can calculate p_a by an independent method making use of absolute absorption intensities from infrared spectra of gases.[23] Thus, p_a is found to be proportional to the absolute absorption intensity of an infrared-active line (which alters the dipole moment of a molecule) and inversely proportional to the square of the frequency, ν, of the line. Therefore, molecular vibrations involving low frequencies and involving atoms carrying partial charges (which tend to cause increased intensity) would make the largest contributions to p_a. Boron and nitrogen,[24] and probably also halogens, carry partial charges. Therefore, contributing modes in B-trihalogenoborazines would be those involving B–X in-plane and out-of-plane bending and B–N ring in-plane and out-of-plane torsion. Three infrared-active lines for B-trichloroborazine have been calculated by Watanabe and co-workers[25] to fall at 106, 118, and 368 cm^{-1}. By mass arguments these three lines should fall at higher frequencies for B-trifluoroborazine and at lower frequencies for B-tribromoborazine. If they were of similar intensity, p_a would reflect the $1/\nu^2$ dependence by increasing from B-trifluoro- to B-trichloro- to B-tribromoborazine.

Acknowledgment.—The authors thank the National Science Foundation and the Advanced Research Projects Agency for financial support for this research.

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Chemistry of Boranes. XXVII.[1] New Polyhedral Borane Anions, $B_9H_9^{2-}$ and $B_{11}H_{11}^{2-}$

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Salts of two novel polyhedral borane anions, $B_9H_9^{2-}$ and $B_{11}H_{11}^{2-}$, have been prepared and characterized. The alkali metal salts of $B_9H_9^{2-}$ possess a high thermal stability comparable to that of the salts of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$. At 600°, $Cs_2B_{11}H_{11}$ is converted to a mixture of $Cs_2B_{10}H_{10}$ and $Cs_2B_{12}H_{12}$. The B_9 and B_{11} anions are hydrolytically unstable in acidic media; the B_9 anion is more rapidly degraded than the B_{11} anion. In solution, the $B_9H_9^{2-}$ ion appears to be best described as a symmetrically tricapped trigonal prism (D_{3h}) of boron atoms each of which has a terminally attached hydrogen atom.

Introduction

The complete series of triangulated coordination polyhedra from the tetrahedron to the icosahedron is established for boron chemistry. This structural series with examples[2–10] is presented in Table I. However, the simple binary hydride series is as yet incomplete; missing members include $B_8H_8^{2-}$, $B_9H_9^{2-}$, and $B_{11}H_{11}^{2-}$. We report in this paper the isolation and characterization of salts of $B_9H_9^{2-}$ and $B_{11}H_{11}^{2-}$. Analogous to $B_9H_9^{2-}$ are the chlorononaboranes[7] B_9Cl_8H and $B_9Cl_8H^{2-}$ and the carborane[11] $B_7H_7C_2(CH_3)_2$, although these boranes may not necessarily comprise an isostructural series. The new $B_{11}H_{11}^{2-}$ ion is isoelectronic with the $B_9C_2H_{11}$ carborane.[9]

Synthesis.—Alkali metal salts of the $B_3H_8^-$ ion decompose smoothly under vacuum at 200–230° with liberation of hydrogen. About 1.6 moles of hydrogen is liberated per mole of triborohydride salt.[12] The solid residue from the pyrolysis consists of a mixture of salts of BH_4^-, $B_{10}H_{10}^{2-}$, $B_{12}H_{12}^{2-}$, and $B_9H_9^{2-}$. Yields of the B_9 salt are substantially greater than those of the B_{10} salt. Under ideal conditions the yield of the B_{12} salt is quite low; however, the presence of ethers in the triborohydride starting material leads to a significant increase in the yield of $B_{12}H_{12}^{2-}$. (The preparation of the $B_{12}H_{12}^{2-}$ ion in good yields by pyrolysis of ether complexes of triborohydride salts[13] and by heating ethereal solutions of triborohydride[14] salts has been described. However, we have found that $B_9H_9^{2-}$ is formed in low yield when a solution of NaB_3H_8 in diglyme is heated to 100°.)

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TABLE I

POLYHEDRAL BORANE STRUCTURES

No. of polyhedral atoms	Polyhedron	Example	Ref
4	Tetrahedron	B_4Cl_4	2
5	Trigonal bipyramid	$B_3C_2H_5$[a]	3
6	Octahedron	$B_6H_6^{2-}$	4
7	Pentagonal bipyramid	$B_5C_2H_7$[a]	5
8	Dodecahedron	B_8Cl_8	6
9	Not definitely established	$B_9Cl_8H^{2-}$	7
10	Bicapped square antiprism	$B_{10}H_{10}^{2-}$	8
11	Not definitely established	$B_9C_2H_{11}$[a]	9
12	Icosahedron	$B_{12}H_{12}^{2-}$	10

[a] The carbon atoms occupy polyhedral positions in this derivative class generically described as carboranes.

The cesium salt[15] of $B_{11}H_{13}^{2-}$ decomposes under vacuum at 250° with the liberation of 1 mole of hydrogen per mole of cesium salt. The solid residue consists substantially of the cesium salt of $B_{11}H_{11}^{2-}$. Pure samples of the cesium salt have been obtained in 70% yield from the pyrolysate residue by fractional recrystallization. As in the case of the B_9 synthesis, the pyrolysis course for $B_{11}H_{13}^{2-}$ is markedly affected by the quality of the starting material. For example, the double salts $Cs_2B_{11}H_{13}\cdot CsCl$ or $CsB_{11}H_{13}\cdot CsBH_4$, which can be present as impurities, decompose thermally to mixtures of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$.

