

Deltahedral and Deltahedral-Fragment Thiaboranes with 12-, 11-, 10-, and 9-Vertex Frameworks, Their Syntheses and Characterization

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Abstract: The nominal structures of 12-, 11-, 10-, and 9-vertex thiaboranes appear to parallel those found for boranes and carboranes of the same framework electron count. The arachno 6-SB₉H₁₂⁻ can be oxidized in high-yield to nido 6-SB₉H₁₁ which gives closo 1-SB₉H₉ upon pyrolysis. Pyrolysis of 6-SB₉H₁₂⁻ leads to nido 7-SB₁₀H₁₂ which in turn gives closo 1-SB₁₁H₁₁ upon pyrolysis. The controlled degradation of 1-SB₉H₉ and 1-SB₁₁H₁₁ can be effected by alcoholic KOH to give nido 4-SB₈H₉⁻ and nido 7-SB₁₀H₁₁⁻, respectively. In NH₃(l), 4-SB₈H₉⁻ and 7-SB₁₀H₁₁⁻ result from 1-SB₉H₉. Protonation of 4-SB₈H₉⁻ gives nido 4-SB₈H₁₀ which is converted to nido Et₃NH⁺SB₈H₉⁻ rather than arachno SB₈H₁₀·NEt₃ when treated with triethylamine. Reduction of 1-SB₉H₉ and 1-SB₁₁H₁₁ in Na-NH₃(l) expels the heteroatom as S²⁻ and yields the corresponding borane anions B₉H₉²⁻ and B₁₁H₁₁²⁻. Reduction by either Na-THF or Na(naphthalene carrier)-THF is not clean and apparently gives coupling and degradation in addition to simple deltahedral opening without extensive elision of the heteroatom.

Attention to framework-electron count in the wide variety of boranes and heteroboranes that have been prepared in the last 15 years shows a striking correlation between that count and the nominal structure of the polyhedron for $2n + 2$, $2n + 4$, and $2n + 6$ framework electrons (closo, nido, and arachno, respectively) where n is the number of framework vertices as outlined previously.^{1,2} In the formalism of the latter scheme it is seen that a sulfur affords the requisite number of electrons for a neutral closo molecule, SB _{$n-1$} H _{$n-1$} , by distribution of the six valence electrons of the atom between four framework electrons and an exopolyhedral lone pair. Molecular orbital descriptions corroborate the latter "assignment" as opposed to the alternative of two lone pairs and two framework electrons.¹ With the major exception of the carboranes, most known heteroboranes have a 12- or 11-atom framework with icosahedral or icosahedral-fragment structures, respectively. The thiaboranes SB₉H₁₂⁻ and SB₉H₁₁ were the first reported heteroboranes (other than carboranes) with 10-atom frameworks³ and can be classified as arachno and nido, respectively.^{1,4} Both the arachno and the nido thiadecaborane appear to have an icosahedral-fragment structure. The more recently prepared closo-1-thiadecaborane(9) afforded the first nonicosahedral heteroborane with other than a carbon heteroelement.⁵ We report here the preparation and characterization of more new thiaboranes (some with 9-atom frameworks) and improved routes to certain others. Parallels between the reaction chemistry of the thiaboranes, carboranes, and boranes are discussed along with the unique aspects of their reaction chemistry.

Results and Discussion

6-Thia-nido-decaborane(11). Electron counting systematics emphasize the oxidation-reduction nature of closo-nido-arachno interconversions within the same size heteroborane framework.^{1,6} For example, 6-SB₉H₁₁⁷ can be obtained from SB₉H₁₂⁻ by protonation followed by pyrolytic disproportionation. The proposed intermediate H(H₂O) _{x} ⁺SB₉H₁₂⁻ is a pyrophoric solid and gives only a 30% yield of 6-SB₉H₁₁.³ We found that the solid H(H₂O) _{x} ⁺SB₉H₁₂⁻ evolves gases upon standing, the predominant component being pentaborane(9) which is not found for pure 6-SB₉H₁₁. The latter observation suggested the presence of other boranes, and indeed it was found that protonation of SB₉H₁₂⁻ also gives appreciable amounts of the previously

unnoticed 4-SB₈H₁₀ (vide infra) which is difficult to separate from 6-SB₉H₁₁. Because of the difficulty surrounding the preparation of 6-SB₉H₁₁ alternative methods for the oxidation of SB₉H₁₂⁻ were explored.

Conversion of SB₉H₁₂⁻ to SB₉H₁₁²⁻ by treatment with n -butyllithium followed by oxidation with SnCl₂ gave a low yield (20%) of SB₉H₁₁·THF which has been independently reported elsewhere.⁸ In benzene SnCl₂ oxidation gave extremely air and moisture sensitive materials and this approach to SB₉H₁₁ was pursued no further.

Adducts of the Lewis acid 6-SB₉H₁₁ can be formed either by direct reaction between the acid and base or by iodine oxidation of SB₉H₁₂⁻ in a donor (base) solvent.^{3,8} The latter method suggested that if the donor solvent were replaced by a nondonor, perhaps oxidation would proceed to give 6-SB₉H₁₁. In fact, iodine oxidation in refluxing benzene gives the desired reaction in over 85% yield after 15 min.



The ¹¹B NMR of 6-SB₉H₁₁ is given in Figure 1 and shows an error in the previously reported spectrum. At 32.1 MHz the six environments expected for the proposed structure (Figure 1) are seen, but the signal at 21.5 ppm saturates easily and disappears at high rf power levels; this doublet of relative intensity 1 was not observed in the previously reported spectrum. The effect of high power levels on the remainder of the 6-SB₉H₁₁ spectrum is minimal. In place of the saturated signal a doublet of relative intensity 1.23 was reported at 40.1 ppm for 6-SB₉H₁₁.³ However, the latter signal is really part of the spectrum for SB₈H₁₀ (vide infra), the other signals of SB₈H₁₀ have chemical shifts close to those of 6-SB₉H₁₁ and are not well resolved at 32.1 MHz. At 70.6 MHz the ¹¹B NMR spectrum of a sample of SB₉H₁₁ prepared by heating protonated SB₉H₁₂⁻ was found to be a 3:1 mixture of SB₉H₁₁:SB₈H₁₀.

A striking similarity in the ¹¹B NMR spectra of 6-SB₉H₁₁ and its isoelectronic analogues B₁₀H₁₄ and 5,6-C₂B₈H₁₂ is the quartet fine structure observed on one signal upon application of line-narrowing.⁹ The boron(s) exhibiting the quartet feature are at the 6,9-positions of B₁₀H₁₄ and the 9-position of 5,6-C₂B₈H₁₂. Thus we assign the -17.3 doublet of quartets in 6-SB₉H₁₁ to the 9-position. The observed pattern probably results from a combination of coupling with several nuclei, namely, the terminal hydro-

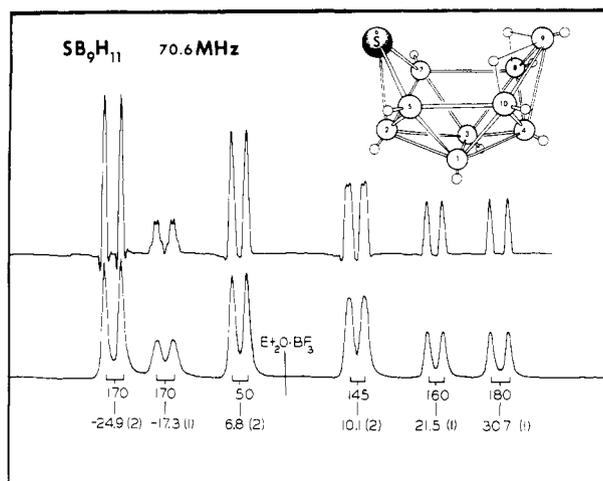


Figure 1. Proposed structure and 70.6-MHz ^{11}B NMR spectrum of 6- SB_9H_{11} (top trace is line-narrowed). The previously reported spectrum (ref 3) was contaminated with 4- SB_8H_{10} and reports chemical shifts relative to $\text{B}(\text{OCH}_3)_3$.

