high potential iron protein (HiPIP) the ratio[7,25] is $60/(3 \times 10^5) = 2 \times 10^{-4}$, consistent with ionic strength effect studies[7] indicating zero charge at the site of reduction. With horse heart cytochrome *c* the ratio is $1.5 \times 10^3/(3.8 \times 10^4) = 3.9 \times 10^{-2}$, consistent with a 2+ charge at the site of reduction. This value is in agreement with that reported by Cummins and Gray[26] from an analysis of the ionic strength dependence of $(H_3N)_5Ru(py)^{2+}$ reduction but is lower than that reported by Holwerda et al.[27] with other reducing agents.

The reduction rates of tetrakis[(*N*-methyl-4-pyridyl)porphine]cobalt(III)[6,28] give $k'/k_{Ru} = 7.7 \times 10^3/(1.2 \times 10^5) = 6.4 \times 10^{-2}$ for the diaquo complex. The ratio indicates a charge of 2+ to 3+ while the oxidant has a net charge of 5+, as a result of the four *N*-methylpyridyl substituents. This example simply illustrates the expected result that net charge on a reactant is not necessarily reflected in its reactivity. It appears that this empirical comparison of k'/k_{Ru} values could be used to determine reactant charge but applications are limited at the moment by the few k_{Ru} values available.

The mechanism assignments suggested here do not preclude the possibility that SO_2^- can react by a bridging mechanism, and in fact, this may be the case with the azido complex. Of course $S_2O_4^{2-}$ must have some outer-sphere reactivity as well. Results to date with $(H_3N)_5CoCl^{2+}$, $Co(NH_3)_6^{3+}$, spinach ferredoxin,[1] and aquometmyoglobin[12] indicate that $k''/k' \leq 0.5$ for totally outer-sphere reactions. Unfortunately, this limit on k''/k' is not useful in mechanism assignment if both paths have bridging-mechanism contributions. It has been shown, however, that the cobalt(III) complexes show a wide range of reactivity with dithionite, and future studies on such systems should be helpful in establishing the mechanisms of dithionite reductions.

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Registry No. $(H_3N)_5CoCl^{2+}$, 14970-14-0; $(H_3N)_5Co(N_3)^{2+}$, 14403-83-9; $(H_3N)_5Co(SO_4)^+$, 18661-07-9; $(H_3N)_5Co(Cl_3C_2O_2)^{2+}$, 19998-53-9; $(H_3N)_5Co(C_6H_5CO_2)^{2+}$, 30931-77-2; $(H_3N)_5Co(C_5H_5N)^{3+}$, 31011-67-3; $(H_3N)_5Co^{3+}$, 14695-95-5; $S_2O_4^{2-}$, 14844-07-6.

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Chemistry of the Boron Subhalides. Preparation, Boron Nuclear Magnetic Resonance, and Thermal Stability of Tetraboron Tetrachloride

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In radio-frequency discharges (~10 MHz) tetraboron tetrachloride is formed from BCl_3 at rates that are significantly higher than previously reported in earlier preparations. The chemical shift of B_4Cl_4 is found to be extremely deshielded for a boron resonance. Tetraboron tetrachloride is shown to be more thermally stable than two small *closo*-carboranes of similar size, $C,3\text{-}(CH_3)_2\text{-}1,2\text{-}C_2B_3H_3$ and $1,5\text{-}C_2B_3H_5$.

Introduction

The properties of molecules or ions containing a central core of atoms that are clustered together in a regular geometric array are of increasing interest in both main-group and transition-metal chemistry. Although many elements have been shown to form clusters, at the present time the majority of the known polyhedral species are boron containing. Rigorous MO calculations have frequently been used to explain and/or predict the structures and stabilities of boron-containing compounds,[1] but there has been a continual search for a more easily visualized approach which does not require such sophisticated methodology to yield qualitatively useful results.

