imparts some stability to the adjacent-carbon structure with respect to rearrangement to the isomer having nonadjacent carbons. Both theoretical[18-21] and experimental[13,22,23] considerations have indicated that the more stable carborane structures are those in which the cage carbons are nonadjacent. Therefore the apparent reluctance of I to rearrange to the 1,5 isomer [1,2-dimethyl-1,5-dicarbaclovopentaborane(5)], either in the discharge or under moderate conditions, is intriguing.[24] It is conceivable that such an isomerization involves an intermediate with a sterically unfavorable configuration which hinders rearrangement. However, although steric effects have recently been observed in the rearrangement[25] of *o*-carborane(12) to neocarborane(12), which is facilitated by the replacement of the C-hydrogen atoms by large substituted silyl groups, the importance of such effects in the case of the much smaller methyl substituents is not obvious. Possibly a more likely explanation is that alkylation in I alters the electronic situation in the cage so as to stabilize the adjacent-carbon structure. Studies on I currently in progress are expected to yield information on possible thermal or base-catalyzed isomerization.

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Photoinduced Nucleophilic Substitution in Halogenated Clovoboranes

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Abstract: Irradiation of polyhalogenated $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ derivatives in aqueous solutions containing CN^-, N_3^-, or OCN^- ions results in replacement of halogen by the appropriate nucleophile. Up to nine halogens were replaced with CN groups, while the introduction of more than two N_3 or OCN groups was prevented, respectively, by competing photolytic or hydrolytic reactions of the new substituent. The results are consistent with a photoinduced heterolysis of the boron-halogen bond followed by addition of an anion to the resulting electron-deficient species, steric factors being important. This mechanism is supported by halogen-exchange experiments.

The clovoboranes, $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$, have displayed a remarkably broad spectrum of derivative chemistry. For instance, the introduction of chloromethyldimethylamino,[1] amino,[2] acyl,[3] hydroxy,[3] alkoxy,[3] alkyl,[3] mercapto,[3] alkylthio,[3,4] diazonium,[5] carbonyl,[5,6] and halo[7] substituents has been reported. However, only halogenation proceeded beyond the disubstitution stage to afford readily poly- and perhalogenated cages. The availability of such derivatives suggested their use as starting materials for the synthesis of otherwise inaccessible, substituted clovoboranes. The direct replacement of halogen by nucleophiles, a valuable synthetic tool in organic as well as boron chemistry, was inapplicable in view of the reported and confirmed inertness of halogenated clovoboranes.[7] Cripps' discovery that $B_{12}Cl_{12}^{2-}$ yields chloride ion on irradiation led to a study in the course of which it was found that *such substitution is effected readily when aqueous solutions of halogenated clovoboranes are irradiated in the presence of nucleophiles*[8] (eq 1, X = Cl,

$$B_{12}X_{12}^{2-} + nY^- \xrightarrow[H_2O]{h\nu} B_{12}X_{12-n}Y_n^{2-} + nX^- \qquad (1)$$

Br; $Y^- = CN^-$, N_3^-, etc.). It was of interest, therefore, to determine the synthetic scope of this reaction and its mechanistic implications.

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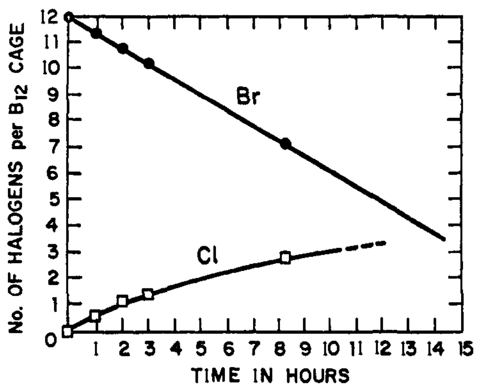

Figure 1. Rate of halogen exchange on irradiation of $B_{12}Br_{12}^{2-}$ with excess chloride ion.

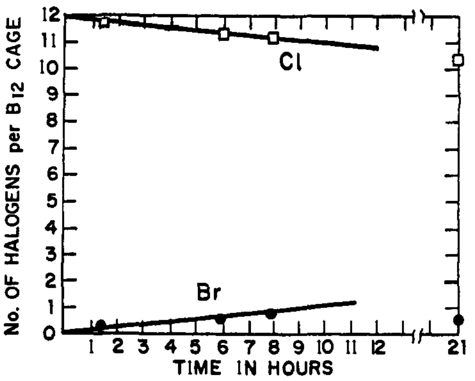

Figure 2. Rate of halogen exchange on irradiation of $B_{12}Cl_{12}^{2-}$ with excess bromide ion.

Results

Cyanide Ion. Cyanide ion was particularly useful in this study since it is a good nucleophile of low steric demand and gives rise to photolytically and hydrolytically stable products.

Prolonged irradiation of $B_{12}Br_{12}^{2-}$ in the presence of excess cyanide ion gave $B_{12}Br_3(CN)_9^{2-}$; even longer irradiation of this species in the presence of cyanide ion gave mixtures of $B_{12}Br_2(CN)_9H^{2-}$ and $B_{12}Br(CN)_9H_2^{2-}$ and, ultimately, $B_{12}Br(CN)_9H_2^{2-}$ only. By contrast, there was quantitative recovery of starting material when $B_{12}Br_{12}^{2-}$ was refluxed 100 hr with excess potassium cyanide without irradiation. Irradiations of $B_{12}Br_{12}^{2-}$ of shorter duration produced gross mixtures of oligocyanated derivatives that could not be separated. Irradiation of $B_{12}Br_{10}H_2^{2-}$ in the presence of cyanide ion gave rise to a mixture of $B_{12}Br_2(CN)_8H_2^{2-}$ and $B_{12}Br(CN)_9H_2^{2-}$ and, ultimately, only the latter compound. When tetra- and pentabromo derivatives of $B_{12}H_{12}^{2-}$ were irradiated in the presence of cyanide ion, there was no reaction and the starting materials were recovered unchanged.

