

Chalcogeno boron hydrides

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Abstract

The syntheses and structures of chains, rings and clusters of compounds containing boron, hydrogen and chalcogens are described. Emphasis is given to the most recent developments involving alkyl and aryl chalcogeno groups as ligands. © 1997 Elsevier Science S.A.

Keywords: Boron hydride; Chalcogeno boron hydrides

1. Introduction

The spectacular growth of metallaborane and metallacarborane cluster chemistry during the last 30 years has sometimes tended to obscure the equally impressive parallel developments in the synthesis and structural characterization of main-group element heteroboranes. It is the aim of this article to summarize some recent developments in this field of chemical research, with the emphasis being restricted to structures that exhibit alkyl (aryl) chalcogeno groups {RX-} (X = S, Se, and Te) as endo-ligands and chalcogeno atoms as cluster units. For example, the compound μ_2 -RSB₂H₅ possesses an alkyl (aryl) chalcogeno group which can be considered as an endo-group replacing one *endo*-hydrogen atom in B₂H₆. In most cases, the interaction of a chalcogeno atom with a borane cage results in the incorporation of the chalcogeno atom into the cluster itself. Either the cage may expand, or else formal substitution of the chalcogeno atom for a boron atom occurs. When chalcogeno atoms occur in heteroborane clusters the electron-counting rules can readily be extended to them [1]. Thus, whereas each {BH} contributes 2e and {XH} contributes 5e (X = S, Se, and Te), {X} contributes 4e; the {XH} group in each case contributing three electrons, the X atom in each case contributing four electrons to the framework plus an exo-polyhedral lone-pair.

While in organic molecules an electronegative heteroatom E (E = N, P, O, S, etc.) is the center of enhanced electron density, quite the opposite situation happens with heteroborane clusters [2] in which the heteroatom seems to be the more plus charged the higher its electronegativity. The reason is that the main-group heteroatom substitutes a skeletal boron atom of the same formal number of skeletal electrons. Thus CH is equivalent to a formal vertex BH^- , and NH or S to a formal vertex BH^{2-} . Such electron-rich boron vertices are, in reality, non-existent in boron hydride clusters since these 'surplus' electrons are dissipated throughout the whole skeleton. The same fate meets the skeletal electrons brought in by an electronegative heteroatom: they are dissipated through the skeleton, changing the heteroatom to the electropositive center [3].

Specific syntheses of chalcogeno boranes and chalcogeno borane anions will be mentioned at appropriate points in the following sections in which the structure and properties of individual compounds are discussed.

The sequence of presentation will be in the order of increasing number of boron atoms. Reactivities for the class of compounds in the headings (Sections 2–14 are not discussed).

2. One-boron-atom systems

The species to be considered are derivatives of the fugitive monomeric borane(3) itself, BH_3 , and the very stable tetrahydroborate(1–) ion, BH_4^- .

2.1. $HB(SH)_2$ 1, H_2BSH 2

The new and unstable compounds $HB(SH)_2$ 1 and $HB(SD)_2$ are formed by CO_2 -laser irradiation of a gaseous mixture of B_2H_6 and H_2S or D_2S respectively [4]. 1 has been identified by infrared (IR) spectroscopy and mass spectrometry. The IR spectrum is interpreted in terms of the assumed C_{2v} structure. 1 is not produced in the thermal reaction of B_2H_6 and H_2S and it is only stable in the gas phase. The great reactivity of the hypothetic monomer H_2BSH 2 precludes its detection by spectroscopic techniques. Ab initio SCF-MO computations suggest that in BH_2SH the overall π effect of the substituent SH is stabilizing [5–7].

2.2. HBS , DBS , $(HBS)_n$

HBS , and DBS (prepared from boron and H_2S or D_2S respectively) have been investigated by IR spectroscopy and calculated by ab initio SCF calculations [8–10]; concerning $(HBS)_n$, see Ref. [11]; photoelectron spectra for the ion HBS^+ show the ν_3 mode at $955 \pm 40 \text{ cm}^{-1}$ [12].

2.3. $(\text{CH}_2\text{S})_2\text{BH } 3$

Reactions of diborane with ethanedithiol lead to $(\text{CH}_2\text{S})_2\text{BH } 3$ which is a monomer only in the vapor phase [13].

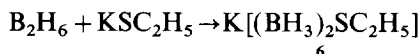
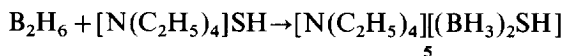
2.4. $\text{H}_3\text{B}-\text{S}(\text{CH}_3)_2$ **4**, $\text{R}_2\text{S}-\text{BH}_2$ and radical **4a**

Base adducts of BH_3 are generally obtained from the direct reaction of diborane (6) with Lewis bases. A convenient borane-carrier is $\text{H}_3\text{B}-\text{S}(\text{CH}_3)_2$ **4** [14,15] which is commercially available. It can be handled more easily and safely than B_2H_6 .

Hydrogen atom abstraction from $\text{R}_2\text{S}-\text{BH}_3$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$) by $(\text{CH}_3)_3\text{CO}^\cdot$ and or $[(\text{CH}_3)_3\text{Si}]_2\text{N}^\cdot$ and radicals gives the $\text{R}_2\text{S}-\text{BH}_2$ and radicals **4a**, the structures and reactions of which were studied in solution using EPR spectroscopy [15].

2.5. $[\text{N}(\text{C}_2\text{H}_5)_4][(\text{BH}_3)_2\text{SH}]$ **5**, $\text{K}[(\text{BH}_3)_2\text{SC}_2\text{H}_5]$ **6**

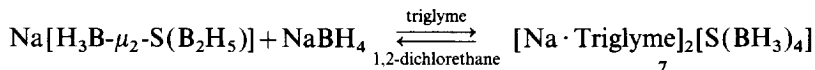
Hydrogen sulfide and alkyl sulfide ions form bisborane adducts $(\text{BH}_3)_2\text{L}^-$ [16–19].



5 decomposes above -78°C [18].

2.6. $[\text{Na} \cdot \text{Triglyme}]_2[\text{S}(\text{BH}_3)_4]$ **7**

Adducts of BH_3 with the S^{2-} ion are not detectable in THF by ^{11}B NMR spectroscopy. The anion $[\text{S}(\text{BH}_3)_4]^{2-}$ **7** can, however, be obtained by the addition of NaBH_4 to $\text{Na}[\text{H}_3\text{B}-\mu_2-\text{S}(\text{B}_2\text{H}_5)]$ **21** [20] in diglyme or triglyme, respectively.



The four BH_3 groups are tetrahedrally disposed about the S^{2-} ion. The anion of **7** may be viewed either as an adduct of B_2H_6 with S^{2-} , or as a bridge substituted thia derivative of the B_2H_7^- anion; furthermore, the anion of **7** is isoelectronic and isostructural with the SO_4^{2-} ion. An X-ray structure analysis at room temperature of the colorless crystals revealed the molecular structure of **7** (Fig. 1).

The effect of bond polarity is nicely to be seen by the result of an electron localization function (ELF) (Figs. 2(a) and (b)). The electron pairs in the planes containing three neighboring atoms (SB_2 and SO_2) of the anion **7** and the SO_4^{2-} ion are either polarized to the boron atoms (SB_2 plane) or to S^{6+} (SO_2 plane).

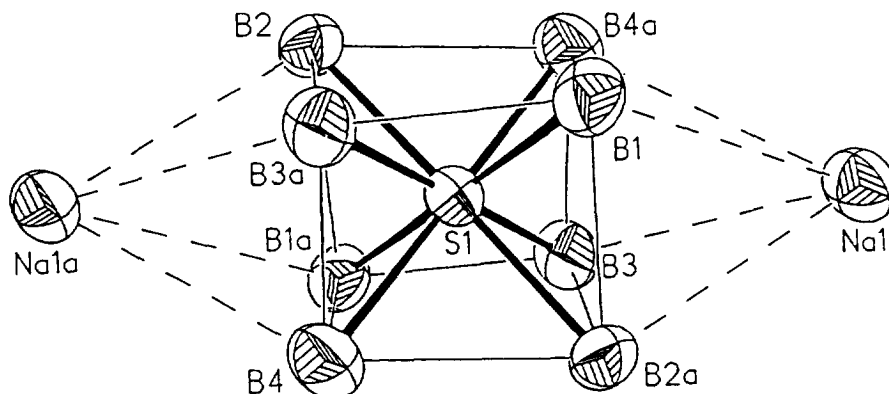


Fig. 1. Disordered, distorted cubic environment of the sulfur atom in $[S(BH_3)_4]^{2-}$ **7**. (From Ref. [20] by permission of Hüthig-Fachverlage, Heidelberg).

2.7. $H_2S_x(BH_3)_2$ **8**, $[H_2B(-S-S_x-S)]^-$ **9b**, $(CH_2-S-)_2BH_2^-$ **9c**

Adducts of the type $H_2S_x(BH_3)_2$ **8** ($x=2, 3$) are formed when B_2H_6 reacts with H_2S_2 or H_2S_3 , respectively; the compounds of type **8** are short-lived species which could be identified by ^{11}B NMR spectroscopy [21].

It was reported that $NaBH_4$ reacts with sulfur at room temperature in the presence of appropriate organic solvents to give a sulfurated borohydride $NaBH_2S_3$ **9a** [22]. The structure of **9** could not be established by X-ray diffraction.

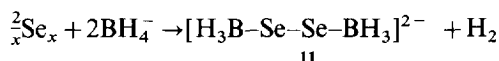
$NaBH_4$ reacts with S_8 in THF or $LiBH_4$ with S_8 in ether via species such as $[H_2B(-S-S_x-S)]^-$ **9b** which exist in the solution for only a few hours and exhibit two ^{11}B NMR triplets [23]. The reducing species of an $NaBH_4/(CH_2SH)_2$ substrate is considered to have the structure $(CH_2-S-)_2BH_2^-$ **9c** [24].

2.8. $BH_{4-n}(SH)_n^-$ ($n=1-4$) **10**

Excess hydrogen sulfide reacts with $NaBH_4$ in THF to form stepwise the anions $BH_{4-n}(SH)_n^-$ ($n=1-4$) **10** [25–27]; $(B(SH)_4)^-$: $\delta^{11}B = -0.6$ (quint), $^2J(^{11}B^1H) = 4$ Hz).

2.9. $Na_2[H_3B-Se-Se-BH_3]$ **11**

$Na_2[H_3B-Se-Se-BH_3]$ **11** is produced by the reaction between elemental selenium and $NaBH_4$ (1 : 1) in triglyme (diglyme), under dehydrogenation.



As can be seen from ^{77}Se NMR there are two rotational isomers of **11** (1 : 1 mixture of gauche and trans isomers) [28].

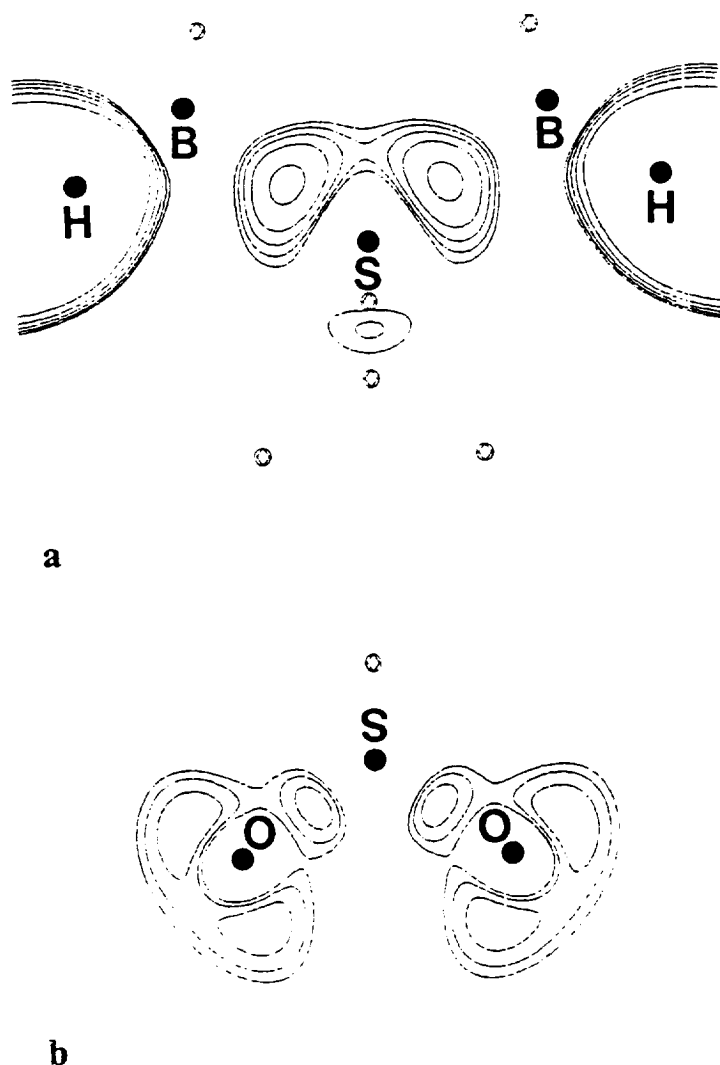


Fig. 2. (a) Contour plot of electron localization function (ELF) in the B–S–B plane of the $[S(BH_3)_4]^{2-}$ anion **7**; the lines represent the values 0.75, 0.8, 0.85, 0.9, and 0.95. (b) Contour plot of ELF in the O–S–O plane of Na_2SO_4 ; the lines represent the values 0.75, 0.8, 0.85, 0.9, and 0.95. (From Ref. [20] by permission of Hüthig-Fachverlage, Heidelberg).

3. Two-boron-atom systems

The species to be considered are derivatives of B_2H_6 .

3.1. μ_2 -HS(B_2H_5) **12**, (H_2BSH)₂ **13**, 1,2-(HS)₂ B_2H_4 **14**, μ_4 -S(B_2H_5)₂ **15**

μ_2 -Mercaptodiborane μ_2 -HS(B_2H_5) **12** was generated by treatment of $[N(C_2H_5)_4][S(BH_3)_2SH]$ **5** with an excess of anhydrous hydrogen chloride at $-78^\circ C$.

The μ_2 -HS(B₂H₅) has an extrapolated b.p. of 27 °C. The thermal stability of **12** in both the gas and the liquid phase is poor [29]. Decomposition in the liquid phase is considerably faster. Gas-phase decomposition yields hydrogen sulfide, diborane, and involatile solid; liquid-phase decomposition yields hydrogen, diborane, and involatile solid. μ_2 -HS(B₂H₅) has also been obtained by CO₂-laser irradiation of a gaseous mixture of B₂H₆ and H₂S [4]. The structure of **12** has been determined by SCF calculations [30] (Fig. 3).

The new and unstable compounds 1 λ^3 ,3 λ^3 ,2 λ^4 ,4 λ^4 -dithiadiboretane (H₂BSH)₂ **13**, the isomer 1,2-dimercaptodiborane 1,2-(HS)₂B₂H₄ **14**, μ_4 -thiabis(diborane) μ_4 -S(B₂H₅)₂ **15**, as well as HB(SH)₂ **1** and μ_2 -HS(B₂H₅) **12** are formed in the reaction of B₂H₆ and H₂S, with or without toluene, in a pressure tube at –15 to –10 °C [30]. SCF calculations indicate that the coordination dimer of **14** exists as a mixture of planar Z and E isomers (C_{2h}) (Fig. 4); **15** has a pyramidal structure (C₂) (Fig. 5); the BSB unit in μ_2 -HS(B₂H₅) **12** and μ_4 -S(B₂H₅)₂ **15**, has some central or open three-center character.

3.2. μ_2 -RS(B₂H₅) **16**

There are relatively few alkylthio derivatives of the simpler boron hydrides. The first to be reported was μ_2 -CH₃SB₂H₅ [31]. The alkylthio group is shown to occupy exclusively a bridging position in μ_2 -RS(B₂H₅) **16**, (R = CH₃, C₂H₅, *n*-C₄H₉) [32,33].

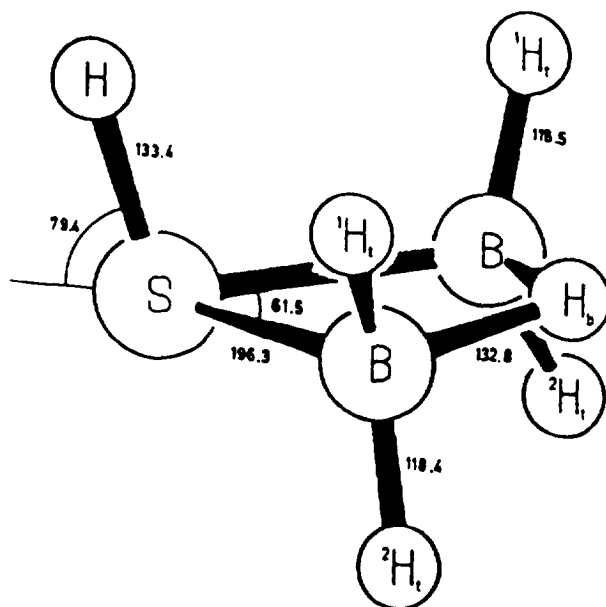


Fig. 3. Calculated structure of μ_2 -HS(B₂H₅) **12**, (C_s). (From Ref. [30] by permission of VCH Verlagsgesellschaft mbH, Weinheim).

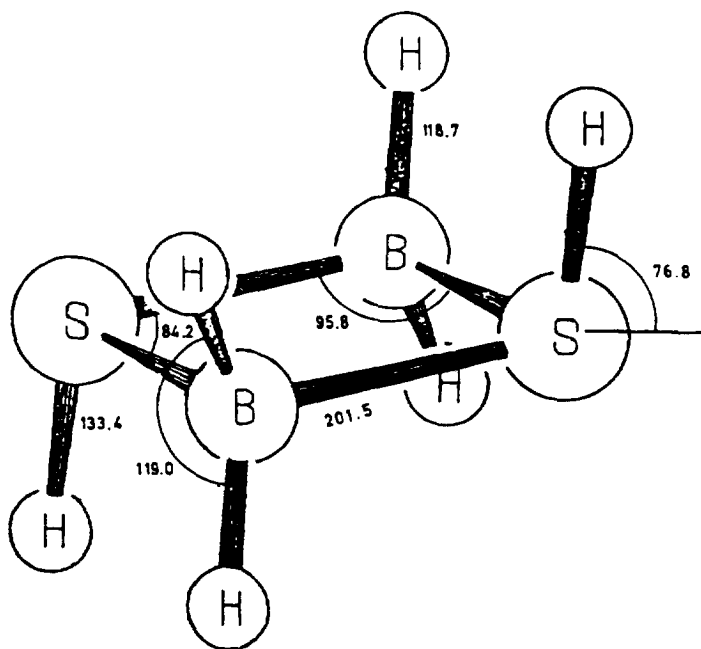
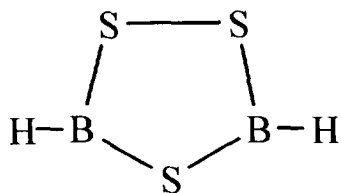


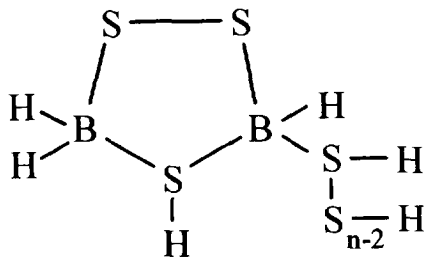
Fig. 4. Calculated structure of $(\text{HSBH}_2)_2$ **13**, (C_{2h}). The four-membered ring SBSB is planar. (From Ref. [30] by permission of VCH Verlagsgesellschaft mbH, Weinheim).

3.3. $\text{H}_2\text{B}_2\text{S}_3$ **17**, $\text{H}_2\text{B}_2\text{S}_4$ **18**

Two routes are now available for the preparation of the parent compound 1,2,4,3,5-trithiadiborolane $\text{H}_2\text{B}_2\text{S}_3$ **17**. Most recently [34], B_2H_6 has been shown to react with H_2S_2 , H_2S_3 or crude sulfane oil in toluene to form selectively $\text{H}_2\text{B}_2\text{S}_3$. The reaction intermediates **17a** were identified by ^{11}B NMR spectroscopy.



17



17a

The reaction of crude sulfane has been utilized to achieve a convenient synthesis of toluene solutions of $\text{H}_2\text{B}_2\text{S}_3$ which are stable on standing at 0°C . The concentrations of $\text{H}_2\text{B}_2\text{S}_3$ should not be greater than 0.5 M because of its propensity to dimerize or to form oligomers which are slightly soluble. $\text{H}_2\text{B}_2\text{S}_4$ **18** is a by-product which was detected by mass spectrometry.

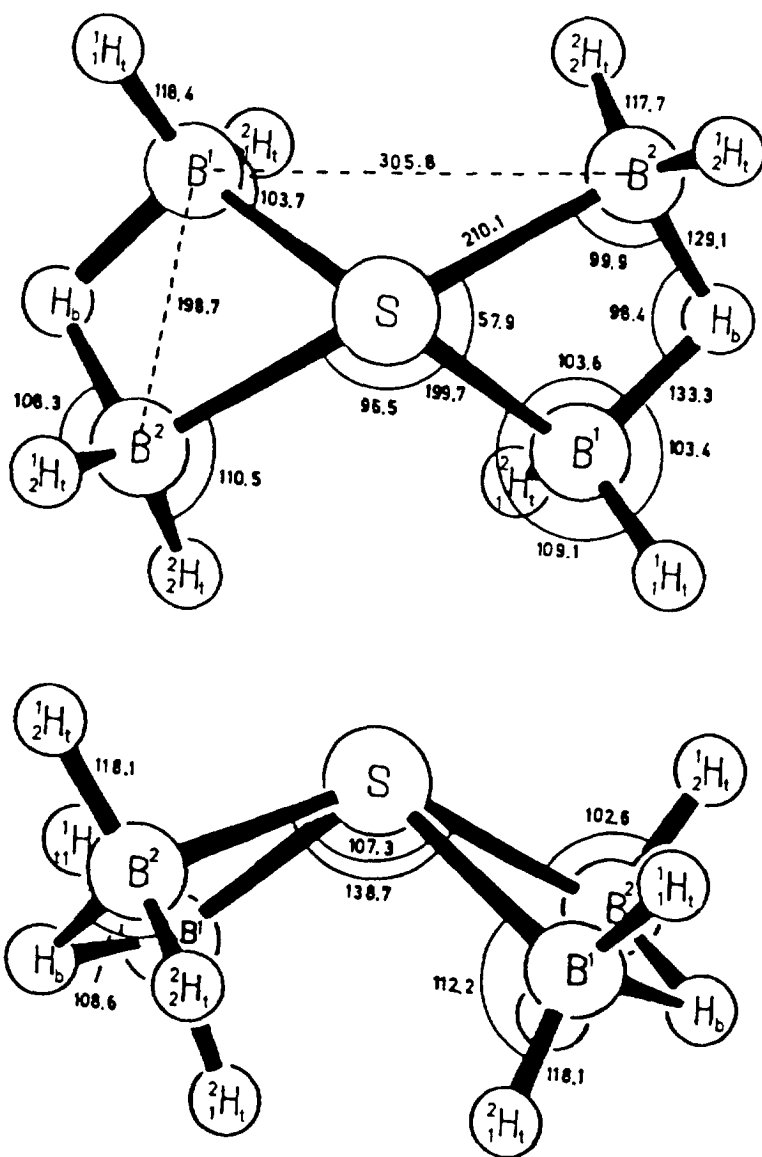


Fig. 5. Calculated structure of $\mu_4\text{-S}(\text{B}_2\text{H}_5)_2$ **15**, (C_2). (From Ref. [30] by permission of VCH Verlagsgesellschaft mbH, Weinheim).

