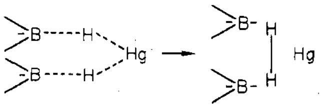
of molecular hydrogen. The nonbridge hydrogens appear to be favored in the nonstatistical distribution of the product. This supports the arguments that the hydrogen molecule is formed in a concerted reaction with $Hg(^3P_1)$. The coordination of the $Hg(^3P_1)$ atom to a pair of hydrogen atoms in pentaborane results in the formation of the hydrogen molecule. Structures I and II in reaction 22 are a schematic repre-



I II (22)

sentation of the interaction. A similar interpretation is reported for the $Hg(^3P_1)$ photosensitization of propane.[20] The side-on orientation of Hg to $H_2$ is consistent with Callear's[21] study of the reaction of $Hg(^3P_{1,0})$ with hydrogen.

**Acknowledgment.** We are grateful for support of this work by the National Science Foundation (Grant No. CHE 76-02477).

**Registry No.** $B_5H_9$, 19624-22-7; $B_5D_9$, 24034-84-2; 1-$DB_5H_8$, 63643-91-4; ($\mu$-D)$B_5H_8$, 16743-79-6; 1-methylpentaborane, 19495-55-7; 2-methylpentaborane, 23753-74-4.

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# Boron Halide Clusters and Radicals: Synthesis and Interconversions of the Three Oxidation States of a Nine-Boron Polyhedron

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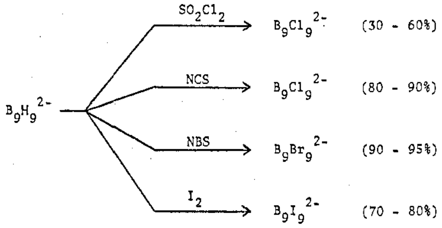
The facile synthesis of the perhalogenated nonahydrononaborates $B_9X_9^{2-}$ (X = Cl, Br, I) under aprotic conditions from $B_9H_9^{2-}$ is described. Oxidations of the perchloro and perbromo anions have yielded the corresponding neutral clusters $B_9Cl_9$ and $B_9Br_9$. Novel borane radicals of the type $B_9X_9^{-}\cdot$ (X = Cl, Br, I) have been isolated as air-stable, colored salts via chemical oxidation of $B_9X_9^{2-}$ or reduction of $B_9X_9$. The redox sequence $B_9X_9^{2-} \rightleftharpoons B_9X_9^{-}\cdot \rightleftharpoons B_9X_9$ has been established. It is likely that all three oxidation states retain the basic tricapped trigonal-prismatic ($D_{3h}$) geometry characteristic of the parent $B_9H_9^{2-}$ structure. This behavior is unusual for nonmetallic polyhedra, and extensive involvement of the halogen substituents in cage bonding is suggested.

## Introduction

The family of polyhedral boranes $B_nH_n^{2-}$ ($6 \leq n \leq 12$) have exceptional stability as predicted by theoretical MO calculations and empirical electron-counting rules.[2,3] These species have closed-shell electron configurations with the requisite $(2n + 2)$ skeletal electrons. Formally, the $(2n + 1)$ family of $B_nH_n^{-}\cdot$ radicals and $2n$ neutral $B_nH_n$ species can be generated by one- and two-electron oxidations, respectively. Indeed an EPR spectrum from the probable $B_{10}H_{10}^{-}\cdot$ radical has been observed in the electrolytic oxidation of $B_{10}H_{10}^{2-}$.[4] A well-resolved, complex EPR spectrum obtained during the air oxidation of $B_9H_9^{2-}$ in ethereal solvents has been used to support the existence of $B_8H_8^{-}\cdot$ as one of the transient products.[5] Nevertheless, neither of these unstable anions was isolable.

Scheme I



The hypothetical $B_nH_n$ neutral boranes should be extremely unstable and none has been observed to date.

In sharp contrast, the perhalogenated derivatives of these boranes are well established in both the dianionic and neutral oxidation states. For example, $B_{10}Cl_{10}^{2-}$, $B_{10}Br_{10}^{2-}$, $B_{12}Cl_{12}^{2-}$, and $B_{12}Br_{12}^{2-}$ are known as are the neutral clusters $B_4Cl_4$, $B_8Cl_8$, $B_9Cl_9$, $B_9Br_9$, and $B_9Cl_8H$.[6,7] Massey's investigations have definitively established the existence and geometry of the neutral nine-boron halide clusters $B_9Cl_9$ and $B_9Br_9$.[7b,7d] The stability of these clusters in spite of their being formally two-electron deficient ($2n$ skeletal electrons) has been postu-

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(1) University of New Hampshire.

(2) (a) W. N. Lipscomb, "Boron Hydrides", Benjamin, New York, 1963; (b) E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes", Marcel Dekker, New York, 1968; (c) D. A. Dixon, D. A. Kleier, T. A. Halgren, J. H. Hall, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **99**, 6226 (1977); (d) Jun-ichi Aihara, *ibid.*, **100**, 3339 (1978); (e) M. J. S. Dewar and M. L. McKee, *Inorg. Chem.*, **17**, 1569 (1978).

