place upon solvent removal. While a few of what may be partially curled ribbons can be found in the micrographs (Figure 2, fiber marked b), most are apparently fully curled. Evidently very strong forces are at work here.

The method of synthesis of the polymer points up its general inertness.[18] The source of this inertness is, no doubt, attributable partly to the structure of the backbone of the polymer since the fission of it into even just two pieces requires the rupture of many bonds. However, also important must be the elemental composition of the polymer—fully 75% of the total being silicon and oxygen.

The fact that the ribbon comes out intact as a unit of substantial dimensions, perhaps a tenth of a micron by several microns, judging from the electron micrographs, leads to the conclusion that the molecular weight of the polymer is many millions. That an ordered product of such high molecular weight is obtained points up just how directed the polymerization process which leads to the formation of the $Si_2O_5^{2-}$ sheet of chrysotile is. Further, the ordered nature of the product brings out the advantages of making ordered organo polymers, as has been done here, by the substitution of polymeric frameworks formed as an integral part of a crystallization process and hence formed in circumstances where the orienting forces are very high. Now, while chrysotile is particularly suited for use in this approach because it has a robust and accessible framework and because the configuration of the framework is such as to tend to prevent intersheet cross-linking (the pendant oxygens are all on one side of the sheet), it is clear that the approach can be used to advantage on other natural and synthetic silicate and nonsilicate crystals containing suitable frameworks.

The Structure of Chrysotile.—In view of the results obtained, it appears that the closed concentric cylinder concept for the structure of chrysotile can be ruled out. The conversion of such cylinders into ribbons would require a lengthwise splitting of the cylinders and this seems most unlikely.

Acknowledgment.—The help of Drs. P. H. Geil, A. G. Walton, J. J. B. P. Blais, and Mr. A. Schwartz in the electron microscope work is gratefully acknowledged.

[18] Linear siloxane polymers rearrange under the type of conditions used.

CONTRIBUTION NO. 1300 FROM THE CENTRAL RESEARCH DEPARTMENT,
EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON, DELAWARE 19898

Chemistry of Boranes. XXIX.[1] Thia- and Azaboranes

BY W. R. HERTLER, F. KLANBERG, AND E. L. MUETTERTIES

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Reaction of decaborane(14) with aqueous ammonium polysulfide gives the thiaborane ion, $B_9H_{12}S$, in essentially quantitative yield. Dehydration of the hydrated conjugate acid of $B_9H_{12}S^-$ gives $B_9H_{11}S$ which in turn reacts with a variety of Lewis bases (L) to give complexes $L \cdot B_9H_{11}S$. Pyrolysis of $CsB_9H_{12}S$ gives the ion $B_{10}H_{11}S^-$, which on acidification is converted to the weak acid $B_{10}H_{12}S$. Treatment of $B_{10}H_{11}S^-$ or $B_{10}H_{12}S$ with strong base affords $B_{10}H_{10}S^{2-}$, which reacts with phenyldichloroborane to give icosahedral $C_6H_5B_{11}H_{10}S$. Reaction of $B_{10}H_{10}S^{2-}$ with a variety of transition metal halides gives a series of icosahedral metalothiaboranes such as $(B_{10}H_{10}S)_2Co^-$. The ion $B_{10}H_{11}S^-$ has also been obtained from the reaction of decaborane(14) with thionitrosodimethylamine along with a new azaborane, $(CH_3)_2NNB_9H_{12}^-$. The N–N bond of the latter compound can be cleaved with sodium metal to give $B_9H_{12}NH^-$, which is isoelectronic and presumably isostructural with $B_9H_{12}S^-$. Acid stability of $B_9H_{12}NH^-$ is considerably lower than that of $B_9H_{12}S^-$.

Introduction

A large number of polyhedral boranes has been synthesized in recent years.[2] These include members of both the simple polyhedral borane series of general formula $B_nH_n^{2-}$ (n = 6–12)[1] and borane anions which are fragments of polyhedra, such as $B_3H_8^-$, $B_9H_{14}^-$, $B_{10}H_{14}^{2-}$, and $B_{11}H_{14}^-$. The binary hydride series is supplemented by a nearly complete series of known carboranes, of general formula $B_nC_2H_{n+2}$ (n = 3–10), in which the carbon atoms occupy polyhedral positions in each respective polyhedron, as well as by a large group of metalocarboranes of icosahedral geometry such as $Co(B_9C_2H_{11})_2^-$,[3] in which some of the metal atom orbitals participate in the icosahedral bonding framework. No compounds in which elements other than carbon fill the polyhedral positions in a framework of boron atoms are known, however.[4] We wish to report

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[1] Paper XXVIII: F. Klanberg, D. R. Eaton, L. F. Guggenberger, and E. L. Muetterties, *Inorg. Chem.*, **6**, 1271 (1967).

[2] See, for example, W. N. Lipscomb, *Science*, **153**, 373 (1966); E. L. Muetterties and W. H. Knoth, *Chem. Eng. News*, **44** (19), 88 (May 9, 1966); E. L. Muetterties, Ed., "Chemistry of Boron," John Wiley and Sons, Inc., New York, N. Y., 1967; M. F. Hawthorne, *Endeavour*, **25**, 146 (1966); E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, Inc., New York, N. Y., 1967.

[3] (a) M. F. Hawthorne, D. C. Young, and P. A. Wegner, *J. Am. Chem. Soc.*, **87**, 1818 (1965); (b) M. F. Hawthorne and T. D. Andrews, *Chem. Commun.*, 443 (1965).

[4] Unstable adducts of $B_{10}H_{14}$ with alane and galane, as well as with zinc and cadmium alkyls, have been reported by N. N. Greenwood and F. A. McGinnety, *J. Chem. Soc., Sect. A*, 1090 (1966), and by N. N. Greenwood and N. F. Travers, *Inorg. Nucl. Chem. Letters*, **2**, 169 (1966). Insufficient evidence has been provided to establish whether these compounds are true heteroatom polyhedral boranes of the type $B_{10}MH_{11}$.

in this paper the synthesis and the chemistry of some novel compounds in which a boron atom in a polyhedral structure has been replaced by a sulfur atom or a nitrogen atom, respectively. By a logical extension of the published systematic nomenclature for polyhedral boranes[5] we propose to name these novel types of compounds thiaboranes and azaboranes.

Results

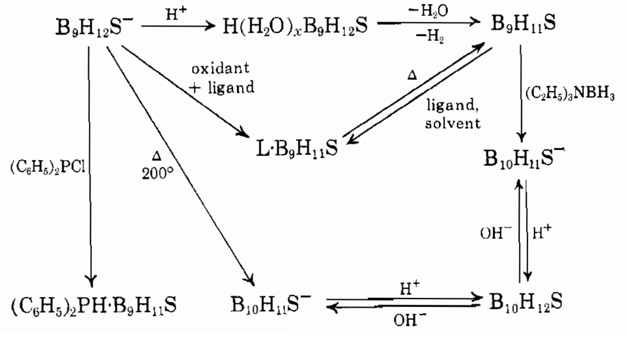
$B_9H_{12}S^-$.—Decaborane reacts essentially quantitatively with ammonium polysulfide in aqueous solution to give the $B_9H_{12}S^-$ ion

$$B_{10}H_{14} + S^{2-} + 4H_2O \longrightarrow B_9H_{12}S^- + B(OH)_4^- + 3H_2 \quad (1)$$

Salts of the anion $B_9H_{12}S^-$ can conveniently be isolated by precipitation with large cations. An unusual feature of the chemistry of the $B_9H_{12}S^-$ ion is its resistance toward hydrolytic attack by hydronium ions. Salts of $B_9H_{12}S^-$ have been converted to a free acid $H(H_2O)_x{}^+B_9H_{12}S^-$, which in concentrated aqueous solution evinces minimal decomposition after several days. The strength of this acid is comparable to that of the acids of $B_{10}H_{10}{}^{2-}$ and $B_{12}H_{12}{}^{2-}$. Unlike the hydrated acid of $B_{12}H_{12}{}^{2-}$, however, the conjugate acid of $B_9H_{12}S^-$ cannot be isolated in crystalline form, because during the dehydration a chemical reaction takes place which gives thiadecaborane(11), $B_9H_{11}S$, in about 30% yield. Thiadecaborane(11) is a very reactive, hygroscopic, low-melting (76.5–77°), and volatile colorless solid which has an exceedingly repulsive odor. Freshly prepared samples do not appear to be air sensitive but the compound yellows on prolonged storage.

The thiaborane $B_9H_{11}S$ is a Lewis acid, which reacts with a variety of donor molecules, such as acetonitrile, triethylamine, dimethylformamide, and dimethyl sulfide to give compounds of general formula $L \cdot B_9H_{11}S$. There is another, usually more convenient, way to prepare these adducts involving oxidation of $B_9H_{12}S^-$ with mild oxidants (iodine, oxalyl chloride) in donor solvents. Some of the adducts $L \cdot B_9H_{11}S$ are thermally stable, sublimable compounds.

Diphenylchlorophosphine reacts with $CsB_9H_{12}S$ in tetrahydrofuran with precipitation of CsCl to give a product which has the composition $(C_6H_5)_2PB_9H_{12}S$. Since this compound has a weak but distinct band in the P–H stretching region (2400 cm^{-1}), which is not found in the other adducts of $B_9H_{11}S$, we consider it to be $(C_6H_5)_2PH \cdot B_9H_{11}S$ rather than $(C_6H_5)_2P \cdot B_9H_{12}S$.[6] The known chemistry of $B_9H_{12}S^-$ is represented graphically below.



$B_{10}H_{11}S^-$ and $B_{10}H_{12}S$.—One of the most interesting and useful reactions of $B_9H_{12}S^-$ is its conversion to another novel thiaborane anion of formula $B_{10}H_{11}S^-$. This can be accomplished by two methods. The first procedure involves the reaction of $B_9H_{11}S$ or its adducts with triethylamine borane at about 200°.

$$L \cdot B_9H_{11}S + (C_2H_5)_3NBH_3 \longrightarrow (C_2H_5)_3NH^+B_{10}H_{11}S^- + H_2 + L \quad (2)$$

The preferred method, however, is the pyrolysis of $CsB_9H_{12}S$ at about 200°. In this pyrolysis, 1.5 moles of hydrogen is liberated per mole of $CsB_9H_{12}S$, and the originally colorless crystals of $CsB_9H_{12}S$ turn yellow, presumably as a result of the formation of colored byproducts. The anion $B_{10}H_{11}S^-$, formed as the major pyrolysis product, is the conjugate base of a weak acid $B_{10}H_{12}S$. Hence, acidification of an aqueous solution of $CsB_{10}H_{11}S$ gives a precipitate of sparingly water-soluble $B_{10}H_{12}S$ which can be purified by sublimation under reduced pressure. Treatment of $B_{10}H_{12}S$ with aqueous base regenerates the anion $B_{10}H_{11}S^-$. Salts are readily obtainable by precipitation with large cations. The over-all yield of $B_{10}H_{12}S$, synthesized from $B_{10}H_{14}$ by the route $B_{10}H_{14} \rightarrow CsB_9H_{12}S \rightarrow CsB_{10}H_{11}S \rightarrow B_{10}H_{12}S$, has been consistently about 50%.