gen, the two bridge hydrogens, and the neighboring boron not on the open face (B-4). A reasonable fit is obtained for $J_{\text{BH}_1} = 165$, $J_{\text{BH}_\mu} = 40$, and $J_{\text{BB}} = 16$ Hz. The doublet of relative intensity two at 10.1 ppm is also affected by secondary bridge hydrogen coupling ($J_{\text{BH}_\mu} = 35$ Hz) which is revealed upon line-narrowing; the signal is assigned to positions 8 and 10, the bridge hydrogens spanning the 8-9 and 9-10 positions. Although assignment of the remainder of the spectrum is admittedly tentative, by correlation with the assignments for $\text{B}_{10}\text{H}_{14}$ and use of the empirical rules of Hermanek and Plesek^{9b} we suggest the following (chemical shift (intensity) position): -24.9 (2) B1,3; -6.8 (2) B5,7; 21.5 (1) B2; 30.7 (1) B4.

The placement of the bridge hydrogen in 6- SB_9H_{11} is not that predicted by the CNPR theory of Williams which favors a spanning of the 7-8 and 9-10 positions.¹⁰ The salient consideration in the CNPR approach is placement of the bridge hydrogens so as to minimize the coordination number of each boron. In 6- SB_9H_{11} it appears that the coordination number of the boron site before "placement" of the bridge hydrogens (rather than after "placement") is more important.

1-Thia-closo-decaborane(9) and 1-Thia-closo-dodecaborane(11). Pyrolysis has often been used as a synthetic technique in borane chemistry, e.g., many of the higher boron hydrides are formed by pyrolysis of diborane under a variety of conditions.¹¹ Simple disproportionations have also been observed, e.g., the synthesis of 2,3- $\text{B}_9\text{C}_2\text{H}_{11}$ from $\text{B}_9\text{C}_2\text{H}_{13}$ by pyrolysis.¹² After several unsuccessful attempts to oxidize 6- SB_9H_{11} with oxidizing agents such as neat Br_2 , FeCl_3 , and SnCl_2 , pyrolysis was investigated. At 450° in vacuo the evolution of H_2 from 6- SB_9H_{11} was observed to be brisk and to give a 60% yield of 1- SB_9H_9 . The structural characterization of 1- SB_9H_9 by NMR has been described previously.⁵ A less volatile component isolated from the pyrolysate has been shown to be a mixture of 2,2', 2,6', and 6,6'-(1- SB_9H_8)₂.¹³ The crystal structure of 2,2'-(1- SB_9H_8)₂ unequivocally confirms the bicapped Archimedean antiprism structure of the closo thia-decaborane framework.^{13,14} By inclusion of the results^{3,8} for 6- $\text{SB}_9\text{H}_{12}^-$ the structural (Figure 2) and chemical relationships between the thia-decaboranes are now evident. Of interest is the axial position of the sulfur in the closo molecule. A simple least-motion closing of the 6- SB_9H_{11} would lead to 2- SB_9H_9 , i.e., an equatorial sulfur with a coordination number of 5. The axial sulfur of 1- SB_9H_9 has a coordination number of 4.

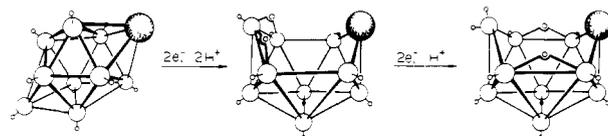


Figure 2. Chemical and structural relationship of closo, nido, and arachno thia-decaboranes.

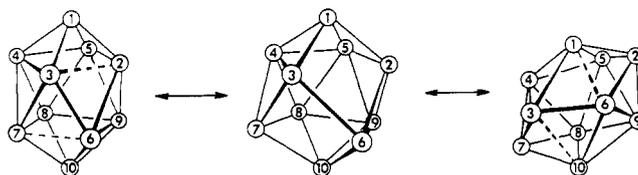


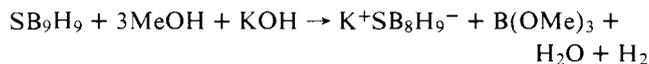
Figure 3. A possible rearrangement mechanism for axial-equatorial interconversion.

Thus, as noted by Williams, heteroatoms, electron-rich relative to boron, appear to preempt framework sites of low coordination number in the thermodynamically preferred isomer.¹⁰ Since 1- SB_9H_9 is formed at a rather high temperature of 450°, 2- SB_9H_9 actually may be formed first and subsequently rearrange to the 1-isomer via some mechanism such as the dsd mechanism proposed by Lipscomb for polyhedral borane rearrangements.¹⁵ The two simultaneous dsd processes illustrated in Figure 3 would interchange axial and equatorial positions.

Attempts to prepare $\text{SB}_{10}\text{H}_{10}$ by the pyrolysis of $\text{SB}_{10}\text{H}_{12}$ were unsuccessful but did give the parent icosahedral thia-borane 1- $\text{SB}_{11}\text{H}_{11}$ which has since been reported independently.¹⁶

Elision of Boron from 1- SB_9H_9 and 1- $\text{SB}_{11}\text{H}_{11}$. Since the carbon heteroatom in carboranes is more electronegative than boron, certain boron sites are rendered more subject to nucleophilic attack than in the isoelectronic borane anions. For instance, while both $\text{B}_{10}\text{H}_{10}^{2-}$ and $\text{B}_{12}\text{H}_{12}^{2-}$ are completely resistant to strong aqueous sodium hydroxide at 95°, 1,2- $\text{B}_{10}\text{C}_2\text{H}_{12}$ and 1,6- $\text{B}_8\text{C}_2\text{H}_{10}$ are degraded by either piperidine or ethanolic KOH.¹⁷⁻²⁰ The influence of a sulfur heteroatom should be similar to that of carbon and render the adjacent boron sites subject to nucleophilic attack. However, there are unique aspects to thia-boranes absent in the isoelectronic closo dicarbaboranes: the presence of a single heteroatom, the larger size of that atom, and the absence of an exohedral²¹ substituent on the heteroatom (unless one considers the lone pair to be a substituent).

Various nucleophiles attack and partially degrade 1- SB_9H_9 in a controlled fashion. Anhydrous methanolic KOH consumes 95% of the thia-decaborane after 9 h at 25° and $\text{Me}_4\text{N}^+\text{4-SB}_8\text{H}_9^-$, tetramethylammonium nonahydro-4-thia-nido-nonaborate(-1) (I), can be isolated after evaporation of the methanol and treatment with a $\text{Me}_4\text{N}^+\text{Cl}^-$ solution. The reaction appears to be



Once dried in vacuo I exhibits extreme sensitivity to air and moisture, sometimes burning vigorously if not handled under a blanket of N_2 . The white solid is best stored in an evacuated ampule. It is insoluble in nonpolar organic solvents but dissolves without decomposition in *dry* acetonitrile. Solubility is low in CH_2Cl_2 , CCl_4 , and diethyl ether. Acetone causes a vigorous exothermic reaction with liberation of H_2S .

