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Chalcogeno boron hydrides

Herbert Binder *, Martin Hein

Institut für Anorganische Chemie der Universität Stuttgart, Pfaffenwaldring 55,
D-70569 Stuttgart, Germany

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* Corresponding author.

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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.

Keywords: Boron hydride; Chalcogeno boron hydrides

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1. Introduction

The spectacular growth of metallaborane and metallacarbaborane 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-RSB_2H_5 possesses an alkyl (aryl) chalcogeno group which can be considered as an endo-group replacing one *endo*-hydrogen atom in B_2H_6. 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 ± 40 cm^{-1} [12].

2.3. $(CH_2S)_2BH$ 3

Reactions of diborane with ethanedithiol lead to $(CH_2S)_2BH$ **3** which is a monomer only in the vapor phase [13].

2.4. $H_3B\text{–}S(CH_3)_2$ 4, $R_2S\text{–}BH_2$ 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 $H_3B\text{–}S(CH_3)_2$ **4** [14,15] which is commercially available. It can be handled more easily and safely than B_2H_6.

Hydrogen atom abstraction from $R_2S\text{–}BH_3$ ($R=CH_3$, C_2H_5) by $(CH_3)_3CO^{\cdot}$ and or $[(CH_3)_3Si]_2N^{\cdot}$ and radicals gives the $R_2S\text{–}BH_2^{\cdot}$ and radicals **4a**, the structures and reactions of which were studied in solution using EPR spectroscopy [15].

2.5. $[N(C_2H_5)_4][(BH_3)_2SH]$ 5, $K[(BH_3)_2SC_2H_5]$ 6

Hydrogen sulfide and alkyl sulfide ions form bisborane adducts $(BH_3)_2L^-$ [16–19].

$$B_2H_6+[N(C_2H_5)_4]SH \rightarrow \underset{\mathbf{5}}{[N(C_2H_5)_4][(BH_3)_2SH]}$$

$$B_2H_6+KSC_2H_5 \rightarrow \underset{\mathbf{6}}{K[(BH_3)_2SC_2H_5]}$$

5 decomposes above −78 °C [18].

2.6. $[Na\cdot Triglyme]_2[S(BH_3)_4]$ 7

Adducts of BH_3 with the S^{2-} ion are not detectable in THF by ^{11}B NMR spectroscopy. The anion $[S(BH_3)_4]^{2-}$ **7** can, however, be obtained by the addition of $NaBH_4$ to $Na[H_3B\text{-}\mu_2\text{-}S(B_2H_5)]$ **21** [20] in diglyme or triglyme, respectively.

$$Na[H_3B\text{-}\mu_2\text{-}S(B_2H_5)]+NaBH_4 \xrightleftharpoons[\text{1,2-dichlorethane}]{\text{triglyme}} \underset{\mathbf{7}}{[Na\cdot Triglyme]_2[S(BH_3)_4]}$$

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).

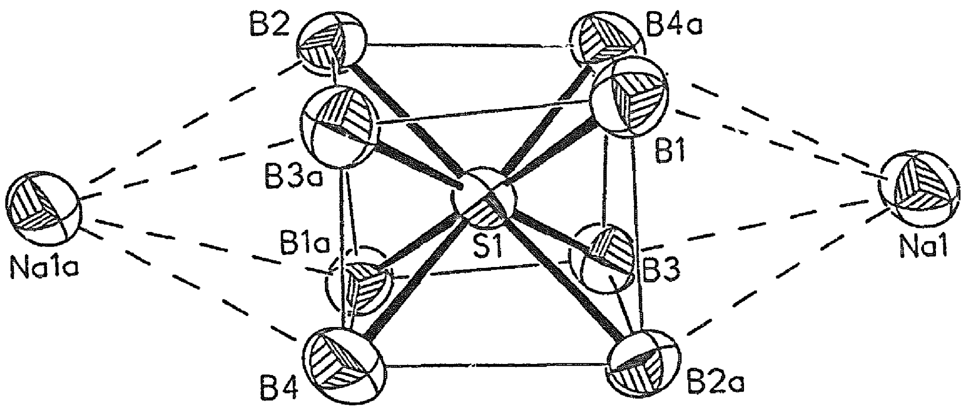


Fig. 1. Disordered, distorted cubic environment of the sulfur atom in $[S(BH_3)_4]^{2-}$ **7**. (From Ref. [20] by permission of Hüthig-Fachverlage, Heidelberg).

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.

$$\tfrac{2}{x}Se_x + 2BH_4^- \rightarrow \underset{11}{[H_3B\text{-}Se\text{-}Se\text{-}BH_3]^{2-}} + H_2$$

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

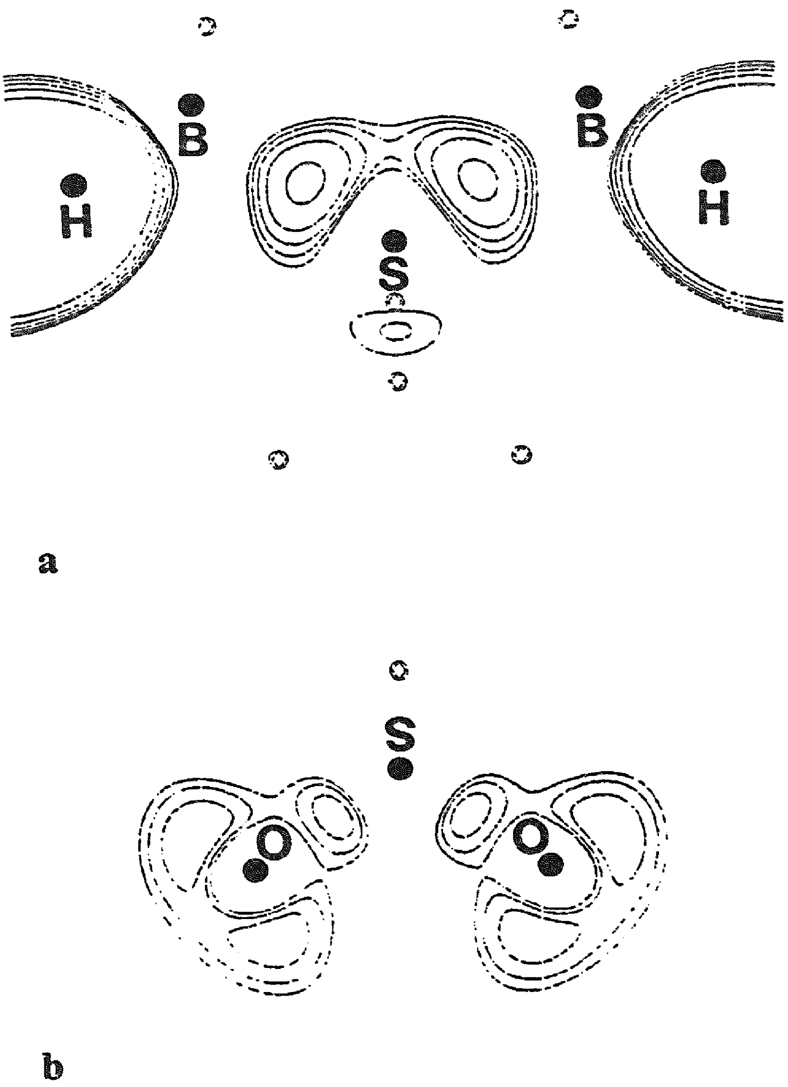


Fig. 2. (a) Contour plot of electron localization function (ELF) in the B–S–B plane of the $[S(BH_3)_4]^{2-}$ anion **7**; the lines represent the values 0.75, 0.8, 0.85, 0.9, and 0.95. (b) Contour plot of ELF in the O–S–O plane of Na_2SO_4; the lines represent the values 0.75, 0.8, 0 85, 0.9, and 0.95. (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)$_2B_2H_4$ 14, μ_4-S(B_2H_5)$_2$ 15

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

The μ_2-HS(B_2H_5) 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(B_2H_5) has also been obtained by CO_2-laser irradiation of a gaseous mixture of B_2H_6 and H_2S [4]. The structure of **12** has been determined by SCF calculations [30] (Fig. 3).

The new and unstable compounds $1\lambda^3,3\lambda^3,2\lambda^4,4\lambda^4$-dithiadiboretane $(H_2BSH)_2$ **13**, the isomer 1,2-dimercaptodiborane 1,2-$(HS)_2B_2H_4$ **14**, μ_4-thiabis(diborane) μ_4-S$(B_2H_5)_2$ **15**, as well as HB$(SH)_2$ **1** and μ_2-HS(B_2H_5) **12** are formed in the reaction of B_2H_6 and H_2S, 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 (C_2) (Fig. 5); the BSB unit in μ_2-HS(B_2H_5) **12** and μ_4-S$(B_2H_5)_2$ **15**, has some central or open three-center character.

3.2. μ_2-RS(B_2H_5) 16

There are relatively few alkylthio derivatives of the simpler boron hydrides. The first to be reported was μ_2-$CH_3SB_2H_5$ [31]. The alkylthia group is shown to occupy exclusively a bridging position in μ_2-RS(B_2H_5) **16**, (R = CH_3, C_2H_5, n-C_4H_9) [32,33].

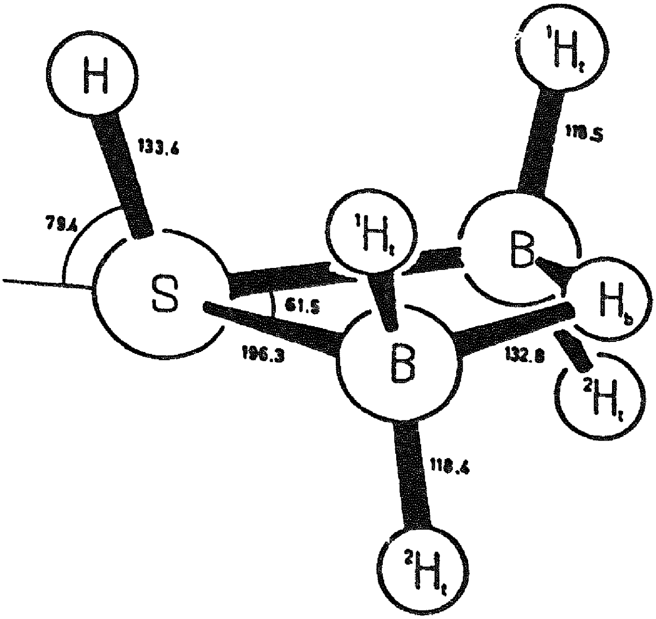


Fig. 3. Calculated structure of μ_2-HS(B_2H_5) 12, (C_s). (From Ref. [30] by permission of VCH Verlagsgesellschaft mbH, Weinheim).

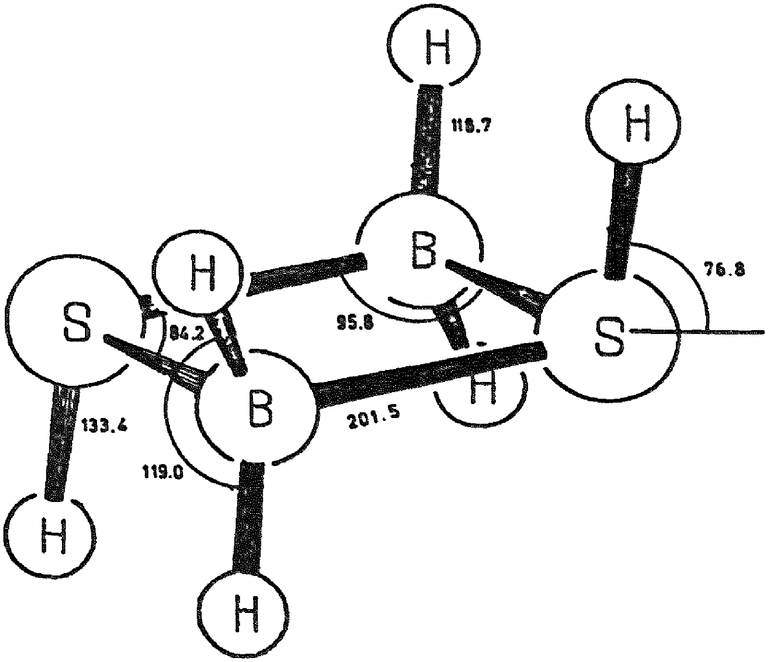
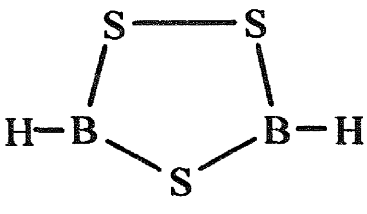


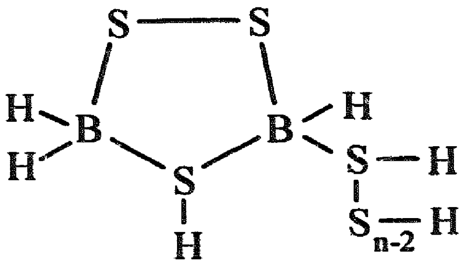
Fig. 4. Calculated structure of $(HSBH_2)_2$ **13**, (C_{2h}). The four-membered ring SBSB is planar. (From Ref. [30] by permission of VCH Verlagsgesellschaft mbH, Weinheim).

3.3. $H_2B_2S_3$ 17, $H_2B_2S_4$ 18

Two routes are now available for the preparation of the parent compound 1,2,4,3,5-trithiadiborolane $H_2B_2S_3$ **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 $H_2B_2S_3$. 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 $H_2B_2S_3$ which are stable on standing at 0 °C. The concentrations of $H_2B_2S_3$ should not be greater than 0.5 M because of its propensity to dimerize or to form oligomers which are slightly soluble. $H_2B_2S_4$ **18** is a by-product which was detected by mass spectrometry.

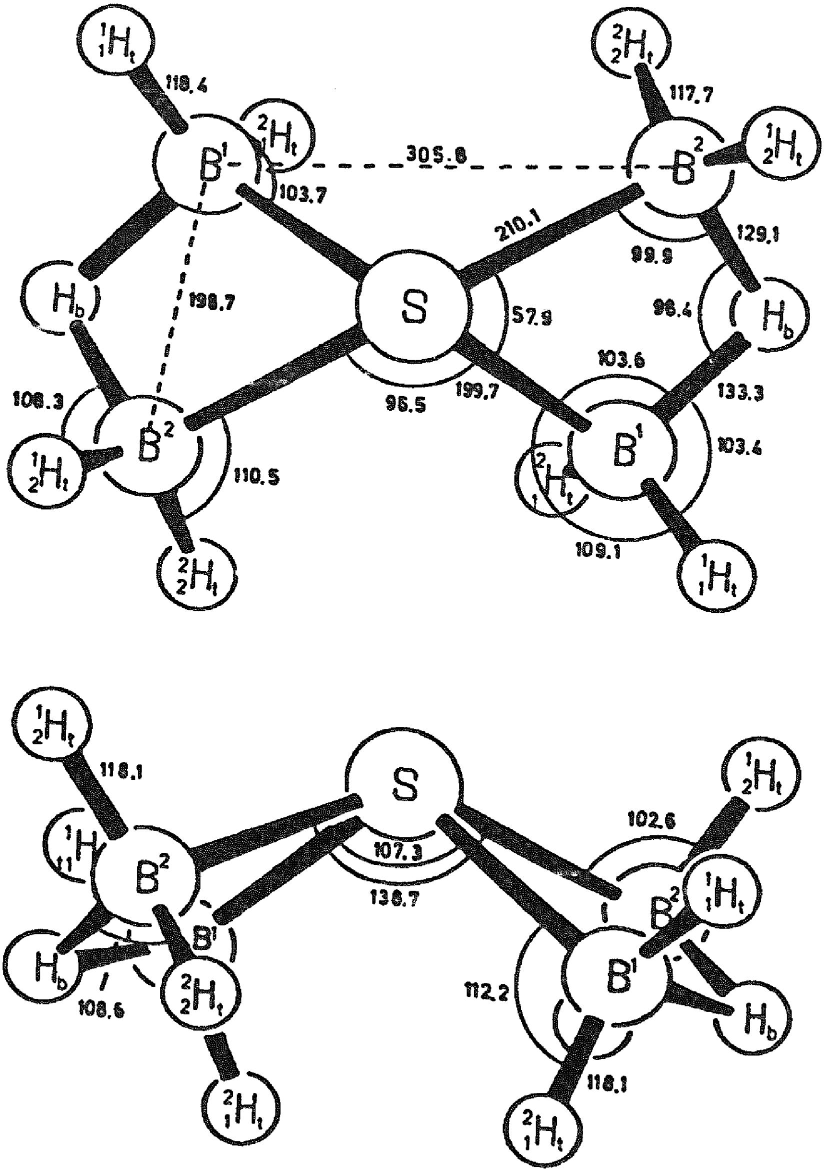


Fig. 5. Calculated structure of μ_4-S$(B_2H_5)_2$ **15**, (C_2). (From Ref. [30] by permission of VCH Verlagsgesellschaft mbH, Weinheim).

$H_2B_2S_3$ **17** has been synthesized for the first time by the ligand exchange reaction: $[(CH_3)_2N]_2B_2S_3$/9-BBN [35]. $H_2B_2S_3$ is a reactive hydroboration agent. Monohydroboration 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. $[CH_2(SCH_3)(BH)_2]_2$ **19**, $H_2B{-}S{-}S{-}BH_2$ **19a**

The compound $[CH_2(SCH_3)(BH)_2]_2$ **19** has been prepared from $(CH_3)_3N{-}BH_2{-}CH_2{-}SCH_3$ 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 $H_2B{-}S{-}S{-}BH_2$ **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. $THF{-}BH_2{-}\mu_2{-}S(B_2H_5)$ 20

A chalcogeno derivative of triborane(7) $THF{-}BH_2{-}\mu_2{-}S(B_2H_5)$ **20** is formed when $\mu_4{-}S(B_2H_5)_2$ **15** interacts with tetrahydrofurane, the following equilibrium operates [30]:

$$\underset{\mathbf{15}}{\mu_4-S(B_2H_5)_2} + THF \rightleftarrows \underset{\mathbf{20}}{THF{-}BH_2{-}\mu_2{-}S(B_2H_5)} + THF\cdot BH_3$$

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

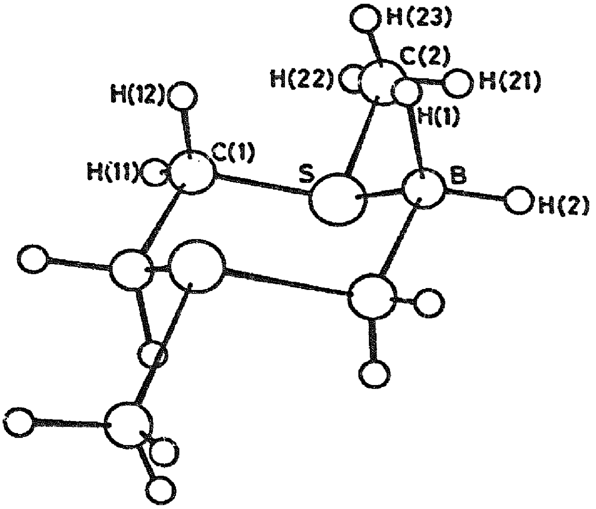


Fig. 6. Structure of $[CH_2(SCH_3)(BH)_2]_2$ **19**.

4.2. $Na[H_3B\text{-}\mu\text{-}S(B_2H_5)]$ **21**

The octahydrotriborate derivative $Na[H_3B\text{-}\mu_2\text{-}S(B_2H_5)]$ **21** is produced by the reaction between anhydrous NaSH and $THF \cdot BH_3$, under dehydrogenation [20].

$$THF \cdot BH_3 + SH^- \rightarrow [H_2B\text{–}S]^- + H_2$$

$$[H_2B\text{–}S]^- + 2THF \cdot BH_3 \rightarrow \underset{\mathbf{21}}{[H_3B\text{-}\mu_2\text{-}S(B_2H_5)]^-}$$

21 is also formed as the first ^{11}B NMR spectroscopically detectable reaction product by the reaction between anhydrous Na_2S and $THF \cdot BH_3$ [20]

$$S^{2-} + 3THF \cdot BH_3 \rightarrow [S(BH_3)_3]^{2-} \rightarrow [S(B_2H_5)]^- + BH_4^-$$

$$[S(B_2H_5)]^- + THF \cdot BH_3 \rightarrow \underset{\mathbf{21}}{[H_3B\text{-}\mu_2\text{-}S(B_2H_5)]^-}$$

Treatment of $THF \cdot BH_3/MBH_4$ (2 : 1) with H_2S results both in formation of **21** and hydrogen evolution [25].

$$2THF \cdot BH_3 + MBH_4 + H_2S \rightarrow \underset{\mathbf{21}}{M[H_3B\text{-}\mu_2\text{-}S(B_2H_5)]} + 2H_2 + 2THF$$

$$M = Li^+, Na^+, Ph_4P^+$$

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. $[H_3B\text{-}\mu_2\text{-}Se(B_2H_5)]^-$ **22**

The corresponding selenium compound $[H_3B\text{-}\mu_2\text{-}Se(B_2H_5)]^-$ **22** can readily be prepared by the reaction between $[H_3B\text{–}Se\text{–}Se\text{–}BH_3]^{2-}$ **11** and B_2H_6 or

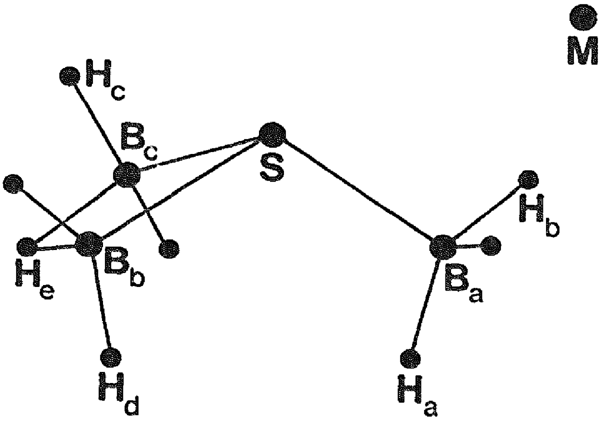


Fig. 7. Calculated structure of $M[H_3B\text{-}\mu_2\text{-}S(B_2H_5)]$ **21**. (From Ref. [20] by permission of Hüthig-Fachverlage, Heidelberg).