Other reactions afford $B_{10}H_{11}S^-$ directly from decaborane though in much lower and erratic yields. In order to introduce a sulfur atom into the B_{10} framework, it appears to be necessary to utilize a reactant having sulfur in some chemically "activated" form. For example, $B_{10}H_{11}S^-$ is produced in the reaction of decaborane with di-*t*-butylsulfur diimine, RN=S=NR,[7] in ether. A small amount of $B_9H_{12}S^-$ is also formed in this reaction. Alternatively, $B_{10}H_{11}S^-$ can be prepared by the reaction of decaborane with thionitrosodimethylamine, $(CH_3)_2NN{=}S$,[8] in ether solution. The second isolable product from the latter reaction is a dimethylamino-substituted B_9 azaborane (*vide infra*).

$B_{10}H_{10}S^{2-}$.—Treatment of $B_{10}H_{11}S^-$ or $B_{10}H_{12}S$ with strong base such as butyllithium gives $B_{10}H_{10}S^{2-}$ by removal of one and two protons, respectively. Although $B_{10}H_{10}S^{2-}$ is stable in solution for a limited time, it has not been isolated and characterized as a solid salt. On prolonged storage in solution, $B_{10}H_{10}S^{2-}$ undergoes an unusual elimination of the sulfur atom to give the polyhedral $B_{10}H_{10}{}^{2-}$ ion. Freshly prepared $B_{10}H_{10}S^{2-}$ reacts readily with phenyldichloroborane to give the B-phenyl-substituted icosahedral thiadodecaborane(11) which is isoelectronic with $C_6H_5B_{10}C_2H_{11}$.[9] Like $B_{10}C_2H_2$, phenylthiadodecaborane(11) is stable toward strong acids and many common electrophilic reagents. It is, however, reactive toward

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(5) R. Adams, *Inorg. Chem.*, **2**, 1087 (1963).

(6) A precedent for this kind of hydrogen transfer from boron to phosphorus is the hydrolysis of the diphenylphosphino derivative of $B_{10}H_{13}^-$ to give $(C_6H_5)_2PH \cdot B_9H_{13}$. See E. L. Muetterties and V. D. Aftandilian, *Inorg. Chem.*, **1**, 731 (1962).

(7) D. H. Clemens, A. J. Bell, and J. L. O'Brien, *Tetrahedron Letters*, 1487 (1965).

(8) W. J. Middleton, *J. Am. Chem. Soc.*, **88**, 3842 (1966).

(9) M. F. Hawthorne and P. A. Wegner, *ibid.*, **87**, 4392 (1965).

strong base. Methanolic sodium hydroxide converts $C_6H_5B_{11}H_{10}S$ to a new anion, $C_6H_5B_{10}H_{10}S^-$, a phenyl-substituted derivative of $B_{10}H_{11}S^-$. A similar reaction was reported for 1,2-$B_{10}C_2H_{12}$.[10] An icosahedral diphenylthiadodecaborane(11), $(C_6H_5)_2B_{11}H_9S$, can be prepared from $C_6H_5B_{10}H_{10}S^-$ by reaction with butyllithium followed by treatment with phenyldichloroborane.

Reaction of $B_{10}H_{10}S^{2-}$ with a variety of transition metal halides gives a series of sandwich compounds structurally similar to the transition metal cyclopentadienides and the complexes of $B_9C_2H_{11}{}^{2-}$ with transition metals.[3] Thus, reaction of $B_{10}H_{10}S^{2-}$ with $FeCl_2$ in tetrahydrofuran gives $(B_{10}H_{10}S)_2Fe^{2-}$, a stable, maroon anion. The same product can be obtained by treating the solution obtained by dissolving $B_{10}H_{12}S$ in aqueous alkali with aqueous ferrous chloride. Polarographic oxidation of $(B_{10}H_{10}S)_2Fe^{2-}$ occurs at +0.21 v to give $(B_{10}H_{10}S)_2Fe^-$. The Fe(III) oxidation state appears to be unstable relative to Fe(II), and reduction of $(B_{10}H_{10}S)_2Fe^-$ occurs readily, particularly in hydroxylic solvents. Probably, partial degradation of $(B_{10}H_{10}S)_2Fe^-$ occurs to give fragments which reduce the bulk of the $(B_{10}H_{10}S)_2Fe^-$ to $(B_{10}H_{10}S)_2Fe^{2-}$. Use of $C_6H_5B_{10}H_9S^{2-}$ in place of $B_{10}H_{10}S^{2-}$ in the reaction with ferrous chloride gives $(C_6H_5B_{10}H_9S)_2Fe^{2-}$. Cobalt(II) chloride and $B_{10}H_{10}S^{2-}$ give yellow $(B_{10}H_{10}S)_2Co^-$. This cobalt(III) sandwich compound is formed directly from cobaltous chloride. Metallic cobalt appears to be an additional product. The cobalt(III) sandwich compound does not seem to undergo reversible polarographic reduction to the corresponding cobalt(II) compound, whereas the analogous $(B_9C_2H_{11})_2Co^-$ ion can be reversibly reduced to $(B_9C_2H_{11})_2Co^{2-}$.[3b]

If the reaction of $B_{10}H_{10}S^{2-}$ with cobalt(II) chloride is carried out in the presence of cyclopentadienide anion, $B_{10}H_{10}SCoC_5H_5$ is obtained. A by-product of this reaction is $(C_5H_5)_2Co^+(B_{10}H_{10}S)_2Co^-$. The two products can be separated by their differing solubilities in benzene. The presence of the cobalticinium ion in $(C_5H_5)_2Co^+(B_{10}H_{10}S)_2Co^-$ is clearly indicated by the ultraviolet spectrum.

Other sandwich compounds can be prepared by reaction of $B_{10}H_{10}S^{2-}$ with transition metal compounds containing labile ligands. The $B_{10}H_{10}S^{2-}$ ion reacts with *cis*-dichlorobis(triethylphosphine)platinum to give yellow $B_{10}H_{10}SPt[P(C_2H_5)_3]_2$, with dichlorobis(triethyl phosphine)cobalt to give brown $B_{10}H_{10}SCo[P(C_2H_5)_3]_2$, and with chloropentacarbonylrhenium to give colorless $B_{10}H_{10}SRe(CO)_3{}^-$.

The transition metal sandwich compounds of $B_{10}H_{10}S^{2-}$ are not as reactive toward electrophilic reagents as are $B_{10}H_{10}{}^{2-}$ and $B_{12}H_{12}{}^{2-}$. However, halogenation of $(B_{10}H_{10}S)_2Fe^{2-}$ can be accomplished; chlorination of $(B_{10}H_{10}S)_2Fe^{2-}$ in acetonitrile gives a mixture of partially chlorinated products with the average composition $(B_{10}H_{7.5}Cl_{2.5}S)_2Fe^{2-}$. Bromination under similar conditions gives $(B_{10}H_{6.5}Br_{3.5}S)_2Fe^{2-}$. Although no deuterium exchange occurs between D_2O and $(B_{10}H_{10}S)_2Fe^{2-}$ under neutral conditions, acid-catalyzed exchange does occur.

$B_9H_{12}NH^-$.—Decaborane reacts exothermally with thionitrosodimethylamine,[8] $(CH_3)_2NN{=}S$, in ether to give $B_{10}H_{11}S^-$ and $B_9H_{12}NN(CH_3)_2{}^-$. The two products are readily separated by the differing solubilities of the tetramethylammonium salts in ethanol, the salt of the $B_{10}H_{11}S^-$ anion being the less soluble of the two. The stability of $B_9H_{12}NN(CH_3)_2{}^-$ is lower than that of $B_{10}H_{11}S^-$ as evidenced by partial decomposition during purification by crystallization from ethanol. The presence of two N-methyl resonances of nonequivalent intensity in the proton nmr spectrum of $B_9H_{12}NN(CH_3)_2{}^-$ suggests the presence of two isomers. Treatment of $B_9H_{12}NN(CH_3)_2{}^-$ with methyl iodide gives the inner salt $B_9H_{12}NN(CH_3)_3$ which (after purification) appears to be isomerically pure. Cleavage of the N–N bond of $B_9H_{12}NN(CH_3)_2{}^-$ occurs on treatment with excess sodium in tetrahydrofuran to give $B_9H_{12}NH^-$ in low yield. The B^{11} nmr spectrum of $B_9H_{12}NH^-$ is sufficiently similar to that of $B_9H_{12}S^-$ to suggest that the two compounds are not only isoelectronic but also isostructural. The tetramethylammonium salt of $B_9H_{12}NH^-$ is stable enough to survive recrystallization from aqueous acetic acid. Nevertheless, $B_9H_{12}NH^-$ is less stable toward acids than is $B_9H_{12}S^-$. Oxidation of $B_9H_{12}NH^-$ with bromine in acetonitrile solution gives $B_9H_{11}NH \cdot CH_3CN$ which is less stable than the analogous thia compound $B_9H_{11}S \cdot CH_3CN$, since it undergoes slow decomposition on storage in air. The lower stability of azaboranes *vs.* isoelectronic thiaboranes may well be a general phenomenon.

Discussion

We do not have crystal structure analyses for any of the new thia- and azaboranes. Furthermore, our spectral data including the B^{11} nmr data do not provide *definitive* structural characterizations. Nevertheless, there exists sufficient precedence in polyhedral borane and carborane chemistry to permit a number of tentative conclusions regarding the most likely structures.

12-Atom Skeletons.—Icosahedral boranes and carboranes are well established.[2] An icosahedral thiaborane seems to be a realistic concept, too, despite the disparity in size of a sulfur and a boron atom. The strict analog to icosahedral $B_{12}H_{12}{}^{2-}$ and $B_{10}H_{10}C_2H_2$ would be the cation $B_{11}H_{11}SH^+$. However, because of the higher nuclear charge on sulfur (obviously it should be more positively charged than either of the two carbon atoms in $B_{10}C_2H_{12}$), one would expect $B_{11}H_{11}SH^+$ to be a strong acid which should readily lose a proton to give neutral $B_{11}H_{11}S$. In the latter molecule the sulfur atom would possess a nonbonding pair of electrons as a quasi-exopolyhedral substituent. In fact, the two 12-skeletal-atom thiaboranes we have prepared, namely, $C_6H_5B_{11}H_{10}S$ and $(C_6H_5)_2B_{11}H_9S$, do not protonate readily. The stereochemistry of these two phenyl-substituted thiaboranes has not been established. The

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[10] R. A. Wiesboeck and M. F. Hawthorne, *J. Am. Chem. Soc.*, **86**, 1642 (1964).

probable structures of the precursors (*vide infra*) as well as the method of preparation suggest, however, that the phenyl groups are attached to boron atoms vicinal to the sulfur atoms.

It seems reasonably certain that the metalothiaboranes are structural analogs of the metalocarboranes[11] for which icosahedral geometry has been proved by X-ray analysis.[12] In metalocarboranes both carbon atoms are in the pentagonal plane adjacent to the metal atom. A similar arrangement probably prevails in the metalothiaborane series (*i.e.*, the sulfur atom is adjacent to the metal atom) as suggested by nmr studies. The structure of $(B_{10}H_{10}S)_2Co^-$ is shown in Figure 1.

