Chemistry of Boranes. XXVI.[1] Inner Diazonium Salts $1,10\text{-}B_{10}H_8(N_2)_2$, $\text{-}B_{10}Cl_8(N_2)_2$, and $\text{-}B_{10}I_8(N_2)_2$

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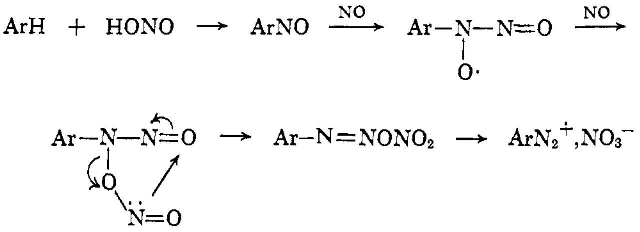
Contribution No. 1145 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898. *Received October 4, 1965*

Abstract: Reaction of $B_{10}H_{10}^{2-}$ with excess nitrous acid followed by reduction gives $1,10\text{-}B_{10}H_8(N_2)_2$. This inner diazonium salt is a useful synthetic intermediate because the nitrogen can be replaced by a variety of nucleophiles. The halogenated analogs $1,10\text{-}B_{10}Cl_8(N_2)_2$ and $1,10\text{-}B_{10}I_8(N_2)_2$ have also been prepared. Evidence is presented for apical–apical conjugation in certain $B_{10}H_{10}^{2-}$ derivatives.

Aromatic diazonium salts have long been of interest principally because of their synthetic versatility. Inorganic counterparts, species in which molecular nitrogen is bonded to an element other than carbon, have not been known except for the special case of azides. In a preliminary communication,[2] we outlined the synthesis and chemistry of the first inorganic diazonium compound, $1,10\text{-}B_{10}H_8(N_2)_2$, a species which is actually an inner salt, $^{+}N_2B_{10}{}^{2-}H_8N_2{}^{+}$. Succeeding articles[3-5] from this laboratory have described other inorganic diazonium compounds and cations such as $1,6\text{-}N_2B_{10}H_8N(CH_3)_3$,[3] $1,10\text{-}N_2B_{10}H_8S(CH_3)_2$,[4] and $1\text{-}(CH_3)_2SB_{10}H_7\text{-}6\text{-}NH_3\text{-}10\text{-}N_2{}^{+}$,[5] all of which are also derivatives of $B_{10}H_{10}{}^{2-}$. Their article reports in detail the chemistry of $1,10\text{-}B_{10}H_8(N_2)_2$ and of its halogenated analogs $1,10\text{-}B_{10}Cl_8(N_2)_2$ and $1,10\text{-}B_{10}I_8(N_2)_2$ and discusses correlations between their chemistry and that reported for the other inner diazonium salts of $B_{10}H_{10}{}^{2-}$.

Preparation and Characterization. The reaction of an aqueous solution of $(NH_4)_2B_{10}H_{10}$ with excess nitrous acid is immediate and exothermic, with the accompanying separation of a brown solid. *This solid is very hazardous because it detonates extremely readily when dry.* However, it is readily reduced by zinc and hydrochloric acid, or preferably by sodium borohydride in alcoholic solution to give the nonexplosive $1,10\text{-}B_{10}H_8(N_2)_2$. Reaction of zinc and hydrochloric acid with the aqueous filtrate from separation of the explosive intermediate gives additional amounts of $1,10\text{-}B_{10}H_8(N_2)_2$ for a total yield of 15–25%.

Although the exact course of this reaction is not known, it may be related to that of the direct preparation of organic diazonium salts by reaction of organic aromatic species, preferably activated ones, with excess nitrous acid.[6] This relationship is probable in view of the general similarity between $B_{10}H_{10}{}^{2-}$ chemistry[2,7-9] and organic aromatic chemistry. Tedder and Theaker[6] have hypothesized possible reaction schemes such as the following for the direct formation of organic diazonium salts.



A scheme such as this may be applicable, in part, to the present case. The obvious differences are that, while the organic system spontaneously proceeds to completion, the formation of $1,10\text{-}B_{10}H_8(N_2)_2$ requires a reduction step, and that it is readily demonstratable that at least two intermediates (water-insoluble and water-soluble) are involved in the latter preparation. At most, therefore, only the initial stages of Tedder's reaction scheme can be applied to our system, the B_{10} intermediates apparently being more stable than those in the organic system. It would be expected that any intermediate similar to those above would be explosive, as is observed, and that any of the intermediates[10] after the first would be readily reducible to a diazonium compound.

A second preparation of $1,10\text{-}B_{10}H_8(N_2)_2$ consists of diazotization of $1,10\text{-}B_{10}H_8(NH_2)_2{}^{2-}$. Unfortunately this is of no present synthetic value since the diamine is prepared from the diazonium compound. It is of interest, however, as additional evidence for the structure of the diazonium compound and because of the contrast in the conditions required for this diazotization and those of the corresponding halogenated diamines, $1,10\text{-}B_{10}Cl_8(NH_2)_2{}^{2-}$ and $1,10\text{-}B_{10}I_8(NH_2)_2{}^{2-}$. Aqueous diazotization does not succeed with $1,10\text{-}B_{10}H_8(NH_2)_2{}^{2-}$, possibly because the concentration of these anions in aqueous acidic solution is negligible because of the extremely weak character of the conjugate acid $1,10\text{-}B_{10}H_8(NH_3)_2$ ($[pK_a]_{CH_3CN} = 12.2$[11]).

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[1] Part XXV: H. C. Miller, W. R. Hertler, E. L. Muetterties, W. H. Knoth, and N. E. Miller, *Inorg. Chem.*, 4, 1216 (1965).

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

[3] W. R. Hertler, W. H. Knoth, and E. L. Muetterties, *ibid.*, 86, 5434 (1964).

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

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

[6] J. M. Tedder and G. Theaker, *Tetrahedron*, 5, 288 (1959).

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

[8] W. R. Hertler and M. S. Raasch, *ibid.*, 86, 3661 (1964).