THF · BH_3 [28].

$$\underset{11}{[H_3B\text{–}Se\text{–}Se\text{–}BH_3]^{2-}} + 2B_2H_6 \rightarrow 2\underset{22}{[H_3B\text{-}\mu_2\text{-}Se(B_2H_5)]^-} + H_2$$

An X-ray structure determination of $[(C_6H_5)_4P][H_3B\text{-}\mu_2\text{-}Se(B_2H_5)]$ failed because of disordering of the cation and anion. ^{11}B and ^{77}Se 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_e 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. $[C_2H_5SBH_2]_3$ **23a**, $[^tBuSBH_2]_3$ **23b***

Reaction of diborane(6) and ethanethiol in a 1 : 2 ratio followed by short-path distillation at 50 °C gives the fluid trimer $[C_2H_5SBH_2]_3$ **23**) [32]. Compounds of this type can be considered as derivatives of the hypothetical B_3H_9 in which the alkylthio groups are shown to occupy exclusively bridging positions. The identity of $[C_2H_5SBH_2]_3$ was established by analysis and molecular weight determinations.

$[^tBuSBH_2]_3$ **23b** (prepared by the reaction of THF · BH_3 with ^tBuSH) is the only colorless solid alkylthioborane which can be sublimed, m.p. 104 °C [40].

*4.5. $[B_3S_2H_6]^-$ **24***

The anion $[B_3S_2H_6]^-$ **24** was reported to be formed when $LiBH_4$ reacts with sulfur in ether solution [41]. However, further experimental work is required in order to characterize more fully this borane.

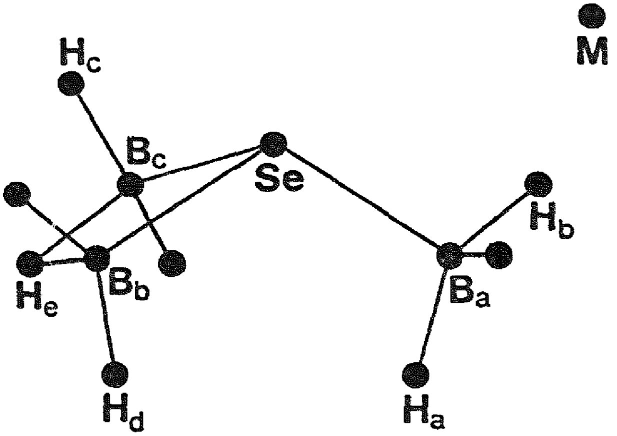


Fig. 8. Calculated structure of $M[H_3B\text{-}\mu_2\text{-}Se(B_2H_5)]$ **22**. (From Ref. [28] by permission of Hüthig-Fachverlage, Heidelberg).

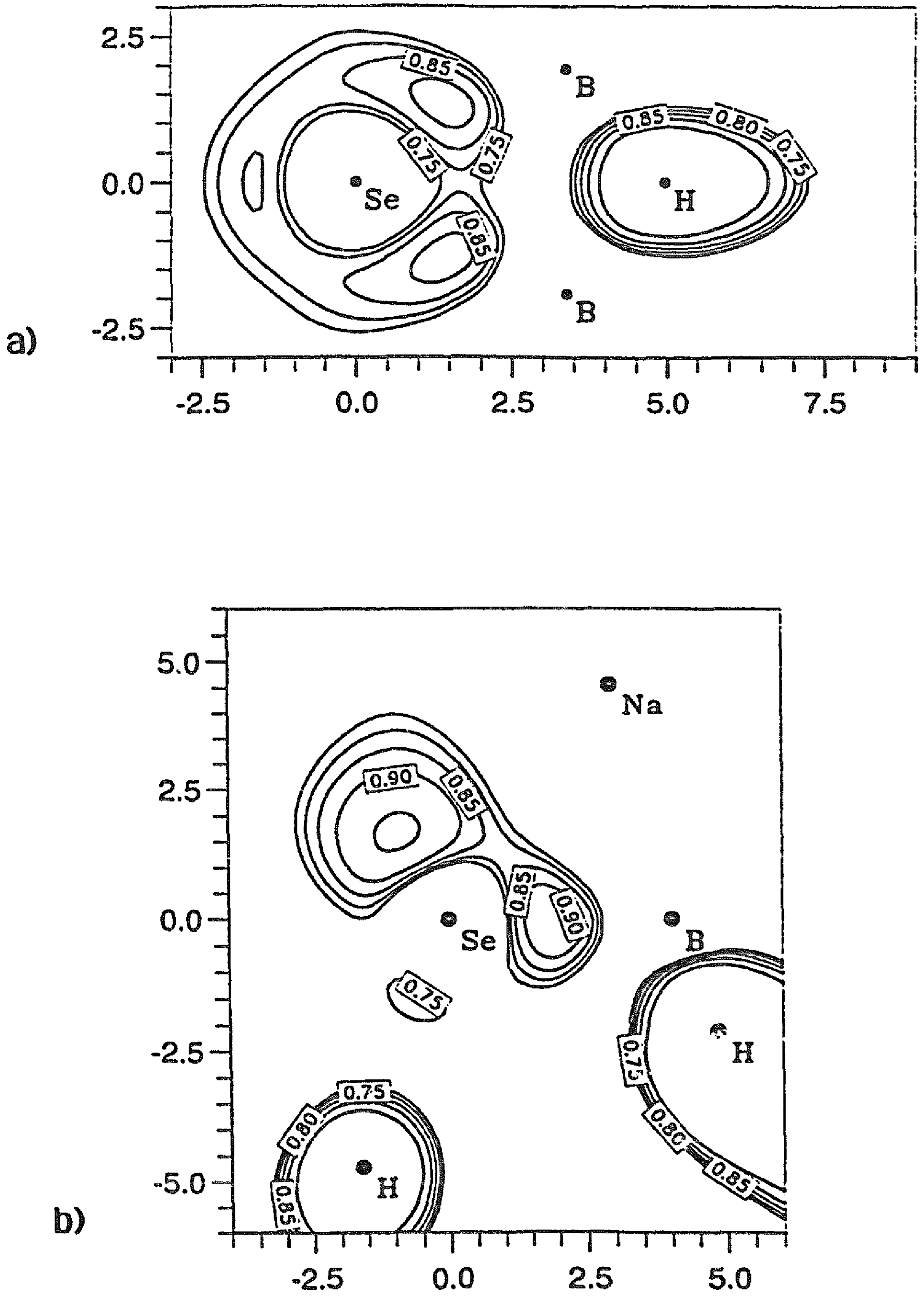


Fig. 9. (a) Contour plot of ELF in the plane $SeB_bB_cH_c$ of $Na[H_3B\text{-}\mu_2\text{-}Se(B_2H_5)]$ 22 (cf. Fig. 8); the lines represent the values 0.75, 0.8, 0.85, 0.9, and 0.95. (b) Contour plot of ELF in the plane SeB_aNa of $Na[H_3B\text{-}\mu_2\text{-}Se(B_2H_5)]$ 22; the lines represent the 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. $H_2B(\mu_2\text{-}SR)_2B_3H_6$ 27

B_4H_{10} reacts with mercaptans by splitting off H_2 to form $H_2B(\mu_2\text{-}SR)_2B_3H_6$ **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 °C, indicating a rapid inversion. On cooling however, the exo–exo, endo–endo and exo–endo invertomers were detected, Fig. 10, Scheme 1 [44].

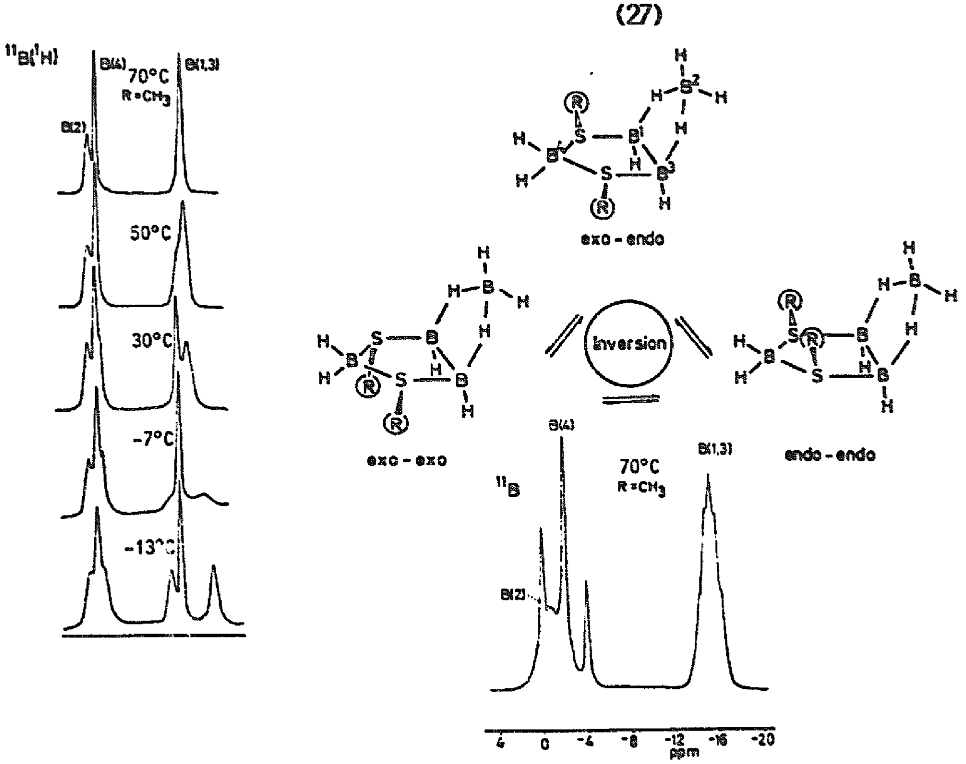
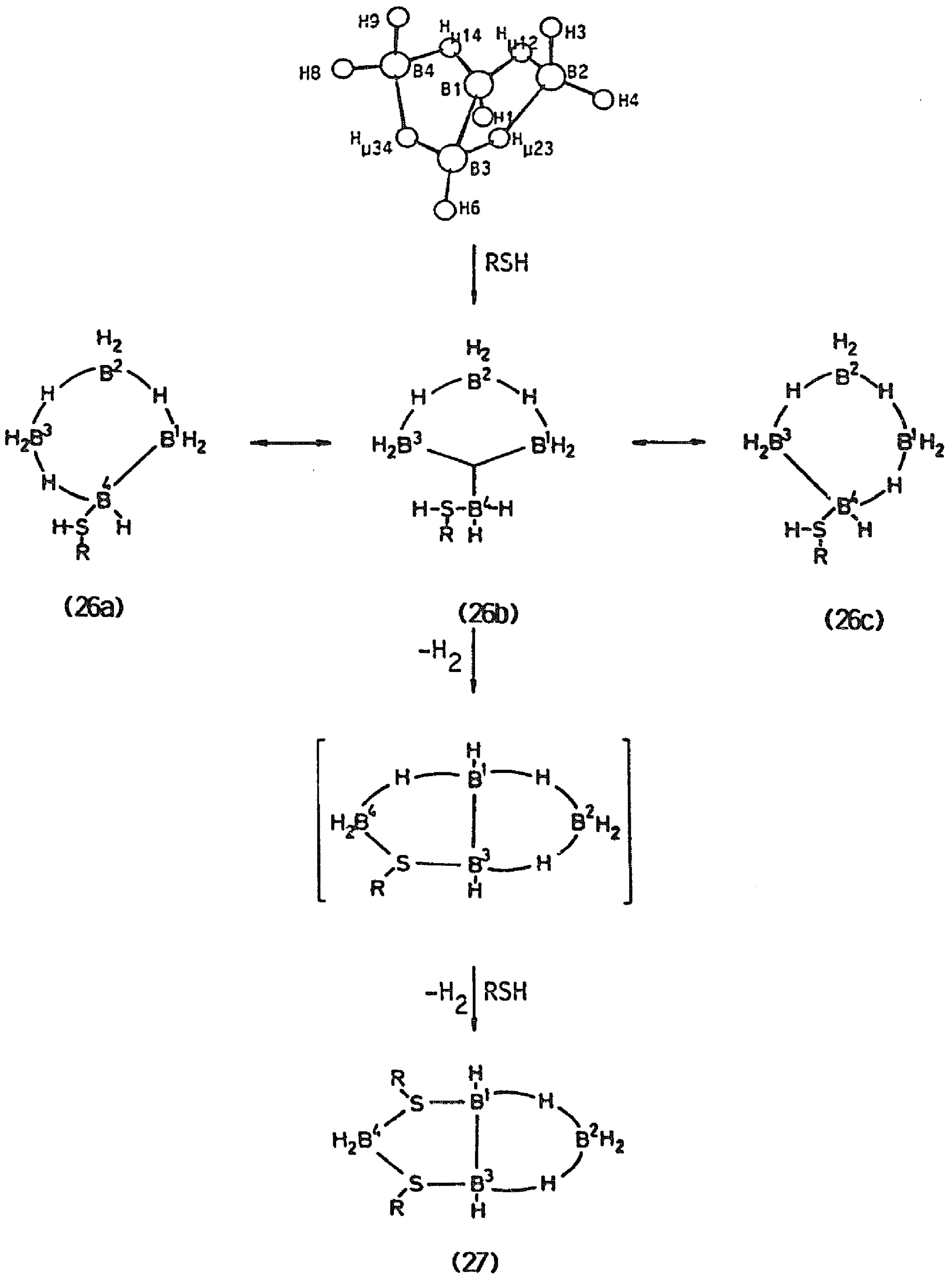


Fig. 10. ^{11}B and $^{11}B\{^1H\}$ NMR spectra of $H_2B(\mu_2\text{-}SR)_2B_3H_6$ **27** for a range of temperature.


H9
Hμ14
Hμ12
H3
H8
B4
B1
B2
H4
H1
Hμ34
Hμ23
B3
H6
RSH
(26a)
(26b)
(26c)
-H2
-H2
RSH
(27)

Scheme 1.

With the ^{11}B spectral data it is possible to calculate the activation energy for inversion in **27**, ($E_a \approx 12.8$–13.3 kcal mol^{-1}; $R=CH_3$, C_2H_5, ^{i}Pr, ^{t}Bu, C_6H_5)).

There was no evidence for the formation of either of the isomers in which $H_{\mu14}$, $H_{\mu12}$ or $H_{\mu14}$, $H_{\mu23}$ was replaced by RS groups.

5.2. $H_2(\mu)_2S_2RBH(B_2H_5)$ 28

B_4H_{10} reacts with bifunctional thiols to give transannularly bridged $H_2(\mu)_2S_2RBH(B_2H_5)$ **28** which exist as cis–trans isomers [bis(diboranyl) structure]; on cooling these compounds rearrange to *cis–trans*-$H_2B(\mu)_2S_2RB_3H_6$ **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 $(B_2H_5)_2$ into the known 'butterfly' structure of B_4H_{10} is realistic [46].

5.3. $[CH_2(SBH_2)_2]_2$ 30

The structure of the cage compound $[CH_2(SBH_2)_2]_2$ **30** (with the adamantane skeleton $C_2B_4S_4$) is shown in Fig. 11, [47]. The crystal structure was determined by X-ray diffraction.

The compound has been obtained from CS_2 and $THF \cdot BH_3$ after 3 weeks, or by the action of methanedithiole on $THF \cdot BH_3$ or $THF \cdot BH_2Cl$.

$$2THF \cdot BH_3 + CS_2 \rightarrow \tfrac{1}{2}\underset{\mathbf{30}}{[H_2B\text{–}S\text{–}CH_2\text{–}S\text{–}BH_2]_2} + 2THF$$

$$2THF \cdot BH_3 + HS\text{–}CH_2\text{–}SH \rightarrow \tfrac{1}{2}\underset{\mathbf{30}}{[H_2B\text{–}S\text{–}CH_2\text{–}S\text{–}BH_2]_2} + 2H_2 + 2THF$$

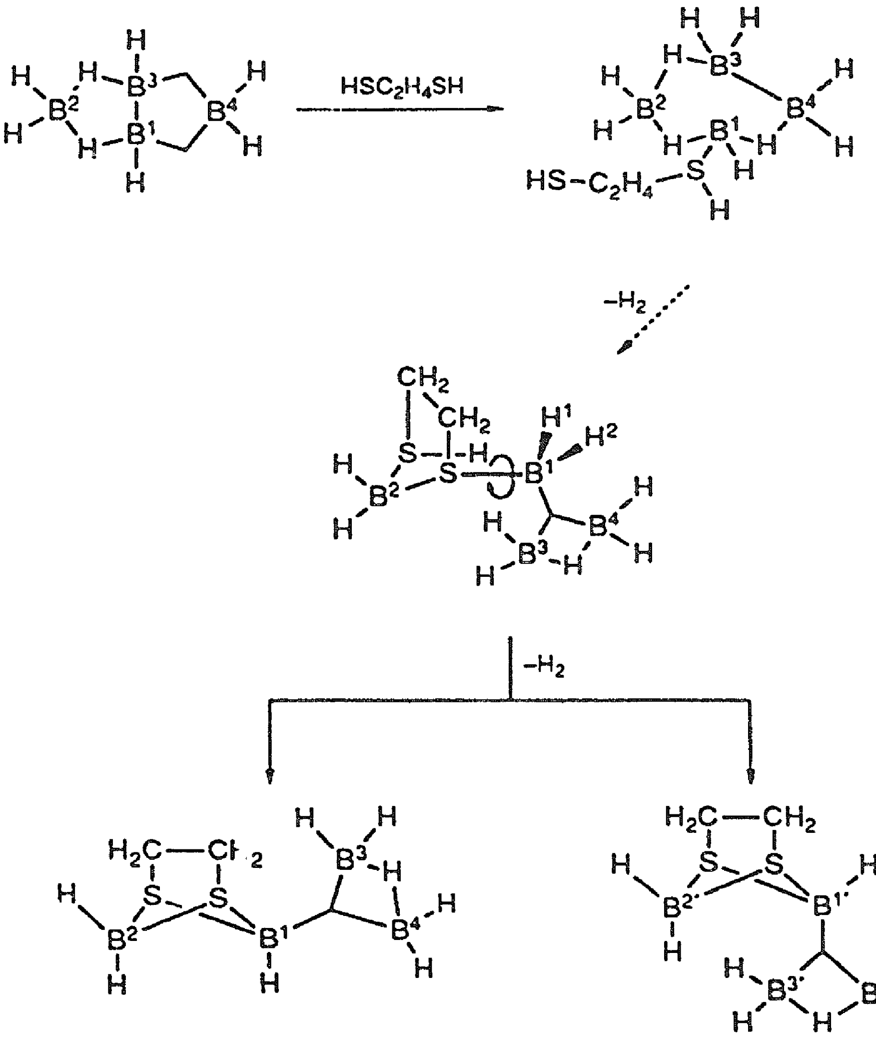
$$2THF \cdot BH_2Cl + HS\text{–}CH_2\text{–}SH \rightarrow \tfrac{1}{2}\underset{\mathbf{30}}{[H_2B\text{–}S\text{–}CH_2\text{–}S\text{–}BH_2]_2} + 2HCl + 2THF$$

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. $Na[CH_2B_5H_{10}S_4] \cdot 3dioxane$ 31

Hydroboration of CS_2 with $Na[B_3H_8]$ yields the sodium salt $Na[CH_2B_5H_{10}S_4] \cdot 3$dioxane **31**, isolated as the tris dioxane adduct; **31** is a novel



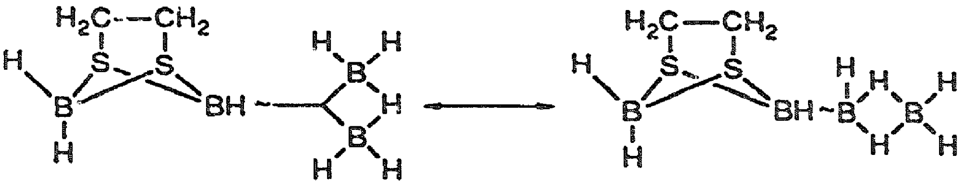
(28-cis)

(28-trans)

Scheme 2.

boron-containing anion with the adamantane skeleton CB_5S_4 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 $[(C_6H_5)_4P]^+$ salt has been determined by X-ray diffraction.

The B–B bond from the $B_3H_8^-$ 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.

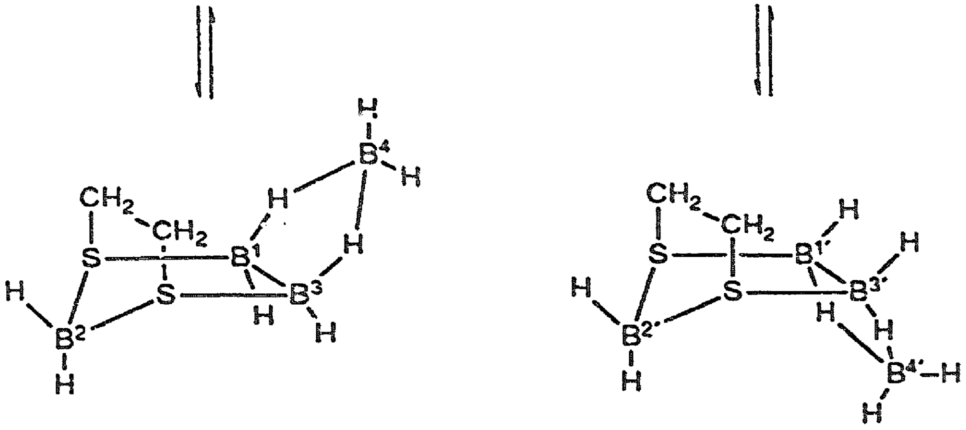


(28)

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 $[H_3B\text{-}\mu_2\text{-}S(B_2H_5)]^-$ **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 $[H_3B\text{-}\mu_2\text{-}S(B_2H_5)]^-$ **21** to $H_2B_2S_3$ **17** (Scheme 7).