The presence of a broad, weak band near 2100 cm^{-1} in the ir spectrum of I (Table I) suggests the presence of a bridge hydrogen in the anion. The ^1H NMR indicated only

Table I. Infrared Spectra^a

$[(\text{CH}_3)_4\text{N}][4\text{-SB}_8\text{H}_9]^-$: ^b 2520 vs, 2450 sh, m, 2413 s, 2125 w, 1740 vw, 1325 m, 1220 vw, 1190 sh, vw, 1150 m, 1115 sh, vw, 1025 vbr, s, 955 s, 925 sh, m, 872 vw, 855 vw, 815 vw, 800 vw, 778 w, 725 m, 687 w, 645 w, 578 w, 530 vw, 489 w, 450 w, 410 w
$4\text{-SB}_8\text{H}_{10}$: ^b 2570 s, 2130 vw, 2015 vw, 1065 sh, vw, 1047 m, 1028 m, 1010 m, 982 m, 950 m, 918 m, 876 w, 868 sh, vw, 845 vw, 829 w, 800 vw, 755 sh, vw, 735 w, 715 vw, 696 vw, 662 sh, vw, 650 w, 632 sh, vw, 588 w, 435 vw, 410 w
$[(\text{C}_2\text{H}_5)_3\text{NH}][4\text{-SB}_8\text{H}_9]^-$: ^b 3450 br, w, 3040 m, 2530 vs, 2440 sh, m, 2390 m, 2115 vw, 1295 vw, 1185 sh, w, 1160 m, 1055 sh, m, 1015 s, 943 w, 913 vw, 895 vw, 873 vw, 838 w, 812 sh, 798 w, 730 sh, vw, 714 w, 696 vw, 683 vw, 641 w, 581 w, 489 w, 441 w, 402 w
$[(\text{CH}_3)_4\text{N}][7\text{-SB}_8\text{H}_9]^-$: ^b 2520 vs, 1322 s, 1160 w, 1110 vw, 1062 w, 1010 m, 953 s, 925 m, 833 vw, 777 w, 745 vw, 720 w, 675 vw, 650 vw, 607 w, 560 vw, 518 w, 463 w
$1\text{-SB}_9\text{H}_9$: ^c 2600 vs, 2560 vs, 1011 w, 972 m, sh, 958 s, 910 w, sh, 902 m, 873 vw, 810 s, 750 w, sh, 738 m, 721 m, 685 s, 660 w, 610 s, 603 s, 532 m
$1\text{-SB}_{11}\text{H}_{11}$: ^b 2600 vs, 2565 vs, 1150 w, 1018 s, 955 w, 906 s, 869 m, 762 w, 720 vs, 641 w, 585 m, 544 m

^a Band intensities are reported in cm^{-1} with relative intensities given by s = strong, m = medium, w = weak, v = very, sh = shoulder, br = broad. ^b Determined as a Nujol mull. ^c Determined in a KBr matrix.

one type of bridge hydrogen at 3 ppm upfield from Me_4Si . The best structural characterization of the molecule is obtained from the ^{11}B NMR spectrum; however, since the same anion is formed by treatment of SB_8H_{10} with NEt_3 (vide infra), and since the latter method gives a cleaner product, discussion of the NMR spectra will be deferred. The spectra of I show a slight contamination of the product by $[\text{B}_9\text{H}_{12}]^-$ and $[\text{SB}_{10}\text{H}_{11}]^-$ ³ the latter of which can be attributed to the presence of about 1% $\text{SB}_{11}\text{H}_{11}$ in the $1\text{-SB}_9\text{H}_9$ used. A separate experiment showed that degradation of $\text{SB}_{11}\text{H}_{11}$ is facile and gives nearly quantitative amounts of $\text{SB}_{10}\text{H}_{11}^-$ under these conditions.

4-Thia-nido-nonaborane(10). Protonation of $4\text{-SB}_8\text{H}_9^-$ gives the corresponding neutral nido thianonaborane SB_8H_{10} (II) ($2n + 4 = 22$ framework electrons). A mixed solvent system consisting of either benzene or methylene chloride and either 98% H_2SO_4 or polyphosphoric acid was used as the protonating medium. The moisture sensitivity of both the starting anion and product thianonaborane necessitate a reasonably anhydrous proton source. $4\text{-SB}_8\text{H}_{10}$ is a hygroscopic, foul-smelling white solid which is easily sublimed in vacuo at 40° . It decomposes rapidly to boric acid and hydrogen sulfide when exposed to air. Solubility is high in benzene, toluene, chlorocarbons, and petroleum ether. Prolonged storage at room temperature leads to moderate decomposition to yellow solids and hydrogen. The yellow solids exhibit broad, unresolved bands in the infrared spectrum and are presumably polymeric. A significant feature of the ir spectrum of SB_8H_{10} is the presence of bridge hydrogen absorption at 2130 and 2015 cm^{-1} (see Table I). Although the low resolution mass spectrum showed the correct m/e cutoff of 132, the profile of the calculated envelope does not agree well with the observed envelope which is considerably more intense than that calculated 2 amu below the parent envelope cutoff. This suggests facile loss of hydrogen from the thianonaborane and the existence of SB_8H_8 which has thus far eluded isolation.

The 70.6-MHz ^{11}B NMR spectrum of SB_8H_{10} (normal and line-narrowed) is shown in Figure 4. Four regions of resonance are seen having relative intensities of 1:2:1:4 reading upfield. Assuming that the upfield signal arises from two nearly coincidental environments of intensity two each, the observed ^{11}B NMR spectrum is consistent with the structure shown in Figure 4. The basic framework is that deltahedral fragment² obtained by removing one boron

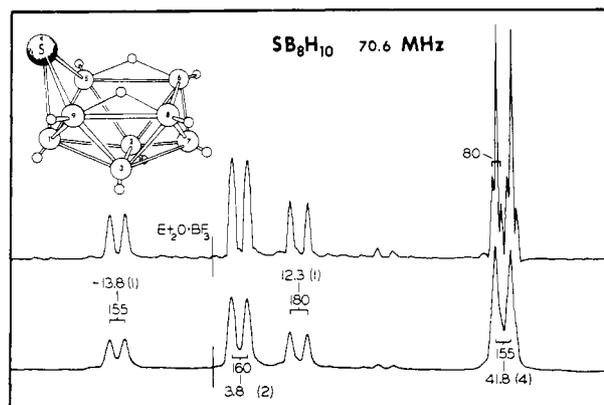


Figure 4. Proposed structure and 70.6-MHz ^{11}B NMR spectrum of $4\text{-SB}_8\text{H}_{10}$ (top trace is line-narrowed).