Chemical Properties of $B_9H_9^{2-}$ and $B_{11}H_{11}^{2-}$.—The thermal stability of $B_9H_9^{2-}$ salts is comparable to that of $B_6H_6^{2-}$, $B_{10}H_{10}^{2-}$, and $B_{12}H_{12}^{2-}$ salts.[16] In 1 hr at 600°, there was no evidence of degradation of $Cs_2B_9H_9$. The cesium salt of $B_{11}H_{11}^{2-}$ is stable to at least 400°; however, at 600°, the salt is completely converted in 1 hr to a mixture of $Cs_2B_{10}H_{10}$ and $Cs_2B_{12}H_{12}$.

Both $B_9H_9^{2-}$ and $B_{11}H_{11}^{2-}$ display a moderately high degree of reactivity in aqueous media. Hydronium ion degrades both anions exhaustively to hydrogen and boric acid. The $B_{11}H_{11}^{2-}$ anion is more resistant to acid attack and survives exposure to acetic acid and to 2 *N* hydrochloric acid. In contrast, the B_9 anion has a lifetime of only a few minutes in dilute solutions of acetic acid. Both B_9 and B_{11} anions are degraded by relatively mild oxidizing agents such as Fe^{3+}, Hg^{2+}, and Cu^{2+}. Silver ions are not reduced by these anions and, in fact, silver salts of $B_9H_9^{2-}$ and $B_{11}H_{11}^{2-}$ have been isolated. The $Ag_2B_9H_9$ salt is quite sensitive to degradation by heat or light. Polarographic studies of polyhedral ions established the relative order of oxidative stability as $B_9H_9^{2-} < B_{11}H_{11}^{2-} < B_{10}H_{10}^{2-} < B_{12}H_{12}^{2-}$. The half-wave potentials are -0.15, $+0.2$, $+0.85$, and >1.1 v for $B_9H_9^{2-}$, $B_{11}H_{11}^{2-}$, $B_{10}H_{10}^{2-}$, amd $B_{12}H_{12}^{2-}$, respectively.

Bromination of $B_9H_9^{2-}$ in alkaline media gives a hexabromo derivative, $B_9Br_6H_3^{2-}$. This derivative like the previously described[7] chloro anion $B_9Cl_8H^{2-}$ is hydrolytically unstable in acid. The sensitivity of B_9 halo anions to acid degradation is somewhat surprising in view of the outstanding hydrolytic stability of other polyhedral haloborane anions, such as $B_6Br_6^{2-}$ [17] and the halogen derivatives[18] of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$. Halogenation of $B_{11}H_{11}^{2-}$ in acidic solution proceeds with abstraction of a boron atom to give B_{10} halo anions. Thus, bromination gives primarily $B_{10}Br_{10}^{2-}$, and chlorination with N-chlorosuccinimide gives $B_{10}Cl_8H_2^{2-}$. Under alkaline conditions, bromination of $B_{11}H_{11}^{2-}$ leads to a product analyzing as $B_{11}Br_9H_2^{2-}$. Reaction of $B_{11}H_{11}^{2-}$ with dimethyl sulfoxide yields dimethylsulfonium derivatives[19] of $B_{10}H_{10}^{2-}$.

Physical Characterization of $B_9H_9^{2-}$.—Unlike the other polyhedral borane anions which show only end absorption, $B_9H_9^{2-}$ displays an ultraviolet absorption maximum. The maximum is at 2260 A (ϵ 4000).

The B^{11} nmr spectrum of $B_9H_9^{2-}$ consists of two doublets of relative intensities 1 and 2 (Figure 1).[20] The B–H coupling constants are 133 ± 3 and 124 ± 2 cps, respectively. These *J* values are comparable to those previously observed[17] for $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$.

In the infrared spectrum of $B_9H_9^{2-}$ in aqueous solution, there are four clearly resolved B–H stretching frequencies at 2580, 2460, 2400, and 2350 cm^{-1}. These data are consistent with but are not definitive of a D_{3h} (*vide infra*) model. The other infrared absorptions are all weak relative to those of $B_{10}H_{10}^{2-}$ or $B_{12}H_{12}^{2-}$; the strongest absorption beyond the B–H stretching region is at 882 cm^{-1}. All the Raman lines of aqueous $B_9H_9^{2-}$ are very weak, precluding accurate polarization measurements.

It is difficult to envisage a plausible structure for $B_9H_9^{2-}$ that does not comprise a closed polyhedron. The only idealized geometries for a B_9 polyhedron of reasonable symmetry are the symmetrically tricapped trigonal prism of D_{3h} symmetry and the monocapped square antiprism[21] of C_{4v} symmetry. The B^{11} nmr spectrum establishes a minimum of two boron atom environments in relative abundances of 1 and 2. Only the D_{3h} trigonal prism is consistent with these data and is probably the ground-state geometry for the solution state of $B_9H_9^{2-}$. This geometry was first proposed[11] for the isoelectronic carborane, $B_7H_7C_2(CH_3)_2$. In the analogous although not isoelectronic species, B_9Cl_8H, nmr data unambiguously rule out any tricapped trigonal prism and indicate a capped square antiprism for the solution state of this haloborane. Actually, the energy difference between the two idealized geometries for a nonaborane, *i.e.*, D_{3h} and C_{4v}, should not be very large. The two geometries are configurationally related through a rather small stretching of a B–B interaction; a motion of about 0.3 A for each atom is sufficient to interconvert the two geom-

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(17) Observation by W. R. Hertler of this laboratory.

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(20) We have measured the hitherto unreported B^{11} nmr spectrum of CsB_9H_{14} in aqueous solution at 25° and have found that it consists of two doublets in the intensity ratio 1:2 at +27.6 ppm and +41.8 ppm. The B–H coupling constants are 142 and 133 cps, respectively.

