

CHAPTER 1

Compounds Containing the Boron–Chalcogen B–E (E=S, Se, Te) Bond

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1.1 Introduction

This chapter focusses on compounds with chalcogen (E=S, Se, Te) to B bonds and reviews the chemical literature over the period 1990–2004. Although every effort has been made to include all important advances in all sections, the review is not claimed to be comprehensive. The literature has been surveyed principally by independent keyword searches of the primary chemical journals and *ISI Web of Science* augmented by *ACS Chemical Abstracts* and *RSC Annual Reports on the Progress of chemistry, Section A (Inorganic Chemistry)*. The review is structured so that relevant books, conference proceedings, and review articles that have appeared over the period are described first, and then the chemistry of specific topics are explored in more detail. Polyhedral boron hydride cluster species forms a major section of this review and this section is conveniently divided into sub-sections depending upon the nature of the B–E linkages. The remaining principal sections of this review cover two other important themes: heterocycles containing B–E linkages, and thioborate and selenoborate chemistry. The review concludes with a miscellaneous section, which includes B–E reagents.

1.2 Books and Review Articles

Sections relating to compounds with B–E bonds can be found in the authoritative review chapters found in *Comprehensive Organometallic Chemistry II* (vol 1); these chapters generally survey the literature over the period 1982–1994. In particular, Chapter 4 has a section reporting on cyclic systems with B–E

(E=S, Se) bonds,¹ and Chapter 7 surveys main group heteroboranes, with a section on thiaboranes and their metal complexes.² Metalloboranes, carboranes, and metallocarboranes are reviewed in Chapters 8, 6, and 9, respectively, with many such clusters containing *exo* B–E bonds.^{3–5} The ‘International Meeting on Boron Chemistry’ (IMEBORON) has met on a number of occasions over the review period and the proceedings of these conferences have been published; these collections give an interesting perspective on the development of boron chemistry in general but with many relevant articles.⁶ A review on chalcogenoboron hydrides was published in 1997 giving a historical viewpoint and covering the literature to 1997.⁷ An overview of heteroboranes in which p-block elements (including S, Se, and Te) have replaced one or more vertices in parent borane cages was reported in 2002.⁸ The topic of thioborate and selenoborates have been reviewed on a number of occasions,^{9–11} with the most recent¹² in 2003 discussing their diverse structures, which range from rings, through clusters to 3d networks.

1.3 Polyhedral Boron Hydride Derivatives

1.3.1 Species with *Exo* B–Chalcogen Bonds

1.3.1.1 Boranes and Heteroboranes

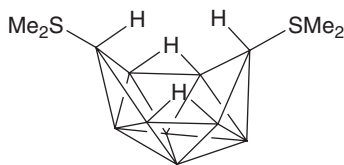
There were a considerable number of reports over the period 1990–2004 on polyhedral boron hydride species with *exo*-chalcogen bonds and the following section is structured in terms of increasing polyhedral size. There were also a few reports on polyhedral carborane species, which are at the end of this section, but there were no reports on other heteroborane species with *exo*-chalcogen bonds.

$\text{Na}[\text{H}_3\text{B}-\mu_2\text{-S}(\text{B}_2\text{H}_5)]$ was obtained from reaction of NaSH with $\text{BH}_3\cdot\text{thf}$,¹³ and $\text{Na}_2[\text{H}_3\text{BSe}_2\text{BH}_3]$, produced by the reaction of elemental Se with $\text{Na}[\text{BH}_4]$, was found to react with excess B_2H_6 to form the related salt $\text{Na}[\text{H}_3\text{B}-\mu_2\text{-Se}(\text{B}_2\text{H}_5)]$.¹⁴ Bi-functional thiols (HSRSH, R=CH₂, CH₂CH₂, CH₂CH₂CH₂, 1,2-C₆H₄) were found to react with B_4H_{10} to afford *trans*-annularly bridged species *e.g.* *cis*- and *trans*- $[(\text{BH}_2)(\mu_2\text{-SRS})(\text{BH})(\text{B}_2\text{H}_5)]$. Upon cooling a fully reversible rearrangement occurred and a ‘butterfly’-type structure, $[(\text{BH}_2)(\mu_2\text{-SRS})(\text{B}_3\text{H}_6)]$ was obtained, again as a mixture of *cis* and *trans* isomers.¹⁵ The adduct, $\text{B}_3\text{H}_7(\text{SMe}_2)$ (**1**) which was isolated as a liquid at room temperature, reacted slowly with additional SMe_2 to yield B_5H_9 with the mechanism of this borane framework expansion believed to involve the diborane(4) adduct, $\text{B}_2\text{H}_4(\text{SMe}_2)_2$.¹⁶ The reaction of **1** with excess NMe_3 in Me_2S at low temperature (–80––30 °C) led to $\text{B}_2\text{H}_4(\text{NMe}_3)_2$, but the ligand-exchanged adduct $\text{B}_3\text{H}_7(\text{NMe}_3)$ was shown not to be an intermediate in this reaction.¹⁷ Treatment of **1** with BCl_3 yielded the chloro-substituted derivative $\text{B}_3\text{H}_6\text{Cl}(\text{SMe}_2)$.¹⁸ Reactions of B_5H_{11} and Me_2S produced $\text{B}_4\text{H}_8(\text{SMe}_2)$ (**2**) and an unstable pentaborane adduct, $\text{B}_5\text{H}_{11}(\text{SMe}_2)$, which was shown to be a precursor to the