from the belt of four equivalent borons adjacent to the sulfur in $1\text{-SB}_9\text{H}_9$, those borons expected to be most susceptible to nucleophilic attack. The placement of the bridge hydrogens is of interest. Upon line-narrowing incipient coupling is observed in the doublet of intensity two at 3.82 ppm. Any incipient coupling in this latter resonance is not due to just simple coupling with a bridge hydrogen or hydrogens; coupling with one bridge hydrogen would cause a diminution of intensity at the center of each arm of this resonance and coupling with two bridge hydrogens would broaden each arm greater than the 65 Hz width observed at half-height, assuming typical bridge hydrogen coupling constants ($J_{\text{BH}_\mu} = 30\text{--}65\text{ Hz}$). One possible explanation involves coupling with one bridge hydrogen and an additional novel coupling between boron and a terminal hydrogen not directly bonded to the boron, i.e., a H-B-B coupling. While such a coupling has not been reported, a H-B-C-H coupling ($J_{\text{HBCH}} = 3.4\text{ Hz}$) has been proposed to account for the observed ^1H NMR spectra of various small metallocarboranes.²² Values of $J_{\text{BH}_\mu} = 30\text{ Hz}$ and $J_{\text{BBH}} = 20\text{ Hz}$ could account for the observed spectrum of SB_8H_{10} . We have observed a similar "triplet" feature for the 3.92 ppm signal of $\text{SB}_{10}\text{H}_{12}$ ($J_{\text{BH}_\mu} = 40$ and $J_{\text{BBH}} = 24\text{ Hz}$). The pentagonal faces in SB_8H_{10} and $\text{SB}_{10}\text{H}_{12}$ should be structurally quite similar (including bridge hydrogens) except for a greater degree of planarity in $\text{SB}_{10}\text{H}_{12}$. The verification of the proposed BBH-coupling must await double resonance experiments especially since line-narrowed spectra can give rise to artifacts.²³ The highest-field signal for SB_8H_{10} also exhibits fine structure due to bridge hydrogen coupling. The great intensity of the center peak in each branch of the signal as well as the asymmetry of the peaks suggests that only one of the two doublets of intensity 2 is affected by the additional coupling. The measured value is $J_{\text{BH}_\mu} = 85\text{ Hz}$, a rather large bridge hydrogen coupling constant; however, other thianonaboranes appear to give large bridge hydrogen coupling constants, e.g., for SB_8H_9^- (vide supra). Such large couplings may be diagnostic of bridge hydrogens which are nearly BH_2^- groups.

Treatment of SB_8H_{10} with either trimethylamine or triethylamine produced a white sublimable solid, III. Characterization of the product suggests a simple deprotonation to form the $4\text{-SB}_8\text{H}_9^-$ anion. For triethylamine, the ^1H NMR spectrum shows three regions of resonance: a singlet of intensity 1 (τ 4.33 (internal Me_4Si) NH), a 1:3:3:1 quartet of intensity 6 (τ 7.02, $J = 7\text{ Hz}$, CH_2), and a 1:2:1 triplet of intensity 9 (τ 8.75, $J = 7\text{ Hz}$, CH_3) with broad BH resonances in the baseline. The ^{11}B NMR spectrum (Figure 5) is essentially identical with that of I, and shows no indication of a B-N linkage. The low resolution mass spectrum

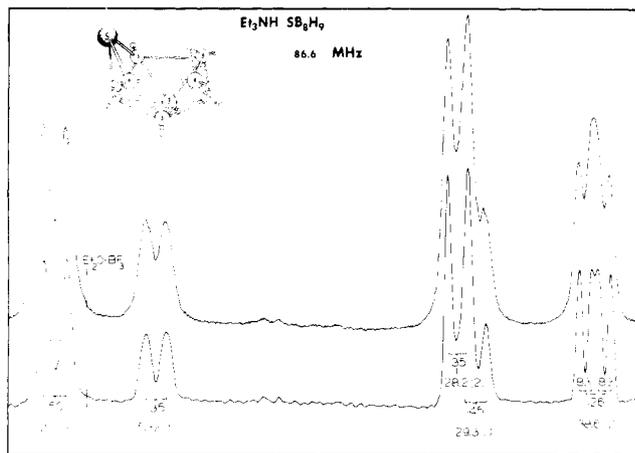


Figure 5. Proposed structure and 86.6-MHz ^{11}B NMR spectrum of $[\text{4-SB}_8\text{H}_9^-]$ (bottom trace is line-narrowed).

showed a parent envelope (m/e cutoff of 233) two orders of magnitude less intense than the two dominant features whose m/e values corresponded with SB_8H_{10} and $(\text{C}_2\text{H}_5)_3\text{N}$. In summary, the data support the removal of a bridging proton from SB_8H_{10} by the amine in formation of a closely associated $[(\text{C}_2\text{H}_5)_3\text{NH}^+][\text{SB}_8\text{H}_9^-]$ complex. The ability to vacuum sublime the "salt" at 85° suggests a zwitterionic character for the substance.

Because of the similarity in their ^{11}B NMR spectra, we formulate both I and III as SB_8H_9^- salts. The slight differences in chemical shifts (Table II) can be attributed to a combination of solvent effects and different counterions. All five of the ^{11}B resonance signals collapse to singlets upon proton decoupling. Thus, the "triplet" signal near 38 ppm arises from two equivalent borons and not from two distinct borons with slightly different chemical shifts. In fact, the identical appearance of this feature at both 70.6 and 32.1 MHz excludes the latter possibility. The evidence strongly suggests the framework structure shown in Figure 5. The sulfur atom could equally well be placed at positions 1, 4, and 7 based solely upon the ^{11}B NMR. In general, elements electron-rich relative to boron prefer low coordination-number sites.¹⁰ Both positions 4 and 7 retain the sulfur at a low-coordinate "axial" site, position 4 being chosen because nucleophilic attack would be expected at the more positive borons adjacent to the sulfur.

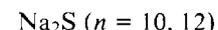
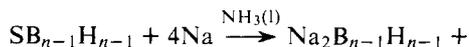
Degradation of 1-SB₉H₉ by NH₃(l). When added to refluxing liquid ammonia 1-SB₉H₉ appears to remain unchanged and not dissolve; however, a subtle degradation reaction occurs and after 9 h gives an insoluble product which is tentatively characterized as a thianonaborate isomeric with 4-SB₈H₉⁻, depending on work-up either the NH₄⁺ or the Me₄N⁺ salt of 7-SB₈H₉⁻. Six-hour liquid ammonia treatment gives the 4-SB₈H₉⁻ discussed above. The ^{11}B NMR spectrum of the 7-isomer is a series of doublets of relative intensity 1:2:2:2:1 (Table II) indicative again of a framework with C_s symmetry but equally consistent with placement of the sulfur at either the 1 or the 7 position. Placement of sulfur at position 7 is proposed in order to maintain a low coordination number for this electron-rich heteroatom. The isolation of the 4-isomer after shorter reaction time suggests that ammonia catalyzes a slow isomerization of the thianonaborane framework. A more detailed characterization of the proposed 7-SB₈H₉⁻ and attempts to define the conditions of its formation are in progress. The liquid ammonia degradations appear to be accompanied by formation of some B₉H₁₂⁻ and B₃H₈⁻ (weak peaks in the ^{11}B NMR).

