the resulting exothermic reaction was complete as shown by persistence of the bromine color in the solution for 30 min. The supernatant liquid was decanted from some undissolved bromine, and aqueous sodium hydroxide was added to the decanted fraction to remove the bromine color. The addition of excess tetramethylammonium chloride precipitated $[(CH_3)_4N]_2B_{12}Br_{10}(OH)_2$ which was recrystallized from water (3.5 g., 19% yield). It darkened at 160° but did not melt to 400°.

Anal. Calcd. for $[(CH_3)_4N]_2B_{12}Br_{10}(OH)_2$: B, 11.7; C, 8.6; H, 2.3; Br, 71.8; N, 2.5. Found: B, 11.8; C, 9.0; H, 3.0; Br, 71.6; N, 2.5. Ultraviolet: $\lambda_{max}^{CH_3CN}$ 254 mμ (ϵ 410). The infrared spectrum of $[(CH_3)_4N]_2B_{12}Br_{10}(OH)_2$ in a Nujol mull includes absorptions at 3570, 1240, 1205, 1090 (broad), 1000, 985, 945, and 845 cm.$^{-1}$.

A solution of benzoyl chloride (40 ml.) and 1,2-dimethoxyethane (10 ml.) was prepared and $(H_3O)_2B_{12}H_{12} \cdot 3H_2O$ (7 g., 30 mmoles) was added at a rate so that the temperature did not exceed 42°. It was necessary to add an additional slight amount of dimethoxyethane to maintain complete solution toward the end of the run. The solution was allowed to stand 3 hr. and was then extracted with toluene and benzene. The residual product was dissolved in aqueous methanol, and excess bromine was added at 75°. The solution was then neutralized with ammonium hydroxide and mixed with aqueous tetramethylammonium chloride. $[(CH_3)_4N]_2B_{12}Br_{10}(OH)_2$, identified by infrared analysis,

precipitated. A similar reaction, differing mainly in that a catalytic amount (0.1 g.) of $AlCl_3$ was present, also gave $[(CH_3)_4$-$N]_2B_{12}Br_{10}(OH)_2$ plus small fractions that had weak absorptions in the C=O region in the infrared.

$B_{12}H_{10}(OCHO)_2^{-2}$.—$[(CH_3)_4N]_2B_{12}H_{10}(OH)_2$ (2.0 g., 6.2 mmoles) was heated on a steam bath for 3 min. in glacial formic acid and then poured into excess water. After filtration, the filtrate was mixed with aqueous tetrapropylammonium bromide to precipitate $[(C_3H_7)_4N]_2B_{12}H_{10}(OCHO)_2$. Recrystallization from water gave 0.5 g., 14%, of glistening platelets, dec. pt. 309–310°.

Anal. Calcd. for $[(C_3H_7)_4N]_2B_{12}H_{10}(OCHO)_2$: B, 21.6; C, 51.8; H, 11.4; N, 4.6. Found: B, 21.6; C, 49.7; H, 11.2; N, 4.6.

$B_{12}Br_6(OH)_6^{-2}$.—The addition of $(H_3O)_2B_{12}H_{12} \cdot 10H_2O$ (30 g., 84 mmoles) to 150 ml. of *t*-butyl alcohol gave an exothermic reaction and much foaming. After being heated on a steam bath for 10 hr., the reaction mixture consisted of two layers. The top layer was evaporated in a stream of air, and a solution of 40 g. of tetramethylammonium chloride in 300 ml. of water was added. The mixture was saturated with bromine and then with a mixture of bromine and chlorine at the boiling point. The addition of ethanol precipitated a tetramethylammonium salt which was too soluble to be recrystallized from water. The addition of cesium fluoride to an aqueous solution of the salt precipitated the corresponding cesium salt which was recrystallized twice from water and dried at 100° to give $Cs_2B_{12}Br_6(OH)_6$.

Anal. Calcd. for $Cs_2B_{12}Br_6(OH)_6$: Cs, 26.2; B, 12.8; Br, 47.4. Found: Cs, 25.3; B, 12.6; Br, 49.2.