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

[10] The only direct evidence as to the nature of the explosive, water-insoluble intermediate is a strong band in the infrared at 2380 cm^{-1}. It has been suggested by Professor R. C. Lord that this may be due to an $NO_2{}^{+}$ cation. A strong absorption band at 2360 cm^{-1} for $NO_2{}^{+}$ in NO_2BF_4, NO_2PF_6, and NO_2SbF_6 has been reported: D. Cook, S. J. Kuhn, and G. A. Olah, *J. Chem. Phys.*, 33, 1669 (1960).

[11] We are indebted to Dr. J. S. Fok, who has determined the p*K* values for a number of $B_{10}H_{10}{}^{2-}$ amine derivatives, for allowing us to use these results prior to publication.

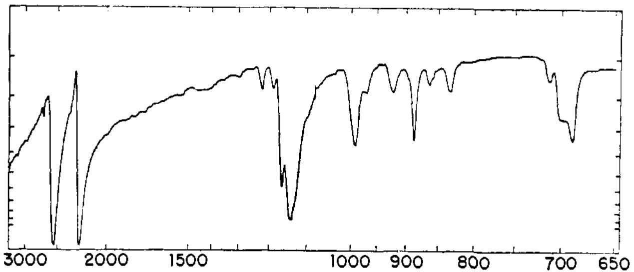

Figure 1. Infrared spectrum (KBr wafer) of 1,10-$B_{10}H_8(N_2)_2$.

Diazotization can be achieved by the reaction of $Na_2B_{10}H_8(NH_2)_2$ with nitrosyl chloride in glyme. The yield is low, presumably because the by-product water hydrolyzes unreacted anion to 1,10-$B_{10}H_8(NH_3)_2$, thereby rendering it inert. The electron-withdrawing effect[12] of the halogen substituents in 1,10-$B_{10}Cl_8(NH_3)_2$[2] and 1,10-$B_{10}I_8(NH_3)_2$[13] make these more acidic ($[pK_a]_{CH_3CN}$ for 1,10-$B_{10}Cl_8(NH_3)_2$ = 10.9[11]) than 1,10-$B_{10}H_8(NH_3)_2$. The concentration of the corresponding halogenated diamine anions in aqueous solution is appreciable, and reaction with nitrous acid in conventional fashion proceeds readily to give good yields of 1,10-$B_{10}Cl_8(N_2)_2$ and 1,10-$B_{10}I_8(N_2)_2$. The hemidiazotized product 1,10-$H_3NB_{10}Cl_8N_2$ has also been isolated.

In common with other derivatives of $B_{10}H_{10}^{2-}$, 1,10-$B_{10}H_8(N_2)_2$ has unusual hydrolytic and oxidative stability for a boron hydride derivative. It is a colorless, crystalline solid, stable toward air, water, dilute acid or base and is not oxidized by alcoholic silver nitrate. It sublimes readily at 100° *in vacuo* and is soluble in common organic solvents including benzene; it is insoluble in water. It begins to decompose at about 125° in a sealed tube. The perhalogenated diazonium compounds, 1,10-$B_{10}Cl_8(N_2)_2$ and 1,10-$B_{10}I_8(N_2)_2$, have greater thermal stability; they begin to decompose at about 180 and 160°, respectively. As in other halogen derivatives of $B_{10}H_{10}^{2-}$,[14] the boron–halogen bonds in these compounds are quite resistant to hydrolysis, and no cleavage of these bonds has been observed.

Thin layer chromatography has indicated that the $B_{10}H_8(N_2)_2$ species under consideration consists essentially of only one isomer, and the stereochemical assignment of this as the 1,10-(bis-apical) isomer follows readily from its B^{11} nuclear magnetic resonance spectrum. The infrared spectrum (Figure 1) has a strong band at 2530 cm^{-1} for the B–H stretching and one at 2250 cm^{-1} for the $-N{\equiv}N$ stretching mode. The latter absorption is shifted to 2280 cm^{-1} in 1,10-$B_{10}Cl_8(N_2)_2$ and 1,10-$B_{10}I_8(N_2)_2$, possibly as a result of inductive electron withdrawal by the halogen substituents.

Reactions. The nitrogen group is a valuable ligand in $B_{10}H_{10}^{2-}$ chemistry because it is the only ligand yet found that is readily displaceable by a variety of nucleophiles. Derivatives of $B_{10}H_{10}^{2-}$ have been prepared which bear dimethyl sulfide,[5] amines,[8] or acetonitrile as ligands, but although it might be expected that these would be readily displaceable by stronger nucleophiles, such is not the case. A pertinent example is the previously reported[4] reaction of 1,10-$N_2B_{10}H_8S(CH_3)_2$ with pyridine to give 1,10-$C_5H_5NB_{10}H_8S(CH_3)_2$. The dimethyl sulfide is not displaced by pyridine in this system, although such a displacement readily occurs in the reaction of $B_{10}H_{12}\cdot 2(CH_3)_2S$ with pyridine.[15] The facile displacement of nitrogen by nucleophiles is common to all the $B_{10}H_{10}^{2-}$ diazonium derivatives studied thus far.[2-5] In this work, the reactions of 1,10-$B_{10}H_8(N_2)_2$ with ammonia, hydrazine, acetonitrile, pyridine, and carbon monoxide have given the corresponding 1,10-$B_{10}H_8$(ligand)$_2$ species.[16] Similarly reaction of the chlorinated diazonium salt with carbon monoxide and with hydrogen sulfide gave 1,10-$B_{10}Cl_8(CO)_2$[17] and 1,10-$B_{10}Cl_8(SH_2)_2$, respectively. Displacement reactions were also observed with azide ion and hydroxide ion as described below.

