6790 *J. Am. Chem. Soc.* **1982**, *104*, 6790-6791

$2n$ Framework Electron Clusters: Directed Synthesis of Octachlorooctaborane, B_8Cl_8. The Activation of CH Bonds

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Received April 5, 1982

The polyhedral boron halides are a series of cluster compounds with the formula B_nX_n, $n = 4$ or 8–12 when X = Cl and $n = 7$–10 when X = Br. They are of interest because they form an entire series of molecular polyhedral species that have only $2n$ framework electrons, two fewer than the $2n + 2$, $n > 4$, that are indicated for optimal deltahedral framework bonding by framework electron count–structural correlations.[1,2] Presumably, by analogy to the differences in chemistry observed between 16-electron transition-metal complexes and their more common 18-electron counterparts, the "electron hyperdeficient"[3] boron monohalide clusters should possess properties or reactivities that are unusual in comparison to the chemistry of electron-rich polyhedra like the borane anions or carboranes.

Of the boron halides the eight vertex species, B_8Cl_8, has had a particularly interesting history. The first indication of the existence of B_8Cl_8 was from an X-ray structural determination of the product formed in the thermal decomposition of neat B_2Cl_4. This product had originally been formulated as $\cdot B_{12}Cl_{11}$.[4] After recrystallization from, or possibly reaction with, BCl_3, however, the molecular formula of the compound then present was established as B_8Cl_8.[5] The experimentally obtained structures of the framework atoms of both the compound reported as B_8Cl_8 and its reduced analogue $B_8H_8^{2-}$ are dodecahedral; the framework geometries are strikingly similar.[6–8]

One of the reasons that virtually nothing is known of the chemistry of B_8Cl_8 is that the method of synthesis has been unclear.[9,10] To date, the only known source of octachlorooctaborane is the thermal decomposition of neat B_2Cl_4. By all accounts the yields of the eight vertex cluster obtained from this reaction have been "very low".[11,12]

We wish to report the synthesis of B_8Cl_8 in good yield (88%) and to communicate the first examples of the chemical reactivity of octaboron octachloride. During many reactions conversion of the eight-atom framework to a nine-vertex product occurs, which may help to explain some of the confusion surrounding the earlier experimental results.

Octaboron octachloride is readily synthesized by the thermal decomposition of dilute B_2Cl_4, 20% by weight in CCl_4, at 100 °C. The choice of solvent is important since in other solvents, e.g., BCl_3 and $SiCl_4$, the course of the decomposition differs.

Boron-11 NMR spectra (28.9 MHz) obtained very early in the reaction show only one resonance, that due to B_2Cl_4, at 62.5 ppm deshielded from external BF_3 etherate. After 90 min at 100 °C, a second absorption at −46.7 ppm (BCl_3) becomes apparent. After ca. 75 h at 100 °C, a third resonance at −65.1 ppm (B_8Cl_8) is resolved (Figure 1A). Over the course of 2 weeks, a fourth resonance at −58.3 ppm (B_9Cl_9) slowly becomes evident (Figure 1B).[13]

Boron-11 NMR data indicate that the diamagnetic portion of the purple-black air-sensitive solid obtained upon opening the sealed tubes, removing solvent, BCl_3, and any unreacted B_2Cl_4 is composed of B_8Cl_8 (95%) and B_9Cl_9 (5%), Figure 1C. Integrations of spectra like Figure 1B indicate that B_8Cl_8 is formed in 88% of the amount expected if the stoichiometry of the reaction is $8B_2Cl_4 \rightarrow B_8Cl_8 + 8BCl_3$. As obtained in Figure 1C, the purity of the compound is typically 90%.[14] Octaboron octachloride is slightly volatile in a standard vacuum line, and fractionation yields material that is 99+% pure.

One of the surprising aspects of the chemistry of B_8Cl_8 is the ready conversion of the eight vertex species to nonaborane derivatives. For example, thermal decomposition of B_8Cl_8 in CCl_4 at 200 °C yields B_9Cl_9 as well as BCl_3 and a tan intractable polymer. After 30 min, the reaction of B_8Cl_8 with a 5-fold excess of *tert*-butyl lithium, followed by removal of the lithium alkyl,[15] yields a product that is most readily shown to be the peralkylated derivative of a nine-atom cage by mass spectrometry. The molecular ion for $B_9(t\text{-Bu})_9$, m/e 611, is the highest mass ion observed, accompanied by ions at the expected ratios for $B_9(t\text{-Bu})_8^+$, m/e 554, and $B_9(t\text{-Bu})_7^+$, m/e 497; the experimental isotopic ratios are as expected. The base peak of the spectrum occurs at m/e 524, which corresponds to $B_9(t\text{-Bu})_8 - 2CH_3$.

