strong, directed bonds is involved. Such bonds are only mobile at high temperature and, in addition, often require the presence of a catalyst to orient atoms for bond formation properly. (3) Regardless of the thermodynamic requirements for the synthesis of a given group IV analog, high pressure is often required just to "contain" reactants which may be quite volatile at the required temperature. Today's high pressure, high temperature equipment is admirably capable of doing this job. Substances such as sulfur are easily contained at temperatures of 1500°.

It is hoped that this paper, in calling attention to the unsymmetrical group IV analogs, will incite inorganic chemists to attempt their synthesis. These compounds far outnumber the symmetrical analogs and should be very important to solid state technology.

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Chemistry of Boranes.[1] XXV. Synthesis and Chemistry of Base Derivatives of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$

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A series of new base derivatives of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ has been prepared from the acid-catalyzed reaction of certain Lewis bases with the parent anions. These derivatives have the composition $B_{10}H_9L^-$, $B_{12}H_{11}L^-$, $B_{10}H_8L_2$, and $B_{12}H_{10}L_2$ in which the ligand may be sulfone, sulfonamide, urea, nitrile, nitrobenzene, or iodobenzene. The stereochemistry of these reactions has been qualitatively assayed. The reactivity of these base derivatives toward electrophilic reagents, such as D_3O^+ and halogen, is lower than that of the parent ions.

Previous papers dealing with the derivative chemistry of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ described derivatives in which one or two hydride ions had been replaced by common Lewis base ligands such as amines, carboxamides, sulfides, phosphines, and arsines and also by nitrogen and carbon monoxide.[1-10] We have found that other Lewis base derivatives of the polyhedral borane anions can be prepared by acid-catalyzed reactions of these anions with sulfones, sulfonamides, nitriles, amides, or nitrobenzene. The synthesis of these new base derivatives and a comparison of their properties with those of the previously described base derivatives are the subjects of this paper.

Synthesis.—Under acidic conditions, the $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ ions react with certain Lewis bases to give hydrogen and $B_{10}H_9L^-$ or $B_{12}H_{11}L^-$ species. Reaction

$$H^+ + B_{12}H_{12}^{2-} + L \longrightarrow H_2 + B_{12}H_{11}L^- \qquad (1)$$

rate varies with the nature of L and is a direct function of acid concentration. Water markedly reduces the reaction rate. For example, sulfone reactions proceed at 25° if water is essentially absent; but, if significant amounts of water are present, moderate reaction rates are not achieved until the temperature is raised to 70–90°. We believe (*vide infra*) that protonated forms of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ are reaction intermediates in (1), and this is consistent with the rate-dependence on acid and water concentrations because the polyhedral borane ions are the conjugate bases of very strong acids.[11]

Under forcing conditions, the monobase derivatives react further with base to give the neutral derivatives

$$H^+ + B_{12}H_{11}L^- + L \longrightarrow H_2 + B_{12}H_{10}L_2 \qquad (2)$$

The course of the base–borane reaction can be accurately followed by the hydrogen evolution since in general the activation energies for reactions 1 and 2 are significantly different for a given base. This difference may be attributable to the relative ease of protonation of $B_{12}H_{12}^{2-}$ and $B_{12}H_{11}L^-$.

Operable Lewis bases for reactions 1 and 2 are sulfones, sulfonamides, tetramethylurea, nitriles, and nitrobenzene. Under nearly anhydrous conditions, amides react in a similar fashion.[5] As discussed below, we believe the linkage is B–O in sulfone, amide, tetramethylurea, and nitrobenzene derivatives and B–N in sulfonamide and nitrile derivatives. Thus it appears

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that the atom of highest electron density in the base is the site of attack by the boron polyhedra. We therefore prefer to categorize reactions 1 and 2 as nucleophilic substitutions catalyzed by acid. The role of the acid may be protonation of the $B_{10}H_{10}^{2-}$ or $B_{12}H_{12}^{2-}$ polyhedron to effectively generate an electrophilic site. A similar proposal was made for a number of other B_{10} and B_{12} substitution reactions.[5]

Reaction of $B_{10}H_{10}^{2-}$ and iodosobenzene occurs under essentially neutral conditions, and no hydrogen is evolved. The product is not $B_{10}H_9OIC_6H_5^-$ but $B_{10}H_9IC_6H_5^-$. Thus, this reaction cannot be grouped with the above acid-catalyzed nucleophilic substitutions. This reaction bears a similarity to the reaction of dimethyl sulfoxide[2] with $B_{10}H_{10}^{2-}$

$$(CH_3)_2SO + B_{10}H_{10}^{2-} \longrightarrow B_{10}H_9S(CH_3)_2^- + OH^-$$

$$C_6H_5IO + B_{10}H_{10}^{2-} \longrightarrow B_{10}H_9IC_6H_5^- + OH^-$$

and may involve electrophilic attack on the B_{10} polyhedron.

Stereochemistry.—In reaction 1, $B_{10}H_{10}^{2-}$ may undergo substitution at either an apical (1) or equatorial (2) site. We found that for all of the oxygen-bonded products (sulfones and amides), the major, if not sole, isomer is the equatorial one. In the nitrile and iodosobenzene products the major isomer appears to be the apical one.[12] This is further evidence[1] that any simple correlation of position of attack in $B_{10}H_{10}^{2-}$ by various reagents with such things as ground-state charge distribution fails.

For initial attack of $B_{12}H_{12}^{2-}$ all positions are equivalent, whereas there are three stereochemically unique positions in $B_{12}H_{11}L^-$. In the bis(tetramethylenesulfone) derivatives of $B_{12}H_{12}^{2-}$ there appears to be one major isomer, probably the 1,7- isomer, whereas in bisamide derivatives all three possible isomers are probably formed.