In studies of the displacement products, ionization of 1,10-$B_{10}H_8(NH_3)_2$[18] was demonstrated by precipitation of the nearly insoluble thallium salt of 1,10-$B_{10}H_8(NH_2)_2^{2-}$ from basic solution. Ionization of 1,10-$B_{10}Cl_8(SH_2)_2$ was demonstrated by preparation of the cesium salt of 1,10-$B_{10}Cl_8(SH)_2^{2-}$. In addition, 1,10-$B_{10}H_8(NCCH_3)_2$ was found to hydrate readily to form 1,10-$B_{10}H_8(NH_2COCH_3)_2$, similar to the previously reported[1] facile hydration of $B_{12}H_{11}NCCH_3^-$. A very diverse chemistry was found for 1,10-$B_{10}H_8(CO)_2$[17] and for the chlorinated carbonyl; this was outlined earlier[2] and will be reported in detail in a subsequent article.[13]

The reactions of 1,10-$B_{10}H_8(N_2)_2$ with molecular nucleophiles were run at 125–140° with no solvent other than excess reagent. This is advantageous where feasible because additional solvents can lead to unexpected products in these reactions. For example, if cyclohexane is present in the carbonylation reaction, the major products obtained are $C_6H_{11}B_{10}H_7(CO)_2$ and 1,10-$B_{10}H_8(CO)_2$ with minor amounts of $(C_6H_{11})_2B_{10}H_6(CO)_2$ also being formed. The stereochemistry of the cyclohexylated products is unknown as is the mechanism of their formation. However, certain speculations can be made. They are almost certainly formed in a radical reaction. The radical initiator may be $N_2B_{10}H_8$ or $B_{10}H_8$ existing in the triplet state as finite-lived intermediates. This possibility is suggested by the observation that nitrogen is evolved when 1,10-$B_{10}H_8(N_2)_2$ is heated alone at 125–150°, coupled with the fact that carbon monoxide is a notoriously poor nucleophile which would not be expected to participate in nucleophilic attack. Furthermore, although the reaction of 1,10-$B_{10}H_8(N_2)_2$ with carbon monoxide proceeds readily at 140°, the reaction of the chlorinated diazonium salt with carbon monoxide does not proceed at this temperature but does occur at 200°. This is

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[12] Inductive electron withdrawal by halogen substituents on $B_{10}H_{10}^{2-}$ derivatives has also been demonstrated by infrared comparison[9] of $B_{10}H_9COC_6H_5^{2-}$ with $B_{10}Cl_9COC_6H_5^{2-}$ and by comparison of nucleophilic cleavage of boron–sulfur bonds in $B_{10}H_8[S(CH_3)_2]_2$ with cleavage of those in $B_{10}H_2Cl_6[S(CH_3)_2]_2$.[4]

[13] W. H. Knoth, J. C. Sauer, J. H. Balthis, H. C. Miller, and E. L. Muetterties, to be published. The preparation parallels that of 1,10-$B_{10}Cl_8(NH_3)_2$.

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

[15] W. H. Knoth, unpublished. This reaction has been explicitly predicted (R. J. Pace, J. W. Williams, and R. E. Williams, *J. Chem. Soc.*, 2196 (1961)) based on work on related displacement reactions (Pace, *et al.*, above; also M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, **80**, 6685 (1958)).

[16] Except that the hydrazine reaction rather surprisingly gave $H_3NB_{10}H_8N_2H_4$.

[17] W. H. Knoth, Jr., U. S. Patent 3,166,378 (1965).

[18] Methylation of this compound and isomers thereof was reported earlier.[8]

consistent with inductive electron withdrawal by the chlorine atoms strengthening the boron–nitrogen bond toward thermal dissociation. In contrast, if the reaction proceeded *via* nucleophilic attack, chlorine substitution should facilitate reaction and this, in fact, is observed in reactions with strong nucleophiles. Azide ion displaces nitrogen quite readily from the chlorinated diazonium compound to give 1,10-$N_2B_{10}Cl_8N_3^-$ at 25° and 1,10-$B_{10}Cl_8(N_3)_2^{2-}$ at 100° in aqueous solution, but does not react at all with 1,10-$B_{10}H_8(N_2)_2$ at 25° and only slowly at reflux temperature in aqueous ethanol to give 1,10-$N_2B_{10}H_8N_3^-$. In addition, hydroxide ion, which does not readily attack the perhydro diazonium compound reacts rapidly with its chlorinated analog to give 1,10-$N_2B_{10}Cl_8OH^{2-}$. It seems likely, therefore, that more than one mechanism may be operable in reactions of these inorganic diazonium compounds.

Conjugative Effects. The question of whether there can be any significant conjugative interaction between various positions of the B_{10} polyhedron has been of interest to us for some time. In an earlier paper,[5] a comparison of the ultraviolet spectrum of 1-$(CH_3)_2$-$SB_{10}H_7$-6-NH_2-10-N_2 (ϵ_{255} 25,000) with that of 1,10-$(CH_3)_2SB_{10}H_8N_2$ (ϵ_{252} 20,600) suggested that no significant interaction can occur between substituents on adjacent equatorial and apical boron atoms. Data from the present work suggest, however, that appreciable interaction can occur between appropriate substituents on apical positions, as shown in Table I. If the diazonium group is considered as an electron acceptor, the spectra of compounds c and d show significant interaction of this group (on an apex) with an electron donor at the other apex when compared with the spectra of compounds a and b. Comparison of the spectra of compounds e and f shows that there is comparatively little effect on the absorption maximum when an NH_3 group on a $B_{10}Cl_8$ nucleus is ionized in the absence of an electron acceptor on the other apex. In fact, the spectra of e and f are quite similar to that of g which completely lacks NH_2 or NH_3 substituents. The correlation between the ultraviolet spectral shifts of compounds c and d in Table I and their B^{11} nuclear magnetic resonance spectra is striking. As shown in Table II, the N_2-bonded apical boron atoms of these species experience a very large, high-field shift compared to other diazonium derivatives of $B_{10}H_{10}^{2-}$. Unfortunately, although this may be due to the proposed apical–apical conjugation, the state of the art does not yet permit an unequivocal statement regarding this.