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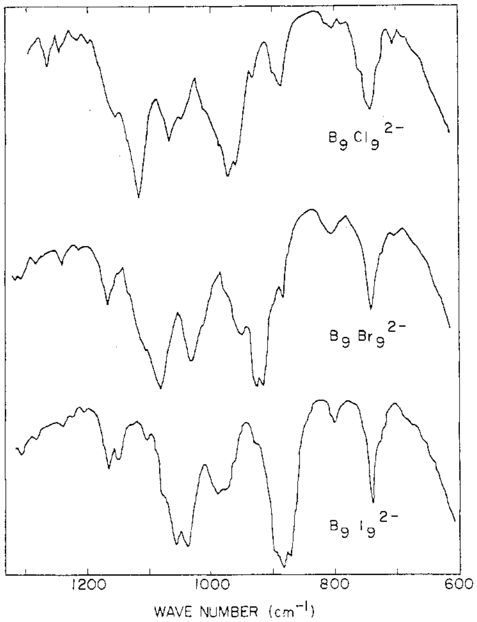

**Figure 1.** Comparison of the IR spectra of $B_9Cl_9^{2-}$, $B_9Br_9^{2-}$, and $B_9I_9^{2-}$.

**Table I.** Electronic Absorption Bands for the $B_9X_9^{2-}$ and $B_9X_9^{-}\cdot$ Boranes in Acetonitrile

| dianion | $\lambda_{max}$, nm | anion | $\lambda_{max}$, nm |
|---|---|---|---|
| $B_9Cl_9^{2-}$ | 225 | $B_9Cl_9^{-}\cdot$ | 275, 425 |
| $B_9Br_9^{2-}$ | 237 | $B_9Br_9^{-}\cdot$ | 278 sh, 349, 480 |
| $B_9I_9^{2-}$ | 227 sh, 266 sh | $B_9I_9^{-}\cdot$ | 228, 255 sh, 563 |

**Table II.** $^{11}B$ NMR Data of $B_9X_9^{2-}$

| anion | chem shifts, ppm[a] | rel intens |
|---|---|---|
| $B_9Cl_9^{2-}$ | −1.45,[b] −5.49 | 3:6 |
| $B_9Br_9^{2-}$ | −0.77, −8.15 | 3:6 |
| $B_9I_9^{2-}$ | −3.14, −16.00 | 3:6 |

[a] Chemical shifts relative to $BF_3\cdot Et_2O$. [b] Shoulder to the resonance at −5.49 ppm.

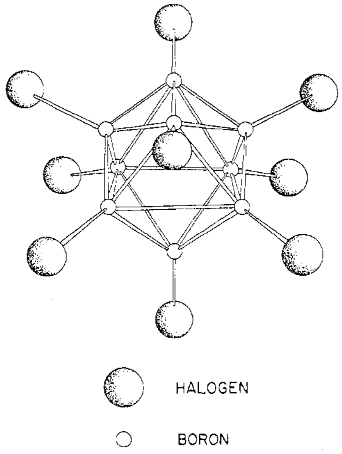

**Figure 2.**

lated as owing to extensive halogen back-donation into the polyhedra.[3e] These two classes of boron clusters are formally related by two-electron redoxes, yet no interconversions have been demonstrated for them. A serendipitous preparation of $B_9Cl_8H^{2-}$ was reported via the "hydrolysis" of $B_9Cl_8H$, but the mode of formation of the dianion from the neutral cluster was obscured.[7e] In order to establish the redox relationship between these neutral clusters and their dianions, we sought to prepare the perhalogenated $B_9H_9^{2-}$ derivatives and to study their oxidations. Further impetus for this work was provided by the dearth of derivative chemistry for the smaller and less symmetrical polyhedral boranes. To date, only the $B_{10}$ and $B_{12}$ dianions have well-defined substitution chemistry.[2b] It was also deemed reasonable that intermediate monoanionic radicals of the type $B_9X_9^{-}\cdot$ may be sufficiently stable for isolation. No polyhedral borane radicals of this type have been reported. Our preliminary communication on the $B_9Cl_9^{2-}$ synthesis and its interconversions with $B_9Cl_9$ has appeared.[8] We report here an improved synthesis and its extension to $B_9Br_9^{2-}$, $B_9I_9^{2-}$, and $B_9Br_9$, as well as the isolation of the first stable radicals of the $B_nX_n^{-}\cdot$ family.

## Results and Discussion

**$B_9X_9^{2-}$.** Since the air and hydrolytic instability of $B_9H_9^{2-}$ precludes its perhalogenation under protic conditions, halogenations were performed with the tetra-*n*-butylammonium salt of $B_9H_9^{2-}$ in methylene chloride under a nitrogen atmosphere. Initially sulfuryl chloride, $SO_2Cl_2$, was used as the chlorinating agent. Nine equivalents of $SO_2Cl_2$ was added to a methylene chloride solution of $(n\text{-}Bu_4N)_2B_9H_9$ at −78 °C and the solution allowed to warm to room temperature. Low to moderate yields of $B_9Cl_9^{2-}$ can be isolated from the nonvolatile residue (Scheme I).

Subsequently it was discovered that *N*-chlorosuccinimide under similar conditions gives very good yields of the desired product. Use of *N*-bromosuccinimide produced the $B_9Br_9^{2-}$ salt in high yields.