The atom through which a base is bonded to a boron of the B_{10} or B_{12} polyhedron has not been rigorously proved in most cases. Simple valence bond considerations suggest that sulfones and nitrobenzene would be bonded through oxygen and that nitriles would be bonded through nitrogen. The dimethylformamide product from $B_{10}H_{10}^{2-}$ was shown by proton resonance[5] to be B–O bonded. This adduct was readily hydrolyzed by aqueous base to replace the amide residue with OH^-.

$$B_{10}H_9OCHN(CH_3)_2^- + OH^- \longrightarrow B_{10}H_9OH^{2-} + OCHN(CH_3)_2$$

The ready replacement of sulfones and all carboxamides by hydroxide ion in aqueous base in both the B_{10} and B_{12} series argues for B–O bonding in all of these derivatives. The single methyl group proton resonance of the $B_{12}H_{11}OC[N(CH_3)_2]_2^-$ is also consistent with B–O bonding. The nitrile derivatives, which must be bonded to boron through nitrogen, are not cleaved by aqueous base. However, another reaction does occur. They cleanly hydrate to amide derivatives which, in contrast to the dimethylformamide derivative mentioned above and known to be bonded through oxygen, are not cleaved by aqueous base.

$$B_{10}H_9N{\equiv}CCH_3^- + H_2O \longrightarrow B_{10}H_9NH_2COCH_3^-$$

The sulfonamide derivatives could be bonded either through oxygen or nitrogen. Their resistance to hydrolysis by aqueous alkali argues for the latter choice.

The monobase derivatives $B_{10}H_9L^-$ and $B_{12}H_{11}L^-$ are susceptible to electrophilic substitutions at the BH sites, but the reactivity of these monoanions is significantly lower than that of the parent dianions $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$. Reactivity is drastically reduced in the neutral derivatives. For example, deuteration of $B_{12}H_{10}L_2$ species does not occur at measurable rates in strongly acidic media up to 100°. Halogenation of the neutral derivatives does occur under mild conditions, but after the introduction of several halogen atoms the rate is greatly lowered and it is difficult to effect complete halogenation. A number of halogenation reactions with various types of $B_{12}H_{11}L^-$ and $B_{12}H_{10}L_2$ species are described in the Experimental section.

Experimental

$2\text{-}B_{10}H_9OS(O)(CH_2)_4^-$.—A mixture of 1.54 g. (10 mmoles) of $(NH_4)_2B_{10}H_{10}$, 15 ml. of tetramethylene sulfone, and 3.92 g. (22 mmoles) of anhydrous *p*-toluenesulfonic acid was stirred in a bath heated at 85° for 70 min., at which time gas evolution had ceased. The mixture was cooled, diluted with water, and treated with a mixture of aqueous tetramethylammonium hydroxide and tetramethylammonium chloride to give 2.77 g. (89%) of $(CH_3)_4N[2\text{-}B_{10}H_9OS(O)(CH_2)_4]$ as a white solid, m.p. 185–186° dec. Recrystallization of a small sample of the product from water did not change the infrared spectrum appreciably. Recrystallization of a portion of the product from acetonitrile–methanol gave large crystals, m.p. 195–196° dec.

Anal. Calcd. for $(CH_3)_4NB_{10}H_9(O_2SC_4H_8)$: C, 30.8; H, 9.4; B, 34.7; N, 4.5; S, 10.3. Found: C, 31.1; H, 9.3; B, 34.7; N, 4.3; S, 10.4.

The infrared spectrum of the product showed absorption at 2500, 1300, 1255, 1030, 1005, 985, and 952 cm.$^{-1}$.

Hydrolysis of $(CH_3)_4N[2\text{-}B_{10}H_9OS(O)(CH_2)_4]$.—A mixture of 3 g. (9.65 mmoles) of $(CH_3)_4N[2\text{-}B_{10}H_9OS(O)(CH_2)_4]$ and 50 ml. of 10% sodium hydroxide solution was boiled for 1 hr. An additional 1 g. of sodium hydroxide was added, and boiling was continued for 30 min. The solution was cooled and poured through an ion-exchange column (acid). The effluent was neutralized with cesium hydroxide and evaporated. The residue was washed with ethanol and ether to give 4.93 g. of white solid. Crystallization of a portion of the product from aqueous ethanol gave colorless needles of $Cs_2[2\text{-}B_{10}H_9OH]$.

Anal. Calcd. for $Cs_2B_{10}H_{10}O$: H, 2.6; B, 27.0. Found: H, 2.7; B, 26.7.

The infrared spectrum of the product was identical with that of authentic $Cs_2[2\text{-}B_{10}H_9OH]$.[5]

An aqueous solution of 1.8 g. of crude $Cs_2[2\text{-}B_{10}H_9OH]$ was passed through a column of sodium cation-exchange resin, and the effluent was evaporated to dryness *in vacuo*. The residue was suspended in acetonitrile containing a small amount of water, and a stream of gaseous chlorine was passed through the suspension until a yellow color persisted. The mixture was treated with water, and the acetonitrile was removed under reduced pressure. Addition of aqueous tetramethylammonium chloride and sodium hydroxide gave a precipitate, which on recrystallization from 50% aqueous ethanol gave 670 mg. of needles of $[(CH_3)_4N]_2[2\text{-}B_{10}Cl_9OH]$.

The infrared spectrum and X-ray powder pattern of the prod-

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(12) There is preferential apical attack in $B_{10}H_{10}^{2-}$ by dimethyl sulfoxide which, as noted above, may react in a similar fashion to iodosobenzene.

uct were identical with those of authentic $[(CH_3)_4N]_2[2\text{-}B_{10}Cl_9\text{-}OH]$.[5]

$B_{12}H_{11}(O_2SC_4H_8)^-$.—The hydrated acid, $H_2B_{12}H_{12}\cdot 7.1H_2O$, was readily soluble in tetramethylene sulfone, even up to equal parts of solute and solvent. The clear solutions showed strong water absorption bands in the infrared region. As a solution of 1.6 g. of the hydrated acid (5.9 mmoles) in 18 g. of tetramethylene sulfone was evaporated under high vacuum at room temperature, the water absorption at 3570 cm.$^{-1}$ decreased steadily in intensity. When the water band had all but disappeared, the solution began to evolve hydrogen. When hydrogen evolution had subsided new bands had appeared in the infrared spectrum at 1020 and 845 cm.$^{-1}$. A clear solution resulted when the reaction mixture was diluted with 2 volumes of water. One-half of the solution was neutralized with aqueous cesium hydroxide. The colorless crystalline solid which separated was recrystallized from water to give 0.6 g. of cesium salt (1.53 mmoles, 52% yield). The strong infrared bands characteristic of the $B_{12}H_{11}(O_2SC_4H_8)^-$ anion occur at 2440, 1300/1280, 1260/1235, 1075, 1055, 1025, 1010, and 990 cm.$^{-1}$.