The interaction of B_8Cl_8 with excess liquid trimethylaluminum yields $(CH_3)_nB_9Cl_{9-n}$, $n = 0$–4, partially alkylated derivatives of again the nine-membered cage. The mass spectra of these derivatives as well as the boron NMR spectra (resonances 76–96 ppm deshielded from external BF_3 etherate) are fully in accord with the formulation of these species as alkylated $2n$ framework electron derivatives. For example, the molecular ion region of $(CH_3)_4B_9Cl_5$ contains the following ions (m/e (intensity)): $(CH_3)_4B_9Cl_5^+$, 336 (10%); $(CH_3)_3B_9Cl_5^+$, 321 (68%); $(CH_3)_2B_9Cl_5^+$, 306 (100%).

Another surprising aspect of the chemistry of B_8Cl_8 is the avidity with which it accepts hydrogen. For example, if n-pentane, which has been shown to be pure by GLC techniques, is added to a sample of the solid material resulting from the thermal decomposition of B_2Cl_4 (Figure 1C), an immediate reaction occurs at ambient temperature.[16,17] Octaboron octachloride is not observed in the solution, and ^1H NMR indicated the formation of pentenes, ca. 4 mol/mol B_8Cl_8. The pentenes formed are identified by GLC techniques (OV-101 column) or by bromination of the hydrocarbon fraction followed by separation and identification of the dibromopentanes produced. Both 1- and 2-pentene are formed. If the B_8Cl_8 is rigorously purified by fractionation prior to the

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[13] ESR measurements (Varian E-4) indicate that a paramagnetic species is also formed during this reaction. The intensity of the absorption rise to a maximum after 30 min at 100 °C and remains approximately constant thereafter. The g value is 1.99; the width of the broad featureless peak is 21 G.

[14] All properties of the sublimed material, e.g., melting point and IR and mass spectra, are as reported: G. F. Lanthier, J. Kane, and A. G. Massey, *J. Inorg. Nucl. Chem.*, **33**, 1569 (1971).

[15] As in T. Davan and J. A. Morrison *J. Chem. Soc., Chem. Commun.*, 250 (1981). In the presence of excess lithium or aluminum alkylating agent, the reaction sequence appears to be fairly complex and includes at least three steps: (1) alkylation of B_8Cl_8; (2) conversion to alkyl derivatives of B_9Cl_9 (along with BR_4^-, δ 17.5, if LiR were the reagent or BR_3, δ −86, if AlR_3 was employed); (3) cage reduction to yield in the lithium reaction $B_9R_9^{2-}$, δ 5.7 (see ref 17).

[16] During the sealed-tube reactions utilizing B_8Cl_8 "as obtained", Figure 1C, as the sample warms from −196 °C, the dark purple-black of the mixture is discharged upon liquefaction. The intensity of the ESR signal is also diminished by at least 2 orders of magnitude. Boron NMR spectra do not contain resonances due to B_8Cl_8. If, however, B_8Cl_8 is fractionated prior to exposure to pentane, B_8Cl_8 is observed in solution, by NMR, until the sample has been heated to 100 °C overnight.

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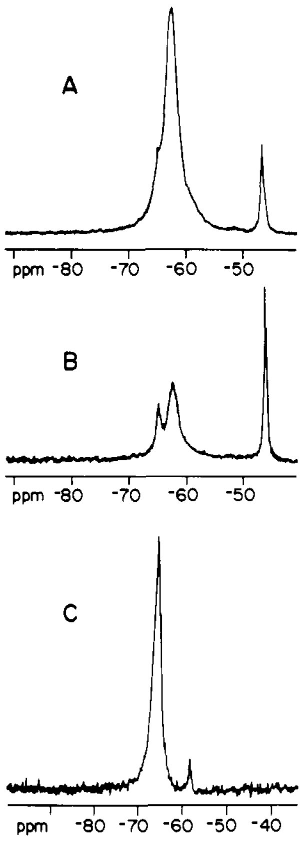

Figure 1. Boron NMR spectra (28.9 MHz): (A) B_2Cl_4, 20% weight in CCl_4, after 75 h at 100 °C (the resonances at −65 sh, −62, and −47 ppm are due to B_8Cl_8, B_2Cl_4, and BCl_3, respectively); (B) after ca. 14 days at 100 °C; (C) after removal of all very volatile material from the reaction (the resonance at −58 ppm is due to B_9Cl_9).

addition of pentane, no reaction is observed at ambient temperature. However, the formation of pentene commences upon raising the temperature to 100 °C.