Exhaustive irradiation of $B_{12}Cl_{12}^{2-}$ in the presence of cyanide ion gave only $B_{12}Cl_5(CN)_7^{2-}$, which was not affected significantly by further irradiation. The $B_{10}Cl_{10}^{2-}$ anion was much less reactive and also less selective yielding on exhaustive irradiation in the presence of cyanide ion mixtures of $B_{10}Cl_9CN^{2-}$, $B_{10}Cl_8(CN)_2^{2-}$, $B_{10}Cl_7(CN)_3^{2-}$, as well as starting material and other products containing BH bands in the infrared spectrum. Their separation was difficult. The $B_{10}Cl_8(CN)_2^{2-}$ species was different from authentic 1,10-$B_{10}Cl_8(CN)_2^{2-}$ by having a strong infrared band at 1160 cm^{-1} (sh 1190 cm^{-1}), absent in the latter.

The cyano groups in these compounds showed a weak, yet sharp band at about 2210 cm^{-1}, *i.e.*, the range of conjugated nitriles.[9] They easily withstood extended boiling in hydrochloric acid or alkali and could be hydrolyzed to the polycarboxylic acids only with difficulty. This was accomplished by prolonged boiling in concentrated sulfuric acid, which seemed to give a mixture of amides and imides, and then by refluxing of the product in strong alkali. The anions $B_{12}Br(COOH)_9H_2^{2-}$ and $B_{12}Br_2(COOH)_8H_2^{2-}$ were obtained in this fashion. Hydrolysis of $B_{10}Cl_8(CN)_2^{2-}$ gave an acid which on heating gave a sublimable, hygroscopic yellow substance, presumably $B_{10}Cl_8(CO)_2$.

Cyanate Ion. When $B_{12}Br_{12}^{2-}$ was irradiated for 80–90 min in the presence of excess potassium cyanate, salts of $B_{12}Br_{11}OCN^{2-}$ and $B_{12}Br_{10}(OCN)_2^{2-}$ could be isolated. The infrared spectra of these products showed strong bands at 2180 cm^{-1} (organic cyanates[10]) and bands at 1050 (m) and 1080 cm^{-1} (w) (C–O stretch[11]). That the OCN group is attached to the cage through the oxygen atom was shown by the facile hydrolysis of $B_{12}Br_{10}(OCN)_2^{2-}$ to $B_{12}Br_{10}(OH)_2^{2-}$. This hydrolysis is so rapid that on irradiating $B_{12}Br_{12}^{2-}$ for 105 min in the presence of excess potassium cyanate (pH $\sim$10) one OCN group gets hydrolyzed in the course of introducing a third OCN group and the product isolated is $B_{12}Br_9(OCN)_2OH^{2-}$ (or $B_{12}Br_9(OCN)(OCONH_2)(OH)^{2-}$).[12] Prolonged irradiation of $B_{12}Br_{12}^{2-}$ in the presence of cyanate ion gave no precipitable products.

Azide Ion. Short (1.5–2 hr) irradiation of $B_{12}Br_{12}^{2-}$ in the presence of excess azide ion produced $B_{12}Br_{11}N_3^{2-}$ and $B_{12}Br_{10}(N_3)_2^{2-}$, anions that could be separated by fractional crystallization. On prolonged irradiation, however, no product could be isolated by precipitation. The well-known photolability of covalent azides suggests the formation of extremely water-soluble product arising *via* the nitrene.

The azide group in $B_{12}Br_{11}N_3^{2-}$ and $B_{12}Br_{10}(N_3)^{2-}$ compounds gave rise to strong absorption at 2140 $cm.^{-1}$ which is normal for azides.[4] The above compound remained unchanged (using the retention of this intense infrared band as a criterion) upon being (a) treated with excess potassium borohydride in water at 40° for 8 hr; (b) treated with excess lithium aluminum hydride in tetrahydrofuran; (c) boiled in 10 *M* hydrochloric acid for 60 hr, and (d) refluxed in 5% sodium hydroxide for 60 hr. By contrast, irradiation of $B_{12}Br_{10}(N_3)_2^{2-}$ caused complete disappearance of the azide band.

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(9) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1959.

(10) J. C. Kauer and W. W. Henderson, *J. Am. Chem. Soc.*, **86**, 4732 (1964), report the –OCN absorption of hindered aliphatic cyanates as a doublet (attributable to Fermi resonance) at 2220–2280 cm^{-1}; similar values (2240, 2773 cm^{-1}) are reported for ethyl cyanate by D. Martin, *Tetrahedron Letters*, No. 39, 2829 (1964).

(11) This falls in the C–O stretch range for aliphatic borates: H. Steinberg, "Organoboron Chemistry," Vol. I, Interscience Publishers, John Wiley and Sons, Inc., New York, N. Y., 1964, p 871 ff.

(12) Generally, products differing by only one functional group had very similar physical properties, making their separation exceedingly difficult and, except for mono- and persubstituted B_{12} cages, complicated by possibilities of isomerism. Furthermore, elemental analysis was usually not sensitive enough to detect, *e.g.*, water of hydration, so that only gross features of the reaction could be established with certainty.

Halide Ion. Irradiation of $B_{12}Br_{12}{}^{2-}$ in the presence of a large excess of chloride ion gave products with a progressively larger chlorine to bromine ratio (Figure 1). While the loss of bromine was linear, half of it having disappeared after 10 hr (extrapolated value), the introduction of chlorine was linear only for the first 2 hr and then tapered off. No precipitable material was present after 17 hr.

Analogous behavior was observed when $B_{12}Cl_{12}{}^{2-}$ was irradiated in the presence of excess bromide ion. Here, too, a linear loss of the original cage halogen occurred, but the time for the loss of six chlorines (extrapolated) was about 70 hr (Figure 2). By contrast, treatment of $B_{12}Cl_{12}{}^{2-}$ with bromine radicals did not cause halogen exchange.

Irradiation of $B_{12}Br_{12}{}^{2-}$ in the presence of fluoride ion caused initially rapid introduction of fluorine into the cage, but the course of the reaction could not be determined as the original product was nonstoichiometric, and after 2 hr no precipitable material was present.