Periodination of $B_9H_9^{2-}$ proceeded smoothly with excess elemental iodine in methylene chloride solution to give $B_9I_9^{2-}$.

**Properties of $B_9X_9^{2-}$.** Salts of all three dianions are air-stable solids. The sodium salt of $B_9Cl_9^{2-}$ is stable to both 12 N HCl and 6 N NaOH in aqueous solutions. The $B_9Br_9^{2-}$ and $B_9I_9^{2-}$ salts are slightly less stable. This contrasts dramatically with the reported rapid acid hydrolysis of $B_9H_9^{2-}$, $B_9Br_6H_3^{2-}$, and $B_9Cl_8H^{2-}$ species.[7e,9] Both the stability of the boron–halogen bonds and the enhanced steric bulk along with the higher symmetry of a perhalogenated polyhedron may contribute to the hydrolytic stability of these dianions.

The infrared absorptions of all three show similar patterns in the boron–halogen and boron-cage vibration regions (850–1150 cm$^{-1}$) as shown in Figure 1. The shift of these absorptions to lower frequencies upon changing the substituent from Cl to Br to I is similar to trends reported for the neutral $B_9X_9$ (X = Cl, Br)[7d] and the dianionic $B_{10}X_{10}^{2-}$ (X = Cl, Br, I) and $B_{12}X_{12}^{2-}$ (X = Cl, Br, I).[5] This strongly suggests the adoption of similar polyhedral geometries for the $B_9X_9^{2-}$ species. In addition, the sensitivity of all these absorptions to the type of halogen also argues for the occurrence of considerable $\pi$-bonding interaction between the $B_9$ cage and the terminal halogens.

Their UV spectra also show a similar trend (Table I). The 28.9-MHz $^{11}B$ NMR data are presented in Table II. The two expected boron resonances (peak ratios 3:6) for a tricapped trigonal-prismatic $D_{3h}$ geometry (Figure 2) are clearly observed for $B_9Br_9^{2-}$ and $B_9I_9^{2-}$. These resonances are less well resolved in $B_9Cl_9^{2-}$, and the lower field signal appears as a shoulder to the higher field resonance. A similar trend of increasing separation between five- and six-coordinate boron shifts is seen in the $B_{10}X_{10}^{2-}$ resonances.[6]

**$B_9X_9$ (X = Cl, Br) and $B_9X_9^{-}\cdot$ (X = Cl, Br, I).** It was originally observed that excess $SO_2Cl_2$ reacted with $B_9H_9^{2-}$ to give only low yields of $B_9Cl_9^{2-}$ (5–15%). Removal of vol-

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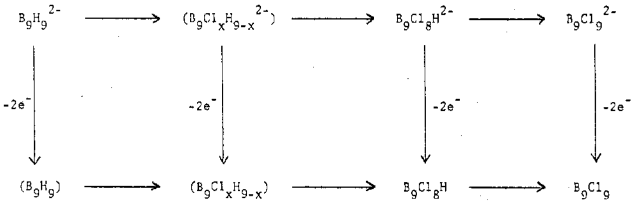
**Scheme II**



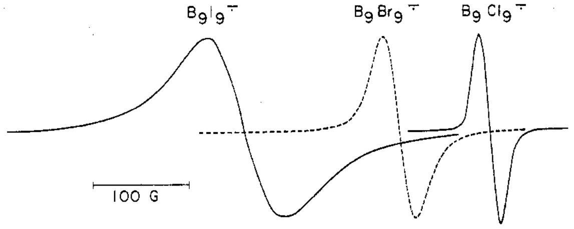


Figure 3. Room-temperature solution EPR spectra of the $B_9X_9^{-}\cdot$ radicals.

Table III. Infrared Spectral Data for $B_9Cl_9^{-}\cdot$, $B_9Br_9^{-}\cdot$, and $B_9I_9^{-}\cdot$ in the 850–1100-cm$^{-1}$ region

| radical anion | freq,[a] cm$^{-1}$ |
|---|---|
| $B_9Cl_9^{-}\cdot$ | 1052 s, bd; 970 s, bd |
| $B_9Br_9^{-}\cdot$ | 1005 s, bd; 930 s, bd |
| $B_9I_9^{-}\cdot$ | 963 s, bd; 885 s, bd |

[a] Nujol mulls of the *n*-$Bu_4N$ salt.

atiles from the reaction mixture at room temperature gives a yellow oily residue which can be extracted by *n*-hexane to give an orange-yellow filtrate. A yellow-orange microcrystalline solid can be isolated from the hexane solution. UV, IR, and mass spectral data identified this as $B_9Cl_9$.[7b] Yields of over 30% can be obtained, and this represents a uniquely convenient and selective synthesis of the neutral cluster without the usual need for electric-discharge apparatus and vacuum-line separations.[7b,7d]

The sulfuryl chloride appears to be both the chlorinating and the oxidizing agent. It seems reasonable that intermediate species of partially chlorinated $B_9$ may be involved as in Scheme II. It can be demonstrated that $B_9Cl_8H$ can indeed be readily chlorinated by $SO_2Cl_2$ to give $B_9Cl_9$. It has also been established that perhalogenated polyhedral boranes are more difficult to oxidize than the parent dianions.[2b]

