and the redox rate constants from ionic strength studies in acetophenone, we find the product of the reactant charges to be approximately 4 when an r value of 25 Å is assumed and even less when smaller values of r are used. These results suggest either that more extensive ion association has occurred in acetophenone relative to the other solvents or that the radius of the activated complex is larger. The latter could occur if acetophenone molecules are between the reactants in the activated complex. In either case, the Z_AZ_B/r ratio would decrease. The smaller Z_AZ_B/r ratio obtained from ionic strength studies relative to that in Figure 1 is consistent with the low position of acetophenone. However, at this point, some mention should be made of the low ionization potential of acetophenone which is less than that of any solvent examined here.[30] A solvent with a relatively low ionization potential could promote removal of an electron from the oxidant (ionization) and thus facilitate the electron transfer.[6c] Using similar arguments, we could find no explanation for the relatively low redox rates in nitromethane and acetonitrile.

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Registry No. Co(terpy)$_2^{2+}$, 18308-16-2; Co(bpy)$_3^{3+}$, 19052-39-2.

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Notes

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Nonaiodononaborane(9), B_9I_9. A Stable Boron Iodide Cluster[1]

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Simple boron halides such as boron trihalides, BX_3, and diboron tetrahalides, B_2X_4 (X = F, Cl, Br, I) are well-known compounds, and several are familiar Lewis acid reagents in chemical synthesis.[2] Much less common are neutral boron halide clusters with polyhedral geometries and the general formulation B_nX_n. These have also been referred to as boron subhalides and include only B_4Cl_4, B_8Cl_8, B_9Cl_9, and B_9Br_9 as well-characterized species.[3] Mass spectral evidence for B_7, B_{10}, B_{11}, and B_{12} chlorides has also been reported.[4]

For both classes of boron halides, formal electron deficiency exists. Boron trihalides, of course, are two electrons short of the octet at the central borons while B_nX_n clusters are formally species with $2n$ skeletal electron counts, two electrons shy of the $2n + 2$ closed-shell configurations.[5] A variety of evidence supports halogen back-donation in simple boron halides as a major stabilizing factor.[6] The general trend of π-bonding significance is believed to be B–F > B–Cl > B–Br > B–I, although Lappert has reported MO calculations that predicted an exactly opposite trend for BX_3.[7] Nonetheless the majority of experimental data support optimal stabilization of BX_3 and B_2X_4 species for X = F and minimal stabilization for X = I, as evidenced by the relative instability of both BI_3 and B_2I_4. Lipscomb has performed ab initio SCF calculations on the tetrahedral clusters B_4H_4, B_4F_4, and B_4Cl_4 and has concluded that indeed the extent of π bonding is significantly greater for B_4F_4 compared to B_4Cl_4.[8] While similar calculations for larger clusters are not yet available, the lack of any literature report of a boron iodide cluster does seem to support the premise that iodine substituents alone may not be capable of stabilizing an electron-deficient boron cage. Literature reports on attempts at synthesizing neutral boron iodide clusters are meager. Schumb reported the room-temperature decomposition of B_2I_4 to give a nonvolatile black polymeric solid with the composition $(BI)_n$.[9] This poorly characterized solid decomposed in solvents such as CS_2, CCl_4, and water while yielding free iodine upon pyrolysis at 125 °C. Recently, Massey obtained mass spectral evidence for clusters of composition $B_9Cl_{9-n}I_n$ (n = 1–6) from the reaction of iodine with a $B_{10}Cl_{10}/B_{11}Cl_{11}$ mixture at 130 °C.[10] However, none was isolated, and furthermore no periodinated clusters were observed.

We recently reported the first stable boron halide radicals $B_9X_9^{-}\cdot$ (X = Cl, Br, I) and have demonstrated the redox relationships $B_9X_9 \rightleftharpoons B_9X_9^{-}\cdot \rightleftharpoons B_9X_9^{2-}$ (X = Cl, Br).[11] We have now successfully extended this to prepare the first boron iodide cluster, B_9I_9. Excess thallic trifluoroacetate reacted with either $(n\text{-}Bu_4N)_2B_9I_9$ or $(n\text{-}Bu_4N)B_9I_9$ in CH_2Cl_2, yielding a red-purple suspension. After solvent removal and CCl_4 extraction, a dark brown microcrystalline solid can be isolated in about 30% yield. Positive identification of the product as B_9I_9 is based on the following data.