$\text{H}_2\text{B}_2\text{S}_3$ **17** has been synthesized for the first time by the ligand exchange reaction: $[(\text{CH}_3)_2\text{N}]_2\text{B}_2\text{S}_3/9\text{-BBN}$ [35]. $\text{H}_2\text{B}_2\text{S}_3$ is a reactive hydroboration agent. Mono-hydroboration of alkynes proceeds by cis addition from the less hindered side of the triple bond. Both hydrogen atoms of **17** react with 1- or 2-alkynes, thus leading to 3,5-dialkenyl-1,2,4,3,5-trithia-diborolane derivatives.

3.4. $[\text{CH}_2(\text{SCH}_3)(\text{BH})_2]_2$ **19**, $\text{H}_2\text{B}-\text{S}-\text{S}-\text{BH}_2$ **19a**

The compound $[\text{CH}_2(\text{SCH}_3)(\text{BH})_2]_2$ **19** has been prepared from $(\text{CH}_3)_3\text{N}-\text{BH}_2-\text{CH}_2-\text{SCH}_3$ by thermal decomposition at 100 °C. As revealed by X-ray crystallography, it contains a six-membered ring in chair conformation and the methyl groups are in equatorial positions. For the molecular structure see Fig. 6 [36,37].

Ab initio calculations were carried out for the non-existent compound $\text{H}_2\text{B}-\text{S}-\text{S}-\text{BH}_2$ **19a** [34,38,39]; the energy minimum is predicted to be at a dihedral angle of 102°, and the barriers to internal rotation around the S–S bond are estimated as 19.1 kcal mol^{−1} and 0.7 kcal mol^{−1} for syn and anti respectively.

4. Three-boron-atom systems

The species to be considered are derivatives of the fugitive triboranes B_3H_7 , B_3H_9 and the stable octahydrotriborate(1−) anion B_3H_8^- .

4.1. $\text{THF}-\text{BH}_2-\mu_2-\text{S}(\text{B}_2\text{H}_5)$ **20**

A chalcogeno derivative of triborane(7) $\text{THF}-\text{BH}_2-\mu_2-\text{S}(\text{B}_2\text{H}_5)$ **20** is formed when $\mu_4-\text{S}(\text{B}_2\text{H}_5)_2$ **15** interacts with tetrahydrofuran, the following equilibrium operates [30]:



20 can only exist in solution, it polymerizes when the solvent is removed.

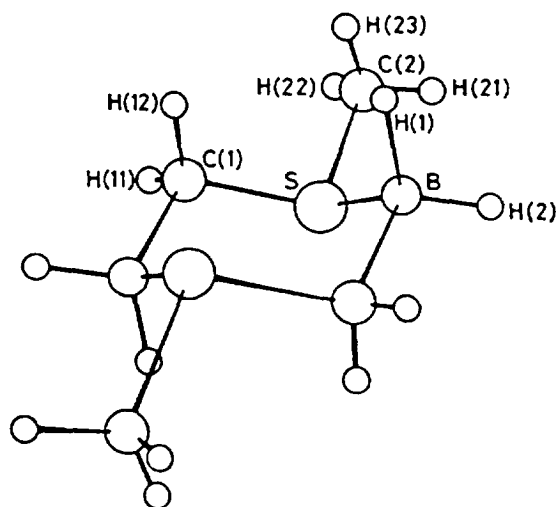
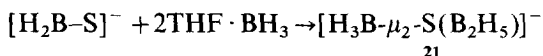
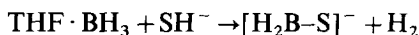


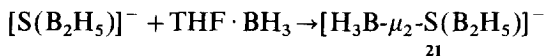
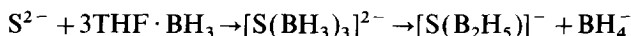
Fig. 6. Structure of $[\text{CH}_2(\text{SCH}_3)(\text{BH})_2]_2$ **19**.

4.2. $\text{Na}[\text{H}_3\text{B}-\mu\text{-S}(\text{B}_2\text{H}_5)]$ **21**

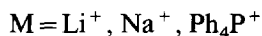
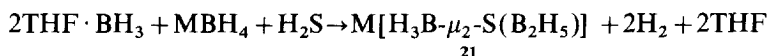
The octahydrotriborate derivative $\text{Na}[\text{H}_3\text{B}-\mu_2\text{-S}(\text{B}_2\text{H}_5)]$ **21** is produced by the reaction between anhydrous NaSH and $\text{THF} \cdot \text{BH}_3$, under dehydrogenation [20].



21 is also formed as the first ^{11}B NMR spectroscopically detectable reaction product by the reaction between anhydrous Na_2S and $\text{THF} \cdot \text{BH}_3$ [20]



Treatment of $\text{THF} \cdot \text{BH}_3/\text{MBH}_4$ (2 : 1) with H_2S results both in formation of **21** and hydrogen evolution [25].



Structural data of **21** have been calculated by SCF methods; the structure can be viewed as being formed by the incorporation of an S atom by the B_3H_8^- ion (Fig. 7).

4.3. $[\text{H}_3\text{B}-\mu_2\text{-Se}(\text{B}_2\text{H}_5)]^-$ **22**

The corresponding selenium compound $[\text{H}_3\text{B}-\mu_2\text{-Se}(\text{B}_2\text{H}_5)]^-$ **22** can readily be prepared by the reaction between $[\text{H}_3\text{B}-\text{Se}-\text{Se}-\text{BH}_3]^{2-}$ **11** and B_2H_6 or

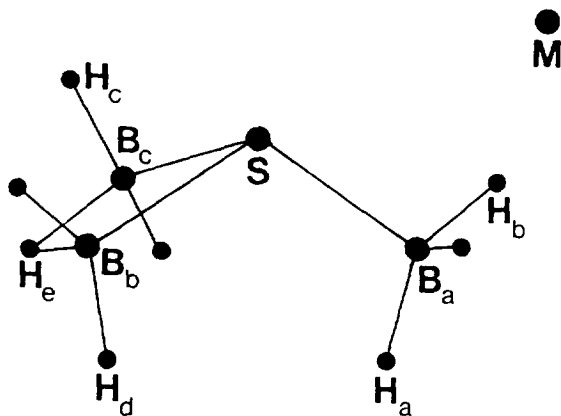
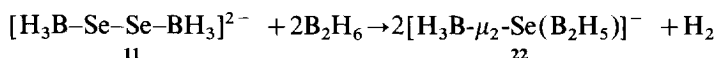


Fig. 7. Calculated structure of $\text{M}[\text{H}_3\text{B}-\mu_2\text{-S}(\text{B}_2\text{H}_5)]$ **21**. (From Ref. [20] by permission of Hüthig-Fachverlage, Heidelberg).

THF · BH₃ [28].



An X-ray structure determination of $[(\text{C}_6\text{H}_5)_4\text{P}][\text{H}_3\text{B}-\mu_2-\text{Se}(\text{B}_2\text{H}_5)]$ failed because of disordering of the cation and anion. ¹¹B and ⁷⁷Se NMR shifts, as well as IR and Raman spectroscopic investigations, convey structural information. Structural data of **22** have been calculated by SCF methods (Fig. 8). The ELF of the planes Se, B_b, B_c and H_c and Se, B_a and Na are shown in Fig. 9(a) and Fig. 9(b): the polarity of the bonds Se–B_b, Se–B_c and Se–B_a is similar, the electron pairs are polarized vs. the boron atoms.

4.4. $[\text{C}_2\text{H}_5\text{SBH}_2]_3$ **23a**, $[\text{'BuSBH}_2]_3$ **23b**

Reaction of diborane(6) and ethanethiol in a 1 : 2 ratio followed by short-path distillation at 50 °C gives the fluid trimer $[\text{C}_2\text{H}_5\text{SBH}_2]_3$ **23** [32]. Compounds of this type can be considered as derivatives of the hypothetical B₃H₉ in which the alkylthio groups are shown to occupy exclusively bridging positions. The identity of $[\text{C}_2\text{H}_5\text{SBH}_2]_3$ was established by analysis and molecular weight determinations.

$[\text{'BuSBH}_2]_3$ **23b** (prepared by the reaction of THF · BH₃ with ^tBuSH) is the only colorless solid alkylthioborane which can be sublimed, m.p. 104 °C [40].

4.5. $[\text{B}_3\text{S}_2\text{H}_6]^{-}$ **24**

The anion $[\text{B}_3\text{S}_2\text{H}_6]^{-}$ **24** was reported to be formed when LiBH₄ reacts with sulfur in ether solution [41]. However, further experimental work is required in order to characterize more fully this borane.

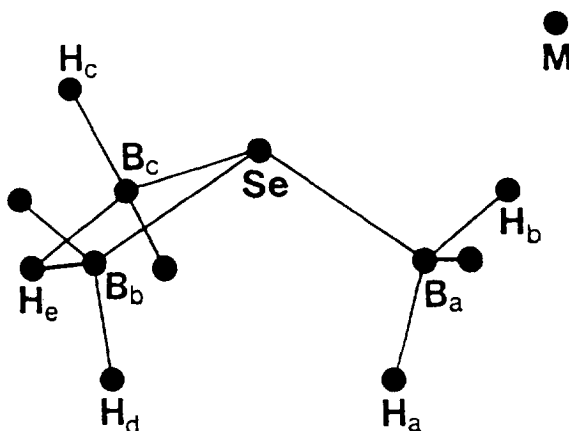


Fig. 8. Calculated structure of $\text{M}[\text{H}_3\text{B}-\mu_2-\text{Se}(\text{B}_2\text{H}_5)]^{-}$ **22**. (From Ref. [28] by permission of Hüthig-Fachverlage, Heidelberg).

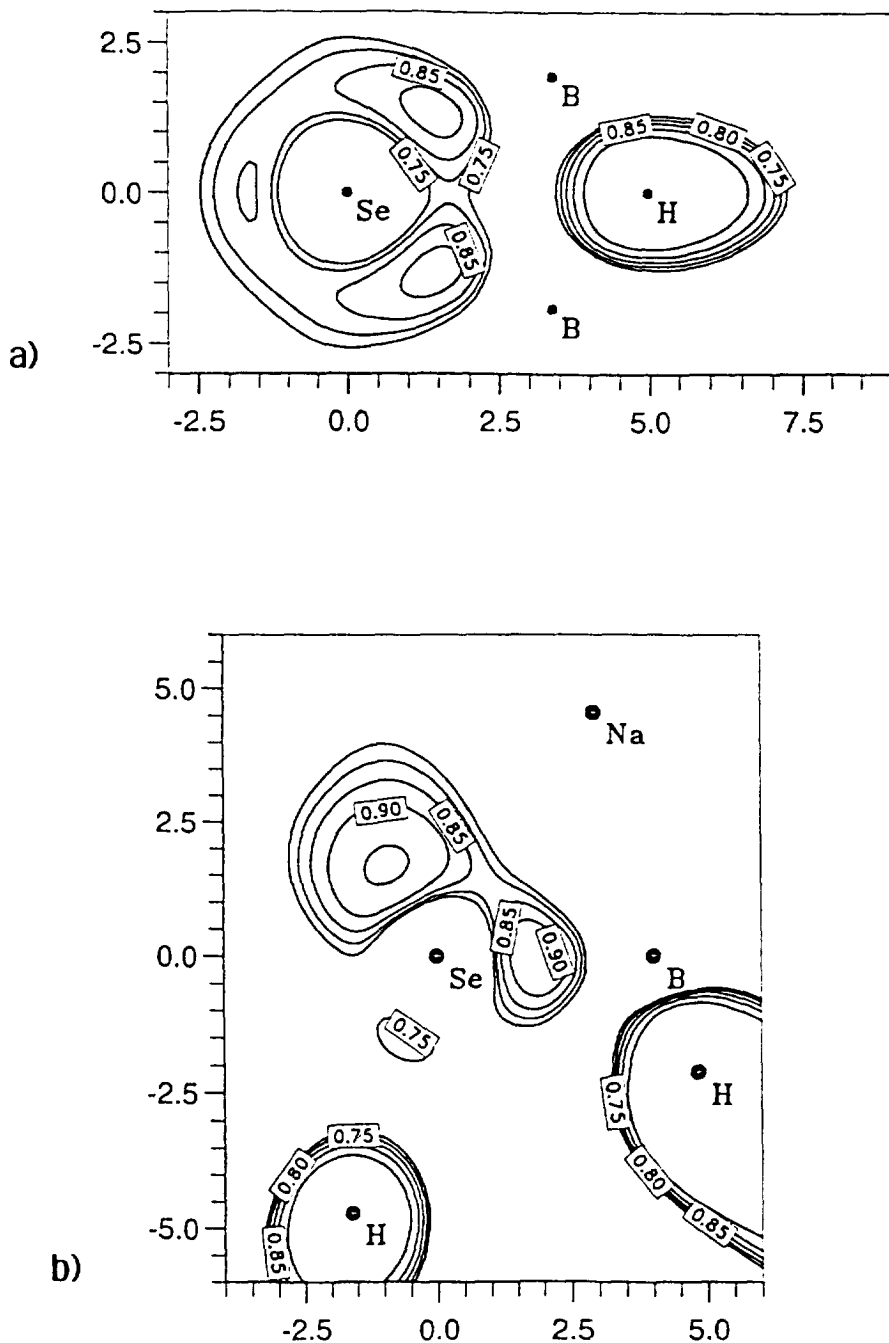


Fig. 9. (a) Contour plot of ELF in the plane $\text{SeB}_6\text{B}_6\text{H}_6$ of $\text{Na}[\text{H}_3\text{B}-\mu_2\text{-Se}(\text{B}_2\text{H}_5)]$ **22** (cf. Fig. 8); the lines represent the values 0.75, 0.8, 0.85, 0.9, and 0.95. (b) Contour plot of ELF in the plane SeB_4Na of $\text{Na}[\text{H}_3\text{B}-\mu_2\text{-Se}(\text{B}_2\text{H}_5)]$ **22**; the lines represent the values 0.75, 0.8, 0.85, 0.9, and 0.95 (cf. Fig. 8). (From Ref. [28] by permission of Hüthig-Fachverlage, Heidelberg).

4.6. $B_3H_6OSC-CH_3$ **25a**, $B_3H_6S_2P(OC_2H_5)_2$ **25b**

B_6H_{14} [42] behaves like a dimer of B_3H_7 and reacts with CH_3COSH or $(C_2H_5O)_2PSSH$ to form the chelate stabilized compounds $B_3H_6OSC-CH_3$ **25a** and $B_3H_6S_2P(OC_2H_5)_2$ **25b**, respectively [43].

5. Four-boron-atom systems

The species considered here are either derivatives of tetraborane(10) or dimers of diborane(6) derivatives.

5.1. $H_2B(\mu_2-SR)_2B_3H_6$ **27**

B_4H_{10} reacts with mercaptans by splitting off H_2 to form $H_2B(\mu_2-SR)_2B_3H_6$ **27**. An unstable adduct $B_4H_{10}RSH$ **26** was identified as a precursor of **27**. The ^{11}B NMR spectra of **27** showed that the B1,3 signals coalesce at $70^\circ C$, indicating a rapid inversion. On cooling however, the exo-exo, endo-endo and exo-endo invertomers were detected, Fig. 10, Scheme 1 [44].

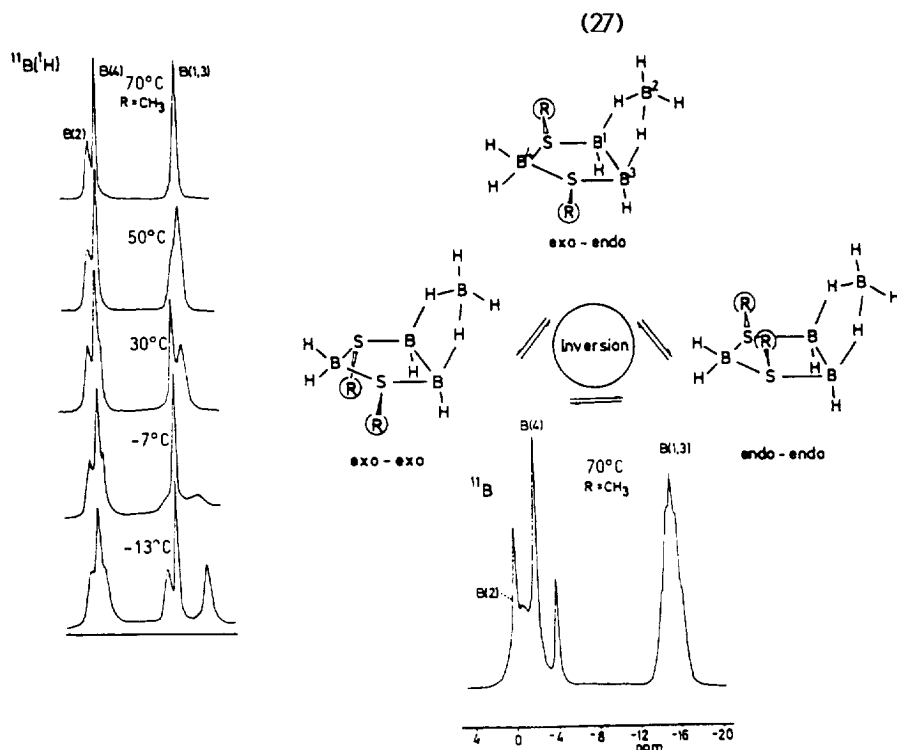
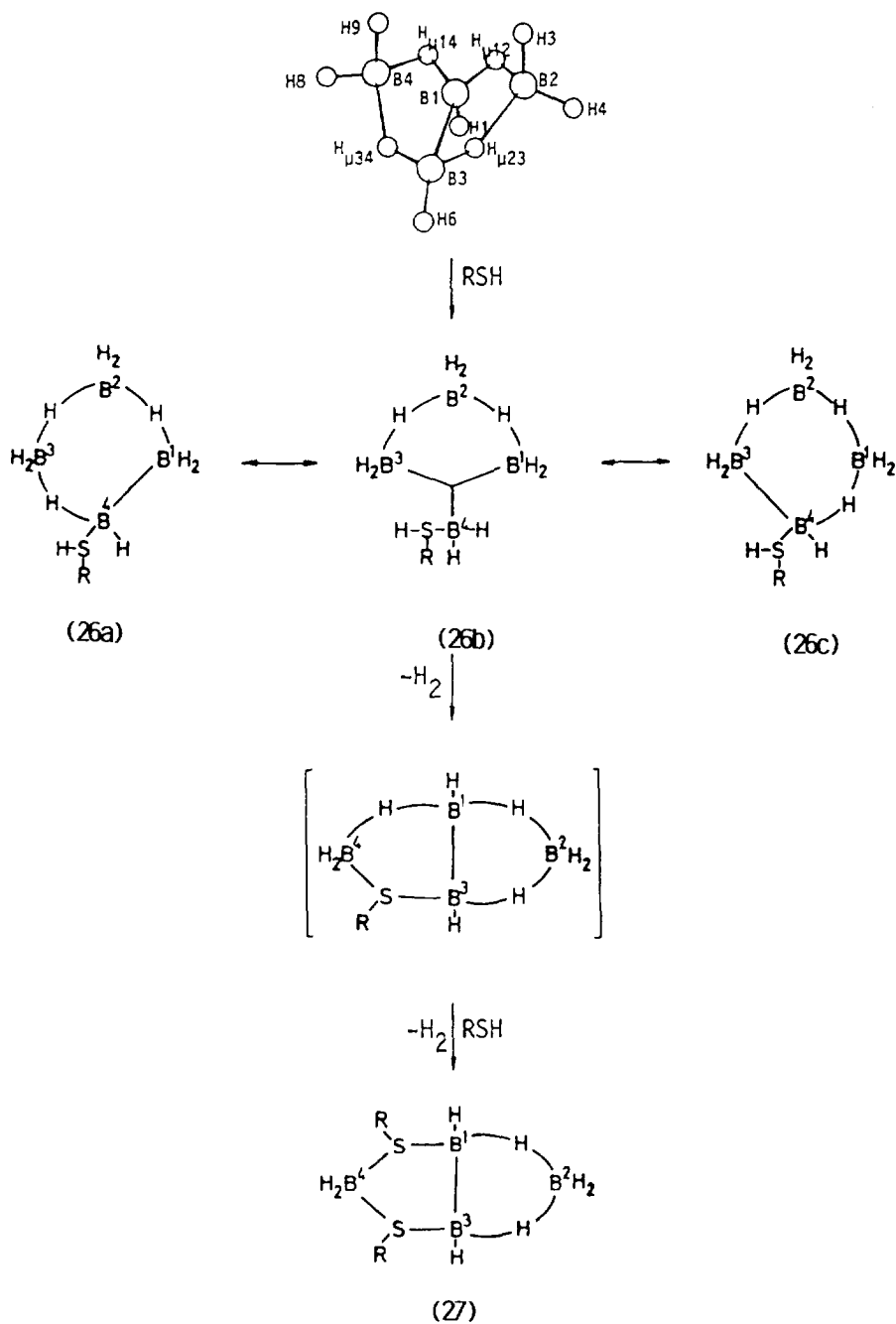


Fig. 10. ^{11}B and $^{11}B\{^1H\}$ NMR spectra of $H_2B(\mu_2-SR)_2B_3H_6$ **27** for a range of temperature.



Scheme 1.

With the ^{11}B spectral data it is possible to calculate the activation energy for inversion in **27**, ($E_a \approx 12.8\text{--}13.3 \text{ kcal mol}^{-1}$; $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, ^i\text{Pr}, ^t\text{Bu}, \text{C}_6\text{H}_5$).

There was no evidence for the formation of either of the isomers in which $\text{H}_{\mu 14}$, $\text{H}_{\mu 12}$ or $\text{H}_{\mu 14}$, $\text{H}_{\mu 23}$ was replaced by RS groups.