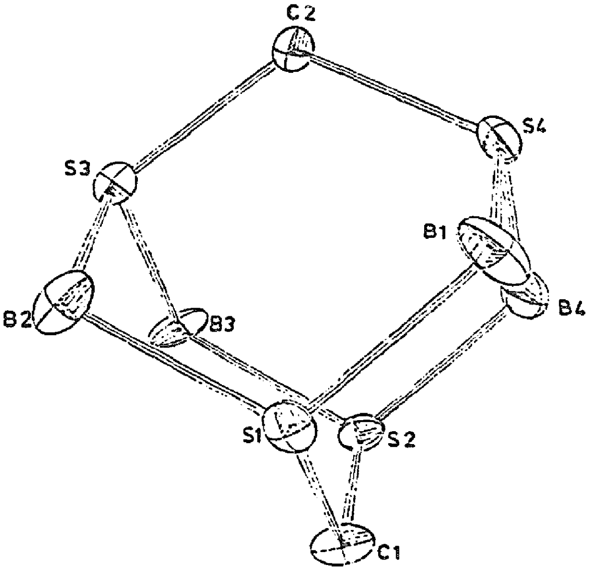


Fig. 11. Structure of $[CH_2(SBH_2)_2]_2$ **30**. (From Ref. [47] by permission of Verlag der Zeitschrift für Naturforschung, Tübingen).

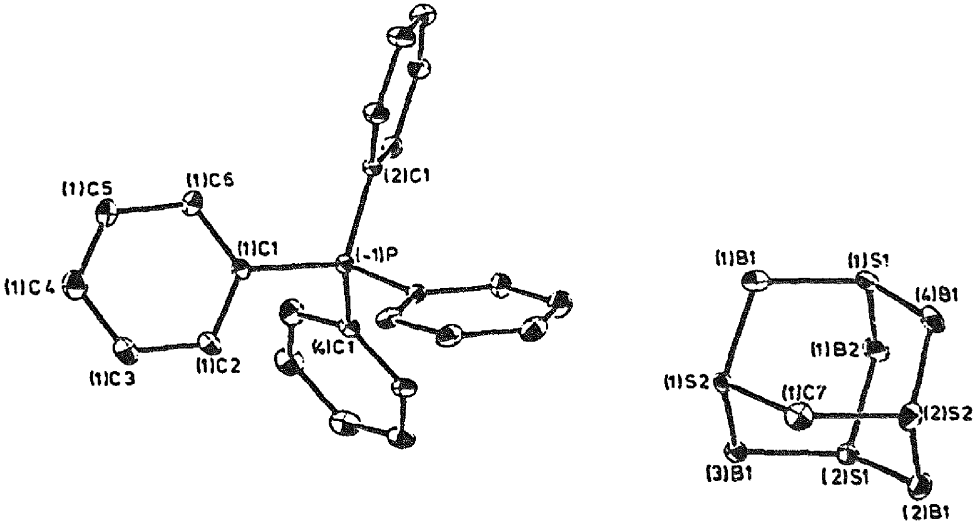


Fig. 12. Structure of $[(C_6H_5)_4P][CH_2B_5H_{10}S_4]$ (31). (From Ref. [48] by permission of Verlag der Zeitschrift für Naturforschung, Tübingen).

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.

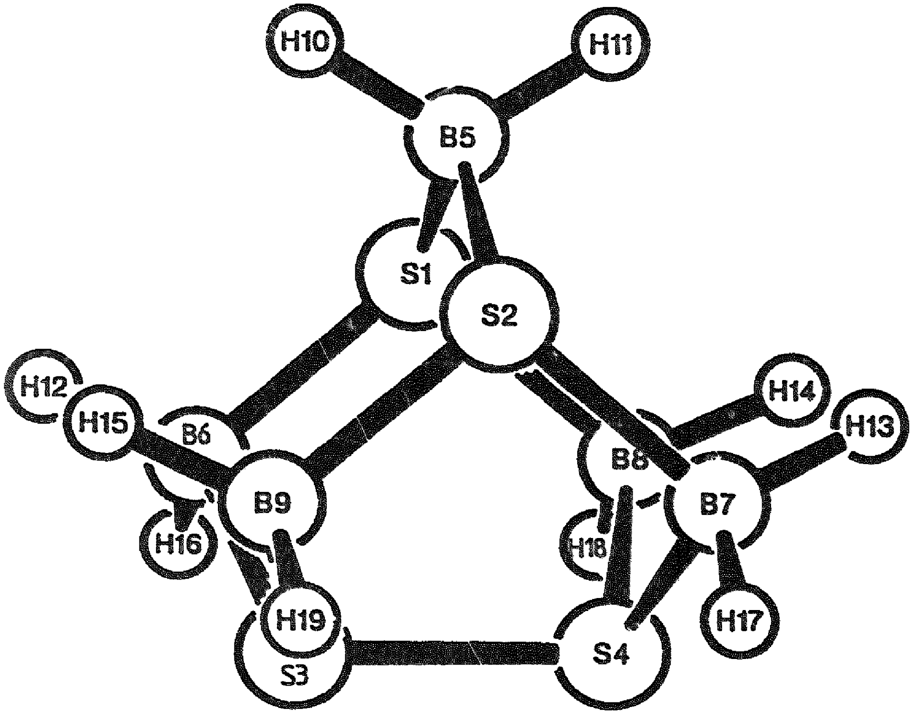


Fig. 13. Calculated structure of [(BH$_2$)$_5$S$_4$]$^-$ **32**. (From Ref. [49] by permission of VCH Verlagsgesellschaft mbH, Weinheim).

7.1. *Cs$_2$[(BH$_2$)$_6$S$_4$]·CsBr* ***34b*** *and Cs$_2$[(BH$_2$)$_6$Se$_4$]·CsBr* ***37b***

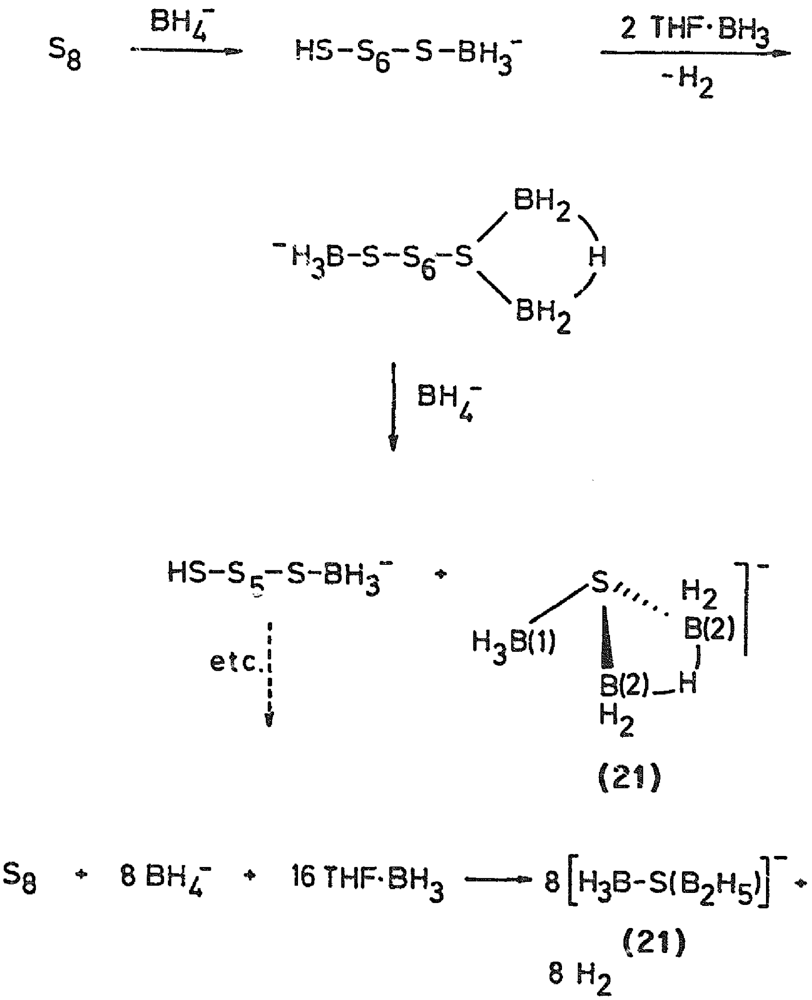
The reaction of THF·BH$_3$/NaBH$_4$ (2 : 1) with H$_2$S produces Na[H$_3$B-μ_2-S(B$_2$H$_5$)] **21** which is also formed in the reaction of THF·BH$_3$ with NaSH or anhydrous Na$_2$S (see Sections 4.2, 4.3 and 4.4). **21** reacts with an excess of H$_2$S to give Na$_2$[(BH$_2$)$_6$S$_4$] (34).

$$\mathbf{21} + \mathrm{H_2S} \rightarrow \underset{\mathbf{33a}}{[\mathrm{HS{-}BH_2}\text{-}\mu_2\text{-}\mathrm{S(B_2H_5)}]^-} \text{ or } \underset{\mathbf{33b}}{[\mathrm{H_3B}\text{-}\mu_2\text{-}\mathrm{S(B_2H_4)}\text{-}\mu\text{-}\mathrm{SH}]^-} + \mathrm{H_2}$$

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

$$2(\mathbf{33a, b}) \rightarrow \underset{\mathbf{34}}{[(\mathrm{BH_2})_6\mathrm{S_4}]^{2-}} + 2\mathrm{H_2}$$

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



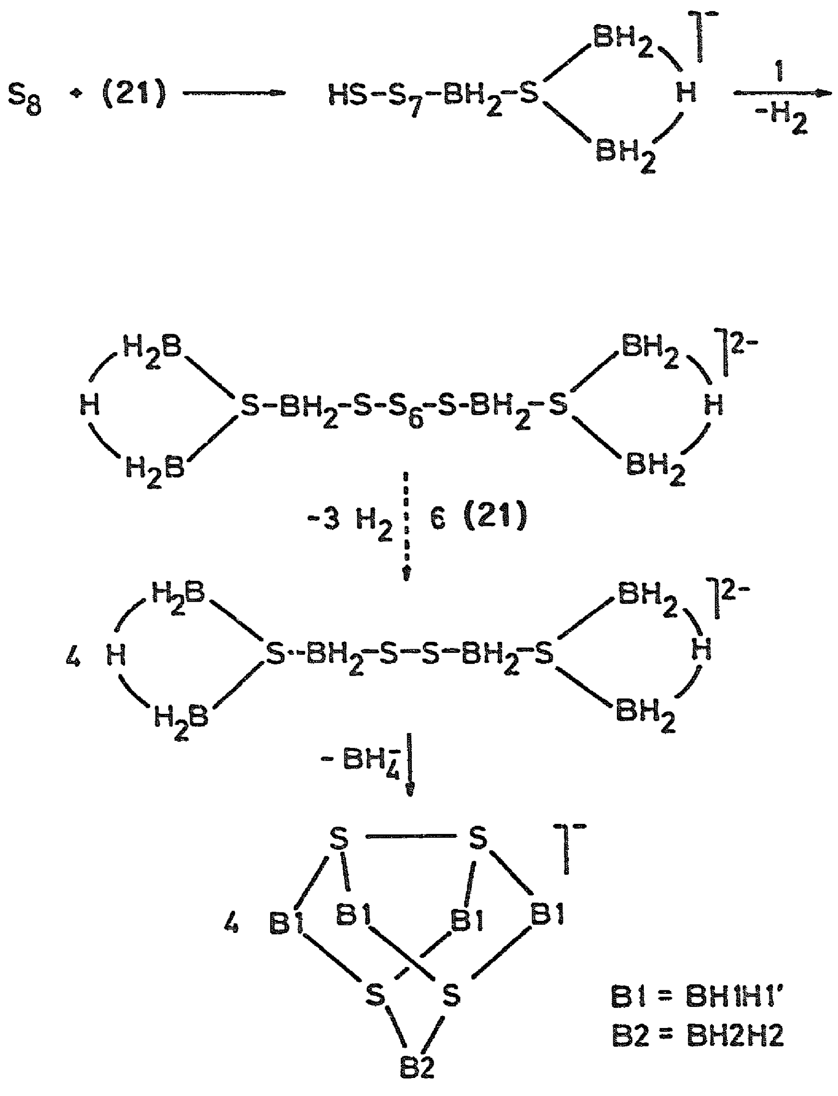
Scheme 5.

$$\mathbf{11} + H^- \rightarrow \underset{\mathbf{35}}{[H_3B\text{–}Se\text{–}H]^-} + \underset{\mathbf{36}}{[H_3B\text{–}Se]^{2-}}$$

$$4\underset{\mathbf{35}}{[H_3B\text{–}Se\text{–}H]^-} + 4\underset{\mathbf{36}}{[H_3B\text{–}Se]^{2-}} \rightarrow \underset{\mathbf{37}}{[(BH_2)_6Se_4]^{2-}} + 2BH_4^- + 4Se^{2-} + 4H_2$$

34 and **37** are stable in water and react with CsBr to form the crystalline compounds $Cs_2[(BH_2)_6S_4]\cdot CsBr$ **34b** and $Cs_2[(BH_2)_6Se_4]\cdot CsBr$ **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



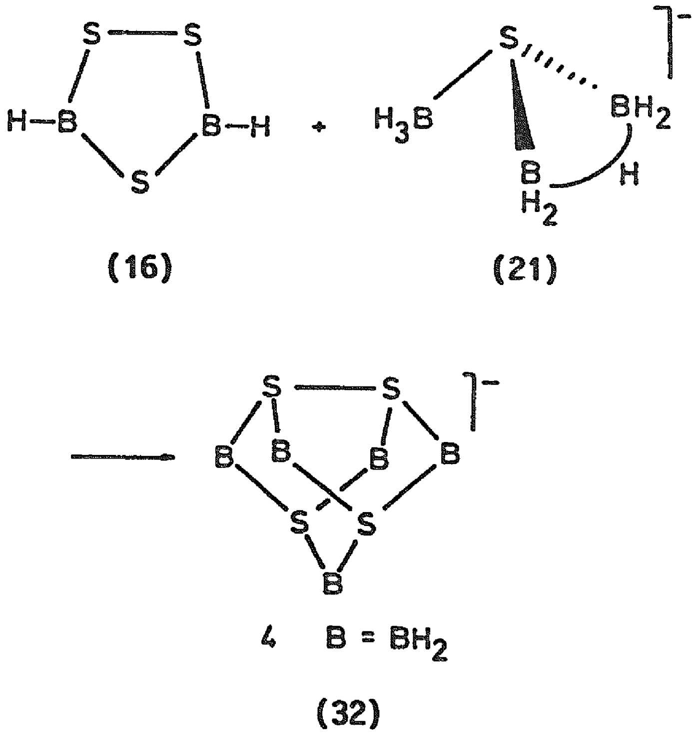
(32)

Scheme 6.

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

7.2. *hypho*-$S_2B_6H_9^-$ **38**, *hypho*-2,3-$(CH_3)_2$–2,3-$S_2B_6H_9$ **39**, *hypho*-1-CH_2–2,5-$S_2B_6H_8$ **40**

The dithiaborane anion *hypho*-$S_2B_6H_9^-$ **38** was produced in high yield by the reaction of *arachno*-$S_2B_7H_8^-$ **39** with excess acetone (Fig. 16). Subsequent reaction



Scheme 7.

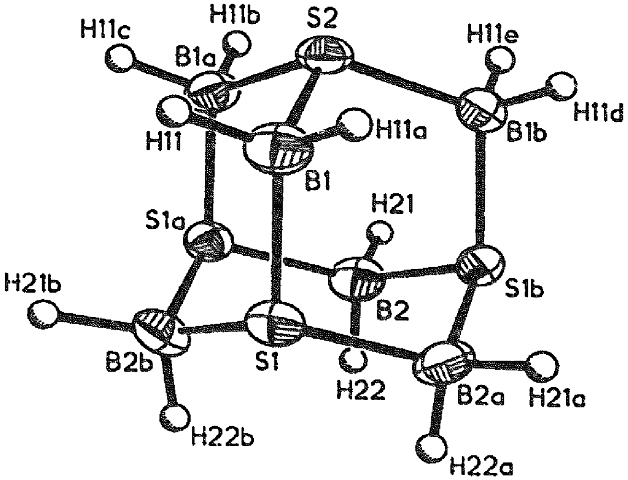


Fig. 14. Structure of the $[(BH_2)_6S_4]^{2-}$ anion 34b. (From Ref. [25] by permission of VCH Verlagsgesellschaft mbH, Weinheim).

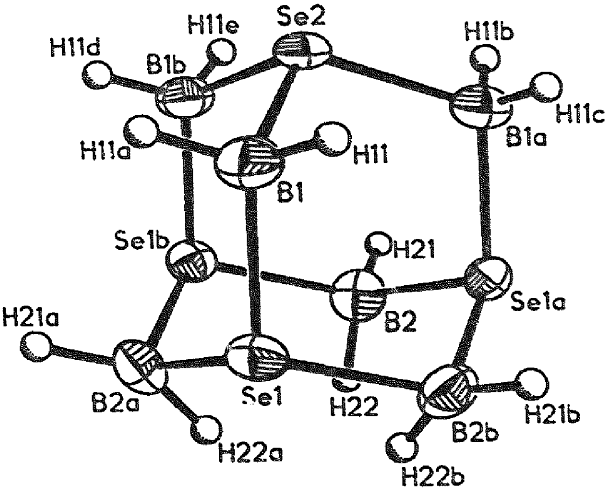


Fig. 15. Structure of the $[(BH_2)_6Se_4]^{2-}$ anion **37b**. (From Ref. [25] by permission of VCH Verlagsgesellschaft mbH, Weinheim).

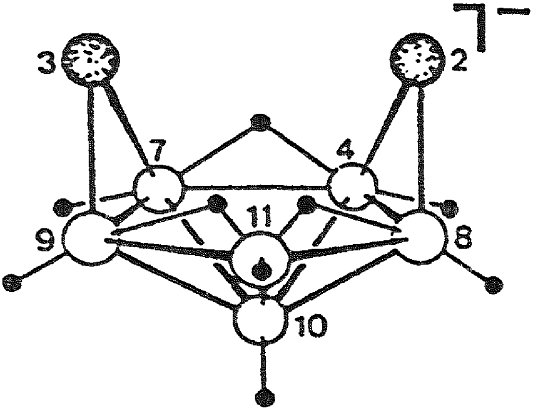


Fig. 16. Eight-vertex hypho-structure of $S_2B_6H_9^-$ **38**. (From Ref. [50] by permission of The American Chemical Society, Washington).

of **38** with excess methyl iodide gave *hypho*-2,3-$(CH_3)_2$–2,3-$S_2B_6H_9$ **39** [51].

$$\textit{arachno}\text{-}S_2B_7H_8 \xrightarrow[\text{2. PPN}^+\text{Cl}^-]{\text{1. }(CH_3)_2CO} \textit{hypho}\text{-}\underset{\mathbf{38}}{S_2B_6H_9^-}\,\text{PPN}^+$$

$$\textit{hypho}\text{-}\underset{\mathbf{38}}{S_2B_6H_9^-} + \text{excess } CH_3I \rightarrow \textit{hypho}\text{-}\underset{\mathbf{39}}{2,3\text{-}(CH_3)_2\text{–}2,3\text{-}S_2B_6H_9} + NaI + HI$$

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*-$S_2B_6H_9^-$ **38** with diiodomethane gave *hypho*-1-CH_2–2,5-$S_2B_6H_8$ **40** in good yield.

$$\underset{\mathbf{38}}{hypho\text{-}S_2B_6H_9^-} + CH_2I_2 \rightarrow \underset{\mathbf{40}}{hypho\text{-}1\text{-}CH_2\text{–}2,5\text{-}S_2B_6H_8} + I^- + HI$$

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 CH_2 unit bridging the two sulfur atoms forming an open five-membered face (Fig. 18).

In **40** the electron-rich bridging S–CH_2–S unit appears to be connected by conventional two-center two-electron bonds. The *hypho*-$S_2B_6H_9^-$ anion has been employed to generate a series of new *arachno*- and *hypho*-metalladithiaborane clusters [50].

7.3. *arachno-4,6,8-*$SC_2B_6H_{10}$ **41a**

The reaction of 7,9-$C_2B_9H_{12}^-$ with Na_2SO_3 in dilute hydrochloric acid affords the new thiacarbaborane 4,6,8-$SC_2B_6H_{10}$ **41a**.

$$nido\text{-}7,9\text{-}C_2B_9H_{12}^- \xrightarrow{\text{dilute HCl, Na}_2} SO_3 4,6,8\text{-}\underset{\mathbf{41a}}{SC_2B_6H_{10}}$$

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

7.4. *hypho-7,8-*$CSB_6H_{11}^-$ **41b**, *8-Me–hypho-7,8-*CSB_6H_{11} **41c**

arachno-4,6-CSB_7H_{11} **42** can be deprotonated and converted in turn to the eight-vertex hypho anion 7,8-$CSB_6H_{11}^-$ **41b**, Fig. 19(b) [53], a carbathiaborane analog of *hypho*-$S_2B_6H_9^-$ **38** [51], in 65% yield by the action of aqueous acetone (reflux, 5 h).