Anal. Calcd. for $CsB_{12}H_{11}(O_2SC_4H_8)$: C, 12.2; H, 4.9; Cs, 33.7; B, 32.9; S, 8.1; neut. equiv., 393. Found: C, 11.6; H, 5.0; Cs, 33.2; B, 32.6; S, 8.4; neut. equiv., 393.

A mixture of 2.06 g. (10 mmoles) of $Na_2B_{12}H_{12}\cdot H_2O$, 15 ml. of tetramethylene sulfone, and 3.92 g. of anhydrous *p*-toluenesulfonic acid was heated in an oil bath at 85° for 115 min., at which time gas evolution had ceased. The mixture was cooled and poured into water. Addition of aqueous cesium fluoride and sodium hydroxide gave a precipitate which was collected by filtration to give 4.86 g. of white solid. Recrystallization of a portion of the product from water gave colorless crystals of $CsB_{12}H_{11}OS(O)(CH_2)_4$, the infrared spectrum of which was identical with that of the compound prepared above.

Hydrolysis of $CsB_{12}H_{11}OS(O)(CH_2)_4$.—A mixture of 200 mg. of $CsB_{12}H_{11}OS(O)(CH_2)_4$ and a stoichiometric excess of 10% sodium hydroxide was boiled briefly until solution occurred. The solution was cooled and treated wih aqueous cesium fluoride to give 160 mg. of $Cs_2B_{12}H_{11}OH$. Recrystallization of the product from water gave crystals, the infrared spectrum of which was identical with that of authentic $Cs_2B_{12}H_{11}OH$.[5]

$B_{12}H_{10}(O_2SC_4H_8)_2$.—A solution of 1.2 g. of $H_2B_{12}H_{12}\cdot 6.7H_2O$ (4.5 mmoles) in 14.3 g. of tetramethylene sulfone was evaporated under reduced pressure at room temperature as described above. When hydrogen evolution was complete at room temperature 4.5 mmoles of hydrogen had been collected. An additional 4.3 mmoles of hydrogen evolved when the mixture was heated to 95–100°. When this solution was cooled to room temperature and diluted with water, an oil separated. Upon further dilution with methanol, the oil solidified. The solid was insoluble in water and alcohol and was recrystallized from aqueous acetone. The colorless crystals melted at 217–219° and had strong characteristic infrared absorption at 2500, 1280 (1300 shoulder), 1250, 1135, 1125, 1100, 1075, 1000 (990 and 1010 shoulders), 910, and 730 cm.$^{-1}$.

Anal. Calcd. for $B_{12}H_{10}(O_2SC_4H_8)_2$: C, 25.2; H, 6.9; B, 34.1; S, 16.8. Found: C, 24.8; H, 6.9; B, 34.1; S, 16.8.

$B_{12}H_{11}[O_2S(n\text{-}C_3H_7)_2]^-$.—A solution of 1.3 g. of $H_2B_{12}H_{12}\cdot 6.7H_2O$ (4.9 mmoles) in 11.6 g. of dipropyl sulfone gave 4.7 mmoles of hydrogen when evaporated at room temperature under high vacuum. The reaction mixture was diluted with water and divided into equal portions and treated as described above to give the cesium (0.6 g., 1.42 mmoles, 58% yield) and tetramethylammonium (0.6 g., 1.64 mmoles, 70% yield) salts of the $B_{12}H_{11}[O_2S(n\text{-}C_3H_7)_2]^-$ anion. The strong infrared bands characteristic of this anion were at 2500, 1220, 1050, 1015, and 975 cm.$^{-1}$.

Anal. Calcd. for $CsB_{12}H_{11}(O_2SC_6H_{14})$: C, 17.0; H, 5.9; Cs, 31.3; B, 30.6; S, 7.6. Found: C, 17.2; H, 6.3; Cs, 30.0; B, 30.7; S, 7.6.

Anal. Calcd. for $(CH_3)_4NB_{12}H_{11}(O_2SC_6H_{14})$: C, 32.9; H, 10.2; N, 3.8; B, 35.5; S, 8.8. Found: C, 32.5; H, 10.0; N, 3.9; B, 35.7; S, 8.8.

$B_{12}H_{11}[n\text{-}C_6H_{13}SO_2N(C_2H_5)_2]^-$.—A sample of hydrated $H_2B_{12}H_{12}$ acid (10.4 g.) did not dissolve in 33 g. of N,N-diethyl-1-hexanesulfonamide at room temperature until most of the water of hydration had been removed by evaporation under high vacuum at room temperature. Hydrogen evolved and the mixture was held at 40° until evolution subsided. Two small samples of the reaction mixture were removed, diluted with 1:1 water–alcohol, and neutralized with aqueous tetramethylammonium hydroxide and cesium hydroxide, respectively. The white solids which separated on cooling were recrystallized from hot water.

Anal. Calcd. for $(CH_3)_4NB_{12}H_{11}[C_6H_{13}SO_2N(C_2H_5)_2]$: C, 38.6; H, 10.7; N, 6.4; B, 29.8; S, 7.3. Found: C, 38.4; H, 10.5; N, 6.4, 6.2; B, 29.7; S, 7.3.

Anal. Calcd. for $CsB_{12}H_{11}[C_6H_{13}SO_2N(C_2H_5)_2]$: C, 24.2; H, 6.9; Cs, 26.8; N, 2.8; B, 26.2; S, 6.5. Found: C, 24.8; H, 7.2; Cs, 26.1; N, 2.8, 3.0; B, 25.2; S, 6.3.

The strong infrared frequencies characteristic of the $B_{12}H_{11}[C_6H_{13}SO_2(NC_2H_5)_2]^-$ anion were at 2500, 1300, 1200, 1090, 1040 (1055 and 1010 shoulders), 980, 955, 850, 840, 795, and 720 cm.$^{-1}$.

The bulk of the reaction mixture was heated to 90° and then to 195°. The evolution of more hydrogen at the elevated temperatures indicated the formation of a neutral $B_{12}H_{10}(\text{ligand})_2$ species, but attempts to isolate it were unsuccessful.