The framework electron count has proven to be extraordinarily effective for the structural classification of many species that contain atoms clustered together at the core of a molecular or ionic entity. The observed geometries of many of the clusters that are formed by the main-group elements have been shown by using this simple but very powerful tool to correlate well with the number of electrons contained in the molecular orbitals that bind the framework atoms together. In particular, most of the species that are observed to occur in the closo (most compact) geometry appear to have $2n + 2$ electrons delocalized in the framework orbitals where n is the number of atoms comprising the framework.[2]

The correlation between the number of framework electrons and the structures of polyhedral compounds has also been analyzed by an algebraic graph-theoretical approach, an analysis which "provides a theoretical basis for the stability of closed deltahedral systems with n vertices and $2n + 2$ skeletal electrons".[3] For the smallest deltahedron, the tetrahedron, the conclusion from graph theory is that ten skeletal electrons are required for delocalized framework bonding, while localized bonding requires twelve framework electrons.

However, as has been explicitly noted,[2,3] one little studied class of compounds, the boron subhalides, appears to consistently violate the "rules" of these formalisms. Representative examples of clustered boron subhalides include B_4Cl_4, B_8Cl_8, and B_9Cl_9. Each of these compounds contains only $2n$ electrons in the framework orbitals, yet the observed structures appear to be based on the fully triangulated closo geometries.[4-6] Further, as Muetterties has noted, the neutral species B_4Cl_4 and B_8Cl_8 appear to be more stable than the corresponding dianions; in the nine-atom system it is not known whether B_9Cl_8H or $B_9Cl_8H^{2-}$ is the thermodynamically favored aggregate.[7]

The smallest polyhedral boron subhalide, tetraboron tetrachloride, appears to be a particularly interesting subhalide. It was the first deltahedral polyborane prepared and it is still the only example of a discrete species that is known to contain four boron atoms in a tetrahedral array. Surprisingly, little is known about this compound, possibly because of the difficulties associated with its preparation. Tetraboron tetrachloride was first isolated from the products of the thermal decomposition of B_2Cl_4[8] and the crystal structure was determined at that time,[4] but later it was reported that no B_4Cl_4 could be isolated from this source.[9] An alternative preparation involved the discharge of BCl_3 in the presence of mercury to give B_2Cl_4 which was then purified and again passed through the same discharge to form B_4Cl_4 at a rate reported to be 10 mg/h;[9] in 1976 this preparation too was repeated with poor success.[10] Many alternative reactions have been attempted, but the best repeatable synthesis currently available appears to be the dc discharge of gaseous BCl_3 in the presence of mercury. This preparation yields B_4Cl_4 at a rate of approximately 1 mg/day.[9,11] So little of this material has ever been prepared that even its thermal stability is in question, as B_4Cl_4 is reported to decompose slowly at 70 °C (no melting point could be obtained[12]), to decompose suddenly at 95 °C (the melting point[10]), and to be thermally stable to 200 °C.[9]

The purpose of the present study was to prepare the smallest of the clustered boron subhalides, B_4Cl_4, to study the boron NMR of this compound, and to ascertain its thermal stability for comparison with the stabilities of compounds that do contain $2n + 2$ electrons in the framework orbitals. However, the amount of B_4Cl_4 produced by the available methods, 1 mg/day, was insufficient, and it was clear that a different synthesis would be required.

Recently, discharge reactions in which radio-frequency ($\sim$10 MHz) power sources were inductively coupled to the plasma in which the reactive species were produced have been shown to be very efficient for the preparation of compounds of relatively limited thermal stability.[13,14] In that study compounds like $(CF_3)_4Sn$ and $(CF_3)_3Bi$, which slowly decompose at moderate temperatures, were successfully prepared and characterized. The preparation of B_4Cl_4, a compound of unknown but probably limited thermal stability, was therefore attempted by using this less harsh type of discharge.

Experimental Section

General Procedures. All manipulations were carried out in the absence of air and moisture by using a standard vacuum line equipped with Teflon valves. Fourier transform ^{11}B NMR spectra at 28.8 MHz were obtained with a Bruker HFX-90 spectrometer modified with a Bruker B-KR 322S pulsed spectrometer. Typical parameters included 512 pulses at a nutation angle of 90° and 8K data points over a bandwidth of 5000 Hz. Chemical shifts are referenced to external boron trifluoride etherate at ambient temperature, 26 °C; positive values reflect resonances that are shielded relative to the standard. Gas-phase infrared spectra were obtained with a Perkin-Elmer 1257 grating spectrophotometer. Mass spectra data for B_4Cl_4 were confirmed with an AEI-30 spectrometer operating at an ionization potential of 70 eV. Boron trichloride (Matheson) was purified by low-temperature distillation, and any hydrogen chloride present was removed at a head temperature of −115 °C; the boron trichloride that distilled between −112 and −90 °C was found to be pure. Carbon tetrachloride was dried over calcium hydride. Mercury was used as received.