(1) Elemental analysis confirmed the formulation as $(BI)_n$.

(2) The infrared spectrum of the compound is simple and contains only one strong, broad band in the cage and B–I vibration region. This is remarkably similar to the spectra of B_9Cl_9 and B_9Br_9 (Figure 1) except for shifting of all the absorption bands to lower frequencies. Similar trends have already been noted for the polyhedral borane derivatives $B_nX_n^{2-}$

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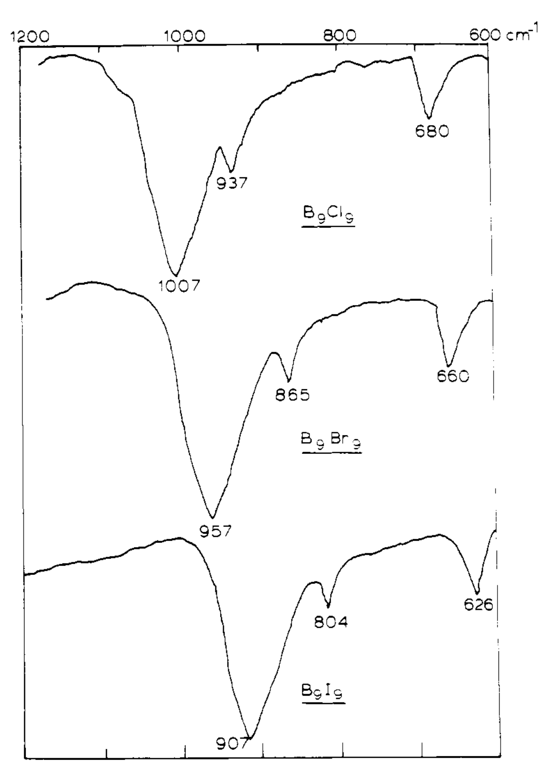

Figure 1. Infrared spectra of the B_9X_9 clusters in the 600–1200-cm^{-1} region.

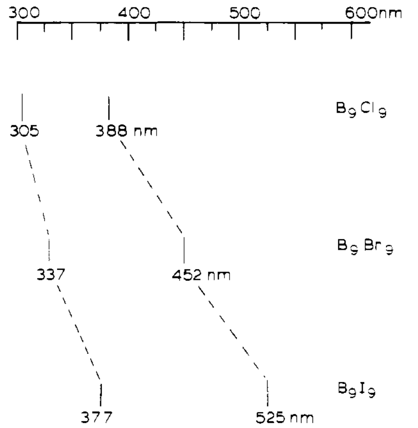

Figure 2. Electronic spectrum absorption maxima of the B_9X_9 clusters.

(n = 9, 10, 12; X = Cl, Br, I), where identical structures are found within each series.[11,12] Such shifts of all absorptions with differing substituents argue for structural similarities and significant multiple-bond character for the B–X bonds in these clusters.

A similar shift is observed in the electronic spectra of the new compound when compared with that of B_9Cl_9 and B_9Br_9 (Figure 2). The progressive shifts of the absorption maximum in the visible region from 388 to 452 to 525 nm account for their different colors; thus B_9Cl_9 is yellow, B_9Br_9 is red-orange, and B_9I_9 is red-purple in chlorinated hydrocarbon solvents.

(3) Mass spectral data clearly indicated a parent ion envelope with isotopomer distribution and intensities consistent with those calculated from natural abundances of ^{10}B and ^{11}B isotopes (Figure 3).

(4) Chemical reduction of the new compound with iodide proceeded quantitatively to give initially the dark blue $B_9I_9^{-}\cdot$ radical previously reported and then to give $B_9I_9^{2-}$.[11] This illustrates the redox relationship of the product to the two nonaiodoborane anions.

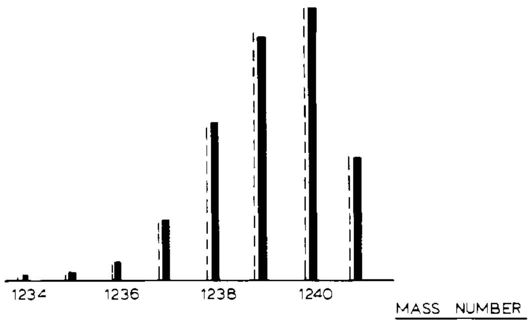

Figure 3. Comparison of theoretical (- - -) and experimental (—) mass spectral peak intensities in the parent ion of B_9I_9.