5.2. $\text{H}_2(\mu)_2\text{S}_2\text{RBH}(\text{B}_2\text{H}_5)$ **28**

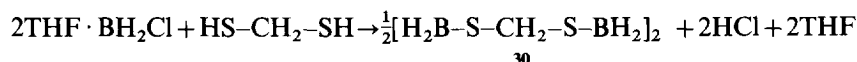
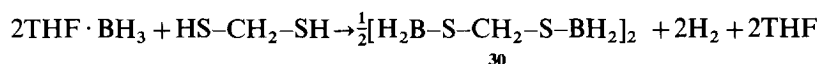
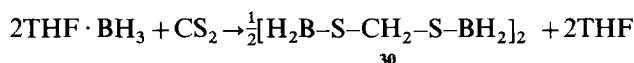
B_4H_{10} reacts with bifunctional thiols to give transannularly bridged $\text{H}_2(\mu)_2\text{S}_2\text{RBH}(\text{B}_2\text{H}_5)$ **28** which exist as *cis-trans* isomers [bis(diboranyl) structure]; on cooling these compounds rearrange to *cis-trans*- $\text{H}_2\text{B}(\mu)_2\text{S}_2\text{RB}_3\text{H}_6$ **29** ('butterfly' structure); this is indicative of a reversible rearrangement, i.e. a reversible ring-expansion–ring-contraction process (Schemes 2–4) [45].

The experimentally demonstrated rearrangement of the bis(diboranyl) structure **28** into the 'butterfly' structure **29** is an indication that the theoretically calculated transformation of the hypothetical valence isomer $(\text{B}_2\text{H}_5)_2$ into the known 'butterfly' structure of B_4H_{10} is realistic [46].

5.3. $[\text{CH}_2(\text{SBH}_2)_2]_2$ **30**

The structure of the cage compound $[\text{CH}_2(\text{SBH}_2)_2]_2$ **30** (with the adamantane skeleton $\text{C}_2\text{B}_4\text{S}_4$) is shown in Fig. 11, [47]. The crystal structure was determined by X-ray diffraction.

The compound has been obtained from CS_2 and $\text{THF} \cdot \text{BH}_3$ after 3 weeks, or by the action of methanedithiole on $\text{THF} \cdot \text{BH}_3$ or $\text{THF} \cdot \text{BH}_2\text{Cl}$.

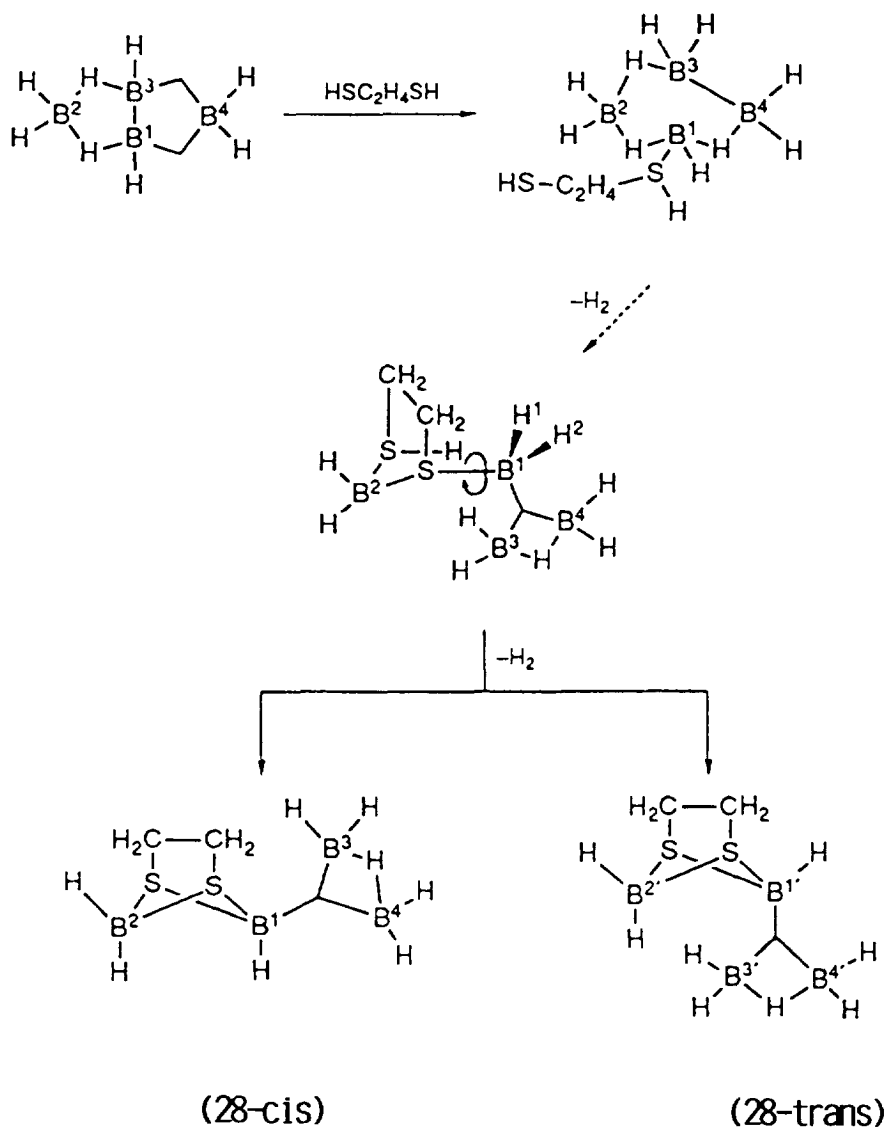


6. Five-boron-atom systems

No chalcogeno pentaborane(9) species are known at the present time. The only well-characterized chalcogeno pentaboranes can be considered as associated chalcogeno di- and triboranes.

6.1. $\text{Na}[\text{CH}_2\text{B}_5\text{H}_{10}\text{S}_4] \cdot 3\text{dioxane}$ **31**

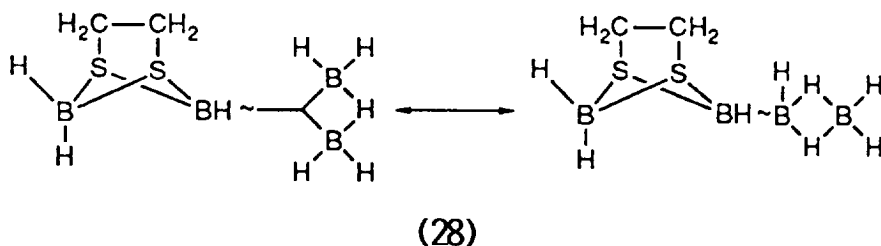
Hydroboration of CS_2 with $\text{Na}[\text{B}_3\text{H}_8]$ yields the sodium salt $\text{Na}[\text{CH}_2\text{B}_5\text{H}_{10}\text{S}_4] \cdot 3\text{dioxane}$ **31**, isolated as the tris dioxane adduct; **31** is a novel



Scheme 2.

boron-containing anion with the adamantane skeleton CB₅S₄ shown in Fig. 12 [48]. Each boron atom carries two terminal hydrogen atoms and there are no bridging hydrogen atoms. The crystal structure of the [(C₆H₅)₄P]⁺ salt has been determined by X-ray diffraction.

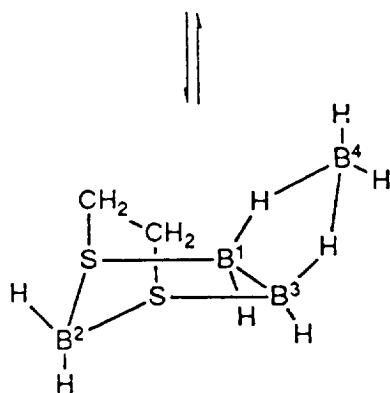
The B–B bond from the B₃H₈[−] ion is not retained in **31** and the S bridges point to C–S bond cleavage. Although the mechanism is unknown, the formation of **31** can partly be described by redox reactions.



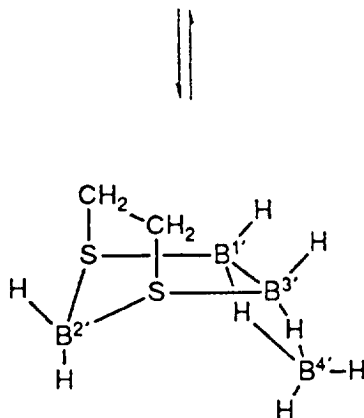
Scheme 3.

(28-cis)

(28-trans)



(29-cis)



(29-trans)

Scheme 4.

6.2. $[(BH_2)_5S_4]^-$ **32**

The new chalcogeno boron hydride anion $[(BH_2)_5S_4]^-$ **32** with the B_5S_4 nor-adamantane skeleton is formed by the reaction of $NaBH_4/THF \cdot BH_3$ with elemental sulfur [49]. These nucleophilic degradation reactions proceed via $[H_3B-\mu_2-S(B_2H_5)]^-$ **21** (Scheme 5 and Scheme 6). An X-ray structure determination of $[(C_6H_5)_4P][(BH_2)_5S_4]$ failed because of disordering of the anion. Structure **32** was deduced from the 1H and ^{11}B NMR spectra. Structural data have been calculated by SCF methods, Fig. 13. **32** can also be obtained by addition of $[H_3B-\mu_2-S(B_2H_5)]^-$ **21** to $H_2B_2S_3$ **17** (Scheme 7).

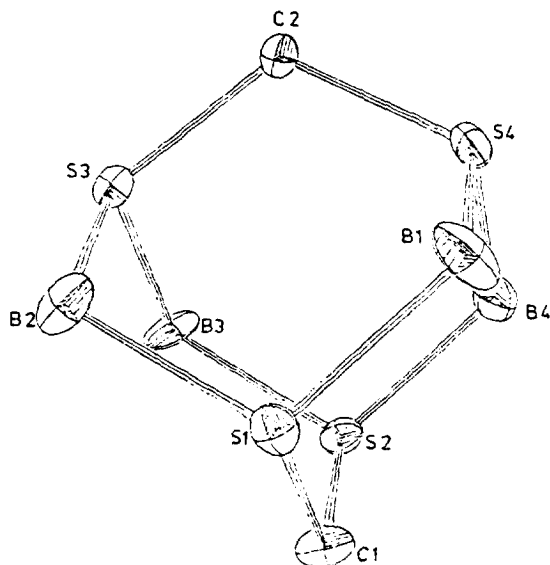


Fig. 11. Structure of $[\text{CH}_2(\text{SBH}_2)_2]_2$ **30**. (From Ref. [47] by permission of Verlag der Zeitschrift für Naturforschung, Tübingen).

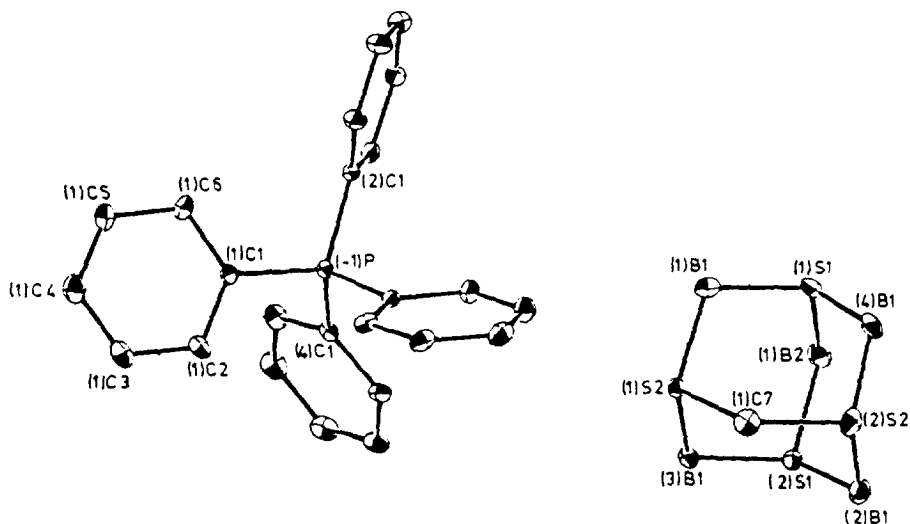


Fig. 12. Structure of $[(\text{C}_6\text{H}_5)_4\text{P}][\text{CH}_2\text{B}_5\text{H}_{10}\text{S}_4]$ (**31**). (From Ref. [48] by permission of Verlag der Zeitschrift für Naturforschung, Tübingen).

7. Six-boron-atom systems

Two types of chalcogeno hexaborane will be considered: associated triboranes and with the hexaboranes we encounter for the first time polyhedral hetero boranes.

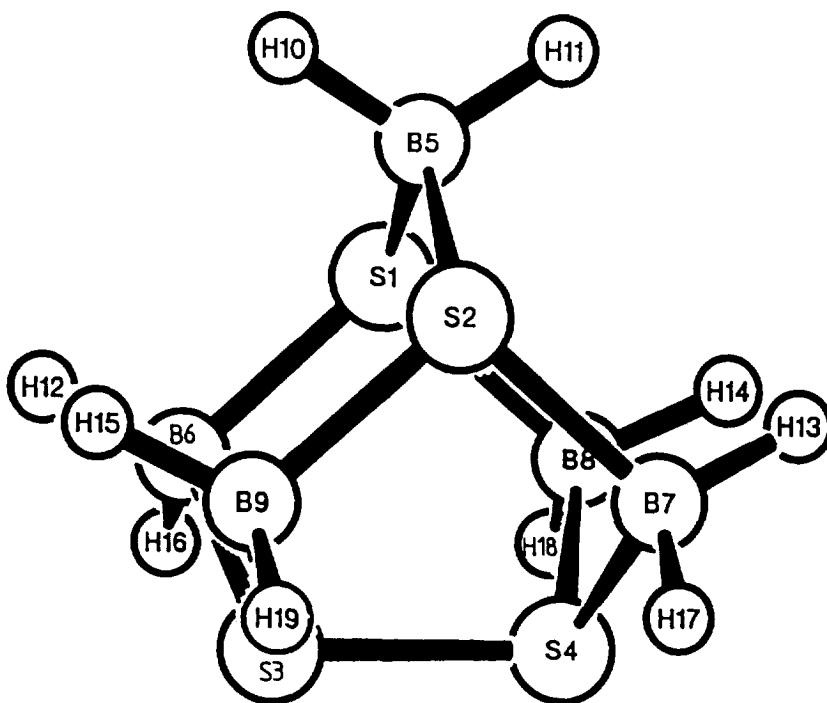
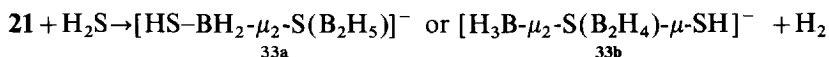


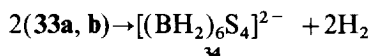
Fig. 13. Calculated structure of $[(\text{BH}_2)_5\text{S}_4]^-$ **32**. (From Ref. [49] by permission of VCH Verlagsgesellschaft mbH, Weinheim).

7.1. $\text{Cs}_2[(\text{BH}_2)_6\text{S}_4] \cdot \text{CsBr}$ **34b** and $\text{Cs}_2[(\text{BH}_2)_6\text{Se}_4] \cdot \text{CsBr}$ **37b**

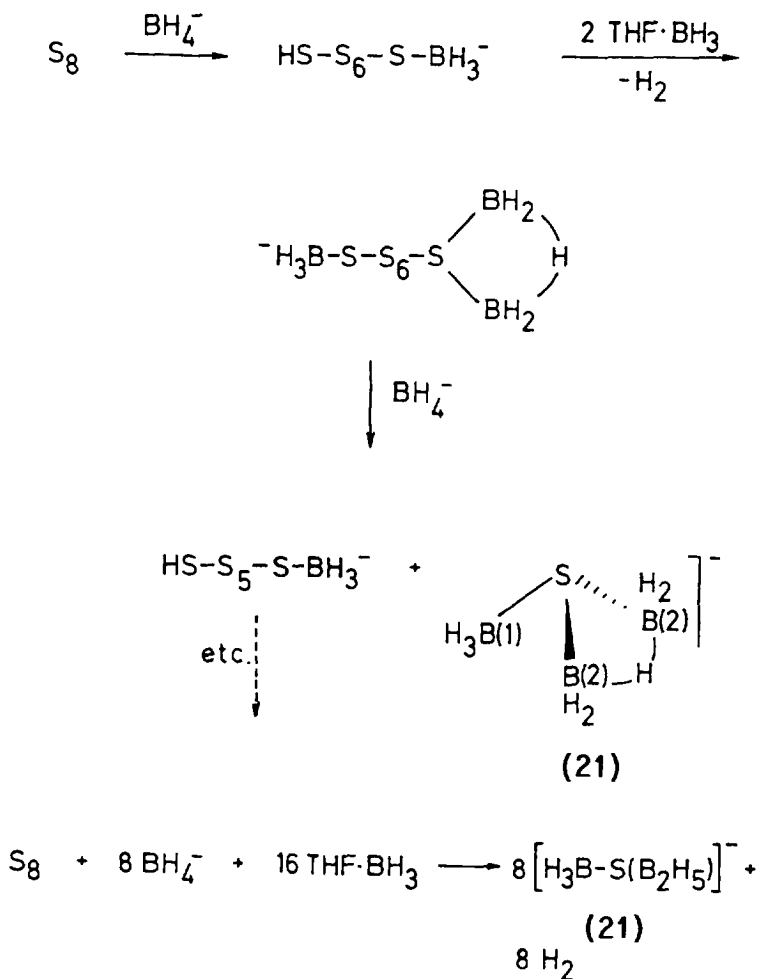
The reaction of $\text{THF} \cdot \text{BH}_3/\text{NaBH}_4$ (2 : 1) with H_2S produces $\text{Na}[\text{H}_3\text{B}-\mu_2\text{-S}(\text{B}_2\text{H}_5)]$ **21** which is also formed in the reaction of $\text{THF} \cdot \text{BH}_3$ with NaSH or anhydrous Na_2S (see Sections 4.2, 4.3 and 4.4). **21** reacts with an excess of H_2S to give $\text{Na}_2[(\text{BH}_2)_6\text{S}_4]$ (**34**).



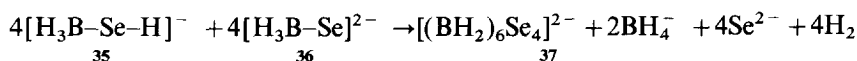
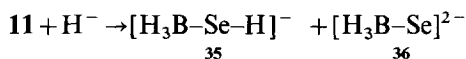
the intermediates (**33a**, **b**) decompose spontaneously to form **34**.



The analogous compound $\text{Na}_2[(\text{BH}_2)_6\text{Se}_4]$ **37** is obtained by treatment of $[\text{H}_3\text{B}-\text{Se}-\text{Se}-\text{BH}_3]^{2-}$ **11** at 100–110 °C.

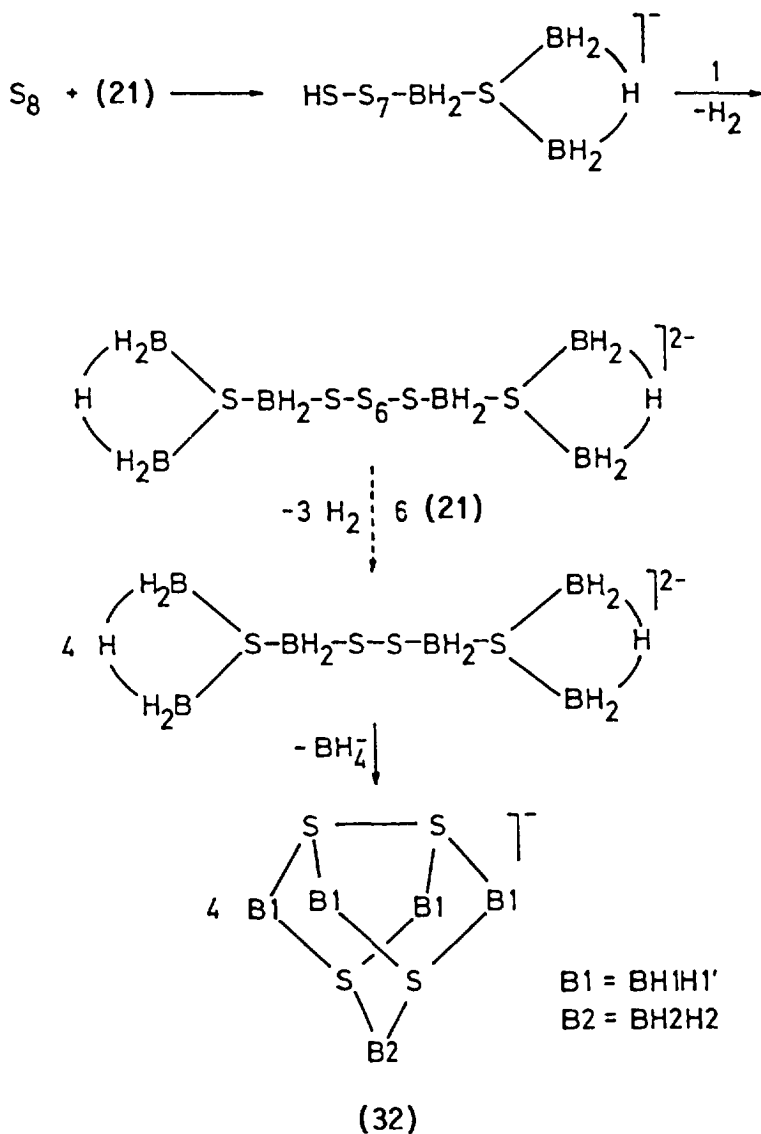


Scheme 5.



34 and **37** are stable in water and react with CsBr to form the crystalline compounds $\text{Cs}_2[(\text{BH}_2)_6\text{S}_4] \cdot \text{CsBr}$ **34b** and $\text{Cs}_2[(\text{BH}_2)_6\text{Se}_4] \cdot \text{CsBr}$ **37b**, characterized by X-ray structure determinations. The anions of **34b** and **37b** consist of the adamantane skeleton B_6S_4 or B_6Se_4 , respectively (Figs. 14 and 15).