(21) Derived from the $B_{10}H_{10}^{2-}$ D_{4d} structure by removal of an apical BH group.

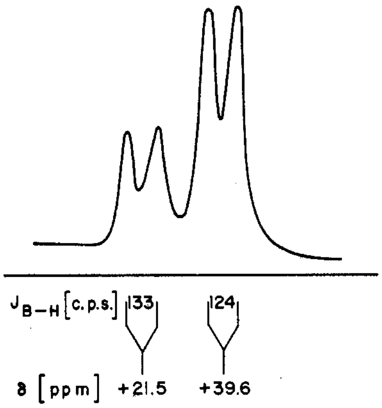

Figure 1.—B^{11} nmr spectrum of $[(CH_3)_3S]_2B_9H_9$ in H_2O at 19.3 Mc. External reference: $B(OCH_3)_3$.

etries (see Figure 2). This stretching mode, repeated a number of times, suffices to "scramble" all boron atom positions. The stereochemical rigidity[22] of a polyhedral nonaborane should be less than that[23-25] of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$, and we are attempting to obtain spectroscopic evidence of configurational exchange in $B_9H_9^{2-}$. It should also be noted that since the energy difference between the D_{3h} and C_{4v} models should be small, packing forces may suffice to distort a D_{3h} nonaborane to C_{4v} symmetry in the solid state.[26]

Physical Characterization of $B_{11}H_{11}^{2-}$.—There are some formal similarities between the $B_{11}H_{11}^{2-}$ ion and the $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ ions. The B_{11} ion shows end absorption in the ultraviolet at 2250 A. The infrared spectrum is simple. There is a B–H stretching frequency at 2450 cm^{-1} with a slight shoulder at 2360 cm^{-1}. The remaining bands down to 600 cm^{-1} occur at 1060, 1020, and 720 cm^{-1}. Some $B_{10}H_{10}^{2-}$ and $B_{11}H_{11}^{2-}$ salts show similar crystal habits. For example, crystals of cesium tetramethylammonium salts of both $B_{10}H_{10}^{2-}$ and $B_{11}H_{11}^{2-}$ are micalike although the former is orthorhombic and the latter is monoclinic.

In the B^{11} spectrum of aqueous $B_{11}H_{11}^{2-}$ ion, there are two doublets of relative intensities 10 and 1 (Figures 3 and 4), and both B–H coupling constants are 125 cps.[27] The proton spectrum is a broad multiplet that collapses on B^{11} irradiation to a single peak at τ 8.18.

Our available data do not provide a unique characterization of structure in $B_{11}H_{11}^{2-}$. Hawthorne and coworkers have proposed for the isoelectronic $B_9C_2H_{11}$ carborane system an octadecahedron in which a decaboranelike framework is closed with the eleventh polyhedral fragment, a boron atom, bridging six other polyhedral atoms (Figure 5). The B^{11} nmr data for $B_{11}H_{11}^{2-}$ can be rationalized in terms of such a structure by assigning the unique boron atom environment to

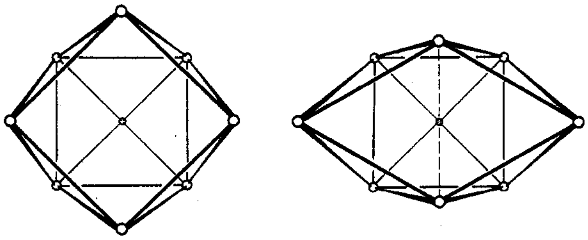

Figure 2.—C_{4v} and D_{3h} model of the B_9 polyhedron (viewed along the C_4 axis of the square antiprism and along one of the C_2 axes of the trigonal prism, respectively).

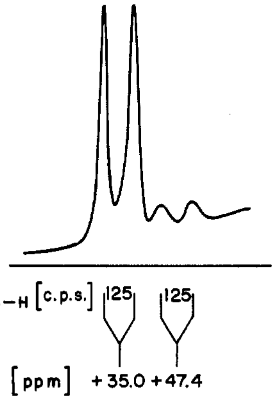

Figure 3.—B^{11} nmr spectrum of $Cs(CH_3)_4NB_{11}H_{11}$ in H_2O at 19.3 Mc.

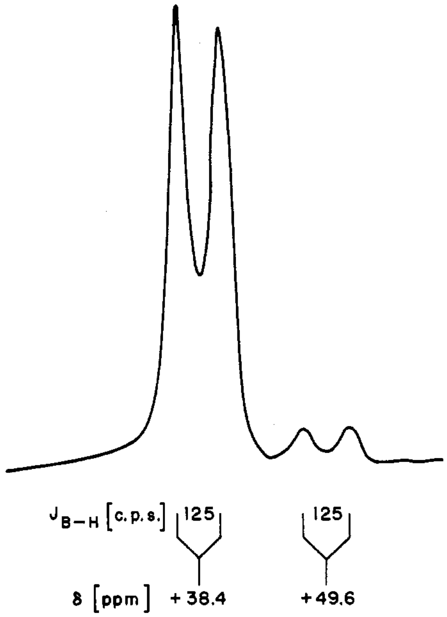

Figure 4.—B^{11} nmr spectrum of $K_2B_{11}H_{13}$ in KOH at 32.1 Mc.

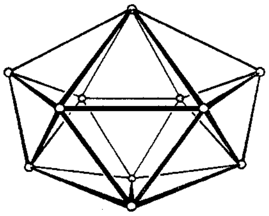

Figure 5.—Octadecahedral structure of $B_{11}H_{11}^{2-}$ (C_{2v} symmetry) as proposed by Berry, Tebbe, and Hawthorne.[9]

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(26) An analysis of three-dimensional X-ray data by Dr. L. Guggenberger of this laboratory suggests that the B_9 polyhedron in $Rb_2B_9H_9$ retains its D_{3h} symmetry.