tetraborane adduct, **2**.¹⁹ The *closo* anion $[\text{B}_6\text{H}_6]^{2-}$ was found to react with $(\text{SeCN})_2$ in organic media to produce $[\text{PPh}_4]_2[(\text{SeCN})\text{B}_6\text{H}_5]$, characterized by single-crystal X-ray diffraction (XRD) studies.²⁰ Treatment of $[\text{NBu}_4][\text{B}_6\text{H}_7]$ with $(\text{SCN})_2$ or $(\text{SeCN})_2$ in dichloromethane solution in the presence of solid KOH resulted in the hexaborate species $[\text{NBu}_4]_2[\text{B}_6(\text{ECN})_6]$ (E=S, Se).²¹ The conventional preparation of 4-(L)-*arachno*- B_9H_{13} derivatives, by ligand exchange on 4-(SMe_2)-*arachno*- B_9H_{13} , was shown by NMR spectroscopy to also generate the previously unreported isomeric species 5-(L)-*arachno*- B_9H_{13} .²²

A series of mono- and di-substituted Me_2S derivatives were obtained from the reaction of DMSO in acid with $\text{Cs}_2[\text{B}_{10}\text{H}_{10}]$, and through a modified procedure the tri-substituted 1,10-(Me_2S)₂-2-(MeS) B_{10}H_7 species was obtained.²³ The *closo* anion $[\text{B}_{10}\text{H}_{10}]^{2-}$ was found to react with $(\text{SeCN})_2$ in organic media and produced $[\text{PPh}_4]_2[(\text{SeCN})\text{B}_{10}\text{H}_9]$ characterized by single-crystal XRD studies.²⁰

The hydroboration of alkenes with 6,9-(SMe_2)₂ $\text{B}_{10}\text{H}_{12}$ (**3**) yielded 6-R-8-(SMe_2)- $\text{B}_{10}\text{H}_{11}$ (R= Pr^n , oct^n , hex^n , 3-methyl-2-butyl, 2,3-dimethyl-2-butyl), which was converted to the corresponding alkyl derivative, 6-R- $\text{B}_{10}\text{H}_{13}$, by treatment with ‘super-hydride’ ($\text{LiEt}_3\text{BH}/\text{thf}$).²⁴ Mechanistic experiments on the formation of **3** from *nido*- $\text{B}_{10}\text{H}_{14}$ and its subsequent reaction with 2,3-dimethylbut-2-ene to form *nido*-5-(Me_2S)-9-($\text{CMe}_2\text{CHMe}_2$) $\text{B}_{10}\text{H}_{11}$ indicated that the movement of the Me_2S from B6 to B5 did not involve a concerted rearrangement of the boron cage, but rather a migration of H and Me_2S on an otherwise static borane cluster.²⁵ A high yield route to *nido*-6-alkyl decarborane(14) derivatives starting from **3** via a one-pot synthesis was reported with XRD results described for *nido*-6-($\text{CMe}_2\text{CHMe}_2$)-8-(SMe_2) $\text{B}_{10}\text{H}_{11}$ (Scheme 1).²⁶

**3**

Scheme 1

Compound **3** reacted with the phosphalkyne PC^tBu to form a product with two B_{10} cages linked by a HPCBu^t bridge, $[\text{B}_{10}\text{H}_{11}(\text{SMe}_2)][\text{CBu}^t\text{PH}][\text{B}_{10}\text{H}_{12}]$.²⁷ The mild thermolysis of **3** in inert hydrocarbon solvents gave the tridecaboranyl species, 6,9-(Me_2S)₂-*arachno*- $\text{B}_{10}\text{H}_{10}$ -1,5-(6'-*nido*- $\text{B}_{10}\text{H}_{13}$)₂ (**4**) in 23% yield (Figure 1).²⁸ The reaction of Me_2Se_2 with *nido*- $\text{B}_{10}\text{H}_{14}$ yielded *arachno*-6,7- μ -(MeSe) $\text{B}_{10}\text{H}_{13}$, whereas Me_2S_2 failed to react under similar conditions; however, the analogous thiomethyl derivative, 6,7- μ -(MeS) $\text{B}_{10}\text{H}_{13}$, was formed by the reaction of *nido*- $\text{B}_{10}\text{H}_{14}$ with Me_2S_3 .²⁹ The kinetics of *ortho*- $\text{C}_2\text{B}_{10}\text{H}_{12}$ formation from acetylenes (propargyl bromide, but-2-yne-1,4-diacetate, or non-1-yne) and *arachno*-6,9- $\text{B}_{10}\text{H}_{12}\text{L}_2$ [$\text{L}=\text{Me}_2\text{S}$ (**3**), Ph_2S , Bu^t_2S , $(\text{C}_6\text{F}_5)_2\text{S}$,