Table II. ^{11}B NMR Data^a

6-SB ₉ H ₁₁ :	^b -24.9, d (2), $J_{\text{BH}} = 170$; -17.3, d (1), $J_{\text{BH}} = 170$; -6.8, d (2), $J_{\text{BH}} = 150$; 10.1, d (2), $J_{\text{BH}} = 145$; 21.5, d (1), $J_{\text{BH}} = 160$; 30.7, d (1), $J_{\text{BH}} = 180$
1-SB ₉ H ₉ :	^b -74.5, d (1), $J_{\text{BH}} = 180$; 4.8, d (4), $J_{\text{BH}} = 180$; 17.6, d (4), $J_{\text{BH}} = 150$
1-SB ₁₁ H ₁₁ :	^b -19.2, d (1), $J_{\text{BH}} = 145$; 3.2, d (5), $J_{\text{BH}} = 140$; 5.8, d (5), $J_{\text{BH}} = 160$
4-SB ₈ H ₁₀ :	^d -13.8, d (1), $J_{\text{BH}} = 155$; 3.8, d (2), $J_{\text{BH}} = 160$; ^c 12.3, d (1), $J_{\text{BH}} = 180$; 41.6, d (2), $J_{\text{BH}} = 155$; 41.8, d of d (2), $J_{\text{BH}} = 155$, $J_{\text{BH}_\mu} = 80$
[Et ₃ NH ⁺][4-SB ₈ H ₉ ⁻]:	^e -2.6, d (2), $J_{\text{BH}} = 150$; 5.3, d (1), $J_{\text{BH}} = 135$; 28.2, d (2), $J_{\text{BH}} = 135$; 29.3, d (1), $J_{\text{BH}} = 145$; 38.6, d of d (2), $J_{\text{BH}} = 126$, $J_{\text{BH}_\mu} = 83$
[Me ₄ N ⁺][4-SB ₈ H ₉ ⁻]:	^f -4.6, d (2), $J_{\text{BH}} = 155$; 5.3, d (1.2), $J_{\text{BH}} = 140$; 26.8, d (2), $J_{\text{BH}} = 140$; 29.2, d (1), $J_{\text{BH}} = 145$; 37.5, d of d (2), $J_{\text{BH}} = 125$, $J_{\text{BH}_\mu} = 80$
[Me ₄ N ⁺][7-SB ₈ H ₉ ⁻]:	^f -23.4, d (1), $J_{\text{BH}} = 145$; -3.1, d (2), $J_{\text{BH}} = 140$; 6.4, d (2), $J_{\text{BH}} = 140$; 33.4, d (2), $J_{\text{BH}} = 155$; 37.3, d (1), $J_{\text{BH}} = 160$
7-SB ₁₀ H ₁₂ :	^b -16.9, d (1), $J_{\text{BH}} = 150$; 1.6, d (2), $J_{\text{BH}} = 176$; 3.9, d (2), $J_{\text{BH}} = 159$; ^c 10.6, d (2), $J_{\text{BH}} = 154$; ^c 17.5, d (1), $J_{\text{BH}} = 154$; 24.9, d (2), $J_{\text{BH}} = 154$

^a The chemical shift data are given in ppm relative to Et₂O·BF₃ (-, values downfield) followed by a description of the multiplet (d = doublet), its relative intensity (in parentheses), and observed coupling constants given in Hz. ^b Determined in benzene-*d*₆ at 70.6 MHz. ^c Additional coupling was evident for this signal upon line-narrowing. ^d Determined in toluene-*d*₈ at 70.6 MHz. ^e Determined in chloroform-*d*₁ at 86.6 MHz. ^f Determined in acetonitrile-*d*₃ at 70.6 MHz.

Reduction of Closo Thiaboranes. Titration of a known amount of Na in liquid ammonia with either 1-SB₉H₉ or 1-SB₁₁H₁₁ resulted in the consumption of 4 mol of sodium per mole of thiaborane. The general reaction is



The borane dianions were identified by NMR and $\text{ir}^{24,25}$ and qualitative tests confirmed the presence of S²⁻ in the filtrates after precipitation of B₉H₉²⁻ and B₁₁H₁₁²⁻ by either Cs⁺ or Me₄N⁺. The closo borane anions and sulfide are apparently generated as a direct result of reduction and do not form through an intermediate which decomposes upon solvation by water since the borane anions can be detected by ^{11}B NMR analysis of a dimethyl sulfoxide solution prepared immediately following evaporation of the NH₃. This process in which the sulfur heteroatom is expelled from the polyhedron is unique in heteroborane chemistry. Since it has been noted that SB₁₀H₁₀²⁻ disproportionates to B₁₀H₁₀²⁻ and S,³ perhaps in this case the SB₉H₉²⁻ similarly goes to B₉H₉²⁻ and S which is reduced further.

The reduction of 1-SB₉H₉ by Na in THF or sodium naphthalide in THF clearly results in the consumption of 2 mol of sodium per mole of 1-SB₉H₉. Unlike reduction in NH₃(l), the elision of sulfur does not appear to be as extensive and the fate of the thiadecaborane is multifarious. The reduction process apparently parallels the complexity suggested regarding the reduction of small dicarbaboranes.²⁶

Sodium in THF slowly reduces 1-SB₉H₉ over a period of days (4–6 days at 25°) to give a red-orange solution. By contrast the deep-green sodium naphthalide color rapidly disappears and gives a pale-yellow solution when 1-SB₉H₉ is added. Upon slow titration of 1-SB₉H₉ in THF by an equal number of moles of sodium naphthalide in THF, one-half of the thiadecaborane is recovered unchanged. In general the recovery of naphthalene is high (85–95%). Analyses of reduction solutions are not highly reproducible and the problem is under further investigation; however, certain facts are apparent. The ^{11}B NMR spectra of the reduction

products of 1-SB₉H₉ exhibit no striking similarity to those of "[SB₉H₉²⁻]" prepared from 6-SB₉H₁₁ by treatment with butyllithium in THF.⁸ Hydrolysis of the reduction solutions followed by ¹¹B NMR analysis shows a mixture of 4-SB₈H₉⁻, 7-SB₈H₉⁻, SB₁₀H₁₁⁻, and doublets perhaps due to "[SB₉H₁₀⁻]" at 7.2, 12.4, 17.1, and 34.4 ppm. The ¹¹B NMR prior to hydrolysis is similar except for the "[SB₉H₁₀⁻]" peaks which are replaced by broad, intense resonances presumably due to "[SB₉H₉²⁻]" at 3.68 and 22.1 ppm. Removal of THF from the products formed by Na reduction followed by protonation with either HCl-benzene or HCl-ether gave 6-SB₉H₁₁, 7-SB₁₀H₁₂, and significantly appreciable amounts of species formulated as S₂B₁₈H₁₈ and S₂B₁₇H₁₇ by GC-mass spec analysis. The latter are suggestive of B-B linked "dimeric" thiaboranes such as SB₉H₈-B₉H₁₀S, SB₁₀H₁₁-B₈H₇S, SB₉H₈-B₈H₉S, etc.

On the basis of these results we suspect that the complexity of the "[SB₉H₉²⁻]" obtained by reduction of 1-SB₉H₉ in THF is due to the formation of a radical anion, (SB₉H₉)^{•-}, which can couple to form "dimeric" thiaboranes or effect a B-atom-transfer reaction to give the observed SB₁₀- and SB₈-frameworks. A similar linking of cages and alteration of cage size has been observed in the synthesis of metallocarboranes by the "polyhedral expansion" technique of reducing a closo carborane to a nido species and inserting a metal into the open face.^{26,27}

No indication of an S-H functionality was seen for any of the compounds discussed here. Since the region of S-H stretching frequency is 2430-2670 cm⁻¹, its presence may be obscured by the B-H stretch. However, the proton NMR spectra show no evidence of any S-H resonance. Therefore we discount the presence of an S-H group in any of the thiaboranes characterized here.

Experimental Section

General. Infrared spectra were determined on a Perkin-Elmer 457 as either KBr disks or Nujol mulls on KBr plates. The ¹¹B NMR spectra were recorded on a Varian HA-100 operating at 32.1 MHz, a Varian HR-220 operating at 70.6 MHz (Indiana University), a Bruker 270 operating at 86.6 MHz (University of Wisconsin), and a JEOL JNM-PS-100 operating at 32.1 MHz. ¹¹B NMR spectra from the latter three instruments were obtained using a pulsed Fourier transform mode. Proton NMR spectra were obtained on a Varian T-60 and a JEOL JNM-PS-100. Chemical shifts are reported relative to external (C₂H₅)₂O·BF₃ and internal Si(CH₃)₄ for ¹¹B and ¹H, respectively. The mass spectra were obtained on an Associated Electronic Industries MS-902. Gas chromatograms and preparative GC separations were performed on a Varian Aerograph Series 2700 with thermal conductivity bridge detector, and employing a 5 ft × 0.25 in. stainless steel column packed with 1.5% OV-101 on Chromosorb G (100-120 mesh). GC-MS analyses were obtained on a AEI MS-30 double beam instrument with Pye series 104 chromatograph using a 5 ft × 0.25 in. column (SE 30, 3%).