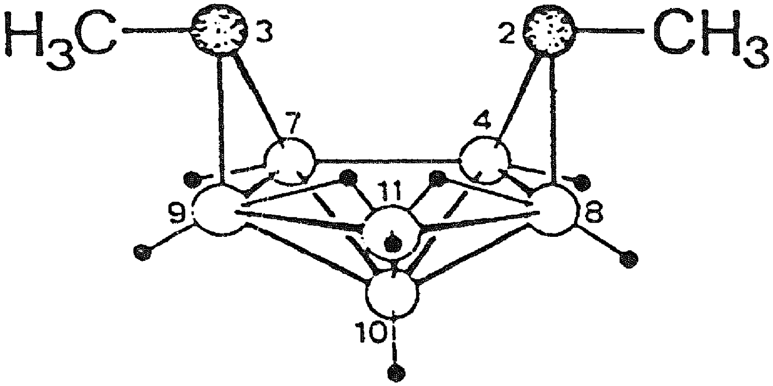


Fig. 17. Eight-vertex hypho-structure of 2,3-$(CH_3)_2$–2,3-$S_2B_6H_9$ **39**. (From Ref. [51] by permission of The American Chemical Society, Washington).

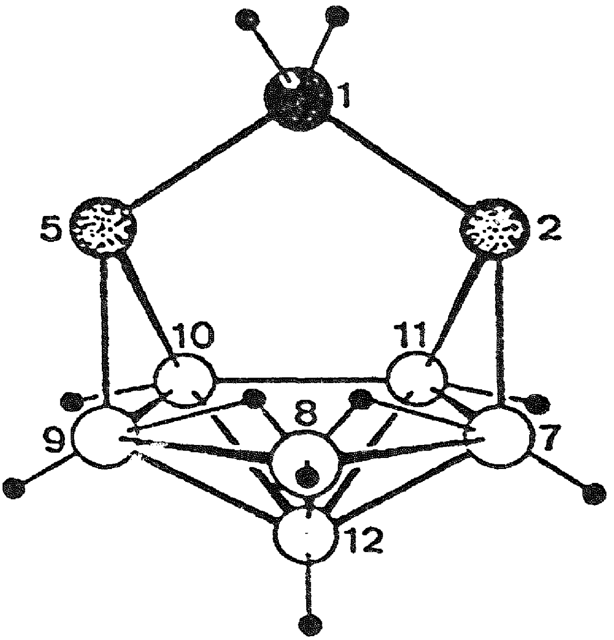


Fig. 18. Nine-vertex hypho-structure of 1-CH_2-2,5-$S_2B_6H_8$ **40**. (From Ref. [51] by permission of The American Chemical Society, Washington).

Methylation of 7,8-$CSB_6H_{11}^-$ **41b** with methyl iodide in THF at room temperature has produced the neutral 8-Me–*hypho*-7,8-CSB_6H_{11} **41c** in 75% yield.

8. Seven-boron-atom systems

The compounds considered are polyhedral hetero boranes.

8.1. *arachno-4,6-CSB$_7$H$_{11}$ 42*

$C_2B_{10}H_{13}^-$ is degraded in acid medium with $K_2S_2O_5$ to give 6,8-CSB_7H_{11} **42** [54]. The structure of this compound is proposed on the basis of ^1H and ^{11}B NMR spectra and topological rules. In compound **42**, which has no symmetry element, two different hydrogen bridges were found and the presence of a CH_2 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-$CSB_8H_9^-$ **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%).

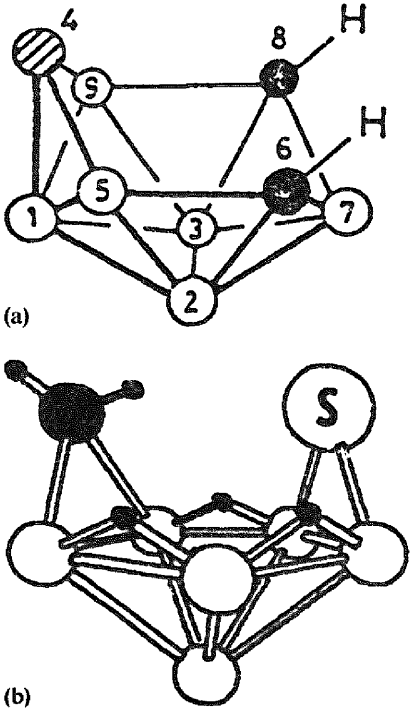


Fig. 19. (a) Proposed structure of *arachno*-4,6,8-$SC_2B_6H_{10}$ **41a**. (From Ref. [52] by permission of The Royal Society of Chemistry, Cambridge). (b) Proposed structure of the *hypho*-7,8-$CSB_6H_{11}^-$ anion **41b**.

*8.2. arachno-6,8-$S_2B_7H_9$ **43**, arachno-$S_2B_7H_8^-$ **43a**, hypho-2,5-$S_2B_7H_{10}^-$ **43b**, hypho-2,5-$S_2B_7H_{11}$ **43c***

In 1977, a high yield synthesis of the first dithiaborane, *arachno*-6,8-$S_2B_7H_9$ **43** was prepared by reaction of $B_9H_{12}S^-$ 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*-$S_2B_7H_9$ cage system might also serve as a primary starting material for the syntheses of a wide range of new hypho-clusters [55].

arachno-$S_2B_7H_8^-$ **43a** was prepared by the reaction in vacuo of excess NaH with *arachno*-6,8-$S_2B_7H_9$ **43** in THF [51].

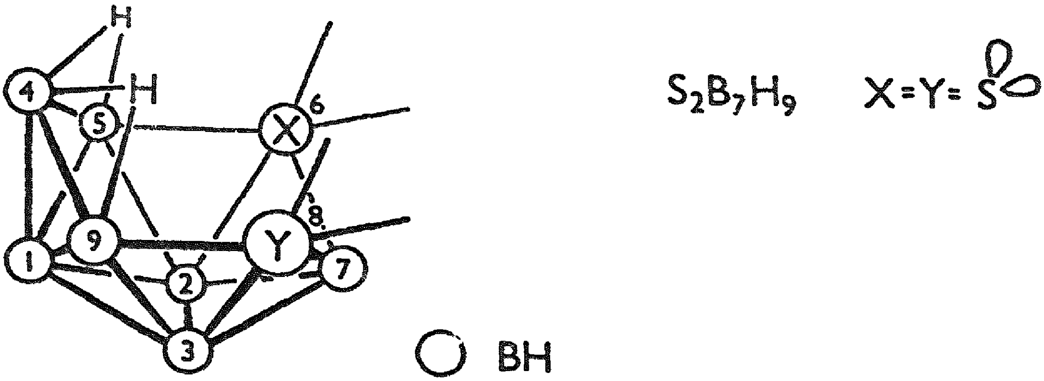


Fig. 20. Proposed structure of *arachno*-6,8-$S_2B_7H_9$ **43**. (From Ref. [54] by permission of Academy of Siences of Czech Republic).

The dithiaborane anion *hypho*-2,5-$S_2B_7H_{10}^-$ **43b** was produced by the reaction of *hypho*-$S_2B_6H_9^-$ **38** with $BH_3 \cdot THF$. Alternatively, **38** may be prepared in better yields either by the reaction of $S_2B_7H_8^-$ **43a** with $BH_3 \cdot THF$ or by the direct reaction of *arachno*-6,8-$S_2B_7H_9$ **43** with $NaBH_4$ [51].

$$\underset{\mathbf{38}}{hypho\text{-}S_2B_6H_9^-} + BH_3 \cdot THF \rightarrow \underset{\mathbf{43b}}{hypho\text{-}2,5\text{-}S_2B_7H_{10}^-} + H_2$$

Protonation of 2,5-$S_2B_7H_{10}^-$ **43b** gives the neutral compound *hypho*-2,5-$S_2B_7H_{11}$ **43c** in good yields [51].

$$\underset{\mathbf{43b}}{hypho\text{-}2,5\text{-}S_2B_7H_{10}^-} + H^+ \rightarrow \underset{\mathbf{43c}}{hypho\text{-}2,5\text{-}S_2B_7H_{11}}$$

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

8.3. *arachno*-$SSeB_7H_9$ **44**

$SSeB_7H_9$ **44** was prepared by reaction of B_9H_9SSe with excess potassium hydroxide in methanol. The structures of **44** are proposed on the basis of ^{11}B NMR results (Fig. 21) [56].

8.4. *arachno*-5,6,9-$SC_2B_7H_{11}$ **45a**, *arachno*-$SeC_2B_7H_{11}$ **45b**

A new ten-vertex *arachno*-dicarbathiaborane, formulated as 5,6,9-$SC_2B_7H_{11}$ **45a**, was prepared from *nido*-5,6-$C_2B_8H_{12}$ in 20% yield by treatment with sulfur and triethylamine in chloroform. NMR measurements suggest the structure shown in Fig. 22(a) [53].

Treatment of $C_2B_7H_{13}$ with polyselenide in aqueous base followed by acidification yielded $SeC_2B_7H_{11}$ **45b** in low yield [57], the structure of which is proposed on the

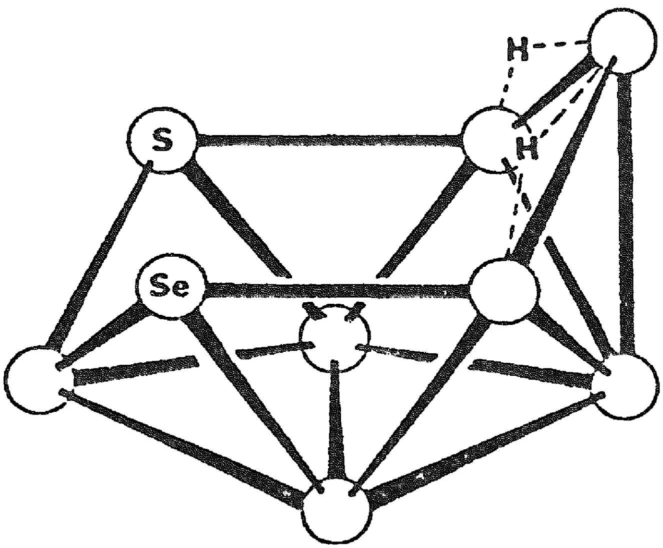


Fig. 21. Proposed structure of *arachno*-$SSeB_7H_9$ **44**. (From Ref. [56] by permission of The American Chemical Society, Washington).

basis of ^1H and ^{11}B 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-(SB_8H_{10}) (?), arachno-4-SB_8H_{12} **46**, *exo-6-L-arachno-4-SB_8H_{10}* **46a**, *arachno-4-$SB_8H_{11}^-$* **46b**, *nido-4-$SB_8H_9^-$* **46c**, *nido-7-$SB_8H_9^-$ (?): metallathiaboranes of the type $L_2PtSB_8H_{10}$* **46d** *(L = PMe_2Ph, Et_3P, Ph_3P) see Ref. [58]*

A key compound for the further development of nine-vertex arachno heteroborane chemistry is *arachno*-4-thianonaborane 4-SB_8H_{12} **46**. This compound was first isolated by Pretzer and Rudolph [59] but was originally incorrectly formulated as *nido*-SB_8H_{10}. The development of an alternative synthesis led to the correct formulation of **46** [60].

$$B_{10}H_{14} + KHSO_3 \xrightarrow{H_2O,\ \text{dilute HCl}} \underset{\mathbf{46}}{4\text{-}SB_8H_{12}}$$

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*-$SB_9H_{12}^-$, using formaldehyde as an oxidizing agent, affords

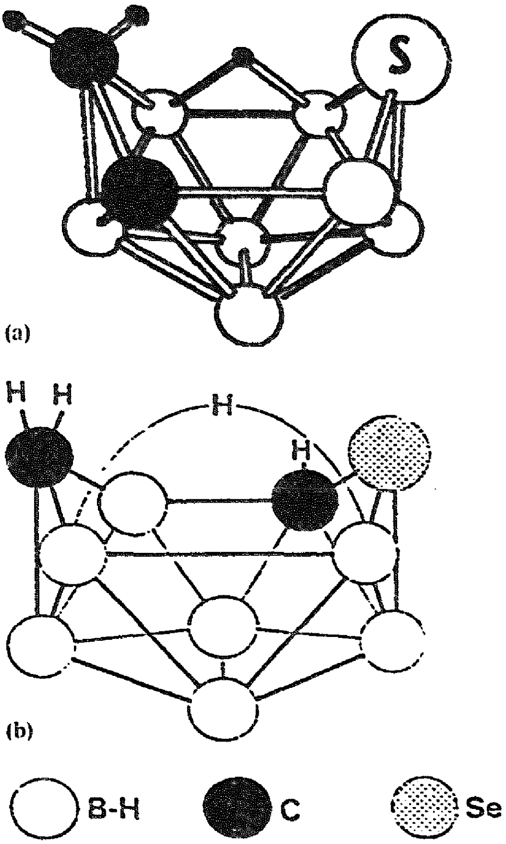


Fig. 22. (a) Proposed structure of 5.6.9-$SC_2B_7H_{11}$ **45a**. (b) Proposed structure of $SeC_2B_7H_{11}$ **45b**. (From Ref. [57] by permission of Chemistry and Industry).

46 in practically quantitative yield.

$$[SB_9H_{12}]^- + HCHO + H_3O^+ + 2H_2O \rightarrow \underset{\mathbf{46}}{SB_8H_{12}} + CH_3OH + B(OH)_3 + H_2$$

Oxidative degradation of the *arachno*-$SB_9H_{12}^-$ anion with acidic aqueous $FeCl_3$ yields the neutral compound directly [62].

$$[SB_9H_{12}]^- + FeCl_3 \xrightarrow[\text{pentane}]{\text{aq HCl}} \underset{\mathbf{46}}{SB_8H_{12}} + FeCl_2 + HCl + H_2 + B(OH)_3$$

On the basis of its ^{11}B and ^{1}H 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-SB_8H_{12} appears to be unstable to storage, and is best prepared freshly.

Reactions between *arachno*-4-SB_8H_{12} and Lewis bases L in benzene or without solvent generate a series of the corresponding *exo*-6-L-*arachno*-4-SB_8H_{10} **46a** [63]

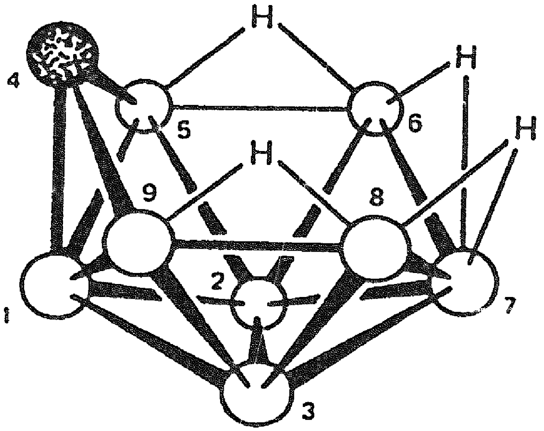


Fig. 23. Proposed structure of *arachno*-4-SB_8H_{12} **46**. (From Ref. [62] by permission of The American Chemical Society, Washington).

(L=SMe_2, PPh_3, MeCN **46a″**, NMe_3, pyridine, urotropine **46a**, **46a′**). All these compounds are characterized by mass spectrometry and ^{11}B 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-SB_8H_{12} **46** can be deprotonated to the *arachno*-4-$SB_8H_{11}^-$ 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-SB_8H_{12}, it has been impractical to develop the chemistry of *arachno*-4-$SB_8H_{11}^-$.

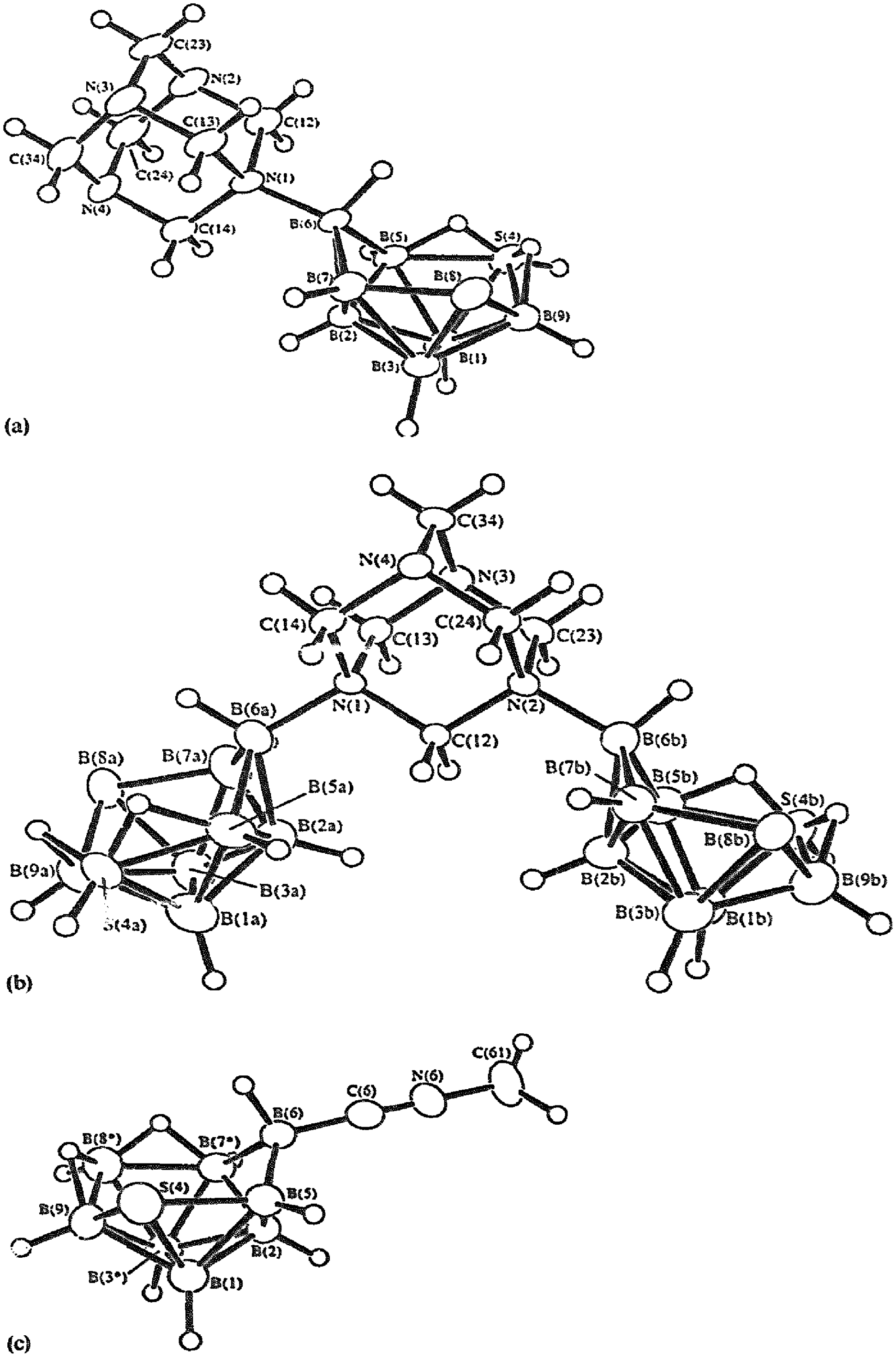
Platinathiadecaboranes $L_2Pt(SB_8H_{10})$ are formed by reaction of L_4Pt with 1-SB_9H_9 in dry refluxing ethanol or methanol. The complexes have been characterized by X-ray crystallography [58]. $L_2Pt(SB_8H_{10})$ complexes also form when $SB_{11}H_{11}$ is substituted for SB_9H_9 as a starting material. 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 SB_8 framework.

The controlled degradation of 1-SB_9H_9 can be effected by alcoholic KOH to give *nido*-4-$SB_8H_9^-$ **46c** [59,58].

$$1\text{-}SB_9H_9 + 3KOH \rightarrow \underset{\mathbf{46c}}{K^+SB_8H_9^-} + B(OMe)_3 + H_2O + H_2$$

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

Fig. 24. (a) Molecular structure of *exo*-6-(uro)-*arachno*-4-SB_8H_{10} **46a**; (b) molecular structure of *exo,exo′*-6-(uro)-*arachno*-(4-SB_8H_{12})$_2$ **46a**; (c) molecular structure of *exo*-6-(MeNC)-*arachno*-4-SB_8H_{12} **46a**. (From Ref. [63] by permission of The American Chemical Society, Washington).


C(23)
N(3)
N(2)
C(13)
C(12)
C(34)
C(24)
N(1)
N(4)
C(14)
B(6)
B(5)
S(4)
B(7)
B(8)
B(9)
B(2)
B(1)
B(3)
(a)
C(34)
N(4)
N(3)
C(14)
C(13)
C(24)
C(23)
N(1)
N(2)
B(6a)
C(12)
B(6b)
B(8a)
B(7a)
B(5a)
B(7b)
B(5b)
S(4b)
B(2a)
B(8b)
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B(3a)
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B(9b)
S(4a)
B(1a)
B(3b)
B(1b)
(b)
C(61)
N(6)
C(6)
B(6)
B(8*)
B(7*)
S(4)
B(5)
B(9)
B(2)
B(3*)
B(1)
(c)

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_9H_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].

$$C_2B_9H_{12}^- + HSO_3^- + 2H^+ \rightarrow \underset{\textbf{47a}}{SC_2B_8H_{10}} + B(OH)_3 + H_2$$

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

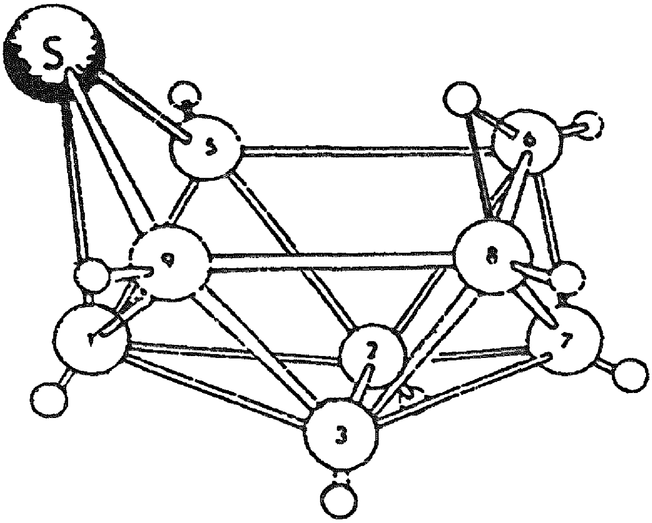


Fig. 25. Proposed structure of *nido*-4-$SB_8H_9^-$ **46c**. (From Ref. [59] by permission of The American Chemical Society, Washington).