Table I. Ultraviolet Maxima of Selected Species

Compd	Formula	λ_{max} (ϵ)
a	1,10-$B_{10}Cl_8(N_2)_2$	283 (29,700), sh 270 (22,400)
b	1,10-$N_2B_{10}Cl_8NH_3$	276 (15,500)
c	Cs-1,10-$N_2B_{10}Cl_8NH_2$	362 (1850), 307 (13,300)
d	$(CH_3)_4N$-1,10-$N_2B_{10}Cl_8OH$	302 (18,200)
e	1,10-$B_{10}Cl_8(NH_3)_2$	217 (6700)[13]
f	$[(CH_3)_4N]_2$-1,10-$B_{10}Cl_8(NH_2)_2$	225 (9600)[13]
g	$[(CH_3)_4N]_2B_{10}Cl_{10}$	224 (11,000)[14]

More compelling evidence for apical–apical conjugation can be obtained from a comparison of the pK_a values (determined in acetonitrile[11]) of 1,10-$B_{10}H_8$-$(NH_3)_2$ (12.2), 1,10-$B_{10}Cl_8(NH_3)_2$ (10.9), and 1,10-$N_2B_{10}Cl_8NH_3$ (7.1). The increase in acidity observed for the perchlorinated diammonium inner salt over its perhydro analog is ascribed to the previously mentioned inductive electron withdrawal by the chlorine atoms. The very large increase in acidity resulting from replacement of one NH_3 group by nitrogen in the chlorinated species can only be accounted for by resonance stabilization of the 1,10-$N_2B_{10}Cl_8NH_2^{2-}$ anion *via* apical–apical conjugation.

Table II. B^{11} Nmr

Species	Formula	δ of B bonded to N_2, ppm[a]	δ of 2nd apical B, ppm[a]
a	1,10-$B_{10}Cl_8(N_2)_2$	~22.1[b]	. . .
b	1,10-$N_2B_{10}Cl_8NH_3$	~24.0[b]	13.9
c	1,10-$N_2B_{10}Cl_8NH_2^-$	42.6	~0
d	1,10-$N_2B_{10}Cl_8OH^-$	45.2	~0
e	1,10-$B_{10}H_8(N_2)_2$	14.2	. . .
f	1,10-$N_2B_{10}H_8S(CH_3)_2$	24.2	~0
g	1-$(CH_3)_2SB_{10}H_7$-6-COOH-10-N_2	24.1	~0

[a] Methyl borate reference. [b] The exact position is obscured by the peaks due to the equatorial boron atoms.

Experimental Section

The preparation of $(NH_4)_2B_{10}H_{10}$ has been described.[19] Boron spectra were determined at 19.2 Mc on a Varian Model V4301 spectrometer unless otherwise noted, with methyl borate as reference. Proton decoupling was effected with an NMR Specialties Model SD60 spin decoupler. Infrared spectra were determined on a Perkin-Elmer Model 21 spectrophotometer.

$B_{10}H_8(N_2)_2$. **a.** Sodium nitrite (150 g, 2.2 moles) was dissolved in a solution of $(NH_4)_2B_{10}H_{10}$ (30 g, 0.2 mole) in 300 ml of water in a 3-l. beaker. Cracked ice (400 ml) was added, and the solution was cooled in an ice–alcohol bath to −10 to −5°. Concentrated hydrochloric acid (150 ml) and cracked ice (500 ml) were mixed and added slowly with vigorous stirring. The reaction temperature was kept below 5° with the addition of more ice as needed. There was a considerable amount of foaming toward the end of the addition. (Caution: as the foam settles, it will leave solid residue on the walls of the beaker. This solid is extremely shock sensitive when dry and should be washed down with a stream of water, not scraped off with a spatula.) Stirring was continued for 10 min and an additional 100 ml of hydrochloric acid plus 300 ml of cracked ice were added, again resulting in severe foaming. The beaker was removed from the cooling bath, and the contents was stirred for 1 hr and filtered. The filter cake was washed twice with water. The filtrate was retained. The filter cake was dissolved in 300 ml of methanol. (Caution: this solid is quite shock sensitive when dry; consequently it should not be pulled completely dry on the filter funnel. The dissolution of the solid in methanol is best conducted by transferring the funnel to a new filter flask, adding the methanol to the damp filter cake in the funnel, and filtering the resulting solution through the same funnel.) Sodium borohydride (5 g) was added to the resulting dark solution with stirring. The color of the solution became light yellow. Stirring was continued for 15 min. The solution was then concentrated to 100 ml and stirred into 700 ml of water. Crude $B_{10}H_8(N_2)_2$ separated (the addition of a coagulant such as ammonium chloride is sometimes necessary to effect a clean precipitation) and was removed by filtration. After drying, the solid was extracted with 100 ml of benzene; the extracts were evaporated to leave 5 g of 1,10-$B_{10}H_8(N_2)_2$.

The filtrate which was retained from the first filtration was cooled to 0–5°. Zinc dust (40 g, 0.61 mole) was added slowly with vigorous stirring. Foaming was severe. After 15 min, the solution was filtered. The filter cake was extracted with two 150-ml

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

portions of methanol. The resulting dark-colored extracts were stirred with 20 g of sodium borohydride until reaction ceased and the color became light yellow. The solution was concentrated to 100 ml and stirred into 700 ml of water to precipitate crude $B_{10}H_8(N_2)_2$ which was dried and extracted with benzene as above. The yield in this step was 3 g for a combined yield of 8 g, 24%. The $B_{10}H_8(N_2)_2$ recovered from the benzene extracts is sufficiently pure for preparative purposes. It can be further purified by recrystallization from 50% aqueous alcohol or, preferably, by sublimation at 100–110° *in vacuo*. *Anal.* Calcd for $B_{10}H_8(N_2)_2$: B, 62.8; H, 4.6; N, 32.6; mol wt, 172. Found: B, 62.1; H, 4.9; N, 33.3; mol wt, 169, 175. Ultraviolet $\lambda_{max}^{CH_3CN}$ 248 mμ (ε 49,000), 300 mμ (sh) (ε 1340). The explosive intermediate has a strong band in the infrared at 2380 cm^{-1}, between the B–H (2530 cm^{-1}) and N≡N (2250 cm^{-1}) absorptions. If there is any absorption at 2380 cm^{-1} in the final product, the reduction step was incomplete and should be repeated. The purified product darkens above 125° without melting.