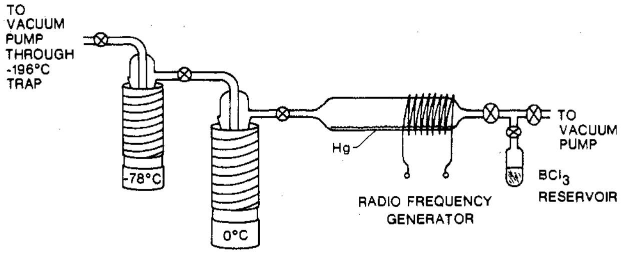

Figure 1. Diagram of plasma apparatus.

Preparation of B_4Cl_4. Tetraboron tetrachloride was prepared in a low-pressure discharge sustained by a modified Lepel 2.5 kW generator operating at approximately 8.6 MHz. The power applied to the $^1/_4$ in. copper tubing load coil which surrounded the reaction vessel (see Figure 1) varied, but the minimum power necessary to maintain the discharge, ca. 25 W, was usually applied. As a precautionary measure the Pyrex reaction vessel was annealed at 660 °C prior to each reaction. In a typical experiment the BCl_3 reservoir was maintained at −78 °C by an external bath, and the traps following the reactor were cooled to 0 and −78 °C, respectively. Removal of any traces of moisture was accomplished by allowing an initial aliquot of BCl_3 to pass through the discharge apparatus and then condensing it in the trap maintained at −196 °C. This material was discarded and the discharge initiated. Within minutes a yellow solid was observed on the walls of the reactor and on the surface of the mercury. As the reaction proceeded, the deposit became much darker and more widespread until eventually yellow and brown solids were found throughout the vacuum line.

After approximately 16 h, the discharge was terminated and the contents of the trap held at 0 °C, mercury and other materials of low volatility, were discarded. The trap that had been maintained at −78 °C was removed from the discharge line and the contents were fractionated at −45 °C. The material retained was allowed to stand at room temperature for a few days and refractionated at −45 °C. The infrared and mass spectra of the yellow crystalline B_4Cl_4 obtained are identical with those found in the literature;[10,15] no boron-containing impurities were observed in the ^{11}B NMR spectrum. Tetraboron tetrachloride melts sharply at 95 °C.

The yields varied, but typically 3–5 mg/h was obtained. Under these conditions, B_2Cl_4 was not observed in some cases. The only volatile boron-containing materials recovered were boron trichloride and tetraboron tetrachloride. More commonly, small amounts of B_2Cl_4 were isolated, but, typically, the amount of B_2Cl_4 formed was less than the amount of B_4Cl_4.

^{11}B NMR Data. At ambient temperature the chemical shift of B_4Cl_4 (1.5% by weight) was measured in each of two chlorinated solvents BCl_3 and CCl_4. Within experimental error, the chemical shift of the singlet, −85.0 ppm, was unaffected by the change of solvent. Line-shape analysis of the resonance indicated that the shape of the curve is Lorentzian. The effect of temperature on the B_4Cl_4 magnetic resonance was also investigated in these same solvents. The temperature range explored in CCl_4 was −20 to +118 °C; for B_4Cl_4 in BCl_3 the temperature was varied from −78 to +26 °C. Within this range, −78 to +118 °C, the chemical shift of B_4Cl_4 is minimally affected by temperature and was -85.0 ± 0.3 ppm for all cases. The observed peak widths at half-height vary as a function of sample temperature: typical line widths are 35 Hz at −78 °C, 16–18 Hz at 25 °C, and ca. 8 Hz at 118 °C.