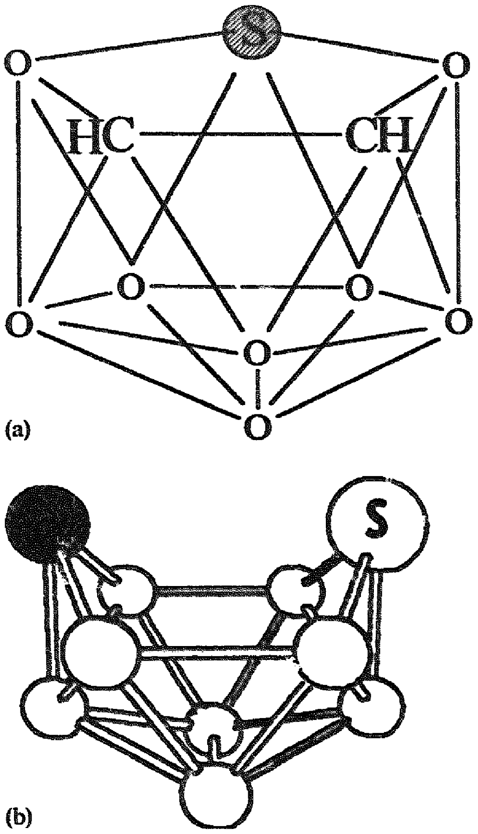


Fig. 26. (a) Proposed structure of *nido*-$SC_2B_8H_{10}$ **47a**. (From Ref. [64] by permission of Plenum Publishing Corp., New York). (b) Proposed structure of *nido*-carbathiaborane 6,9-$CSB_8H_9^-$ **47b**.

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

9.3. *nido*-$SeC_2B_8H_{10}$ **48**

The treatment of $Na_2SeO_3 \cdot 5H_2O$ with 7,8-$C_2B_9H_{12}^-K^+$ in an aqueous solution of citric acid resulted in the formation of $SeC_2B_8H_{10}$ **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].

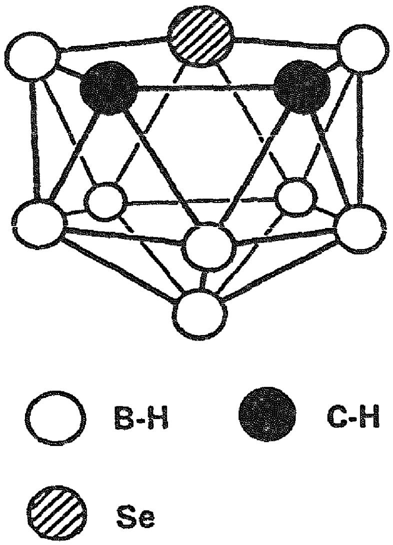


Fig. 27. Proposed structure of *nido*-$SeC_2B_8H_{10}$ **48**. (From Ref. [65] by permission of Chemistry and Industry).

9.4. *arachno*-$Se_2B_8H_{10}$ **49a**, *arachno*-6,9-NSB_8H_{11} **49b**, *arachno*-6,9-CSB_8H_{12} **49c**, *arachno*-6,9-$CSB_8H_{11}^-$ **49d**

The $Se_2B_8H_{10}$ **49a** molecule is formed as a coproduct during the $SeB_9H_{12}^-$ synthesis [57,67]. The reaction of $B_9H_{13}(SMe_2)$ 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 azathiaborane *arachno*-6,9-NSB_8H_{11} **49b**, along with its 6-HO– derivative (yields 15% and

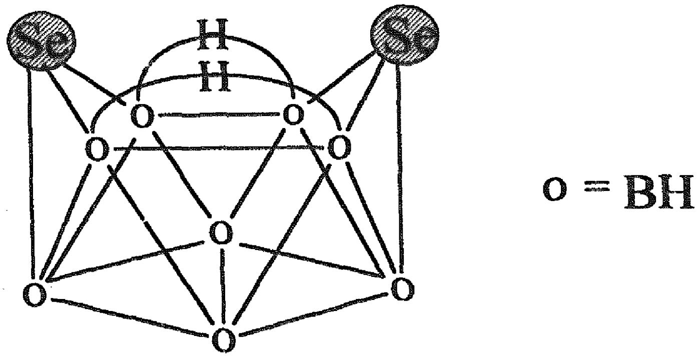


Fig. 28. Proposed structure of *arachno*-$Se_2B_8H_{10}$ **49a**. (From Ref. [57] by permission of Chemistry and Industry).

35% respectively); lower yields of the former compound (10%) were obtained in a similar way, using *arachno*-4-SB_8H_{12} as a boron-cluster reagent [53].

Much more developed has been the chemistry of *arachno*-6,9-CSB_8H_{12} **49c**, which can be obtained in a reasonable yield (48%) by treatment of 4-CB_8H_{14} with elemental sulfur in the presence of triethylamine in chloroform [68]. Bridge-deprotonation of this carbathiaborane with NaH leads to the *arachno*-6,9-$CSB_8H_{11}^-$ anion **49d**.

10. Nine-boron-atom systems

The compounds considered are polyhedral hetero boranes.

10.1. closo-1-SB$_9$H$_9$ 50, 6,7,8,9,10-D$_5$-1-SB$_9$H$_4$ 50a, closo-SeB$_9$H$_9$ 50b

The preparation of 1-thia-*closo*-decaborane(9) **50** was effected by pyrolysis of SB_9H_{11} at 375 °C in vacuo [69].

$$SB_9H_{11} \rightarrow \underset{\mathbf{50}}{SB_9H_9} + H_2$$

The formation of *closo*-SeB_9H_9 **50b** by pyrolysis (380 °C) of SeB_9H_{11} 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 ^{11}B NMR spectrum.

The ^{11}B NMR spectrum of SB_9H_9 **50** and SeB_9H_9 **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-SB_9H_9 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-SB_9H_9 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-D_5-1-SB_9H_4 **50a** was obtained [73].

10.2. closo-6-X–1-SB$_9$H$_8$ 51, closo-10-X–1-SB$_9$H$_8$ 52 (X=Cl, Br, I); closo-6,10-X$_2$–1-B$_9$H$_7$ 53 (X=Br, I)

The halogenation of 1-SB_9H_9 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-SB_9H_9. 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

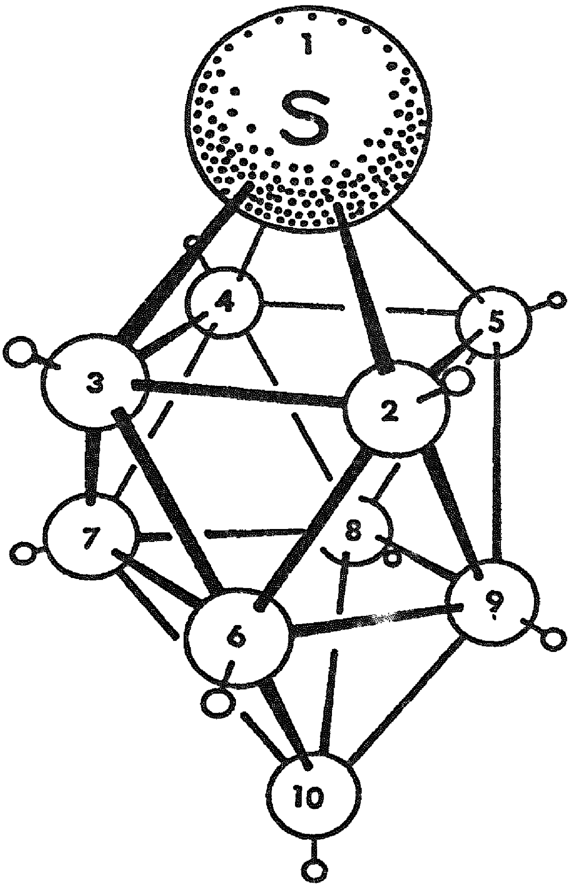


Fig. 29. Proposed structure for 1-thia-*closo*-decaborane(9) SB_9H_9 **50**. (From Ref. [69] by permission of The American Chemical Society, Washington).

give the thermodynamically more stable 10-isomer in the reaction mixture ($\Delta H_{\text{isomerization}} = 6.8$ 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 $(B_9H_8S)_2$ in about 5% yield [70,69,75]. ^{11}B NMR spectroscopy cannot distinguish between two of the possible isomers, 2,2′-(1-SB_9H_8)$_2$ **54a** and 6,6′-(1-SB_9H_8)$_2$ **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 SB_9H_8 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 SB_9H_8 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-SB_9H_8)(1′-$SB_{11}H_{10}$) 55

Three isomeric forms of **55** are obtained from the 450 °C pyrolysis of $SB_{10}H_{12}$, the best characterized of which appears to be either the 2,2′- or the 2,7′-isomer [75].

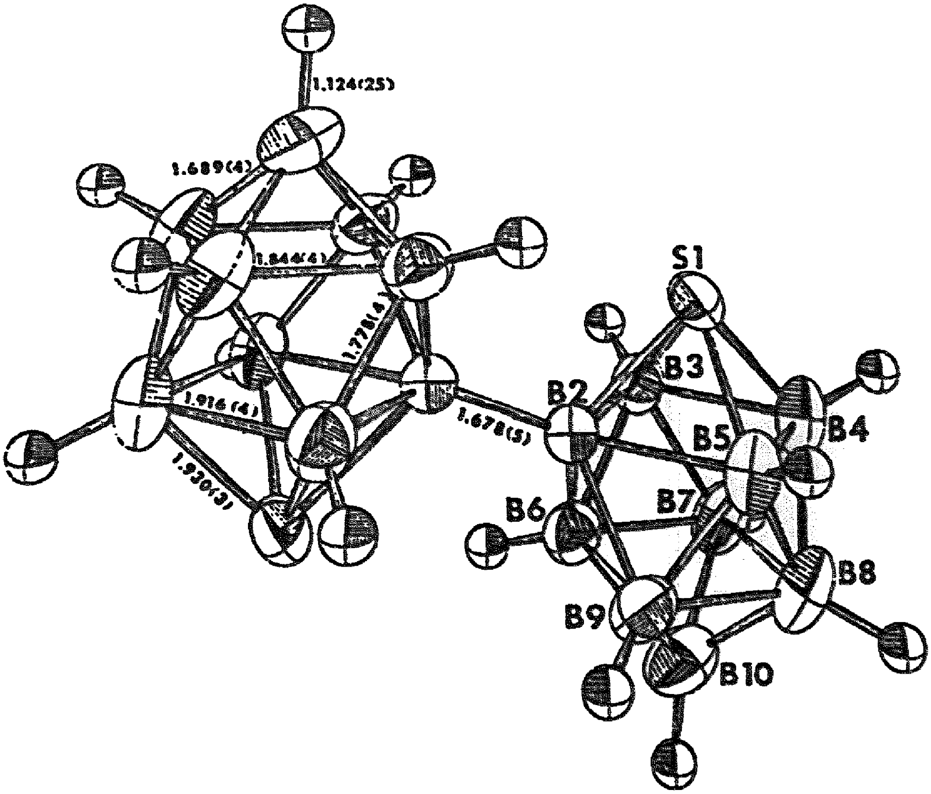


Fig. 30. ORTEP plot depicting the molecular structure and thermal ellipsoids for *closo*-2,2′-(1-SB_9H_8)$_2$ **54a**. (From Ref. [71] by permission of The American Chemical Society, Washington).

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. $(1\text{-}SB_9H_8)(1',7'\text{-}C_2B_{10}H_{11})$ 56a, $(1\text{-}SB_9H_8)(2',3'\text{-}C_2B_9H_{10})$ 56b

Copyrolysis of 6-SB_9H_{11} and 1,7-$C_2B_{10}H_{12}$ gives three isomers of (1-SB_9H_8)(1′,7′-$C_2B_{10}H_{11}$) **56**, but more definitive structural characterization is rather tenuous. Complete structural characterization is also lacking for the two (1-SB_9H_8)(2′,3′-$C_2B_9H_{10}$) **56b** isomers formed upon copyrolysis of 6-SB_9H_{11} and 7,9-$C_2B_9H_{13}$ [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-SB_9H_{9-n} (n=1–5) 57a, *closo*-$(C_2H_5)_n$–1-SB_9H_{9-n} (n=1–5) 57b

Electrophilic alkylation of *closo*-1-SB_9H_9 with either methyl or ethyl iodide in the presence of $AlCl_3$ produces alkylated derivatives of the type *closo*-$(CH_3)_n$–1-SB_9H_{9-n} ($n=1$–5) **57a**, *closo*-$(C_2H_5)_n$–1-SB_9H_{9-n} ($n=1$–5) **57b**, which were identified by GC-MS, ^{11}B and ^{1}H NMR spectroscopy [76]. The initial product is 6-R–1-SB_9H_8 rather than the 10-R–1-SB_9H_8 predicted on the basis of ground-state charge considerations. Thus, these results are as found for halogenation of 1-SB_9H_9. Therefore, in *closo*-thioboranes 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-SB_9H_{11} 58

nido-6-SB_9H_{11} **58** can be obtained from *arachno*-6-$SB_9H_{12}^-$ by protonation followed by pyrolytic disproportionation. The proposed intermediate $H(H_2O)_x^+$–$SB_9H_{12}^-$ is a pyrophoric solid and gives only a 30% yield of 6-SB_9H_{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-SB_9H_{11} and 4-SB_8H_{12} were prepared [78].

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

$$Cs^+SB_9H_{12}^- + \tfrac{1}{2}I_2 \rightarrow \underset{58}{6\text{-}SB_9H_{11}} + \tfrac{1}{2}H_2 + Cs^+I^-$$

The NMR study of *nido*-6-SB_9H_{11} using ^{11}B, ^{11}B{^{1}H}, ^{1}H{^{11}B}, [^{11}B–^{11}B]-COSY, and [^{1}H–^{1}H]-COSY techniques has enabled unequivocal assignment of the ^{11}B and ^{1}H spectra [79]; Fig. 31 shows the proposed structure of the 6-SB_9H_{11} cluster.

10.8. $SB_9H_{11}\cdot$ligand 59, (ligand$=H^-$, OH^-, CH_3CN, DMF, $(CH_3)_2S$, THF, Et_3N, and PPh_3)

Iodine oxidation of $CsSB_9H_{12}$ in THF affords white crystalline $SB_9H_{11}\cdot THF$ in good yield [77,80]. Like the known compound $SB_9H_{11}\cdot S(CH_3)_2$ [77], the THF adduct was very moisture sensitive and was characterized by its ^{1}H and ^{11}B NMR spectra. Treatment of $SB_9H_{11}\cdot THF$ with acetonitrile or triphenylphosphine easily generated $SB_9H_{11}\cdot CH_3CN$ and $SB_9H_{11}\cdot PPh_3$ in good yield. Reaction of $SB_9H_{11}\cdot PPh_3$ with tetraethylammonium hydroxide in aqueous acetonitrile formed $[(C_2H_5)_4N][HOSB_9H_{11}]$ in moderate yield. The pattern of the ^{11}B NMR spectrum of this hydroxi derivative is very similar to the spectrum of $SB_9H_{11}\cdot(CH_3)_2NCHO$. This suggests that $HOSB_9H_{11}^-$ is a member of the $SB_9H_{11}\cdot$ligand class of compounds with the ligand being OH^-. $SB_9H_{12}^-$ is also a member of the $SB_9H_{11}\cdot$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 $SB_9H_9^{2-}$ ion 60

For *M*=*Pd*: $(SB_9H_9)Pd(\text{ligand})_x^n$; *ligand*=$PPh_3$ ($x=2$, $n=0$), phen ($x=1$, $n=0$), and $C_2S_2(CN)_2$ ($x=1$, $n=2-$)] see Refs. [80,81], $[(C_2H_5)_3P]_2Pt(H)SB_9H_{10}$ [82]

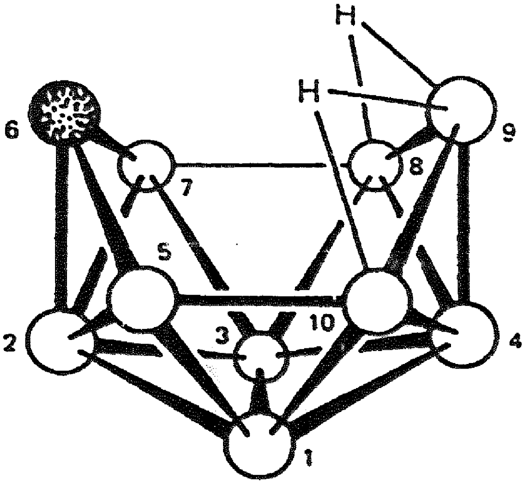


Fig. 31. Proposed structure of *nido*-6-SB_9H_{11} 58. (From Ref. [59] by permission of The American Chemical Society, Washington).

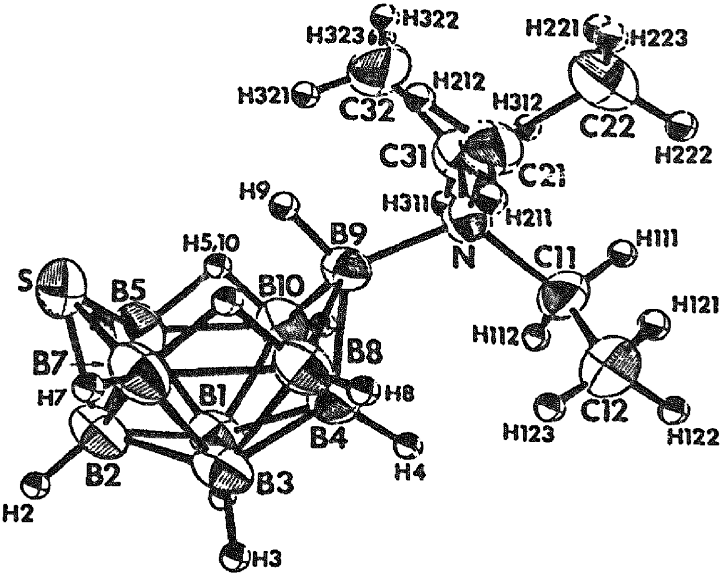


Fig. 32. ORTEP plot of the molecular structure of *arachno*-9-Et_3N-6-SB_9H_{11} 59 with non-hydrogen ellipsoids at 50% confidence level. (From Ref. [81] by permission of The American Chemical Society, Washington).

10.10. 6-SB_9H_{11} as a hydroboration agent 61, nido-6-$SB_9H_{10}^-$ 61a (see Section 10.14)

Since *nido*-6-SB_9H_{11} has the same framework structure as *nido*-$B_{10}H_{14}$ it was anticipated that treatment of 6-SB_9H_{11} 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-SB_9H_{11} undergoes a facile hydroboration reaction when treated with alkynes and alkenes [83–85]. Hydroboration of alkenes and alkynes by 6-SB_9H_{11} 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-SB_9H_{11} cluster: (μ_2-(4,exo-9)-1-$SiMe_3$-3-H-N_3)-arachno-6-SB_9H_{11} 62

It is reported that *nido*-6-SB_9H_{11} 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-$SiMe_3$-3-H-N_3)-*arachno*-6-SB_9H_{11} 62 [86].

nido-6-SB_9H^{11} + Me_3SiN_3 → (μ_2-(4,*exo*-9)-1-$SiMe_3$-3-H-N_3)-*arachno*-6-SB_9H_{11}
62

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

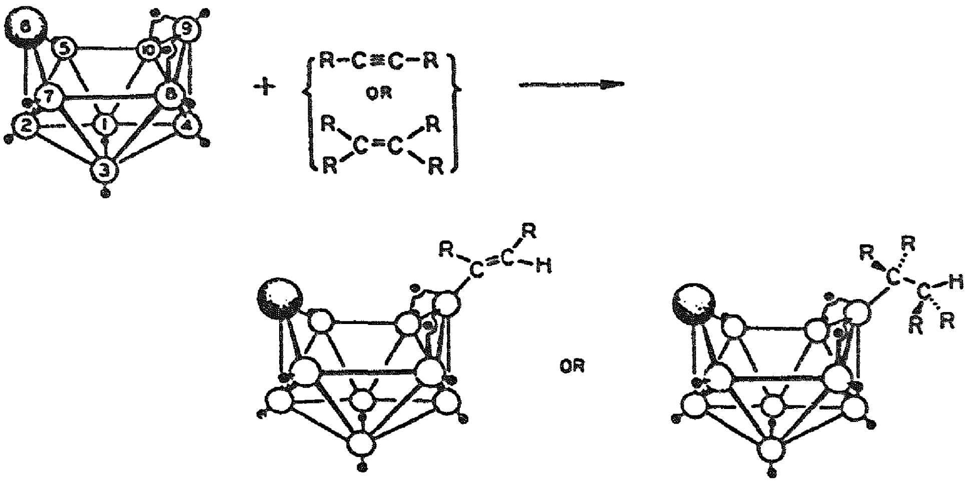


Fig. 33. Hydroboration by *nido*-6-SB$_9$H$_{11}$ **61**. (From Ref. [83,84] by permission of The American Chemical Society, Washington).