All preparations were conducted under an atmosphere of nitrogen unless specified otherwise. The published procedure³ was used for SB₉H₁₂⁻. Solvents were generally vacuum distilled from reservoirs containing appropriate drying agents over which the solvents were stored. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride (LAH), diethyl ether from LAH, benzene from sodium bis(2-methoxyethoxy)aluminum hydride (Vitride, trademark of National Patent Development Co., manufactured by Reaco Chemical Co., and purchased from Eastman Kodak Co.), petroleum ether from LAH, amines from KOH, chlorocarbons from P₂O₅, toluene from LAH, and methanol from molecular sieves and CaSO₄. Benzene not distilled directly into a reaction flask was dried by percolation through sodium hydride. Decaborane was freshly sublimed prior to use. Liquid ammonia was taken from a cylinder of anhydrous grade (Union Carbide, Linde Division) without further purification. Samples for NMR analysis were prepared from dried solvents, sealed under nitrogen, and stored at

-78 °C prior to analysis. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

6-SB₉H₁₁. The procedure for a typical synthesis is given. In a 500-ml three-neck flask, equipped with a condenser, nitrogen inlet and outlet, magnetic stirrer, and heating mantle were placed 200 ml of dry benzene and 11.82 g (46.6 mmol) of I₂. After thorough purging with nitrogen, 25.56 g (93.1 mmol) of CsSB₉H₁₂ was quickly added to the stirred iodine solution and the mixture brought to reflux. Gas evolution could be seen, even at room temperature, and the intense iodine color slowly faded yielding a yellow solution and a white solid. The mixture was quickly filtered and the filtrate rotary evaporated, giving a yellow solid. Sublimation of this solid at 40 °C in vacuo (0.1 mm) yielded 11.32 g (86.5%) of 6-SB₉H₁₁.

1-SB₉H₉. In a typical pyrolysis, 7.91 g (56.3 mmol) of SB₉H₁₁ was placed in the bottom of a 24 mm o.d. borosilicate glass tube 70 cm long, closed with a "test tube bottom", and with an outer 24/40 standard-taper joint at the open end. The open end of this tube was fitted through an inner 24/40 standard-taper joint to the bottom of a sublimator. Prior to connection of the tube to the sublimator, glass wool was loosely packed in the tube, starting 25 cm from the bottom and extending upwards for 15 cm.

The entire apparatus was then evacuated through the sublimator. A furnace was placed around the tube in the region of the glass wool packing, and heating tape wrapped around the bottom of the tube to gently sublime the SB₉H₁₁ into furnace hot zone. The furnace was heated to 450 °C. This system was continuously evacuated during the entire pyrolysis and the sublimator's cold finger maintained at -78 °C. After about 9 h no further hydrogen evolution was observed, heating was stopped, and the system was back-filled with nitrogen. 1-SB₉H₉ (4.62 g, 59.2%) was scrapped from the sublimator probe. Impurities imparting a slight yellow color to the product were removed by treatment with acetonitrile, rotary evaporation, and vacuum sublimation at room temperature affording 4.35 g (55.8%) of pure white crystals.

Anal. Calcd: B, 70.31; H, 6.39; S, 23.15. Found: B, 70.47; H, 6.39; S, 22.96.

The low-resolution mass spectrum shows typical boron envelopes; the parent-peak profile is the most intense feature with a cutoff at *m/e* 140 corresponding to ¹¹B₉¹H₉³²S⁺ and a weaker cutoff of the correct relative intensity for ¹¹B₉¹H₉³⁴S⁺ at *m/e* 142. The melting point is 216.5-217.0 °C (uncorrected) in a sealed capillary. The ¹H NMR (DCCl₃) shows three sets of 1:1:1:1 quartets at -7.97 (*J*_{H-B} = 171 Hz), **1**; -2.47 (*J*_{H-B} = 177 Hz), **4**; and -0.13 (*J*_{H-B} = 156 Hz), **4** (chemical shifts in parts per million relative to internal Me₄Si). The ultraviolet spectrum in heptane exhibits a single absorption (λ_{max} 2140 Å) having a molar extinction coefficient of 8100 l. mol⁻¹ cm⁻¹.

1-SB₁₁H₁₁. SB₁₀H₁₂ was prepared by the method described in the literature³ except that during the acidification of the crude SB₁₀H₁₁⁻ anion, a mixed solvent system was employed (water-benzene). The SB₁₀H₁₂ was recovered from the benzene layer by rotary evaporation and vacuum sublimation.

The pyrolysis apparatus was that used for the preparation of SB₉H₉. Typically, 3.88 g of SB₁₀H₁₂ (25.5 mmol) was placed in the pyrolysis tube and pyrolyzed at 380 °C in a manner analogous to that employed for SB₉H₁₁ (vide supra). Pale yellow material (169 mg) was collected from the -78 °C cold finger after 4 h of heating. This material was resublimed in vacuo at 50 °C to yield 149 mg of pure white SB₁₁H₁₁ (0.92 mmol).

Typical boron envelopes are observed in the low-resolution mass spectrum, the parent peak profile with cutoff *m/e* 164 corresponding to ¹¹B₁₁¹H₁₁³²S⁺. A weaker cutoff of the correct relative intensity is seen at *m/e* 166 corresponding to ¹¹B₁₁¹H₁₁³⁴S⁺. Our characterization of the molecule agrees with that published¹⁶ and includes a melting point of 325-326 °C (uncorrected, sealed capillary).

[Me₄N⁺][4-SB₈H₉⁻] and [SB₁₀H₁₁⁻]. Into a 250-ml three-neck flask containing a magnetic stir bar and fitted to a vacuum line and solvent still was distilled ca. 50 ml of CH₃OH. The flask was back-filled with nitrogen and 513 mg (9.16 mmol) of KOH quickly added. After complete dissolution of the KOH in the methanol, 1.269 g (9.16 mmol) of 1-SB₉H₉ was quickly added to the stirred solution (25°). Upon addition of the thiaborane the solution turned pale yellow, warmed, and bubbled vigorously. After a half-hour the solution cooled to 25° and the bubbling subsided to a slower

rate. The system was then evacuated of nitrogen, closed from the pump, and the progress of the reaction monitored by a mercury manometer which showed a continual pressure increase. The vapors generated were hydrogen sulfide and hydrogen. After 9 h the flask was connected to a rotary evaporator, pumped to dryness, and placed under nitrogen. Water (10 cm^3) was added, any unreacted SB_9H_9 recovered by filtration, and $4\text{-SB}_8\text{H}_9^-$ precipitated from the filtrate by addition of a concentrated solution of tetramethylammonium chloride. The product was collected by rapid filtration in air, washed several times with cold water, and vacuum dried 24 h. $(\text{CH}_3)_4\text{N-4-SB}_8\text{H}_9$ (615 mg, 3.05 mmol) was obtained, a 33.3% yield.

The above procedure gives 90% or better yields of $\text{SB}_{10}\text{H}_{11}^-$ (identified by ^{11}B NMR³) when applied to $1\text{-SB}_{11}\text{H}_{11}$.