11-Atom Skeletons.—The ion $B_{10}H_{10}S^{2-}$ is isoelectronic with $B_9C_2H_{11}^{2-}$, and these two ions are probably isostructural. In metalocarborane sandwiches the $B_9C_2H_{11}$ moiety is an open icosahedral fragment, but the structure of the *free ion* $B_9C_2H_{11}^{2-}$ has not yet been conclusively determined.[13]

Pursuing the concept of isoelectronic relationships between thiaborane and carborane chemistry further, the ion $B_{10}H_{11}S^-$ is the isoelectronic analog of $B_9C_2H_{12}^-$.[10] Thus, we propose for the structure of $B_{10}H_{11}S^-$ (Figure 2) an icosahedral fragment with the extra hydrogen atom placed on the pentagonal face either in a fixed position or rapidly traversing the three possible bridging positions among the four boron atoms in the pentagonal face.[14]

The neutral thiaborane $B_{10}H_{12}S$ is isoelectronic and presumably isostructural with the carborane $B_9C_2H_{13}$, a known compound of relatively low stability and uncertain structure. Wiesboeck and Hawthorne[10] have suggested that $B_9C_2H_{13}$ and its conjugate base, $B_9C_2H_{12}^-$, are icosahedral fragments. These authors have also pointed out that both compounds are isoelectronic with $B_{11}H_{13}^{2-}$, the structure of which has recently been shown[15] to contain a boron framework of a nearly regular icosahedron with one vertex missing. The two extra hydrogen atoms in $B_{11}H_{13}^{2-}$ bridge nonadjacent edges of the open pentagonal face.

For $B_{10}H_{12}S$, one structural possibility is essentially as found in the $B_{11}H_{13}^{2-}$ ion, *i.e.*, an icosahedral fragment with the two extra hydrogen atoms bridging nonadjacent edges of the pentagonal face. Alternatively, one boron atom in the open pentagonal face might become protonated to give a BH_2 group. There is somewhat inconclusive evidence for such a BH_2 group in the decoupled B^{11} nmr spectrum of $B_{10}H_{12}S$.[16]

10-Atom Skeletons.—The ion $B_9H_{12}S^-$ is best regarded as a structural analog (Figure 3) of $B_{10}H_{14}^{2-}$ with which it is isoelectronic. Infrared and B^{11} nmr data unambiguously show the presence of bridging hydrogen atoms as well as one BH_2 group in $B_9H_{12}S^-$. There is an alternative structure for this ion which is also shown in Figure 3. However, we believe that the structure of $B_9H_{12}S^-$ is most adequately described by the analogy to the $B_{10}H_{14}^{2-}$ ion.

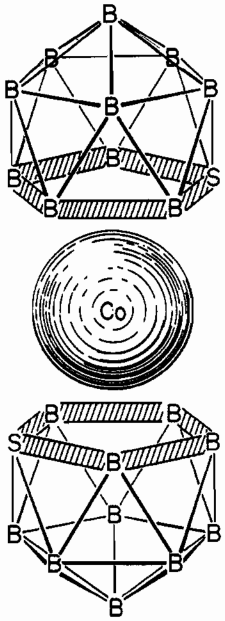

Figure 1.—Proposed structure of the $(B_{10}H_{10}S)_2Co^-$ ion.

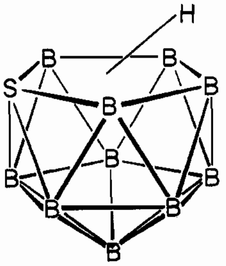

Figure 2.—Proposed structure of $B_{10}H_{11}S^-$.

Finally, we correlate the neutral thiaborane $B_9H_{11}S$ with the isoelectronic $B_{10}H_{13}^-$ ion. The structure of this ion is unknown although presumably the basic decaborane framework is retained. There is infrared evidence for the presence of BHB bridge bonds, but there is no evidence for a BH_2 group in the nmr spectrum of $B_9H_{11}S$. Support for the proposed correlation of $B_9H_{11}S$ with $B_{10}H_{13}^-$ is derived from the fact that both species readily form ligand complexes, namely, $B_9H_{11}S\cdot$(ligand) and $B_{10}H_{13}$(ligand)$^-$.

Experimental Section

Salts of $B_9H_{12}S^-$.—Decaborane (12 g, 0.10 mole) was added slowly in small portions to the stirred solution of 200 ml of yellow ammonium sulfide solution. After the evolution of hydrogen had ceased, the warm solution (50–60°) was filtered to remove small amounts of insoluble material. The filtrate was treated with an aqueous solution of 60 g of cesium fluoride, and the resulting pre-

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(11) A short notation for the thia derivatives would be metal "thi-ollides" by analogy with the name metal carbollides suggested by M. F. Hawthorne and R. L. Pilling, *J. Am. Chem. Soc.*, **87**, 3987 (1965), for derivatives of $B_9C_2H_{11}^{2-}$.

(12) A. Zalkin, D. H. Templeton, and T. E. Hopkin, *ibid.*, **87**, 3988 (1965).

(13) *Neutral* $B_9C_2H_{11}$ has a structure of a closed polyhedron of C_{2v} symmetry which is closely related to the icosahedral fragment configuration. See C. Tsai and W. E. Streib, *J. Am. Chem. Soc.*, **88**, 4513 (1966).

(14) There is another, rather unprecedented, alternative for the structure of $B_{10}H_{11}S^-$. It consists of an adamantane-like framework of 10 BH units with the sulfur atom in the center of this array. The sulfur atom would be bonded either to the six nonbridgehead boron atoms or to the four bridgehead boron atoms.

(15) C. F. Fritchie, Jr., *Inorg. Chem.*, **6**, 1199 (1967).

(16) Another alternative geometry also consistent with the nmr data places the sulfur atom in a decaborane-like framework such that the sulfur atom bridges the 8, 9, and 10 positions. It would then be necessary to postulate that the 6 position bears a BH_2 group and the twelfth hydrogen atom in $B_{10}H_{12}S$ alternately bridges the 5,6 and 6,7 positions. We consider this structure unlikely.

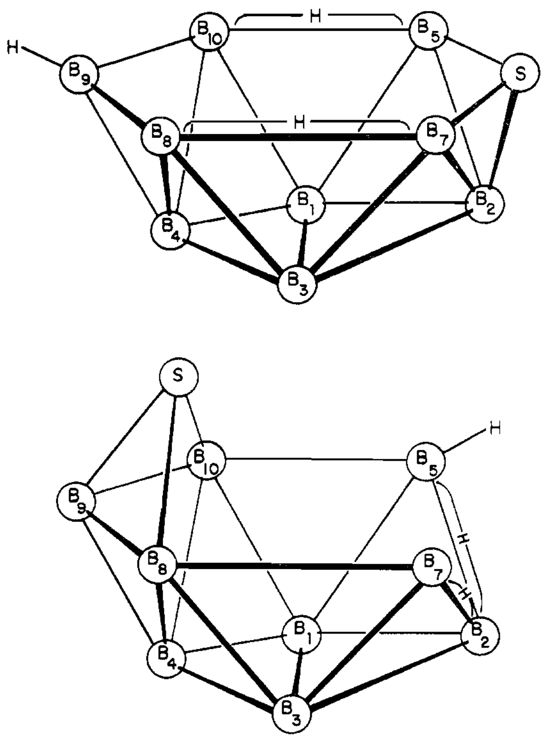

Figure 3.—Possible structures of the $B_9H_{12}S^-$ ion. On the top is the structure preferred by us which is based on the $B_{10}H_{14}^{2-}$ geometry. On the bottom is an alternative structure.

cipitate was recrystallized from 150 ml of water. The yield was 20 g of $CsB_9H_{12}S$ (90%).

Anal. Calcd for $CsB_9H_{12}S$: Cs, 48.8; B, 35.5; H, 4.4; S, 11.7; mol wt, 275. Found: Cs, 47.2; B, 35.5; H, 4.6; S, 11.7.

The molecular weight, determined ebullioscopically in acetonitrile, was 132, indicating complete dissociation of the salt. The molecular weight, calculated from the neutralization equivalent of the acid $HB_9H_{12}S$ (prepared from a weighed amount of $CsB_9H_{12}S$ by ion exchange), was 277.

Rubidium and tetramethylammonium salts of $B_9H_{12}S^-$ were prepared similarly to the cesium salt. The rubidium salt was recrystallized from water, and the tetramethylammonium salt from acetone or acetonitrile.

Anal. Calcd for $RbB_9H_{12}S$: Rb, 37.7; B, 42.9; H, 5.3; S, 14.1; hydrolytic H_2, 1875 cc/g. Found: Rb, 35.4; B, 43.3; H, 6.0; S, 13.9; hydrolytic H_2, 1876 cc/g.

Crystals of $RbB_9H_{12}S$ are monoclinic with the parameters $a = 8.82$, $b = 10.85$, $c = 10.98$ A, $\beta = 92.70°$, and $Z = 4$. The calculated density is $\rho_x = 1.54$, and the experimentally determined density (by the flotation method) is $\rho_E = 1.48$. The space group is $P2_1/C$.

Anal. Calcd for $(CH_3)_4NB_9H_{12}S$: C, 22.3; H, 11.2; N, 6.5; B, 45.2; S, 14.9; hydrolytic H_2, 1973 cc/g; mol wt, 216. Found: C, 22.5; H, 11.1; N, 6.3; B, 44.4; S, 14.4; hydrolytic H_2, 1942 cc/g; mol wt, ebullioscopic in acetonitrile, 103.

The yield of $B_9H_{12}S^-$ decreased when the reaction was run at lower temperatures (5°). Part of the decaborane was hydrolyzed under those reaction conditions to $B_9H_{14}^-$ which, after addition of a soluble cesium salt, coprecipitated as the sparingly soluble double salt $CsB_9H_{12}S \cdot CsB_9H_{14}$.

Anal. Calcd for $Cs_2B_{18}H_{26}S$: Cs, 51.2; B, 37.5; H, 5.1; S, 6.2; hydrolytic H_2, 1737 cc/g. Found: Cs, 48.6; B, 37.9; H, 4.9; S, 6.3; hydrolytic H_2, 1753 cc/g.

The compound is identical with one obtained from cocrystallization of authentic samples of $CsB_9H_{12}S$ and CsB_9H_{14}. The infrared spectrum of $Cs_2B_{18}H_{26}S$ differs from that of $CsB_9H_{12}S$ only in some band contours, whereas the ultraviolet and B^{11} nmr spectra of $Cs_2B_{18}H_{26}S$ consist of a superposition of the spectra of $CsB_9H_{12}S$ and CsB_9H_{14}.

Polarographic Data.—$CsB_9H_{12}S$ was examined in acetonitrile with $(C_4H_9)_4NClO_4$ as supporting electrolyte at a rotating platinum electrode *vs.* a saturated calomel electrode. An oxidation wave was observed at +0.90 v. The electrode reaction was irreversible and probably involved many electrons.

Under similar conditions, $(CH_3)_4NB_{10}H_{11}S$ showed a well-defined oxidation wave at +0.98 v.

Spectral Data.—In aqueous solution, $CsB_9H_{12}S$ absorbs ultraviolet radiation at 2270 A (ϵ 6000). The infrared spectrum of $B_9H_{12}S^-$ shows a complex region of B–H stretching absorption. Four bands are readily detectable between 2500 and 2300 cm^{-1}, the precise position of which varies somewhat from one salt to another. For $CsB_9H_{12}S$, the positions are 2525 (vs), 2470 (s), 2380 (s), and 2355 (m) cm^{-1}. A mull of $(CH_3)_4NB_9H_{12}S$ also has a weak pair of bands at 2130 and 2075 cm^{-1}, which we assign to B–H–B bridging absorption. These two bands are not well resolved in mulls of alkali metal salts of $B_9H_{12}S^-$. Other absorptions due to the anion $B_9H_{12}S^-$ occur at 1189 (m), 1049 (s), 1010 (vs), 990 (sh), 966 (w), 938 (w), 920 (m), 905 (sh), 784 (m), 758 (m), 726 (m), 690 (w), and 657 (w) cm^{-1}.