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,

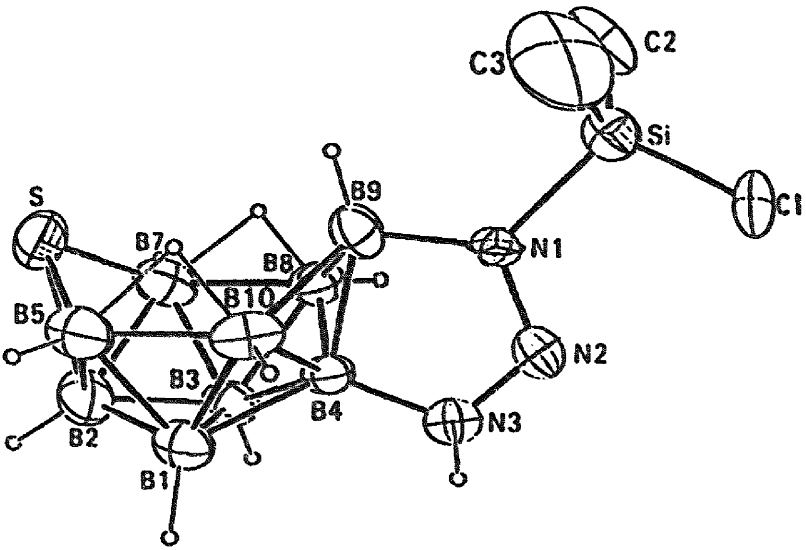


Fig. 34. ORTEP drawing of the molecular structure of (μ_2-(4,*exo*-9)-1-SiMe$_3$-3-H-N$_3$)-*arachno*-6-SB$_9$H$_{11}$ **62**. (From Ref. [86] by permission of The American Chemical Society, Washington).

26-skeletal-electron systems such as *exo*-9-Et_3N-*arachno*-6-SB_9H_{11} [77], thus indicating that the triazene group is functioning as a two-skeletal-electron donor to the cage.

10.12. *nido*-XB_9H_{11} **63a** (X=Se, Te), $XB_9H_{11} \cdot L$ **63b** (L=Lewis base)

Aqueous polyselenide or polytelluride solutions react with $B_9H_{13} \cdot S(CH_3)_2$ to form the $XB_9H_{12}^-$ anions, which can be isolated as tetramethylammonium salts. Oxidation of these salts with iodine produces the XB_9H_{11} molecules in benzene or the $XB_9H_{11} \cdot CH_3CN$ **63b** molecules in the presence of acetonitrile. Reaction of $SeB_9H_{11} \cdot CH_3CN$ with triethylamine produces $SeB_9H_{11} \cdot N(C_2H_5)_3$ in a rapid ligand displacement reaction [67,53,68]. There are similarities in the ^{11}B NMR spectra of the $XB_9H_{12}^-$ ions relative to that of the $XB_9H_{11} \cdot L$ (L=Lewis base) molecules.

10.13. *nido*-$S_2B_9H_9$ **64a**, *nido*-$SSeB_9H_9$ **64b**, *nido*-$Se_2B_9H_9$ **64c**

Reaction of $SB_9H_{12}^-$ **59** with potassium polysulfide, with a small amount of polyselenide present, generated $S_2B_9H_9$ **64a**.

Treatment of $SB_9H_{12}^-$ **59** with potassium polyselenide formed $SSeB_9H_9$ **64b**. The formation of $Se_2B_9H_9$ **64c** was first reported as an unexpected minor product during the synthesis of $SeB_{10}H_{11}^-$ **70b** [88,56]. This diselenaborane can now be made in good yield by reaction of $B_9H_{14}^-$ with potassium polyselenide [57].

Thermolysis of *arachno*-2,3-$S_2B_9H_{10}$ **65b** in refluxing toluene results in dehydrogenation and formation of *nido*-$S_2B_9H_9$ **64a** [89].

$$arachno\text{-}2\text{-}H\text{–}2,3\text{-}S_2B_9H_{10} \rightarrow 7,9\text{-}\underset{\mathbf{64a}}{nido\text{-}S_2B_9H_9} + H_2$$

Treatment of $Se_2B_9H_9$ (or $SSeB_9H_9$) with potassium hydroxide followed by reaction of the products with triethylamine, C_5H_6, and $CoCl_2$ formed $Se_2B_9H_9CoCp$ (or $SSeB_9H_9CoCp$) [56]. The structure of *nido*-7,9-$Se_2B_9H_9$ **64c** has been determined unambiguously to be the 7,9-isomer by ^{11}B NMR spectroscopy [90] Fig. 35.

Both the 7,9- and 7,8-isomers of $S_2B_9H_9$ 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-$S_2B_9H_9$ 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-$S_2B_9H_{10}^-$ **65a**, *arachno*-2-H–2,3-$S_2B_9H_{10}$ **65b**, *arachno*-2-CH_3–2,3-$S_2B_9H_{10}$ **65c**, *arachno*-2-CH_2I–2,3-$S_2B_9H_{10}$ **65d**

The reaction of *nido*-6-$SB_9H_{10}^-$ **61a** with elemental sulfur results in sulfur insertion into the *nido*-SB_9 cage framework to produce the new *arachno*-dithiaborane cluster

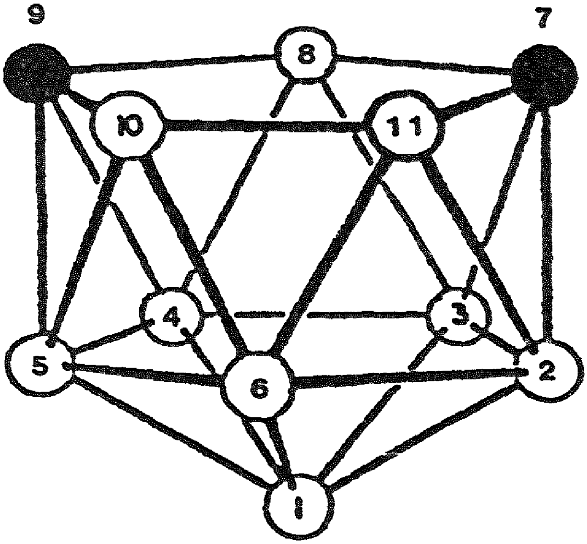


Fig. 35. Proposed structure of *nido*-7,9-$Se_2B_9H_9$ **64c**. (From Ref. [90] with kind permission of Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington OX5 1GB, UK).

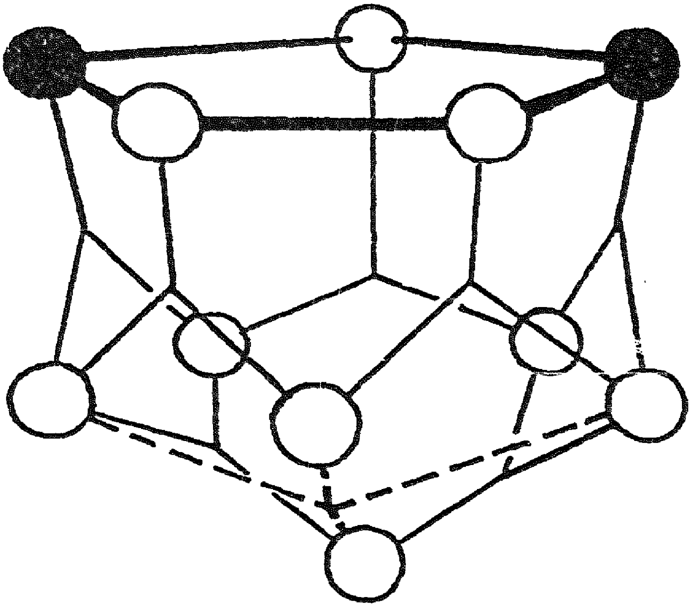


Fig. 36. A scheme of localized cluster bonding in *nido*-7,9-$Se_2B_9H_9$ **64c** calculated with the MNDO programme. (From Ref. [90] with kind permission of Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington OX5 1GB, UK).

anion, *arachno*-2,3-$S_2B_9H_{10}^-$ **65a** [89].

$$\underset{\mathbf{61a}}{nido\text{-}6\text{-}SB_9H_{10}^-} + \tfrac{1}{8}S_8 \rightarrow \underset{\mathbf{65a}}{arachno\text{-}2,3\text{-}S_2B_9H_{10}^-}$$

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-$S_2B_9H_{10}^-$ with concentrated H_2SO_4 in CH_2Cl_2, protonation occurs at one of the cage sulfur sites to give *arachno*-2-H-2,3-$S_2B_9H_{10}$ **65b**. **65b** also reacts with CH_3I or CH_2I_2 to give 2-CH_3-2,3-$S_2B_9H_{10}$ **65c** and *arachno*-2-CH_2I-2,3-$S_2B_9H_{10}$ **65d** respectively. A single crystal X-ray structure determination of CH_3-2,3-$S_2B_9H_{10}$ **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-$S_2B_9H_{10}$ **65b** Fig. 38(a).

In contrast to the structure observed for *arachno*-2,3-$S_2B_9H_{10}^-$ **65a**, in 2-CH_3-2,3-$S_2B_9H_{10}$ **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-$S_2B_9H_{10}^-$. 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-$S_2B_9H_{10}^-$ results not only in substitution at sulfur, but alters the nature of the sulfur-cage bonding interactions.

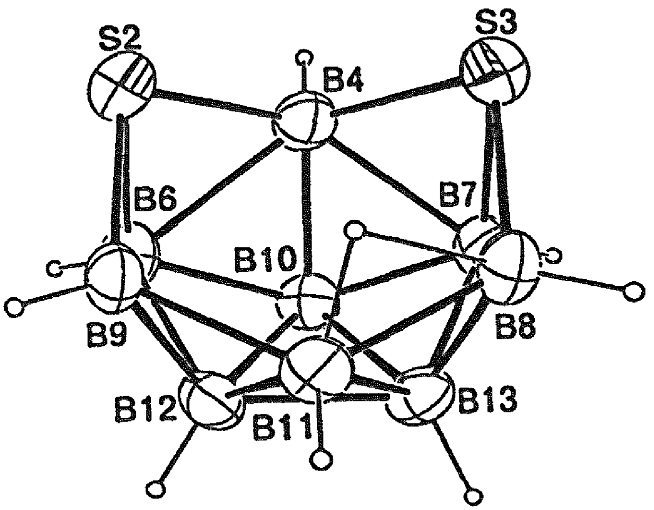


Fig. 37. ORTEP drawing of the anion structure of *arachno*-2,3-$S_2B_9H_{10}^-$ **65a**. (From Ref. [89] by permission of The American Chemical Society, Washington).

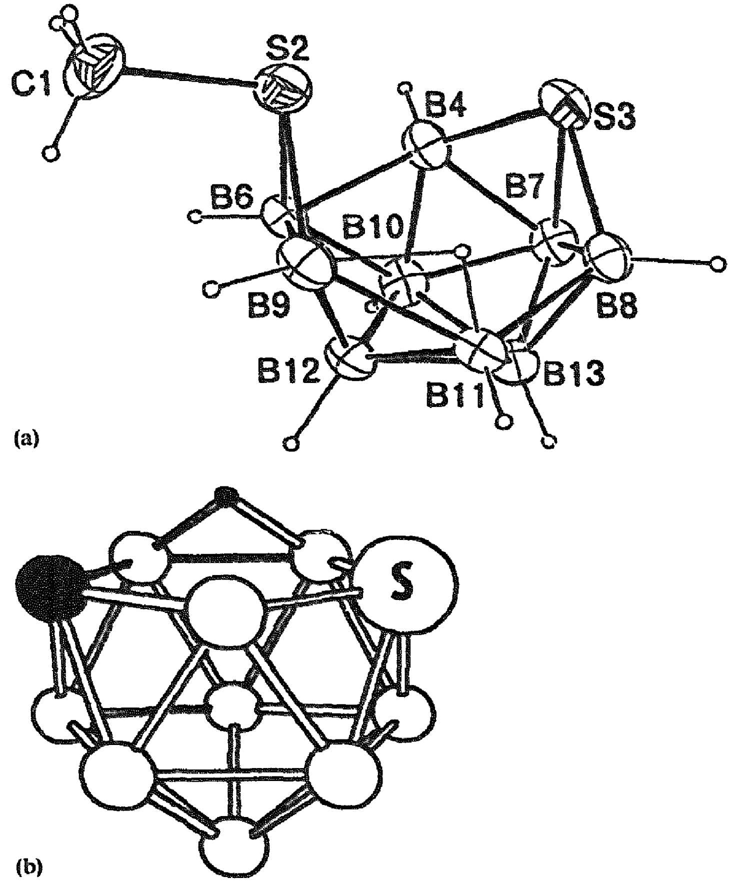


Fig. 38. (a) ORTEP drawing of the structure of *arachno*-2-CH_3–2,3-$S_2B_9H_{10}$ **65c**. (From Ref. [89] by permission of The American Chemical Society, Washington). (b) Proposed structure of *nido*-7,9-CSB_9H_{11} **66b**.

10.15. $SB_9H_{11}^{2-}$ 66, $(SB_9H_{11})_2M^{2-}$ (M = Ni, Pd) 66a, nido-7,9-CSB_9H_{11} 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*-$CSB_8H_{11}^-$ anion can be converted to *nido*-7,9-CSB_9H_{11} **66b** by heating at 120 °C; the structure is shown in Fig. 38(b).

10.16. arachno-6-$SB_9H_{12}^-$ 67a, arachno-6-$SB_9H_{11}Br^-$ 67b, arachno-$SB_9H_{11}(OH)^-$ 67c, arachno-6-$SeB_9H_{12}^-$ 67d, arachno-6-$TeB_9H_{12}^-$ 67e

For coinage metal derivatives of *arachno*-6-$SB_9H_{12}^-$, see Refs. [80,91–93].

Reaction of decaborane(14) with aqueous ammonium polysulfide gives the thiaborane ion, $SB_9H_{12}^-$ **67a**, in essentially quantitative yield [77].

$$\underset{}{B_{10}H_{14}} + S^{2-} + 4H_2O \rightarrow \underset{\textbf{67a}}{SB_9H_{12}^-} + B(OH)_4^- + 3H_2$$

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 $(PPh_3)_3AuSB_9H_{12}$ [91,92]. The compound is a salt consisting of $[(C_6H_5)_3P]_3Au^+$ cations and $SB_9H_{12}^-$ anions. $(C_2H_5)_4N[SB_9H_{11}Br]$ **67b** was prepared from 2-$BrB_{10}H_{13}$ [94] which is believed to be the 1-$SB_9H_{11}Br^-$ isomer.

arachno-$SB_9H_{11}(OH)^-$ **67c**: after standing in acetone solution for some months, partial decomposition of 6-$SB_9H_{12}^-$ **67a** was noted. The ^{11}B NMR behavior of species **67c** was very similar to that of 6-$SB_9H_{12}^-$ **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 $^{11}B(9)$ [95] then indicated **67c** is a 9-endo-substituted *arachno*-6-$SB_9H_{11}(OH)^-$ cluster anion closely related to 6-$SB_9H_{12}^-$ **67a** Fig. 40.

An anion of this 9-(OH)-*arachno*-6-$SB_9H_{11}(OH)^-$ 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 $B_9H_{13}\cdot S(CH_3)_2$ to form the $XB_9H_{12}^-$ (X=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 $SB_9H_{12}^-$ ion **59**.

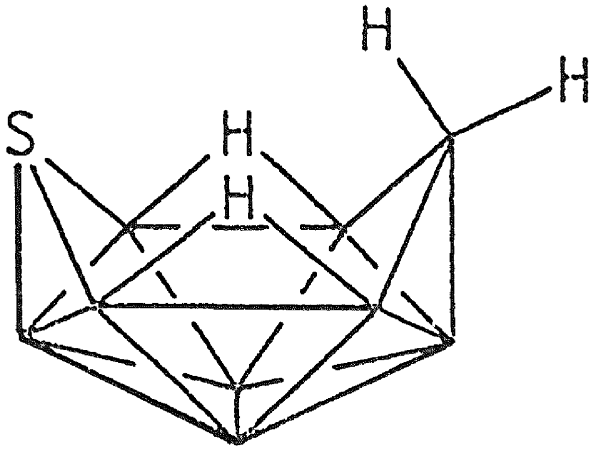


Fig. 39. Schematic representation of the ten-vertex *arachno*-6-$SB_9H_{12}^-$ **67a**. (From Ref. [79] by permission of The Royal Society of Chemistry).

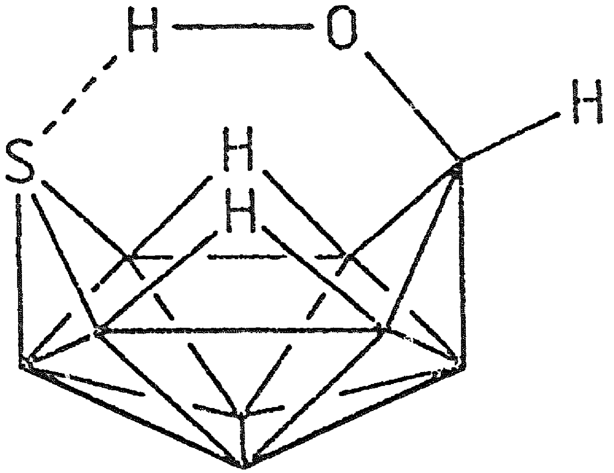


Fig. 40. Proposed structure of the 9-endo-substituted *arachno*-6-$SB_9H_{11}(OH)^-$ cluster anion **67c**. (From Ref. [79] by permission of The Royal Society of Chemistry).

10.17. *$(C_2H_5)_2S\cdot B_9H_{13}$* ***68***

$(C_2H_5)_2S\cdot B_9H_{13}$ **68** was synthesized in fair yield by a degradation of bis(diethylsulfide) decaborane(12) with methanol [96].

$$[(C_2H_5)_2S]_2\cdot B_{10}H_{12}+3CH_3OH\rightarrow$$

$$\underset{\mathbf{68}}{(C_2H_5)_2S\cdot B_9H_{13}}+H_2+(C_2H_5)_2S+(CH_3O)_3B$$

68 is a stable intermediate in the total methanolysis since it may be degraded completely to $(CH_3O)_3B$ under prolonged reaction with methanol.

11. Ten-boron-atom systems

The compounds considered are polyhedral hetero boranes.

11.1. *nido-7-$SB_{10}H_{12}$* ***69a***, *nido-7-$SeB_{10}H_{12}$* ***69b***, *nido-7-$TeB_{10}H_{12}$* ***69c***, *2-R-7-$SB_{10}H_{11}$* ***69d***, *$(SB_{10}H_{11})_2$* ***69e***, *$SB_{10}H_{11}^-$* ***70a***, *$SeB_{10}H_{11}^-$* ***70b***, *$TeB_{10}H_{11}^-$* ***70c***, *$M(EB_{10}H_{10})^{2-}$ (M=Fe, Co; E=Se, Te)* ***71***, *$CpCoEB_{10}H_{10}$* ***72***

Pyrolysis of $CsSB_9H_{12}$ **67a** gives the ion $SB_{10}H_{11}^-$ **70a**, which on acidification is converted to the weak acid *nido*-7-$SB_{10}H_{12}$ **69a** [77]. Improved synthetic routes have been developed for the preparation of **69a**. Good yields (greater than 60%) of *nido*-7-$SB_{10}H_{12}$ **69a** can be obtained by acidification of the anion that is formed either by the reaction of *nido*-6-SB_9H_{11} **58** with $NaBH_4$ under reflux conditions or by the reaction of *nido*-6-$SB_9H_{10}^-$ **61a** with THF · BH_3.

$$\underset{\mathbf{58}}{6\text{-}SB_9H_{11}} + NaBH_4 \xrightarrow[\text{dioxane}]{\text{reflux}} \underset{\mathbf{70a}}{Na^+SB_{10}H_{11}^-} + 2H_2$$

$$\underset{\mathbf{61a}}{6\text{-}SB_9H_{10}^-} + THF \cdot BH_3 \xrightarrow[\text{dioxane}]{\text{reflux}} \underset{\mathbf{70a}}{SB_{10}H_{11}^-} + H_2 + THF$$

The anion **70a** can then be converted to the neutral thiaborane by acidification with aqueous HCl in CH_2Cl_2 to give *nido*-7-$SB_{10}H_{12}$ **69a** [62].

As is shown in Fig. 41, *nido*-7-$SB_{10}H_{12}$ **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 ^{11}B NMR spectra of $SB_{10}H_{12}$ **69a** and $SeB_{10}H_{12}$ **69b** contain very similar doublet patterns. The spectrum of $TeB_{10}H_{12}$ also is similar but somewhat compressed. Treatment of $SeB_{10}H_{12}$ or $TeB_{10}H_{12}$ with aqueous KOH and either $CoCl_2$ or $FeCl_2$ forms $M(EB_{10}H_{10})^{2-}$ (M = Fe, Co; E = Se, Te). Triethylamine, cyclopentadiene monomer $CoCl_2$, and $SeB_{10}H_{12}$ or $TeB_{10}H_{12}$ in tetrahydrofuran solution form $CpCoEB_{10}H_{10}$ [88].

Oxidation of *nido*-7-$SB_{10}H_{10}^{2-}$ **73** by Ag^+ in benzene and toluene leads to coupled polyhedra $(SB_{10}H_{11})_2$ **69e** and attack upon the solvent to give arylthiaboranes 2-R–7-$SB_{10}H_{11}$ **69d**.