(27) The B^{11} nmr spectrum of the anion $B_{11}H_{13}^{2-}$, which has not been reported before, shows also two doublets in the intensity ratio 10:1. The chemical shifts are +38.4 and +49.6 ppm, respectively, and both B–H coupling constants are 125 cps.

the "bridging" boron atom of coordination number seven and assuming that the ten remaining boron atoms are accidentally equivalent. Alternatively, the $B_{11}H_{11}^{2-}$ ion might be described as an open icosahedral fragment. In this structure, the unique boron atom environment could be assigned to the boron atom on the fivefold axis opposite to the icosahedral "hole." It would then be necessary to postulate that the ten boron atoms in the two nonequivalent pentagonal planes are accidentally equivalent.

The two possible geometries for $B_{11}H_{11}^{2-}$ discussed above are configurationally related by a simple bending motion (see Figure 6) which may be visualized for the icosahedral geometry as a distortion of the upper pentagonal plane. Since this distortion mode is relatively large, the barrier to configurational isomerism of this type may prove to be fairly high.

Hydrolytic Stability.—We now have a more complete qualitative picture of hydrolytic stability in polyhedral borane anions. Stability decreases in the order $B_{12}H_{12}^{2-} > B_{10}H_{10}^{2-} >> B_{11}H_{11}^{2-} > B_9H_9^{2-} \sim B_6H_6^{2-}$. The B_{12} and H_{10} anions are particularly distinguished in that they can be isolated in the form of crystalline hydronium salts which are acids comparable to sulfuric acid in acidity function. The significantly lower stability of the $B_9H_9^{2-}$ and $B_6H_6^{2-}$ ions to acid hydrolysis probably is a complex reflection of the lower resonance energy in these structures, greater charge density on the boron atoms and hydridic character of the hydrogen atoms, and lower average coordination number for the boron atoms.[28]

Experimental Section

Salts of B_3H_8.—Sodium triborohydride[8] in the form of the tris-dioxane complex was prepared by the literature procedure,[13] and the corresponding potassium salt was prepared in a similar fashion by using KBH_4 instead of $NaBH_4$ in the reaction. The potassium salt was isolated by evaporating an aqueous solution to dryness and then vaccum drying the solid at 100° (<1 μ). Rubidium, cesium, and thallium salts were prepared from the sodium salt by adding soluble salts of the large cations to a solution of sodium triborohydride in water. These were recrystallized twice from water. *Anal.* Calcd for RbB_3H_8: B, 25.8; hydrolytic H_2, 1600 ml/g. Found: B, 25.8; hydrolytic H_2, 1611 ml/g. Calcd for TlB_3H_8: Tl, 83.5; B, 13.3; H, 3.3. Found: Tl, 83.4; B, 13.5; H, 3.7.

Pyrolysis of CsB_3H_8. Preparation of $Cs_2B_9H_9$.—In an evacuated flask connected to a vacuum line of sufficient volume to hold about 10 l. of gas, CsB_3H_8 (37.8 g, 0.218 mole) was heated to a temperature of ~230° within 30 min and then held at that temperature for another 30 min. Hydrogen evolution commenced slowly around 180° and proceeded very vigorously above 210°. The total pressure was kept at about 300 mm initially, but in the later stages of the pyrolysis it approached (but never exceeded) atmospheric pressure. A total of 7.75 l. (0.346 mole) of hydrogen was collected. The solid pyrolysate was treated with 180 ml of boiling water, and the resulting hot suspension was filtered. The insoluble material was twice recrystallized from 300 ml of water to give 5.7 g (0.015 mole) of $Cs_2B_9H_9$ as glittering, faintly yellowish crystals. *Anal.* Calcd for $Cs_2B_9H_9$: Cs, 71.4; B, 26.2; H, 2.4; hydrolytic H_2, 1143 ml/g. Found: Cs, 71.6; B, 26.3; H, 2.6; hydrolytic H_2, 1148 ml/g.

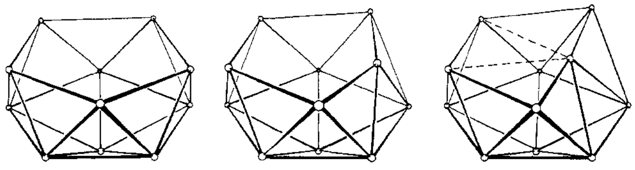

Figure 6.—Interconversion of geometrical configurations for the B_{11} cage. The C_{5v} model is on the left, and the C_{2v} model is on the right; the figure in the center represents an intermediate configuration.

The filtrate from above was cooled in an ice bath to give a precipitate shown by infrared analysis to consist largely of $Cs_2B_{12}H_{12}\cdot CsBH_4$. This solid was allowed to react with dilute hydrochloric acid to give the known double salt $Cs_2B_{12}H_{12}\cdot CsCl$. The yield was 1.0 g. *Anal.* Calcd for $Cs_2B_{12}H_{12}\cdot CsCl$: Cs, 69.2; B, 22.5; H, 2.1; Cl, 6.2. Found: Cs, 67.5; B, 22.5; H, 2.1; Cl, 6.2. The double salt was identical with an authentic sample as shown by comparison of the infrared spectra and the X-ray powder patterns.