Miscellaneous Anions. Exhaustive irradiation of $B_{12}Br_{12}{}^{2-}$ in the presence of thiocyanate ion led to mixtures of sulfur-containing products that could not be identified with certainty. However, the number of bromine atoms lost was roughly equal to the number of sulfur atoms introduced into the molecule.

Irradiation in the presence of bulky anions, such as phenoxide or carbamyldicyanomethanide,[13a] gave monosubstituted products which crystallized as 1:1 complexes with the starting material.

It should be noted at this point that B^{11} nmr was of only partial usefulness in structure elucidation.[13b] For instance, monosubstituted derivatives such as $B_{12}Br_{11}OCN^{2-}$, $B_{12}Br_{11}N_3{}^{2-}$, and $B_{12}Br_{11}(OC_6H_5)^{2-}$ ions gave only one peak at +31 ppm which is the position of the $B_{12}Br_{12}{}^{2-}$ ion.[7] On the other hand, B^{11} nmr proved useful with polycyano compounds as the boron attached to a cyano group was significantly shifted to higher field as compared with boron attached to halogen. A particularly good example of this was $B_{12}Cl_5(CN)_7{}^{2-}$ which showed two well-separated peaks in 5:7 ratio at +28.6 and +40.6 ppm, respectively, the latter being assigned to the CN-bearing borons. It is noteworthy that in this compound the peak due to Cl-bearing borons has been shifted to lower field, as compared with $B_{12}Cl_{12}{}^{2-}$ which has a singlet at +31.0 ppm.

The direction of photoinduced nucleophilic substitution in $B_{10}Cl_{10}{}^{2-}$ was also established by B^{11} nmr. Thus, the authentic 1,10-$B_{10}Cl_8(CN)_2{}^{2-}$ ion has a peak at +26.2 ppm with a small shoulder on the high-field side. This is consistent with the structure assigned, as the position of the apical borons has shifted from a low-field shoulder (present in $B_{10}Cl_{10}{}^{2-}$) to a high-field shoulder in going from B–Cl to B–CN. In the $B_{10}Cl_8(CN)_2{}^{2-}$ species obtained on irradiation of $B_{10}Cl_{10}{}^{2-}$ in cyanide solution the main peak is at +28.3 ppm and the low-field shoulder due to apical Cl-bearing borons is still present at about +22 ppm. There is, however, a new peak at +42.8 ppm which must be due to CN-bearing equatorial borons. The area ratio of the main peak (including low-field shoulder) to the high-field peak is 8:2.

Authentic 1,10-$B_{10}Br_8(CN)_2{}^{2-}$ ion has only one featureless broad peak at +29.6 ppm. In $B_{12}Br_3(CN)_9{}^{2-}$ the B–Br and B–CN peaks are partly overlapping and appear in 3:9 area ratio at +27.5 and 33.0 ppm, respectively. In $B_{12}Br(CN)_9H_2{}^{2-}$ the main peak is at +36.1 ppm with a shoulder at +28.4 ppm due to both B–Br and B–H, since on decoupling it moves slightly toward higher field, indicating collapse of a doublet derived from B–H.

Discussion

If one considers the SN* mechanism[14] in, for instance, $B_{12}Br_{12}{}^{2-}$, it becomes obvious that the spherical nature of the cage makes the molecule immune to SN2-type attack while the protective shell of halogens precludes any four-center mechanism. Thus, a necessary prerequisite for the bonding of a new substituent to boron is that its prospective attachment site be already vacated by the halogen. The first step of the reaction must, therefore, consist of a boron–halogen bond scission in the photoexcited molecule.

A priori this may happen in two ways,[15] leading to intermediates analogous to a carbonium ion or a radical, *viz.*

$$B_{12}X_{12}{}^{2-} \xrightarrow{h\nu} B_{12}X_{12}{}^{2-*} \longrightarrow B_{12}X_{11}{}^{-} + X^{-} \qquad \text{(A)}$$

$$B_{12}X_{12}{}^{2-} \xrightarrow{h\nu} B_{12}X_{12}{}^{2-*} \longrightarrow B_{12}X_{11}{}^{2-} + X\cdot \qquad \text{(B)}$$

Experimental evidence favors the first mode of dissociation (scheme A) since the second step involves the addition of *an anion*, as, *e.g.*, cyanide or fluoride radicals would not be formed under the experimental conditions. The facile and rapid addition of anions demands a reactive, electron-deficient intermediate and is thus incompatible with scheme B, the dianion radical being a poor electrophile.[16] However, scheme B may be operating as a slow secondary reaction during extended irradiations (after cessation of boron–halogen bond heterolysis) and it would account for the replacement of halogen by hydrogen in $B_{12}Br_3(CN)_9{}^{2-}$ and $B_{10}Cl_{10}{}^{2-}$. The main course of the reaction, though, is accommodated best by the SN1* mechanism, which, except for the anomalous fluoride case, is compatible with some generalizations that have emerged from this study.

1. *Perbrominated cages react faster and to a greater extent than the perchlorinated ones.* This is in line with the greater strength of the B–Cl bond as compared with the B–Br[17] bond and the greater ease of bromide (*vs.* chloride) solvolysis in bridgehead systems.[18]

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(13) (a) S. Trofimenko, E. L. Little, and H. F. Mower, *J. Org. Chem.*, **27**, 433 (1962). (b) The B^{11} nmr spectra were determined at 19.25 Mc and the chemical shifts are referred to external methyl borate. The samples were dissolved in acetonitrile.

(14) The notation of Ingold is used (C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 306 ff); an asterisk denotes the photoinduced nature of the reaction.

(15) The third scheme, $B_{12}X_{12}{}^{2-}$ ($h\nu$) $\longrightarrow B_{12}X_{12}{}^{2-*} \longrightarrow B_{12}X_{11}{}^{3-} + X^{+}$, can be ignored. Not only is this particular type of dissociation lacking in precedent, but the attack of an anion on the most electronegative site in the molecule would not be expected.