The Br^- ion is octahedrally coordinated by Cs^+ ions. The Cs_6Br octahedra share

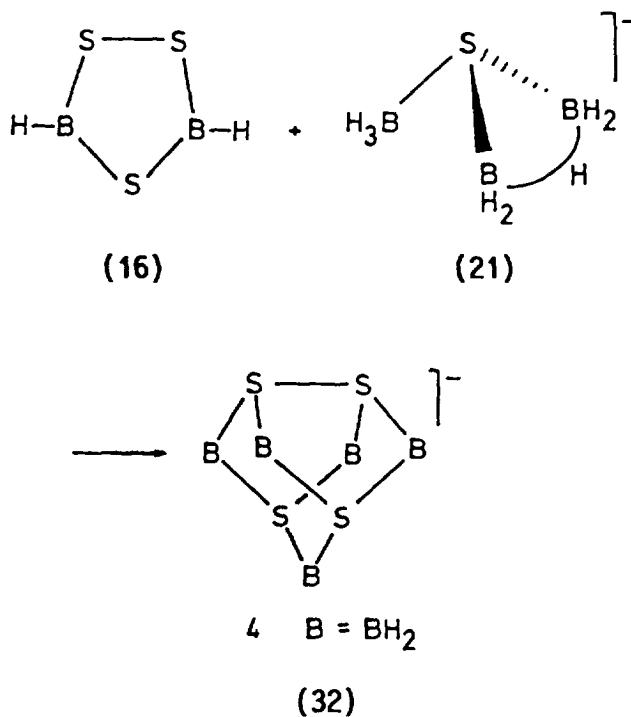


Scheme 6.

faces to form columns along the hexagonal c axis. The crystal structures of the isotopic compounds **34b** and **37b** are closely related to the structure of CsNiCl_3 .

7.2. *hypho-S₂B₆H₉⁻* **38**, *hypho-2,3-(CH₃)₂-2,3-S₂B₆H₉* **39**,
hypho-1-CH₂-2,5-S₂B₆H₈ **40**

The dithiaborane anion *hypho-S₂B₆H₉⁻* **38** was produced in high yield by the reaction of *arachno-S₂B₇H₈⁻* **39** with excess acetone (Fig. 16). Subsequent reaction



Scheme 7.

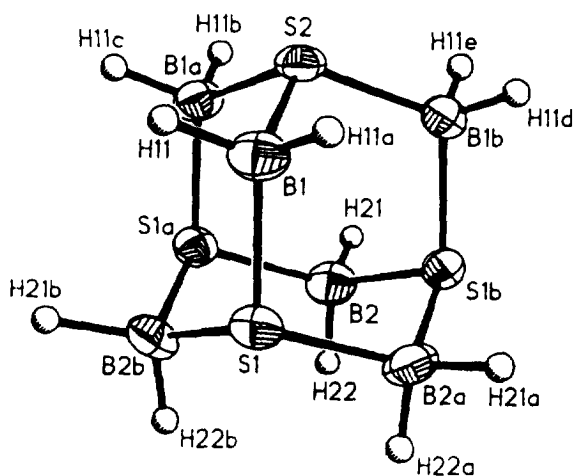


Fig. 14. Structure of the $[(\text{BH}_2)_6\text{S}_4]^{2-}$ anion **34b**. (From Ref. [25] by permission of VCH Verlagsgesellschaft mbH, Weinheim).

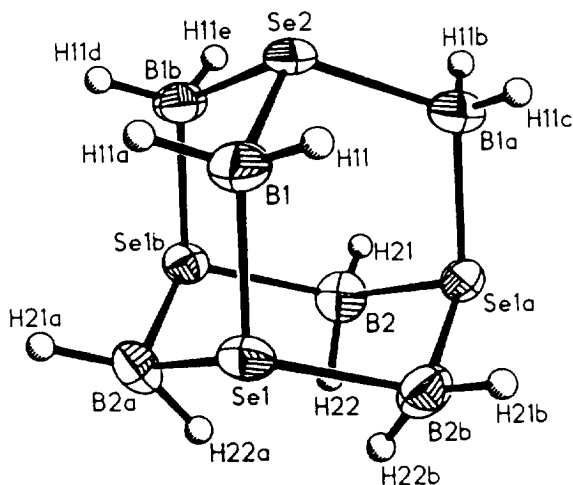


Fig. 15. Structure of the $[(\text{BH}_2)_6\text{Se}_4]^{2-}$ anion **37b**. (From Ref. [25] by permission of VCH Verlagsgesellschaft mbH, Weinheim).

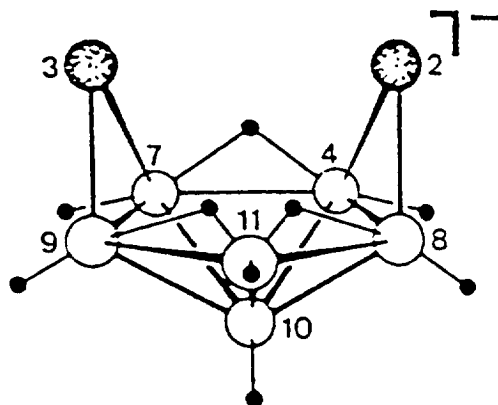
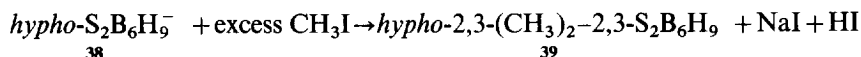
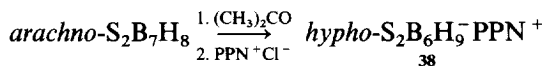


Fig. 16. Eight-vertex hypho-structure of $\text{S}_2\text{B}_6\text{H}_9^-$ **38**. (From Ref. [50] by permission of The American Chemical Society, Washington).

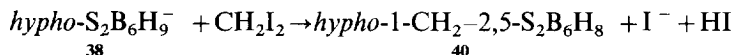
of **38** with excess methyl iodide gave *hypho*-2,3- $(\text{CH}_3)_2$ -2,3- $\text{S}_2\text{B}_6\text{H}_9$ **39** [51].



A single-crystal X-ray determination of **39** showed that the compound has an eight-vertex hypho cage geometry, which can be derived from an octadecahedron

by removing three vertices. Alternatively, **39** can be considered a dibridged derivative of hexaborane(10) Fig. 17.

The reaction of *hypho*-S₂B₆H₉[−] **38** with diiodomethane gave *hypho*-1-CH₂-2,5-S₂B₆H₈ **40** in good yield.

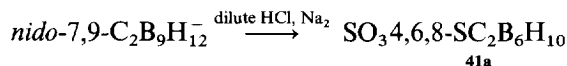


A single-crystal X-ray structural determination of **40** showed that it has a nine-vertex *hypho* cage geometry derived from an icosahedron by removal of three vertices. Furthermore, the cage is observed to have a unique CH₂ unit bridging the two sulfur atoms forming an open five-membered face (Fig. 18).

In **40** the electron-rich bridging S-CH₂-S unit appears to be connected by conventional two-center two-electron bonds. The *hypho*-S₂B₆H₉[−] anion has been employed to generate a series of new *arachno*- and *hypho*-metalladithiaborane clusters [50].

7.3. *arachno*-4,6,8-SC₂B₆H₁₀ **41a**

The reaction of 7,9-C₂B₉H₁₂[−] with Na₂SO₃ in dilute hydrochloric acid affords the new thiacarborane 4,6,8-SC₂B₆H₁₀ **41a**.



The structure of **41a** is proposed on the basis of ¹H and ¹¹B NMR spectra (Fig. 19(a)) [52].

7.4. *hypho*-7,8-CSB₆H₁₁[−] **41b**, 8-Me-*hypho*-7,8-CSB₆H₁₁ **41c**

arachno-4,6-CSB₇H₁₁ **42** can be deprotonated and converted in turn to the eight-vertex *hypho* anion 7,8-CSB₆H₁₁[−] **41b**, Fig. 19(b) [53], a carbathiaborane analog of *hypho*-S₂B₆H₉[−] **38** [51], in 65% yield by the action of aqueous acetone (reflux, 5 h).

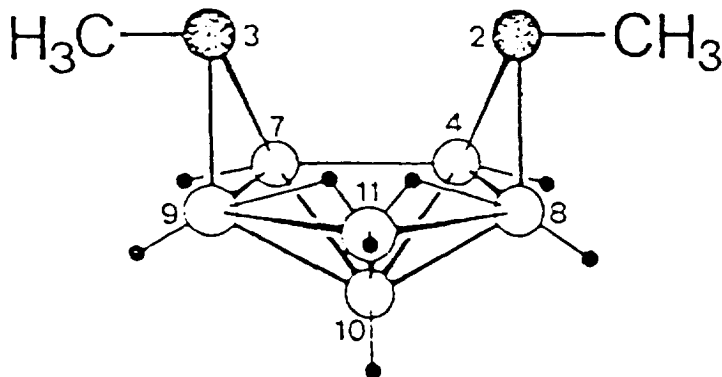


Fig. 17. Eight-vertex *hypho*-structure of 2,3-(CH₃)₂-2,3-S₂B₆H₉ **39**. (From Ref. [51] by permission of The American Chemical Society, Washington).

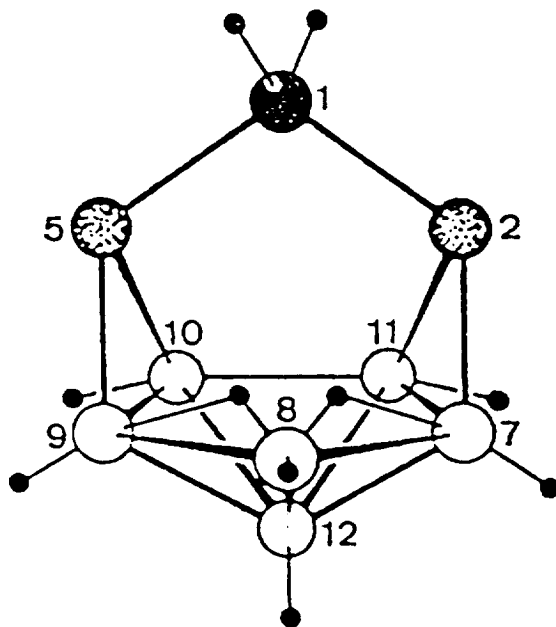


Fig. 18. Nine-vertex hypho-structure of 1-CH₂-2,5-S₂B₆H₈ **40**. (From Ref. [51] by permission of The American Chemical Society, Washington).

Methylation of 7,8-CSB₆H₁₁[−] **41b** with methyl iodide in THF at room temperature has produced the neutral 8-Me-*hypho*-7,8-CSB₆H₁₁ **41c** in 75% yield.

8. Seven-boron-atom systems

The compounds considered are polyhedral hetero boranes.

8.1. *arachno*-4,6-CSB₇H₁₁ **42**

C₂B₁₀H₁₃[−] is degraded in acid medium with K₂S₂O₅ to give 6,8-CSB₇H₁₁ **42** [54]. The structure of this compound is proposed on the basis of ¹H and ¹¹B NMR spectra and topological rules. In compound **42**, which has no symmetry element, two different hydrogen bridges were found and the presence of a CH₂ group was demonstrated.

The possibility of the presence of one or two lone pairs on the sulfur atom is discussed.

The reaction of *nido*-6,9-CSB₈H₉[−] **47b** with hydrochloric acid at room temperature resulted in one-boron cluster degradation to afford the previously reported [54] nine-vertex species **42** (yield 55%).

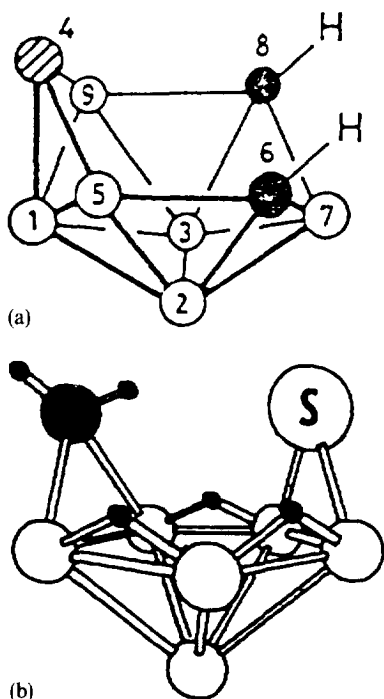


Fig. 19. (a) Proposed structure of *arachno*-4,6,8- $\text{SC}_2\text{B}_6\text{H}_{10}$ **41a**. (From Ref. [52] by permission of The Royal Society of Chemistry, Cambridge). (b) Proposed structure of the *hypho*-7,8- $\text{CSB}_6\text{H}_{11}^-$ anion **41b**.

8.2. *arachno*-6,8- $\text{S}_2\text{B}_7\text{H}_9$ **43**, *arachno*- $\text{S}_2\text{B}_7\text{H}_8^-$ **43a**, *hypho*-2,5- $\text{S}_2\text{B}_7\text{H}_{10}$ **43b**,
hypho-2,5- $\text{S}_2\text{B}_7\text{H}_{11}$ **43c**

In 1977, a high yield synthesis of the first dithiaborane, *arachno*-6,8- $\text{S}_2\text{B}_7\text{H}_9$ **43** was prepared by reaction of $\text{B}_9\text{H}_{12}\text{S}^-$ with potassium hydrogen sulfite in aqueous acid [54]. The constitution followed from topological rules derived for heteroboranes and from interpretation of ^1H and ^{11}B NMR spectra. The presence of two equivalent hydrogen bridges was demonstrated for **43**, which has one plane of symmetry (Fig. 20).

This cluster contains both two sulfur atoms and two two-boron–boron bridging hydrogens on the open face and would appear to be a versatile starting material for the generation of a range of new types of hybrid cluster. Since a cage-sulfur atom is a four skeletal-electron donor (isoelectronic with BH_2^-) the incorporation of two sulfur atoms into a boron hydride framework necessitates the formation of open cage geometries, suggesting that the *arachno*- $\text{S}_2\text{B}_7\text{H}_9$ cage system might also serve as a primary starting material for the syntheses of a wide range of new hypho-clusters [55].

arachno- $\text{S}_2\text{B}_7\text{H}_8^-$ **43a** was prepared by the reaction in vacuo of excess NaH with *arachno*-6,8- $\text{S}_2\text{B}_7\text{H}_9$ **43** in THF [51].

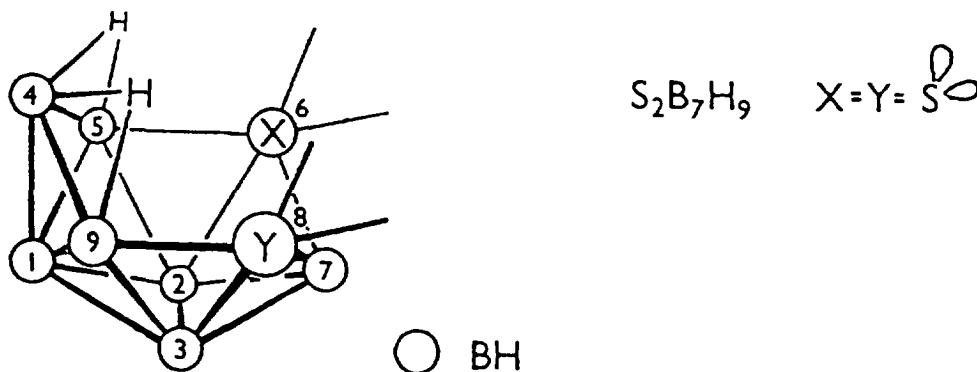
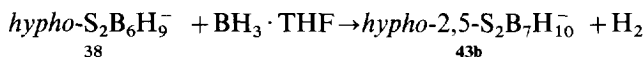
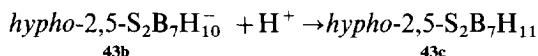


Fig. 20. Proposed structure of *arachno*-6,8-S₂B₇H₉ **43**. (From Ref. [54] by permission of Academy of Sciences of Czech Republic).

The dithiaborane anion *hypho*-2,5-S₂B₇H₁₀[−] **43b** was produced by the reaction of *hypho*-S₂B₆H₉[−] **38** with BH₃ · THF. Alternatively, **38** may be prepared in better yields either by the reaction of S₂B₇H₈[−] **43a** with BH₃ · THF or by the direct reaction of *arachno*-6,8-S₂B₇H₉ **43** with NaBH₄ [51].



Protonation of 2,5-S₂B₇H₁₀[−] **43b** gives the neutral compound *hypho*-2,5-S₂B₇H₁₁ **43c** in good yields [51].



42c was found to decompose slowly at room temperature, but may be kept indefinitely under high vacuum at dry-ice temperature.

8.3. *arachno*-SSeB₇H₉ **44**

SSeB₇H₉ **44** was prepared by reaction of B₉H₉SSe with excess potassium hydroxide in methanol. The structures of **44** are proposed on the basis of ¹¹B NMR results (Fig. 21) [56].

8.4. *arachno*-5,6,9-SC₂B₇H₁₁ **45a**, *arachno*-SeC₂B₇H₁₁ **45b**

A new ten-vertex *arachno*-dicarbathiaborane, formulated as 5,6,9-SC₂B₇H₁₁ **45a**, was prepared from *nido*-5,6-C₂B₈H₁₂ in 20% yield by treatment with sulfur and triethylamine in chloroform. NMR measurements suggest the structure shown in Fig. 22(a) [53].

Treatment of C₂B₇H₁₃ with polyselenide in aqueous base followed by acidification yielded SeC₂B₇H₁₁ **45b** in low yield [57], the structure of which is proposed on the

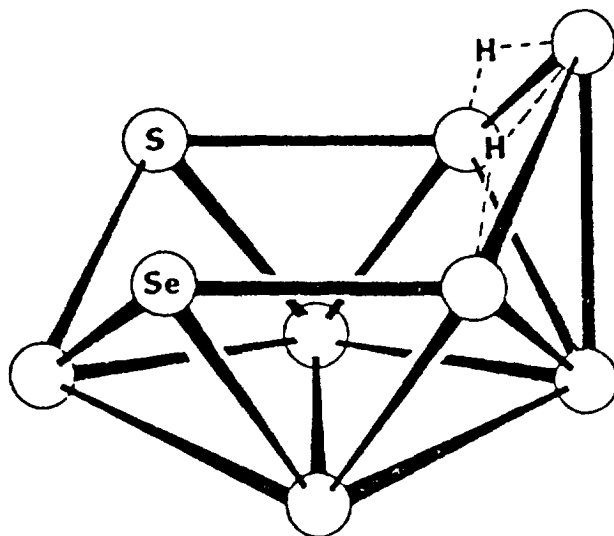


Fig. 21. Proposed structure of *arachno*-SSeB₇H₉ **44**. (From Ref. [56] by permission of The American Chemical Society, Washington).

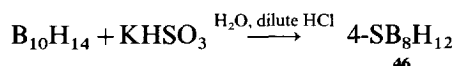
basis of ¹H and ¹¹B NMR spectra. These results are interpreted in terms of the *arachno* structure given in Fig. 22(b).

9. Eight-boron-atom systems

The compounds considered are polyhedral hetero boranes.

9.1. *nido*-(SB₈H₁₀) (?), *arachno*-4-SB₈H₁₂ **46**, *exo*-6-*L*-*arachno*-4-SB₈H₁₀ **46a**, *arachno*-4-SB₈H₁₁⁻ **46b**, *nido*-4-SB₈H₉⁻ **46c**, *nido*-7-SB₈H₉⁻ (?): metallathiaboranes of the type L₂PtSB₈H₁₀ **46d** (L = PMe₂Ph, Et₃P, Ph₃P) see Ref. [58]

A key compound for the further development of nine-vertex *arachno* heteroborane chemistry is *arachno*-4-thianonaborane 4-SB₈H₁₂ **46**. This compound was first isolated by Pretzer and Rudolph [59] but was originally incorrectly formulated as *nido*-SB₈H₁₀. The development of an alternative synthesis led to the correct formulation of **46** [60].



More recently, a convenient high-yield synthesis was reported that makes this thiaborane one of the most accessible thiaborane synthons [61]. The oxidative degradation of *arachno*-SB₉H₁₂, using formaldehyde as an oxidizing agent, affords

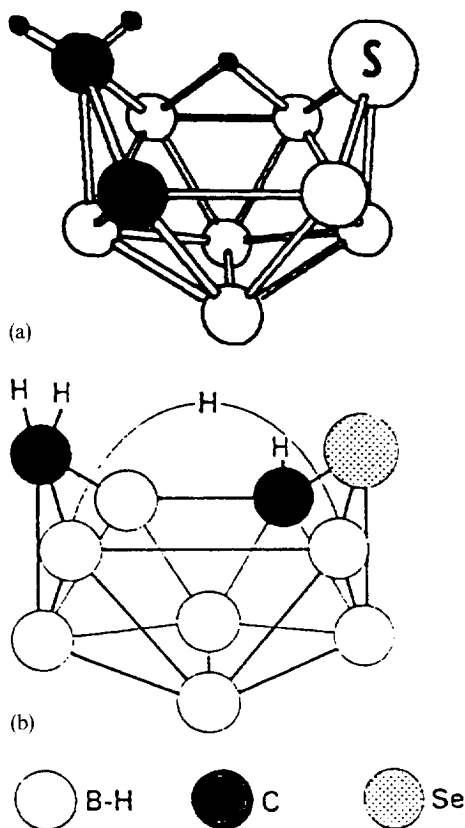
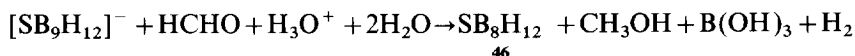
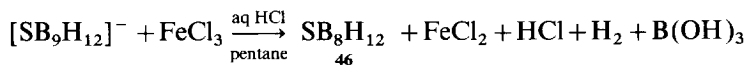


Fig. 22. (a) Proposed structure of 5,6,9-SC₂B₇H₁₁ **45a**. (b) Proposed structure of SeC₂B₇H₁₁ **45b**. (From Ref. [57] by permission of Chemistry and Industry).

46 in practically quantitative yield.



Oxidative degradation of the *arachno*-SB₉H₁₂[−] anion with acidic aqueous FeCl₃ yields the neutral compound directly [62].



On the basis of its ¹¹B and ¹H NMR spectra, **46** has the structure shown in Fig. 23.

The compound is isolated as a white volatile solid that decomposes to intractable materials upon moderate heating. Pure 4-SB₈H₁₂ appears to be unstable to storage, and is best prepared freshly.

Reactions between *arachno*-4-SB₈H₁₂ and Lewis bases L in benzene or without solvent generate a series of the corresponding *exo*-6-L-*arachno*-4-SB₈H₁₀ **46a** [63]

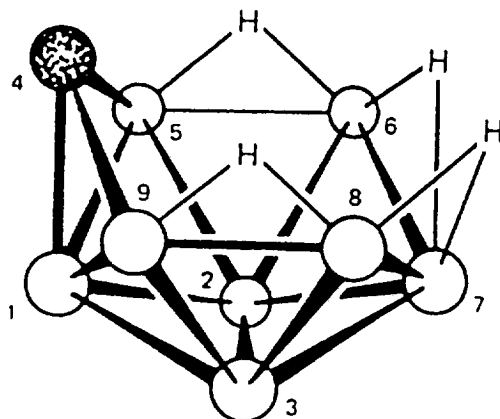


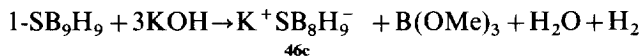
Fig. 23. Proposed structure of *arachno*-4-SB₈H₁₂ **46**. (From Ref. [62] by permission of The American Chemical Society, Washington).