Aqueous tetramethylammonium hydroxide was then added to the filtrate from the $Cs_2B_{12}H_{12}\cdot CsBH_4$ isolation step, and the resulting precipitate was collected and recrystallized from 150 ml of water to give 3.7 g (0.011 mole) of $Cs(CH_3)_4NB_{10}H_{10}$. *Anal.* Calcd for $Cs(CH_3)_4NB_{10}H_{10}$: Cs, 40.9; C, 14.8; H, 6.8; N, 4.3; B, 33.3; hydrolytic H_2, 1447 ml/g. Found: Cs, 39.7; C, 14.9; H, 6.8; N, 4.3; B, 33.1; hydrolytic H_2, 1463 ml/g.

This synthesis of $B_9H_9^{2-}$ was run routinely many times as described above as well as on a smaller scale. The yields of the individual products varied only within very narrow limits.

Pyrolysis of RbB_3H_8. Preparation of $Rb_2B_9H_9$.—With the apparatus described in the preceding example, RbB_3H_8 (7.0 g, 0.055 mole) was heated to 230° for about 1 hr. Hydrogen was evolved slowly up to 200°, but very briskly at 220–225°. A total of 1880 ml (0.084 mole) of H_2 was collected. The solid reaction product was dissolved in 80 ml of boiling water, and the resulting solution was allowed to cool to 40–50°. The resulting precipitate was collected by filtration and recrystallized from 30 ml of water to give 1.0 g (0.005 mole) of $Rb_2B_9H_9$. *Anal.* Calcd for $Rb_2B_9H_9$: Rb, 61.6; B, 35.1; H, 3.3; hydrolytic H_2, 1534 ml/g. Found: Rb, 60.2; B, 35.2; H, 3.4; hydrolytic H_2, 1520 ml/g.

Concentration and cooling of the filtrate from the $Rb_2B_9H_9$ isolation step gave 1.9 g of solid consisting of a mixture of $Rb_2B_{10}H_{10}$ and $Rb_2B_{12}H_{12}\cdot RbBH_4$, as indicated by infrared analysis. It was not further separated.

Pyrolysis of KB_3H_8. Synthesis of $K_2B_9H_9$.—Potassium triborohydride (16.5 g, 0.21 mole) was heated to 227° for 1 hr under the conditions employed for the pyrolysis of CsB_3H_8 and RbB_3H_8. A very vigorous evolution of hydrogen was observed slightly above 200° (about 4 l. of H_2/min). The total volume of hydrogen generated was 6.3 l. (0.28 mole). The solid pyrolysate, after dissolution in 50 ml of water, was treated with an aqueous cesium fluoride solution, and the resulting crude salt was separated and purified in the same fashion as the CsB_3H_8 pyrolysate. The yields were 2.0 g of $Cs_2B_9H_9$ as well as 1.5 g of $Cs_2B_{12}H_{12}\cdot CsCl$ and 0.1 g of $Cs(CH_3)_4NB_{10}H_{10}$. *Anal.* Found for $Cs_2B_9H_9$: B, 26.5; hydrolytic H_2, 1126 ml/g.

Preparation of $[(CH_3)_3S]_2B_9H_9$ and $Zn(NH_3)_4B_9H_9$.—A solution of 10 g of $Cs_2B_9H_9$ in 1 l. of hot water, the pH of which had been adjusted to about 8, was passed through a sodium ion exchange column prepared by saturating Rexyn 101 (H) resin with sodium chloride solution and washing with water until the washings were free of chloride ion. The solution was vacuum concentrated on a rotating evaporator to yield a viscous yellow oil, which on standing crystallized to give a hydrated salt of $Na_2B_9H_9$.

Aqueous solutions of $Na_2B_9H_9$ and trimethylsulfonium iodide

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[28] Hydrolysis mechanism has not been established for any of the polyhedral anions. Two possibilities are: (1) direct hydronium ion or proton attack of a BH hydrogen atom and hydrogen elimination with water attack of the boron atom; (2) protonation of the polyhedron, *e.g.*, at an edge, attack of water at a now relatively electrophilic boron site, and hydrogen elimination. The concept of polyhedral protonation is not unreasonable since H–D exchange occurs for $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ only in acidified D_2O.

were mixed to give a precipitate which was recrystallized from water. *Anal.* Calcd for $[(CH_3)_3S]_2B_9H_9$: B, 37.3; S, 24.6. Found: B, 37.4; S, 24.6.

In similar fashion, the tetraamminezinc salt was prepared by mixing dilute ammonium hydroxide solutions of $Na_2B_9H_9$ and tetraamminezinc chloride. The precipitate was recrystallized from dilute ammonium hydroxide. *Anal.* Calcd for $Zn(NH_3)_4B_9H_9$: Zn, 27.3; N, 23.4; H, 8.8; B, 40.6. Found: Zn, 27.4; N, 23.1; H, 9.1; B, 40.6.

Spectral Data of $B_9H_9^{2-}$.—The ultraviolet absorption spectra of some $B_9H_9^{2-}$ salts were as follows: $Cs_2B_9H_9$, $\lambda_{max}^{H_2O}$ 2240 A (ϵ 3950); $Rb_2B_9H_9$, $\lambda_{max}^{H_2O}$ 2260 A (ϵ 4040); $[(CH_3)_3S]_2B_9H_9$, $\lambda_{max}^{H_2O}$ 2260 A (ϵ 4540).

The infrared spectrum of $Rb_2B_9H_9$ was recorded (Nujol mull) on a Perkin-Elmer Model 20 grating instrument from 4000 to 200 cm^{-1}. In the B–H stretching region, a very sharp spike occurred at 2540 cm^{-1}; other well-defined absorption peaks were at 2478, 2445, and 2415 cm^{-1}; in the region of cage vibrations, bands were observed at 1050 (w), 995 (w) with a shoulder at 960, 882 (m), 760 (w), 660 (w), and 590 (vw) cm^{-1}. The positions of the B–H stretching vibrations of $Rb_2B_9H_9$ in aqueous solution were 2580, 2460, 2400 (vs), and 2350 cm^{-1}. The spectrum of $Cs_2B_9H_9$ was identical with that of $Rb_2B_9H_9$.