We therefore believe this to be the first example of a neutral boron cluster solely stabilized by iodine substituents and favor the tricapped trigonal-prismatic geometry (D_{3h}) found exclusively for nine-boron clusters in the solid state.[11] This dark brown solid is surprisingly air stable, and samples can be kept for months without special precautions. Solutions of B_9I_9 in chlorinated hydrocarbons are also air stable at least for hours. Reaction with water is very slow due probably to insolubility. Donor organic solvents like THF, ether, dimethoxyethane, and CH_3CN give red-purple solutions that last only for minutes before development of the characteristic dark blue coloration of the $B_9I_9^{-}\cdot$ species, indicating cage reduction. The compound also has high thermal stability and can be transferred under high vacuum without extensive decomposition at 200 °C.

The apparent stability of B_9I_9 may in part be attributed to the steric congestion created by the nine iodine substituents around the boron polyhedron, effectively precluding nucleophilic attack. Estimates of intramolecular halogen–halogen contacts indicate that all three B_9X_9 should be comparatively shielded from attack. Furthermore, all three are reluctant to undergo halide-exchange reactions commonly observed for simple boron halides. B_9Br_9, for example, is recovered unchanged from extended treatment with BCl_3 at 80 °C.[13] In view of the high coordination numbers (5 and 6) of the boron vertices, the bridging intermediate required for halogen exchange is probably not favored. That neutral B_9I_9 exists at all must attest to the ability of the iodines to help alleviate the electron-deficient character of the B_9 cage. The kinetic nature of this stability is reflected in competitive oxidations carried out between the B_9X_9 and $B_9X_9^{-}\cdot$ clusters:

$$B_9X_9 + B_9X'_9{}^{-}\cdot \rightarrow B_9X_9{}^{-}\cdot + B_9X'_9$$

$$B_9X_9{}^{-}\cdot + B_9X'_9{}^{2-} \rightarrow B_9X_9{}^{2-} + B_9X'_9{}^{-}\cdot$$

The oxidative power follows the order $B_9I_9 > B_9Br_9 > B_9Cl_9$ and $B_9I_9^{-}\cdot > B_9Br_9^{-}\cdot > B_9Cl_9^{-}\cdot$. Hence iodines in the $2n$-electron B_9I_9 and $(2n + 1)$-electron $B_9I_9^{-}\cdot$ clusters are indeed the least able to relieve the electron deficiencies as expected from observed trends in simple boron halides.

It is also instructive to compare the manner electron deficiency is compensated for in boron hydrides and boron halides (Figure 4). BH_3 simply dimerizes to give B_2H_6 using three-center BHB bonds. Boron trihalides are sufficiently stabilized by back-donation to exist as monomers. Both classes of compounds behave as Lewis acids and adduct readily. In polyhedral boranes, $B_nH_n^{2-}$ (n = 10, 12), oxidations lead typically to coupled cages. Chemical or electrolytic oxidation of $B_{10}H_{10}^{2-}$ presumably yielded the electron-deficient $B_{10}H_{10}^{-}\cdot$ species which rapidly dimerizes to $B_{20}H_{19}^{3-}$, again with

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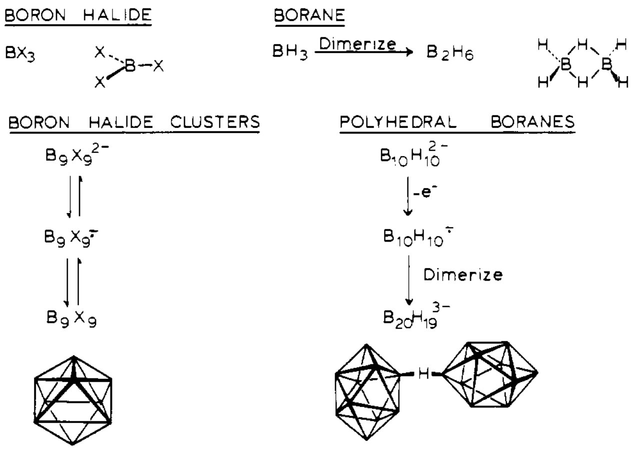

Figure 4. Electron-deficient species in boron hydrides and boron halides.

three-center BHB bonds.[14] Similarly, $B_{12}H_{12}^{2-}$ can be electrolytically oxidized to give the $B_{24}H_{23}^{3-}$ species.[15] Only the transient radical $B_8H_8^{-}\cdot$ reported by Muetterties seemed to remain monomeric at least in ethereal solvents.[16] The B_9X_9 boron halide clusters, as we have seen, are sufficiently stabilized by halogen back-donation to exist as both neutral and monoanionic electron-deficient species, favoring reduction rather than adduct formation as their predominant reaction.