The B^{11} nmr spectrum of $B_9H_{12}S^-$ at 32.1 Mc (Figure 4) shows three distinct regions of absorption, a low-field doublet, a multiplet, and two overlapping high-field doublets. The relative intensities of the three areas are 1:4:4. Proton-decoupling experiments, performed on the corresponding spectrum at 19.2-Mc B^{11} excitation frequency, suggest that the multiplet is composed of a doublet of intensity 2 at 27.5 ppm, a doublet of intensity 1 at 32.0 ppm, and a triplet of intensity 1 at 34.0 ppm. This spectrum of $B_9H_{12}S^-$ is consistent with a decaborane type framework in which the sulfur atom occupies the 6 position and two of the extra hydrogen atoms (*i.e.*, those in excess of one terminal hydrogen atom per each boron atom) bridge the 5,10 and 7,8 positions. There would also be a BH_2 group in the 9 position.

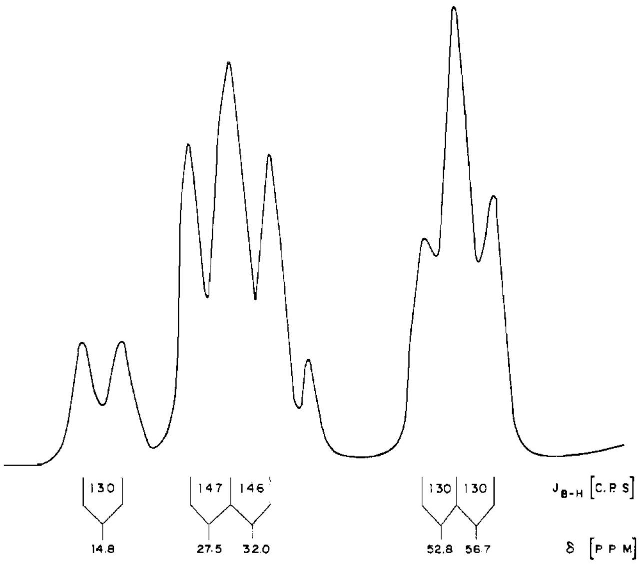

Figure 4.—B^{11} nmr spectrum of $CsB_9H_{12}S$ in CH_3CN at 32.1 Mc. External reference: $B(OCH_3)_3$.

$B_9H_{11}S$.—A solution of 10 g of $CsB_9H_{12}S$ in 100 ml of water–acetonitrile (1:1) was passed through an ion-exchange column packed with Rexyn 101 H resin. The effluent was evaporated to dryness on a rotating evaporator leaving a white powdery residue which was spontaneously flammable in air. Sublimation of the residue at 70–90° (0.1 mm) gave 1.5 g (30%) of large transparent hexagons of thiadecaborane(11). *Pure* $B_9H_{11}S$ is hygroscopic, but not spontaneously flammable in contact with dry air. It melts at 76.5–77° with partial decomposition, and it is easily soluble in a wide variety of organic solvents.

Anal. Calcd for $B_9H_{11}S$: B, 69.3; H, 8.4; S, 22.8; hydrolytic H_2, 2874 cc/g; mol wt, 140.5. Found: B, 69.0; H, 7.9; S, 22.7; hydrolytic H_2, 2897 cc/g; mol wt, cryoscopic in benzene, 185.

The compound has ultraviolet absorption in cyclohexane at 2230 A (ϵ 2165) and at 3220 A (ϵ 2360). The mass spectrum shows the expected isotopic distribution for nine boron atoms at m/e 140 and 141. The infrared spectrum is very reminiscent of the spectrum of decaborane. There is only one B–H stretching absorption at 2530 cm^{-1}, as well as two B–H–B bridge absorptions at 1950 and 1900 cm^{-1}. There are other bands at 1049 (s), 1028 (sh), 1012 (s), 952 (w), 936 (m), 903 (s), 882 (m), 834 (s), 806 (s), 790 (w), 749 (s), 730 (sh), 721 (s), and 702 (s) cm^{-1}.

The B^{11} nmr spectrum at 32.1 Mc in benzene shows the features given in Table I. The accuracy of the coupling constants in this spectrum is limited to ±10 cps.

TABLE I

Position, ppm	Rel intens	BH coupling constant, cps	Remarks
−6.2	2.0	161	Doublet
+0.9	1.0	133	Doublet
+12.0	2.0	147	Doublet
+28.9	2.1	178	Very broad doublet
+47.3	0.94	160	Doublet
+58.2	1.23	200	Doublet
+65.0	0.46	160	Broad doublet, presumably impurity

$CH_3CN \cdot B_9H_{11}S$.—A solution of $CsB_9H_{12}S$ (6.5 g, 0.024 mole) in 50 ml of acetonitrile was heated on a steam bath while a solution of iodine (3.0 g, 0.012 mole) in 75 ml of acetonitrile was gradually added. Heating was continued until all of the iodine was reduced. The resulting precipitate of cesium iodide was removed by filtration and the filtrate was poured into 400 ml of aqueous potassium acetate solution containing a little sodium bisulfite. The precipitate was collected, dried, and recrystallized from 40 ml of benzene to give 1.0 g of white needles of $CH_3CN \cdot B_9H_{11}S$, mp 152° dec.

Anal. Calcd for $CH_3CN \cdot B_9H_{11}S$: C, 13.2; H, 7.8; N, 7.7; B, 53.6; S, 17.7; mol wt, 181. Found: C, 13.0; H, 7.7; N, 7.5; B, 52.9; S, 17.4; mol wt, 262 (cryoscopic in C_6H_6) and 306 (ebullioscopic in CH_3CN).

Ultraviolet absorption occurs at $\lambda_{max}^{CH_3CN}$ 2420 A (ϵ 10,950). The infrared spectrum has a strong, sharp B–H stretching absorption at 2500 cm^{-1}, C≡N absorption at 2338 cm^{-1} with a shoulder at 2360 cm^{-1}, and B–H–B bridge absorption at 2110 and 2020 cm^{-1}. In the region from 1100 to 650 cm^{-1}, the spectrum is practically identical with that of $CsB_9H_{12}S$, differences occurring only in some band intensities.

The B^{11} nmr spectrum of $CH_3CN \cdot B_9H_{11}S$ at 19.2 Mc shows an incompletely resolved multiplet similar in appearance to that displayed by $CsB_9H_{12}S$. In $CDCl_3$ the proton nmr spectrum shows two broadened CH_3 peaks at τ 7.28 and 7.92 (intensity ratio 5:1), whereas in acetone-d_6 the CH_3 peaks appear as a pair of doublets (Δ = 1.8 cps) at τ 7.53 and 7.63, respectively. The reason for the splitting is not well understood; it may reflect molecular asymmetry and ligand-exchange equilibria.

Alternative methods of preparing $CH_3CN \cdot B_9H_{12}S$ are dissolution of $B_9H_{11}S$ in acetonitrile or oxidation of $CsB_9H_{12}S$ with oxalyl chloride (instead of iodine) in the same solvent. Work-up and purification are as described above.

$(C_2H_5)_3N \cdot B_9H_{11}S$.—Thiadecaborane(11) (0.6 g, 0.004 mole) in 5 ml of benzene was treated with 4 ml of triethylamine. The solvent and excess triethylamine were evaporated *in vacuo* leaving a yellow crystalline solid which was purified by vacuum sublimation. The yield was 0.5 g, mp 111–113°.

Anal. Calcd for $(C_2H_5)_3N \cdot B_9H_{11}S$: C, 29.8; H, 10.8; N, 5.8; B, 40.3; S, 13.3. Found: C, 30.0; H, 10.9; N, 5.8; B, 40.4; S, 13.4.

The ultraviolet spectrum in acetonitrile shows absorption at 2260 A (ϵ 7000), with a shoulder at 2920 A (ϵ 160). Infrared absorptions include a sharp B–H stretching frequency at 2565 cm^{-1} with a shoulder at 2535 cm^{-1} and a weak band at 2040 cm^{-1} presumably indicative of B–H–B stretching absorption.

The H^1 nmr spectrum in $CDCl_3$ shows a normal ethyl resonance at τ 8.52 (CH_3) and 6.81 (CH_2). The B^{11} nmr spectrum corresponds to that of $CH_3CN \cdot B_9H_{11}S$.

$(C_2H_5)_3N \cdot B_9H_{11}S$ was also prepared by a ligand displacement reaction

$$CH_3CN \cdot B_9H_{11}S + (C_2H_5)_3N \longrightarrow (C_2H_5)_3N \cdot B_9H_{11}S + CH_3CN$$

$(CH_3)_2NCHO \cdot B_9H_{11}S$.—Iodine (6.4 g, 0.025 mole) was added to a solution of $CsB_9H_{12}S$ (2.7 g, 0.010 mole) in 20 ml of dimethylformamide until the iodine color was no longer discharged. The solution was poured into 400 ml of 5% potassium acetate solution, and the resulting precipitate was collected, washed with water, and dried *in vacuo*. Recrystallization from benzene gave 0.9 g of $(CH_3)_2NCHO \cdot B_9H_{11}S$, mp 171–173° dec.

Anal. Calcd for $(CH_3)_2NCHO \cdot B_9H_{11}S$: C, 16.9; H, 8.5; N, 6.6; B, 45.6; S, 15.0; hydrolytic H_2, 1887 cc/g. Found: C, 17.3; H, 8.5; N, 6.4; B, 45.9; S, 14.7; hydrolytic H_2, 1865 cc/g.

The ultraviolet spectrum in acetonitrile has a peak at 2380 A (ϵ 8650). In the H^1 nmr spectrum in acetone-d_6, the formyl hydrogen atom appears as a broad peak at τ 1.94 and the methyl resonances appear as two doublets (J = 0.9 cps) at τ 7.23 and 6.96. The B^{11} nmr spectrum (19.2 Mc) in benzene shows two overlapping doublets at δ 51.6 and 56.6 ppm (J_{B-H} = 131 cps), each of intensity 2, and an unresolved multiplet of intensity 5, centered at δ 22.2 ppm.

Infrared absorptions include two sharp B–H stretching bands at 2555 and 2485 cm^{-1}, two weak but well-resolved bands at 2125 and 2082 cm^{-1} attributed to B–H–B stretching vibrations, and a C=O frequency at 1725 cm^{-1}.

$(CH_3)_2S \cdot B_9H_{11}S$.—Iodine (2.5 g, 0.01 mole) was added to a solution of $CsB_9H_{12}S$ (5.4 g, 0.02 mole) in 120 ml of a 1:1 mixture of dimethyl sulfide and tetrahydrofuran. Precipitated cesium iodide was removed by filtration, and the filtrate was poured into 500 ml of water giving two liquid phases. The organic phase was separated and evaporated to dryness leaving a white solid, recrystallizable from diethyl ether. The solid was hydrolytically very unstable. It melted in the range 65–70° with decomposition. Attempted sublimation at 0.01 mm pressure gave $B_9H_{11}S$ and some polymeric material. The adduct was characterized by spectral data. The infrared spectrum corresponds in its essential features to the spectra of other adducts; the H^1 nmr spectrum shows one CH_3 peak at τ 7.36 in $CDCl_3$. The B^{11} nmr spectrum shows two overlapping high-field doublets at δ 54 ppm of intensity 4 as well as a low-field multiplet of intensity 5. The ultraviolet spectrum had a peak at 2310 A (ϵ 5000), with a shoulder at 2850 A (ϵ 400).