(L = SMe₂, PPh₃, MeCN **46a''**, NMe₃, pyridine, urotropine **46a**, **46a'**). All these compounds are characterized by mass spectrometry and ¹¹B and ¹H NMR spectroscopy. Single-crystal X-ray diffraction studies have been carried out on three representatives of the series Figs. 24(a)–(c).

It has previously been shown that *arachno*-4-SB₈H₁₂ **46** can be deprotonated to the *arachno*-4-SB₈H₁₁[−] anion **46b** by reaction with NaH in quantitative yield [61]; **46b** is stable for weeks as its Na⁺ salt. Owing to the difficult and poor-yield routes to *arachno*-4-SB₈H₁₂, it has been impractical to develop the chemistry of *arachno*-4-SB₈H₁₁[−].

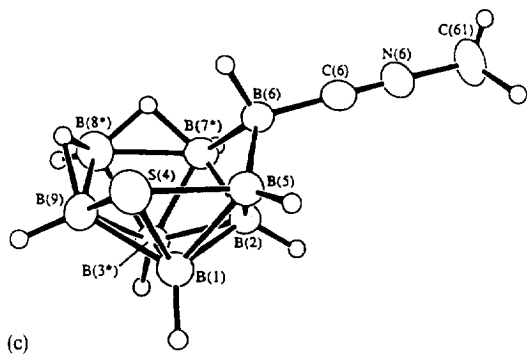
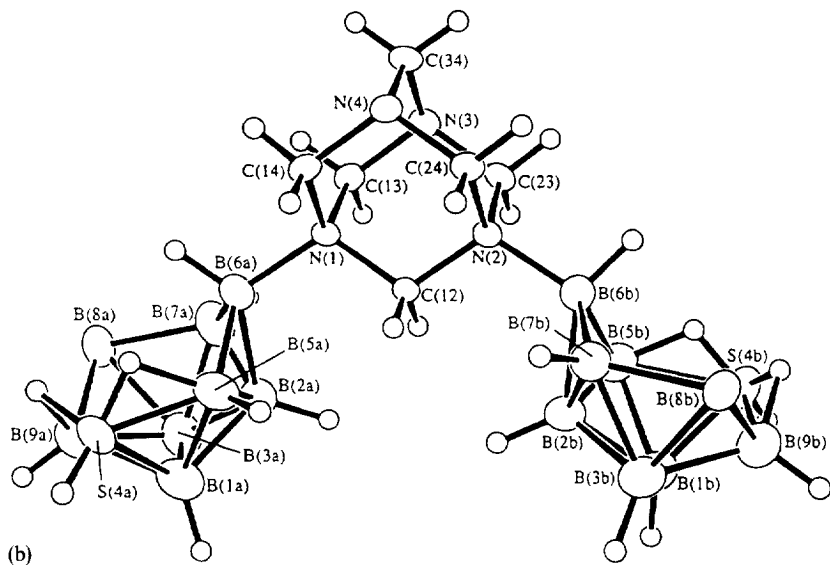
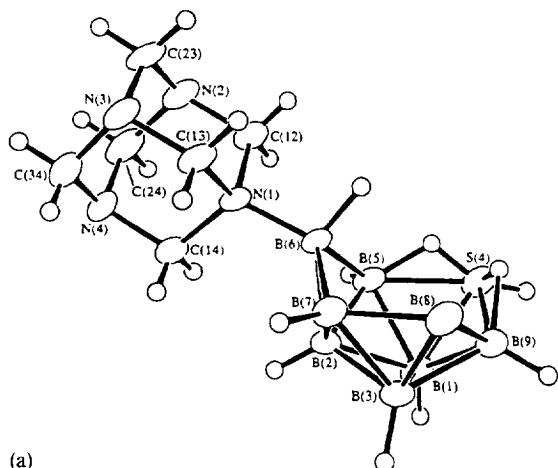
Platinathiadecaboranes L₂Pt(SB₈H₁₀) are formed by reaction of L₄Pt with 1-SB₉H₉ in dry refluxing ethanol or methanol. The complexes have been characterized by X-ray crystallography [58]. L₂Pt(SB₈H₁₀) complexes also form when SB₁₁H₁₁ is substituted for SB₉H₉ as a starting material. It appears that the synthetic method is a degradative insertion reaction where the Pt moiety is able to form a kinetically stable coordination complex after the thiaborane has been degraded to an SB₈ framework.

The controlled degradation of 1-SB₉H₉ can be effected by alcoholic KOH to give *nido*-4-SB₈H₉[−] **46c** [59,58].



46c exhibits extreme sensitivity to air and moisture, sometimes burning vigorously

Fig. 24. (a) Molecular structure of *exo*-6-(uro)-*arachno*-4-SB₈H₁₀ **46a**; (b) molecular structure of *exo,exo'*-6-(uro)-*arachno*-(4-SB₈H₁₂)₂ **46a'**; (c) molecular structure of *exo*-6-(MeNC)-*arachno*-4-SB₈H₁₂ **46a**. (From Ref. [63] by permission of The American Chemical Society, Washington).

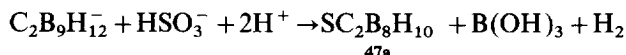


if not handled under a blanket of N_2 . The white solid is best stored in an evacuated ampoule. The best structural characterization of the molecule was obtained from the ^{11}B NMR spectrum; the proposed structure is shown in Fig. 25.

The isomeric $7-SB_8H_9^-$ anion is reported to be formed as a degradation product from $1-SB_8H_9$ in liquid ammonia. A 6 h liquid ammonia treatment gives the $4-SB_8H_9^-$ discussed above [59,58]. From this work, it is assumed that the reported $4-SB_8H_9^-$ and $7-SB_8H_9^-$ anions seem more likely to be $4-SB_8H_{11}^-$ **46b** and $4-SB_8H_9^-$ **46c** [60].

9.2. *nido*- $SC_2B_8H_{10}$ **47a**, 6,9- $CSB_8H_9^-$ **47b**

The *nido*-8-thia-1,2-dicarba-undecaborane $8,1,2-SC_2B_8H_{10}$ **47a** is formed in the reaction of $1,2-C_2B_9H_{12}K$ with sodium bisulfite in aqueous solution [64].



According to its ^{11}B NMR spectrum the molecule of **47a** has a plane of symmetry. As a result of the incorporation of the sulfur atom, the C and S atoms find themselves in the position that is most advantageous to them: in the open pentagonal face, where there is enhanced electron density (Fig. 26(a)).

arachno-6,9- $CSB_8H_{11}^-$ **49d** can be oxidized by acetone (ambient temperature, 24 h, yield 38%) to give the anionic *nido*-carbathiaborane 6,9- $CSB_8H_9^-$ **47b**, Fig. 26(b) [54]. The reaction of this anion with hydrochloric acid at room temperature resulted

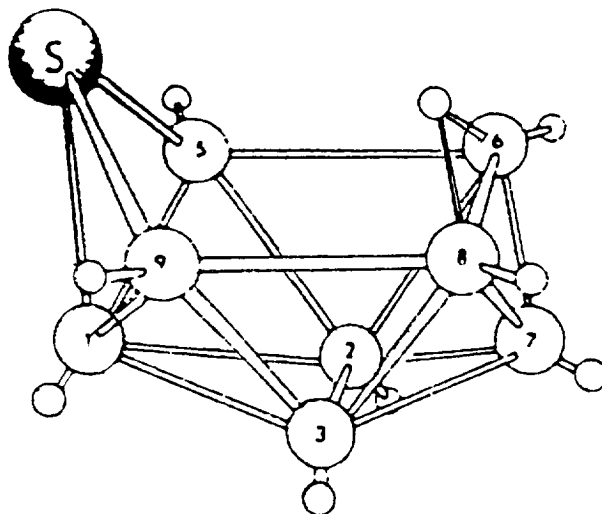


Fig. 25. Proposed structure of *nido*- $4-SB_8H_9^-$ **46c**. (From Ref. [59] by permission of The American Chemical Society, Washington).

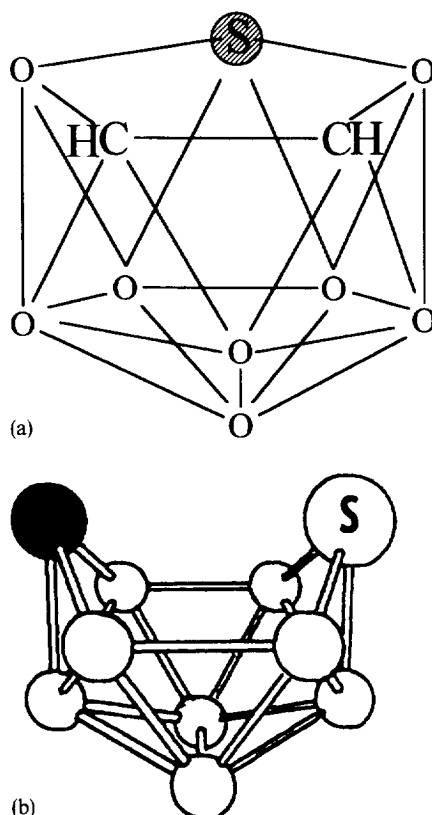


Fig. 26. (a) Proposed structure of *nido*- $\text{SC}_2\text{B}_8\text{H}_{10}$ **47a**. (From Ref. [64] by permission of Plenum Publishing Corp., New York). (b) Proposed structure of *nido*-carbathiaborane 6,9- CSB_8H_5^- **47b**.

in one-boron cluster degradation to afford the previously reported [54] nine-vertex species.

9.3. *nido*- $\text{SeC}_2\text{B}_8\text{H}_{10}$ **48**

The treatment of $\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$ with $7,8\text{-C}_2\text{B}_9\text{H}_{12}^-\text{K}^+$ in an aqueous solution of citric acid resulted in the formation of $\text{SeC}_2\text{B}_8\text{H}_{10}$ **48** in ca. 9% yield. The ^{11}B NMR spectrum showed five doublets of relative area 1 : 2 : 2 : 2 : 1; the ^1H NMR spectrum showed one singlet of equivalent CH groups and overlapped signals of terminal B–H groups. These results are consistent with the structure shown in Fig. 27 [65].

The above reaction represents another example of the degradative insertion of heteroatoms into the borane framework. Although **48** contains no extra hydrogen atoms in the open pentagonal face, it is a *nido* compound with 26 framework electrons. This corresponds with the arrangement with one exohedral electron pair on each selenium atom [66].

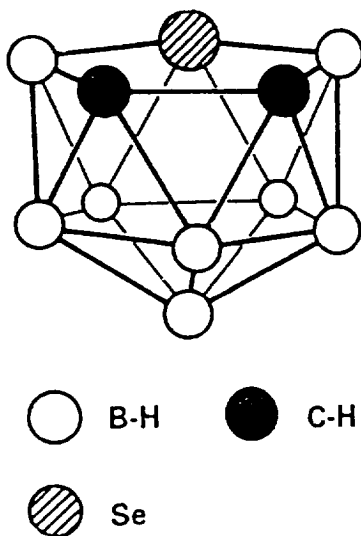


Fig. 27. Proposed structure of *nido*- $\text{SeC}_2\text{B}_8\text{H}_{10}$ **48**. (From Ref. [65] by permission of Chemistry and Industry).

9.4. *arachno*- $\text{Se}_2\text{B}_8\text{H}_{10}$ **49a**, *arachno*-6,9- $\text{NSB}_8\text{H}_{11}$ **49b**, *arachno*-6,9- $\text{CSB}_8\text{H}_{12}$ **49c**, *arachno*-6,9- $\text{CSB}_8\text{H}_{11}^-$ **49d**

The $\text{Se}_2\text{B}_8\text{H}_{10}$ **49a** molecule is formed as a coproduct during the $\text{SeB}_9\text{H}_{12}^-$ synthesis [57,67]. The reaction of $\text{B}_9\text{H}_{13}(\text{SMe}_2)$ with polyselenide ion gave **49a** in 27% yield. The ^{11}B NMR spectrum contained three doublets of relative areas 2 : 4 : 2; one signal had additional bridge hydrogen coupling. This evidence is consistent with the structure given in Fig. 28.

The reaction between BuONO and *nido*-6- SB_9H_{11} in ether yielded the first azathia-borane *arachno*-6,9- $\text{NSB}_8\text{H}_{11}$ **49b**, along with its 6-HO- derivative (yields 15% and

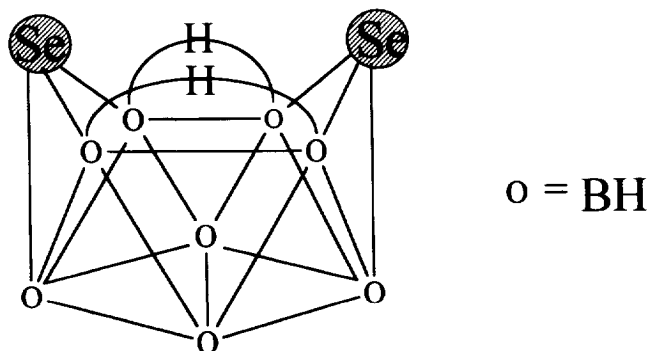


Fig. 28. Proposed structure of *arachno*- $\text{Se}_2\text{B}_8\text{H}_{10}$ **49a**. (From Ref. [57] by permission of Chemistry and Industry).

35% respectively); lower yields of the former compound (10%) were obtained in a similar way, using *arachno*-4-SB₈H₁₂ as a boron-cluster reagent [53].

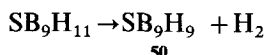
Much more developed has been the chemistry of *arachno*-6,9-CSB₈H₁₂ **49c**, which can be obtained in a reasonable yield (48%) by treatment of 4-CB₈H₁₄ with elemental sulfur in the presence of triethylamine in chloroform [68]. Bridge-deprotonation of this carbathiaborane with NaH leads to the *arachno*-6,9-CSB₈H₁₁[−] anion **49d**.

10. Nine-boron-atom systems

The compounds considered are polyhedral hetero boranes.

10.1. *closo*-1-SB₉H₉ **50**, 6,7,8,9,10-D₅-1-SB₉H₄ **50a**, *closo*-SeB₉H₉ **50b**

The preparation of 1-thia-*closo*-decaborane(9) **50** was effected by pyrolysis of SB₉H₁₁ at 375 °C in vacuo [69].



The formation of *closo*-SeB₉H₉ **50b** by pyrolysis (380 °C) of SeB₉H₁₁ in a flow-through reactor system also parallels that of known thiaborane chemistry [69–71]; however, the presence of cage-coupled products was not observed by mass spectral or GLC experiments [67,53,68]; **50b** was identified by its ¹¹B NMR spectrum.

The ¹¹B NMR spectrum of SB₉H₉ **50** and SeB₉H₉ **50b** in benzene consists of three doublets (74.5, −4.8, and −17.6 ppm **50**; 73.3, −5.4 and −19.9 ppm **50b**) in intensity ratios of (1 : 4 : 4). The data are entirely consistent with an axial placement of the sulfur (selenium) atom in the bicapped Archimedean antiprism structure of C_{4v} symmetry shown in Fig. 29.

Pure 1-SB₉H₉ is a clear crystalline solid with a distinctively ‘sweet’ odor. The *closo* structure of the molecule seems to render it remarkably robust in comparison with *nido*-thiaboranes [72]. It is reasonably air-stable with decomposition occurring only over a period of several weeks.

1-SB₉H₉ has been deuterated under Friedel–Crafts conditions using DCl. The site of initial deuteration was not established clearly, but under forceful conditions deuteration was not complete and 6,7,8,9,10-D₅-1-SB₉H₄ **50a** was obtained [73].

10.2. *closo*-6-X-1-SB₉H₈ **51**, *closo*-10-X-1-SB₉H₈ **52** (X = Cl, Br, I); *closo*-6,10-X₂-1-B₉H₇ **53** (X = Br, I)

The halogenation of 1-SB₉H₉ could be followed sequentially, and thus provides a good probe for the theory of directive effects in substitution reactions in deltahedral boranes [73,74]. The directive effect of the sulfur heteroatom does not correlate with the ground-state charge distribution of 1-SB₉H₉. It appears that initial attack is at the 6-position instead of the anticipated 10-position. In the case of monobromination and monoiodination there is a significant degree of rearrangement to also

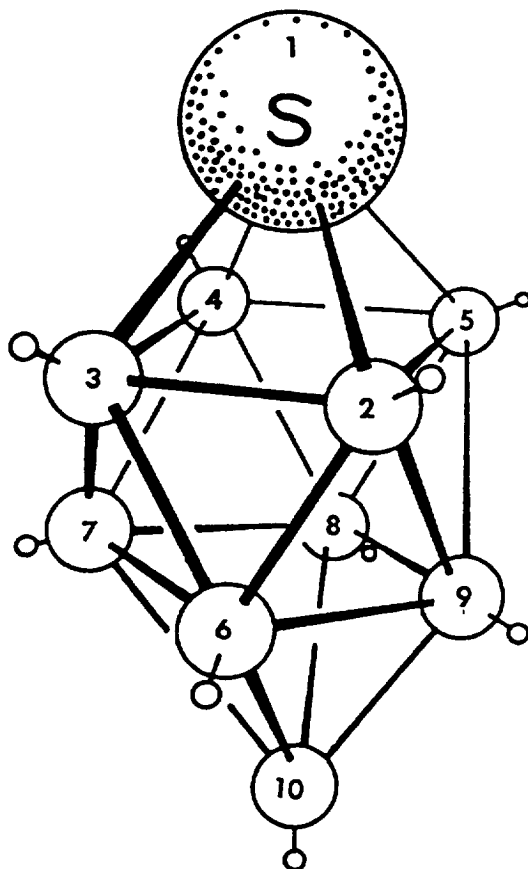


Fig. 29. Proposed structure for 1-thia-closo-decaborane(9) SB_9H_9 , **50**. (From Ref. [69] by permission of The American Chemical Society, Washington).

give the thermodynamically more stable 10-isomer in the reaction mixture ($\Delta H_{\text{isomerization}} = 6.8 \text{ kcal mol}^{-1}$). Only the 6-isomer results from monochlorination. Rearrangement is also a significant factor as halogenation becomes more extensive. A linear correlation between the Pauling electronegativity of X and the chemical shift of the substituted boron is observed for both axial and lower belt (lb) regions (lb = B6,7,8,9). For the axial isomers, the ^{11}B NMR spectra were quite simple and showed the expected downfield singlet and two upfield doublets of relative intensity 1 : 4 : 4. All the halothiadecaboranes described here were characterized additionally by mass spectrometry.

10.3. 2,2'-(1- SB_9H_8)₂ **54a**, 2,6'-(1- SB_9H_8)₂ **54b**, 6,6'-(1- SB_9H_8)₂ **54c**

The vacuum pyrolysis of thiadecaborane(11) SB_9H_{11} produces three isomers of $(\text{B}_9\text{H}_8\text{S})_2$ in about 5% yield [70,69,75]. ^{11}B NMR spectroscopy cannot distinguish

between two of the possible isomers, 2,2'-(1-SB₉H₈)₂ **54a** and 6,6'-(1-SB₉H₈)₂ **54c**. Separation of the 2,2'-isomer from the others was accomplished by elution with heptane–chloroform (9 : 1) on preparative silica gel t.l.c. plates. The molecular structure of **54a** shown in Fig. 30 was determined by single-crystal X-ray diffraction techniques [70,71].

The molecule has *C*_i($\bar{1}$) space group imposed point symmetry; the center of inversion of the molecule is at the midpoint of a B–B bond (1.678(5) Å) joining the two bicapped square antiprism frameworks of the SB₉H₈ moieties. The sulfur atom is in an 'axial' position and the equatorial belt of four boron atoms closest to the sulfur atom contains the boron through which the SB₉H₈ units are connected. The average B–S distance is 1.923(3) Å. The B–B distances of the cage range from 1.940(3) to 1.689(4) Å.

10.4. (1-SB₉H₈)(1'-SB₁₁H₁₀) **55**

Three isomeric forms of **55** are obtained from the 450 °C pyrolysis of SB₁₀H₁₂, the best characterized of which appears to be either the 2,2'- or the 2,7'-isomer [75].

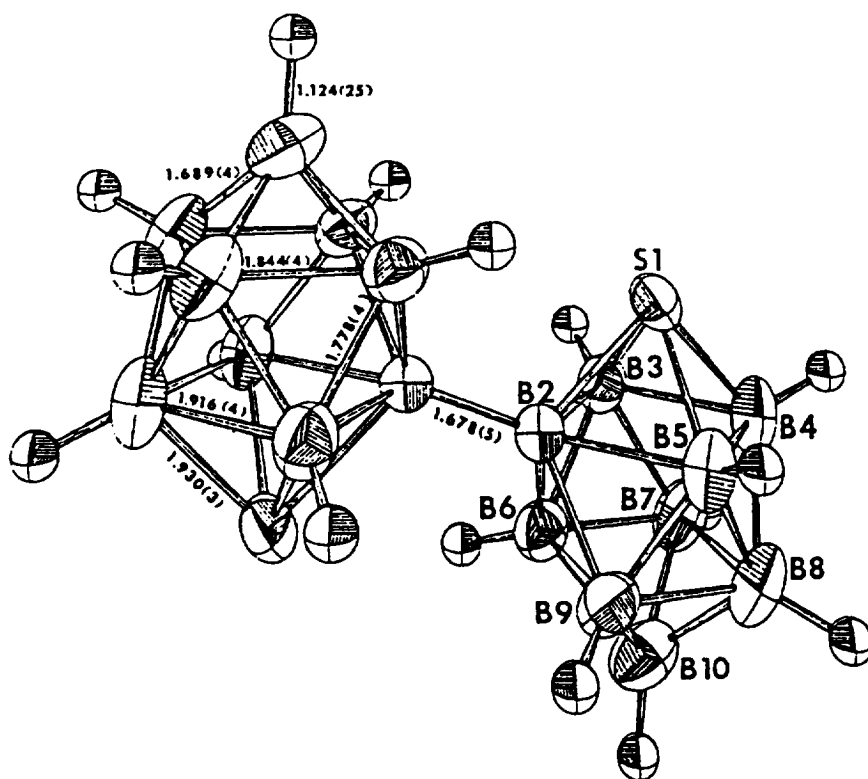


Fig. 30. ORTEP plot depicting the molecular structure and thermal ellipsoids for *closo*-2,2'-(1-SB₉H₈)₂ **54a**. (From Ref. [71] by permission of The American Chemical Society, Washington).

The ^{11}B NMR of the mixture of isomers exhibits poor resolution due to extensive overlap. The regions typical of the axial boron resonance for both cages are sufficiently resolved to show that the axial boron of the SB_9H_8 moiety is not part of a B–B bond.