Bromination of $B_{12}H_{11}$(N,N-diethyl-1-hexanesulfonamide)$^-$.—Bromine (0.35 ml., 6.8 mmoles) was added to a refluxing solution of 0.49 g. (1 mmole) of $CsB_{12}H_{11}\cdot N(C_2H_5)_2SO_2C_6H_{13}$ in about 20 ml. of 1,2-dichloroethane until the color of excess bromine persisted. The hydrogen bromide and excess bromine were carried off in a stream of nitrogen. The solvent was removed under reduced pressure, and the residue, in aqueous methanol, was treated with an excess of tetramethylammonium chloride. Upon chilling, 0.6 g. of product (0.6 mmole, 60%) separated.

Anal. Calcd. for $(CH_3)_4NB_{12}H_{4.5}Br_{6.5}C_{10}H_{23}NSO_2\cdot 3H_2O$: C, 16.8; H, 4.6; B, 13.0; Br, 51.8; N, 2.8; S, 3.2. Found: C, 18.1; H, 4.2, 4.6; B, 13.0; Br, 51.9; N, 3.3, 3.4; S, 2.5.

$B_{12}H_{11}[C_6H_5SO_2N(C_2H_5)_2]^-$.—A few grams each of hydrated $H_2B_{12}H_{12}$ and N,N-diethylbenzenesulfonamide were mixed and held under high vacuum at 60° for about 2 hr. The mixture was taken up in alcohol to give a clear solution. A solid separated upon neutralization with aqueous cesium hydroxide. It was recrystallized from aqueous alcohol. The strong infrared bands characteristic of the $B_{12}H_{11}[C_6H_5SO_2N(C_2H_5)_2]^-$ anion occurred at 2500, 1300, 1190, 1150, 1105, 1050, 1030, 1020, 995, 945, 855, 840, 795, 735, and 685 cm.$^{-1}$.

Anal. Calcd. for $CsB_{12}H_{11}[C_6H_5SO_2N(C_2H_5)_2]$: C, 24.6; H, 5.4; Cs, 27.1; N, 2.9; B, 26.6; S, 6.6. Found: C, 22.7; H, 5.7; Cs, 26.3; N, 3.0, 3.2; B, 24.6; S, 7.0.

$B_{12}H_{11}OC[N(CH_3)_2]_2^-$.—A mixture of 30 ml. of tetramethylurea, 2 ml. of concentrated sulfuric acid, and 4 g. (21 mmoles) of $Na_2B_{12}H_{12}$ was heated at 165° until 250 ml. of gas had evolved. The mixture was cooled and treated with dilute aqueous cesium fluoride, and the precipitate was collected to give 7.1 g. (18.2 mmoles, 87%) of $CsB_{12}H_{11}OC[N(CH_3)_2]_2$. A portion of the product was purified by two recrystallizations from water.

Anal. Calcd. for $CsB_{12}H_{11}OC[N(CH_3)_2]_2$: C, 15.4; H, 5.9; B, 33.3; N, 7.2. Found: C, 15.1; H, 5.9; B, 32.8; N, 7.1.

The infrared spectrum of the product showed absorption at 2500, 1620, and 1530 cm.$^{-1}$. The proton magnetic resonance spectrum of the sodium salt of the product in D_2O showed a single sharp peak at τ 6.82 (external tetramethylsilane). The proton magnetic resonance spectrum of the tetramethylammonium salt of the product showed two nearly equal peaks in pyridine–D_2O solution consistent with $(CH_3)_4NB_{12}H_{11}OC[N(CH_3)_2]_2$.

$1\text{-}B_{10}H_9IC_6H_5^-$.—To a solution of 1.54 g. (10 mmoles) of $(NH_4)_2B_{10}H_{10}$ in 6 ml. of water and 40 ml. of acetonitrile containing a small amount of ethanol was added 2.2 g. (10 mmoles) of iodosobenzene. The resulting mixture was warmed on a steam bath until solution was nearly complete. The mixture was then filtered, and the filtrate was evaporated under reduced pressure. The residue was suspended in water and filtered to remove insoluble material (790 mg.). The filtrate was treated with cesium fluoride, and the resulting precipitate was collected by filtration to give 690 mg. of $Cs[1\text{-}B_{10}H_9IC_6H_5]$ as a white solid. Recrystallization from water gave well-formed crystals.

Anal. Calcd. for $CsB_{10}H_9IC_6H_5$: C, 15.9; H, 3.1; B, 23.8; I, 27.9; Cs, 29.3. Found: C, 15.6; H, 3.3; B, 23.8; I, 27.1; Cs, 31.3.

The ultraviolet spectrum of the product had $\lambda_{\max}^{CH_3CN}$ 296 mμ (ϵ 4090). The B^{11} n.m.r. spectrum (19.25 Mc.) of $Cs[1\text{-}B_{10}H_9IC_6H_5]$ in aqueous acetonitrile showed a doublet at 14.6 p.p.m. (J = 117 c.p.s.), a broad peak just to high field of the 14.6 p.p.m. doublet partially buried beneath the high-field half of the doublet, and a large multiplet centered at 44 p.p.m. The 14.6 p.p.m. doublet could be decoupled to a single sharp peak by double irradiation. The 44 p.p.m. multiplet could also be decoupled to a single peak. The broad peak was unaffected by irradiation at 60 Mc. The intensity ratio of the 14.6 p.p.m. doublet and the broad peak to the 44 p.p.m. multiplet was 2:8.8 (theory requires 2:8). The 14.6 p.p.m. doublet could be assigned to one unsubstituted apical boron atom, the broad peak to one substituted apical boron atom, and the 44 p.p.m. multiplet to eight unsubstituted equatorial boron atoms (two doublets). In agreement with this assignment, the intensity ratio of the low-field half of the 14.6 p.p.m. doublet to the 44 p.p.m. multiplet was 1:19 (theory requires 1:16). Thus, the 14.6 p.p.m. doublet must represent only a single unsubstituted boron atom rather than two as would be required in $2\text{-}B_{10}H_9IC_6H_5^-$.