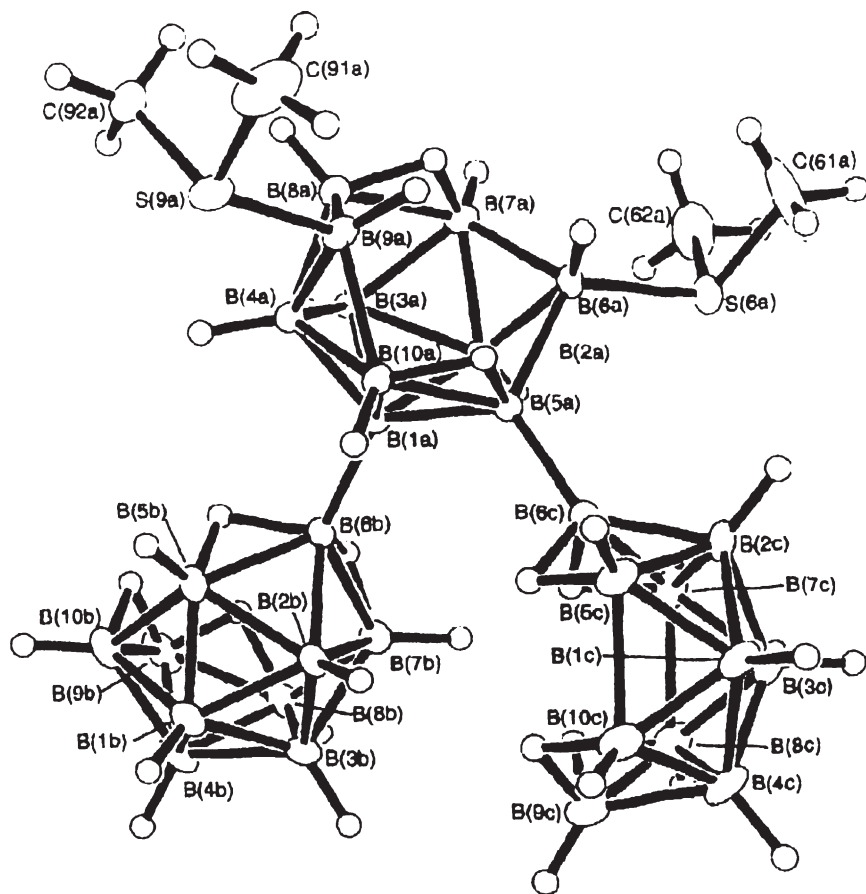


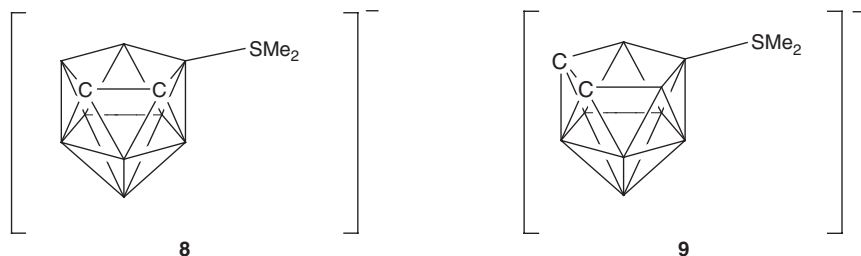
Figure 1 Molecular structure of 6,9-(SMe₂)₂-arachno-B₁₀H₁₀-1,5-(6'-nido-B₁₀H₁₃)₂ (**4**)
(Reproduced with permission from Chem. Commun., 2001, 1788.)

MePhS, Me(C₆F₅)S, or MeBu^tS] have been investigated in detail: the rate constants decreased both with increased electronegativity and/or increased size of the substituent on S, with the yield increased as the size and/or basicity of the Lewis base increased.³⁰

Excess H₂SO₄ and Me₂S were found to react with [Me₃NH][B₁₁H₁₄] to yield 7-(SMe₂)₂-B₁₁H₁₃ in good yield; upon warming to 110 °C, the adduct rearranged to a mixture of 1- and 7-isomers.³¹

A one-step preparation of the Me₂S-substituted icosahedral boranes 1,7-(SMe₂)₂B₁₂H₁₀ (**5**), 1,12-(SMe₂)₂B₁₂H₁₀ (**6**), and [SMe₃][B₁₂H₁₁(SMe₂)] has been reported from the self-condensation reaction of BH₃.SMe₂.³² The 1,2-isomer, 1,2-(Me₂S)₂B₁₂H₁₀ (**7**) obtained from a mixture of products from the pyrolysis of BH₃.SMe₂ was characterized by XRD and multinuclear NMR, and

these charge-compensated derivatives, the *nido* 11-vertex $\{C_2B_9\}$ carborane (1-) anion is coordinated η^5 to a metal centre and in the process forms an icosahedral *closo* 12-vertex $\{MC_2B_9\}$ cluster.