(16) It is conceivable that the reaction may proceed sequentially *via* (a) homolytic boron–halogen bond scission to give an intimate radical pair, followed by (b) a one-electron transfer from the boron to the halogen (still within the common solvent cage), and finally, (c) separation of the solvated ions. The net result, however, would be indistinguishable from scheme A.

(17) Dissociation energies of the boron–halogen bond in BCl_3 and BBr_3 have been estimated at 103 and 81 kcal/mole, respectively (T. L. Cottrell, "The Strength of Chemical Bonds," Butterworths, London, 1954).

(18) R. C. Fort and P. von R. Schleyer, *Chem. Rev.*, **64**, 277 (1964); *J. Am. Chem. Soc.*, **86**, 4194 (1964), and references cited therein. Since $B_{12}Br_{12}{}^{2-}$ and $B_{12}Cl_{12}{}^{2-}$ cannot give rise to a common $B_{12}X_{11}{}^{-}$ ion, the assumption is made that the stabilities of $B_{12}Br_{11}{}^{-}$ and $B_{12}Cl_{11}{}^{-}$ are roughly comparable.

2. *The reactivity of halogenated cages falls off with decreasing number of halogens.* One may assume that the departure of halide ion is facilitated through stabilization of the transition state by π-electron donation from the remaining halogens to the incipient $B_{12}X_{11}^-$ ion.[19] That such stabilization of the $B_{12}X_{11}^-$ ion is not significant[20a] follows from the rather similar reaction rates of $B_{12}Br_{12}^{2-}$ with poor nucleophiles such as Cl^- and strong nucleophiles[20b] such as N_3^- or OCN^-. This implies high reactivity of $B_{12}Br_{11}^-$ coupled with low selectivity as far as nucleophilicity of the adding anion is concerned.

3. *Polysubstitution is effected readily by small ions.* The intermediate electron-deficient species, while not very discriminating in terms of electrophilic demand on the adding ion, places restrictions on its size. Molecular models show that removal of a halide ion from $B_{12}Br_{12}^{2-}$ gives rise to a well-shielded "positive hole" which can accommodate only small nucleophiles. The steric inaccessibility of atoms bonded to boron is attested by the extraordinary inertness of CN groups in $B_{12}(CN)_9Br_3^{2-}$ to hydrolysis and is in contrast to the ease with which OCN substituents are hydrolyzed. In the latter case, the carbon atom, which is the target of nucleophilic attack, stays outside the protective shell and is readily accessible.

4. *The perhalogenated B_{12} cages are more reactive than their B_{10} counterparts.* The reactions of $B_{10}Cl_{10}^{2-}$ are quite sluggish and nonspecific as compared with those of $B_{12}Cl_{12}^{2-}$; only a minor part of the B_{10} cage is accounted for and, apart from products containing new B–CN and B–H bonds, even some starting material is found to survive the irradiation. This probably reflects lack of adequate excitation of $B_{10}Cl_{10}^{2-}$ ion by the light source used and is also the probable cause of termination of the SN1* reaction at stages such as $B_{12}(CN)_9Br_3^{2-}$ and $B_{12}Cl_5(CN)_7^{2-}$ which, in contrast to $B_{12}Br_{12}^{2-}$ and $B_{12}Cl_{12}^{2-}$, have no ultraviolet maxima.

Experimental Section

The irradiations were carried out in cylindrical quartz tubes (20 × 5 and 30 × 8 cm), sealed at the bottom and fitted with a standard taper joint at the top connected to a water-cooled condenser. The light source was a 9-mm tube filled with mercury vapor and wound into a coil of five to eight turns fitting snugly the appropriate quartz tube. It was, essentially, a variant of the Hanovia Sc 2537 lamp which emits 95% of its ultraviolet output at 2537 A. It was operated at 5000 v and had an intensity of about 5 w. The coil was enclosed in a cylindrical aluminum reflector. The temperatures of the reaction mixtures ranged from 25 to 35° (for 1- to 3-hr irradiations) to around 70° for prolonged irradiations.

$B_{12}H_8Br_4^{2-}$ and $B_{12}H_7Br_5^{2-}$. A solution of 100 g (0.486 mole) of $Na_2B_{12}H_{12}\cdot H_2O$ in 1 l. of 9:1 water–methanol was cooled to −10°. Bromine was added slowly to the stirred solution until a break in bromine absorption was noticeable, the temperature being maintained at −10 to −2°. The product was precipitated with cesium fluoride and recrystallized from water to yield 77 g (21%) of colorless crystals. *Anal.* Calcd for $Cs_2H_8B_{12}Br_4$: B, 17.9; Br, 44.2; H, 1.100. *Anal.* Calcd for $Cs_2H_7B_{12}Br_5$: B, 16.2; Br, 49.8; H, 0.87. Found: B, 16.4; Br, 46.2; H, 1.25. This corresponds to a 65:35 mixture of $B_{12}H_8Br_4^{2-}$ and $B_{21}H_7Br_5^{2-}$ salts.

$B_{12}Br(CN)_9H_2^{2-}$. A solution of 113 g (0.10 mole) of $(NH_4)_2B_{12}Br_{12}$ and 78.0 g (1.2 moles) of potassium cyanide in 1 l. of water was stirred and irradiated for 100 hr. The solution was acidified with hydrochloric acid, and all volatile materials were distilled at reduced pressure. The residue was dissolved in water and the product precipitated as the tetramethylammonium salt, which was purified by chromatography on alumina (using acetonitrile as eluent). The product was converted to the free acid *via* ion exchange and irradiated again in 1 l. of water with 113 g of potassium cyanide for 72 hr. Addition of tetramethylammonium chloride to the yellow solution gave a solid which was purified by recrystallization from water; yield 9.3 g (16%). *Anal.* Calcd for $C_{17}H_{26}B_{12}BrN_{11}$: C, 34.3; H, 4.37; B, 21.9; Br, 13.5; N, 25.6. Found: C, 34.2; H, 4.54; B, 21.9; Br, 14.5; N, 25.5.