$1\text{-}B_{10}H_9NCCH_3^-$.—A mixture of 5.33 g. (18.2 mmoles) of $[(CH_3)_4N]_2B_{10}H_{10}$, 80 ml. of acetonitrile, and 16 g. of *p*-toluenesulfonic acid was refluxed while gas evolution was measured with a wet test meter. When 50 cc. of gas had evolved, evolution ceased. The mixture was cooled and filtered to give 1.42 g. of solid. Treatment of the filtrate with ether gave 4.21 g. of additional solid. The combined solids were recrystallized from acetonitrile to give, in two crops, 1.59 g. of crystals of $(CH_3)_4N[1\text{-}B_{10}H_9NCCH_3]$. Further recrystallization from acetonitrile gave needles with m.p. >415°.

Anal. Calcd. for $(CH_3)_4NB_{10}H_9NCCH_3$: C, 31.0; H, 10.4; B, 46.5; N, 12.1. Found: C, 31.0; H, 10.5; B, 46.3; N, 12.1.

The infrared spectrum of the product showed no absorption attributable to C═N or N—H.

The B^{11} n.m.r. spectrum (19.25 Mc.) of $(CH_3)_4N[1\text{-}B_{10}H_9\text{-}NCCH_3]$ in dimethylformamide solution showed a broad multiplet in the vicinity of 16 p.p.m. (relative intensity 2.16) and a slightly distorted doublet at 44.9 p.p.m. (J = 126 c.p.s., relative intensity 7.84). On irradiating at 60 Mc., the ~16 p.p.m. multiplet became a broad single peak, and the 44.9 p.p.m. doublet collapsed to a sharp single peak. The ~16 p.p.m. multiplet can be assigned to a doublet representing one unsubstituted apical boron atom and an overlapping single peak representing one substituted apical boron atom. The 44.9 p.p.m. doublet then represents eight unsubstituted equatorial boron atoms.

$1\text{-}B_{10}H_9NH_2COCH_3^-$.—$(CH_3)_4NB_{10}H_9NCCH_3$ (450 mg.) was dissolved in boiling acetonitrile and treated with 2 ml. of water. The resulting solution was boiled nearly to dryness and then treated with acetonitrile. By gradual addition of benzene to the hot acetonitrile solution there was obtained 445 mg. of crystals of $(CH_3)_4NB_{10}H_9NH_2COCH_3$. Recrystallization from acetonitrile–benzene gave crystals with m.p. >450°.

Anal. Calcd. for $(CH_3)_4NB_{10}H_9NH_2COCH_3$: C, 28.8; H, 10.5; B, 43.2; N, 11.2. Found: C, 29.6; H, 10.7; B, 42.9; N, 11.3.

The infrared spectrum of the product showed absorption at 3100, 3280, 2400–2500, and 1645 cm.$^{-1}$.

$B_{10}H_9NH_2COC_6H_5^-$.—A mixture of 5.33 g. (20 mmoles) of $[(CH_3)_4N]_2B_{10}H_{10}$, 60 ml. of benzonitrile, and 8 g. of *p*-toluenesulfonic acid was stirred at 100–110°. When 620 cc. of gas had evolved, no further evolution occurred, and the solution was cooled and poured into excess ether. The resulting precipitate was collected by filtration and washed with ether and water to give 6.1 g. (98%) of $(CH_3)_4NB_{10}H_9NH_2COC_6H_5$ as a yellow solid. Two recrystallizations from acetonitrile–benzene gave pale yellow crystals with m.p. 232–233°.

Anal. Calcd. for $(CH_3)_4NB_{10}H_9NH_2COC_6H_5$: C, 42.3; H, 9.0; B, 34.6; N, 9.0. Found: C, 43.5; H, 9.4; B, 34.2; N, 9.3.

The infrared spectrum of the product showed absorption at 3300, 3200, 2500, 1630, 1570, 1500, and 1600 cm.$^{-1}$.

$(CH_3)_3NB_{12}H_{10}\cdot NO_2C_6H_5$.—A mixture of 2.3 g. (10.6 mmoles) of $NaB_{12}H_{11}N(CH_3)_3$, 40 ml. of nitrobenzene, and 4 g. of *p*-toluenesulfonic acid was heated at 97–100° for 1 hr. during which time 120 cc. of gas evolved. The mixture was cooled and treated with ether and water and filtered. Evaporation of the ethereal layer of the filtrate gave a dark gum which was recrystallized three times from acetone–cyclohexane to give 345 mg. of light bronze crystals of $(CH_3)_3NB_{12}H_{10}\cdot NO_2C_6H_5\cdot$acetone, m.p. >405°.

Anal. Calcd. for $(CH_3)_3NB_{12}H_{10}O_2NC_6H_5\cdot C_3H_6O$: C, 38.0; H, 8.0; B, 34.2; N, 7.4. Found: C, 38.4; H, 8.2; B, 32.8; N, 7.4.

The ultraviolet spectrum of the product in acetonitrile showed absorption at 378 mμ (ϵ 935) and 313 mμ (ϵ 8550). The infrared spectrum of the product showed absorption at 2500, 1700, 1575, 1545, and 1480 cm.$^{-1}$.

$(CH_3)_3NB_{12}H_{10}Br^-$.—To a stirred solution of 2.65 g. (10.4 mmoles) of $NaB_{12}H_{11}N(CH_3)_3\cdot H_2O\cdot {}^1/_3C_2H_5OH$ in 50 ml. of water in an ice bath was added dropwise over 30 min. a solution of 1.78 g. of N-bromosuccinimide in 50 ml. of acetonitrile. After the addition was complete, the solution was stirred for 30 min. at room temperature, and the organic solvent was removed under reduced pressure. The remaining solution was treated with aqueous cesium hydroxide, and the resulting precipitate was collected and washed with water to give 3.41 g. (8.3 mmoles, 80%) of $Cs(CH_3)_3NB_{12}H_{10}Br$. A sample was prepared for analysis by recrystallization from water.

Anal. Calcd. for $CsB_{12}H_{10}BrN(CH_3)_3$: C 8.8; H, 4.7; B, 31.5; N, 3.40; Br, 19.4. Found: C, 9.6; H, 4.7; B, 31.7; N, 3.6; Br, 19.8.