Experimental Section

All reactions were carried out under air- and moisture-free conditions in Schlenk glassware. Reagent grade methylene chloride was distilled from CaH_2 and CCl_4 from P_4O_{10}. $(n\text{-}Bu_4N)B_9I_9$ and $(n\text{-}Bu_4N)_2B_9I_9$ were prepared from $(n\text{-}Bu_4N)_2B_9H_9$ as reported.[11] $Tl(CF_3COO)_3$ was obtained from Aldrich Chemical Co.

Elemental analyses were performed at Schwarzkopf Microanalytical Laboratories. Infrared spectra were recorded as Nujol mulls and KBr pellets on a Perkin-Elmer 337 spectrometer. Field-desorption mass spectra were run in CH_2Cl_2 solution on a CEC 21-110B high-resolution mass spectrometer at the Massachusetts Institute of Technology.[17]

Synthesis of B_9I_9. A solution of 200 mg, 0.12 mmol, of $(n\text{-}Bu_4N)_2B_9I_9$ in 8 mL of CH_2Cl_2 was added to 400 mg, 0.74 mmol, of $Tl(TFA)_3$. The suspension was stirred to give a red-purple suspension within minutes. After 0.5 h, the solvent was removed in vacuo and the residue extracted with 2 × 20 mL of CCl_4. The combined filtrates were evaporated to dryness. The residue was washed with hexane to give 40 mg, 0.036 mmol, of dark brown, microcrystalline solid. Anal. Calcd for B_9I_9: B, 7.85; I, 92.15. Found: B, 7.94; I, 91.50.

Reduction of B_9I_9. To a solution of 20.0 mg, 0.016 mmol, of B_9I_9 in 5 mL of CH_2Cl_2 was added dropwise a solution of 5.9 mg, 0.016 mmol, of $(n\text{-}Bu_4N)I$ in 3 mL of CH_2Cl_2. A rapid color change to dark blue was observed. After solvent removal, the residue was extracted with 2 × 3 mL of ethanol and filtered to give 22.5 mg, 0.015 mmol, of dark blue $n\text{-}Bu_4NB_9I_9$ identical with an authenic sample (95% theoretical).

Competitive Redox Reactions of B_9X_9. Equivalent amounts of B_9I_9 and $(n\text{-}Bu_4N)B_9Cl_9$ were placed in a flask. CH_2Cl_2 was added and the solution stirred for 10 min. After solvent removal, the residue was extracted twice with 5 mL of CCl_4 and filtered. The residue was then washed with ether and identified as crude $(n\text{-}Bu_4N)B_9I_9$. From the CCl_4 filtrate B_9Cl_9 can be isolated. Similar reactions were carried out with other combinations of B_9X_9 and $B_9X_9^{-}\cdot$.

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Registry No. B_9I_9, 75918-65-9; B_9Br_9, 12589-31-0; B_9Cl_9, 31304-34-4; $n\text{-}Bu_4NB_9I_9$, 72403-00-0; $n\text{-}Bu_4NB_9Br_9$, 72402-95-0; $n\text{-}Bu_4NB_9Cl_9$, 72402-98-3; $(n\text{-}Bu_4N)_2B_9I_9$, 72402-94-9.

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Kinetic Isotope Effects for Silylene Insertions into Oxygen–Hydrogen and Silicon–Hydrogen Bonds

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Silylenes, the divalent silicon species analogous to carbenes, are known to insert into a variety of heteronuclear single bonds.[1] Oxygen–hydrogen bonds of alcohols and silicon–hydrogen bonds of silanes are efficient traps for silylenes.[2–6] In this note, we report kinetic isotope effects for the insertion of photochemically generated dimethylsilylene[7] and methylphenylsilylene[8] into Si–H and O–H single bonds.

Kinetic isotope effects have been measured for the insertion of carbenes and nitrenes into various intramolecular and intermolecular traps.[9–16] In general, the observed effects, k_H/k_D, are between 1.1 and 2.5. The magnitude of k_H/k_D in these and other related studies[17–21] has been interpreted as an in-

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