Scheme 3

The chemistry of monoanionic carborane ligands has been investigated by exploring the conformation adopted by formal two-orbital metal cluster bonding contributors by reactions of $Tl[9-(SMe_2)\text{-}nido\text{-}7,8\text{-}C_2B_9H_{10}]$ (**118**) with complexes of Rh(I) and Pd(II).⁴² The synthesis and structure of the ferracarborane $Fe\mathbf{8}_2$ and its charge transfer salt with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (**9**) has been reported with its magnetic properties discussed (Scheme 3).⁴³ The mixed-sandwich ferracarborane complex $CpFe\mathbf{8}$ has been synthesized and characterized by cyclic voltametry, IR, and 1H and ^{11}B NMR spectroscopy; it formed stable 1:1 charge transfer salts with **9** and 7,7,8,8-tetracyano-2,3,5,6-tetrafluoroquinodimethane.⁴⁴ The complex $[(cod)Rh\mathbf{8}]$ has been used to prepare the halide complexes $[[X_2Rh\mathbf{8}]_2]$ ($X=Cl, Br, I$) by reaction with HX .⁴⁵ These complexes have been further used to prepare several sandwich and half-sandwich complexes containing the 'Rh $\mathbf{8}$ ' fragment.⁴⁵ The reaction of **8** with $[(\text{arene})RuCl_2]_2$ ($\text{arene}=C_6H_6, 1,3,5\text{-}C_6H_3Me_3$) afforded the cationic ruthenium arene cluster complexes $[(\text{arene})Ru\mathbf{8}][BF_4]$.⁴⁶ Reaction of $[[RuCl_2(C_6H_6)]_2]$ with $[10-(Me_2S)\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]^-$ (**10**) afforded the expected cationic complex $[(C_6H_6)Ru\mathbf{10}]^+$ and the unexpected neutral complex $[(C_6H_6)Ru\{10-(HS)\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}\}]$.⁴⁷ Ruthenacarborane clusters of the formula $[3,3,3\text{-}H(PPh_3)_2\text{-}8\text{-}L\text{-}closo\text{-}3,1,2\text{-}RuC_2B_9H_{10}]$ ($L=SMe_2, SET_2, S(CH_2)_4, SEtPh$) and $[1\text{-}Me\text{-}3,3,3\text{-}H(PPh_3)_2\text{-}8\text{-}L\text{-}closo\text{-}3,1,2\text{-}RuC_2B_9H_9]$ ($L=SMe_2, SET_2$) were prepared by the reaction of the corresponding ligands with $[RuCl_2(PPh_3)_3]$.⁴⁸ A series of $\{(PPh_3)_2Rh^{(I)}\}$ fragment half-sandwich complexes were similarly prepared by reaction of these charge-compensated ligands with $[RhCl(PPh_3)_3]$.⁴⁹ Ruthenium complexes with monoanionic carborane ligands *e.g.* $[RuH(PPh_3)_3\mathbf{8}]$, $[RuH(PPh_3)_3\{9-(SR_2)\text{-}7\text{-}Me\text{-}7,8\text{-}C_2B_9H_9\}]$, have been shown to efficiently catalyze the Kharasch addition of CCl_4 across olefins.⁵⁰ The cluster substitution product, $[Mo(CO)_2(\eta^3\text{-}C_3H_5)\{(7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-}(SMe_2))\}]$, was obtained from treatment of the salt $[NEt_4][Mo(CO)_2(\eta^3\text{-}C_3H_5)\{(7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)\}]$ with $[CPh_3][BF_4]$ and SMe_2 in CH_2Cl_2 .⁵¹ Three dialkylsulfane-substituted *nido* carboranes $7,8\text{-}Ph_2\text{-}10\text{-}(SR_2)\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}$

($R_2=Me_2$, Me/Et, Et₂) have been synthesized and characterized and the SMe_2 -labelled B atoms gave useful stereochemical information on the course of 12-vertex MC_2B_9 isomerizations.⁵² The synthesis and reactivity of the sterically encumbered charge-compensated carborane 7-Ph-11-(SMe_2)-*nido*- $C_2B_9H_{10}$ and its conversion to [1-Ph-3,3-(CO)₂-7-(SMe_2)-3,1,2-*closo*- $RhC_2B_9H_8$] has been described.⁵³

The donor molecule Me_2S reacted with the anion $[Fe(CO)_3(\eta^5-7-CB_{10}H_{11})]^-$ in the presence of acids and hydride-abstrating reagents and gave the zwitterionic complex $[Fe(CO)_3(\eta^5-9-(SMe_2)-7-CB_{10}H_{11})]$ in which the SMe_2 was bound to a B atom lying in a β site with respect to the C.⁵⁴ Reaction of the monocarborane derivative $[Pt_2(PEt_3)_4(\eta^5:\eta^5-9,9-I(H)-7-CB_{10}H_{10})_2]$ with $PhSeCl$, Ph_2Se_2 , and $PhTeI$ yielded products with chalcogen substituents on Pt, or Pt and B.⁵⁵

The electronically saturated chromaborane $[Cp^*_2Cr_2B_4H_8]$, when reacted with CS_2 , produced in high yield the saturated cluster $[Cp^*_2Cr_2(CH_2S_2)B_4H_6]$ (**11**), which contained the intracuster bridging methanedithiolato $\{CH_2S_2\}$ ligand (Figure 2).⁵⁶ The reaction of CS_2 with the open *nido*-6-iridadecaboranes $[H(PPh_3)_2\text{-}nido\text{-}6\text{-}IrB_9H_{13}]$ and $[H(PPh_3)(ortho\text{-}Ph_2PC_6H_4)\text{-}nido\text{-}6\text{-}IrB_9H_{12}\text{-}5]$ yielded *closo* 10-vertex species with boron to metal dithioformate bridges.⁵⁷ The *isocloso* species $[1,1,1\text{-}H(PPh_3)(ortho\text{-}Ph_2PC_6H_4)\text{-}isocloso\text{-}1\text{-}IrB_9H_8\text{-}2]$ reacted similarly and produced the *closo* species $[10\text{-}(PPh_3)\text{-}2,6:2,9\text{-}(\mu\text{-}S_2CH_2)_2\text{-}2\text{-}(ortho\text{-}Ph_2PC_6H_4)\text{-}closo\text{-}2\text{-}Ir\text{-}B_9H_5\text{-}1]$ with an unusual *isocloso* \rightarrow *closo* conversion.⁵⁷