Preparation of $B_{12}H_3Br_8N(CH_3)_3^-$.—To a solution of 3 g. of $NaB_{12}H_{11}N(CH_3)_3$[4] in 60 ml. of water and 10 ml. of methanol was added bromine. An exothermic reaction occurred, and the temperature rose to about 45°. After the initial heat of reaction subsided, the temperature was raised to about 90° for 15 min., and bromine was periodically added to maintain the bromine color. Then, the reaction mixture was cooled to 45°, and chlorine was added. The temperature rose to approximately 60°. The chlorine addition was maintained at such a rate that chlorine vapor was visually discernible above the surface of the solution. The addition was continued for 15 min., and then excess chlorine was removed under reduced pressure. The reaction mixture was filtered, and the filtrate was divided into two portions; a cesium salt was precipitated from one and a tetramethylammonium salt from the other. The salts were recrystallized from a hot water–methanol mixture.

Anal. Calcd. for $(CH_3)_4NB_{12}H_3Br_8N(CH_3)_3$: C, 9.3; H, 2.7; B, 14.3; Br, 70.7; N, 3.1. Found: C, 9.4; H, 2.5; B, 14.3; Br, 70.0; N, 3.1.

Anal. Calcd. for $CsB_{12}H_3Br_8N(CH_3)_3$: C, 3.7; H, 1.3; Cs, 13.8; B, 13.4; Br, 66.3; N, 1.4. Found: C, 5.2; H, 1.5; Cs, 15.4; B, 13.3; Br, 65.1; N, 1.5.

$B_{12}H_{10}IN(CH_3)_3^-$.—To a solution of 1.1 g. (5 mmoles) of $NaB_{12}H_{11}N(CH_3)_3$[4] in 10 ml. of 1 *M* aqueous sodium acetate was added 9 ml. of 1 *N* iodine in potassium iodide solution, and the resulting solution was heated to boiling. When the color had faded the solution was filtered, and the filtrate was treated with aqueous tetramethylammonium chloride. The resulting precipitate was collected by filtration and recrystallized from water to give 1.32 g. (77%) of crystals of $(CH_3)_4N(CH_3)_3NB_{12}H_{10}I$. A sample was prepared for analysis by one additional recrystallization from water.

Anal. Calcd. for $(CH_3)_4NB_{12}H_{10}IN(CH_3)_3$: C, 21.0; H, 7.8; B, 32.5; N, 7.0; I, 31.7. Found: C, 21.1; H, 7.8; B, 31.6; N, 5.4; I, 33.4.

$B_{12}H_4I_7N(CH_3)_3^-$.—Iodine (50.8 g., 200 mmoles) was added to a slurry of $NaB_{12}H_{11}N(CH_3)_3$[4] (22.3 g., 100 mmoles) in 150 ml. of tetrachloroethylene. After the initial reaction subsided, iodine monochloride was added (0.2 mole) and the temperature was slowly raised to 70° and held there for 2 hr. The reaction mixture was cooled to room temperature and filtered. The solid product was heated with 80 ml. of water for 1 hr. at 75°, and this slurry was filtered while hot. The filtrate was divided in half. To one part of the filtrate was added aqueous tetramethylammonium chloride to give a precipitate of the corresponding salt, and to the other part aqueous cesium fluoride was added to give the cesium salt. These salts were recrystallized from a methanol–water mixture.

Anal. Calcd. for $(CH_3)_4NB_{12}H_4I_7N(CH_3)_3$: C, 7.3; H, 2.2; I, 76.9. Found: C, 6.9; H, 2.0; I, 77.0.

Anal. Calcd. for $CsB_{12}H_4I_7N(CH_3)_3$: C, 2.1; Cs, 10.9; B, 10.7; I, 73.2. Found: C, 3.4; Cs, 9.4; B, 9.3; I, 73.4.

$B_{12}Cl_7H_4N(C_2H_5)_3^-$.—A stream of chlorine was passed into a solution of $(C_2H_5)_3NHB_{12}H_{11}N(C_2H_5)_3$[4] (20 mmoles) in 50 ml. of methanol to which sufficient water had been added to cause incipient precipitation of the salt. After a few minutes the reaction temperature was raised to about 70° and held there for 1 hr. while the chlorine was passed through at a relatively rapid rate. At the end of the reaction the solution was concentrated, and then water was added to precipitate the crude salt which was then recrystallized from methanol–water.

Anal. Calcd. for $(C_2H_5)_3NHB_{12}H_4Cl_7N(C_2H_5)_3$: C, 24.7; H, 6.1; B, 22.3; Cl, 42.4. Found: C, 25.0; H, 6.3; B, 21.6; Cl, 42.5.

$B_{12}H_5Br_6N(C_2H_5)_3^-$.—The triethylammonium salt[4] of $B_{12}H_{11}N(C_2H_5)_3^-$ (20 mmoles) was dissolved in 50 ml. of methanol, and water was added until there was incipient precipitation of the salt. Bromine (*ca.* 1.4 g.) was then added to the solution, and the temperature rose to approximately 50°. The reaction mixture was heated to reflux and held there for 1 hr. Bromine was added at periodic intervals to maintain the bromine coloration. The solution was evaporated, and the crude solid was recrystallized from hot methanol–water.

Anal. Calcd. for $(C_2H_5)_3NHB_{12}H_5Br_6N(C_2H_5)_3$: C, 17.6; H, 4.4; Br, 58.7; B, 15.9. Found: C, 17.6; H, 4.6; Br, 59.5; B, 15.3.

The triethylammonium salt was dissolved in a water–methanol solution and passed through a strong-acid ion-exchange column. To the effluent was added aqueous cesium fluoride to give a precipitate which was recrystallized from water.

Anal. Calcd. for $CsB_{12}H_5Br_6N(C_2H_5)_3$: C, 8.5; H, 2.4; B, 15.3; Br, 56.6. Found: C, 8.8; H, 2.6; B, 14.9; Br, 57.4.

Bromination of $B_{12}H_{11}P(CH_3)_3^-$.—To a solution of $NaB_{12}H_{11}P(CH_3)_3$[4] in methanol cooled to 0° bromine was added dropwise until the color of excess bromine persisted. Two samples of the reaction mixture were removed. One was treated with aqueous tetramethylammonium chloride, the other with aqueous trimethylsulfonium iodide. The colorless precipitates were recrystallized from water to give the corresponding salts of $B_{12}H_7Br_4P(CH_3)_3^-$ which had characteristic infrared absorption bands at approximately 2500, 1290, 1000, 980, 950, 875, 835, 795, and 765 cm.$^{-1}$.