The compound was too unstable to give meaningful analytical data.

$(C_6H_5)_2PH \cdot B_9H_{11}S$.—A mixture of $CsB_9H_{12}S$ (2.7 g, 0.01 mole) and diphenylchlorophosphine (2.2 g, 0.01 mole) in 70 ml of tetrahydrofuran was refluxed for 30 min and subsequently stirred overnight at room temperature. Cesium chloride precipitated and was removed by filtration. The filtrate was chilled to −20° to give 250 mg of $(C_6H_5)_2PH \cdot B_9H_{11}S$, melting at 148–150°.

Anal. Calcd for $(C_6H_5)_2PH \cdot B_9H_{11}S$: C, 44.1; H, 6.8; P, 9.5; B, 29.8; S, 9.8. Found: C, 44.4; H, 6.9; P, 9.2; B, 27.5; S, 8.9.

Ultraviolet spectrum: $\lambda_{max}^{CH_3OH}$ 2260 A (ϵ 22,800) and 2730 A (ϵ 1420).

Infrared absorptions (KBr wafer) occur at 2535 cm^{-1} (B–H stretching) and at 2440 cm^{-1}. This latter weak but distinct band is assigned to a P–H stretching vibration, because none of the other adducts $L \cdot B_9H_{11}S$ displays a band at this frequency.

The remainder of the spectrum from 1500 to 650 cm^{-1} consists of a superposition of phenyl and $B_9H_{11}S$ bands.

$B_{10}H_{11}S^-$.—The bright yellow solution of $CH_3CN \cdot B_9H_{11}S$ (1.8 g, 0.01 mole) in 25 ml of triethylamine borane was refluxed for 90 min under nitrogen. After the solution was cooled to room temperature, it was poured into 300 ml of water containing excess tetramethylammonium chloride. The resulting precipitate was recrystallized from acetonitrile to give 0.5 g (22%) of $(CH_3)_4NB_{10}H_{11}S$.

Anal. Calcd for $(CH_3)_4NB_{10}H_{11}S$: C, 21.3; H, 10.3; N, 6.2; B, 48.0; S, 14.2. Found: C, 20.9; H, 10.8; N, 6.0; B, 48.7; S, 14.1.

$B_{10}H_{12}S$ by Pyrolysis of $CsB_9H_{12}S$.—In an evacuated flask connected to a vacuum line, $CsB_9H_{12}S$ (4.7 g, 0.017 mole) was gradually heated to 227°. Hydrogen (578 ml, 0.026 mole) was slowly generated and a deep yellow pyrolysate was formed. The crude pyrolysate was dissolved in water, and the solution was acidified with concentrated hydrochloric acid. The resulting precipitate was filtered off, washed with 2 *N* hydrochloric acid, and purified by sublimation at 160° (0.01 mm). The yield was 1.0 g of $B_{10}H_{12}S$.

Anal. Calcd for $B_{10}H_{12}S$: B, 71.0; H, 7.9; S, 21.1; hydrolytic H_2, 2940 cc/g; mol wt, 152. Found: B, 71.0; H, 8.00; S, 21.0; hydrolytic H_2, 2955 cc/g; mol wt, cryoscopic in C_6H_6, 149.

In cyclohexane solution, ultraviolet absorption occurs at 2240 A (ϵ 2340).

The infrared spectrum shows a strong, sharp B–H stretching absorption at 2565 cm^{-1} and a broad, weak B–H–B absorption centered at 1940 cm^{-1}. Other bands are at 1020 (vs), 1010 (sh), 994 (vs), 945 (m), 929 (m), 910 (w), 875 (m), 866 (m), 804 (w), 787 (w), 765 (s), 726 (sh), 707 (s), and 656 (w) cm^{-1}.

The B^{11} nmr spectrum (Figure 5) shows four doublets with relative intensities 1:4:2:2; proton-decoupling experiments indicate a triplet arising from a BH_2 group.

In subsequent experiments, $CsB_9H_{12}S$ was usually pyrolyzed at atmospheric pressure under a nitrogen blanket without any reduction in the yield of $B_{10}H_{12}S$. The progress of the reaction may be followed conveniently by measuring the hydrogen evolved with a wet-test meter.

$(CH_3)_4NB_{10}H_{11}S$.—To a solution of 1.2 g (0.010 mole) of decaborane(14) in 30 ml of ether was added 16 ml of 0.63 *M* thionitrosodimethylamine in ether. The mixture was stirred at room temperature for about 1 hr. The gummy precipitate which had formed was collected, washed with ether, and extracted with dilute aqueous sodium hydroxide solution. The extract was filtered, the filtrate was treated with tetramethylammonium chloride, and the resulting precipitate was collected to give 840 mg of solid. This solid was extracted with ethanol, and the undissolved part of it was recrystallized from acetonitrile–benzene to give (in two crops) 0.2 g (9×10^{-4} mole) of $(CH_3)_4NB_{10}H_{11}S$. The yield, based on $B_{10}H_{14}$, was 9%.

Anal. Calcd for $(CH_3)_4NB_{10}H_{11}S$: B, 48.0; H, 10.3; C, 21.3; N, 6.2; S, 14.2. Found: B, 48.2; H, 9.9; C, 22.1; N, 6.5; S, 14.2.

The H^1 nmr spectrum of the product in CD_3CN–$(CD_3)_2SO$ shows a single peak at τ 7.03 corresponding to $(CH_3)_4N^+$. There is no resonance peak attributable to SH. The infrared spectrum shows peaks at 2530 (sharp, B–H), 1480 ($(CH_3)_4N$), 1420 (w), 1290 (w), 1060, 1025, 1010, 990, 950 ($(CH_3)_4N$), 920, 875 (vw), 815 (w), 775 (w), 750 (w), and 740 cm^{-1} (w). The ultraviolet spectrum of the product in acetonitrile shows absorption at 2360 A (ϵ 2320) and 2700 A (ϵ 1320). In large-scale preparations, it has been found advantageous to add a solution of decaborane in ether to a solution of about 2 molar equiv of $(CH_3)_2NNS$ in ether within 30 min. This results in improved yields of $(CH_3)_4NB_{10}H_{11}S$ and poorer yields of $(CH_3)_4N(CH_3)_2NNB_9H_{12}$ (*vide infra*).

$CsB_{10}H_{11}S$.—A warm solution of 1 g of $(CH_3)_4NB_{10}H_{11}S$ in aqueous acetonitrile was passed through a column of sodium ion exchange resin. The effluent was evaporated *in vacuo* to a small volume and treated with excess cesium sulfate. The resulting precipitate was collected by filtration to give 0.9 g of colorless $CsB_{10}H_{11}S$. The product was further purified by recrystallization from water.

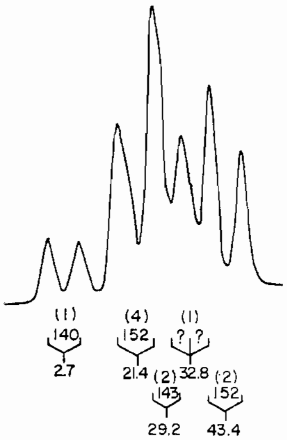

Figure 5.—B^{11} nmr spectrum of $B_{10}H_{12}S$ in CH_3CN at 19.3 Mc.

Anal. Calcd for $CsB_{10}H_{11}S$: B, 38.0; H, 3.9; S, 11.3. Found: B, 38.4; H, 4.3; S, 11.4.

The 32.1-Mc B^{11} nmr spectrum of $CsB_{10}H_{11}S$ shows four doublets with relative intensities 2:3:4:1. The assignments indicated in Figure 6 were confirmed by proton-decoupling experiments performed upon the 19.3-Mc B^{11} nmr spectrum. The proposed structure would require that the doublet of intensity 4 arise from accidental equivalence of two doublets of intensity 2. The doublet of intensity 1 probably arises from the boron atom *para* to the sulfur atom. The spectrum is also consistent with a similar structure in which the sulfur atom is *meta* to the icosahedral vacancy, but it is inconsistent with an icosahedral fragment in which the sulfur atom is *para* to the vacancy.

$B_{10}H_{12}S$ and $B_9H_{12}S^-$ from $B_{10}H_{14}$ and (t-C_4H_9N=)$_2$S.—To a solution of 40 g of decaborane in 700 ml of ether cooled in an ice bath was added over 30 min a solution of 28.7 g of N,N′-di-*t*-butylsulfur diimine[7] in 100 ml of ether. The resulting mixture was stirred at room temperature for 2 days and then evaporated to dryness. The residue was treated with cold 10% aqueous sodium hydroxide solution. The resulting mixture was washed with pentane and filtered through Celite. The filtrate was treated with tetramethylammonium chloride, and the resulting precipitate was collected and washed with ethanol. The filter cake was dissolved in hot aqueous acetonitrile and passed through a sodium cation exchange column, and the effluent was concentrated *in vacuo* to a small volume. Addition of cold concentrated hydrochloric acid gave a precipitate which was collected by filtration and washed with cold 10% hydrochloric acid. Sublimation of the filter cake at 160° (0.1 mm) gave 7.5 g of $B_{10}H_{12}S$ as a waxy solid. The product was identified by comparison of its infrared spectrum with that of an authentic sample of $B_{10}H_{12}S$.

Addition of tetramethylammonium chloride to the acid filtrate gave a precipitate of 4.8 g of $(CH_3)_4NB_9H_{12}S$ identified by comparison of the infrared spectrum with that of an authentic sample.

2-Phenylthiadodecaborane(11).—To a solution of 40 ml of tetrahydrofuran containing 13 ml of 1.6 *M* butyllithium in hexane was added 1.5 g of $B_{10}H_{12}S$. After being stirred for 20 min at room temperature, the slurry was cooled in an ice bath and treated with 1.6 g of phenyldichloroborane, dissolved in a small amount of benzene. The resulting solution was allowed to warm to room temperature and then evaporated *in vacuo*. The residue was extracted with benzene and filtered. The filtrate was evaporated, and the residue was recrystallized from heptane to give 720 mg of colorless crystals of $C_6H_5B_{11}H_{10}S$, mp 102.7–105.5°. An additional crystallization from heptane raised the melting point to 105.3–106.3°.

Anal. Calcd for $C_6H_5B_{11}H_{10}S$: B, 50.0; H, 6.4; C, 30.2; S, 13.5; mol wt, 238.3. Found: B, 50.9; H, 6.4; C, 30.2; S, 13.5; mol wt, 237 (cryoscopic in benzene).

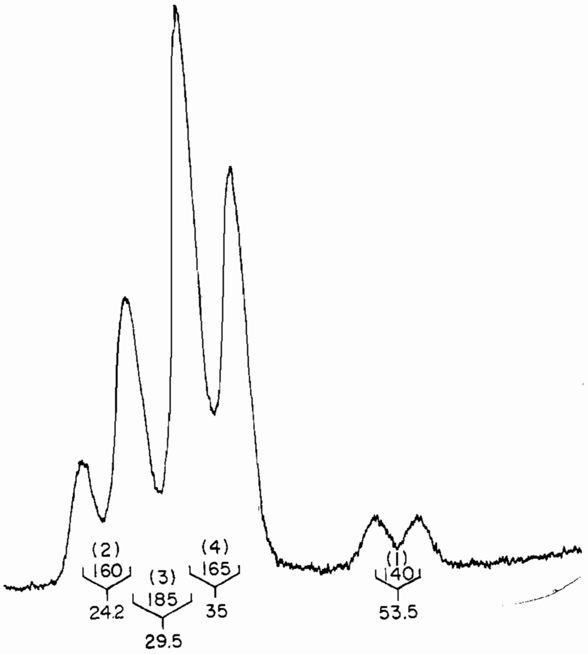

Figure 6.—B^{11} nmr spectrum of $CsB_{10}H_{11}S$ in CH_3CN at 32.1 Mc.