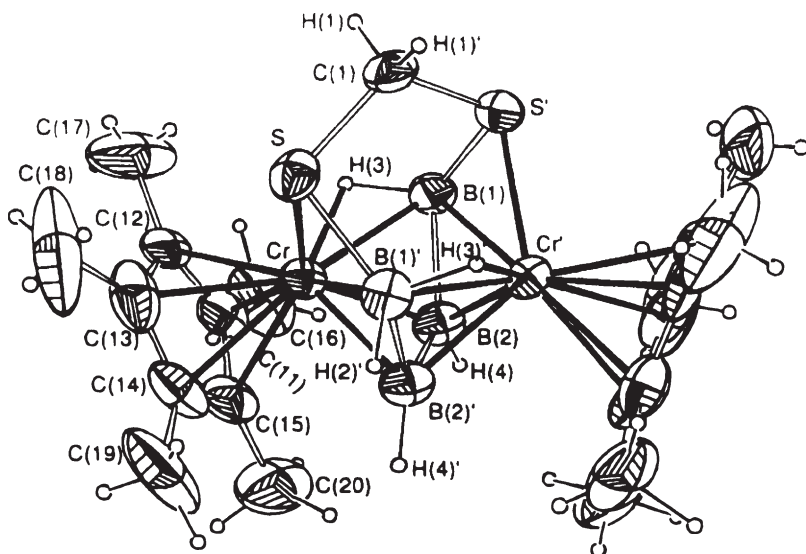


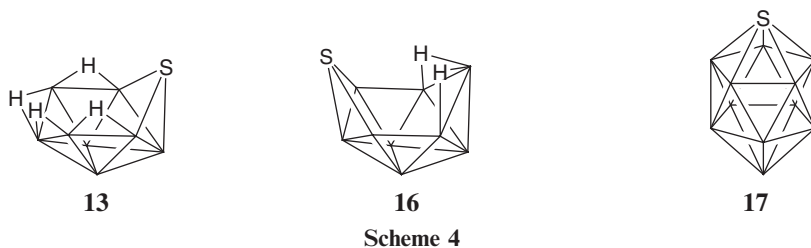
Figure 2 Molecular structure of $[Cp^*_2Cr_2(CH_2S_2)B_4H_6]$ (**11**)
(Reproduced with permission from *Organometallics*, 1996, **15**, 1964.)

1.3.2 Species with Chalcogen Atoms within the Cage

1.3.2.1 Chalcogenoboranes

This important area of boron–chalcogen chemistry has made some tremendous advances, particularly in macropolyhedral systems, in recent years. The topic was recently reviewed^{7,8} in 1997 and 2002. This section is again ordered in increasing numbers of boron atoms within the cage.

A series of *exo*-6-(L)-*arachno*-4-SB₈H₁₀ adducts (L=SMe₂ (**12**) PPh₃, MeCN, NMe₃, py, urotropine, MeNC, quin) have been prepared from *arachno*-4-SB₈H₁₂ (**13**) and the corresponding Lewis bases with the X-ray structures of three representative examples (L=urotropine, 1/2urotropine, MeNC) reported (Scheme 4).⁵⁸ The thianonaborane anion *nido*-[9-SB₈H₉][−] was prepared by deprotonation of **12** with Na metal or NaH; the reaction was reversed by treatment of the product with Me₂S and CF₃COOH.⁵⁹ Thermolysis of **13** in cyclohexane generated the 18-vertex macropolyhedral *anti*-9,9′-S₂B₁₆H₁₆ (**14**) in modest yield,⁶⁰ and mild thermolysis of **12** resulted in the formation of the macropolyhedral S₂B₁₇H₁₇(SMe₂) (**15**) in low yield.⁶¹ The structure of **15** is a conventional *nido*-type 11-vertex {SB₁₀H₉} sub-cluster fused to an *arachno*-type 10-vertex {SB₉H₈(SMe₂)} sub-cluster with two boron atoms in common.⁶¹



The microwave spectrum of 1-SB₉H₉ has been reported together with high-level *ab initio* and DFT calculations.⁶² The reactions of *nido*-6-SB₉H₁₁ (**16**) with imines and trimethylsilylazide have been investigated; the latter reagent gave the first examples of a new class of fused-ring cluster triazene-thiaborane, (μ₂-(4,*exo*-9)-1-SiMe₃-3-H-N₃)-*arachno*-6-SB₉H₁₀, in 42% yield.⁶³ *N*-butylformalimine gave a unique zwitterionic compound, 9-(BuⁿNH₂CH₂)-*nido*-6-SB₉H₉, which formed an adduct upon treatment with CH₃CN.⁶⁴ Reactions between **16** and Lewis bases (L) gave a series of corresponding *arachno* compounds, *exo*-9-(L)-*arachno*-6-SB₉H₁₁ (L=NEt₃, quinoline, isoquinoline, urotropine, py, MeCN, MeNC, NH₃, SMe₂, PPh₃).⁶⁵ The compound *arachno*-9-(PPh₃)-6-SB₉H₁₁ was obtained upon thermolytic decomposition of *arachno*-[*exo*-9-{Cl-*trans*,*cis*-(PPh₃)₂H₂Ir}-6-SB₉H₁₁].⁶⁶ The crystal structure of 9-(PCy₂Ph)-6-SB₉H₁₁ has been determined and the cluster had the expected *arachno* 10-vertex {SB₉} geometry with the phosphine substituent *exo*.⁶⁷ The structure of Cs[6-SB₉H₁₂] has been established by XRD studies.⁶⁶ Dehydrogenation of *arachno*-2-H-2,3-S₂B₉H₁₀

afforded the previously reported *nido*-7,9-S₂B₉H₉.⁶⁸ The structure of *nido*-Se₂B₉H₉ has been unambiguously determined as the 7,9-isomer using high-field ¹¹B NMR⁶⁹ and results from MNDO MO calculations of the S₂B₉H₉ thiaborane analogue have shown that all the 2c/2e bonds were localized around the {B₃S₂} open face. The *arachno* dithiaborane cluster anion [2,3-S₂B₉H₁₀][−] was obtained from the reaction of *nido*-[6-SB₉H₁₀][−] anion with S₈, and reactions of this dithiaborane with MeI, CH₂I₂, and H₂SO₄ have been reported.⁶⁸ The *nido* 11-vertex thiaboranes [7-SB₁₀H₁₁][−] and 7-SB₁₀H₁₂ were produced by synthetic sequences involving the reaction of SCl₂ with B₁₀H₁₄ followed by *in situ* dehydrohalogenation initiated by ‘proton-sponge’.⁷⁰