10.5. $(1\text{-SB}_9\text{H}_8)(1',7'\text{-C}_2\text{B}_{10}\text{H}_{11})$ **56a**, $(1\text{-SB}_9\text{H}_8)(2',3'\text{-C}_2\text{B}_9\text{H}_{10})$ **56b**

Copyrolysis of $6\text{-SB}_9\text{H}_{11}$ and $1,7\text{-C}_2\text{B}_{10}\text{H}_{12}$ gives three isomers of $(1\text{-SB}_9\text{H}_8)(1',7'\text{-C}_2\text{B}_{10}\text{H}_{11})$ **56**, but more definitive structural characterization is rather tenuous. Complete structural characterization is also lacking for the two $(1\text{-SB}_9\text{H}_8)(2',3'\text{-C}_2\text{B}_9\text{H}_{10})$ **56b** isomers formed upon copyrolysis of $6\text{-SB}_9\text{H}_{11}$ and $7,9\text{-C}_2\text{B}_9\text{H}_{13}$ [75]. However, the carboranyl thiaboranes are believed to be B–B linked clusters. There is no evidence for polydeltahedral thiaboranes where the B–B link involves a vertex order other than five.

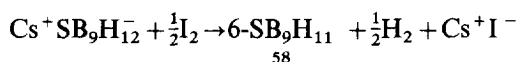
10.6. *closo*-(CH_3) $_n$ - $1\text{-SB}_9\text{H}_{9-n}$ ($n=1-5$) **57a**, *closo*-(C_2H_5) $_n$ - $1\text{-SB}_9\text{H}_{9-n}$ ($n=1-5$) **57b**

Electrophilic alkylation of *closo*- $1\text{-SB}_9\text{H}_9$ with either methyl or ethyl iodide in the presence of AlCl_3 produces alkylated derivatives of the type *closo*-(CH_3) $_n$ - $1\text{-SB}_9\text{H}_{9-n}$ ($n=1-5$) **57a**, *closo*-(C_2H_5) $_n$ - $1\text{-SB}_9\text{H}_{9-n}$ ($n=1-5$) **57b**, which were identified by GC-MS, ^{11}B and ^1H NMR spectroscopy [76]. The initial product is $6\text{-R-}1\text{-SB}_9\text{H}_8$ rather than the $10\text{-R-}1\text{-SB}_9\text{H}_8$ predicted on the basis of ground-state charge considerations. Thus, these results are as found for halogenation of $1\text{-SB}_9\text{H}_9$. Therefore, in *closo*-thiaboranes the site of substitution does not agree with the ground-state charge distribution and rearrangement is important in determining the substitution site. The best results were obtained with a 1 : 1 ratio of AlCl_3 to thiaborane and an HCl pressure between 1.1 and 1.2 atm.

10.7. *nido*- $6\text{-SB}_9\text{H}_{11}$ **58**

nido- $6\text{-SB}_9\text{H}_{11}$ **58** can be obtained from *arachno*- $6\text{-SB}_9\text{H}_{12}^-$ by protonation followed by pyrolytic disproportionation. The proposed intermediate $\text{H}(\text{H}_2\text{O})_x^+-\text{SB}_9\text{H}_{12}^-$ is a pyrophoric solid and gives only a 30% yield of $6\text{-SB}_9\text{H}_{11}$ [77]. By the reaction of decaborane(14) with KHSO_3 in water and by a subsequent protonation of the formed intermediate with either concentrated H_2SO_4 or diluted HCl the respective thiaboranes $6\text{-SB}_9\text{H}_{11}$ and $4\text{-SB}_8\text{H}_{12}$ were prepared [78].

Iodine oxidation in refluxing benzene gives the desired reaction in over 85% yield after 15 min [59].



The NMR study of *nido*- $6\text{-SB}_9\text{H}_{11}$ using ^{11}B , $^{11}\text{B}\{^1\text{H}\}$, $^1\text{H}\{^{11}\text{B}\}$, $[^{11}\text{B}\text{--}^{11}\text{B}]\text{-COSY}$, and $[^1\text{H}\text{--}^1\text{H}]\text{-COSY}$ techniques has enabled unequivocal assign-

ment of the ^{11}B and ^1H spectra [79]; Fig. 31 shows the proposed structure of the 6- SB_9H_{11} cluster.

10.8. $\text{SB}_9\text{H}_{11} \cdot \text{ligand } 59$, (ligand = H^- , OH^- , CH_3CN , DMF , $(\text{CH}_3)_2\text{S}$, THF , Et_3N , and PPh_3)

Iodine oxidation of $\text{CsSB}_9\text{H}_{12}$ in THF affords white crystalline $\text{SB}_9\text{H}_{11} \cdot \text{THF}$ in good yield [77,80]. Like the known compound $\text{SB}_9\text{H}_{11} \cdot \text{S}(\text{CH}_3)_2$ [77], the THF adduct was very moisture sensitive and was characterized by its ^1H and ^{11}B NMR spectra. Treatment of $\text{SB}_9\text{H}_{11} \cdot \text{THF}$ with acetonitrile or triphenylphosphine easily generated $\text{SB}_9\text{H}_{11} \cdot \text{CH}_3\text{CN}$ and $\text{SB}_9\text{H}_{11} \cdot \text{PPh}_3$ in good yield. Reaction of $\text{SB}_9\text{H}_{11} \cdot \text{PPh}_3$ with tetraethylammonium hydroxide in aqueous acetonitrile formed $[(\text{C}_2\text{H}_5)_4\text{N}][\text{HOSB}_9\text{H}_{11}]$ in moderate yield. The pattern of the ^{11}B NMR spectrum of this hydroxi derivative is very similar to the spectrum of $\text{SB}_9\text{H}_{11} \cdot (\text{CH}_3)_2\text{NCHO}$. This suggests that $\text{HOSB}_9\text{H}_{11}$ is a member of the $\text{SB}_9\text{H}_{11} \cdot \text{ligand}$ class of compounds with the ligand being OH^- . SB_9H_{12} is also a member of the $\text{SB}_9\text{H}_{11} \cdot \text{ligand}$ class in which H^- is the ligand. The position of the base attachment was determined in 9- Et_3N -6- SB_9H_{11} [81] Fig. 32.

The triethylamine ligand is attached to the thiaborane cage in an exo-polyhedral manner at the B9 position. The sulfur occupies the 6-position. The bridging hydrogens on the open face are significantly displaced toward B9 and away from the sulfur.

10.9. Metal derivatives of the $\text{SB}_9\text{H}_9^{2-}$ ion 60

For $M = \text{Pd}$: $(\text{SB}_9\text{H}_9)\text{Pd}(\text{ligand})_x^n$; ligand = PPh_3 ($x=2$, $n=0$), phen ($x=1$, $n=0$), and $\text{C}_2\text{S}_2(\text{CN})_2$ ($x=1$, $n=2-$) see Refs. [80,81], $[(\text{C}_2\text{H}_5)_3\text{P}]_2\text{Pt}(\text{H})\text{SB}_9\text{H}_{10}$ [82]

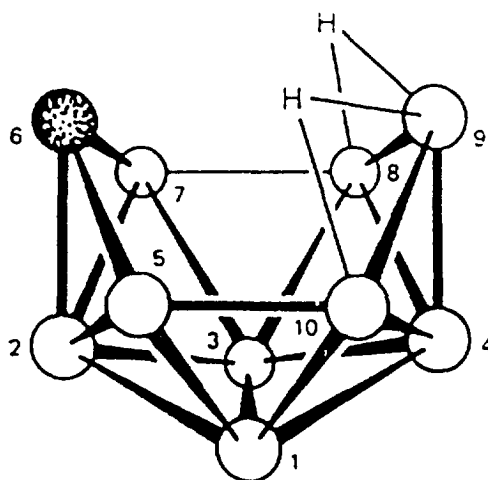


Fig. 31. Proposed structure of *nido*-6- SB_9H_{11} 58. (From Ref. [59] by permission of The American Chemical Society, Washington).

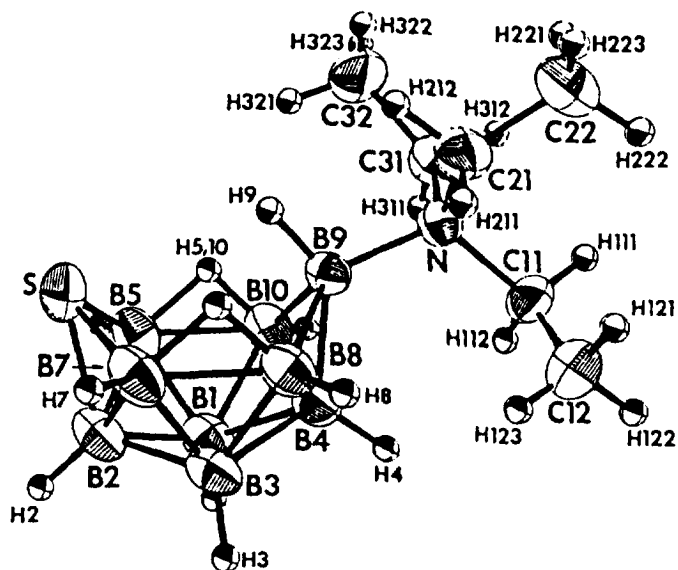


Fig. 32. ORTEP plot of the molecular structure of *arachno*-9-Et₃N-6-SB₉H₁₁ **59** with non-hydrogen ellipsoids at 50% confidence level. (From Ref. [81] by permission of The American Chemical Society, Washington).

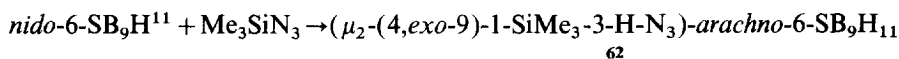
10.10. 6-SB₉H₁₁ as a hydroboration agent **61**, *nido*-6-SB₉H₁₀ **61a** (see Section 10.14)

Since *nido*-6-SB₉H₁₁ has the same framework structure as *nido*-B₁₀H₁₄ it was anticipated that treatment of 6-SB₉H₁₁ with acetylenes in the presence of Lewis bases would produce a new heteroborane with 12-atom framework, a dicarbathiaborane. Contrary to these expectations, it was found that 6-SB₉H₁₁ undergoes a facile hydroboration reaction when treated with alkynes and alkenes [83–85]. Hydroboration of alkenes and alkynes by 6-SB₉H₁₁ clearly occurs by addition of the *exo*-BH at the 9-position across the unsaturated C–C bond. A particularly definitive observation is the fact that the hydroboration is a regiospecific anti-Markownikoff syn-addition, as shown schematically in Fig. 33.

10.11. Triazene-*arachno*-6-SB₉H₁₁ cluster:

(μ_2 -(4,*exo*-9)-1-SiMe₃-3-H-N₃)-*arachno*-6-SB₉H₁₁ **62**

It is reported that *nido*-6-SB₉H₁₁ reacts readily with an organic derivative of hydrazoic acid, trimethylsilyl azide, to give the first example of a new class of hybrid fused-ring cluster triazene-thiaborane compounds, (μ_2 -(4,*exo*-9)-1-SiMe₃-3-H-N₃)-*arachno*-6-SB₉H₁₁ **62** [86].



In contrast to free triazenes [87], **62** exhibits both thermal and photolytic stability.

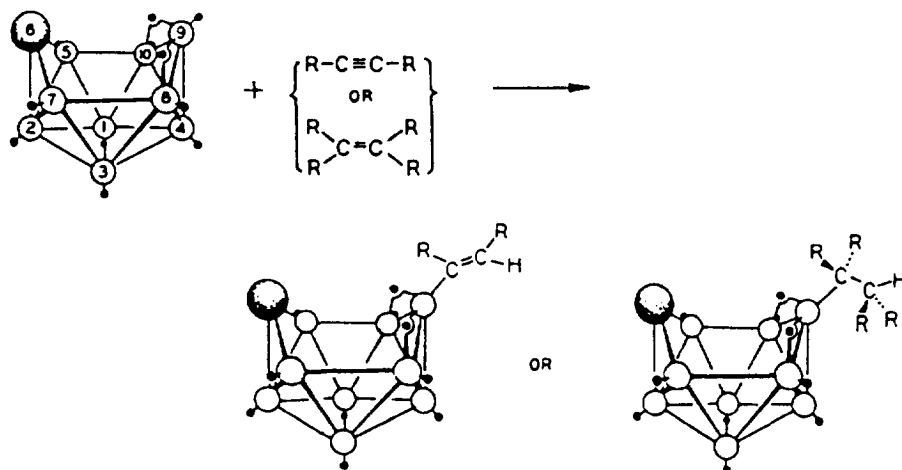


Fig. 33. Hydroboration by *nido*-6-SB₉H₁₁ **61**. (From Ref. [83, 84] by permission of The American Chemical Society, Washington).

For example, no nitrogen was evolved nor any decomposition observed upon xylene reflux for 3 days or upon photolysis in toluene solution for 3 h. The structure is shown in Fig. 34.

The cage framework is consistent with those observed for other 10-vertex,

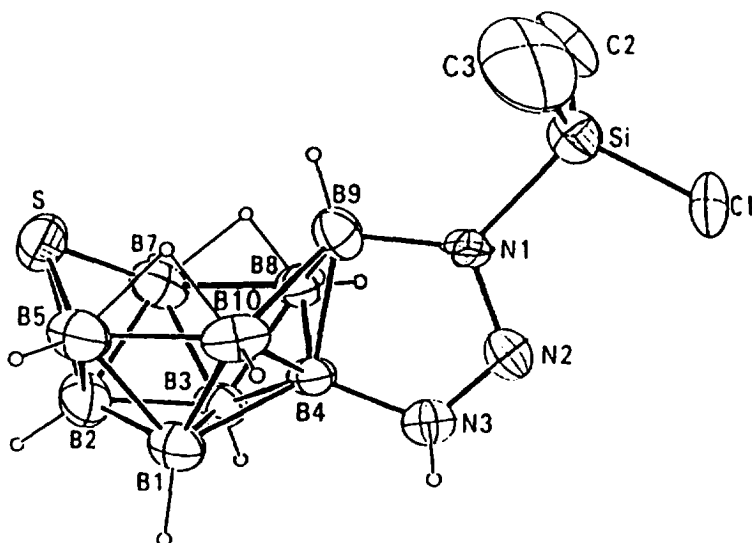


Fig. 34. ORTEP drawing of the molecular structure of $(\mu_2-(4,exo-9)-1-SiMe_3-3-H-N_3)-archo-6-SB_9H_{11}$ **62**. (From Ref. [86] by permission of The American Chemical Society, Washington).

26-skeletal-electron systems such as *exo*-9-Et₃N-*arachno*-6-SB₉H₁₁ [77], thus indicating that the triazene group is functioning as a two-skeletal-electron donor to the cage.

10.12. *nido*-XB₉H₁₁ **63a** (X = Se, Te), XB₉H₁₁ · L **63b** (L = Lewis base)

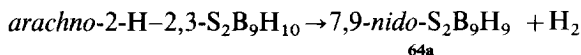
Aqueous polyselenide or polytelluride solutions react with B₉H₁₃ · S(CH₃)₂ to form the XB₉H₁₂[−] anions, which can be isolated as tetramethylammonium salts. Oxidation of these salts with iodine produces the XB₉H₁₁ molecules in benzene or the XB₉H₁₁ · CH₃CN **63b** molecules in the presence of acetonitrile. Reaction of SeB₉H₁₁ · CH₃CN with triethylamine produces SeB₉H₁₁ · N(C₂H₅)₃ in a rapid ligand displacement reaction [67,53,68]. There are similarities in the ¹¹B NMR spectra of the XB₉H₁₂[−] ions relative to that of the XB₉H₁₁ · L (L = Lewis base) molecules.

10.13. *nido*-S₂B₉H₉ **64a**, *nido*-SSeB₉H₉ **64b**, *nido*-Se₂B₉H₉ **64c**

Reaction of SB₉H₁₂[−] **59** with potassium polysulfide, with a small amount of polyselenide present, generated S₂B₉H₉ **64a**.

Treatment of SB₉H₁₂[−] **59** with potassium polyselenide formed SSeB₉H₉ **64b**. The formation of Se₂B₉H₉ **64c** was first reported as an unexpected minor product during the synthesis of SeB₁₀H₁₁[−] **70b** [88,56]. This diselenaborane can now be made in good yield by reaction of B₉H₁₄[−] with potassium polyselenide [57].

Thermolysis of *arachno*-2,3-S₂B₉H₁₀ **65b** in refluxing toluene results in dehydrogenation and formation of *nido*-S₂B₉H₉ **64a** [89].



Treatment of Se₂B₉H₉ (or SSeB₉H₉) with potassium hydroxide followed by reaction of the products with triethylamine, C₅H₆, and CoCl₂ formed Se₂B₉H₉CoCp (or SSeB₉H₉CoCp) [56]. The structure of *nido*-7,9-Se₂B₉H₉ **64c** has been determined unambiguously to be the 7,9-isomer by ¹¹B NMR spectroscopy [90] Fig. 35.

Both the 7,9- and 7,8-isomers of S₂B₉H₉ were calculated with the MNDO program. The heat of formation of the 7,9-isomer was calculated to be −28.2 kcal mol^{−1}, which was 48.2 kcal mol^{−1} more stable than the 7,8-isomer. A scheme of localized cluster bonding in 7,9-S₂B₉H₉ calculated with the MNDO program is shown in Fig. 36, [90].

It is noteworthy that while there are many examples of heteroboranes with two or more heteroatoms from Groups IV/14 or V/15 in adjacent positions, apparently there are no heteroboranes with two adjacent atoms from Group VI/16 nor any metal–heteroborane derivatives with two adjacent Group VI/16 atoms.

10.14. *arachno*-2,3-S₂B₉H₁₀[−] **65a**, *arachno*-2-H-2,3-S₂B₉H₁₀ **65b**,
arachno-2-CH₃-2,3-S₂B₉H₁₀ **65c**, *arachno*-2-CH₂I-2,3-S₂B₉H₁₀ **65d**

The reaction of *nido*-6-SB₉H₁₀[−] **61a** with elemental sulfur results in sulfur insertion into the *nido*-SB₉ cage framework to produce the new *arachno*-dithiaborane cluster

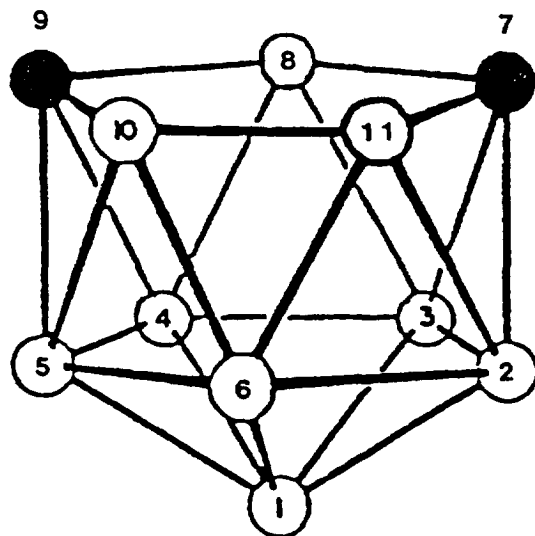


Fig. 35. Proposed structure of *nido*-7,9- $\text{Se}_2\text{B}_9\text{H}_9$ **64c**. (From Ref. [90] with kind permission of Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington OX5 1GB, UK).

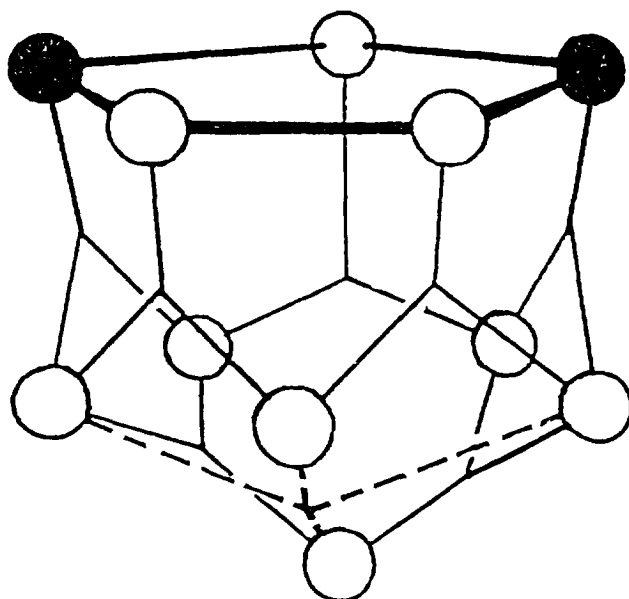
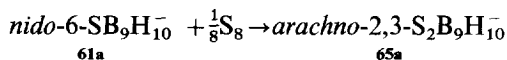


Fig. 36. A scheme of localized cluster bonding in *nido*-7,9- $\text{Se}_2\text{B}_9\text{H}_9$ **64c** calculated with the MNDO programme. (From Ref. [90] with kind permission of Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington OX5 1GB, UK).

anion, *arachno*-2,3-S₂B₉H₁₀[−] **65a** [89].



A single crystal X-ray study has confirmed that, consistent with its formal *arachno* skeletal-electron count, the anion adopts a structure that may be derived from a 13-vertex closo-deltahedron by removal of two vertices, Fig. 37.

The two sulfur atoms adopt non-adjacent three-coordinate positions on the open six-membered face of the cage. In the solid state, a single bridge-hydrogen was located at the B8–B11 edge; however, in solution the NMR spectra indicate *C_s* cage symmetry, suggesting that the bridging hydrogen is interconverting between positions at the B8–B11 and B9–B11 edges. The spectroscopic data indicate that, upon reaction of *arachno*-2,3-S₂B₉H₁₀[−] with concentrated H₂SO₄ in CH₂Cl₂, protonation occurs at one of the cage sulfur sites to give *arachno*-2-H-2,3-S₂B₉H₁₀ **65b**. **65b** also reacts with CH₃I or CH₂I₂ to give 2-CH₃-2,3-S₂B₉H₁₀ **65c** and *arachno*-2-CH₂I-2,3-S₂B₉H₁₀ **65d** respectively. A single crystal X-ray structure determination of CH₃-2,3-S₂B₉H₁₀ **65c** confirmed that the methyl is bound to a sulfur atom and thus provides additional support for the structure proposed for *arachno*-2-H-2,3-S₂B₉H₁₀ **65b** Fig. 38(a).