The B^{11} nmr spectrum in acetone consists of a symmetrical doublet at 36.8 ppm (J = 152 cps) for the equatorial boron atoms and a broad peak at 14.2 ppm for the nitrogen-substituted apical boron atoms.

b. A solution of 1,10-$B_{10}H_8(NH_3)_2$ (0.5 g, 3.3 mmoles) in 20 ml of anhydrous glyme was prepared in a nitrogen atmosphere. The solution was chilled in an ice bath, and excess sodium hydride was added. Hydrogen was evolved. The mixture was filtered under nitrogen after 15 min. Nitrosyl chloride was passed through the filtrate, causing an exothermic reaction. After reaction ceased, the mixture was filtered, and the filtrate was diluted with water to precipitate 0.15 g (26%) of 1,10-$B_{10}H_8(N_2)_2$, identified by infrared analysis.

1,10-$B_{10}H_8$ $(NCCH_3)_2$. A solution of 1,10-$B_{10}H_8(N_2)_2$ (5.0 g, 29.0 mmoles) in acetonitrile (40 ml) was heated to 150° for 3.5 hr at autogeneous pressure in a stainless steel pressure vessel. The resulting red solution was concentrated in a stream of air to give a slurry which was filtered. The cream-colored crystals (4 g) thus obtained were recrystallized from acetonitrile to give 2.1 g (37%) of 1,10-$B_{10}H_8(NCCH_3)_2$ (darkens without melting above 308°). *Anal.* Calcd for $B_{10}H_8(CH_3CN)_2$: C, 24.2; H, 7.1; B, 54.5; N, 14.1. Found: C, 22.5; H, 7.0; B, 54.4; N, 14.2. Ultraviolet $\lambda_{max}^{CH_3CN}$ 239 mμ (ε 49,000). The infrared spectrum had no absorption for N–H, C≡N, or C=N. The B^{11} nmr spectrum in acetonitrile consisted of a symmetrical doublet at 42.8 ppm (J = 140 cps) for the equatorial boron atoms and a singlet at 13.8 ppm for the substituted apical boron atoms.

1,10-$(B_{10}H_8NH_2COCH_3)_2$. A solution of 1,10-$B_{10}H_8(NCCH_3)_2$ (3.3 g, 16.7 mmoles) in aqueous acetonitrile was evaporated on a steam bath to leave crystalline 1,10-$B_{10}H_8(NH_2COCH_3)_2$. This was dissolved in water, and the solution was filtered. The filtrate was divided in half; one-half was evaporated to recover 1,10-$B_{10}H_8(NH_2COCH_3)_2$ (mp 236–238°), and the other was mixed with excess ammonium hydroxide and then evaporated to leave $(NH_4)_2$-1,10-$B_{10}H_8(NHCOCH_3)_2\cdot H_2O$ (mp 238–242°). *Anal.* Calcd for $B_{10}H_8(NH_2COCH_3)_2$: C, 20.5; H, 7.7; B, 46.2; N, 12.0. Found: C, 20.2; H, 7.6; B, 45.1; N, 12.0. Ultraviolet $\lambda_{max}^{H_2O}$ 230 mμ (ε 19,200), sh 260 mμ (ε 11,500). *Anal.* Calcd for $(NH_4)_2B_{10}H_8(NHCOCH_3)_2\cdot H_2O$: C, 16.7; H, 9.1; B, 37.7; N, 19.6. Found: C, 17.2; H, 9.4; B, 37.2; N, 20.0. Ultraviolet $\lambda_{max}^{H_2O}$ 231 mμ (ε 20,400), sh at 260 mμ (ε 12,500).

1,10-$B_{10}H_8(NC_5H_5)_2$. A solution of 1,10-$B_{10}H_8(N_2)_2$ (2.0 g, 11.6 mmoles) in pyridine (50 ml) was refluxed 24 hr during which time 630 ml of gas (110%) was evolved. The solution was cooled and filtered to obtain 1,10-$B_{10}H_8(NC_5H_5)_2$ which was recrystallized from dimethyl sulfoxide, mp 352–353° (2.0 g, 63%). *Anal.* Calcd for $B_{10}H_8(NC_5H_5)_2$: C, 43.8; H, 6.6; B, 39.4; N, 10.2. Found: C, 43.7; H, 6.5; B, 39.4; N, 10.2.

1,10-$B_{10}H_8(NH_3)_2$. Ammonia (15 ml) and 1,10-$B_{10}H_8(N_2)_2$ (1 g, 5.8 mmoles) were sealed in a platinum tube which was heated to 200° for 15 min under 1000 psi external pressure. The tube was opened, and the ammonia was evaporated, leaving 0.8 g (92%) of 1,10-$B_{10}H_8(NH_3)_2$. The analytical sample was recrystallized from dilute sodium hydroxide and dried at 100° *in vacuo* (no mp to 400°). *Anal.* Calcd for $B_{10}H_8(NH_3)_2$: B, 72.0; N, 18.7. Found: B, 71.4; N, 18.6. The B^{11} nmr (14.2 Mc) consisted of a symmetrical doublet at 49.4 ppm (J = 120 cps) and a broad peak at 10.5 ppm.

A solution of 1,10-$B_{10}H_8(NH_3)_2$ (0.2 g, 1.3 mmoles) in 25 ml of 10% aqueous sodium hydroxide was prepared hot and allowed to cool. A few crystals separated and were removed. Excess thallium nitrate solution was added causing the precipitation of Tl_2-1,10-$B_{10}H_8(NH_2)_2$ as a light yellow solid. This was washed thoroughly with water five times before analysis. *Anal.* Calcd for $Tl_2B_{10}H_8(NH_2)_2$: B, 19.4; N, 5.0. Found: B, 19.5; N, 5.1.