The UV–PES spectra of the thiaborane *nido*-7-SB₁₀H₁₂ has been reported and compared with spectra from more open thiacarboranes.⁷¹ The previously known *nido*-[7-SB₁₀H₁₁][−] anion was obtained in 45% yield from the reaction of S₈ with a solution of *anti*-[B₁₈H₂₀]^{2−}.⁷²

The molecular structure of the *closo* 12-vertex 1-SB₁₁H₁₁ cluster (**17**) has been studied by electron diffraction methods augmented by *ab initio* calculations. Substantial distortions away from the regular icosahedron occurred by expansion of the pentagonal belt adjacent to sulfur.⁷³ The UV–PES spectra of **17** has also been reported,⁷¹ and its microwave spectrum has been investigated and demonstrated that the molecule had C_{5v} symmetry.⁷⁴

The 18-vertex non-metallated adduct S₂B₁₆H₁₄(PPh₃) was a coproduct in the reaction of [NiBr₂(PPh₃)₂] with **14**.^{75,76}

The reaction of metabisulfite with *syn*-B₁₈H₂₂ gave a good yield of the macropolyhedral thiaborane anion [SB₁₇H₁₉][−], which exhibited an *arachno*–*nido* two-borons-in-common cluster-fusion mode.⁷⁷ The reaction of S₈ on a solution of *anti*-[B₁₈H₂₀]^{2−} gave as the major product the macropolyhedral anion [S₂B₁₇H₁₈][−] (**18**), isolated in 48% yield as its [PPh₄]⁺ salt and characterized crystallographically.⁷² The cluster structures of the macropolyhedral thiaborane **15** and thiaborane anion [S₂B₁₈H₁₉][−] were investigated at the B3LYP/6-311 and G**//B3LYP/6-31G* density functional theory level.⁷⁸ The treatment of **18** with oxidizing acids quantitatively yielded S₂B₁₇H₁₇ characterized as its anion [S₂B₁₇H₁₆][−].⁷⁹

The double-cluster anion [S₂B₁₈H₁₉] (**19**) (Figure 3) was prepared from the interaction of S₈ with [*syn*-B₁₈H₂₁][−].⁸⁰

1.3.2.2 Metallochalcogenoboranes

A series of new *arachno* and *hypho* metalladithiaborane clusters have been generated from the *hypho*-[S₂B₆H₉][−] anion (**20**): reactions with [{(C₆Me₆)RuCl₂]₂}, [Cp*Co(CO)L], [(dppe)NiCl₂], and [(PMe₃)₂Rh(CO)Cl] have been reported and products, including *hypho*-[1,1-(C₆Me₆)Cl-1,2,5-RuS₂B₆H₉] and *arachno*-[7-(C₆Me₆)-7,6,8-RuS₂B₆H₈], were characterized by XRD studies.⁸¹ A dimeric product [{Pd(PPh₃)(S₂B₆H₈)₂] was obtained from the attempted recrystallization of a product obtained from the reaction of [PdCl₂(PMe₂Ph)₂]

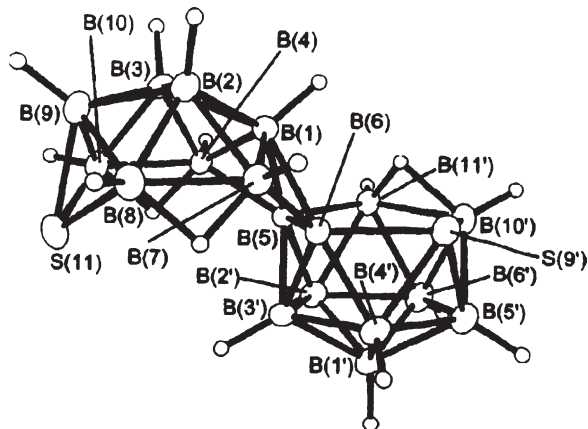


Figure 3 Crystallographically determined structure of the anion $[S_2B_{18}H_{19}]^-$ (**19**) (Reproduced with permission from J. Chem. Soc., Dalton Trans., 1998, 2965.)

with **20**.⁸² The molecular structure of the open 9-vertex cluster *arachno* [5,5-(PMe₂Ph)₂-4,6,5-S₂PdB₆H₈] has been established.⁸³

The synthesis, X-ray structure, and dynamic NMR properties of the *arachno* 10-vertex cluster [9,9-(PMe₂Ph)₂-9,6,8-PtS₂B₇H₇] has been reported; the compound was fluxional *via* a vertex flip of the {Pt(PMe₂Ph)₂} moiety.⁸⁴