$B_{12}Br_3(CN)_9^{2-}$ and $B_{12}Br_2(CN)_9H^{2-}$. A solution of 58.0 g (0.0426 mole) of $Cs_2B_{12}Br_2$ and 64.0 g of potassium cyanide (0.985 mole) in 550 ml of water was stirred and irradiated for 6 days. The clear yellow solution was stirred with excess cesium fluoride yielding 21.0 g (56%) of $Cs_2B_{12}Br_3(CN)_9$. The filtrate was stirred with excess tetramethylammonium chloride, yielding 5.6 g (20%) of $[(CH_3)_4N]_2B_{12}Br_2(CN)_9H$. Both materials were purified by recrystallization from water and drying *in vacuo*.

(a) *Anal.* Calcd for $C_9H_2B_{12}Br_3Cs_2N_9O$ (a monohydrate): C, 12.1; H, 0.23; Cs, 29.9; B, 14.6; Br, 27.0; N, 14.2. Found: C, 12.2; H, 0.40; Cs, 29.0; B, 14.2; Br, 29.5; N, 14.2.

(b) *Anal.* Calcd for $C_{17}H_{25}B_{12}Br_2N_{11}$: C, 30.3; H, 3.71; B, 19.3; Br, 23.8; N, 22.9. Found: C, 29.7; H, 3.62; B, 18.0; Br, 23.8; N, 23.1.

$B_{12}Br_2(CN)_8H_2^{2-}$ and $B_{12}Br(CN)_9H_2^{2-}$. A mixture of 100 g of $Cs_2B_{12}H_2Br_{10}$ and 113 g of KCN was stirred in 1 l. of water and irradiated for 120 hr. The solution was then acidified and evaporated to dryness, and the residue was extracted with acetonitrile. The extracts were evaporated to dryness; the residue was dissolved in water and converted to the $(CH_3)_4N$ salt, obtained in 22.0 g yield.

Another identical reaction (but with irradiation time only 60 hr) gave 23.3 g of product.

Both products were combined and recrystallized from a mixture of aqueous acetonitrile and ethanol; First crop, 13 g, second crop, 10 g. *Anal.* Calcd for $C_{16.5}H_2B_{12}Br_{1.5}N_{10.5}$: C, 31.9; H, 4.18; B, 20.9; Br, 19.3; N, 23.7. Found: C, 32.1; H, 4.30; B, 21.1; Br, 19.1; N, 23.7.

This corresponds to a 1:1 mixture of $B_{12}H_2Br(CN)_9^{2-}$ and $B_{12}H_2Br_2(CN)_8^{2-}$ species.

$B_{12}Cl_5(CN)_7^{2-}$. A mixture of 15.8 g (0.025 mole) of $K_2B_{12}Cl_{12}$ and 32 g (0.48 mole) of KCN was stirred and irradiated for 44 hr. The clear solution was stirred with excess CsF and the resulting precipitate was recrystallized five times from water to yield 4.0 g of light tan crystals. This material is very soluble in alcohols, acetone, ethyl acetate, and tetrahydrofuran. It contains a CN band at 2220 cm^{-1}. *Anal.* Calcd for $C_7B_{12}Cl_5Cs_2N_7$: C, 11.1; H, 0.00; B, 17.2; Cl, 23.5; Cs, 35.2, N, 13.0. Found: C, 11.1; H, 0.46; B, 17.3; Cl, 24.1; Cs, 33.4; N, 12.8.

When the above experiment was repeated, extending the irradiation time to 64 hr, the crude cesium salt was converted to the free acid by means of ion exchange. The acid solution was decolorized with Darco (the cesium salt cannot be decolorized in this fashion) and the product was reprecipitated as the cesium salt. Its infrared spectrum was not significantly different from that of the product from the first experiment. *Anal.* Found: C, 10.9; H, 0.35; B, 16.8; Cl, 24.7; Cs, 33.2; N, 12.5.

$B_{10}Cl_8(CN)_2^{2-}$. A mixture of 80 g of $Cs_2B_{10}Cl_{10}$ and 60 g of KCN was irradiated in 900 ml of water for 90 hr. The solution was acidified with hydrochloric acid and then evaporated to dryness. The residue was extracted with ethanol, and the extracts were evaporated, dissolved in water, and converted to a solution of the free acid *via* ion exchange. This solution was exhaustively chlorinated; the product was precipitated as the Cs salt and recrystallized from water, in 20.0-g yield. Both filtrates were treated with $(CH_3)_4NCl$ to yield an additional 10.5 g of the salt. It was purified by chromatography on alumina using acetonitrile as eluent; yield of purified product, 6.0 g. *Anal.* Calcd for $C_{10}H_{24}B_{10}Cl_{10}N_4$ (*i.e.*, $[(CH_3)_4N]_2B_{10}Cl_8(CN)_2$): C, 20.3; H, 4.06; B, 18.3; Cl, 48.0. Found: C, 20.3; H, 4.38; B, 18.1; Cl, 47.8.

The infrared spectrum of this material has a strong 1160 (sh 1190) cm^{-1} band absent in $B_{10}Cl_8(CN)_2^{2-}$ containing diapical nitriles; hence the irradiation product must contain at least one equatorial nitrile.

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(19) π-Electron donation by halogen has been invoked to account for, *e.g.*, the direction of electrophilic aromatic substitution in halo aromatics, and the decrease of F^{19} shielding parameters in fluorophenylplatinum(II) complexes: G. W. Parshall, *J. Am. Chem. Soc.*, **86**, 5367 (1964).

(20) (a) See A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 38 ff; (b) E. R. Thornton, "Solvolysis Mechanisms," The Ronald Press Co., New York, N. Y., 1964, p 163.