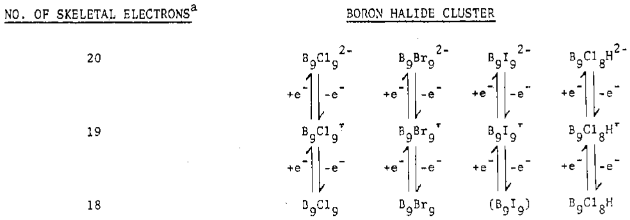
Direct oxidation of $(n\text{-}Bu_4N)_2B_9Cl_9$ with thallic trifluoroacetate produced a dark brown product which was paramagnetic and was analyzed as $(n\text{-}Bu_4N)B_9Cl_9$. Similar oxidations of $B_9Br_9^{2-}$ and $B_9I_9^{2-}$ produced paramagnetic brown and violet species, respectively. It is also possible to use *N*-chlorosuccinimide (NCS) or *N*-bromosuccinimide (NBS) for these latter oxidations.

An alternate synthesis for $B_9Cl_9^{-}\cdot$ is via the one-electron reduction of $B_9Cl_9$ with a stoichiometric amount of *n*-$Bu_4NI$. Similarly, $B_9Br_9^{-}\cdot$ can be prepared from $B_9Br_9$.

These species represent the first stable polyhedral borane radicals isolated. Previous reports of neutral boron radicals like $B_{12}Cl_{11}$ have been put in doubt by recent work.[7c,10]

As expected, further oxidation of the $B_9Cl_9^{-}\cdot$ and $B_9Br_9^{-}\cdot$ radicals with excess thallic trifluoroacetate produced the neutral $B_9Cl_9$ and $B_9Br_9$ clusters, respectively. We have not yet successfully isolated pure samples of the unknown $B_9I_9$ cluster by this method. A red-purple product of the oxidation of $B_9I_9^{-}\cdot$ has proved to be relatively unstable. The decreased ability of iodine to back-bond and stabilize the $B_9$ cage may well render it less accessible.

**Chart I**



[a] No. of formal skeletal electrons for a nine-boron polyhedra. See ref. 3b.

**Properties of $B_9X_9^{-}\cdot$.** Solution ESR spectra of these paramagnetic monoanions exhibited broad single resonances without fine structure (Figure 3). The signals shift to lower field and broaden increasingly upon going from $B_9Cl_9^{-}\cdot$ to $B_9Br_9^{-}\cdot$ to $B_9I_9^{-}\cdot$. Measured *g* values for the radicals are 2.018, 2.080, and 2.191, respectively. Their electronic spectra are presented in Table I. The IR absorptions in the cage and B–X region again show similarities with expected shifts to lower frequencies from Cl to Br to I substitution (Table III).

While it has not been possible to rigorously establish the geometries of these radical monoanions, all known nine-boron polyhedra possess the tricapped trigonal-prism ($D_{3h}$) geometry. These include $B_9H_9^{2-}$,[11] $B_9Cl_9^{2-}$, $B_9Br_9^{2-}$, and $B_9I_9^{2-}$ (vide supra). Additionally, neutral $B_9Cl_9$ and $B_9Br_9$ clusters have been shown by X-ray diffraction to have essentially $D_{3h}$ geometries.[12] It seems quite unlikely that these $B_9X_9^{-}\cdot$ species, which represent the intermediate oxidation state of the redox series $B_9X_9^{2-}$, $B_9X_9^{-}\cdot$, and $B_9X_9$, will adopt a geometry *significantly* different from the favored tricapped trigonal prism.

**Chemical Properties of $B_9X_9^{-}\cdot$.** All three monoanions exhibit good air stability both as solids and in aprotic solvents. Methylene chloride solutions of $B_9Cl_9^{-}\cdot$ and $B_9Br_9^{-}\cdot$ slowly decompose in air to give colorless solutions over a period of days. Under dry nitrogen atmosphere, all $B_9X_9^{-}\cdot$ solutions are stable indefinitely at room temperature.

Facile reductions to the parent dianions can be achieved with stoichiometric amounts of iodide. As described above, $B_9Cl_9^{-}\cdot$ and $B_9Br_9^{-}\cdot$ can be further oxidized to the neutral clusters. Their relative oxidizing strengths vary in the order $B_9Cl_9^{-}\cdot < B_9Br_9^{-}\cdot < B_9I_9^{-}\cdot$. This may again be an indication of the optimal ability of the chlorine substituents to back-donate into the electron-deficient $B_9$ cage and stabilize the radical anion.

The existence and isolation of these radicals and the known neutral $B_9X_9$ species thus further support the multiple-bonding character of boron halide clusters. Limited structural data of the neutral boron chloride clusters indicate B–Cl distances ranging from 1.70 to 1.75 Å (for example: $B_4Cl_4$, 1.70–1.71 Å;[13] $B_8Cl_8$, 1.65–1.75 Å;[14] $B_9Cl_9$, 1.72–1.75 Å[12]). Comparing these to the B–Cl range of 1.77–1.88 Å in the $(2n + 2)$-electron borane derivatives such as 5,12-$Cl_2$-*m*-$C_2B_{10}H_{10}$ (1.80–1.81 Å),[15] 9,10-$Cl_2$-1,7-$CHPB_{10}H_8$ (1.77–1.80 Å),[16] *m*-$B_{10}Cl_{10}C_2H_2$ (1.79–1.84 Å),[17] $C_2B_4H_5Cl$ (1.82 Å),[18] and the polyhedral borane $B_{10}H_7Cl_3^{2-}$ (1.83–1.88 Å),[19] we can conclude that significant multibonding must exist in the boron halide clusters to compensate for their electron deficiency.