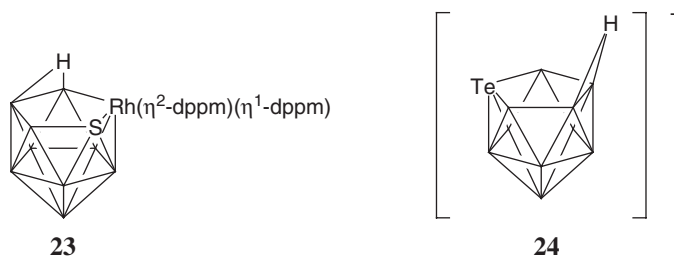
The formation of 9-, 10-, and 11-vertex metallathiaborane clusters, by insertion of the S atom into existing metalloborane frameworks, has been achieved for clusters containing eight boron atoms. Thus, the reaction of *arachno*-[(PMe₃)₂(CO)HrB₈H₁₂] with H₂S yielded *nido*-[2,2,2-(PMe₃)₂H-2,6-IrSB₈H₁₀], *closo*-[2,2,2-(PMe₃)₂H-2,1-IrSB₈H₈], and *nido*-[(PMe₃)₂(CO)-HrS₂B₈H₈].⁸⁵ The reaction of [RhCl(PPh₃)₃] with *arachno*-[S₂B₉H₁₀]⁻ (**21**) yielded *nido*-[(PPh₃)₂HRhS₂B₈H₈],⁸⁶ while [(C₆Me₆)RuCl₂]₂ reacted with *arachno*-[6-SB₉H₁₂]⁻ (**22**) to yield *closo*-[2-(C₆Me₆)-2,1-RuSB₈H₈].⁸⁷ The platinathiaborane species [(PMe₂Ph)₂PtSB₈H₁₂] was obtained from [PtMe₂(PMe₂Ph)₂] with **13**.⁸⁸

Reaction of [(*p*-cymene)RuCl₂]₂ with **22** yielded *closo*-[2,3-(*p*-cymene)₂-2,3,1-Ru₂SB₉H₉] and [2,3-(*p*-cymene)₂-2,3,1-Ru₂SB₉H₈Cl-7], and the open *nido* species [7-(*p*-cymene)-7,8-RuSB₉H₁₀Cl-11].⁸⁷ The reaction of **16** with [(IrCp*Cl₂)₂] yielded *nido*-[8-Cp*-8,7-IrSB₉H₁₁], whereas reaction with **22** yielded a mixture of products *e.g.* *nido*-[8-Cp*-8,7-IrSB₉H₁₀-Cl-9], *nido*-[8-Cp*-8,7-IrSB₉H₁₀-Cl-10], and *closo*-[1-Cp*-1,2-IrSB₉H₉].⁶⁶ The structure of *nido*-[8-Cp*-8,7-IrSB₉H₁₀-Cl-9] was established by XRD studies.⁶⁶ Cs[6-SB₉H₁₂] reacted with Vaska's compound to afford *arachno*-[*exo*-9-[Cl-*trans*-, *cis*-(PPh₃)₂H₂Ir]-6-SB₉H₁₁]⁶⁶ and with [Rh(PPh₃)₃Cl] at room temperature in ethanol solution to produce the orange air-stable compound [8,8-(PPh₃)₂Cl-8,7-RhSB₉H₁₀] in high yield.⁸⁹ This cluster's *nido* 11-vertex cage geometry was established by XRD studies and in solution it exhibited a fluxionality involving swinging the metal-ligand fragment from one side to the other of the {SB₉}

heteroborane cage.⁸⁹ The *nido* species [8,8,8-(PMe₂Ph)₃-8,7-RhSB₉H₁₀] was prepared in good yield by the addition of excess PMe₂Ph to [8,8-(PPh₃)₂-8,7-RhSB₉H₁₀]⁹⁰, and this crystal structure compared to that of [8,8-(PPh₃)₂-9-(EtO)-8,7-RhSB₉H₉].0.95CH₂Cl₂ showed that the addition of a third *exo* ligand on Rh had minimal effect on the cluster geometry.⁹¹ The reaction of [8,8-(PPh₃)₂-8,7-RhSB₉H₁₀] with CO resulted in [8,8,8-(CO)(PPh₃)₂-8,7-RhSB₉H₁₀] in quantitative yield and thermolysis of this *nido* species afforded a closed 11-vertex cluster [1,1,3-(CO)(PPh₃)₂-*closo*-1,2-RhSB₉H₈] in 46% yield.⁹² The synthesis and solid-state structure of *nido*-[8,8-(dppe)-8,7-RhSB₉H₁₀].2CH₂Cl₂ has been reported. This 11-vertex {RhSB₉} polyhedron showed a gross *nido* icosahedral geometry while apparently possessing a cluster count more appropriate to a *closo* geometry; two one-electron agostic-type Rh–H–C interactions were proposed as a source of the additional electron pair.^{93,94} Two new isoelectronic *nido* species [μ-9,10-(SMe)-8,8-(PPh₃)₂-8,7-IrSB₉H₉] and [μ-9,10-(SMe)-8-(η⁴-Cp*H)-8,7-IrSB₉H₉] have been characterized by XRD studies.⁹⁵ The reactions of the unsaturated cluster [8,8-(PPh₃)₂-*nido*-8,7-RhSB₉H₁₀] with bidentate phosphine ligands (dppm, dppe, dppp) have been studied and substitution of the two PPh₃ ligands occurred to give the related bidentate complexes and/or clusters with the bidentate phosphines ligands bridging.^{96,97} The cluster [8,8-(η²-dppm)-8-(η¹-dppm)-*nido*-8,7-RhSB₉H₁₀] (**23**), containing a pendant PPh₂ group, reacted with BH₃.thf and gave the species [8,8-(η²-dppm.BH₃)-*nido*-8,7-RhSB₉H₁₀] with a bidentate dppm.BH₃ ligand.⁹⁸ Compound **23** also reacted with [{MCp*Cl₂]₂] (M=Rh, Ir) and gave bimetallic species.^{99,100} The metal reagent [RhCl(PPh₃)₃] inserted into the quadrilateral face of the *isonido* 11-vertex cluster [1-(PPh₃)-1,3-(μ-dppm)-*isonido*-1,2-RhSB₉H₈] and yielded the icosahedral product [2,2,3-(PPh₃)Cl₂-2,3-(μ-Cl)-3,7-(μ-dppm)-*closo*-2,3,1-Rh₂SB₉H₈].¹⁰¹ Reactions with [MCl(PPh₃)₃] (M=Rh, Ir) with **21** yielded *nido*-[(PPh₃)₂HIrS₂B₉H₉] and *nido*-[(PPh₃)₂RhSB₉H₁₁].⁸⁶