$B_{10}Cl_8(CN)_2^{2-}$ and $B_{10}Cl_7(CN)_3^{2-}$. A mixture of 21.9 g (0.03 mole) of $Cs_2B_{10}Cl_{10}$ and 32.9 (0.57 mole) of potassium cyanide was stirred and irradiated in 275 ml of water for 30 hr. The product was precipitated with tetramethylammonium ion and recrystallized from water. Light tan crystals were obtained. The product was converted to the free acid *via* ion exchange, and the acid eluate was decolorized with Darco. Reprecipitation with tetramethylammonium ion gave colorless crystals which were recrystallized again from water and obtained in 3.2-g yield. *Anal.* Calcd for $C_{10.4}H_{24}B_{10}Cl_{7.6}N_{4.4}$ (*i.e.*, a 6:4 mixture of $[(CH_3)_4N]_2B_{10}Cl_8(CN)_2$ and $[(CH_3)_4N]_2B_{10}Cl_7(CN)_3$): C, 21.2; H, 4.07; B, 18.3; Cl, 45.7; N, 10.5. Found: C, 21.4; H, 4.17; B, 18.7; Cl, 45.5; N, 10.5.

$B_{10}Cl_9CN^{2-}$, $B_{10}Cl_8(CN)_2^{2-}$, and $B_{10}Cl_7(CN)_3^{2-}$. Three 100-g batches of $Cs_2B_{10}Cl_{10}$ were irradiated each with 113 g of KCN in 1 l. of water for 120 hr. Each solution was stirred with an excess of 50% aqueous cesium fluoride. The solid was filtered, and the filtrate was treated with $[(CH_3)_4N]Cl$. Both products contained B–H and CN bands, but the $[(CH_3)_4N]$ salt had a stronger nitrile band.

The cesium salts were combined, converted to the free acid, and exhaustively chlorinated until the B–H band in the infrared had disappeared. The product was converted to the tetramethylammonium salt, then purified by chromatography on alumina and processed further with the original tetramethylammonium salt which also was exhaustively chlorinated.

The combined products were converted to the cesium salt (*via* free acid), which was recrystallized from water. Since this salt contained much starting material (by infrared) it was not analyzed. To the filtrate from recrystallization, tetramethylammonium chloride was added and the resultant solid recrystallized from aqueous acetonitrile, yielding two crops (6.0 and 2.0 g) of recrystallized product. *Anal.* Calcd for $[(CH_3)_4N]_2B_{10}Cl_{8.3}(CN)_{1.7}$ (*i.e.*, a 7:3 mixture of $B_{10}Cl_8(CN)_2^{2-}$ and $B_{10}Cl_9(CN)^{2-}$ species): C, 19.5; H, 4.05; B, 18.2; Cl, 49.5; N, 8.76. Found: C, 19.1; H, 3.94; B, 17.9; Cl, 47.1; N, 8.68. Both crops were combined, converted to the free acid and then to the cesium salt which was recrystallized from water. *Anal.* Calcd for $Cs_2B_{10}Cl_9CN$: C, 1.67; B, 15.0; Cl, 44.3; N, 1.94. Found: C, 2.04; B, 14.9; Cl, 44.3; N, 1.65. The filtrate from the original separation of the first cesium salt was treated with tetramethylammonium chloride yielding 28 g of a product with a strong nitrile band in the infrared. It was recrystallized from an acetonitrile–water–alcohol mixture. *Anal.* Calcd. for $[(CH_3)_4N]_2B_{10}Cl_8(CN)_2$: C, 20.3; H, 4.06; B, 18.3; Cl, 48.0; N, 9.47. Calcd for $[(CH_3)_4N]_2B_{10}Cl_7(CN)_3$: C, 22.7; H, 4.14; B, 18.6; Cl, 42.7; N, 12.0. Calcd for a 3:7 mixture of the above products: C, 22.0; H, 4.12; B, 18.5; Cl, 44.2; N, 11.3. Found: C, 22.0; H, 4.51; B, 18.6; Cl, 44.1; N, 10.8.

1,10-$B_{10}Cl_8(CN)_2^{2-}$. 1,10-$Cs_2B_{10}H_8(CN)_2$[5] (2.4 g, 0.0055 mole) was dissolved in 40 ml of a 1:1 water–acetonitrile mixture. Chlorine was bubbled into the stirred solution for 90 min. The solution was evaporated and the product recrystallized from boiling water. The yield of the dry product was 2.7 g (69%). *Anal.* Calcd for $Cs_2B_{10}C_2Cl_8N_2$: B, 15.2; C, 3.38; Cl, 40.0. Found: B, 14.9; C, 3.34; Cl, 37.4.

1,10-$B_{10}Br_8(CN)_2^{2-}$. 1,10-$Cs_2B_{10}H_8(CN)_2$[5] (0.68 g, 0.13 mole) was dissolved in 40 ml of acetonitrile–water mixture and exhaustively brominated. The product contained a B–H band. Further bromination was done with sodium bromide and chlorine. The product was isolated as the Cs salt and recrystallized three times from water. *Anal.* Calcd for $Cs_2B_{10}C_2Br_8N_2$: B, 10.1; C, 2.25; Br, 60.1. Found: B, 10.3; C, 2.49; Br, 57.5. Infrared (KBr): 2210, 1605, 1212, 970 (vs, sh at 990), 992, and 841 (vs) cm^{-1}.

Halogen-Exchange Reactions. 1. A mixture of 13.6 g of $Cs_2B_{12}Br_{12}$ (0.01 mole) and 24 g (0.5 mole) of sodium chloride was dissolved in 200 ml of water at 40°, stirred, and irradiated. Samples were withdrawn after various time intervals. The product was precipitated with tetramethylammonium chloride, recrystallized from water, and analyzed to determine the number of halogens per B_{12} unit.

1. 1 hr. Found: B, 10.8; Br, 74.6; Cl, 1.86, *i.e.*, $B_{12}Br_{11.4}Cl_{0.6}$.
2. 2 hr. Found: B, 10.9; Br, 72.3; Cl, 3.36; *i.e.*, $B_{12}Br_{10.8}Cl_{1.1}$.
3. 3 hr. Found: B, 11.3; Br, 71.4; Cl, 3.90; *i.e.*, $B_{12}Br_{10.2}Cl_{1.3}$.
4. 8 hr 15 min. Found: B, 11.8; Br, 51.0; Cl, 8.90; *i.e.*, $B_{12}Br_{7.0}Cl_{2.8}$.
5. 17 hr. No precipitation with Me_4NCl.