In contrast to the structure observed for *arachno*-2,3-S₂B₉H₁₀[−] **65a**, in 2-CH₃-2,3-S₂B₉H₁₀ **65c**, the methylated sulfur adopts only a two-coordinate position bridging a B–B edge, while the other sulfur is in a three-coordinate position similar to those observed in 2,3-S₂B₉H₁₀[−]. The similarity of the NMR spectra of **65b**, **c**, and **d** suggests that **65b** and **65d** adopt cage structures similar to that confirmed for **65c**. Thus, either alkylation or protonation of 2,3-S₂B₉H₁₀[−] results not only in substitution at sulfur, but alters the nature of the sulfur-cage bonding interactions.

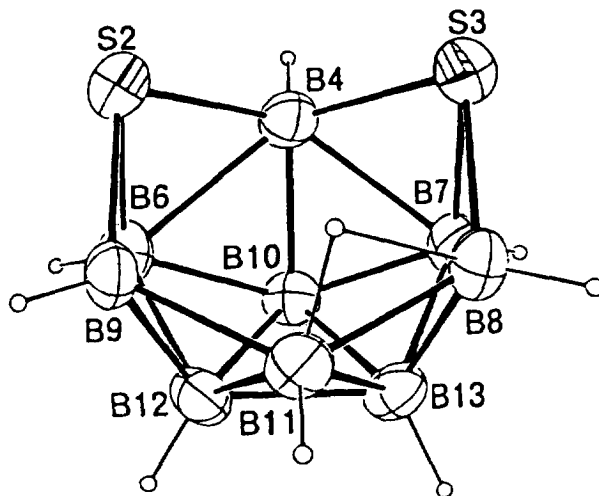


Fig. 37. ORTEP drawing of the anion structure of *arachno*-2,3-S₂B₉H₁₀[−] **65a**. (From Ref. [89] by permission of The American Chemical Society, Washington).

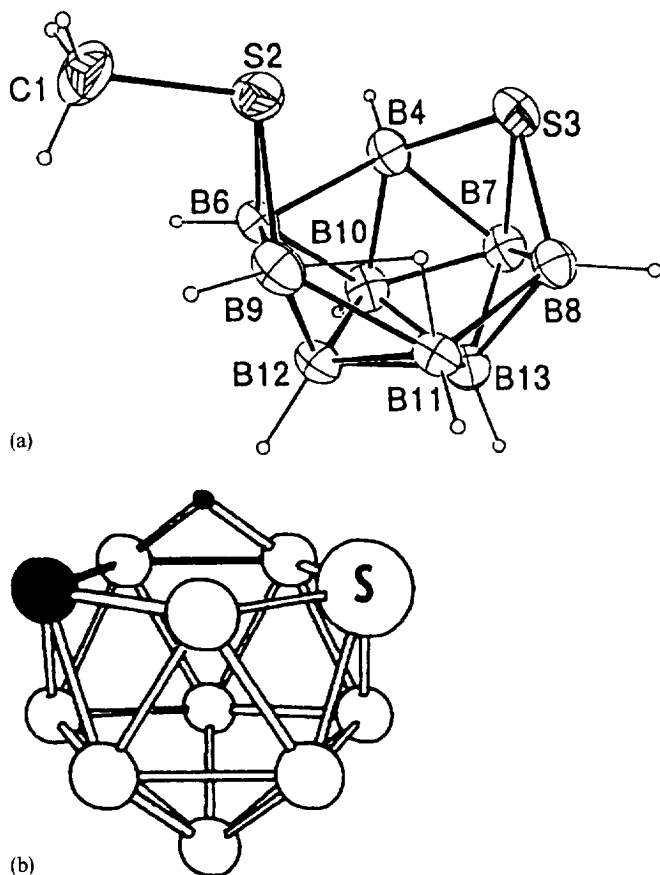


Fig. 38. (a) ORTEP drawing of the structure of *arachno*-2-CH₃-2,3-S₂B₉H₁₀ **65c**. (From Ref. [89] by permission of The American Chemical Society, Washington). (b) Proposed structure of *nido*-7,9-CSB₉H₁₁ **66b**.

10.15. $SB_9H_{11}^{2-}$ **66**, $(SB_9H_{11})_2M^{2-}$ ($M = Ni, Pd$) **66a**, *nido*-7,9-CSB₉H₁₁ **66b**

Chemical procedures are outlined for the in situ formation of the reactive anion $SB_9H_{11}^{2-}$ **66**. This compound is used to produce the new derivatives $(SB_9H_{11})M^{2-}$ ($M = Ni, Pd$) **66a** [80].

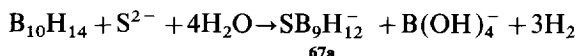
The *arachno*-CSB₈H₁₁[−] anion can be converted to *nido*-7,9-CSB₉H₁₁ **66b** by heating at 120 °C; the structure is shown in Fig. 38(b).

10.16. *arachno*-6-SB₉H₁₂[−] **67a**, *arachno*-6-SB₉H₁₁Br[−] **67b**,
arachno-SB₉H₁₁(OH)[−] **67c**, *arachno*-6-SeB₉H₁₂[−] **67d**, *arachno*-6-TeB₉H₁₂[−] **67e**

For coinage metal derivatives of *arachno*-6-SB₉H₁₂[−], see Refs. [80,91–93].

Reaction of decaborane(14) with aqueous ammonium polysulfide gives the thia-

borane ion, $\text{SB}_9\text{H}_{12}^-$ **67a**, in essentially quantitative yield [77].



The ^{11}B NMR spectrum consists of six resonances of relative areas 1 : 2 : 1 : 1 : 2 : 2 reading upfield [94, 79]. The ^{11}B NMR relative intensity pattern was consistent with the molecular symmetry shown in Fig. 39. The pattern of the NMR spectrum is consistent with the solid-state structure of $(\text{PPh}_3)_3\text{AuSB}_9\text{H}_{12}$ [91, 92]. The compound is a salt consisting of $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{Au}^+$ cations and $\text{SB}_9\text{H}_{12}^-$ anions. $(\text{C}_2\text{H}_5)_4\text{N}[\text{SB}_9\text{H}_{11}\text{Br}]$ **67b** was prepared from 2- $\text{BrB}_{10}\text{H}_{13}$ [94] which is believed to be the 1- $\text{SB}_9\text{H}_{11}\text{Br}^-$ isomer.

arachno- $\text{SB}_9\text{H}_{11}(\text{OH})^-$ **67c**: after standing in acetone solution for some months, partial decomposition of 6- $\text{SB}_9\text{H}_{12}^-$ **67a** was noted. The ^{11}B NMR behavior of species **67c** was very similar to that of 6- $\text{SB}_9\text{H}_{12}^-$ **59**, but with the COSY correlations indicating a different shielding ordering of the three resonances of relative intensity 1 [79]. The absence of an endo-terminal ^1H resonance associated with $^{11}\text{B}(9)$ [95] then indicated **67c** is a 9-endo-substituted *arachno*-6- $\text{SB}_9\text{H}_{11}(\text{OH})^-$ cluster anion closely related to 6- $\text{SB}_9\text{H}_{12}^-$ **67a** Fig. 40.

An anion of this 9-(OH)-*arachno*-6- $\text{SB}_9\text{H}_{11}(\text{OH})^-$ formulation has previously been reported [80, 94]. The essential identity of the ^{11}B shielding behavior of **67c** with this previously reported species confirms the formulation.

Aqueous polyselenide or polytelluride solutions react with $\text{B}_9\text{H}_{13} \cdot \text{S}(\text{CH}_3)_2$ to form the $\text{XB}_9\text{H}_{12}^-$ ($\text{X} = \text{Se}$ (**67d**), Te (**67e**)) anions [67, 53, 68]. Both **67d** and **67e** appear to have limited stability; the identity of these compounds is confirmed by their subsequent chemistry and the similarity of their ^{11}B NMR spectra with that of the $\text{SB}_9\text{H}_{12}^-$ ion **59**.

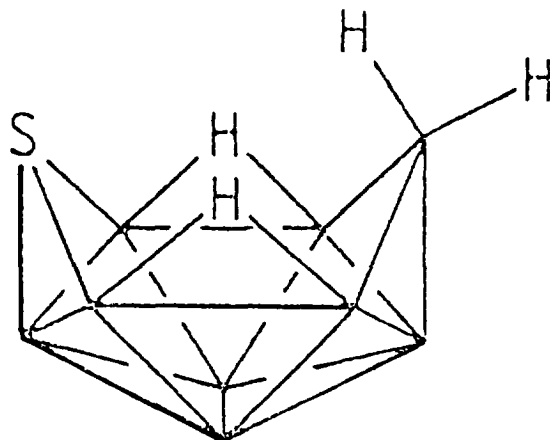


Fig. 39. Schematic representation of the ten-vertex *arachno*-6- $\text{SB}_9\text{H}_{12}^-$ **67a**. (From Ref. [79] by permission of The Royal Society of Chemistry).

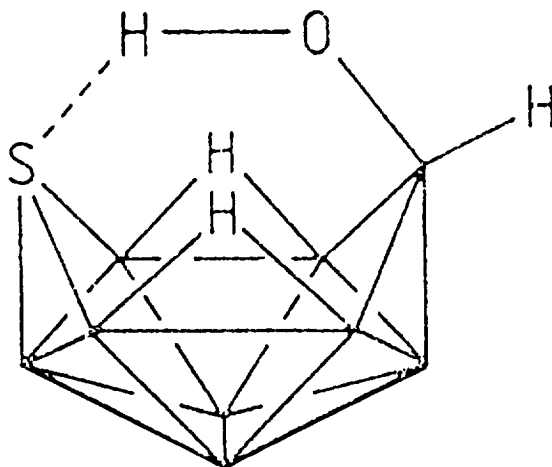
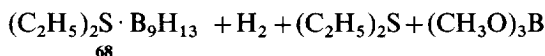
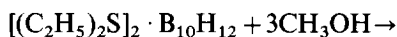


Fig. 40. Proposed structure of the 9-endo-substituted *arachno*-6-SB₉H₁₁(OH)[−] cluster anion **67c**. (From Ref. [79] by permission of The Royal Society of Chemistry).

10.17. (C₂H₅)₂S · B₉H₁₃ **68**

(C₂H₅)₂S · B₉H₁₃ **68** was synthesized in fair yield by a degradation of bis(diethylsulfide) decaborane(12) with methanol [96].



68 is a stable intermediate in the total methanolysis since it may be degraded completely to (CH₃O)₃B under prolonged reaction with methanol.

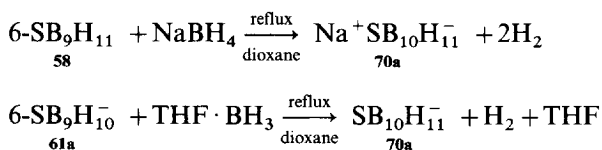
11. Ten-boron-atom systems

The compounds considered are polyhedral hetero boranes.

11.1. *nido*-7-SB₁₀H₁₂ **69a**, *nido*-7-SeB₁₀H₁₂ **69b**, *nido*-7-TeB₁₀H₁₂ **69c**,
2-*R*-7-SB₁₀H₁₁ **69d**, (SB₁₀H₁₁)₂ **69e**, SB₁₀H₁₁[−] **70a**, SeB₁₀H₁₁[−] **70b**, TeB₁₀H₁₁[−] **70c**,
M(EB₁₀H₁₀)^{2−} (M = Fe, Co; E = Se, Te) **71**, CpCoEB₁₀H₁₀ **72**

Pyrolysis of CsSB₉H₁₂ **67a** gives the ion SB₁₀H₁₁[−] **70a**, which on acidification is converted to the weak acid *nido*-7-SB₁₀H₁₂ **69a** [77]. Improved synthetic routes have been developed for the preparation of **69a**. Good yields (greater than 60%) of *nido*-7-SB₁₀H₁₂ **69a** can be obtained by acidification of the anion that is formed either by the reaction of *nido*-6-SB₉H₁₁ **58** with NaBH₄ under reflux conditions or

by the reaction of *nido*-6-SB₉H₁₀[−] **61a** with THF · BH₃.



The anion **70a** can then be converted to the neutral thiaborane by acidification with aqueous HCl in CH₂Cl₂ to give *nido*-7-SB₁₀H₁₂ **69a** [62].

As is shown in Fig. 41, *nido*-7-SB₁₀H₁₂ **69a** has been proposed to adopt a structure based on an icosahedron missing one vertex, with the sulfur occupying a position on the open face. The ¹¹B NMR spectra of SB₁₀H₁₂ **69a** and SeB₁₀H₁₂ **69b** contain very similar doublet patterns. The spectrum of TeB₁₀H₁₂ also is similar but somewhat compressed. Treatment of SeB₁₀H₁₂ or TeB₁₀H₁₂ with aqueous KOH and either CoCl₂ or FeCl₂ forms M(EB₁₀H₁₀)^{2−} (M = Fe, Co; E = Se, Te). Triethylamine, cyclopentadiene monomer CoCl₂, and SeB₁₀H₁₂ or TeB₁₀H₁₂ in tetrahydrofuran solution form CpCoEB₁₀H₁₀ [88].

Oxidation of *nido*-7-SB₁₀H₁₀^{2−} **73** by Ag⁺ in benzene and toluene leads to coupled polyhedra (SB₁₀H₁₁)₂ **69e** and attack upon the solvent to give arylthiaboranes 2-R-7-SB₁₀H₁₁ **69d**.

The ¹¹B NMR spectrum of the phenyl or the analogous tolyl derivative is found to be a perturbed version of that of the parent 7-SB₁₀H₁₂ **69a**. The nine clearly discernible boron resonances of unit intensity confirm substitution at other than the symmetric B1 or B5 boron positions (see Fig. 42) [97].

In aqueous ammonia, Na₂Se₄ and Na₂Te₄ react with decaborane(14) to give

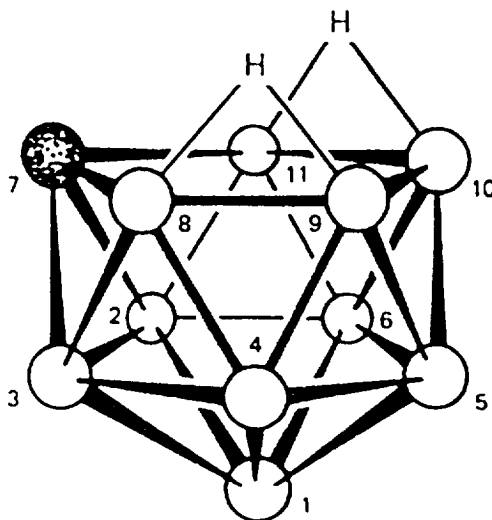


Fig. 41. Proposed structure of *nido*-7-SB₁₀H₁₂ **69a**. (From Ref. [62] by permission of The American Chemical Society, Washington).

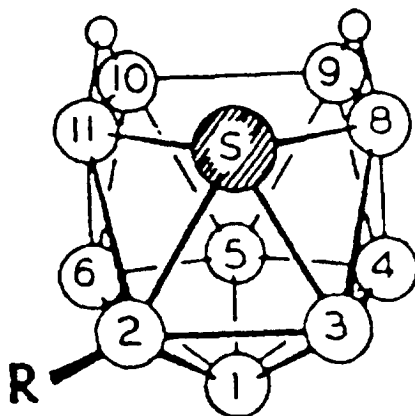


Fig. 42. Proposed structure of *nido*-2-R-7-S B₁₀H₁₁ **69d**. (From Ref. [97] by permission of The American Chemical Society, Washington).

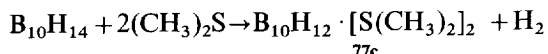
SeB₁₀H₁₁[−] **70b** and TeB₁₀H₁₁[−] **70c** respectively. These anions form *nido*-7-SeB₁₀H₁₂ **69b** and *nido*-7-TeB₁₀H₁₂ **69c** upon acidification [88]. The ¹¹B NMR spectra of the EB₁₀H₁₁[−] ions (E=S, Se, Te) are all very similar. The spectrum of the tellurium derivative displays the most detail with a 2 : 3 : 2 : 2 : 1 pattern of doublets. The area 3 doublet is not symmetrical, suggesting the overlap of two resonances.

11.2. *nido*-7-SB₁₀H₁₀^{2−} **73**, (SB₁₀H₁₀)₂M^{n−} **74**

Treatment of SB₁₀H₁₁[−] **70a** or SB₁₀H₁₂ **69a** with strong base affords *nido*-7-SB₁₀H₁₀^{2−} **73**. Reaction of SB₁₀H₁₀^{2−} with a variety of transition metal halides gives a series of icosahedral metala thiaboranes (SB₁₀H₁₀)₂M^{n−} **74** [77]. SB₁₀H₁₀^{2−} **73** is stable in solution for a limited time; it has not been isolated and characterized as a solid salt.

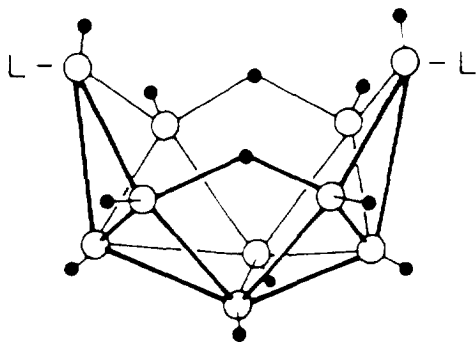
11.3. μ₂-6,7-(CH₃E)B₁₀H₁₃ **75a, b** (E = S, Se), μ₂-6,9-CH₃EB₁₀H₁₂[−] **76a, b**, {Cs[μ₂-6,9-CH₃SB₁₀H₁₂]}₃ · Cs[μ₂-6,7-OH-μ₂-6,9-CH₃SB₁₀H₁₁] **77a**, B₁₀H₁₂ · [S(CH₃)₂]₂ **77c**

While strong bases readily deprotonate B₁₀H₁₄, certain weaker bases react with B₁₀H₁₄ according to the following equation:

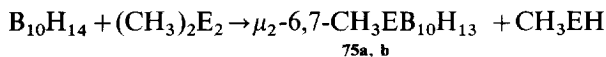


Effectively, hydrogen atoms are replaced by electron pair donor atoms at the 6- and 9-positions of the B₁₀H₁₄ framework, while hydrogen atoms bridge boron only between 7–8 and 5–10 boron atom positions, Fig. 43 [98].

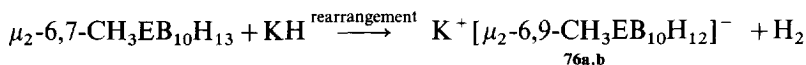
In contrast to this type of reaction, B₁₀H₁₄ reacts with (CH₃)₂E₂ (E = S, Se) to

Fig. 43. Structure of $B_{10}H_{12}[S(CH_3)_2]_2$ **77c**.

form $B-\mu_2-6,7-CH_3EB_{10}H_{13}$ **75a, b**



The structure of $\mu_2-6,7-CH_3SeB_{10}H_{13}$ **75b** has been determined by X-ray crystallography (Fig. 44) [99]. The first reaction step is considered to be an adduct formation $B_{10}H_{14} \cdot (CH_3)_2E_2$. Treatment of **75a, b** with potassium hydride yields $\mu_2-6,9-CH_3EB_{10}H_{12}^-$ **76a, b**.



The formation of the anion **76a, b** is accompanied by a rearrangement of the bridging ligand CH_3E from the 6–7 to the 6–9 boron atom position.

76a, b is stable to hydrolysis. However, upon recrystallization of $Cs^+[\mu_2-6,9-CH_3SB_{10}H_{12}]^-$ **76a** from an aqueous solution, it was partially hydrolyzed. A 'stable' form, a 'double salt' of the composition $\{Cs[\mu_2-6,9-CH_3SB_{10}H_{12}]\}_3 \cdot Cs[\mu_2-6,7-OH-\mu_2-6,9-CH_3SB_{10}H_{11}]$ **77a** was isolated, the structure of which is shown in Fig. 45 [100].

This 'double salt' **77a** is the first example of a heteroborane polyeder with a bridging OH group. The orthorhombic unit cell contains 32 molecules of **77a**.

11.4. nido-6,6'-O($B_{10}H_{13}$)₂ **78**

By the action of sulfuric acid on compounds of the type $B_{10}H_{12} \cdot (SR_2)_2$ **77c** a novel compound has been prepared, 6,6'-oxido-bis(tridecahydrodecaborane) $O(B_{10}H_{13})_2$ **78** [101]. The IR, UV and NMR spectra establish evidence of the compound **78** as being the anhydride of an unknown monohydroxytridecahydrodecaborane, and of the oxide bridge, which bonds the $B_{10}H_{13}$ fragments together, as being situated at the 6- and 6'-positions. It is not only the first known purely inorganic oxygenous derivative of the tetradecehydrodecaborane, the species is believed to be the very first existing anhydride of any hypothetical hydroxyborane. **78**

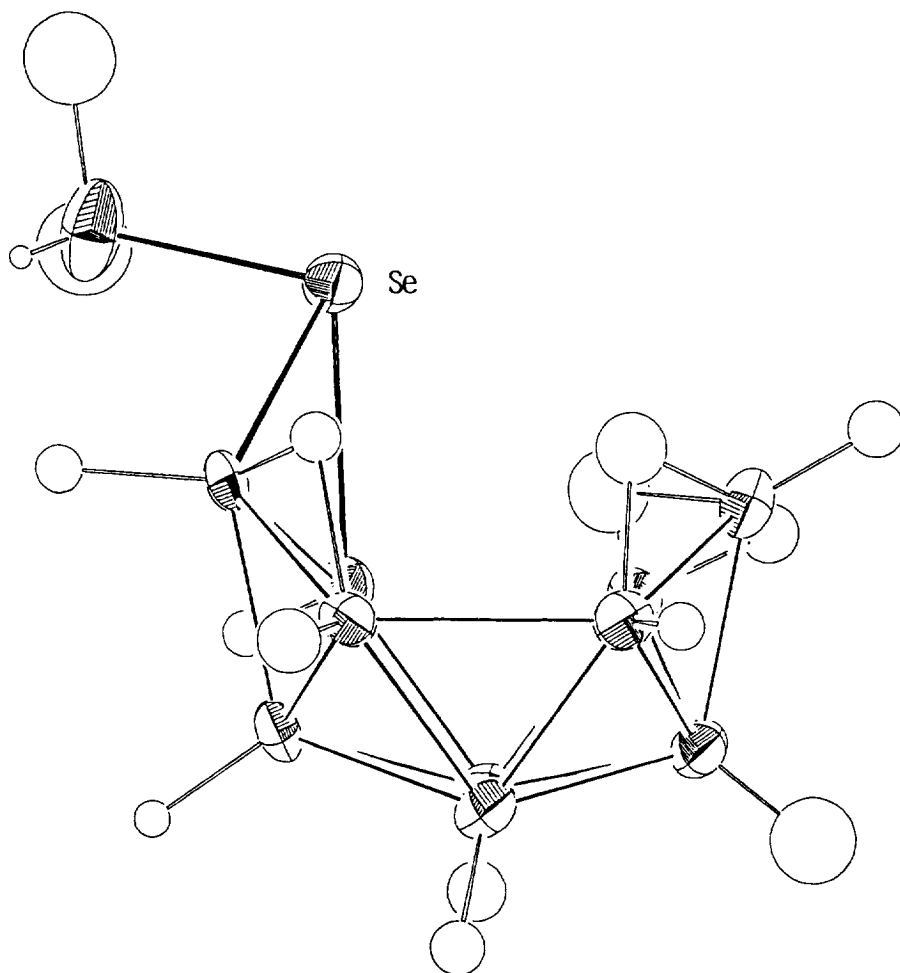


Fig. 44. Molecular structure of μ_2 -6,7- $\text{CH}_3\text{SeB}_{10}\text{H}_{13}$ **75b**.

is extremely resistant towards inorganic acids and their halogenides. This unusual stability towards action of agents that are apt of primarily attacking the anhydridic function of a molecule may be explained by the B–O–B bond as being effectively shielded by the bulky $\text{B}_{10}\text{H}_{13}$ -groups and, moreover, as being literally wrapped in the hydrogen bridges of both fragments.