A Raman spectrum of a concentrated aqueous solution of $Na_2B_9H_9$ was obtained using a Cary Raman spectrometer equipped with a helical Toronto mercury arc source. The intensity of all the Raman bands appeared very low; the positions were 2510 (b), 2455 (b), 890, 800, 760, and 460 (vw, b) cm^{-1}.

Bromination of $B_9H_9^{2-}$.—A sample of $Cs_2B_9H_9$ (670 mg, 1.8 mmoles) in 50 ml of 2 *N* sodium hydroxide solution was refluxed with 50 ml of sodium hypobromite solution. More bromine was added dropwise until the yellow color of NaOBr persisted. Addition of tetramethylammonium chloride precipitated a solid which was recrystallized from 40 ml of a 1:1 mixture of acetonitrile and water. Recovery was 0.4 g. *Anal.* Calcd for $[(CH_3)_4N]_2B_9Br_6H_3$: C, 13.2; H, 3.7; N, 3.9; B, 13.4; Br, 65.8. Found: C, 13.5; H, 4.5; N, 3.9; B, 13.6; Br, 65.3.

This bromo derivative had ultraviolet absorption at 2180 A (ϵ 10,200) and a shoulder at 3030 A (ϵ 138). The B^{11} nmr spectrum at 19.2 Mc consisted of two broad peaks centered at +16.9 and +28.2 ppm which remained unchanged when a superimposed field at 60 Mc was applied. The infrared spectrum of the salt, in addition to cation bands, had a moderately strong and sharp B–H absorption at 2550 cm^{-1} as well as a multitude of weak bands between 1100 and 700 cm^{-1}.

In aqueous solution, the $B_9Br_6H_3^{2-}$ ion slowly evolved hydrogen upon acidification with hydrochloric acid.

Preparation of $Cs_2B_{11}H_{13}$ and $Cs(CH_3)_4NB_{11}H_{13}$.—For the preparation of $Cs_2B_{11}H_{13}$ we employed a synthesis similar to the one that has been described[15] for $Rb_2B_{11}H_{13}$. Recrystallization of $Cs_2B_{11}H_{13}$ from aqueous tetramethylammonium hydroxide gave a less soluble double salt as large, platelike crystals. *Anal.* Calcd for $Cs(CH_3)_4NB_{11}H_{13}$: Cs, 39.2; C, 14.2; H, 7.4; N, 4.1; B, 35.1; hydrolytic H_2, 1585 ml/g. Found: Cs, 38.0; C, 14.0; H, 7.5; N, 4.2; B, 35.0; hydrolytic H_2, 1584 ml/g.

Pyrolysis of $Cs_2B_{11}H_{13}$. Preparation of $Cs_2B_{11}H_{11}$.—In an evacuated flask connected to a vacuum line, $Cs_2B_{11}H_{13}$ (10 g, 0.025 mole) was heated to 268° for about 1 hr. Hydrogen (544 ml, 0.024 mole) was collected during this time, with a concomitant pressure increase to about 600 mm. The solid pyrolysate was dissolved in 35 ml of hot water, and the solution was filtered through Celite to remove colloids. Slow cooling of the solution to room temperature produced 6.0 g of pure crystalline $Cs_2B_{11}H_{11}$. The filtrate contained 3.6 g of a mixture of cesium salts of $B_{10}H_{10}^{2-}$, $B_{12}H_{12}^{2-}$, and some additional $B_{11}H_{11}^{2-}$, which was identified by isolation of the salt mixture and comparison of the infrared and B^{11} nmr spectra with those of mixtures of samples of known composition. *Anal.* Calcd for $Cs_2B_{11}H_{11}$: Cs, 67.1; B, 30.1; H, 2.8; hydrolytic H_2, 1301 ml/g. Found: Cs, 65.4; B, 29.9; H, 2.9; hydrolytic H_2, 1287 ml/g.

Preparation of $Cs(CH_3)_4NB_{11}H_{11}$.—Under the same conditions as described above, $Cs_2B_{11}H_{13}$ (5.6 g, 0.014 mole) generated 364 ml (0.016 mole) of hydrogen. Tetramethylammonium hydroxide was added to the filtered aqueous solution of the solid reaction product. The resulting precipitate was recrystallized from 75 ml of water to give, in two crops, a total of 3.8 g of cesium tetramethylammonium hendecahydrohendecaborate. *Anal.* Calcd for $Cs(CH_3)_4NB_{11}H_{11}$: Cs, 39.4; C, 14.3; H, 6.9; N, 4.2; B, 35.3; hydrolytic H_2, 1528 ml/g. Found: Cs, 38.3; C, 14.8; H, 6.8; N, 4.2; B, 35.6; hydrolytic H_2, 1528 ml/g. The infrared spectrum (KBr disk, Perkin-Elmer Model 21 spectrophotometer) of this salt showed anion absorptions at 2450 cm^{-1} with a shoulder at 2360 cm^{-1}, at 1060 cm^{-1} with a shoulder at 1020 cm^{-1}, and at 720 cm^{-1}.