1,10-$N_2B_{10}H_8N_3^-$. A mixture of 1,10-$B_{10}H_8(N_2)_2$ (1.0 g, 5.8 mmoles), sodium azide (4 g, 62 mmoles), water (50 ml), and ethanol (50 ml) was refluxed for 3 days to obtain a clear yellow solution. The addition of aqueous tetramethylammonium hydroxide precipitated $(CH_3)_4N$-1,10-$N_2B_{10}H_8N_3$ which was recrystallized from water and dried *in vacuo*. The product was quite shock sensitive and exploded at 180°. *Anal.* Calcd for $(CH_3)_4NN_2B_{10}H_8N_3$: C, 18.4; H, 7.7; B, 41.5. Found: C, 18.8; H, 7.9; B, 41.3. Ultraviolet $\lambda_{max}^{CH_3CN}$ 284 mμ (ε 21,900), 218 mμ (ε 14,100). The infrared spectrum had strong absorptions for both $-N_2$ (2220 cm^{-1}) and $-N_3$ (2100 cm^{-1}).

1,10-$B_{10}H_8(CO)_2$. A silver-lined, pressure vessel (100 ml) was charged with 10 g (58 mmoles) of 1,10-$B_{10}H_8(N_2)_2$. It was then evacuated and pressured with carbon monoxide followed by a 3-hr reaction period at 140° and 1000 atm. (In one of many otherwise similar experiments, a violent explosion occurred. It is believed this was caused by too rapid heating of the pressure vessel. Consequently it is recommended that a slow rate of heating be used while bringing the reaction temperature to 140°. A heat-up time of 1.5 hr seems satisfactory.) The vessel was then cooled and vented. The crude product was extracted with water. The extract was filtered and evaporated, followed by sublimation of the residue at 80–100° and nominal 0.5-mm pressure. Yields ranged from 55 to 75%. The melting point of the sublimed product in a sealed tube was 155–156°. *Anal.* Calcd for $B_{10}H_8(CO)_2$: C, 14.0; H, 4.6; B, 62.7; mol wt, 172. Found: C, 14.2; H, 4.8; B, 62.9; mol wt, 186. Ultraviolet $\lambda_{max}^{cyclohexane}$ 246 mμ (ε 62,000), 315 mμ (sh) (ε 1270). The infrared spectrum had an intense —C≡O stretching vibration at 2140 cm^{-1}. The B^{11} nmr spectrum in benzene consisted of a doublet for the equatorial boron atoms at 29.1 ppm (J = 162 cps) which is unsymmetrical because of coincidence of the low-field member of the doublet with a single peak at 25 ppm representing the substituted apical boron atoms. This interpretation is confirmed by a proton-decoupled spectrum which has a single peak at 29.1 ppm and a low-field shoulder. In addition the B^{11} nmr spectrum in water (14.2 Mc), in which $B_{10}H_8(CO)_2$ is hydrated to form $(H^+)_2B_{10}H_8(COOH)^{2-}\cdot xH_2O$[2], consists of a symmetrical doublet at 44.3 ppm (J = 110 cps) and a singlet at 13 ppm.

$C_6H_{11}B_{10}H_7(CO)_2$ and $(C_6H_{11})_2B_{10}H_6(CO)_2$. A solution of 1,10-$B_{10}H_8(N_2)_2$ (4.6 g, 26.7 mmoles) in 50 ml of cyclohexane was heated at 140° for 1.5 hr in a glass-lined, pressure vessel under 1000 atm of carbon monoxide pressure. The recovered solution was filtered to obtain 0.6 g of 1,10-$B_{10}H_8(CO)_2$. The filtrate was concentrated in an air stream and filtered again when another 0.5 g of solid had appeared. This was 1,10-$B_{10}H_8(CO)_2$ by infrared analysis; total conversion to $B_{10}H_8(CO)_2$ was 23.6%. Concentration of the filtrate to dryness left a residue which was stirred with 5 ml of water, resulting in partial dissolution. Filtration gave a solid which was crude $(C_6H_{11})_2B_{10}H_6(CO)_2$. The filtrate was concentrated on a steam bath until it separated into two layers while hot. One of these layers crystallized on standing overnight and was found to be 2.0 g (29%) of $C_6H_{11}B_{10}H_7(CO)_2$, mp 62–64°. The crude $(C_6H_{11})_2B_{10}H_6(CO)_2$ was fractionally sublimed at 100° *in vacuo* to obtain 0.7 g (7.2%) of the pure dialkylated dicarbonyl, mp 44–46°. *Anal.* Calcd for $C_6H_{11}B_{10}H_7(CO)_2$: C, 37.6; H, 7.4; B, 42.3; mol wt, 254. Found: C, 37.2; H, 6.9; B, 42.6; mol wt, 268. Calcd for $(C_6H_{11})_2B_{10}H_6(CO)_2$: C, 50.2; H, 8.4; B, 32.3; mol wt, 336. Found: C, 49.5; H, 8.3; B, 31.7; mol wt, 318.

The infrared spectra of the cyclohexylated carbonyls had intense absorption peaks at 2150 cm^{-1} for C≡O stretching.

1,10-$N_2H_4B_{10}H_8NH_3$. A solution of 1,10-$B_{10}H_8(N_2)_2$ (6.0 g, 35 mmoles) in 98% hydrazine (60 ml) was refluxed in a nitrogen atmosphere for 2.5 hr. The hydrazine was removed under vacuum, and the residual solid was recrystallized five times from water to obtain 1.0 g (17%) of 1,10-$N_2H_4B_{10}H_8NH_3$ (no mp to 400°). *Anal.* Calcd for $N_2H_4B_{10}H_8NH_3$: B, 65.4; H, 9.1; mol wt, 165. Found: B, 65.0; H, 9.5; mol wt, 167 (X-ray), 155 (cryoscopic in tetramethylene sulfone). Nitrogen analysis of this species and of its derivatives below has given erratic and unreliable results.