In all of these reactions dihydrogen (material not condensable at −196 °C) is unobserved. The identity of all of the boron-containing products has not, as yet, been unequivocally proven; however, mass spectrometric and NMR evidence is consistant with the presence of partially hydrogenated nonaboron chlorides, e.g., $B_9H_4Cl_5$. Boron trichloride and HCl are also formed.

In conclusion, the chemistry of the polyhedral boron halides has been selected for study because these clusters lack the requisite or "magic" numbers of electrons ($2n + 2$) associated with the frameworks of many of the most stable deltahedral compounds,[1,2] and it seemed most likely that unusual reactivity patterns might emerge.

We believe that some of the reactions above do illustrate that the polyhedral boron halides may well prove to have a most interesting and diverse chemistry. In particular they illustrate that at 100 °C B_8Cl_8 can accept hydrogen from pentane, liberating pentene in the process. The activation of CH bonds[18] in this system is under further study.

Acknowledgment. The financial assistance of the donors of the Petroleum Research Foundation, admistered by the American Chemical Society, and the National Science Foundation is gratefully acknowledged.

Registry No. B_8Cl_8, 32915-80-3; B_2Cl_4, 13701-67-2; BCl_3, 10294-34-5; $B_9(t\text{-}Bu)_9$, 83416-55-1; $CH_3B_9Cl_8$, 83416-56-2; $(CH_3)_2B_9Cl_7$, 83416-57-3; $(CH_3)_3B_9Cl_6$, 83416-58-4; B_9Cl_9, 31304-34-4; $(CH_3)_4B_9Cl_5$, 83416-59-5; *n*-pentane, 109-66-0; 1-pentene, 109-67-1; 2-pentene, 109-68-2.

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Magnetic Interactions in Metalloporphyrin π-Radical Cations of Copper and Iron

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Received June 4, 1982

When a paramagnetic metalloporphyrin complex is oxidized to a π-radical cation, the opportunity exists for magnetic interactions between the unpaired electrons of the metal and the ligand. There is little understanding of the nature of this phenomenon, and also, there is conflict in the literature over the characterization of species that display it. For example, $[Cu^{II}(TPP)]^+$ (TPP = tetraphenylporphyrinate) and related copper porphyrins have been variously described as $S = 0$ or $S = 1$ systems.[1-4] Experimentally, *three* different states can be distinguished: (a) the diamagnetic $S = 0$ antiferromagnetic state, (b) the $S = 1$ ferromagnetic state having a spin-only magnetic moment $\mu_s = 2.83\ \mu_B$, and (c) the independent spin $S = {}^1/_2, S = {}^1/_2$ state having $\mu_s = 2.45\ \mu_B$.[5] The distinction between b and c does not appear to have been considered previously. Unexpectedly, the present work reveals that a noninteracting $S = {}^1/_2, S = {}^1/_2$ state should be considered for the solution phase but that a strongly antiferromagnetically coupled $S = 0$ state exists in crystalline $[Cu(TPP\cdot)][SbCl_6]$. A further intriguing case is provided by the pair of closely related complexes $Fe^{III}(OClO_3)_2(TPP\cdot)$ and $[Fe^{III}Cl(TPP\cdot)][SbCl_6]$.[6,7] Although the latter was previously taken to be an iron(IV) complex,[8] both are high-spin iron(III) radical cations, bringing together an $S = {}^5/_2$ metal and an $S = {}^1/_2$ ligand. The interesting observation is that the perchlorate complex behaves like an independent spin $S = {}^5/_2, S = {}^1/_2$ system, whereas the chloride complex is a strongly coupled overall $S = 2$ system. Moreover, the magnetic behavior of both complexes differs from that of compound I of horseradish peroxidase (HRP I), an $S = 1$ iron(IV)/$S = {}^1/_2$ porphyrin radical, which has been interpreted in terms of a weak antiferromagnet ($-J \sim 1.5\ cm^{-1}$).[9]

Synthetically, we are finding that selected organic radicals allow metalloporphyrin radical cations to be isolated in analytically pure crystalline form, many for the first time. Treatment of Cu(TPP) or Cu(TTP) (TTP = tetra-*p*-tolylporphyrinate) with tris(*p*-bromophenyl)amminium hexachloroantimonate[10] or thianthrenium perchlorate,[11] respectively, in dichloromethane gives good yields of purple crystalline $[Cu(TPP\cdot)][SbCl_6]$ and $[Cu(TTP\cdot)][ClO_4]$.[12]

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