Thermal Decomposition of B_4Cl_4. The thermal stability of B_4Cl_4 was assessed by heating samples of this compound, neat and dissolved in carbon tetrachloride or boron trichloride. In all cases the contents of the vessels were vacuum sublimed into 4-mm tubes which were then sealed with a torch.

Pure B_4Cl_4, 10 mg, showed no signs of decomposition after 4 h at 100 °C; after a further 6 h at 125 °C, approximately 10% of the liquid sample had decomposed with the deposition of a tan solid. A second sample, 18 mg, was held at 125 °C for 18 h and the temperature was then raised to 150 °C for 21 h. The tube was opened and 8.3 mg,

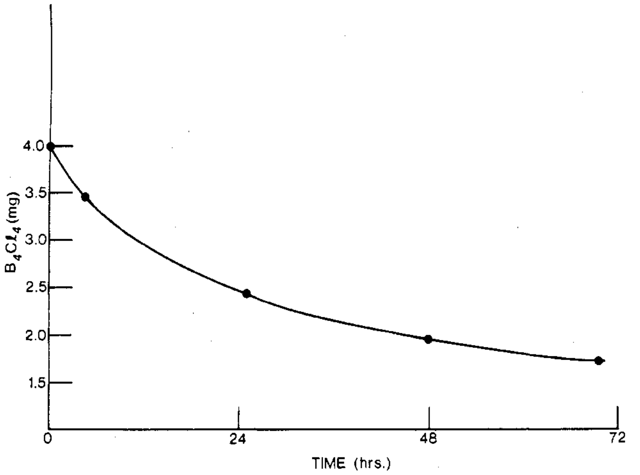

Figure 2. Thermal decomposition of tetraboron tetrachloride (1% in boron trichloride) at 125 °C.

46%, of the B_4Cl_4 was recovered. After 28 h at 152 °C, about 80% of a third sample had decomposed with the deposition of a yellow oil and a tan solid. At 200 °C decomposition was evident within 10 min. The identity of the B_4Cl_4 recovered was confirmed by a melting point of 95 °C and mass spectrometry.

A sample of B_4Cl_4, 1.2 mol % in CCl_4, was maintained at 125 °C for 120 h and the decomposition periodically monitored by ^{11}B NMR. After 18 h, a small, but distinct, resonance due to BCl_3, $\delta = -46.7$ ppm,[16] was observed and a very small amount of dark brown solid had deposited above the liquid level. After 120 h, the molar ratio of B_4Cl_4 to BCl_3 in solution was 1.5:1. After 7 weeks at 125 °C, a much larger amount of dark solid had deposited, and the only boron-containing species in solution was BCl_3.

Tetraboron tetrachloride, 4 mg, 1 mol % in boron trichloride, was similarly heated to 125 °C for 72 h. The amount of B_4Cl_4 remaining in solution at 125 °C (as determined by integration of the relative peak areas) vs. time is presented in Figure 2. A very small resonance at −63 ppm[17] indicated the presence of a minute amount of B_2Cl_4 formed during the thermal decomposition of tetraboron tetrachloride in BCl_3. The solution remained clear during the 72-h period, but after 1 week at 125 °C, yellow solids had begun to precipitate.

Results and Discussion

Preparation of B_4Cl_4. The rate of production of tetraboron tetrachloride from boron trichloride in the radio-frequency plasma is significantly higher than the rates attainable in alternative discharge systems. Even in the absence of a detailed study to optimize the experimental parameters, the yield of B_4Cl_4 has been enhanced approximately 100-fold compared to yields in earlier preparations. While the amount of material produced is still small in an absolute sense, this method does easily produce enough of the product for the survey of the chemistry of the compound, whereas earlier yields were variously characterized as "small",[11] "minute",[12] and "trace amounts if any".[18]