2. In a similar experiment, 0.01 mole of $K_2B_{12}Cl_{12}$ and 0.5 mole of sodium bromide were irradiated. The solution was sampled as above.

1. 1 hr 25 min. B, 18.3; Cl, 58.0; Br, 4.92; *i.e.*, $B_{12}Cl_{11.6}Br_{0.4}$.
2. 5 hr 45 min. B, 18.2; Cl, 57.3; Br, 6.69; *i.e.*, $B_{12}Cl_{11.4}Br_{0.6}$.
3. 8 hr. B, 17.8; Cl, 57.0; Br, 8.92; *i.e.*, $B_{12}Cl_{11.2}Br_{0.8}$.
4. 21 hr. B, 18.6; Cl, 52.8; Br, 6.05; *i.e.*, $B_{12}Cl_{10.4}Br_{0.5}$.

Irradiation of $B_{12}Br_{12}^{2-}$ with Excess Fluoride Ion. $(NH_4)_2B_{12}Br_{12}$ (2.0 g) was irradiated for 45 min with 4 g of sodium fluoride in 100 ml of water. A portion of this solution was treated with $(CH_3)_4NCl$ to yield a precipitate, the separation of which was slow.[21] It was purified by recrystallization from water. *Anal.* B, 10.7; Br, 50.3; F, 9.94. This fits no rational formula but indicates loss of 4.4 atoms of bromine and introduction of 6.3 atoms of fluorine per B_{12} unit.

The original solution was irradiated for another hour, at which time it gave no precipitate with $(CH_3)_4N^+$ or $(C_2H_5)_4N^+$ and very little with $(C_3H_7)_4N^+$ ion. The precipitate contained little fluorine (1.78%) and the amount was to small too permit conclusions.

$B_{12}Br(COOH)_9H_2^{2-}$ and $B_{12}Br_2(COOH)_8H_2^{2-}$. One gram of a 1:1 mixture of $[(CH_3)_4N]_2B_{12}Br(CN)_9H_2$ and $[(CH_3)_4N]_2B_{12}Br_2(CN)_8H_2$ was stirred for 1 hr in 20 ml of concentrated sulfuric acid above 200°. The solution was cooled and poured onto ice along with tetrapropylammonium bromide. The resulting solid was collected, washed with water, and then converted to the free acid *via* ion exchange. The acid eluate was evaporated to dryness and then refluxed overnight in 15% sodium hydroxide. Tetrapropylammonium bromide was added to the solution which was then acidified with hydrochloric acid. A solid precipitated. It was filtered and air-dried (in the course of drying, it seemed to liquefy, then to resolidify, and remain unchanged thereafter), then dried at 113°(1 mm). There was obtained 0.85 g of white solid, which softened above 320° and decomposed sharply at 355°. *Anal.* Calcd for $C_{32.5}H_{66.5}B_{12}Br_{1.5}N_2$ (*i.e.*, a 1:1 mixture of $[(C_3H_7)_4N]_2B_{12}H_2Br(COOH)_9$ and $[(C_3H_7)_4N]_2B_{12}H_2Br_2(COOH)_8$): C, 38.8; H, 6.61; B, 12.9; Br, 11.9; N, 2.78. Found: C, 39.0; H, 6.85; B, 12.7; Br, 11.9; N, 2.83.

The infrared spectrum shows intense carbonyl absorption with peaks at 1700, 1660, and 1600 cm^{-1} along with broad absorption in the 2400–3000-cm region.

$B_{12}Br_{11}N_3^{2-}$. A mixture of 113 g (0.1 mole) of $(NH_4)_2B_{12}Br_{12}$ and 156 g (2.4 moles) of sodium azide was dissolved in 1 l. of water and irradiated for 2 hr. The solution was cooled, and the product was precipitated by adding excess cesium fluoride. It was recrystallized from water and obtained as a colorless solid in 81-g (61%) yield. An additional 15 g was obtained by adding excess tetramethylammonium chloride to the filtrate. *Anal.* Calcd for $Cs_2B_{12}Br_{11}N_3$: B, 9.88; Cs, 20.2; N, 3.19; Br, 66.6. Found: B, 10.0; Cs, 20.5; N, 3.06; Br, 64.8.

$B_{12}Br_{10}(N_3)_2^{2-}$. A mixture of 0.01 mole of $(NH_4)_2B_{12}Br_{12}$ and 0.36 mole of sodium azide was dissolved in 150 ml of water and irradiated for 90 min. The product was precipitated by adding excess cesium fluoride and was purified by recrystallization from water. There was obtained 6.7 g of dried salt. *Anal.* Calcd for $Cs_2B_{12}Br_{10}N_6$: B, 10.2; Br, 62.5; N, 6.55. Found: B, 11.2; Br, 62.4; N, 5.55.

$B_{12}Br_{11}OCN^{2-}$. A solution of 0.01 mole of $(NH_4)_2B_{12}Br_{12}$ and 0.36 mole of potassium cyanate in 270 ml of water was irradiated for 90 min. The product was precipitated by addition of excess tetramethylammonium chloride and recrystallized from aqueous acetonitrile to give 6.0 g of a white solid. The infrared spectrum is characterized by bands at 2275 (s), 1080, 1050, 1006, and 987 cm^{-1}. *Anal.* Calcd for $C_9H_{24}B_{12}Br_{11}N_3O$: C, 9.02; H, 2.00; B, 10.8; Br, 73.3; N, 3.50. Found: C, 9.36; H, 2.36; B, 10.9; Br, 71.0; N, 3.32.

$B_{12}Br_{10}(OH)_2^{2-}$. A mixture of 100 g of $(NH_4)_2B_{12}Br_{12}$ and 230 g of potassium cyanate was dissolved in 1 l. of water and irradiated for 80 min. It was then left at room temperature for 48 hr. The product was precipitated by adding excess tetramethylammonium chloride and recrystallized from aqueous acetonitrile. It was obtained in 27-g (25%) yield. The material was converted to the cesium salt *via* the free acid and recrystallized twice from water. Its infrared spectrum contains a hydroxyl band at 3300 cm^{-1}. *Anal.* Calcd for $Cs_2B_{12}Br_{10}(OH)_2$: B, 10.5; Br, 64.8; N, 0.00. Found: B, 10.5; Br, 64.3; N, 0.10.