The B^{11} nmr spectrum consists of two doublets and a singlet of relative intensities 1:9:1. The low-field doublet can be assigned to the boron atom *para* to the sulfur atom, the singlet to the phenyl-substituted boron atom, and the high-field doublet to the remaining nine boron atoms which, albeit not strictly environmentally equivalent, possess a very similar environment that could give rise to accidental degeneracies. The spectrum is shown in Figure 7.

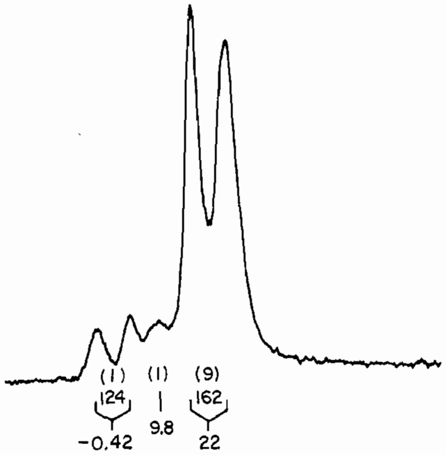

Figure 7.—B^{11} nmr spectrum of $C_6H_5B_{11}H_{10}S$ in CH_2Cl_2 at 19.3 Mc.

The ultraviolet spectrum of the product in cyclohexane shows absorption at 2770 (ε 897), 2700 (ε 1320), 2450 (ε 5960), and 2150 A (ε 14,700).

Thin layer chromatography of the product on silica gel with benzene shows a single spot suggesting that the product is isomerically pure.

Tetramethylammonium Phenylthiaundecaborate(11).—A mixture of 250 mg of $C_6H_5B_{11}H_{10}S$, 2.5 g of sodium hydroxide, and 25 ml of methanol was refluxed for 1.5 hr and then evaporated under reduced pressure. The residue was dissolved in water and treated with excess tetramethylammonium chloride. The resulting precipitate was recrystallized from ethanol to give 120 mg of colorless plates of $(CH_3)_4NC_6H_5B_{10}H_{10}S$, mp 186–188°.

Anal. Calcd for $(CH_3)_4NC_6H_5B_{10}H_{10}S$: B, 35.9; H, 9.04; C, 39.9; N, 4.7; S, 10.6. Found: B, 36.0; H, 9.06; C, 40.2; N, 4.7; S, 10.8.

The ultraviolet spectrum of the product in acetonitrile solution shows absorption at 2850 (sh, ε 3820), 2540 (ε 5500), and 2200 A (sh, ε 9850).

$(C_6H_5)_2B_{11}H_9S$.—To a solution of 400 mg $(CH_3)_4NC_6H_5B_{10}H_{10}S$ in 10 ml of tetrahydrofuran was added 0.9 ml of 1.6 *M* butyllithium in hexane. The resulting mixture was cooled to −40° and treated with 230 mg of phenyldichloroborane in benzene.

The mixture was warmed to room temperature and the solvents were evaporated. The residue was extracted with water and then with cyclohexane. The organic layer was evaporated to an oil which was crystallized from acetonitrile by dropwise addition of water. This gave 95 mg of crystals of $(C_6H_5)_2B_{11}H_9S$, mp 97–100°.

Anal. Calcd for $(C_6H_5)_2B_{11}H_9S$: B, 37.8; H, 6.1; C, 45.9; S, 10.2. Found: B, 38.1; H, 6.2; C, 45.2; S, 10.6. The ultraviolet spectrum in cyclohexane shows absorption at 2200 (ε 26,800), 2720 (sh, ε 4860), and 2780 A (sh, ε 2610).

Bis(tetramethylammonium)bis(π-(1)-2-thiollyl)iron(II), $[(CH_3)_4N]_2(B_{10}H_{10}S)_2Fe$–$C_4H_9Li$ Method.—To a stirred mixture of 40 ml of anhydrous tetrahydrofuran and 25 ml of 1.6 *M* butyllithium in hexane was added with cooling 1.5 g (0.010 mole) of $B_{10}H_{12}S$. Heat was evolved and a precipitate formed. The mixture was stirred for 10 min at room temperature, and 2.6 g of anhydrous ferrous chloride was added. An exothermic reaction occurred, and a dark color appeared. The mixture was evaporated *in vacuo*, and the residue was extracted with water. The deep maroon extract was filtered and treated with tetramethylammonium chloride. The resulting precipitate was collected by filtration to give 1.35 g of $[(CH_3)_4N]_2(B_{10}H_{10}S)_2Fe$ as a pink solid. Recrystallization from acetonitrile–ethanol gave maroon needles, which darken without melting above 300°. Thin layer chromatography on silica gel shows a single, red boron-containing spot.

Anal. Calcd for $[(CH_3)_4N]_2(B_{10}H_{10}S)_2Fe$: B, 42.9; H, 8.8; C, 19.1; N, 5.6; S, 12.7; Fe, 11.1. Found: B, 42.3; H, 9.0; C, 19.0; N, 5.5; S, 12.6.

The ultraviolet spectrum of the product in acetonitrile solution shows peaks at 2300 (ε 20,800), 2520 (sh, ε 18,000), 4050 (ε 97), and 5100 A (ε 189). The infrared spectrum shows complex absorption at 2450–2550 cm^{-1} (BH str) and sharp peaks at 1015 (cage) and 885 cm^{-1}.

Polarographic oxidation of the product in acetonitrile solution with 0.1 *M* $(C_4H_9)_4NClO_4$ as electrolyte (rpe *vs.* sce) shows a well-defined wave at $E_{1/2}$ = +0.2 v which is probably a reversible one-electron oxidation. Additional nonreversible oxidations occur at +1.35 and +1.8 v. Under similar conditions $(CH_3)_4NB_{10}H_{11}S$ shows a well-defined oxidation wave at +0.98 v.

$[(CH_3)_4N]_2(B_{10}H_{10}S)_2Fe$–Na method.—A mixture of 284 mg of $CsB_{10}H_{11}S$, 30 ml of tetrahydrofuran, and about 1 ml of 50% sodium dispersed in mineral oil was stirred at reflux overnight. The resulting mixture was treated with 500 mg of anhydrous ferrous chloride and refluxed for 15 min. The resulting black mixture was treated with ethanol and evaporated *in vacuo*. The residue was extracted with water and pentane. The rose-colored aqueous layer was treated with tetramethylammonium chloride, and the resulting precipitate was collected by filtration to give 70 mg of pink $[(CH_3)_4N]_2(B_{10}N_{10}S)_2Fe$. Recrystallization from acetonitrile–ethanol gave red microcrystals. The infrared spectrum of the product was identical with that of the iron compound prepared above.

Anal. Found: Fe, 11.2 (by X-ray fluorescence).

$Cs_2(B_{10}H_{10}S)_2Fe$.—To a solution of 42 ml of 1.6 *M* butyllithium–hexane in 120 ml of anhydrous tetrahydrofuran was added with ice-bath cooling 4.56 g of $B_{10}H_{12}S$. After stirring for 15 min at room temperature, 2.04 g of ferrous chloride was added, and the mixture was refluxed for 15 min. It was then evaporated under reduced pressure, the resulting residue was extracted with water and filtered, and the filtrate was treated with cesium sulfate. The precipitate was recrystallized from water to give 6.29 g (34%) of $Cs_2(B_{10}H_{10}S)_2Fe\cdot H_2O$ as maroon crystals.

Anal. Calcd for $Cs_2(B_{10}H_{10}S)_2Fe \cdot H_2O$: B, 33.8; H, 3.5; S, 10.0; Fe, 8.7. Found: B, 33.3; H, 3.9; S, 10.2; Fe, 8.8.

The ultraviolet spectrum in acetonitrile shows absorption at 5080 (ϵ 183), 4150 (ϵ 88.5), 2540 (ϵ 16,300), and 2300 A (ϵ 18,400).

Recrystallization of $Cs_2(B_{10}H_{10}S)_2Fe \cdot H_2O$ from D_2O gave $Cs_2(B_{10}H_{10}S)_2Fe \cdot D_2O$ which contained no boron-bound deuterium (by infrared analysis). Recrystallization from D_2O containing sulfuric acid gave $Cs_2(B_{10}H_{10}S)_2Fe \cdot D_2O$ containing some boron-bound deuterium. The approximate area ratio of the B–H and B–D stretching frequencies was 5.6:1.

Bromination of $(B_{10}H_{10}S)_2Fe^{2-}$.—To 16 ml of 0.125 *M* bromine in acetonitrile was added 100 mg of $[(CH_3)_4N]_2(B_{10}H_{10}S)_2Fe$. A deep green color formed. Benzene was added, and the mixture was evaporated *in vacuo*. The residue was suspended in aqueous tetramethylammonium chloride and filtered to give 200 mg of a violet solid. Recrystallization from acetonitrile–ethanol gave 65 mg of maroon crystals of $[(CH_3)_4N]_2(B_{10}H_{6.5}Br_{3.5})_2Fe$.

Anal. Calcd for $[(CH_3)_4N]_2(B_{10}H_{6.5}Br_{3.5})_2Fe$: B, 20.5; Br, 53.0; N, 2.7. Found: B, 23.9; Br, 52.9; N, 3.0.

Chlorination of $(B_{10}H_{10}S)_2Fe^{2-}$.—Chlorine gas was bubbled through a solution of 200 mg of $[(CH_3)_4N]_2(B_{10}H_{10}S)_2Fe$ in 50 ml of acetonitrile for 4 min. The solution was evaporated, and the residue was treated with aqueous sodium bisulfite and tetramethylammonium chloride. Filtration gave 255 mg of lavender solid. Recrystallization from acetonitrile–ethanol gave 120 mg of maroon crystals of $[(CH_3)_4N]_2(B_{10}H_{7.5}Cl_{2.5})_2Fe$.

Anal. Calcd for $[(CH_3)_4N]_2(B_{10}H_{7.5}Cl_{2.5})_2Fe$: B, 32.3; H, 5.9; C, 14.3; Cl, 26.2. Found: B, 31.5; H, 6.0; C, 14.7; Cl, 27.7.

The ultraviolet spectrum in acetonitrile shows absorption at 5100 (ϵ 157), 3100 (ϵ 11,300), 2720 (ϵ 10,800), 2500 (ϵ 11,700), and 2230 A (ϵ 17,600).

$Cs(B_{10}H_{10}S)_2Co$—C_4H_9Li Method.—To a mixture of 40 ml of tetrahydrofuran and 13.5 ml of a 1.6 *M* solution of butyllithium in hexane in an ice bath was added 1.5 g of $B_{10}H_{12}S$. After being stirred at room temperature for 20 min, the mixture was immersed in an ice bath and treated with 1.1 g of anhydrous cobaltous chloride. The solution darkened at once. After being stirred for 10 min at room temperature, the mixture was evaporated, and the residual dark, oily product was extracted with water and filtered through Celite. The deep amber filtrate was treated with excess tetramethylammonium chloride. The resulting precipitate of $(CH_3)_4N(B_{10}H_{10}S)_2Co$ was collected by filtration, dissolved in aqueous acetonitrile, and passed through a column packed with a commercial strongly acidic ion-exchange resin which had been pretreated with excess sodium chloride. The resulting effluent was evaporated *in vacuo* to a small volume and treated with excess cesium sulfate. The resulting brown precipitate was recrystallized from water to give 750 mg of rust-colored crystals of $Cs(B_{10}H_{10}S)_2Co$.