Pyrolysis of $Cs_2B_{11}H_{13}\cdot CsCl$.—The double salt $Cs_2B_{11}H_{13}\cdot CsCl$ (4.2 g, 7.4 mmoles) was heated to 285–313° for 3 hr. A total of 170 ml (7.6 mmoles) of hydrogen was collected, no significant hydrogen evolution being observed below 280°. The solid pyrolysate was dissolved in 50 ml of water, and the solution was treated with a solution of tetramethylammonium hydroxide. The infrared spectrum of the resulting precipitate showed absorptions typical of both the $B_{10}H_{10}^{2-}$ cage and the $B_{12}H_{12}^{2-}$ cage in about equal intensities. There was no evidence for $B_{11}H_{11}^{2-}$ in the mixture.

Preparation of $B_{11}H_{11}^{2-}$ Salts.—The sodium salt of $B_{11}H_{11}^{2-}$ was prepared by passing a solution of $Cs_2B_{11}H_{11}$ through a sodium ion exchange column. The effluent was evaporated to dryness to give a hydrated and hygroscopic form of $Na_2B_{11}H_{11}$. Aqueous solutions of this salt were used for the preparation of the salts described below by metathesis with soluble salts of the respective cations. The amminezinc salt was twice recrystallized from dilute ammonium hydroxide solution, the amminecadmium salt from concentrated ammonium hydroxide, the phosphonium salt from a mixture of acetonitrile (80%) and ethanol (20%), and the arsonium salt from a mixture of ethanol (80%) and acetonitrile (20%). The zinc and cadmium salts were obtained as colorless needles, the phosphonium salt as bright yellow plates, and the arsonium salt as light yellow needles. *Anal.* Calcd for $Zn(NH_3)_4B_{11}H_{11}$: Zn, 24.8; N, 21.3; H, 8.8; B, 45.2; hydrolytic H_2, 1954 ml/g. Found: Zn, 24.6; N, 21.1; H, 8.8; B, 44.4; hydrolytic H_2, 1952 ml/g. Calcd for $Cd(NH_3)_{5.5}(H_2O)_{0.5}B_{11}H_{11}$: Cd, 32.6; N, 22.3; H, 8.3; B, 34.5. Found: Cd, 32.1; N, 22.5; H, 8.4; B, 34.4. Calcd for $[(C_6H_5)_3PCH_3]_2B_{11}H_{11}$: C, 66.7; H, 6.9; P, 9.1; B, 17.4. Found: C, 66.1; H, 7.1; P, 8.3; B, 17.7. Calcd for $[(C_6H_5)_4As]_2B_{11}H_{11}$: C, 64.3; H, 5.7; B, 13.3; As, 16.7. Found: C, 64.4; H, 6.4; B, 12.5; As, 15.3. Calcd for $[(CH_3)_3S]_2B_{11}H_{11}$: S, 22.6; B, 41.8. Found: S, 22.9; B, 42.2.

Halogenation of $B_{11}H_{11}^{2-}$.—$Cs_2B_{11}H_{11}$ (4.6 g, 0.011 mole) was dissolved in 100 ml of water. Bromine was slowly added to the hot solution until the bromine color was no longer discharged. The solution was heated to reflux while gaseous chlorine was bubbled through it for 1 hr. The excess free halogen was then destroyed with $NaHSO_3$. Addition of aqueous tetramethylammonium chloride to the reaction solution precipitated 4.0 g of $[(CH_3)_4N]_2B_{10}Br_{10}$ which was recrystallized from a large volume of water. *Anal.* Calcd for $[(CH_3)_4N]_2B_{10}Br_{10}$: C, 9.1; H, 2.3; N, 2.7; B, 10.3; Br, 75.7. Found: C, 8.9; H, 2.0; N, 2.3; B, 10.1; Br, 75.7. Infrared and B^{11} nmr spectra were superimposable with those of authentic samples.

N-Chlorosuccinimide (15 g, 0.11 mole) in 100 ml of water was added to an aqueous solution of $Na_2B_{11}H_{11}$ containing *ca.* 1.8 g of $Na_2B_{11}H_{11}$. After an induction period of about 1 min, a very vigorous exothermic reaction ensued, heating the solvent to reflux. Addition of tetramethylammonium chloride precipitated 0.7 g of a solid recrystallizable from water. The analysis and infrared and ultraviolet spectra of this solid indicated a composition of $[(CH_3)_4N]_2B_{10}Cl_8H_2$. *Anal.* Calcd for $[(CH_3)_4N]_2B_{10}Cl_8H_2$: C, 17.5; H, 5.9; N, 5.1; B, 19.7; Cl, 51.7. Found: C, 17.5; H, 5.2; N, 5.3; B, 19.5; Cl, 51.7.

Sodium hypobromite solution (50 ml) was added to an aqueous solution containing *ca.* 1 g of $Na_2B_{11}H_{11}$, and the mixture was refluxed for 30 min. Addition of tetramethylammonium chloride precipitated 3.2 g of a white solid which was recrystallized from a

1:1 mixture of water and acetonitrile. The analysis indicated a composition of $[(CH_3)_4N]_2B_{11}Br_9H_2$. *Anal.* Calcd. for $[(CH_3)_4N]_2B_{11}Br_9H_2$: C, 9.7; H, 2.7; N, 2.8; B, 12.0; Br, 72.8. Found: C, 9.7; H, 3.0; N, 2.9; B, 11.8; Br, 72.5. The infrared spectrum of this compound showed a weak B–H absorption at 2580 cm^{-1}; cage bands occurred at 1150 (w), 1120 (m), 1010 (m), 990 (m), 960 (s), 845 (s), 820 (sh), and 720 cm^{-1}. The compound had ultraviolet absorption at 2360 A (ϵ 4350) and a shoulder at 2860 A (ϵ 108). The B^{11} nmr spectrum consisted of a broad peak at +30.7 ppm with a shoulder at +20.8 ppm.