The addition of sodium hydroxide to an aqueous solution of 1,10-$N_2H_4B_{10}H_8NH_3$ and thallium nitrate precipitated $TlN_2H_3B_{10}H_8NH_3$. *Anal.* Calcd for $TlN_2H_3B_{10}H_8NH_3$: B, 29.3. Found: B, 29.3. The addition of 10% aqueous sodium hydroxide (1.5 ml, 3.7 mmoles) to a solution of 1,10-$N_2H_4B_{10}H_8NH_3$ (0.2 g, 1.2 mmoles) in 15 ml of methanol containing 1.5 ml of cyclohexanone resulted in the precipitation of crystalline $C_6H_{10}{=}NNH_2B_{10}H_8NH{=}C_6H_{10}\cdot H_2O$ (mp 268–270°). *Anal.* Calcd for $C_6H_{10}{=}NNH_2B_{10}H_8NH{=}C_6H_{10}\cdot H_2O$: C, 42.0; H, 9.6; B, 31.5. Found: C, 43.1; H, 10.0; B, 31.3.

1,10-$B_{10}Cl_8(N_2)_2$ and 1,10-$N_2B_{10}Cl_8NH_3$. Sodium nitrite (10 g, 0.14 mole) was added to a solution of 1,10-$B_{10}Cl_8(NH_3)_2$[2] in 300 ml of water. Glacial acetic acid (20 ml) was added, and the solution was stirred for 2 hr. A solid precipitated and was filtered. The filtrate was mixed with an additional 10 g of sodium nitrite and 5 ml of glacial acetic acid, stirred for 1 hr, and again filtered. The solids obtained were combined and extracted three times with alcohol to leave virtually pure 1,10-$B_{10}Cl_8(N_2)_2$ (10.8 g, 70%). The use of hydrochloric acid in place of acetic lowered the yield to about 45%. The analytical sample (dec pt 180–200°) was recrystallized from ethanolic ethyl acetate with low recovery. This compound sublimes slowly at 120–130° *in vacuo*. *Anal.* Calcd for $B_{10}Cl_8(N_2)_2$: B, 24.1; Cl, 63.4; N, 12.5. Found: B, 24.4; Cl, 63.5; N, 12.7. Ultraviolet $\lambda_{max}^{CH_3CN}$ 283 mμ (ε 29,700), sh at 270 mμ (ε 22,400). The infrared spectrum had a sharp absorption at 2280 cm^{-1} for $N{\equiv}N$. The B^{11} nmr spectrum in acetone consisted of a single peak at 22.7 ppm.

The alcoholic extracts were evaporated to about 5 ml and filtered. The filtrate was diluted with a large excess of water, and crystalline 1,10-$N_2B_{10}Cl_8NH_3$ (2.1 g, 14%) separated. The analytical sample (darkened at 240°, no mp to 360°) was recrystallized from water. *Anal.* Calcd for $N_2B_{10}Cl_8NH_3$: B, 24.8; Cl, 64.9; N, 9.6. Found: B, 24.2; Cl, 64.6; N, 9.5. Ultraviolet $\lambda_{max}^{CH_3CN}$ 276 mμ (ε 15,500). The infrared spectrum had a sharp absorption band at 2275 cm^{-1} for $N{\equiv}N$ stretching as well as bands for N–H stretching in the 3100- to 3500-cm^{-1} region and N–H deformation in the 1600-cm^{-1} region. The B^{11} nmr spectrum in aqueous HCl–CH_3CN consisted of a major peak at 24.0 ppm plus a smaller peak at 13.9 ppm. The B^{11} nmr spectrum in aqueous NaOH–CH_3CN ($N_2B_{10}Cl_8NH_2^-$) consisted of a major singlet at 25.1 ppm, a quite broad smaller peak at 42.6 ppm, and a moderately broad smaller peak at 0 ppm. The 42.6-ppm peak is assigned to the boron bearing the diazonium group by analogy with the $HOB_{10}Cl_8N_2^-$ spectrum (see below).

The addition of 1,10-$N_2B_{10}Cl_8NH_3$ to aqueous sodium hydroxide gave a clear, yellow solution. The addition of cesium chloride precipitated Cs-1,10-$N_2B_{10}Cl_8NH_2$ (dec pt 180°) which was recrystallized from water. *Anal.* Calcd for $CsN_2B_{10}Cl_8NH_2$: B, 19.0; N, 7.4. Found: B, 19.1; N, 7.4. Ultraviolet $\lambda_{max}^{CH_3CN}$ 362 mμ (ε 1850), 307 mμ (ε 13,300). The infrared spectrum had a sharp absorption band at 2250 cm^{-1} for $N{\equiv}N$ stretching and bands at 3420 and 3315 cm^{-1} for N–H stretching and at 1575 cm^{-1} for NH_2 deformation.

1,10-$N_2B_{10}Cl_8N_3^-$. A mixture of 1,10-$B_{10}Cl_8(N_2)_2$ (2.0 g, 4.5 mmoles), sodium azide (1 g, 15 mmoles), and acetonitrile (60 ml) was stirred at room temperature for 20 min. Gas was evolved. and the solution became yellow. It was then refluxed for 30 min, cooled, and filtered. The filtrate was concentrated in a stream of air to leave a viscous liquid. Mixing this with aqueous cesium chloride precipitated Cs-1,10-$N_2B_{10}Cl_8N_3$, a shock-sensitive solid which was recrystallized from water (0.9 g, 33% yield). *Anal.* Calcd for $Cs_2N_2B_{10}Cl_8N_3$: Cs, 22.2; B, 18.1; N, 11.7; Cl, 47.4. Found: Cs, 21.1; B, 17.8; N, 11.5; Cl, 48.2. Ultraviolet $\lambda_{max}^{H_2O}$ 285 mμ (ε 18,800). The infrared spectrum had absorption bands for both $-N{\equiv}N$ (2275 cm^{-1}) and $-N_3$ (2125 cm^{-1}) groups.