12. Eleven-boron-atom systems

The compounds considered are polyhedral hetero boranes.

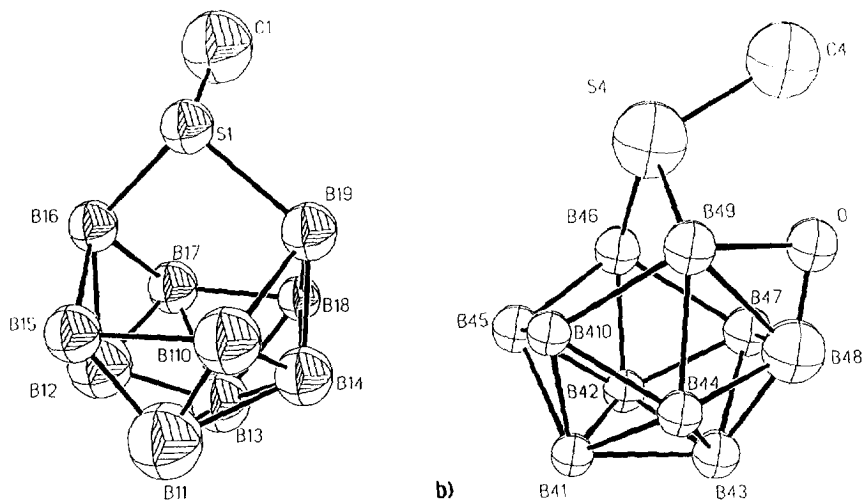
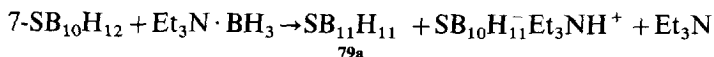


Fig. 45. (a) Molecular structures of the anion $[\mu_2-6,9-\text{CH}_3\text{SB}_{10}\text{H}_{11}]^-$ and (b) $[\mu_2-6,7-\text{OH}-\mu_2-6,9-\text{CH}_3\text{SB}_{10}\text{H}_{11}]^-$ from the "double salt": $\{\text{Cs}[\mu_2-6,9-\text{CH}_3\text{SB}_{10}\text{H}_{11}]\}_3 \cdot \text{Cs}[\mu_2-6,7-\text{OH}-\mu_2-6,9-\text{CH}_3\text{SB}_{10}\text{H}_{11}]$ **77a**.

12.1. *closo-SB₁₁H₁₁* **79a**, 12-Br-1-SB₁₁H₁₀ **79b**, *closo-B-C₆H₅SB₁₁H₁₀* **79c**, *closo-B,B'(C₆H₅)₂SB₁₁H₉* **79d**, *closo-SeB₁₁H₁₁* **79e**, *closo-TeB₁₁H₁₁* **79f**

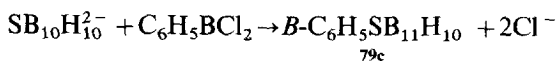
The reaction of 7-SB₁₀H₁₂ **69a** with Et₃N · BH₃ produced the parent compound *closo-SB₁₁H₁₁* **79a** [102]



Pyrolysis of 6-SB₉H₁₂[−] **67a** leads to *nido*-7-SB₁₀H₁₂ **69a**, which in turn gives *closo-SB₁₁H₁₁* **79a** upon pyrolysis [59]. The ¹¹B NMR spectrum has three doublets of relative intensities 1 : 5 : 5 and supports the proposed structure of **79a** (see Fig. 46). The influence of a sulfur heteroatom should be similar to that of a carbon and render the adjacent boron sites subject to nucleophilic attack.

The bromination of **79a** in methylene chloride in the presence of Al powder gave 12-Br-1-SB₁₁H₁₀ **79b**. The position of the bromine atom follows from the ¹¹B NMR spectrum, which indicates that the B12 atom is the most negative B atom in the molecule [102]. However, the initial halogenation of SB₁₁H₁₁ is analogous to that of 1-SB₉H₉ **50**. While the halogenation and deuteration of SB₁₁H₁₁ have not been studied thoroughly, the experiments in Ref. [73] indicate that the 1b is the site of initial substitution.

Phenylboron dichloride reacted with SB₁₀H₁₀^{2−} **73** to yield *B-closo-C₆H₅SB₁₁H₁₀* **79c** [77]. This material probably possesses icosahedral geometry with the phenyl substituent bound to a boron atom adjacent to sulfur.



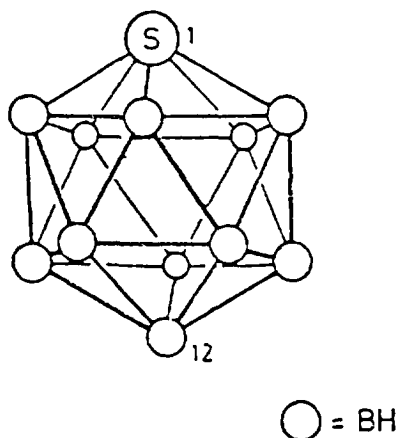


Fig. 46. Proposed structure of *closo*-SB₁₁H₁₁ **79a**. (From Ref. [102] by permission of The Royal Society of Chemistry, Cambridge).

The degradation of *B*-C₆H₅SB₁₁H₁₀ in methanolic sodium hydroxide produced *B*-C₆H₅SB₁₀H₁₀[−] ion. A *B,B'*-diphenyl derivative, *closo*-*B,B'*-(C₆H₅)₂SB₁₁H₉ **79d** was prepared by reacting *B*-C₆H₅SB₁₀H₁₀[−] with *n*-butyllithium followed by reaction with phenylboron dichloride [77]. The probable structures of the precursors, as well as the method of preparation, suggest, however, that the phenyl groups are attached to boron atoms vicinal to the sulfur atoms.

During the past few years a number of examples of insertion of nitrogen and sulfur units into borane and heteroatom borane cage structures by the use of NaNO₂ and KHSO₃ have been reported. The insertion of S, Se, or Te into borane cages has previously been accomplished by the use of polychalcogenido ions [77,88]. Reaction of NaB₁₁H₁₄ with an excess of NaHSeO₃ or solid TeO₂ in water–heptane under nitrogen produced *closo*-SeB₁₁H₁₁ **79e** or *closo*-TeB₁₁H₁₁ **79f** respectively [103]. Compounds **79e, f** have also been prepared by the reaction of SeB₁₀H₁₂ **69b** or TeB₁₀H₁₂ **69c** with Me₃N · BH₃ in refluxing xylenes [103]. The ¹¹B NMR spectra of **79e, f** are very similar to that reported previously for SB₁₁H₁₁ **79a** [102]. **79e, f** have *closo*, nearly-icosahedral cage structures.

12.2. *nido*-OB₁₁H₁₂[−] **80**

During the reaction of Et₄N⁺B₁₁H₁₄[−] with the oxides M₂O₃ (M=As, Sb, Bi), besides the expected icosahedral heteroboranes, a new anionic species was isolated, initially formulated as Et₄N⁺B₁₁H₁₃OH[−] [104,105]. However, on the basis of ¹H, ¹¹B and ¹⁷O NMR spectroscopy, the correct formulation is *nido*-OB₁₁H₁₂M⁺ **80** (M=Na, Et₄N, C₆H₅CH₂NEt₃). The proposed structure is shown in Fig. 47.

Interestingly, this anionic OB₁₁H₁₂[−] species appears as the first reported example of an oxaborane, the related oxaborane clusters always including an additional transition metal such as Fe or Rh [106,107] in the cage. Further, the reaction of

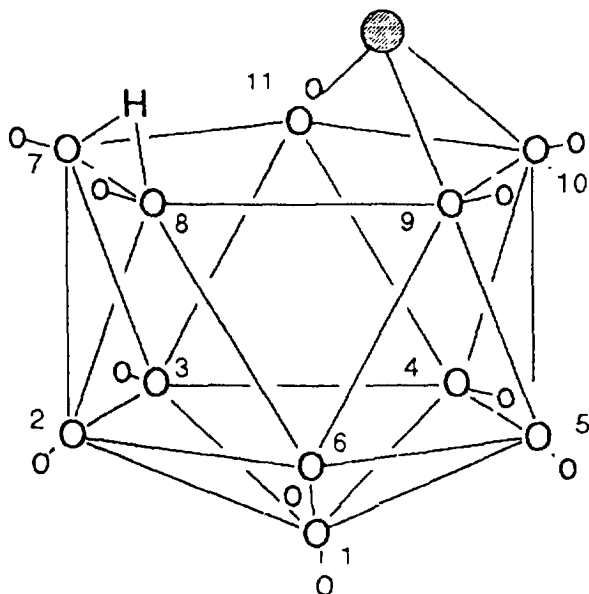


Fig. 47. Proposed structure of *nido*-OB₁₁H₁₂M⁺ **80** (M = Na, Et₄N, C₆H₅CH₂NEt₃).

methanol with MeNB₁₁H₁₁ was recently shown to lead to the anionic MeNB₁₁H₁₁OMe[−] [108] which is isoelectronic with OB₁₁H₁₂[−].

13. Twelve-boron-atom systems

The compounds considered are exo-substituted polyhedral boranes.

13.1. closo-B₁₂H₁₁SH^{2−} 81a, closo-B₁₂H₁₁SCH₃^{2−} 81b, closo-B₁₂H₁₀(SCH₃)₂^{2−} 81c, closo-B₁₂H₉(SCH₃)₃^{2−} 81d, closo-B₁₂H₁₁S(CH₃)₂[−] 81e, closo-B₁₂H₁₀[S(CH₃)₂]₂ 81f

B₁₂H₁₂^{2−} reacts under acidic conditions with a number of sulfur-containing species to form substitution derivatives. B₁₂H₁₁SH^{2−} **81a** can be prepared from (H₃O)₂B₁₂H₁₂ and hydrogen sulfide. Dimethyldisulfide reacts with (H₃O)₂B₁₂H₁₂ to give B₁₂H₁₁SCH₃^{2−} **81b** or B₁₂H₁₀(SCH₃)₂^{2−} **81c** and B₁₂H₉(SCH₃)₃^{2−} **81d**, depending on reaction conditions. Transmethylation of trimethylsulfonium iodide with B₁₂H₁₁SCH₃^{2−} and B₁₂H₁₀(SCH₃)₂^{2−} gives the inner sulfonium salts B₁₂H₁₁S(CH₃)₂[−] **81e** and B₁₂H₁₀[S(CH₃)₂]₂ **81f**. B₁₂H₁₁S(CH₃)₂[−] **81e** can also be obtained by methylation of B₁₂H₁₁SH^{2−} [109].

13.2. $(Cs^+)_4[H_{11}B_{12}-S-S-B_{12}H_{11}]$ **82a**; radicals:
 $B_{12}H_{11}S^{\cdot 2-}$ **82b** or $B_{12}H_{11}SH^{\cdot -}$ **82c**

The formation of the disulfide-linked tetravalent anion $H_{11}B_{12}-S-S-B_{12}H_{11}^{4-}$ **82a** by the oxidation of *closo*- $B_{12}H_{11}SH^{2-}$ **81a** with iodosobenzoate is supported by both chemical and spectral evidence [110]. The ^{11}B NMR spectrum showed a singlet of area 1 corresponding to the sulfur-bound boron, two doublets of area 5 and a doublet of area 1, all of which appeared as singlets on hydrogen decoupling. $H_{11}B_{12}-S-S-B_{12}H_{11}^{4-}$ is of particular interest in the neutron-capture therapy of gliomas as it possess favorable biological properties [111–113].

The rapid appearance of a free radical upon adding the disulfide $(Na^+)_4[H_{11}B_{12}-S-S-B_{12}H_{11}]$ **82a**, but not the thiol, $Na_2B_{12}H_{11}SH$ **81a**, to acidified solvents clearly indicates that the free-radical $B_{12}H_{11}SH^{\cdot -}$ **82c** formation is dependent on the presence of the disulfide linkage. It is suggested that either a thiyl

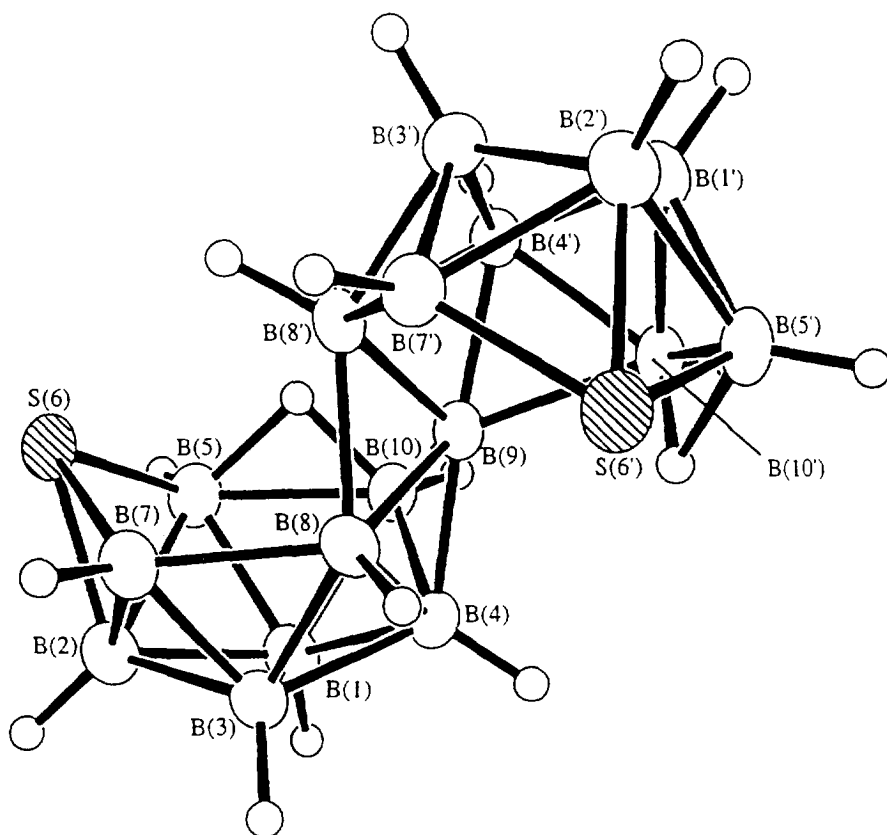


Fig. 48. ORTEP-type drawing of the molecular structure of the *arachno*- $[9,9'-S_2B_{17}H_{18}]^-$ anion in $Ph_4P^+[9,9'-S_2B_{17}H_{18}]^-$ **83**. (From Ref. [114] by permission of VCH Verlagsgesellschaft mbH, Weinheim.

radical, $B_{12}H_{11}S^{\cdot 2-}$ **82b**, or a thiol radical, $B_{12}H_{11}SH^{\cdot -}$ **82c**, is formed from the disulfide $H_{11}B_{12}-S-S-B_{12}H_{11}^{4-}$ in acidified organic solvents.

14. Seventeen-boron-atom system

A macropolyhedral thiaborane

14.1. *arachno*-[9,9'- $S_2B_{17}H_{18}$] $^-$ **83**

An interesting expansion of the scope of borane chemistry is the linkage of various clusters to form 'polypolyhedra'. The unprecedented macropolyhedral dithiaborane anion $S_2B_{17}H_{18}^-$ **83** (19-vertex) was recently synthesized and structurally characterized [114].

83 is the first structurally characterized macropolyhedral heteroborane, and it also demonstrates for the first time a mode by which two *arachno*-type subclusters may fuse to form a macropolyhedral boron-atom agglomeration. Previous macropolyhedrals have been limited to fusions among *nido*- and *closo*-type clusters. The $S_2B_{17}H_{18}^-$ anion, isolated in 48% yield as its Ph_4P^+ salt, is obtained by the action of elemental sulfur on a solution in THF of the *anti*- $B_{18}H_{20}^{2-}$ anion, followed by chromatographic separation of the products. It was identified and characterized by X-ray diffraction analysis (Fig. 48) and NMR spectroscopy.

The structure of the $S_2B_{17}H_{18}^-$ anion derives formally from the fusion, with two

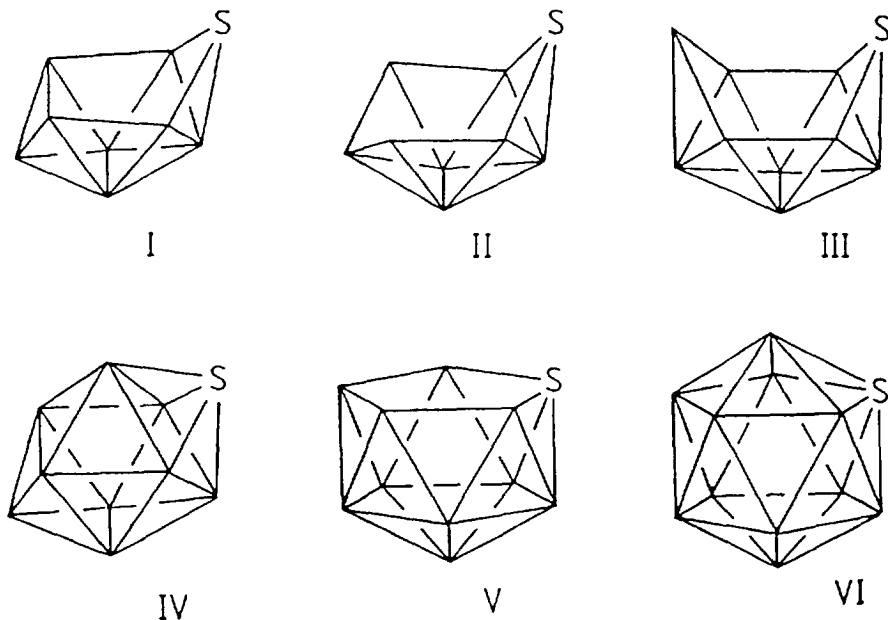


Fig. 49. Structures I–VI. (From Ref. [114] by permission of VCH Verlagsgesellschaft mbH, Weinheim).

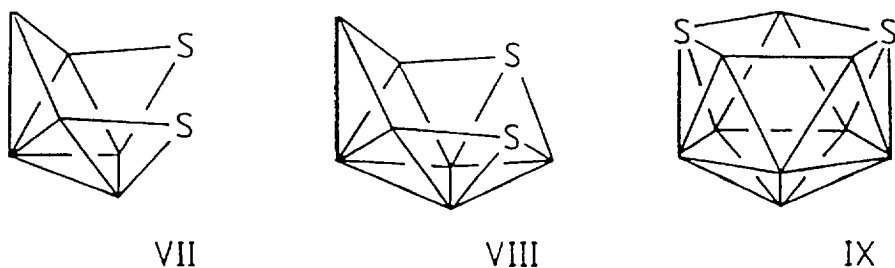


Fig. 50. Structures VII–IX. (From Ref. [114] by permission of VCH Verlagsgesellschaft mbH, Weinheim).

common vertices, between a ten-vertex *arachno*- $\{\text{SB}_9\}$ cluster and an 11-vertex *arachno*- $\{\text{SB}_{10}\}$ cluster.

15. Conclusions

The known and potential structural variety of polyhedral boron hydride chemistry is extensive. In principle this variety is also available to any combinations of main group elements that have the same numbers of valence electrons available. However, heteroborane chemistry, other than that of the carbaboranes (particularly that of the dicarbaboranes, which exceeds that of the boranes themselves), is surprisingly limited. Apart from the carbaboranes, the best-exemplified and most diverse main-group polyhedral heteroborane chemistry is that of the thiaboranes [114].

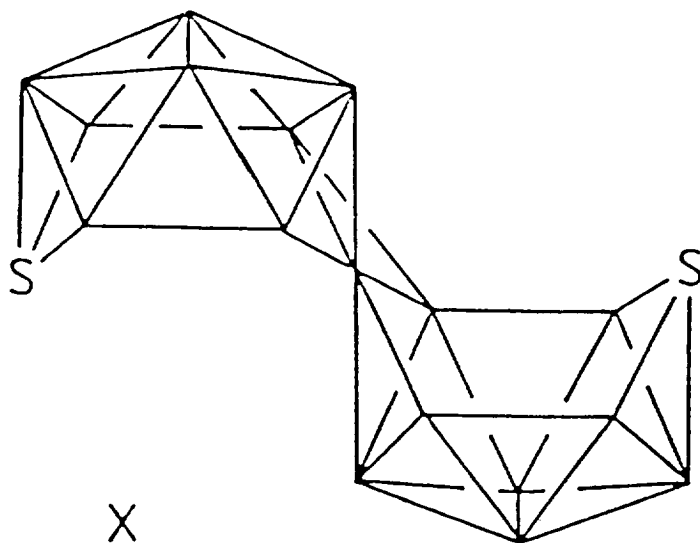


Fig. 51. Structure X. (From Ref. [114] by permission of VCH Verlagsgesellschaft mbH, Weinheim).

However, only six basic contiguous monothaborane building blocks are available (schematic cluster geometries I–VI) Fig. 49.

These comprise the nine-vertex *nido*- and *arachno*-{SB₈} system (I and II respectively), the ten-vertex *closo*-{SB₉} system IV, the ten-vertex *nido*- and *arachno*-{SB₉} (both of gross geometry III), the 11-vertex *nido*-{SB₁₀} system (V), and the 12-vertex *closo*-{SB₁₁} system (VI).

In contrast to the very extensive known dicarbaborane chemistry, only three dithaborane building blocks (schematic geometries VII–IX) are currently reported. These comprise the eight-vertex *hypho*-{S₂B₆} system (VII), the nine-vertex *arachno*-{S₂B₇} system (VIII), and the 11-vertex *nido*-{S₂B₉} system (IX) (Fig. 50).

The schematic cluster connectivity of the presently unique large 19-vertex {S₂B₁₇} system is outlined as in (X) (Fig. 51).

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