$B_{12}H_{11}SH^{-2}$.—A mixture of $(H_3O)_2B_{12}H_{12} \cdot 5H_2O$ (15 g., 55 mmoles) and hydrogen sulfide (30 g.) was heated to 100° for 4 hr. in a 100-ml. stainless steel pressure vessel. The crude product was neutralized with cesium hydroxide and the resulting cesium salt was filtered and recrystallized from water. Three additional runs were made in the same manner, and the four runs were composited to obtain 95 g. (50%) of $Cs_2B_{12}H_{11}SH$. A second recrystallization reduced this to 53 g. (28%) but did not cause any change in the infrared spectrum.

Anal. Calcd. for $Cs_2B_{12}H_{11}SH$: B, 29.7; S, 7.3; H, 2.7; Cs, 60.5. Found: B, 30.1; S, 7.5; H, 2.8; Cs, 60.0.

A solution of 1 g. of $Cs_2B_{12}H_{11}SH$ and 3 g. of trimethylsulfonium iodide in 15 ml. of water was refluxed for 3 hr. The mixture was cooled and a precipitated solid was separated and recrystallized from water. The infrared spectrum of the product was identical with that of an authentic sample of $[(CH_3)_3S]B_{12}H_{11}S(CH_3)_2$.[6]

$B_{12}H_{11}SCH_3^{-2}$.—Dimethyl disulfide (11.3 g., 120 mmoles) was added over a 5-min. period to $(H_3O)_2B_{12}H_{12} \cdot 3.5H_2O$ (24.3 g., 100 mmoles) with cooling in an ice–water bath. The mixture was allowed to warm to room temperature and was stirred for 25 hr. Methyl mercaptan was evolved and characterized as its 2,4-dinitrophenyl thioether (m.p. 126–127°, lit.[20] 128°). Neutralization with 50% aqueous cesium hydroxide precipitated $Cs_2B_{12}H_{11}$-SCH_3 which was recrystallized from water (26 g., 57%).

Anal. Calcd. for $Cs_2B_{12}H_{11}SCH_3$: C, 2.7; H, 3.4; S, 7.0. Found: C, 2.9; H, 3.4; S, 6.8. A solution of $Cs_2B_{12}H_{11}SCH_3$ (1.0 g., 2.2 mmoles) in water (100 ml.) was mixed with an excess of aqueous trimethylsulfonium iodide. The resulting precipitate was recrystallized from water to obtain $(CH_3)_3SB_{12}H_{11}S(CH_3)_2$, identical by infrared analysis with an authentic sample.[6]

Anal. Calcd. for $(CH_3)_3SB_{12}H_{11}S(CH_3)_2$: C, 21.4; H, 9.3; S, 22.8. Found: C, 23.3; H, 10.0; S, 22.5.

$B_{12}H_9(SCH_3)_3^{-2}$ and $B_{12}H_{10}(SCH_3)_2^{-2}$.—Dimethyl disulfide (100 g., 1.1 moles) was added over a 30-min. period to $(H_3O)_2$-$B_{12}H_{12} \cdot 5.5H_2O$ (69.2 g., 250 mmoles) with cooling in a wet ice bath. After 15 min. the cooling bath was removed and the mixture was stirred at room temperature for 48 hr. The reaction mixture was neutralized with cesium hydroxide; the resulting precipitate was filtered and recrystallized from water to obtain 20 g. (15%) of $Cs_2B_{12}H_9(SCH_3)_3$.

Anal. Calcd. for $Cs_2B_{12}H_9(SCH_3)_3$: C, 6.6; H, 3.3; S, 17.5. Found: C, 6.3; H, 4.5; S, 16.0.

Concentration of the filtrate gave 39.0 g. (31%) of $Cs_2B_{12}H_{10}$-$(SCH_3)_2$.

Anal. Calcd. for $Cs_2B_{12}H_{10}(SCH_3)_2$: C, 4.8; H, 3.2; S, 12.8. Found: C, 5.0; H, 3.5; S, 12.6.

$Cs_2B_{12}H_{10}(SCH_3)_2$ (1.0 g.) was dissolved in water (100 ml.), and a slight excess of concentrated aqueous trimethylsulfonium

(20) R. W. Bost, J. O. Turner, and R. D. Norton, *J. Am. Chem. Soc.*, **54**, 1985 (1932).