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(11) L. J. Guggenberger, *Inorg. Chem.*, **7**, 2260 (1968).

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## Conclusions

We have prepared the perhalogenated $B_9X_9^{2-}$ derivatives and novel $B_9X_9^{-}\cdot$ radicals and established the interconversions between $B_9X_9^{2-}$, $B_9X_9^{-}\cdot$, and $B_9X_9$.

This represents the first successful demonstration of the redox relationship between formally $(2n + 2)$, $(2n + 1)$, and $2n$ polyhedral boranes. We have also confirmed the relationship between the previously reported $B_9Cl_8H^{2-}$ and $B_9Cl_8H$ species. A summary of these redox conversions is presented in Chart I.

If confirmed, the postulated retention of the parent $D_{3h}$ geometry for all three cluster classes would constitute a rare example of a nonmetallic cluster able to maintain its basic structure over at least three oxidation states. Furthermore, the observed stability of all the perhalogenated boranes studied here convincingly attests to the effectiveness of halogen substituents in back-bonding to and in stabilizing of polyhedral boranes.

## Experimental Section

All reactions were run under an atmosphere of dry nitrogen in Schlenk glassware. Methylene chloride was distilled under nitrogen from phosphorus pentoxide. $Tl(CF_3COO)_3$, $(n\text{-}Bu_4N)Cl$, $(n\text{-}Bu_4N)I$, and $SO_2Cl_2$ were obtained from Aldrich Chemical Co. *n*-Hexane was dried by distillation from $CaH_2$. $(n\text{-}Bu_4N)_2B_9H_9$ was obtained by literature methods.[20] $(n\text{-}Bu_4N)_2B_9Cl_8H$ and $B_9Cl_8H$ were prepared by Muetterties' procedure.[7e]

IR spectra were recorded as Nujol mulls or $CH_2Cl_2$ solutions on a Perkin-Elmer 337 spectrometer. The 28.9-MHz $^{11}B$ spectra were recorded on a Bruker WH 90-DX spectrometer with Fourier transform and deuterium lock. $^{11}B$ shifts were referenced to external $BF_3\cdot Et_2O$. Visible and ultraviolet spectra were taken with a Cary 14 spectrophotometer by using spectrograde $CH_3CN$ solvent. EPR data were obtained on a Varian E-4 spectrometer using DPPH as frequency marker.

Chemical analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

**Preparation of $(n\text{-}Bu_4N)_2B_9Cl_9$. From $SO_2Cl_2$.** An amount of 200 mg (0.34 mmol) of $(n\text{-}Bu_4N)_2B_9H_9$ was dissolved in 5 mL of $CH_2Cl_2$ in a Schlenk tube and chilled in a dry ice–acetone bath. A 275-$\mu$L (3.4-mmol) sample of $SO_2Cl_2$ was slowly added via a syringe. A brown coloration developed instantaneously. After warming to room temperature over a period of 1 h, the solution was evacuated to dryness with a mechanical pump. The brown oily residue was extracted with 5 mL of $CH_2Cl_2$ and filtered through Celite. Addition of ether precipitated 180 mg (0.20 mmol, 59%) of $(n\text{-}Bu_4N)_2B_9Cl_9$ as a white powder. Recrystallization from $CH_2Cl_2$–ether gave microcrystalline product of good purity.

**From *N*-Chlorosuccinimide.** A solution of $(n\text{-}Bu_4N)_2B_9H_9$ (1.0 g, 1.7 mmol) in 25 mL of $CH_2Cl_2$ was cooled to −78 °C. *N*-Chlorosuccinimide (2.1 g, 15.7 mmol) was added and the reaction mixture allowed to warm to room temperature and stirred for 1 h. Addition of ethyl ether precipitated the product. This was washed with ethanol followed by ether to give $(n\text{-}Bu_4N)_2B_9Cl_9$ (1.35 g, 1.5 mmol, 88%). Anal. Calcd for $C_{32}H_{72}N_2B_9Cl_9$: C, 42.64; H, 7.99; Cl, 35.46. Found: C, 42.91; H, 8.06; Cl, 34.94.

**Preparation of $(n\text{-}Bu_4N)_2B_9Br_9$.** A solution of $(n\text{-}Bu_4N)_2B_9H_9$ (0.50 g, 0.85 mmol) in 25 mL of $CH_2Cl_2$ was cooled to −78 °C. *N*-Bromosuccinimide (1.36 g, 7.62 mmol) was added and the suspension warmed to room temperature. After 1 h of additional stirring, diethyl ether was added to precipitate the product. After ethanol and ether washing, the yield of $(n\text{-}Bu_4N)_2B_9Br_9$ was 1.10 g (0.84 mmol, 98%). Recrystallization from acetone–*n*-hexane gave crystals. Anal. Calcd for $C_{32}H_{72}N_2B_9Br_9$: C, 29.53; H, 5.53; Br, 55.26. Found: C, 29.86; H, 5.74; Br, 54.88.