$B_{12}Br_9(OCN)_2OH^{2-}$. A mixture of 0.01 mole of $(NH_4)_2B_{12}Br_{12}$ and 0.36 mole of potassium cyanate was dissolved in 200 ml of water and irradiated for 105 min. The product was precipitated with tetramethylammonium chloride and recrystallized from 1 l. of water. There was obtained 2.8 g of colorless solid. *Anal.* Calcd

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(21) No precipitate could be obtained using CsF as precipitant. It was found in a separate experiment that sodium fluoride *per se* did not hinder precipitation of $Cs_2B_{12}Br_{12}$.

for $C_{10}H_{25}B_{12}Br_9N_4O_3$ (*i.e.*, $[(CH_3)_4N]_2B_{12}Br_9(OCN)_2OH$): C, 10.9; H, 2.27; B, 11.8; Br, 65.3; N, 5.08. Calcd for $C_{10}H_{27}$-$B_{12}Br_9N_4O_4$ (*i.e.*, $[(CH_3)_4N]_2B_{12}Br_9(OCN)_2OH \cdot H_2O$): C, 10.7; H, 2.42; B, 11.6; Br, 64.5; N, 5.02. Found: C, 10.6; H, 2.24; B, 11.6; Br, 65.0; N, 4.52. Analysis thus does not permit a distinction between anhydrous material and the monohydrate.

$B_{12}Br_{11}(OC_6H_5)^{2-}$. A mixture of 11.6 g of $(NH_4)_2B_{12}Br_{12}$, 22.5 g of phenol, and 13.5 g of potassium hydroxide was dissolved in 270 ml of water and irradiated for 26 hr. The dark brown suspension was filtered, and the product was precipitated with tetramethylammonium chloride. It was further purified by recrystallization from aqueous acetonitrile, conversion to the free acid *via* ion exchange, and then to the cesium salt which was recrystallized from water. *Anal.* Calcd for $Cs_2B_{12}Br_{11.5}(OC_6H_5)_{0.5}$: B, 9.54; Br, 67.4; C, 2.64; H, 0.18. Found: B, 9.40; Br, 66.7; C, 2.77; H, 0.80. This corresponds to a 1:1 mixture of $B_{12}Br_{12}{}^{2-}$ and $B_{12}Br_{11}(OC_6H_5)^{2-}$.

$B_{12}Br_{11}OCNH_2{=}C(CN)_2{}^{2-}$. A mixture of 11.3 g of $(NH_4)_2$-$B_{12}Br_{12}$ and 35.3 g (0.1 mole) of potassium carbamyldicyanomethanide (0.24 mole) was dissolved in 250 ml of water and irradiated for 26 hr. Addition of excess tetramethylammonium chloride precipitated 11.0 g of crude product which was purified by recrystallization from aqueous acetonitrile. There was obtained 6.0 g of crystalline material containing a weak CN band at 2200 cm^{-1}. *Anal.* Calcd for $B_{12}Br_{11.5}C_{10}H_{25}O_{0.5}N_{3.5}$: C, 9.59; H, 2.00; B, 10.4; Br, 73.5; N, 3.92. Found: C, 9.46; H, 2.22; B, 10.2; Br, 73.5; N, 3.36. This corresponds to a 1:1 mixture of $B_{12}Br_{12}{}^{2-}$ and $B_{12}Br_{11}OCNH_2{=}C(CN)_2{}^{2-}$.

Irradiation of $B_{12}Br_{12}{}^{2-}$ in the Presence of Excess Thiocyanate Ion. A mixture of 20 g of $Cs_2B_{12}Br_{12}$ and 20 g of potassium thiocyanate was stirred and irradiated for 41 hr in 270 ml of water. The clear yellow solution was treated with excess cesium fluoride and the precipitated solid was recrystallized from water yielding 5.8 g of crystalline material. *Anal.* Found: C, 0.56; H, 0.67; B, 11.4; Br, 59.8; Cs, 21.6; S, 5.86. $Cs_2B_{12}Br_{10}(SCN)_2$ requires: C, 1.83; B, 9.92; Br, 61.2; Cs, 20.3; S, 4.38. $Cs_2B_{12}Br_9(SCN)_3$ requires: C, 2.79; B, 10.1; Br, 55.8; Cs, 20.6; S, 7.44. Partial hydrolysis of the thiocyanate groups to mercapto groups may have occurred and the exact nature of substituents is hard to decide from the analytical data. The presence of some SCN groups is indicated by a band at 2130 cm^{-1}. The Cs:B:Br:S ratio is 2:12:9.4:2.3 so that a rough correspondence exists between the number of bromine atoms lost and sulfur atoms gained.

$B_{10}Cl_8(CO)_2$ (Equatorial CO)? One gram of $Cs_2B_{10}Cl_8(CN)_2$ (equatorial CN) was stirred in 8 ml of boiling, concentrated sulfuric acid for several minutes. A deep violet solution formed which was left standing overnight and the poured dropwise into ice-water. There was obtained 0.63 g of a solid which had no CN bands in the infrared and contained a broad band at 1630 cm^{-1}.

This material (0.55 g) was refluxed overnight in 20 ml of 5% sodium hydroxide. Ammonia was evolved. The solution was then run through an ion-exchange resin and the acidic eluate was collected and evaporated to dryness. Pyrolysis of the residue in a sublimer tube at *ca.* 200° (1 mm) gave a small amount of purple sublimate which was followed at *ca.* 250° (1 mm) by a yellowish orange sublimate. The latter was exceedingly hygroscopic.

The infrared spectrum was characterized by bands at 2170 (s), 1130 (w), 1020 (s), 950 (w), and 840 (m) cm^{-1}, which would suggest a dicarbonyl structure.