TABLE II

$\epsilon_{p/2}$ (Volts)

pH	$B_{10}H_{10}^{-2}$ [a]	$B_{10}H_9OH^{-2}$	$B_{10}H_8(OH)_2^{-2}$	$B_{10}Cl_{10}^{-2}$ [b]	$B_{10}Cl_9OH^{-2}$	$B_{10}Cl_8(OH)_2^{-2}$	$B_{12}H_{12}^{-2}$ [a]	$B_{12}H_{11}OH^{-2}$	$B_{12}H_{10}(OH)_2^{-2}$	$B_{12}Br_{10}(OH)_2^{-2}$
4.5	+0.85	+0.60	+0.47	>+1.1	+1.03	+0.74	>+1.4	+0.98	+0.76	>+1.25
7	+0.85	+0.66	+0.62	>+1.1	+1.0	+0.70	>+1.4	....	+0.77	......
10	+0.85	+0.66	+0.63	>+1.1	+1.02	+0.68	>+1.4	....	+0.74	......

[a] See ref. 2.   [b] See ref. 3.

iodide was added. The resulting precipitate was filtered and washed with hot water to leave $B_{12}H_{10}[S(CH_3)_2]_2$.

Anal. Calcd. for $B_{12}H_{10}[S(CH_3)_2]_2$: C, 18.1; H, 8.3; S, 24.2. Found: C, 17.8; H, 8.3; S, 24.2.

$B_{12}H_9(C_8H_9)_3^{-2}$, $B_{12}H_{10}(C_8H_9)_2^{-2}$, and $B_{12}Cl_{10}(C_8H_9)_2^{-2}$.—A solution of $(H_3O)_2B_{12}H_{12}\cdot5H_2O$ (5 g., 18.5 mmoles) and 5 ml. of 2-propanol was prepared at 0°. Styrene (5 g., 48 mmoles) was added and the temperature was maintained at 0–5° for 18 hr. and then at room temperature for 5 hr. (Under these conditions, 2-propanol alone does not react with $(H_3O)_2B_{12}H_{12}\cdot5H_2O$.) Neutralization with cesium hydroxide precipitated $Cs_2B_{12}H_9$-$(C_8H_9)_3$ which was recrystallized from 50% aqueous 2-propanol (6.9 g., 52%).

Anal. Calcd. for $Cs_2B_{12}H_9(C_8H_9)_3$: B, 18.1; C, 40.0; H, 5.0. Found: B, 17.6; C, 41.6; H, 4.1.

In a similar experiment, a fraction was isolated from the recrystallization of the cesium salt which analyzed for a mixture of mono- and dialkylated $B_{12}H_{12}^{-2}$ derivatives. The boron:styrene ratio was 12:1.4. Chlorination of this salt in acetonitrile at 25–40° gave a product with the same boron:styrene ratio and a boron:chlorine ratio of 12:10.6. A solution of hydrobromic acid (100 ml.) and 12 g. of the unchlorinated cesium salt with a boron:styrene ratio of 12:1.4 was distilled slowly over 3.5 hr., collecting 50 ml. of distillate. An oil separated from the distillate. This was separated, dried over potassium hydroxide pellets, and distilled. Ethylbenzene (1.0 g., 45%, $n^{25}D$ 1.4908, b.p. 132°) was isolated. The infrared spectrum was identical with that of authentic ethylbenzene.

In another alkylation of $(H_3O)_2B_{12}H_{12}$ (23 g., 85 mmoles) with styrene (15 g., 144 mmoles) in 2-propanol (18 ml.), the temperature during addition of the styrene was 8–12°. Subsequently, the mixture was stirred 4 hr. at 0–5° and 3 hr. at room temperature. It was then neutralized with 10% aqueous sodium hydroxide and steam distilled for 30 min. Precipitation of a cesium salt from the distillation residue with 50% aqueous cesium fluoride followed by recrystallization from water gave 28 g. (53%) of a salt analyzing for a 1:2 $Cs_2B_{12}H_{12}$-styrene addition product.

Anal. Calcd. for $Cs_2B_{12}H_{10}(C_8H_9)_2$: B, 21.1; C, 31.2; H, 4.5. Found: B, 21.1; C, 32.2; H, 4.6.

Part of this product was converted to the corresponding tetramethylammonium salt by passage, in aqueous solution, through a sodium-charged cation-exchange column followed by precipitation of the tetramethylammonium salt from the effluent with tetramethylammonium hydroxide. This salt was then chlorinated in acetonitrile at 5 to 35° and recrystallized from water.