**Preparation of $(n\text{-}Bu_4N)_2B_9I_9$.** A solution of $(n\text{-}Bu_4N)_2B_9H_9$ (300 mg, 0.51 mmol) in 25 mL of $CH_2Cl_2$ was cooled to −78 °C. Nine equivalents of iodine (1.20 g, 4.7 mmol) was added and the mixture allowed to warm to room temperature. The brown suspension was stirred for 1 h and ether added to complete precipitation of the product. After $CHCl_3$ washing, 0.70 g of $(n\text{-}Bu_4N)_2B_9I_9$ (0.41 mmol, 80%) was obtained. Anal. Calcd for $C_{32}H_{72}N_2B_9I_9$: C, 22.29; H, 4.18; I, 66.23. Found: C, 22.38; H, 4.42; I, 66.58.

**Preparation of $B_9Cl_9$. From $B_9H_9^{2-}$.** A solution of $(n\text{-}Bu_4N)_2B_9H_9$ (200 mg, 0.34 mmol) in 10 mL of $CH_2Cl_2$ was cooled to −78 °C. Twenty equivalents of $SO_2Cl_2$ (550 $\mu$L, 6.8 mmol) was added via a syringe. The mixture was allowed to warm to room temperature and stirred for 2 h. The solvent and volatiles were removed with a mechanical-pump vacuum, and the orange oily residue was extracted with 10 mL of dry *n*-hexane. Filtration and removal of solvent yielded yellow-orange microcrystalline $B_9Cl_9$ (49 mg, 0.12 mmol, 33%) identified by its IR, UV, and mass spectra. This can be further purified by sublimation in a vacuum line.

**From $B_9Cl_9^{-}\cdot$.** A mixture of 50 mg (0.076 mmol) of $(n\text{-}Bu_4N)B_9Cl_9$ and 100 mg (0.185 mmol) of $Tl(CF_3COO)_3$ was stirred in 5 mL of $CH_2Cl_2$. After 0.5 h, the solvent was evaporated off and the residue extracted with 10 mL of hexane. From the extract was isolated 14 mg (0.033 mmol, 44%) of $B_9Cl_9$.

**Preparation of $(n\text{-}Bu_4N)B_9Cl_9$. From $B_9Cl_9^{2-}$.** A solution of $(n\text{-}Bu_4N)_2B_9Cl_9$ (200 mg, 0.22 mmol) in 10 mL of $CH_2Cl_2$ was added to $Tl(CF_3COO)_3$ (110 mg, 0.2 mmol) in a Schlenk tube. After stirring for 2 h, the solution was filtered through Celite and evaporated to dryness. The dark brown residue was washed with ethanol and ether to give 100 mg (0.15 mmol, 75%) of $(n\text{-}Bu_4N)B_9Cl_9$ as brown flakes.

**From $B_9Cl_9$.** A 10-mL $CH_2Cl_2$ solution of $B_9Cl_9$ (120 mg, 0.29 mmol) was added to $(n\text{-}Bu_4N)I$ (100 mg, 0.27 mmol), and the resulting solution was evacuated to dryness. The residue was washed with ether to give 155 mg (0.23 mmol, 80%) of $(n\text{-}Bu_4N)B_9Cl_9$ as a brown microcrystalline solid. Anal. Calcd for $C_{16}H_{36}NB_9Cl_9$: C, 29.17; H, 5.46; Cl, 48.43. Found: C, 29.39; H, 5.75; Cl, 47.73.

**Preparation of $(n\text{-}Bu_4N)B_9Br_9$.** A solution of $(n\text{-}Bu_4N)_2B_9H_9$ (500 mg, 0.85 mmol) in 25 mL of $CH_2Cl_2$ was cooled to −78 °C and 20 equiv (3.0 g, 16.9 mmol) of *N*-bromosuccinimide added. After warming of the mixture to room temperature and 1 h of additional stirring, ether was added to precipitate the brown product. This was filtered and washed with ethanol to give 0.80 g of $(n\text{-}Bu_4N)B_9Br_9$ (0.75 mmol, 90%) as a dark brown solid. Anal. Calcd for $C_{16}H_{36}NB_9Br_9$: C, 18.15; H, 3.40; Br, 67.91. Found: C, 18.19; H, 3.51; Br, 65.95.

**Preparation of $B_9Br_9$.** A solution of 200 mg (0.19 mmol) of $(n\text{-}Bu_4N)B_9Br_9$ in 10 mL of $CH_2Cl_2$ was added to 0.3 g (5.5 mmol) of $Tl(CF_3COO)_3$ and the resulting suspension stirred for 2 h. The dark orange-red solution was evaporated to dryness and the residue extracted with 10 mL of *n*-hexane. Filtration and removal of solvent yielded 73 mg (0.09 mmol, 48%) of an orange-red solid identified as $B_9Br_9$ by its IR, UV, and mass spectra. It can be further purified by sublimation.