The most interesting aspect of the synthesis is that under the conditions reported, the amount of B_4Cl_4 produced from BCl_3 is greater than the amount of B_2Cl_4 formed simultaneously. In all previous experiments using dc arcs, ozonizer discharges, or microwave cavities, the amount of B_2Cl_4 synthesized is at least 10^3 times larger than the amount of B_4Cl_4 formed concurrently. While B_2Cl_4 and B_4Cl_4 could arise from different precursors, a simple scheme that easily incorporates these observations is that the boron subhalides may be formed through a series of reactions involving boron monochloride. This species, BCl, could regenerate BCl_3 by reaction with atomic or molecular chlorine, it could insert into a BCl_3 bond to form B_2Cl_4, or it could polymerize to form B_4Cl_4 and the yellow deposits, presumably $(BCl)_n$, observed on the walls of the reactor. Equations 1–4 present reactions by which BCl could yield all of the boron-containing products found.

$$BCl_3 \xrightarrow{rf} BCl + 2Cl \text{ (or } Cl_2) \quad (1)$$

$$BCl + BCl_3 \rightarrow B_2Cl_4 \quad (2)$$

$$4BCl \rightarrow B_4Cl_4 \quad (3)$$

$$B_4Cl_4 + mBCl \rightarrow (BCl)_{4+m} \quad (4)$$

The formation of BCl from BCl_3 has been observed in vacuum UV photoionization–mass spectrometric investigations, microwave discharges, and flash photolysis experiments.[19-21] In the first study the results indicated that BCl^+ was formed from BCl_3 by the stepwise loss of two chlorine atoms rather than the concerted loss of molecular chlorine.[19] In the latter two experiments BCl was identified among the products formed by BCl_3, but BCl_2 was not observed. Although the postulated reaction sequence does easily explain the products, the presence of other proposed intermediates such as BCl_2,[22] while not required, cannot be excluded, nor can the possibility that B_2Cl_4 is formed from singlet BCl, while B_4Cl_4 arises from, e.g., triplet BCl.

Boron NMR of Tetraboron Tetrachloride. The chemical shift of B_4Cl_4 (−85 ppm) is found to be very deshielded in comparison to the chemical shifts of perhalogenated borane anions and carboranes, compounds that do contain $2n + 2$ framework electrons. The chemical shift of the anion $B_{12}Cl_{12}^{2-}$, for example, is reported to be +12.9 ppm, while the resonances of $B_{10}Cl_{10}^{2-}$ are found at +10.6 and +5.3 ppm.[23] Similarly, the chemical shifts of the *m*-carborane $Cl_2C_2B_{10}Cl_{10}$ are observed to be 10.7 and 2.5 ppm.[24] In the absence of heavy-metal atoms, boron chemical shifts as deshielded as −85 ppm have been found only for tricoordinate species like $B(CH_3)_3$.[16] Presumably, the position of the B_4Cl_4 resonance is a reflection of the very electron-poor (hyperdeficient) environment of the boron atoms in this compound.

Variation of the temperature over a 200 °C range resulted in essentially no change in chemical shift. The differences in peak widths could be ascribed to the temperature dependence of the quadrupolar relaxation processes. No evidence for an alternative polytope was observed.

Thermal Stability of B_4Cl_4. Tetraboron tetrachloride is found to be moderately thermally stable. After an 18-h exposure to a temperature of 125 °C, followed by a further 21 h at 150 °C, 46% of a neat liquid sample can be recovered. Approximately half of a 1% solution of B_4Cl_4 in BCl_3 survives 48 h at 125 °C (see Figure 2). The known *closo*-carboranes closest in size to B_4Cl_4, e.g., *C*,3-$(CH_3)_2$-$C_2B_3H_3$ and 1,5-$C_2B_3H_5$, all have five vertices. After 2.5 h at 130 °C, 96% of an 18-mg sample of neat *C*,3-$(CH_3)_2$-1,2-$C_2B_3H_3$ decomposed.[25] After 20 h at 150 °C, all of a pure aliquot, 50 μmol, of 1,5-$C_2B_3H_5$ had decomposed.[26] Tetraboron tetrachloride is thus more thermally stable than either of two *closo*-carboranes of similar size.

The smallest predicted borane anion, $B_5H_5^{2-}$, has yet to be prepared, but the larger anions $B_nH_n^{2-}$ (n = 6–12) have all been isolated.[27] The thermal stabilities vary, but $B_{11}H_{11}^{2-}$ decomposes at 250 °C in a complex fashion[27,28] while $B_7H_7^{2-}$ is reported only to be less stable.