1,10-$B_{10}Cl_8(N_3)_2^{2-}$. A mixture of 1,10-$B_{10}Cl_8(N_2)_2$ (2.0 g, 4.5 mmoles), sodium azide (1 g, 15 mmoles), and acetonitrile (60 ml) was refluxed for 1 hr and filtered. The filtrate was concentrated in a stream of air and then mixed with water (50 ml) and an additional 1 g (15 mmoles) of sodium azide. The resulting solution was refluxed until gas evolution ceased and a salt, precipitated from an aliquot of the solution with tetramethylammonium chloride, had no infrared absorption for $N{\equiv}N$ groups (∼2280 cm^{-1}). The remaining solution was cooled and mixed with excess aqueous cesium chloride to precipitate a solid which was recrystallized from water to obtain 1.1 g (33% yield) of Cs_2-1,10-$B_{10}Cl_8(N_3)_2$, a shock-sensitive solid which explodes on heating to 224°. *Anal.* Calcd for $Cs_2B_{10}Cl_8(N_3)_2$: Cs, 35.8; B, 14.6; Cl, 38.2; N, 11.3. Found: Cs, 35.6; B, 14.6; Cl, 38.1; N, 11.1. Ultraviolet $\lambda_{max}^{H_2O}$ 260 mμ (ε 4470), 238 mμ (ε 15,900). The infrared spectrum had a strong azide band at 2150 cm^{-1}.

$B_{10}Cl_8(SH)_2^{2-}$. Hydrogen sulfide (100 g) and 1,10-$B_{10}Cl_8(N_2)_2$ (3.1 g, 6.9 mmoles) were charged into a glass-lined pressure vessel and heated at 150° for 4 hr. The excess hydrogen sulfide was removed, leaving a solid presumed to be $B_{10}Cl_8(SH_2)_2$. This was dissolved in water; the solution was filtered, and a cesium salt was precipitated from the filtrate by the addition of excess aqueous cesium chloride. The precipitated salt was recrystallized twice from water to obtain, after drying *in vacuo* at 130° for 3 hr, 1.2 g (24%) of Cs_2-1,10-$B_{10}Cl_8(SH)_2\cdot H_2O$. *Anal.* Calcd for $Cs_2B_{10}Cl_8(SH)_2\cdot H_2O$: Cs, 35.8; B, 14.6; Cl, 38.2; S, 8.6. Found: Cs, 35.0; B, 14.6; Cl, 38.4; S, 8.7. Ultraviolet $\lambda_{max}^{CH_3CN}$ 231 mμ (ε 18,900). The infrared spectrum confirmed the presence of water of hydration and had a weak absorption for S–H at 2530 cm^{-1}.

1,10-$N_2B_{10}Cl_8OH^-$. A 10% aqueous sodium hydroxide (4 ml) was added to a solution of 1,10-$B_{10}Cl_8(N_2)_2$ (1.1 g, 2.5 mmoles) in 15 ml of glyme. The mixture (two layers) was stirred vigorously; a yellow color developed rapidly. The mixture was then boiled briefly with continued stirring until a drop of the glyme layer gave a clear solution when added to excess water. The reaction mixture was diluted with 100 ml of water. The addition of tetramethylammonium chloride precipitated $(CH_3)_4N$-1,10-$N_2B_{10}Cl_8OH$ (reddens at 210°, mp 340–345°), which was recrystallized from water for analysis. *Anal.* Calcd for $(CH_3)_4NN_2B_{10}Cl_8OH$: B, 21.2; N, 8.2. Found: B, 21.1; N, 8.4. Ultraviolet $\lambda_{max}^{CH_3CN}$ 302 mμ (ε 18,200). The infrared spectrum had absorption for O–H stretching at 3440 cm^{-1} and for $N{\equiv}N$ stretching at 2240 cm^{-1}. The B^{11} nmr spectrum in acetonitrile consisted of a major peak at 26.5 ppm, a very broad minor peak at 45.2 ppm, and a minor peak at 0 ppm. The 45.2-ppm peak is assigned to the boron attached to nitrogen because of its extreme broadness.

1,10-$B_{10}Cl_8(CO)_2$. A glass-lined pressure vessel was charged with 1,10-$B_{10}Cl_8(N_2)_2$ (0.5 g, 1.1 mmoles). It was then evacuated and pressured with carbon monoxide followed by a 4-hr reaction period at 200° and 1000 atm. The product was water-soluble; it was shown to be (after exposure to atmospheric moisture) a hydrate of 1,10-$B_{10}Cl_8(CO)_2$ by comparison of its infrared spectrum with that of an authentic sample.[2,18]

1,10-$B_{10}I_8(N_2)_2$. Sodium nitrite (4 g, 59 mmoles) and glacial acetic acid (10 ml) were added to a solution of 1,10-$B_{10}I_8(NH_3)_2$[18] (6.2 g, 5.4 mmoles) in 150 ml of 50% aqueous alcohol. The solution was stirred for 20 min and then filtered to obtain a first fraction of 1,10-$B_{10}I_8(N_2)_2$ as a yellow solid. The filtrate was mixed with additional sodium nitrite (2 g, 29 mmoles) and 5 ml of acetic acid and allowed to stand overnight. Additional product precipitated. The combined yield of 1,10-$B_{10}I_8(N_2)_2$ was 5.9 g (94%). Extraction with a hot mixture of 100 ml of acetonitrile and 50 ml of ethanol gave 1.2 g of 1,10-$B_{10}I_8(N_2)_2$ as dingy yellow needles. Recrystallization of the extraction residue from 200 ml of acetonitrile gave an additional 1.2 g of bright yellow needles for a combined recrystallized yield of 38% (dec pt 160–190°). This loss during recrystallization appeared to be due to reaction with the solvents; recrystallization should not be necessary for most preparative purposes. *Anal.* Calcd for $B_{10}I_8(N_2)_2$: B, 9.2; I, 86.1; N, 4.8. Found: B, 9.1; I, 84.1; N, 5.0. Ultraviolet $\lambda_{max}^{CH_3CN}$ 393 mμ (ε 5550), 295 (ε 9550), 260 (sh) (ε 10,800), 232 (ε 15,100). The infrared spectrum had an absorption band at 2280 cm^{-1} for the diazonium group.