**Preparation of $(n\text{-}Bu_4N)B_9I_9$. With NBS.** A solution of 200 mg (0.116 mmol) of $(n\text{-}Bu_4N)_2B_9I_9$ in 10 mL of $CH_2Cl_2$ was added to 41 mg (0.23 mmol) of *N*-bromosuccinimide and the mixture stirred overnight at room temperature. Addition of ether precipitated a violet solid of crude $(n\text{-}Bu_4N)B_9I_9$. This was washed with ethanol and ether to give 140 mg (0.094 mmol, 81%) of the product.

**With $Tl(CF_3COO)_3$.** A solution of 250 mg (0.13 mmol) of $(n\text{-}Bu_4N)_2B_9I_9$ in 6 mL of acetone was added to 70 mg (0.13 mmol) of $Tl(CF_3COO)_3$. After 0.5 h, the solvent was removed, and the violet residue was washed with ethanol to yield 160 mg (0.11 mmol, 82%) of $(n\text{-}Bu_4N)B_9I_9$. Anal. Calcd for $C_{16}H_{36}NB_9Br_9$: C, 12.96; H, 2.43; I, 77.07. Found: C, 13.27; H, 2.56; I, 76.29.

**Reduction of $(n\text{-}Bu_4N)B_9X_9$.** Stoichiometric amounts of the $(n\text{-}Bu_4N)B_9X_9$ salt and $(n\text{-}Bu_4N)I$ were dissolved in $CH_2Cl_2$. After 5 min, the solvent was removed and the residue washed with $CHCl_3$. The crude $(n\text{-}Bu_4N)_2B_9X_9$ was recrystallized from $CH_2Cl_2$–ether. Yields of over 90% were obtained.

**Interconversion of $B_9Cl_8H^{2-}$ and $B_9Cl_8H$. From $B_9Cl_8H$ to $B_9Cl_8H^{2-}$.** A solution of $B_9Cl_8H$ (38 mg, 0.1 mmol) in 10 mL of $CH_2Cl_2$ was added to $(n\text{-}Bu_4N)I$ (100 mg, 0.27 mmol), and the resulting yellow-orange solution was evaporated to dryness and the residue washed with ether to give 56 mg (0.09 mmol, 90%) of $(n\text{-}Bu_4N)_2B_9Cl_8H$ as a white solid.

**From $B_9Cl_8H^{2-}$ to $B_9Cl_8H$.** A solution of $(n\text{-}Bu_4N)_2B_9Cl_8H$ (150 mg, 0.17 mmol) in 10 mL of $CH_2Cl_2$ was added to 50 mg (0.09 mmol) of $Tl(CF_3COO)_3$. After stirring for 2 h, the red-brown solution was filtered through Celite and evaporated to dryness. The red-brown residue was washed with ethanol and ether to give 85 mg (0.13 mmol, 74%) of $(n\text{-}Bu_4N)B_9Cl_8H$. This was redissolved in 10 mL of $CH_2Cl_2$ and added to 100 mg (0.18 mmol) of $Tl(CF_3COO)_3$. After 0.5 h, the solvent was removed and the brown residue extracted with *n*-

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(20) J. C. Carter and P. H. Wilks, *Inorg. Chem.*, 9, 1777 (1970).

hexane. Filtration and evaporation of solvent yielded a yellow-orange solid identified as $B_9Cl_8H$ (15 mg, 0.04 mmol, 34%).

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**Registry No.** $(n\text{-}Bu_4N)_2B_9Cl_9$, 68694-93-9; $(n\text{-}Bu_4N)_2B_9Br_9$, 72402-96-1; $(n\text{-}Bu_4N)_2B_9I_9$, 72402-94-9; $B_9Cl_9$, 31304-34-4; $(n\text{-}Bu_4N)B_9Cl_9$, 72402-98-3; $(n\text{-}Bu_4N)B_9Br_9$, 72402-95-0; $B_9Br_9$, 12589-31-0; $(n\text{-}Bu_4N)B_9I_9$, 72403-00-0; $B_9Cl_8H$, 72275-11-7; $(n\text{-}Bu_4N)_2B_9Cl_8H$, 72402-97-2; $(n\text{-}Bu_4N)B_9Cl_8H$, 72402-99-4; $(n\text{-}Bu_4N)_2B_9H_9$, 68380-71-2.

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# Molecular Addition Compounds. 7. Synthesis of Addition Compounds of Boron Trifluoride, Borane, and Alane with *N,N,N′,N′*-Tetramethylethylenediamine and Triethylenediamine by Precipitation from Ether Solvents[1]

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Triethylenediamine (TED) precipitates $BF_3$ from diethyl ether ($Et_2O$) as $TED\cdot2BF_3$ and as $TED\cdot BF_3$ from tetrahydrofuran (THF). *N,N,N′,N′*-Tetramethylethylenediamine (TMED) and TED precipitate $BH_3$ from both $Et_2O$ and THF as $TMED\cdot2BH_3$ and $TED\cdot2BH_3$, respectively. From $Et_2O$, TMED precipitates $AlH_3$ as $TMED\cdot2AlH_3$. In THF, TMED reacts with $AlH_3$ to afford $TMED\cdot AlH_3$. Thus the patterns of behavior exhibited by $BF_3$, $BH_3$, and $AlH_3$ with TED and TMED in $Et_2O$ and in THF are all different. Since $TMED\cdot AlH_3$ is modestly soluble in THF, TMED cannot precipitate alane quantitatively from this solvent. However, TED reacts instantly and quantitatively with alane in $Et_2O$ and THF to give the highly insoluble mono adduct $TED\cdot AlH_3$. Consequently, the quantitative precipitation of alane from ether solvents is feasible with TED.