Anal. Calcd for $Cs(B_{10}H_{10}S)_2Co$: B, 44.0; H, 4.1; S, 13.0; Co, 12.0. Found: B, 43.1; H, 4.1; S, 12.9; Co, 11.8.

The B^{11} nmr spectrum at 32.1 Mc (Figure 8) consists of four doublets with relative intensities 4:2:2:2. This spectrum is entirely consistent with the proposed icosahedral structure (Figure 1) with a stereochemistry in which the sulfur atom is adjacent to the cobalt. Thus the highest field doublet may be assigned to the two boron atoms adjacent to both sulfur and cobalt, the 24.4-ppm doublet can be assigned to two boron atoms adjacent to sulfur, the 15-ppm peak can be assigned to two boron atoms adjacent to cobalt, and the remaining four boron atoms which are not strictly equivalent have a very similar chemical shift leading to spectroscopic equivalence and giving rise to the doublet at 5.14 ppm. This assignment is consistent with the observed broadening of the resonance signals of the boron atoms adjacent to cobalt. The ultraviolet spectrum in acetonitrile shows absorption at 2260 (ϵ 9160), 3150 (ϵ 22,600), 3700 (ϵ 268, sh), and 4450 A (ϵ 445). Polarographic reduction of the product occurs in acetonitrile solution at −0.77 v.

$Cs(B_{10}H_{10}S)_2Co$–NaOH Method.—A solution of 760 mg of $B_{10}H_{12}S$ in a minimum of 10% aqueous sodium hydroxide was treated with twice the volume of 50% aqueous sodium hydroxide and then added to a solution of 4.5 g of $CoCl_2 \cdot 6H_2O$ in a minimum of water. The resulting mixture was filtered through Celite, and the filtrate was treated with $^1/_2$ volume of 50% aqueous cesium hydroxide. The resulting brown precipitate was collected by filtration, dissolved in ethanol, and filtered. The dark filtrate was evaporated; the residue was extracted with ether and filtered. Evaporation of the filtrate gave 1.6 g of $Cs(B_{10}H_{10}S)_2Co$, identified by comparison of the infrared spectrum with that of an authentic sample. Further purification was achieved by dissolving the product in ethanol, filtering, diluting the filtrate with water, and concentrating the solution on a rotary evaporator at ambient temperature. The resulting crystals were collected by filtration to give 1.25 g of yellow-orange $Cs(B_{10}H_{10}S)_2Co$. The infrared spectrum of the product was identical with that of $Cs(B_{10}H_{10}S)_2Co$ prepared by the butyllithium method.

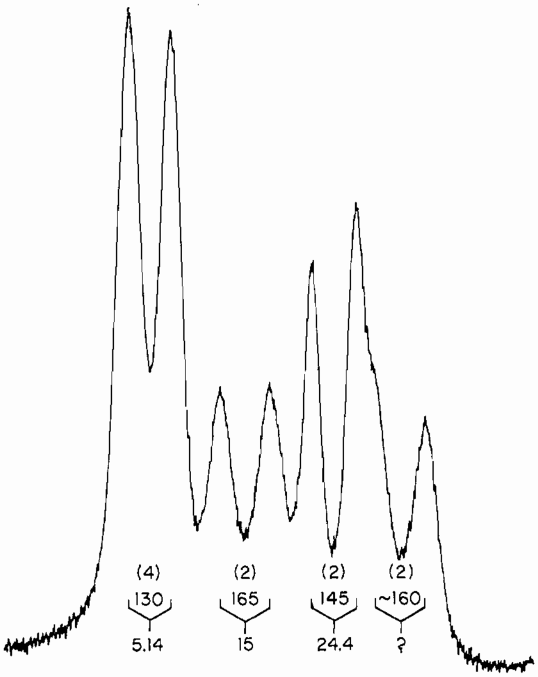

Figure 8.—B^{11} nmr spectrum of $Cs(B_{10}H_{10}S)_2Co$ in CH_3CN at 32.1 Mc.

$B_{10}H_{10}SCoC_5H_5$ and $(C_5H_5)_2Co^+(B_{10}H_{10}S)_2Co^-$.—To a solution of 35.5 ml of 1.6 *M* butyllithium (in hexane) in 40 ml THF was added 2.7 g of $B_{10}H_{12}S$ with ice-bath cooling. After 15 min, 1.6 ml of cyclopentadiene was added. After an additional 15 min 2.3 g of cobaltous chloride was added; the mixture was heated to reflux, cooled, and filtered, and the filtrate was evaporated. The residue was washed with water and then extracted with benzene. The benzene extract was chromatographed on neutral alumina using 5:1 benzene–ethylene chloride. Crystallization of the chromatographed product from benzene–cyclohexane gave 340 mg of orange plates of $B_{10}H_{10}SCoC_5H_5$, mp 267.5–268.5°.

Anal. Calcd for $B_{10}H_{10}SCoC_5H_5$: B, 39.4; C, 21.9; H, 5.5; S, 11.7; mol wt, 274. Found: B, 38.7; C, 22.8; H, 5.8; S, 11.7; mol wt, 274 (mass spectral) and 272 (cryoscopic in benzene).

The H^1 nmr spectrum of the product in acetonitrile-d_3 shows a single resonance peak at τ 4.48 (C_5H_5). The ultraviolet spectrum of the product in acetonitrile shows absorption at 3240 (ϵ 431), 2870 (ϵ 24,000), and 2320 A (ϵ 6370).

The benzene-insoluble residue was extracted with ethylene chloride, and the extract was chromatographed on neutral alumina (elution with ethylene chloride). Crystallization of the chromatographed material from benzene–acetonitrile gave 590 mg of orange needles of $(C_5H_5)_2Co^+(B_{10}H_{10}S)_2Co^-$, mp 287–287.5° (under N_2). When heated in air, blackening occurs above ~175°.

Anal. Calcd for $(C_5H_5)_2Co^+(B_{10}H_{10}S)_2Co^-$: B, 39.4; H, 5.5; C, 21.9; S, 11.7; Co, 21.4; half mol wt, 274. Found: B, 39.1; H, 5.8; C, 22.0; S, 11.8; Co, 21.4; mol wt (cryoscopic in DMSO), 275.

The H^1 nmr spectrum in acetonitrile-d_3 shows a single resonance at τ 4.53 (C_5H_5). The ultraviolet spectrum in acetonitrile shows absorption at 4365 (sh, ϵ 720), 3605 (sh, ϵ 3020, 3140, 23,700), and 2620 A (ϵ 40,400).

The principal absorption peak in the ultraviolet spectrum of cobalticinium perchlorate in water is reported to be at $\sim$2620 A (ϵ 39,810).[17]

The B^{11} nmr spectrum is identical with that of $Cs(B_{10}H_{10}S)_2Co$.

$B_{10}H_{10}SPt[P(C_2H_5)_3]_2$.—To a mixture of 15 ml of tetrahydrofuran and 1.3 ml of a 1.6 *M* solution of butyllithium in hexane was added 304 mg of $B_{10}H_{12}S$. After 10 min, 1.0 g of *cis*-dichlorobis(triethylphosphine)platinum was added. The resulting solution was refluxed for 5 min and then evaporated *in vacuo*. Water was added to the residue, and the resulting mixture was extracted with methylene chloride. The extract was evaporated, and the residue was recrystallized from a mixture of methylene chloride and acetonitrile to give 340 mg of yellow plates. The acetonitrile solvate was heated at 100° (0.1 mm) to give $[(C_2H_5)_3P]_2PtB_{10}H_{10}S$.

Anal. Calcd for $[(C_2H_5)_3P]_2PtB_{10}H_{10}S$: B, 18.6; H, 6.9; C, 24.8; S, 5.5; Pt, 33.6. Found: B, 18.3; H, 6.8; C, 25.8; S, 5.8; Pt, 32.6.

The ultraviolet spectrum in chloroform shows absorption at 2670 A (ϵ 17,500) and 4070 A (ϵ 150).

$(CH_3)_4NB_{10}H_{10}SRe(CO)_3$.—To a solution of 13 ml of 1.6 *M* butyllithium in hexane and 40 ml of tetrahydrofuran was added 1.5 g of $B_{10}H_{12}S$. The solution was stirred for 15 min at room temperature, 3.6 g of $Re(CO)_5Cl$ was added, and the solution was refluxed for 2.5 hr during which period carbon monoxide was evolved. The mixture was evaporated *in vacuo*, and the residue was dissolved in water and treated with excess tetramethylammonium chloride. The resulting precipitate was dissolved in acetonitrile and treated with ether to precipitate 835 mg of $(CH_3)_4NB_{10}H_{11}S$. The mixture was filtered, and the filtrate was evaporated *in vacuo*. The residue was twice recrystallized from ethanol to give 100 mg of crystals of $(CH_3)_4NB_{10}H_{10}SRe(CO)_3$.

Anal. Calcd for $(CH_3)_4NB_{10}H_{10}SRe(CO)_3$: B, 21.9; H, 4.5; C, 17.0. Found: B, 21.9; H, 4.7; C, 20.5.

The ultraviolet spectrum in acetonitrile shows only end absorption. The infrared spectrum of the product shows absorption at 2520 (B–H), 2100 (w), 1980 (C=O), 1480, and 950 cm^{-1} $[(CH_3)_4N^+]$.

$B_{10}H_{10}SCo[P(C_2H_5)_3]_2$.—To a mixture of 15 ml of tetrahydrofuran and 3.3 ml of 1.6 *M* butyllithium in hexane was added 400 mg of $B_{10}H_{12}S$. After being stirred for 15 min at room temperature, the mixture was cooled in an ice bath and treated with 965 mg of $[(C_2H_5)_3P]_2CoCl_2$. The solution turned deep green at once. It was evaporated *in vacuo*, and the residue was treated with water and filtered to give 1 g of brown solid. Recrystallization from benzene followed by recrystallization from heptane–benzene and ether–benzene gave 200 mg of dark brown needles of $[(C_2H_5)_3P]_2CoB_{10}H_{10}S$. The infrared spectrum is nearly identical with that of $[(C_2H_5)_3P]_2PtB_{10}H_{10}S$.

Anal. Calcd for $[(C_2H_5)_3P]_2CoB_{10}H_{10}S$: B, 24.3; H, 9.1; C, 32.3; Co, 13.2. Found: B, 24.0; H, 8.7; C, 32.1; Co, 13.1.

$[(CH_3)_4N]_2(C_6H_5B_{10}H_9S)_2Fe$.—To a solution of 302 mg of $(CH_3)_4NC_6H_5B_{10}H_{10}S$ in 15 ml of tetrahydrofuran was added 1 ml of 1.6 *M* butyllithium in hexane. After 10 min, 200 mg of ferrous chloride was added; the mixture was warmed briefly, and then cooled and filtered. The filtrate was evaporated *in vacuo* and the residue was suspended in aqueous tetramethylammonium chloride and filtered to give 215 mg of $[(CH_3)_4N]_2(C_6H_5B_{10}H_9S)_2Fe$ as red solid. The product was recrystallized from acetonitrile–ethanol.