The ^{11}B NMR spectrum of the phenyl or the analogous tolyl derivative is found to be a perturbed version of that of the parent 7-$SB_{10}H_{12}$ **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, Na_2Se_4 and Na_2Te_4 react with decaborane(14) to give

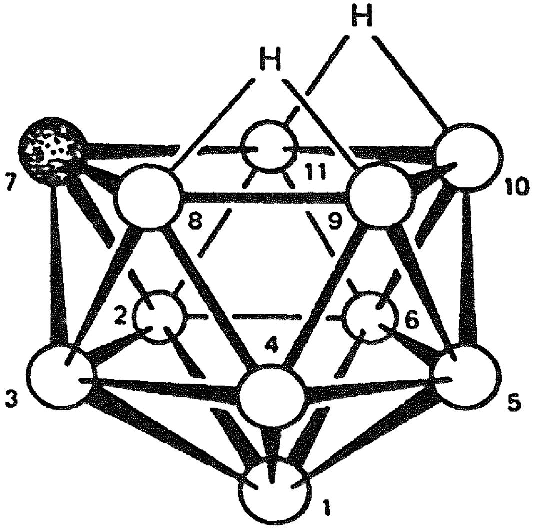


Fig. 41. Proposed structure of *nido*-7-$SB_{10}H_{12}$ **69a**. (From Ref. [62] by permission of The American Chemical Society, Washington).

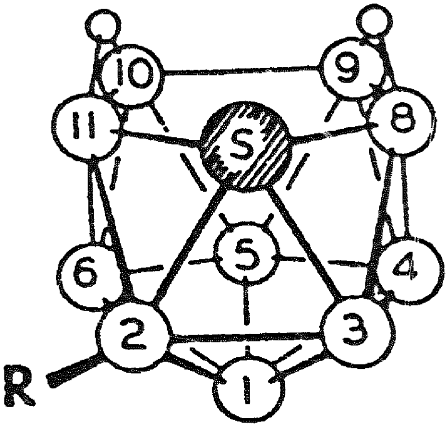


Fig. 42. Proposed structure of *nido*-2-R-7-S $B_{10}H_{11}$ **69d**. (From Ref. [97] by permission of The American Chemical Society, Washington).

$SeB_{10}H_{11}^-$ **70b** and $TeB_{10}H_{11}^-$ **70c** respectively. These anions form *nido*-7-$SeB_{10}H_{12}$ **69b** and *nido*-7-$TeB_{10}H_{12}$ **69c** upon acidification [88]. The ^{11}B NMR spectra of the $EB_{10}H_{11}^-$ 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-$SB_{10}H_{10}^{2-}$ 73, $(SB_{10}H_{10})_2M^{n-}$ 74

Treatment of $SB_{10}H_{11}^-$ **70a** or $SB_{10}H_{12}$ **69a** with strong base affords *nido*-7-$SB_{10}H_{10}^{2-}$ **73**. Reaction of $SB_{10}H_{10}^{2-}$ with a variety of transition metal halides gives a series of icosahedral metala thiaboranes $(SB_{10}H_{10})_2M^{n-}$ **74** [77]. $SB_{10}H_{10}^{2-}$ **73** is stable in solution for a limited time; it has not been isolated and characterized as a solid salt.

11.3. μ_2-6,7-$(CH_3E)B_{10}H_{13}$ 75a, b (E=S, Se), μ_2-6,9-$CH_3EB_{10}H_{12}^-$ 76a, b, $\{Cs[\mu_2\text{-}6,9\text{-}CH_3SB_{10}H_{12}]\}_3 \cdot Cs[\mu_2\text{-}6,7\text{-}OH\text{-}\mu_2\text{-}6,9\text{-}CH_3SB_{10}H_{11}]$ 77a, $B_{10}H_{12} \cdot [S(CH_3)_2]_2$ 77c

While strong bases readily deprotonate $B_{10}H_{14}$, certain weaker bases react with $B_{10}H_{14}$ according to the following equation:

$$B_{10}H_{14} + 2(CH_3)_2S \rightarrow \underset{\mathbf{77c}}{B_{10}H_{12} \cdot [S(CH_3)_2]_2} + H_2$$

Effectively, hydrogen atoms are replaced by electron pair donor atoms at the 6- and 9-positions of the $B_{10}H_{14}$ 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, $B_{10}H_{14}$ reacts with $(CH_3)_2E_2$ (E=S, Se) to

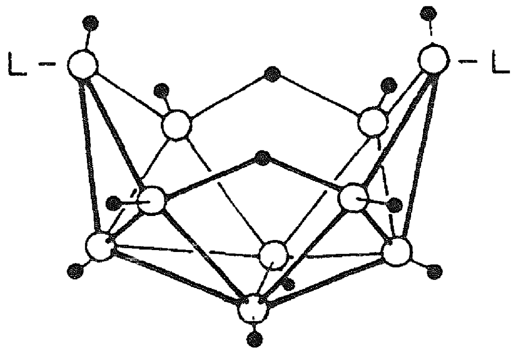


Fig. 43. Structure of $B_{10}H_{12}[S(CH_3)_2]_2$ **77c**.

form *B*-μ_2-6,7-$CH_3EB_{10}H_{13}$ **75a, b**

$$B_{10}H_{14}+(CH_3)_2E_2 \rightarrow \underset{\mathbf{75a,\ b}}{\mu_2\text{-6,7-}CH_3EB_{10}H_{13}} + CH_3EH$$

The structure of μ_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 μ_2-6,9-$CH_3EB_{10}H_{12}^-$ **76a, b**.

$$\mu_2\text{-6,7-}CH_3EB_{10}H_{13} + KH \xrightarrow{\text{rearrangement}} \underset{\mathbf{76a,b}}{K^+[\mu_2\text{-6,9-}CH_3EB_{10}H_{12}]^-} + H_2$$

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 $Cs^+[\mu_2\text{-6,9-}CH_3SB_{10}H_{12}]^-$ **76a** from an aqueous solution, it was partially hydrolyzed. A 'stable' form, a 'double salt' of the composition $\{Cs[\mu_2\text{-6,9-}CH_3SB_{10}H_{12}]\}_3\cdot Cs[\mu_2\text{-6,7-}OH\text{-}\mu_2\text{-6,9-}CH_3SB_{10}H_{11}]$ **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 tetradecahydrodecaborane, the species is believed to be the very first existing anhydride of any hypothetic hydroxyborane. **78**

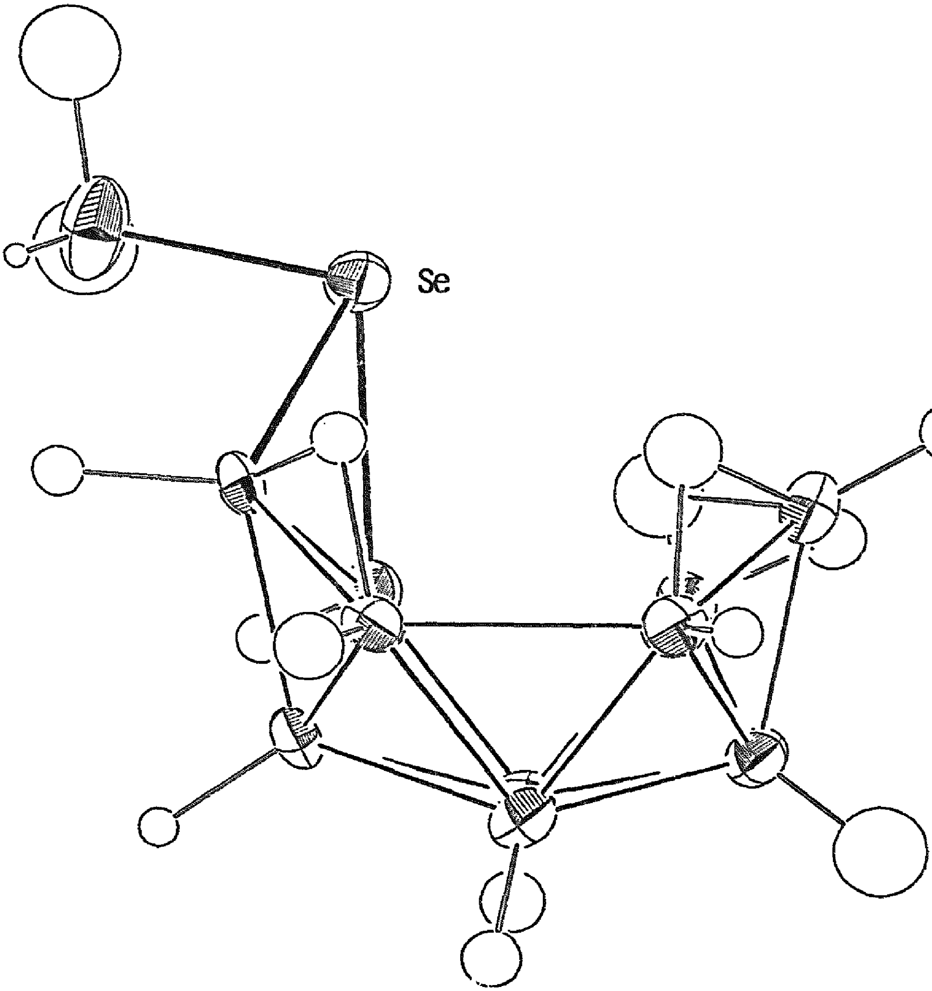


Fig. 44. Molecular structure of μ_2-6,7-$CH_3SeB_{10}H_{13}$ **75b**.

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 $B_{10}H_{13}$-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.

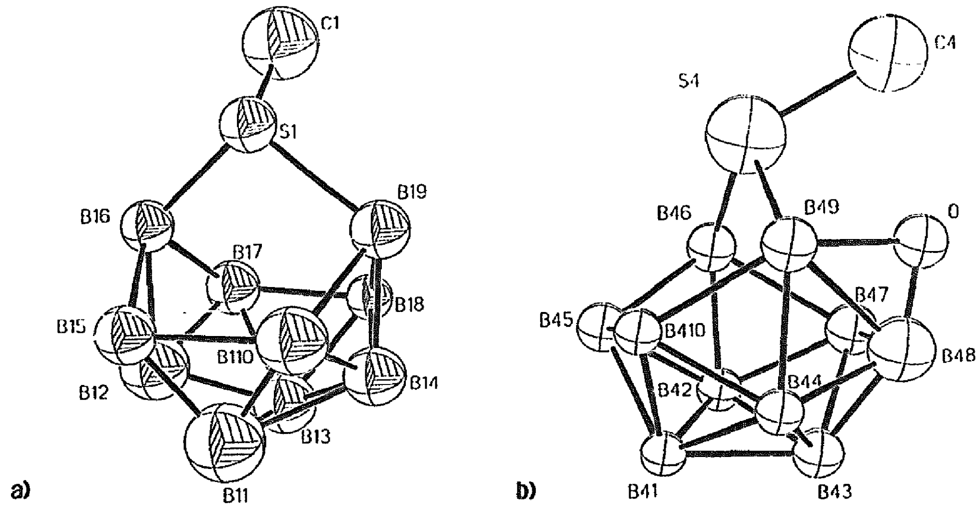


Fig. 45. (a) Molecular structures of the anion [μ_2-6,9-$CH_3SB_{10}H_{12}$] and (b) [μ_2-6,7-OH-μ_2-6,9-$CH_3SB_{10}H_{11}$] from the "double salt": {Cs[μ_2-6,9-$CH_3SB_{10}H_{12}$]}$_3\cdot$ Cs[μ_2-6,7-OH-μ_2-6,9-$CH_3SB_{10}H_{11}$] **77a**.

12.1. *closo*-$SB_{11}H_{11}$ *79a*, *12-Br–1*-$SB_{11}H_{10}$ *79b*, *closo-B*–$C_6H_5SB_{11}H_{10}$ *79c*, *closo-B,B'*$(C_6H_5)_2SB_{11}H_9$ *79d*, *closo*-$SeB_{11}H_{11}$ *79e*, *closo*-$TeB_{11}H_{11}$ *79f*

The reaction of 7-$SB_{10}H_{12}$ **69a** with $Et_3N\cdot BH_3$ produced the parent compound *closo*-$SB_{11}H_{11}$ **79a** [102]

$$7\text{-}SB_{10}H_{12} + Et_3N\cdot BH_3 \rightarrow \underset{\mathbf{79a}}{SB_{11}H_{11}} + SB_{10}H_{11}^{-}Et_3NH^{+} + Et_3N$$

Pyrolysis of 6-$SB_9H_{12}^{-}$ **67a** leads to *nido*-7-$SB_{10}H_{12}$ **69a**, which in turn gives *closo*-$SB_{11}H_{11}$ **79a** upon pyrolysis [59]. The ^{11}B 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-$SB_{11}H_{10}$ **79b**. The position of the bromine atom follows from the ^{11}B NMR spectrum, which indicates that the B12 atom is the most negative B atom in the molecule [102]. However, the initial halogenation of $SB_{11}H_{11}$ is analogous to that of 1-SB_9H_9 **50**. While the halogenation and deuteration of $SB_{11}H_{11}$ have not been studied thoroughly, the experiments in Ref. [73] indicate that the lb is the site of initial substitution.

Phenylboron dichloride reacted with $SB_{10}H_{10}^{2-}$ **73** to yield *B-closo*-$C_6H_5SB_{11}H_{10}$ **79c** [77]. This material probably possesses icosahedral geometry with the phenyl substituent bound to a boron atom adjacent to sulfur.

$$SB_{10}H_{10}^{2-} + C_6H_5BCl_2 \rightarrow \underset{\mathbf{79c}}{B\text{-}C_6H_5SB_{11}H_{10}} + 2Cl^{-}$$

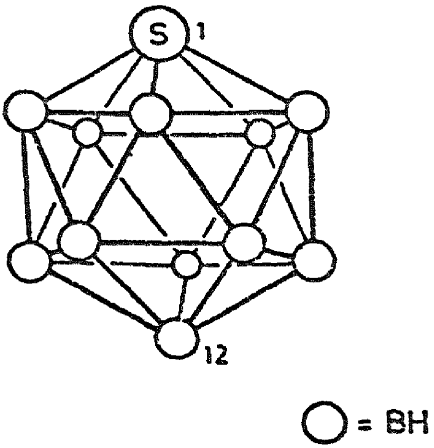


Fig. 46. Proposed structure of *closo*-$SB_{11}H_{11}$ **79a**. (From Ref. [102] by permission of The Royal Society of Chemistry, Cambridge).

The degradation of *B*-$C_6H_5SB_{11}H_{10}$ in methanolic sodium hydroxide produced *B*-$C_6H_5SB_{10}H_{10}^-$ ion. A *B,B'*-diphenyl derivative, *closo-B,B'*$(C_6H_5)_2SB_{11}H_9$ **79d** was prepared by reacting *B*-$C_6H_5SB_{10}H_{10}^-$ 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 $NaNO_2$ and $KHSO_3$ 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 $NaB_{11}H_{14}$ with an excess of $NaHSeO_3$ or solid TeO_2 in water–heptane under nitrogen produced *closo*-$SeB_{11}H_{11}$ **79e** or *closo*-$TeB_{11}H_{11}$ **79f** respectively [103]. Compounds **79e, f** have also been prepared by the reaction of $SeB_{10}H_{12}$ **69b** or $TeB_{10}H_{12}$ **69c** with $Me_3N \cdot BH_3$ in refluxing xylenes [103]. The ^{11}B NMR spectra of **79e, f** are very similar to that reported previously for $SB_{11}H_{11}$ **79a** [102]. **79e, f** have closo, nearly-icosahedral cage structures.

12.2. *nido*-$OB_{11}H_{12}^-$ 80

During the reaction of $Et_4N^+B_{11}H_{14}^-$ with the oxides M_2O_3 (M = As, Sb, Bi), besides the expected icosahedral heteroboranes, a new anionic species was isolated, initially formulated as $Et_4N^+B_{11}H_{13}OH^-$ [104,105]. However, on the basis of ^1H, ^{11}B and ^{17}O NMR spectroscopy, the correct formulation is *nido*-$OB_{11}H_{12}^-M^+$ **80** (M = Na, Et_4N, $C_6H_5CH_2NEt_3$). The proposed structure is shown in Fig. 47.

Interestingly, this anionic $OB_{11}H_{12}^-$ 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

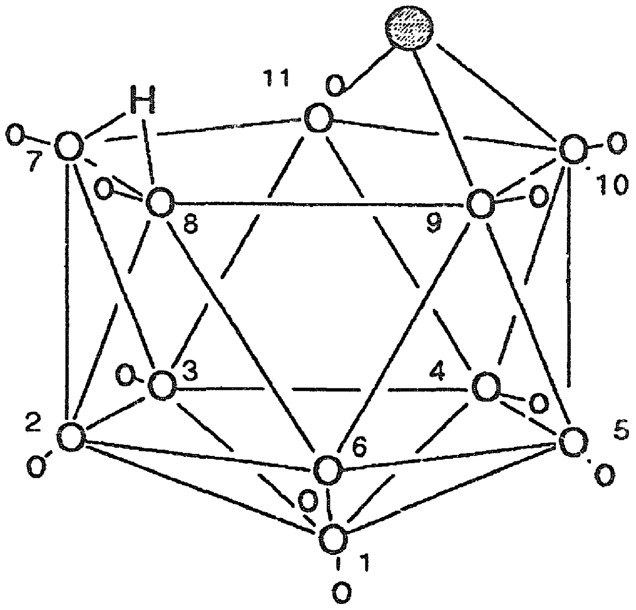


Fig. 47. Proposed structure of *nido*-$OB_{11}H_{12}^{-}M^{+}$ **80** (M = Na, Et_4N, $C_6H_5CH_2NEt_3$).

methanol with $MeNB_{11}H_{11}$ was recently shown to lead to the anionic $MeNB_{11}H_{11}OMe^{-}$ [108] which is isoelectronic with $OB_{11}H_{12}^{-}$.

13. Twelve-boron-atom systems

The compounds considered are exo-substituted polyhedral boranes.

13.1. closo-$B_{12}H_{11}SH^{2-}$ 81a, closo-$B_{12}H_{11}SCH_3^{2-}$ 81b, closo-$B_{12}H_{10}(SCH_3)_2^{2-}$ 81c, closo-*$B_{12}H_9(SCH_3)_3^{2-}$ 81d, closo-$B_{12}H_{11}S(CH_3)_2^{-}$ 81e, closo-$B_{12}H_{10}[S(CH_3)_2]_2$ 81f*

$B_{12}H_{12}^{2-}$ reacts under acidic conditions with a number of sulfur-containing species to form substitution derivatives. $B_{12}H_{11}SH^{2-}$ **81a** can be prepared from $(H_3O)_2B_{12}H_{12}$ and hydrogen sulfide. Dimethyldisulfide reacts with $(H_3O)_2B_{12}H_{12}$ to give $B_{12}H_{11}SCH_3^{2-}$ **81b** or $B_{12}H_{10}(SCH_3)_2^{2-}$ **81c** and $B_{12}H_9(SCH_3)_3^{2-}$ **81d**, depending on reaction conditions. Transmethylation of trimethylsulfonium iodide with $B_{12}H_{11}SCH_3^{2-}$ and $B_{12}H_{10}(SCH_3)_2^{2-}$ gives the inner sulfonium salts $B_{12}H_{11}S(CH_3)_2^{-}$ **81e** and $B_{12}H_{10}[S(CH_3)_2]_2$ **81f**. $B_{12}H_{11}S(CH_3)_2^{-}$ **81e** can also be obtained by methylation of $B_{12}H_{11}SH^{2-}$ [109].

13.2. $(Cs^+)_4[H_{11}B_{12}\text{–}S\text{–}S\text{–}B_{12}H_{11}]$ 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 $H_{11}B_{12}\text{–}S\text{–}S\text{–}B_{12}H_{11}^{4-}$ **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. $H_{11}B_{12}\text{–}S\text{–}S\text{–}B_{12}H_{11}^{4-}$ 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 $(Na^+)_4[H_{11}B_{12}\text{–}S\text{–}S\text{–}B_{12}H_{11}]$ **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

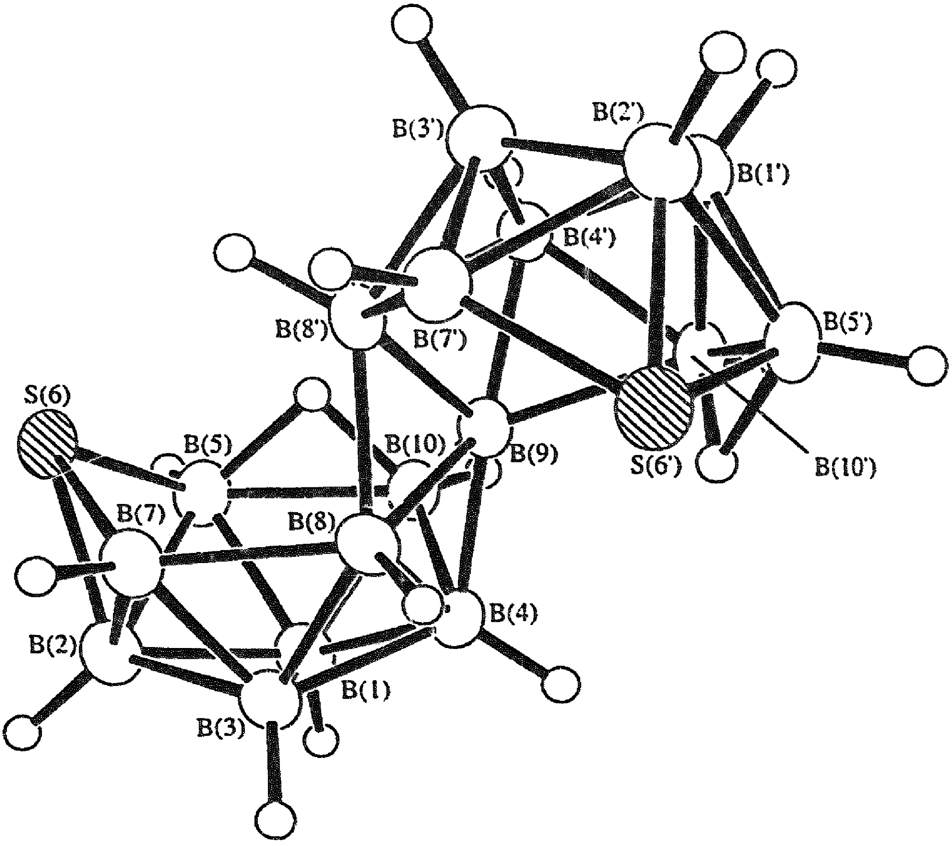


Fig. 48. ORTEP-type drawing of the molecular structure of the *arachno*-$[9,9'\text{-}S_2B_{17}H_{18}]^-$ anion in $Ph_4P^+[9,9'\text{-}S_2B_{17}H_{18}]^-$ 83. (From Ref. [114] by permission of VCH Verlagsgesellschaft mbH, Weinheim.