## Introduction

Over the years, various workers have carried out experiments involving addition compounds of *N,N,N′,N′*-tetramethylethylenediamine (TMED) and triethylenediamine (TED) with boron trifluoride, borane, and alane.[3-8] These adducts are highly insoluble in the usual organic solvents (THF, $Et_2O$, $CHCl_3$, pentane, and benzene). During the course of our work, it became desirable to achieve the convenient precipitation of borane and alane from ether solvents. Surprisingly, no work has been reported in the literature on the precipitation of borane and alane from their solution in ether solvents using TMED or TED.

Recently we reported the successful precipitation of $BF_3$ from such ether solvents by TMED and ethylenediamine (EDA).[1,3] Irrespective of the mode of addition or the amount of the reactants, TMED always precipitates $BF_3$ as $TMED\cdot2BF_3$.[3] The reaction between EDA and $BF_3$ affords either the mono or the bis adduct, depending upon the solvents utilized.[1] In continuation of the above study, we now wish to report our exploration of the precipitation under standardized conditions of boron trifluoride, borane, and alane from ether solvents ($Et_2O$, THF) with TMED and TED.

## Experimental Section

The reaction flasks and other glass equipment used for experiments were oven-dried and assembled in a stream of dry nitrogen gas. The special techniques for the manipulation of air-sensitive materials are described elsewhere.[9] $Et_2O\cdot BF_3$ and TMED were distilled from calcium hydride. TED was purified by sublimation under reduced pressure. Aluminum hydride was prepared according to the published procedure.[10] The $^1H$ NMR, $^{11}B$ NMR, and $^{27}Al$ NMR spectra were recorded on Varian T-60 and FT-80A instruments. The $^1H$, $^{11}B$, and $^{27}Al$ chemical shifts are in $\delta$ relative to $Me_4Si$, $Et_2O\cdot BF_3$, and $Al(NO_3)_3$ standards, respectively. Infrared spectra were recorded with the Perkin-Elmer 700 spectrometer.

**Precipitation of Boron Trifluoride with Triethylenediamine. (a) Determination of Stoichiometry by $^1H$ NMR.** Two different reactions were carried out in individual centrifuge vials maintained at 25 °C. The vials were charged with TED (5 mmol), benzene (3.0 mmol, internal standard), and $CCl_4$ (5 mL). An aliquot (0.6 mL) was taken from the first vial, and the amount of TED was estimated via $^1H$ NMR. To the second vial was added 5.0 mmol of $Et_2O\cdot BF_3$ with stirring. The $^1H$ NMR spectrum of the supernatant liquid, following centrifugation, indicated that all TED had been precipitated from solution, and no signal attributable to TED was detectable.

**(b) Determination of Stoichiometry by GLC.** In a 50-mL centrifuge vial were dissolved 5.0 mmol of TED and 3.0 mmol of *n*-dodecane (internal standard) in 10 mL of THF. The amount of TED present in the solution was determined by GLC analysis with a 6 ft × 0.25 in. column packed with 10% SE-30 on Chromosorb W. The solution was then treated with 5.0 mmol of $Et_2O\cdot BF_3$ with constant stirring; a white solid precipitated. GLC analysis of the supernatant liquid indicated that it was free of TED. The adduct was collected by centrifugation, washed several times with *n*-pentane, and dried. There was obtained 0.88 g (98% yield) of $TED\cdot BF_3$: mp 199–201 °C;[11] IR and $^1H$ NMR spectra superimposable with those reported in literature;[11] $^{11}B$ NMR ($CH_3CN$) $\delta$ −0.32 (q, $J = 13$ Hz).

When the same reaction was carried out in diethyl ether, a different result was realized. Thus, treatment of 5.0 mmol of TED in $Et_2O$ with 5.0 mmol of $Et_2O\cdot BF_3$ yielded a precipitate. GLC analysis of the supernatant liquid revealed the presence of 2.5 mmol of residual TED. The reaction mixture was treated further with 5.0 mmol of $Et_2O\cdot BF_3$. The GLC analysis now indicated no TED in the solution. The adduct was collected by centrifugation, washed several times with $Et_2O$, and dried. There was obtained 1.23 g (99% yield) of $TED\cdot2BF_3$: mp >300 °C; IR spectrum identical with that reported in the literature;[4] $^1H$ NMR (acetone-$d_6$) $\delta$ 3.47 (s, 12 H); $^{11}B$ NMR ($CH_3CN$) $\delta$ −0.24 (q, $J = 12$ Hz).

**Precipitation of Borane with *N,N,N′,N′*-Tetramethylethylenediamine and Triethylenediamine. Determination of Stoichiometry.** Identical reactions were carried out in THF and in $Et_2O$ at 25 °C. The following

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