Anal. Calcd. for $(CH_3)_4NB_{12}H_7Br_4P(CH_3)_3$: P, 5.1; B, 21.4; N, 2.3; Br, 52.7. Found: P, 4.6; B, 20.8; N, 2.3; Br, 53.7.

Anal. Calcd. for $(CH_3)_3SB_{12}H_7Br_4P(CH_3)_3$: C, 11.8; H, 4.1; S, 5.3; B, 21.3; P, 5.1; Br, 52.4. Found: C, 11.9; H, 4.4; S, 5.4; B, 20.8; P, 5.3; Br, 47.9.

The balance of the reaction mixture was heated to reflux, and an excess of bromine was added. The mixture was cooled and treated with an excess of aqueous trimethylsulfonium iodide. The white precipitate was recrystallized from water. Elemental analysis indicates the product to be a mixture averaging 5.6 atoms of bromine per 12 boron atoms.

Anal. Calcd. for $(CH_3)_3SB_{12}H_{5.4}Br_{5.6}P(CH_3)_3$: P, 4.3; B, 18.0; S, 4.4; Br, 59.7. Found: P, 4.3; B, 18.0; S, 4.7; Br, 59.9.

$B_{12}H_6Cl_4[S(CH_3)_2]_2$ and $B_{12}H_4Cl_6[S(CH_3)_2]_2$.—Chlorine was added to a solution of $B_{12}H_{10}[S(CH_3)_2]_2$[4] (1.8 g., 7 mmoles) in tetrachloroethane at such a rate that the temperature rose rapidly to about 60°. Under these conditions a gummy solid phase separated. The temperature was slowly raised to 144° and held there for 15 min. while a slow stream of chlorine was passed through the solution. The reaction mixture was cooled to 80° and filtered. The solid product was recrystallized from an acetonitrile–carbon tetrachloride mixture.

Anal. Calcd. for $B_{12}H_6Cl_4[S(CH_3)_2]_2$: C, 11.9; H, 4.9; Cl, 35.3; B, 32.4; S, 15.9. Found: C, 12.0; H, 4.5; Cl, 36.2; B, 31.4; S, 15.9.

To the filtrate from the crude reaction product was added carbon tetrachloride. A solid phase precipitated which was recrystallized from dichloromethane.

Anal. Calcd. for $B_{12}H_4Cl_6[S(CH_3)_2]_2$: C, 10.2; H, 3.4; Cl, 45.2; S, 13.6. Found: C, 11.1; H, 3.9; Cl, 44.1; S, 13.5.

Preparation of Bromo Derivatives of $B_{12}H_{10}[S(CH_3)_2]_2$.—Excess bromine was added to a solution of $B_{12}H_{10}[S(CH_3)_2]_2$[4] (2.1 g., 8 mmoles) in 50 ml. of tetrachloroethane, and the temperature was raised to 130° for about 10 min. Bromine was added periodically to maintain the bromine coloration. The reaction mixture was filtered. Concentration of the filtrate gave solids that approximated the pentabromo derivative on analysis. The solids obtained from the reaction mixture were recrystallized from an acetonitrile–methanol mixture. One fraction analyzed fairly well for the tetrabromo derivative and a number of other fractions were obtained that approximated the tribromo derivative.

Anal. Calcd. for $B_{12}H_6Br_4[S(CH_3)_2]_2$: C, 8.3; H, 3.1; S, 11.1; Br, 55.2. Found: C, 8.1; H, 3.2; S, 11.9; Br, 52.9.

Bromine was added slowly at room temperature to a dichloromethane solution of 0.40 g. of $B_{12}H_{10}[S(CH_3)_2]_2$, in which was suspended an excess of anhydrous sodium carbonate. When the color of excess bromine persisted, addition was discontinued. The mixture was filtered, the filtrate was evaporated to dryness, and the residue was recrystallized from hot ethanol to give 0.25 g. of colorless crystals, m.p. 205–240° dec.

Anal. Calcd. for $B_{12}H_8Br_2[S(CH_3)_2]_2$: C, 11.4; H, 4.5; Br, 37.9; S, 15.2. Found: C, 12.0; H, 4.7; Br, 38.7; S, 14.1.

Preparation of $B_{12}H_4Br_7S(n\text{-}C_3H_7)_2^-$.—Bromine was slowly added to a solution of $CsB_{12}H_{11}S(n\text{-}C_3H_7)_2$[4] (1 mmole) in 40 ml. of water and 5 ml. of methanol. The reaction mixture was slowly warmed to near reflux, and bromine was added periodically over a period of 15 min. to maintain the bromine color. The reaction mixture was filtered, and tetramethylammonium chloride was added to the filtrate to precipitate the corresponding salt which was recrystallized from methanol–water, m.p. 185–187.5°.

Anal. Calcd. for $(CH_3)_4NB_{12}H_4Br_7S(n\text{-}C_3H_7)_2$: C, 13.6; H, 3.0; Br, 63.1; S, 3.6. Found: C, 14.7; H, 3.7; Br, 62.6; S, 3.7.

Bromination of $B_{10}H_9$(N-methylpyrrolidone)$^-$.—A solution of 3.9 g. (10 mmoles) of $(n\text{-}C_3H_7)_4NB_{10}H_9\cdot C_5H_9NO$ in about 25 ml. of 1,2-dichloroethane was heated to reflux while bromine (4.1 ml., 80 mmoles) was added dropwise until the color of free bromine persisted. The hydrogen bromide which had formed and the excess bromine were carried out of the hot mixture with a stream of nitrogen. The product was not completely soluble in the hot mixture. Filtration of the hot suspension gave 4.8 g. of insoluble solid, and cooling the hot filtrate gave an additional 1.7 g. of white solid having an infrared spectrum identical with that of the first crop. The combined 6.5 g. of crude material (60% yield) was recrystallized in 55% recovery from aqueous acetonitrile as glistening transparent needles.