Polarographic Data.—A polarographic oxidation reduction study on $Cs(CH_3)_4NB_{11}H_{11}$ in acetonitrile solution in the potential range +0.6 to −2.0 v, with $(C_4H_9)_4NClO_4$ as supporting electrolyte, showed a well-defined oxidation wave at $E_{1/2}$ = 0.20 v corresponding to approximately a two-electron oxidation. The reduction observed at $E_{1/2}$ = −1.9 v was less well defined and probably represented a many-electron step. In an aqueous 0.5 *M* K_2SO_4 solution, the $B_9H_9^{2-}$ anion was oxidized at −0.15 v. The process was diffusion controlled at a platinum surface, and the oxidation might have been autocatalytic in nature. The use of a phosphate buffer solution did not significantly alter the results obtained in K_2SO_4 solution.

X-Ray Data.—As an additional characterization of some of the salts described in this article, lattice constants were determined from precession and Weissenberg photographs. The results are as follows (the experimentally determined density (by flotation) is abbreviated d_E, the calculated density is designated d_X): $Rb_2B_9H_9$: tetragonal, $a = 6.33$, $c = 11.51$, $Z = 2$, $d_X = 1.98$, $d_E = 1.99$; $Cs_2B_9H_9$: tetragonal, $a = 6.50$, $c = 12.06$; $Z = 2$, $d_X = 2.43$, $d_E = 2.43$; $Cs(CH_3)_4NB_{10}H_{10}$: orthorhombic, $a = 27.72$, $b = 7.47$, $c = 7.42$, $Z = 4$, $d_X = 1.406$, $d_E = 1.390$; $Cs(CH_3)_4NB_{11}H_{13}$: orthorhombic, $a = 5.715$, $b = 5.779$, $c = 12.370$, $Z = 1$, $d_X = 1.378$, $d_E = 1.382$; $Cs(CH_3)_4NB_{11}H_{11}$: monoclinic, $a = 12.59$, $b = 5.69$, $c = 5.68$, $\beta = 96.62°$, $Z = 1$, $d_X = 1.385$, $d_E = 1.368$; $Zn(NH_3)_4B_{11}H_{11}$: hexagonal, $a = 7.46$, $c = 14.40$, $Z = 2$, $d_X = 1.26$, $d_E = 1.29$.[29]

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(29) NOTE ADDED IN PROOF.—A recent experiment with the tetra-*n*-butylammonium salt of $B_9H_9^{2-}$ in dimethyl sulfoxide has established a minimum lifetime for the ground state (D_{3h}) geometry *at 200°* of $\sim 10^{-4}$ sec. The characteristic B^{11} spectrum of $B_9H_9^{2-}$ is unperturbed at 200° and 32 Mc. We would estimate from this information that the barrier to polyhedral rearrangement in unsubstituted (*exo* or skeletal polyhedral) $B_9H_9^{2-}$ is at least 30 kcal. This experiment was performed with the cooperation of Professor M. F. Hawthorne and Phillip Garrett and with their 32-Mc radiofrequency unit. (*Caution:* Mixtures of $B_9H_9^{2-}$ salts and dimethyl sulfoxide react irreversibly and explosively fast after relatively long (minutes) induction periods at 200° and above.)

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Approximate Force Constants for Tetrahedral Metal Carbonyls and Nitrosyls

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Approximate carbonyl and nitrosyl force constants have been calculated for the molecules in the tetrahedral isoelectronic series $Mn(NO)_3(CO)$, $Fe(NO)_2(CO)_2$, $Co(NO)(CO)_3$, $Ni(CO)_4$, and their substituted derivatives. The required secular equations are given for species having two different oscillators. These force constants provide a quantitative means for comparing relative π-acceptor strengths of the substituent ligands. Explicit inclusion of the CN oscillator of isonitriles is shown to be important in derivatives of ligands of this type. Empirical relationships have been determined which allow the prediction of force constants and frequencies in substituted derivatives provided information on a related molecule is available.

Introduction

In a recent series of articles[1–3] Cotton demonstrated the usefulness of easily calculated "nonrigorous" force constants for carbonyl complexes. In this method force constants are calculated from secular equations in which only the CO oscillators and their interactions are considered. Couplings between the CO vibrations and other deformations of the molecule are not included. Observed frequencies, uncorrected for anharmonicity, for molecules in solution are used, and so long as a similar procedure is employed for a series of compounds, meaningful comparisons of the calculated force constants may be made. We have extended this type of treatment to the tetrahedral isoelectronic series $Mn(NO)_3(CO)$, $Fe(NO)_2(CO)_2$, $Co(NO)(CO)_3$, $Ni(CO)_4$, and their substituted derivatives. Quite recently Beck and Lottes[4] reported such calculations for a large number of carbonyl, nitrosyl, and halogen compounds of manganese, iron, and cobalt. We incorporate their data with ours and with that culled from the literature by us for cobalt and nickel carbonyl and nitrosyl compounds to present a fairly complete summary of all known tetrahedral molecules of this general type. The appropriate secular equations are presented explicitly here for future use and reference.

Experimental Section

Materials.—$Co(CO)_3(NO)$ was prepared as described by Horrocks and Taylor.[5] The ditertiary phosphines 1,1-bis(diphenylphosphino)methane (dpm), 1,2-bis(diphenylphosphino)ethane (dpe), and 1,3-bis(diphenylphosphino)propane (dpp) were prepared using the method of Hewertson and Watson.[6] 1,3-Bis-

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(1) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

(2) C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).

(3) F. A. Cotton, *ibid.*, **3**, 702 (1964). One of the secular equations for $Ni(CO)_4$ given in ref 3 is in error and should read, in Cotton's notation, $\lambda_{T_2} = \mu(k - k_i)$.

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