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

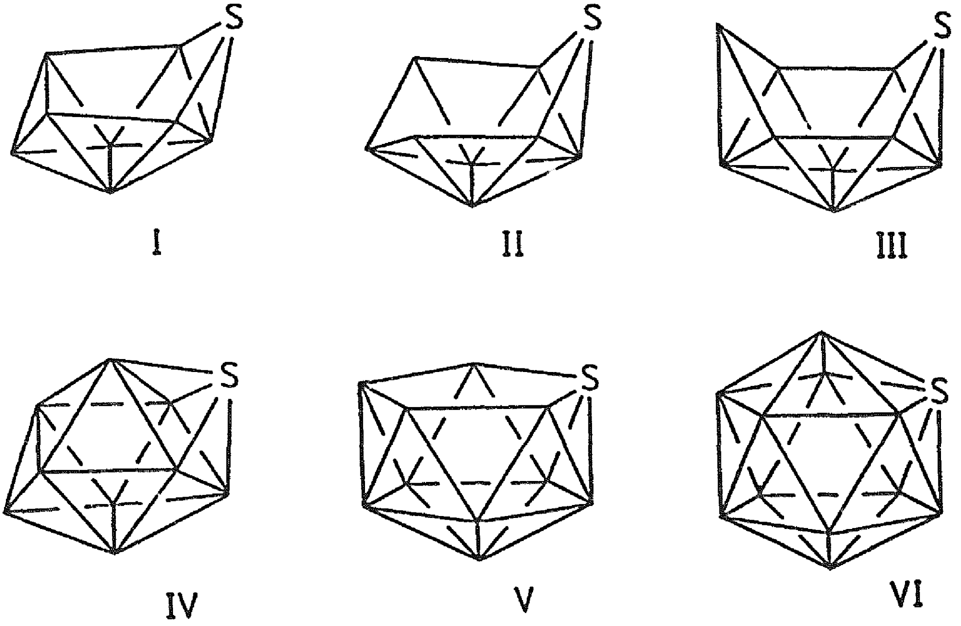
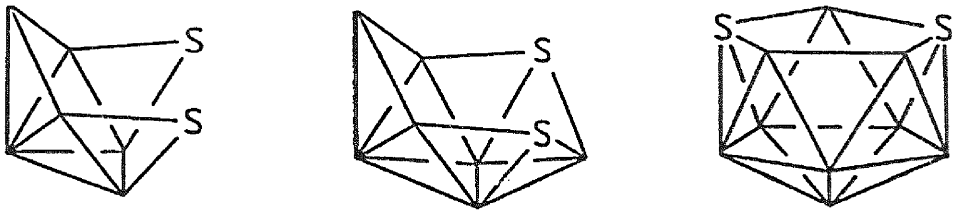


Fig. 49. Structures I–VI. (From Ref. [114] by permission of VCH Verlagsgesellschaft mbH, Weinheim).



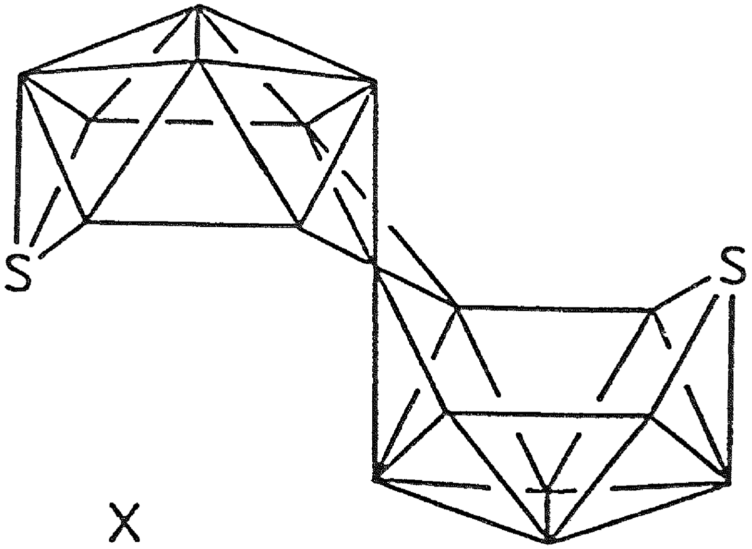
VII VIII IX

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

common vertices, between a ten-vertex *arachno*-{SB_9} cluster and an 11-vertex *arachno*-{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].



X

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

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

These comprise the nine-vertex *nido-* and *arachno-*{SB_8} system (I and II respectively), the ten-vertex *closo-*{SB_9} system IV, the ten-vertex *nido-* and *arachno-*{SB_9} (both of gross geometry III), the 11-vertex *nido-*{SB_{10}} system (V), and the 12-vertex *closo-*{SB_{11}} system (VI).

In contrast to the very extensive known dicarbaborane chemistry, only three dithiaborane building blocks (schematic geometries VII–IX) are currently reported. These comprise the eight-vertex *hypho-*{S_2B_6} system (VII), the nine-vertex *arachno-*{S_2B_7} system (VIII), and the 11-vertex *nido-*{S_2B_9} system (IX) (Fig. 50).

The schematic cluster connectivity of the presently unique large 19-vertex {S_2B_{17}} system is outlined as in (X) (Fig. 51).

References

[1] K. Wade, Structural and bonding patterns in cluster chemistry, Adv. Inorg. Chem. Radiochem., 18 (1976) 1.
[2] R.E. Williams, Adv. Inorg. Radiochem., 18 (1976) 67.
[3] S. Hermanek and J. Plesek, in G.W. Kabalka (Ed.), Current Topics in the Chemistry of Boron, The Royal Society of Chemistry, Cambridge, 1994, p. 353.
[4] H.-R. Bachmann, F. Bachmann, K.L. Kompa, H. Nöth and R. Rinck, Chem. Ber., 109 (1976) 3331.
[5] F. Bernardi, A. Bottoni and N.D. Epiotis, J. Am. Chem. Soc., 100 (1978) 7205.
[6] O. Gropen, E.W. Nilssen and H.M. Seip, J. Mol. Struct., 23 (1974) 289.
[7] K. Brendhaugen, E.W. Nilssen and H.M. Seip, Acta Chem. Scand., 27 (1973) 2965.
[8] P. Turner and I. Mills, Mol. Phys., 46 (1982) 161.
[9] T.-K. Ha, M.-T. Nguyen and L.G. Vanquinckenborne, J. Mol. Struct., 90 (1982) 99.
[10] D.C. Frost, C. Kirby, W.M. Lau, C.A. McDowell and N.P.C. Westwood, J. Mol. Struct., 100 (1983) 87.
[11] Gmelin Handbook of Inorganic Chemistry, Boron Compounds, 3rd Supplement, Vol. 4, Springer, Berlin, 1988, p. 115.
[12] M.E. Jacox, J. Phys. Chem. Ref. Data, 13 (1984) 945.
[13] Z. Egan, S.G. Shore and J.E. Bonnell, Inorg. Chem., 3 (1964) 1024.
[14] J. Beres, A. Dodds, A.J. Morabito and R.M. Adams, Inorg. Chem., 10 (1971) 2072.
[15] A. Baban and B.P. Roberts, J. Chem. Soc. Perkin Trans. II, (1987) 497.
[16] P.C. Keller, J. Chem. Soc. Chem. Commun., (1969) 209.
[17] P.C. Keller, Inorg. Chem., 8 (1969) 1695.
[18] J.D. Cotton and T.C. Waddington, J. Chem. Soc. A, (1966) 789.
[19] (a) L.D. Schwartz and P.C. Keller, Inorg. Chem., 10 (1971) 645; (b) N.R. Thompson, J. Chem. Soc. (London), (1965) 6290; (c) J.W. Gilje, K.W. Morse and R.W. Parry, Inorg. Chem., 6 (1967) 1761; (d) R.E. Hester and E. Mayer, Spectrochim. Acta Part A, 23 (1967) 2218; (e) E. Mayer and A.W. Laubengayer, Monatsh. Chem., 101 (1970) 1138; (f) E. Mayer and R.E. Hester, Spectrochim. Acta Part A, 25(1969) 237.
[20] H. Binder, H. Loos, H. Borrmann, A. Simon, H.-J. Flad and A. Savin, Z. Anorg. Allg. Chem., 619 (1993) 1353.
[21] H. Binder, W. Ehmann and K. Dermentzis, Z. Naturforsch. Teil B, 46 (1991) 581.
[22] M. Lalancette, A. Frêche and R. Monteux, Can. J. Chem., 46 (1968) 2754.
[23] H. Binder and W. Diamantikos, Z. Naturforsch. Teil B, 38 (1983) 203.
[24] C. Wayne, E.E. Entreken and A.R. Guida, J. Org. Chem., 49 (1984) 3024.
[25] H. Binder, H. Loos, K. Dermentzis, H. Borrmann and A. Simon, Chem. Ber., 124 (1991) 427.

[26] B.F. Spielvogel and E.F. Rothgery, J. Chem. Soc. Chem. Commun., (1966) 765.
[27] P.C. Keller, Inorg. Chem., 8 (1969) 1695.
[28] H. Binder, I. Duttlinger, H. Loos, K. Locke, A. Pfitzner, H.-J. Flad, A. Savin and M. Kohout, Z. Anorg. Allg. Chem., 621 (1995) 400.
[29] P.C. Keller, J. Chem. Soc. Chem. Commun., (1969) 209.
[30] H. Binder, A. Ziegler, R. Ahlrichs and H. Schiffer, Chem. Ber., 120 (1987) 1545.
[31] A.B. Burg and R.I. Wagner, J. Am. Chem. Soc., 76 (1954) 3307.
[32] E.L. Muetterties, N.E. Miller, K.J. Packer and H.C. Miller, Inorg. Chem., 3 (1964) 870.
[33] R. Köster, G. Seidel and R. Boese, Chem. Ber., 121 (1988) 1137.
[34] H. Binder, W. Ehmann and K. Dermentzis, Z. Naturforsch. Teil B, 46 (1991) 581.
[35] H. Nöth and R. Staudigl, Chem. Ber., 115 (1982) 813.
[36] H. Nöth and D. Sedlak, Chem. Ber., 116 (1983) 1479.
[37] W. Biffar, H. Nöth and D. Sedlak, Organometallics, 2 (1983) 579.
[38] O. Gropen, E.W. Nielssen and H.M. Seip, J. Mol. Struct., 23 (1974) 289.
[39] O. Gropen, Acta Chem. Scand. Ser. A, 29 (1975) 873.
[40] H. Binder, unpublished results.
[41] H. Nöth and G. Mikulaschek, Z. Anorg. Allg. Chem., 311 (1961) 241.
[42] B. Brellochs and H. Binder, Angew. Chem. Int. Ed. Engl., 27 (1988) 262; Angew. Chem., 100 (1988) 270.
[43] H. Binder, B. Brellochs, B. Frei, A. Simon and B. Hettich, Chem. Ber., 122 (1989) 1049.
[44] H. Binder, P. Melidis, S. Söylemez and G. Heckmann, Phosphorus Sulfur Silicon, 64 (1992) 1.
[45] H. Binder, P. Melidis, S. Söylemez and G. Heckmann, J. Chem. Soc. Chem. Commun., (1991) 1091.
[46] M.L. McKee, Inorg. Chem., 25 (1986) 3545.
[47] H. Binder, W. Diamantikos, K. Dermentzis and H.-D. Hausen, Z. Naturforsch. Teil B, 37 (1982) 1548.
[48] K. Wolfer, H.-D. Hausen and H. Binder, Z. Naturforsch. Teil B, 40 (1985) 235.
[49] H. Binder, K. Wolfer, W. Ehmann, W.-P. Pfeffer. K. Peters, H. Horn and R. Ahlrichs, Chem. Ber., 125 (1992) 651.
[50] K. Mazghi, P.J. Carroll and L.G. Sneddon, Inorg. Chem., 31 (1992) 3197.
[51] S.O. Kang and L.G. Sneddon, J. Am. Chem. Soc., 111 (1989) 3281.
[52] K. Base, S. Hermanek and F. Hanousek, J. Chem. Soc. Chem. Commun., (1984) 299.
[53] J. Holub, T. Jelinek, B. Stibr, J.D. Kennedy and M. Thornton-Pett, in G.W. Kabalka (Ed.), Current Topics in the Chemistry of Boron, The Royal Society of Chemistry, Cambridge, 1994, p. 359.
[54] J. Plesek, S. Hermanek and Z. Janousek, Coll. Czech. Chem. Commun., 42 (1977) 785.
[55] S.O. Kang and L.G. Sneddon, in G.A. Olah, K. Wade and R.E. Williams (Eds.), Electron Deficient Boron and Carbon Clusters, Wiley, New York, 1991, pp. 195–213 and references cited therein.
[56] G.D. Friesen, A. Barriola, P. Daluga, P. Ragatz and J.C. Huffman, Inorg. Chem., 19 (1980) 458.
[57] G.D. Friesen, A. Barriola and L.J. Todd, Chem. Ind., (1978) 631.
[58] D.A. Thompson, T.K. Hilty and R.W. Rudolph, J. Am. Chem. Soc., 99 (1977) 6774.
[59] W.R. Pretzer and R.W. Rudolph, J. Am. Chem. Soc., 98 (1976) 1441.
[60] K. Base, S. Hermanek and V. Gregor, Chem. Ind., (1979) 743.
[61] K. Base, M.G.H. Wallbridge, X.L.R. Fontaine, N.N. Greenwood, J.D. Kennedy and B. Stibr, Polyhedron, 8 (1989) 2089.
[62] S.O. Kang and L.G. Sneddon, Inorg. Chem., 27 (1988) 3298.
[63] J. Holub, B. Stibr, J.D. Kennedy, M. Thornton-Pett, T. Jelinek and J. Plesek, Inorg. Chem., 33 (1994) 4545.
[64] V.A. Brattsev, S.P. Knyazev, G.N. Danilova and V.I. Stanko, J. Gen. Chem. USSR, (1975) 1364.
[65] K. Base and B. Stibr, Chem. Ind., (1977) 919.
[66] B. Stibr, K. Base, J. Plesek, S. Hermanek, J. Dolansky and Z. Janousek, Pure Appl. Chem., 49 (1977) 803.
[67] G.D. Friesen, R.L. Kump and L.J. Todd, Inorg. Chem., 19 (1980) 1485.
[68] J. Holub, T. Jelinek, J. Plesek, B. Stibr, S. Hermanek and J.D. Kennedy, J. Chem. Soc. Chem. Commun., (1991) 1389.
[69] W.R. Pretzer and R.W. Rudolph, J. Am. Chem. Soc., 95 (1973) 931.

[70] W.R. Pretzer and R.W. Rudolph, J. Chem. Soc. Chem. Commun., (1974) 629.
[71] W.R. Pretzer, T.K. Hilty and R.W. Rudolph, Inorg. Chem., 14 (1975) 2459.
[72] R.E. Williams, Inorg. Chem., 10 (1971) 210.
[73] W.L. Smith, B.J. Meneghelli, D.A. Thompson, P. Klymko, N. McClure, M. Bower and R.W. Rudolph, Inorg. Chem., 16 (1977) 3008.
[74] W.L. Smith, B.J. Meneghelli, N. McClure and R.W. Rudolph, J. Am. Chem. Soc., 98 (1976) 624.
[75] W.R. Pretzer and R.W. Rudolph, Inorg. Chem., 15 (1976) 1775.
[76] B.J. Meneghelli and R.W. Rudolph, J. Organomet. Chem., 133 (1977) 139.
[77] W.R. Hertler, F. Klanberg and E.L. Muetterties, Inorg. Chem., 11 (1967) 1696.
[78] K. Base, Coll. Czech. Chem. Commun., 48 (1983) 2593.
[79] M. Bown, X.L.R. Fontaine and J.D. Kennedy, J. Chem. Soc. Dalton Trans., (1988) 1467.
[80] A.R. Siedle, D. McDowell and L.J. Todd, Inorg. Chem., 13 (1974) 2735.
[81] T.K. Hilty and R.W. Rudolph, Inorg. Chem., 18 (1979) 1106.
[82] A.R. Kane, L.J. Guggenberger and E.L. Muetterties, J. Am. Chem. Soc., 92 (1970) 2571.
[83] B.J. Meneghelli and R.W. Rudolph, J. Am. Chem. Soc., 100 (1978) 4626.
[84] B.J. Meneghelli, M. Bower, N. Canter and R.W. Rudolph, J. Am. Chem. Soc., 102 (1980) 4355.
[85] N.Canter, C.G.Overberger and R.W.Rudolph, Organometallics, 2 (1983) 569.
[86] S. Küpper, P.J. Carroll and L.G. Sneddon, J. Am. Chem. Soc., 114 (1992) 4914.
[87] N. Wiberg, Adv. Organomet. Chem., 24 (1985) 179.
[88] J.L. Little, G.D. Friesen and L.J. Todd, Inorg. Chem., 16 (1977) 869.
[89] J. Holub, A.E. Wille, B. Stibr, P.J. Carroll and L.G. Sneddon, Inorg. Chem., 33 (1994) 4920.
[90] O.N. Dhubhghaill, D. Reed and T.R. Spalding, Polyhedron, 12 (1993) 1977.
[91] F. Klanberg, E.L. Muetterties and L.J. Guggenberger, Inorg. Chem., 7 (1968) 2272.
[92] L.J. Guggenberger, J. Organomet. Chem., 81 (1974) 271.
[93] E.L. Muetterties, W.G. Peet, P.A. Wegner and C.W. Alegranti, Inorg. Chem., 9 (1970) 2447.
[94] A.R. Siedle, G.M. Bodner, A.R. Garber and L.J. Todd, Inorg. Chem., 13 (1974) 1756.
[95] X.L.R. Fontaine and J.D. Kennedy, J. Chem. Soc. Dalton Trans., (1987) 1573.
[96] B.M. Graybill, J.K. Ruff and M.F. Hawthorne, J. Am. Chem. Soc., 83 (1961) 2669.
[97] D.A. Thompson, W.R. Pretzer and R.W. Rudolph, Inorg. Chem., 15 (1976) 2948.
[98] (a) J. Van der Maas Reddy and W.N. Lipscomb, J. Am. Chem. Soc., 81 (1959) 754; (b) J. Van der Maas Reddy and W.N. Lipscomb, J. Chem. Phys., 31 (1959) 610; (c) D.E. Sands and A. Zalkin, Acta Crystallogr., 15 (1962) 410.
[99] (a) H. Binder, S. Söylemez, M. Hofmann and A. Pfitzner, unpublished results; (b) S. Söylemez, Dissertation, University of Stuttgart, 1994.
[100] H. Binder, R. Stöckle, S. Söylemez and A. Pfitzner, unpublished results.
[101] J. Plesek, S. Hermanek and B. Stibr, Coll. Czech. Chem. Commun., 33 (1968) 691.
[102] J. Plesek and S. Hermanek, J. Chem. Soc. Chem. Commun., (1975) 127.
[103] G.D. Friesen and L.J. Todd, J. Chem. Soc. Chem. Commun., (1978) 349.
[104] A. Ouassas, C. R'Kha, H. Mongeot and B. Frange, Inorg. Chim. Acta, 180 (1991) 257.
[105] A. Ouassas, B. Fenet, H. Mongeot and B. Frange, in G.W. Kabalka (Ed.), Current Topics in the Chemistry of Boron, The Royal Society of Chemistry, Cambridge, 1994, p. 363.
[106] R.P. Micciche, J.J. Briguglio and L.G. Sneddon, Inorg. Chem., 23 (1984) 3992.
[107] E.J. Ditzel, X.L.R. Fontaine, H. Fowkes, N.N. Greenwood, J.D. Kennedy, P. MacKinnon, Z. Sisan and M. Thornton-Pett, J. Chem. Soc. Chem. Commun., (1990) 1692.
[108] F. Meyer, J. Müller, P. Paetzold and R. Boese, Angew. Chem., 104 (1992) 1221.
[109] W.H. Knoth, J.C. Sauer, D.C. England, W.R. Hertler and E.L. Muetterties, J. Am. Chem. Soc., 86 (1964) 3973.
[110] G.R. Wellum, E.I. Tolpin and A.H. Soloway, Inorg. Chem., 16 (1977) 2120.
[111] A.H. Soloway, Progr. Boron Chem., 1 (1964) Chapter 4.
[112] A.H. Soloway, N.A. Spinelli and A. Kaczmarczyk, paper presented in part at the 136th Meet. American Association of Science, Boston, 1969.
[113] H. Hatanaka and S. Keiji, Z. Neurol., 204 (1973) 309.
[114] T. Jelinek, J.D. Kennedy, B. Stibr and M. Thornton-Pett, Angew. Chem., 106 (1994) 1663.