Obviously any detailed comparison of the stability of tetraboron tetrachloride with the stabilities of other polyhedral species would include only compounds with similar ligands, but in most cases either the analogous species are not known or their stability is not recorded. The intent here is solely to note that B_4Cl_4 and those deltahedral compounds mentioned above that do contain $2n + 2$ framework electrons are all of similar stability.

In conclusion, the radio-frequency discharge method does generate tetraboron tetrachloride from BCl_3 more efficiently than any previous synthesis. Over a 200 °C temperature range, no evidence for fluctionality on the NMR time scale is observed. Tetraboron tetrachloride, a compound that contains only eight ($2n$) framework electrons and a compound which in the construct of the graph-theoretical approach is held together by bonds that are neither localized nor delocalized in nature,[3] is surprisingly more thermally stable than two *closo*-carboranes of similar size.

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Registry No. B_4Cl_4, 17156-85-3; BCl_3, 10294-34-5.

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Reactions of Diborane with Some Chelating Bidentate Ligands. A One-Step Synthesis of $[(LL)BH_2]B_2H_7$ Salts

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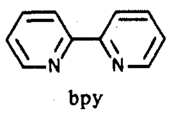
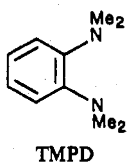
The reactions of diborane with the chelating ligands 2,2′-bipyridyl (bpy), *N,N,N′,N′*-tetramethyl-*o*-phenylenediamine (TMPD), and 1,8-bis(dimethylamino)naphthalene (BDN) have been investigated. bpy reacts with excess diborane to give the ether-insoluble air-stable bis(borane) adduct $bpy{\cdot}2BH_3$. TMPD reacts with an equimolar quantity of diborane to form the ether-insoluble air-stable ionic product $[(TMPD)BH_2]BH_4$. Acid hydrolysis of this material gives a solution of the $(TMPD)BH_2^+$ cation which has been isolated and characterized as the PF_6^- salt. TMPD reacts with excess diborane to yield the air-sensitive ether-insoluble $[(TMPD)BH_2]B_2H_7$. Mild solvolysis with 2-propanol or treatment with $(CH_3)_3N$ converts this to the BH_4^- salt. BDN reacts remarkably slowly with excess diborane in diethyl ether to form $[(BDN)BH_2]B_2H_7$. The $(BDN)BH_2^+$ cation has been isolated and characterized as the PF_6^- salt.

Introduction

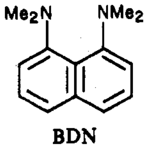
While the chemical literature contains many reports on the reactions of monodentate Lewis bases with diborane to give both covalent (symmetrical cleavage) and ionic (unsymmetrical cleavage) products,[1] with a few exceptions[2,3] studies with polydentate chelating ligands have been neglected in spite of their possible potential for geometrical control of the type of cleavage. This paper is an account of the reactions of diborane with the well-known bidentate donors 2,2′-bipyridyl (bpy), *N,N,N′,N′*-tetramethyl-*o*-phenylenediamine (TMPD), and 1,8-bis(dimethylamino)naphthalene (BDN). Normal donor–acceptor reactions occur with these bases, but with others, notably some heteroaromatics like 1,10-phenanthroline, 1,8-naphthyridine, and 8-hydroxyquinoline, hydroboration has been found to occur. The latter results will be detailed elsewhere.



bpy



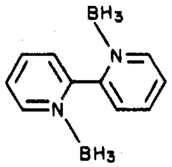
TMPD



BDN

Results and Discussion

Bipyridine–Diborane. bpy forms an ether-insoluble air-stable product with excess diborane having the composition $bpy{\cdot}B_2H_6$. The boron-11 NMR spectrum (acetonitrile) shows a single quartet ($\delta = -13.0$, $J = 95$ Hz), and the IR spectrum contains no bands characteristic of borohydride ion, so the product is the bis(borane) adduct I. The boron-11 NMR parameters of I are strikingly close to those of pyridine–borane ($\delta = -13.0$, $J = 90$ Hz).[4]



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