Anal. Calcd. for $[(CH_3)_4N]_2B_{12}Cl_{10}(C_8H_9)_2$: C, 34.1; H, 4.9; N, 3.2; Cl, 42.2. Found: C, 34.0; H, 4.4; N, 3.8; Cl, 42.6.

$B_{12}H_{11}(C_3H_7)^{-2}$ and $B_{12}Cl_7H_4(C_3H_7)^{-2}$.—A mixture of $(H_3O)_2$-$B_{12}H_{12}\cdot5H_2O$ (15 g., 55 mmoles) and 30 g. of propylene was shaken under autogenous pressure at 35° for 48 hr. The crude product was dissolved in 10% aqueous sodium hydroxide and filtered. The addition of 50% aqueous cesium fluoride gave a gel-like precipitate which recrystallized from water to give 8.5 g. (37%) of $Cs_2B_{12}H_{11}(C_3H_7)$.

Anal. Calcd. for $Cs_2B_{12}H_{11}(C_3H_7)$: B, 28.8; C, 8.0; H, 4.0. Found: B, 27.5; C, 8.1; H, 4.2.

Chlorination of $Cs_2B_{12}H_{11}(C_3H_7)$ in acetonitrile at 25–40° until no further chlorine was absorbed gave $Cs_2B_{12}Cl_7H_4(C_3H_7)$.

Anal. Calcd. for $Cs_2B_{12}Cl_7H_4(C_3H_7)$: C, 5.2; H, 1.6; Cl, 35.9. Found: C, 4.6; H, 1.6; Cl, 35.5.

Polarographic Studies.—The half-wave potentials $(\epsilon_{p/2})$ shown in Table II were determined using a graphite–Nujol paste electrode vs. a saturated calomel electrode. The values at pH 4.5 were determined in 0.1 M KH_2PO_4 and the studies at pH 7 and 10 were done using standard Britton–Robinson buffers. These values were determined at several concentrations and found to be essentially independent of concentration. The value of +0.47 for $B_{10}H_8(OH)_2^{-2}$ at pH 4.5 is inconsistent with the values at pH 7 and 10. It may be that $B_{10}H_8(OH)_2^{-2}$ is unstable at this pH because different values were obtained on rerunning the pH 4.5 solutions. In many cases, more than one oxidation peak was observed for these anions; only the first is reported.

[Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois]

The Rates and Mechanism of Substitution Reactions of Palladium(II)-Acetylacetonate Complexes

By Ralph G. Pearson and Dale A. Johnson[1]

The rates of some substitution reactions of palladium(II)–acetylacetonate complexes have been measured in 91% water–9% methanol. The reactions studied include acid hydrolysis, base hydrolysis, and halide substitution in acidic media. The order of nucleophile reactivity found is $H_2O \approx OH^- < Cl^- < Br^- < I^- < SCN^-$. The parallelism of this order of reactivity to that observed for platinum(II) complexes and the kinetic form of the observed rate constants suggest that palladium and platinum systems react by similar S_N2 mechanisms. Because the leaving group is a chelate, the rate equation is a function of the hydrogen ion concentration and the concentration of added nucleophile. The role of hydrogen ion is to trap the half-open chelate ring.

The majority of the studies of the substitution reactions of planar complexes have dealt with Pt(II) systems.[2] The form of the observed rate constant

(1) Sinclair Fellow 1960–1961, United States Rubber Fellow 1961–1962 Union Carbide Fellow 1962–1963.

(2) (a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 4; (b) R. G. Pearson, H. B. Gray, and F. Basolo, *J. Am. Chem. Soc.*, **82**, 787 (1960); (c) F. Basolo, H. B. Gray, and R. G. Pearson, *ibid.*, **82**, 4200 (1960); (d) H. B. Gray and R. J. Olcott, *Inorg. Chem.*, **1**, 481 (1962).

for most Pt(II) substitution reactions is

$$k_{obsd} = k_1 + k_2[X] \tag{1a}$$

where X is the entering nucleophile. The substitution reactions of Pt(II) complexes are interpreted in terms of a two-path mechanism in which the first-order rate constant k_1 is associated with nucleophilic attack by the solvent, and the second-rate constant k_2 describes direct attack by the entering nucleophile.[2] The five-co-