Anal. Calcd. for $(C_3H_7)_4NB_{10}H_{0.5}Br_{8.5}C_5H_9NO$: C, 19.0; H, 3.5; B, 10.0; Br, 63.3; N, 2.6. Found: C, 18.9, 19.1; H, 3.4, 3.4; B, 10.0; Br, 63.2; N, 2.7, 2.9.

Bromination of $B_{10}H_8$(N-methylpyrrolidone)$_2$.—Bromine was added dropwise to a refluxing solution of 3.1 g. (10 mmoles) of $B_{10}H_8$(N-methylpyrrolidone)$_2$ in 25 ml. of 1,2-dichloroethane until the color of excess bromine persisted. The bulk of the product (4.9 g., 59% yield) was insoluble in the hot reaction mixture, and 0.5 g. of material of similar infrared spectrum separated on chilling the hot filtrate. A suitable recrystallization solvent was not found. The major crop was insoluble in hot acetone, acetonitrile, and 1,2-dichloroethane. It was soluble in a hot mixture of acetonitrile and 1,2-dichloroethane but did not separate on cooling. The crude material was extracted for several hours with 1,2-dichloroethane in a Soxhlet extractor. No solid separated from the solvent on chilling. The material in the thimble was dried and analyzed.

Anal. Calcd. for $B_{10}H_{1.5}Br_{6.5}(C_5H_9NO)_2$: C, 14.6; H, 2.4; B, 13.1; Br, 62.7; N, 3.4. Found: C, 14.4, 14.8; H, 2.8, 2.7; B, 13.1; Br, 62.7; N, 2.8, 2.8, 3.2.

Notes

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The Iodides of Phosphorus. II. The Reaction of Bromine with Diphosphorus Tetraiodide

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Although a large number of mixed phosphorus trihalides are possible only a few have been prepared. Those that have been isolated include $PClF_2$,[1,2] PCl_2F,[1,2] $PBrF_2$,[3] and PBr_2F.[3] Others have been identified in the course of ebullioscopic,[4] Raman spectral,[4] and n.m.r.[5] studies. In each case their preparation or identification has involved either halogen exchange or reorganization reactions. We have investigated the reaction of bromine with P_2I_4 as a possible route to the new mixed trihalide $PBrI_2$, since reaction of stoichiometric quantities of halogen with other compounds involving one P–P bond, such as organo-substituted diphosphines, results in excellent yields of the corresponding monohalo compounds.[6]

Experimental

The compound P_2I_4 was prepared by the procedure of Germann and Traxler.[7] The bromine and CS_2 were both reagent grade chemicals. The CS_2 was dried over CaH_2 and carefully fractionated before use. All operations were carried out either *in vacuo* or under a dry nitrogen atmosphere.

In a typical run 5.709 g. (35.7 mmoles) of Br_2 in 100 ml. of CS_2 was added dropwise with stirring to 20.347 g. (35.7 mmoles) of P_2I_4 dissolved in 400 ml. of CS_2. The orange color of the P_2I_2 was gradually darkened during the addition. Removal of the CS_2 under reduced pressure left a deep red liquid, $d = 3.53$ g./ml. and f.p. 8–12°; yields were ~90% assuming the product to be $PBrI_2$.

Anal. Calcd. for $PBrI_2$: Br, 21.91; I, 69.60; P, 8.49. Found: Br, 21.74, 21.92; I, 69.50, 69.40; P, 8.48, 8.57.

The infrared spectra (in CS_2 or CH_2Cl_2 solution) were measured in a CsI solution cell on a Beckman IR 7 spectrophotometer equipped with CsI optics. The P^{31} n.m.r. spectra were recorded on a Varian V-4300B spectrometer operating at 24.3 Mc. For the percentage composition measurements the signal-to-noise ratio was improved by time averaging with a Nuclear Data, Inc., Model 800 digital memory oscilloscope. The mass spectra were measured on a CEC 21-102 instrument equipped with a heated inlet system.

Results and Discussion

The infrared spectrum of the reaction product showed peaks at 379 and 329 cm.$^{-1}$ with a shoulder at 306 cm.$^{-1}$. The 379 cm.$^{-1}$ peak is assigned to P–Br stretching and the 329 cm.$^{-1}$ absorption plus the 306 cm.$^{-1}$ shoulder is assigned to P–I stretching.

Although the analytical and infrared data are in agreement with the formulation $PBrI_2$, subsequent n.m.r. and mass spectral studies have indicated that the product is a mixture. The mass spectrum (room temperature) of the reaction product showed peaks, together with the appropriate isotopic intensity distributions, corresponding to PI_3^+, $PBrI_2^+$, PBr_2I^+, PI_2^+, I_2^+, $PBrI^+$, PBr_2^+, PI^+, I^+, PBr^+, and Br^+, suggesting that the liquid is a mixture of PI_3, PBr_3, and the two new mixed trihalides, $PBrI_2$ and PBr_2I. This result was confirmed by the P^{31} n.m.r. spectrum of the pure liquid (Figure 1), which showed peaks at -184, -208, -223, and -227 p.p.m. relative to 85% H_3PO_4. We assign the -184 and -227 p.p.m. peaks to PI_3 (-178 p.p.m.[8]) and PBr_3 (-227 p.p.m.[9]); hence it is reasonable to attribute the -208 and -223 p.p.m. peaks to $PBrI_2$ and PBr_2I, respectively, on the basis that there is evidence for these molecules in the mass spectrum. As estimated from the areas under the n.m.r. peaks the composition of the mixture is 8.2% PBr_3, 13.8% PBr_2I, 33.2% $PBrI_2$, and 44.8% PI_3. Because of the discrepancy between our value for the chemical shift of PI_3 in the reaction mixture (-184 p.p.m.) and that reported[8] for pure PI_3 (-178 p.p.m.), we decided to redetermine the chemical shift of PI_3 (in CS_2 solution). However, since our value (-179 p.p.m.) confirmed the earlier result, the PI_3 resonance is apparently shifted downfield by dissolution in the other halides.

The fact that good analyses are obtained for the composition $PBrI_2$ suggests that reaction proceeds to $PBrI_2$ initially. If this is the case two reactions that could give rise to the observed products are

$$2PBrI_2 \rightleftharpoons PBr_2I + PI_3$$

$$3PBr_2I \rightleftharpoons 2PBr_3 + PI_3$$

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