4-SB₈H₁₀. In a 100-ml three-neck flask thoroughly purged with nitrogen and containing a magnetic stir bar were placed 15 cm^3 of concentrated sulfuric acid and 15 ml of petroleum ether (boiling range 30–60 °C). Then 895 mg (4.44 mmol) of $(\text{CH}_3)_4\text{N}^+\text{-4-SB}_8\text{H}_9^-$ was slowly added via a tip-up tube over a period of 20 min. The mixture was stirred an additional 20 min (during which slow gas evolution was seen) and quickly separated in air by a separatory funnel, and the organic layer rotary evaporated to a yellow-orange residue. The flask containing this residue was connected to a vacuum line. A tared, detachable U-trap fitted with stopcocks on each arm of the "U" was interposed between the flask containing the residue and the pump. The trap was evacuated, cooled to $-196 \text{ }^\circ\text{C}$, and allowed to collect the volatile components of the reaction residue. The residue was gently heated to $45 \text{ }^\circ\text{C}$ to facilitate the sublimation procedure. The material collected formed a single white band in the trap, was a colorless solid at room temperature, and exhibited no detectable vapor pressure on a Hg manometer (25°). SB_8H_{10} (146 mg, 1.14 mmol) was recovered (25.6%). Gas chromatography performed on the product showed a single peak with a retention time of 5.3 ($1.0 = \text{CH}_2\text{Cl}_2$, column $100 \text{ }^\circ\text{C}$ and flow rate $45 \text{ cm}^3/\text{min}$). SB_8H_{10} was stored at $-78 \text{ }^\circ\text{C}$ in the trap to retard thermal decomposition.

$[(\text{C}_2\text{H}_5)_3\text{NH}^+][4\text{-SB}_8\text{H}_9^-]$. From a storage trap 41 mg (0.32 mmol) of SB_8H_{10} was sublimed onto a vacuum sublimator cold finger ($-78 \text{ }^\circ\text{C}$). Then about 2 ml of dry triethylamine (dried over KOH) was distilled into the sublimator and allowed to reflux and wash the $-78 \text{ }^\circ\text{C}$ cold finger free of SB_8H_{10} . This refluxing action was continued 45 min and then the amine was pumped away leaving a white residue. Vacuum sublimation ($85\text{--}90 \text{ }^\circ\text{C}$) afforded 35 mg (0.15 mmol) of $[(\text{C}_2\text{H}_5)_3\text{NH}^+][4\text{-SB}_8\text{H}_9^-]$ (48%). The low resolution mass spectrum showed a weak boron envelope with m/e cutoff of 231 corresponding to $^{11}\text{B}_8^{12}\text{C}_6^{14}\text{H}_{25}^{14}\text{N}^{32}\text{S}^+$. The dominant features were boron envelopes with m/e 130 and 132 corresponding to $^{11}\text{B}_8^1\text{H}_{10}^{32}\text{S}^+$ and $^{11}\text{B}_8^1\text{H}_{10}^{34}\text{S}^+$, respectively, and a sharp peak at m/e 101 corresponding to $^{12}\text{C}_6^1\text{H}_{15}^{14}\text{N}^+$.

Reduction of 1-SB₉H₉ and 1-SB₁₁H₁₁ by Na in NH₃(l). About 50 ml of ammonia was condensed into a 100-ml three-neck flask equipped with a nitrogen inlet, nitrogen outlet, and a condenser cooled with a dry ice-isopropyl alcohol mixture; then 173 mg (7.54 mmol) of clean Na were added. With the flask maintained at $-78 \text{ }^\circ\text{C}$ by an external dry ice-isopropyl alcohol bath, finely powdered $1\text{-SB}_9\text{H}_9$ was slowly added through one neck via a tip-up tube to the deep-blue ammonia solution. The mixture was stirred until all of the thiaborane, only slightly soluble in ammonia, was consumed (several minutes) and then an additional quantity of thiaborane added. The titration proceeded until the deep-blue turned a blue-green color which was observed to turn clear to pale yellow within 30 s. $1\text{-SB}_9\text{H}_9$ (255 mg, 1.84 mmol) was consumed, giving a Na: SB_9H_9 mole ratio of 4.1:1. The ammonia was evaporated and the resulting residue divided into two portions. The first portion was dissolved in 1 ml of water, subjected to ^{11}B NMR analysis, then treated with CsF and the resulting precipitate was filtered and examined by infrared which showed good agreement with the literature description²⁴ for $\text{B}_9\text{H}_9^{2-}$, as did the ^{11}B NMR: literature, $+3.4 \text{ ppm}$ ($J_{\text{B-H}} = 133 \text{ Hz}$) area 1, and $+21.5 \text{ ppm}$ ($J_{\text{B-H}} = 124 \text{ Hz}$) area 2; observed $+3.6 \text{ ppm}$ ($J_{\text{B-H}} = 137 \text{ Hz}$) area 1, and $+20.6 \text{ ppm}$ ($J_{\text{B-H}} = 122 \text{ Hz}$) area 2 (all chemical shifts relative to external $\text{BF}_3\cdot\text{OEt}_2$). The filtrate gave positive qualitative tests for sulfide (H_2S , CdS, and ZnS). The second portion of the residue remaining after ammonia evaporation was dissolved in Me_2SO and subjected to ^{11}B NMR analysis, which confirmed the presence of the $\text{B}_9\text{H}_9^{2-}$ anion prior to addition of water.

The reduction of $\text{SB}_{11}\text{H}_{11}$ was followed with the same procedure and apparatus using 50 ml of NH_3 and 28.3 mg (1.23 mmol) of Na. $\text{SB}_{11}\text{H}_{11}$ (48.3 mg, 0.030 mmol) was consumed during the titration giving a Na: $\text{SB}_{11}\text{H}_{11}$ mole ratio of 4.1:1. The ammonia was evaporated, a ^{11}B NMR sample in D_3CCN prepared from the white residue, and the remaining white solid dissolved in water to give a solution showing positive sulfide tests. The ^{11}B NMR showed a single predominant doublet at $+17.2 \text{ ppm}$ ($J_{\text{B-H}} = 125 \text{ Hz}$); that reported for $\text{B}_{11}\text{H}_{11}^{2-}$ is $+16.9 \text{ ppm}$ ($J_{\text{B-H}} = 125 \text{ Hz}$).²⁵ Weaker signals (15% total) of $\text{B}_{11}\text{H}_{13}^{2-}$ and $\text{B}_{10}\text{H}_{10}^{2-}$ were also seen in the spectrum: $+20.8$ ($J_{\text{B-H}} = 120 \text{ Hz}$, area 10) and $+32.0$ ($J_{\text{B-H}} = 130 \text{ Hz}$, area 1) vs. reported values of $+20.3$ ($J_{\text{B-H}} = 125 \text{ Hz}$) and $+31.7$ ($J_{\text{B-H}} = 125 \text{ Hz}$) for $\text{B}_{11}\text{H}_{13}^{2-}$; and $+1.2$ ($J_{\text{B-H}} = 125 \text{ Hz}$, area 1) and $+29.5$ ($J_{\text{B-H}} = 125 \text{ Hz}$, area 4) vs. 0.9 ($J_{\text{B-H}} = 139 \text{ Hz}$) and $+29.9$ ($J_{\text{B-H}} = 128 \text{ Hz}$) reported for $\text{B}_{10}\text{H}_{10}^{2-}$.²⁵

Reduction of 1-SB₉H₉ by Na in THF. Dry THF (40 ml) was distilled into a 100-ml three-neck round-bottom flask cooled to $-78 \text{ }^\circ\text{C}$, connected to a vacuum line, and equipped with a glass covered magnetic stir bar. The flask was back-filled with nitrogen and a known amount of freshly cut and cleaned sodium the size of a pea was added. Typically, 293 mg (2.12 mmol) of $1\text{-SB}_9\text{H}_9$ was added to the Na-THF mixture and stirring started (25°). A yellowing of the THF was noted within 4 h and after 24 h a definite orange color was present. Stirring was continued until no more sodium was consumed, a process requiring 4 days, during which time 92 mg (4.00 mmol) of sodium was consumed giving a Na: SB_9H_9 ratio of 1.9 to 1. Treatment of the final red-orange solution, IV, depended upon the nature of the experiment. The solution was concentrated to about 1 ml by vacuum evaporation if NMR analysis was desired.