Anal. Calcd for $[(CH_3)_4N]_2(C_6H_5B_{10}H_9S)_2Fe$: C, 36.6; H, 8.0. Found: C, 36.5; H, 8.1.

$(CH_3)_4N(CH_3)_2NNB_9H_{12}$.—To a stirred solution of 18.5 g of decaborane(14) in 450 ml of ether was added dropwise 200 ml of 0.7 *M* N,N-thionitrosodimethylamine[6] in ether. The mixture was stirred for an additional 30 min. The supernatant liquid was decanted from the gum which had separated, and the gum was washed with ether. The gum was extracted with 10% aqueous sodium hydroxide. The extract was filtered, and the filtrate was treated with excess tetramethylammonium chloride. The resulting precipitate was extracted with warm ethanol and filtered. The filtered ethanol extract was concentrated under reduced pressure and then treated with 1:1 benzene–cyclohexane to give 4.9 g of $(CH_3)_4N^+(CH_3)_2NNB_9H_{12}^-$. The product was recrystallized from ethanol–cyclohexane and then from a small volume of ethanol to give crystals melting at 197–198° (bubbling).

Anal. Calcd for $(CH_3)_4N(CH_3)_2NNB_9H_{12}$: B, 40.3; H, 12.5; C, 29.9; N, 17.4; hydrolytic H_2, 1762 cc/g. Found: B, 40.4; H, 12.1; C, 30.1; N, 17.4; hydrolytic H_2, 1753 cc/g.

The product shows ultraviolet absorption in acetonitrile solution at 2850 A (ϵ 1510) with a shoulder at 2250 A (ϵ 6100). The H^1 nmr spectrum in acetonitrile-d_3 shows three peaks at τ 7.1 $[(CH_3)_4N^+$, relative intensity 4], τ 7.86 ($N-CH_3$, relative intensity 0.74), and τ 7.97 ($N-CH_3$, relative intensity 1.1) suggesting the presence of two isomers.

$(CH_3)_3NNB_9H_{12}$.—A solution of 1.5 g of $(CH_3)_4N(CH_3)_2NNB_9H_{12}$ and 5 ml of methyl iodide in 35 ml of acetonitrile was refluxed for 45 min. The mixture was evaporated under reduced pressure, and the residue was suspended in water and filtered. The filter cake was washed with water to give 1.17 g of $(CH_3)_3NNB_9H_{12}$ as a pale yellow solid. The product was recrystallized from acetonitrile–ethanol to give colorless crystals, which decomposed quite suddenly at 176.5° with formation of copious amounts of gas.

Anal. Calcd for $(CH_3)_3NNB_9H_{12}$: B, 53.3; H, 11.6; C, 19.7; N, 15.4; hydrolytic H_2, 2330 cc/g. Found: B, 53.3, 52.8; H, 11.4, 11.3; C, 18.6, 20.6; N, 16.8; hydrolytic H_2, 2350 cc/g.

The ultraviolet spectrum in acetonitrile shows absorption at 2230 A (ϵ 7100). The H^1 nmr spectrum of the product in acetonitrile-d_3 shows a single peak at τ 7.02 $[-N(CH_3)_3]$. The infrared spectrum shows absorption characteristic of the $-N(CH_3)_3$ group at 1481 cm^{-1}. There is no absorption attributable to N–H.

$(CH_3)_4NB_9H_{12}NH$.—A mixture of 3 g of $(CH_3)_4N(CH_3)_2NNB_9H_{12}$ (mixture of isomers), 100 ml of THF, and 10 ml of 50% sodium dispersed in mineral oil was stirred at reflux for 20 hr under a nitrogen atmosphere. The mixture was cooled, treated portionwise with ethanol, and evaporated *in vacuo*. The residue was treated with water and pentane. The aqueous layer was treated with tetramethylammonium chloride to give a precipitate of 1.9 g of colorless solid. This was boiled with 100 ml of ethanol. Undissolved $(CH_3)_4NB_9H_{12}NH$ was filtered off. On cooling, the filtrate deposited 235 mg of crystals of $(CH_3)_4NB_9H_{12}NH$, mp >300°.

Anal. Calcd for $(CH_3)_4NB_9H_{12}NH$: B, 49.0; H, 12.7; C, 24.2; N, 14.1; hydrolytic H_2, 2140 cc/g. Found: B, 50.1; H, 12.4; C, 24.5; N, 14.6, 13.5, 13.7; hydrolytic H_2, 2084, 2106 cc/g.

The infrared spectrum shows sharp absorption at 3390 cm^{-1} (N-H str) and no absorption attributable to NH_2 deformation. The ultraviolet spectrum of the product in acetonitrile shows peaks at 2180 A (ϵ 8200) and 2750 A (sh, ϵ 105). The H^1 nmr spectrum in CD_3CN shows peaks at τ 7.11 ($(CH_3)_4N$, relative intensity 12) and 7.91 (NH, relative intensity 1). The latter peak is shifted to τ 6.95 on addition of a little D_2O. The B^{11} nmr spectrum is shown in Figure 9.

$CsB_9H_{12}NH$.—A solution of 600 mg of $(CH_3)_4NB_9H_{12}NH$ in aqueous acetonitrile was passed through a sodium cation exchange column, and the effluent was concentrated *in vacuo* to about 25 ml. The solution was treated with excess cesium sulfate to give 630 mg (81%) of $CsB_9H_{12}NH$. The product was recrystallized from ethanol–benzene–cyclohexane.

Anal. Calcd for $CsB_9H_{12}NH$: H, 5.1; N, 5.5. Found: H, 5.4; N, 5.4.

The ultraviolet spectrum in water shows absorption at 2180 A (ϵ 8570) and $\sim$2800 A (ϵ 5).

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(17) G. Wilkinson, *J. Am. Chem. Soc.*, **74**, 6148 (1952).

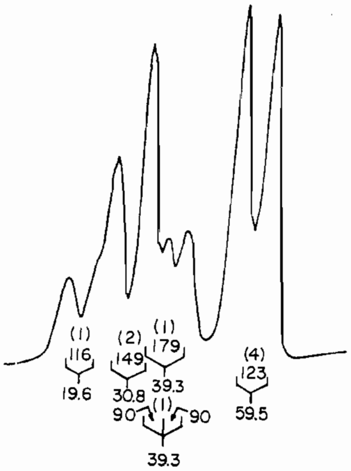

Figure 9.—B^{11} nmr spectrum of $(CH_3)_4NB_9H_{12}NH$ in CH_3CN at 19.3 Mc.

$CH_3CNB_9H_{11}NH$.—To a solution of 600 mg of $(CH_3)_4NB_9H_{12}NH$ in a small volume of acetonitrile cooled in an ice bath was added dropwise a cold, concentrated solution of bromine in acetonitrile until the bromine color was no longer discharged. The mixture was poured into a cold aqueous solution of sodium acetate and sodium bisulfite. The resulting precipitate was collected and dried first at 0° (0.1 mm) and then at 25° (0.1 mm). The product was then sublimed onto a −80° cold finger at 80° (0.1 mm) to give 300 mg of $CH_3CN\cdot B_9H_{11}NH$, mp 85–88°.

Anal. Calcd for $CH_3CN\cdot B_9H_{11}NH$: B, 59.1; H, 9.2; C, 14.6; N, 17.0; hydrolytic H_2, 2450 cc/g. Found: B, 61.1; H, 9.5; C, 15.2; N, 16.0; hydrolytic H_2, 2288 cc/g.

The product must be stored in an inert atmosphere as it decomposes in air. A pentane solution of $CH_3CN\cdot B_9H_{11}NH$ in air rapidly deposits a flocculent solid which contains OH groups (by infrared analysis).

The mass spectrum of $CH_3CNB_9H_{11}NH$ (solid injection) shows no parent peak, but an intense peak occurs at *m/e* 41 corresponding to CH_3CN^+, and the spectrum cuts off at *m/e* 125 corresponding to $^{11}B_9H_{11}NH^+$. Thus, complete fragmentation occurs to CH_3CN and $B_9H_{11}NH$.

The H^1 nmr spectrum in CD_3CN shows a single peak at τ 6.98 (CH_3CN). The infrared spectrum shows peaks at 3400 (N–H str), 2550 (B–H str), and 2340 cm^{-1} ($C\equiv N$ str). The ultraviolet spectrum in acetonitrile solution has λ_{max} 2410 A (ϵ 10,400).

$CH_3CN\cdot B_9H_{11}NH$ can also be prepared by treatment of an acetonitrile solution of $B_9H_{12}NH^-$ with iodine, N-chlorosuccinimide, N-bromosuccinimide, or N-iodosuccinimide.

Treatment of a solution of $CH_3CN\cdot B_9H_{11}NH$ in benzene with triethylamine gave $(C_2H_5)_3NB_9H_{11}NH$ as a colorless solid identified by the presence of resonance peaks characteristic of ethyl groups in its H^1 nmr spectrum and by the absence of infrared absorption characteristic of $C\equiv N$.

Reaction of $CH_3CNB_9H_{11}NH$ with lithium aluminum hydride or lithium borohydride in THF gave $B_9H_{12}NH^-$, isolated as the tetramethylammonium salt and identified by comparison with an authentic sample.

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The Interaction of Phosgene with Lewis Acids

By KARL O. CHRISTE

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Vapor pressure–composition isotherms indicate the following relative order of Lewis acidity toward phosgene: $AlCl_3 > SbCl_5 > BCl_3$. Whereas $AlCl_3$ forms a well-defined 1:1 adduct with $COCl_2$, the BCl_3–$COCl_2$ system shows a positive deviation from Raoult's law. Contrary to earlier literature reports $COCl_2$ forms only a 1:1 adduct with $AlCl_3$. The adduct is a white solid melting at 25° and has a dissociation pressure of 36 and 440 mm at 0 and 25°, respectively. Its infrared spectrum agrees only with an oxygen-bridged coordination complex and not with any ionic structure postulated earlier.

Introduction

Complex formation between $COCl_2$ and the Lewis acid $AlCl_3$ was first described by Baud.[1] The existence and characterization of the following complexes were reported: (i) $Al_2Cl_6\cdot 5COCl_2$, liquid, mp −2°, vapor pressure 760 mm at 30°; (ii) $Al_2Cl_6\cdot 3COCl_2$, liquid, mp 9°, and (iii) $2Al_2Cl_6\cdot COCl_2$, solid, decomposing at 150°. Later, the properties of solutions of $AlCl_3$ in liquid $COCl_2$ were extensively studied by Germann and coworkers.[2–8] Based on their work these solutions were considered as a solvent system of acids and bases,[9,10] assuming for the solvent a self-ionization comparable to that of H_2O. Consequently, the $AlCl_3$–$COCl_2$ adducts were generally believed to be ionic, containing $COCl^+$ or CO^{2+} cations and $AlCl_4^-$ anions. More recently, Huston[11] has shown in a tracer study of the $COCl_2$–$AlCl_3$ system that the exchange rate of radioactive chlorine between $AlCl_3$ and $COCl_2$ is slow. It was therefore suggested that the active agent in solutions of $AlCl_3$ in liquid $COCl_2$ is $AlCl_3$ itself and not CO^{2+} or $COCl^+$. However, interaction between $COCl_2$ and $AlCl_3$ through a chlorine atom, without actually break-

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