Hydrolysis of IV. A solution of IV was prepared from 149 mg (1.08 mmol) of $1\text{-SB}_9\text{H}_9$ in the manner described above. After allowing 5 days for reaction with sodium, the excess sodium was removed, the red-orange solution rotary evaporated to a gum and completely dissolved in 10 ml of water, giving a yellow solution which slowly bubbled. Addition of aqueous tetramethylammonium chloride afforded 68 mg of pale yellow solid after vacuum drying for 24 h. Solutions in D_3CCN were prepared for NMR analysis.

Protonation of IV. (a) Ethereal Solution. The reduction in THF was performed as usual using 123 mg (0.89 mmol) of $1\text{-SB}_9\text{H}_9$. The excess sodium was removed and the solution then taken to dryness by rotary evaporation. Diethyl ether (35 ml) was distilled into the flask, one of the side arms of the flask was equipped with a gas outlet and the other with a standard taper drip-tip, one end of which extended below the surface of the ether and the other end connected to a lecture bottle of anhydrous HCl. The gas outlet was opened and while a steady purge of nitrogen was maintained, a slow stream of hydrogen chloride was bubbled through the ethereal solution. Initially the ether boiled, but it soon cooled as a white salt formed with the continued stream of HCl. After 15 min the hydrogen chloride stream was stopped, the contents of the flask rotary evaporated to dryness and the residue placed in a vacuum sublimator. Sublimation up to 50° afforded 15 mg of white sublimate which was shown by gas chromatography, infrared, and mass spectra to be about an equimolar mixture of $\text{SB}_{10}\text{H}_{12}$ and SB_9H_{11} . Further sublimation up to $135 \text{ }^\circ\text{C}$ gave 22 mg of white sublimate which gas chromatography showed to be a mixture of SB_9H_{11} (90%), $\text{SB}_{10}\text{H}_{12}$ (5%), and three other components of about equal abundance (totaling 5%) with retention times of 2.0, 2.3, and 3.3 ($1.0 = \text{SB}_{10}\text{H}_{12}$, column at $155 \text{ }^\circ\text{C}$). The low resolution mass spectrum showed boron envelopes corresponding to SB_9H_{11} and $\text{SB}_{10}\text{H}_{12}$. In addition two other weak envelopes were seen with m/e cutoff of ca. 226 and 270 (probably $\text{SB}_{10}\text{H}_{10}\text{Cl}_2$ and $\text{B}_{17}\text{H}_{19}\text{S}_2$). The infrared spectrum showed only $\text{B}_9\text{H}_{11}\text{S}$.

(b) Benzene Solution. The reduction of 306 mg (2.20 mmol) by sodium in THF was performed as usual and the THF removed by rotary evaporation. Into the flask containing the red-orange reduction product was distilled 35 ml of diethyl ether, the solution stirred, and the ether removed by vacuum evaporation. This washing process was repeated three times and following the final removal of ether, 40 ml of benzene was distilled into the flask. The system was then pressurized (50 mmHg less than 1 atm) by anhydrous HBr, and stirred 12 h during which a white solid replaced the orange solid. The mixture was then placed under nitrogen and filtered. The yellow filtrate was rotary evaporated and the residue vacuum sublimed up to $170 \text{ }^\circ\text{C}$, affording 35 mg of yellow subli-

mate. Mass spectral analysis showed a strong parent boron envelope with m/e cutoff of 282 (probably $B_{18}H_{20}S_2$); features with lower m/e ratios were not readily apparent due to the fragmentation pattern of this species. The infrared spectrum was similar to $SB_{10}H_{12}$ but not identical. The ^{11}B NMR in benzene appeared to be a 2:1 mixture of $SB_{10}H_{12}$: SB_9H_{11} .

Reduction of 1- SB_9H_9 by Sodium Naphthalide. Dry THF was added to a flask as described above for the other reductions. The system was back-filled with nitrogen, warmed to 25°, and 47.7 mg (2.08 mmol) of Na and 265.8 mg (2.08 mmol) of naphthalene were added. Stirring was continued for 5 h during which time the deep-green sodium naphthalide was generated. Then 143.6 mg (1.04 mmol) of 1- SB_9H_9 was quickly added and reduction occurred within 10 s giving a yellow solution. Subsequent treatment of this solution depended upon the nature of the experiment. Concentration of the solution by vacuum evaporation of the solvent afforded an NMR sample.

A separate experiment was conducted in which 10 ml of THF containing 1.1 mmol of sodium naphthalide was added dropwise by an equalized pressure addition funnel to a stirred 10 ml THF solution containing 1.1 mmol of 1- SB_9H_9 . The rate of addition was such that each drop of sodium naphthalide solution was completely decolorized before further addition (approximately 10 s between drops). The resulting pale yellow solution was stirred 8 h and concentrated to ca. 2 ml by vacuum evaporation and a NMR sample prepared. The remaining THF was removed by vacuum and the residue Soxhlet extracted 3 h with petroleum ether. Gas chromatography of the extracted material showed it to be about a 2:1 mixture of naphthalene to 1- SB_9H_9 .

Complete removal of the solvent from the crude reduced 1- SB_9H_9 , washing several times with dry benzene, and Soxhlet extraction of the resulting yellow solid with petroleum ether (bp 30–60 °C) for 6 h under nitrogen yielded only naphthalene in the extract (87% recovery as shown by 1H NMR, infrared spectroscopy, and gas chromatography). The material not extracted, a highly hygroscopic, bright yellow, crusty salt, V, was dissolved in either dimethyl- d_6 sulfoxide or D_2O in the case of NMR analysis. Starting with 320 mg (2.32 mmol) of 1- SB_9H_9 , 430 mg of V was obtained (2.33 mmol assuming V to be $Na_2B_9H_9S$). Experiments such as the hydrolysis described above for IV were conducted in the same manner on V.

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The Electron Spin Resonance of Tetra(*p*-carboxylphenyl)porphinatocobalt(II) in Pyridine at 77 K

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Abstract: Electron spin resonance (ESR) spectra of tetra(*p*-carboxyphenyl)porphinatocobalt(II) ($Co(p-COOH)TPP$) in pyridine showed well-resolved superhyperfine (shf) structure due to two nitrogen nuclei from two solvent molecules coordinated to the fifth and the sixth positions of the square planar complex. From these spectra, complete ESR parameters were determined, and an attempt was made to calculate the relative orbital energies of the d orbitals with assumed values of the Racah, the inverse cube radial, and the spin-orbit coupling parameters.

Assour,¹ in 1965, studied the ESR of cobalt phthalocyanine (CoPc) in several heterocyclic amines at 77 K. Shf splittings were observed and were interpreted as due to two N nuclei. The spectra, however, looked more like those due to the complex being coordinated to only one N. Walker,²

much later, studied the ESR of tetra(*p*-methoxyphenyl)porphinatocobalt ($Co(p-OCH_3)TPP$) in toluene glass in the presence of various concentrations of amines and showed that both five- and six-coordinated complexes could be formed. They were designated as the 1:1 and 2:1 ad-