A series of closed polyhedra {EMB₁₀} ((E=S, Se, or Te; M=Rh, Ru, Pd, Mo, Cu, or Pt) have been reported.^{102–111} *Nido*-[7-TeB₁₀H₁₁][−] (**24**) reacted with [{RhCp*Cl₂]₂] in CH₂Cl₂ solution to give *closo*-[2-Cp*-1,2-TeRhB₁₀H₁₀] in moderate yield, and with [{Ru(η⁶-arene)Cl₂]₂] (arene = 4-MeC₆H₄¹Pr, or C₆H₆) to give *closo*-[2-(arene)-1,2-TeRuB₁₀H₁₀].¹⁰² Both clusters were structurally characterized by XRD as closed {TeMB₁₀} polyhedra based on a distorted icosahedron with Te and M adjacent. The reaction of *closo*-[2,2,2-H(PPh₃)₂-1,2-TeRhB₁₀H₁₀] with metal carbonyl species (e.g. [Os₃H₂(CO)₁₀], [Mo(CO)₆]) led to the unexpected products: *closo*-[(PPh₃)(CO)Rh₂Te₂B₂₀H₂₀] and [{*closo*-(PPh₃)RhTeB₁₀H₁₀]₂], which both contained two {RhTeB₁₀} cages.¹⁰³ The synthesis of a series of 12-vertex *closo* tellura- and selenapalladaborane cluster derivatives [2,2-(PR₃)₂-2,1-PdEB₁₀H₁₀] and [2,2-X(PPh₃)-2,1-PdTeB₁₀H₉(PPh₃)] (R₃ = Me₂Ph, MePh₂, Ph₃; E=Se, Te; X=Cl, Br, I, CN, SCN, O₂CMe) has been achieved starting from the *nido*-[7-EB₁₀H₁₁][−] anions and appropriate Pd(II) complexes, or from [2,2-I(PPh₃)-2,1-PdTeB₁₀H₉(PPh₃)].¹⁰⁴ The reaction of [2,2-I(PPh₃)-2,1-PdTeB₁₀H₉(PPh₃)] with Ag[BF₄] in toluene/H₂O solution at room temperature led to a cationic cluster *closo*-[2,2-(H₂O)(PPh₃)-2,1-PdTeB₁₀H₉(PPh₃)] [BF₄] in excellent yield and from

which many cationic clusters were obtained by displacement of the coordinated H_2O by neutral donor ligands (CO , CN^tBu , $\text{CNC}_6\text{H}_{11}$, NCMe , thf , SC_4H_8).¹⁰⁵ An alternative route to cationic clusters *e.g.* *closo*-[2,2-(PR_3)₂-2,1-PdTeB₁₀H₉(PPh₃)]⁺ involved the reaction of [2,2-I(PPh₃)₂-2,1-PdTeB₁₀H₉(PPh₃)] with excess phosphine ($\text{PR}_3 = \text{PMe}_2\text{Ph}$, PMe_3).¹⁰⁶ The synthesis and structural characterization of the rhodatelluraborane cluster *closo*-[2,2-(PPh₃)(PhNHCS₂)-2,1-RhTeB₁₀H₁₀] has been reported.¹⁰⁷ The fluxional behaviour of {M(PR₃)₂} in *closo* 12-vertex {MZB₁₀} (Z=S, Se, Te) metalloheteroboranes has been characterized and a mechanism for the rotation of the {M(PPh₃)₂} units above the heteroborane cage was suggested.¹⁰⁸ The *closo* complex [2,2,2-{ η^1 -SC(H)NPh}(PMe₂Ph)₂-2,1-RhTeB₁₀H₁₀] has been characterized by XRD and was described as one of the first thioformamidate complexes to be isolated.¹⁰⁹ The paramagnetic *B*-fluorinated mixed-sandwich compound [2-(C₇H₇)-7,11-F₂-*closo*-2,1-MoTeB₁₀H₈] (**25**), formed from reaction of **24** (Scheme 5) with [Mo(CO)₃(η^7 -C₇H₇)] [BF₄]⁻ had the 2{BF} units in adjacent positions within the *closo* 12-vertex {MoTeB₁₀} cluster (Figure 4); the compound exhibited a reversible one-electron reduction at $E^\circ = -0.39$ V in CH₂Cl₂ solution.¹¹⁰ The platinathiaborane species [(PMe₂Ph)₂PtSB₁₀H₁₀] was obtained by reaction of [PtMe₂(PMe₂Ph)₂] with *nido*-7-SB₁₀H₁₂.⁸⁸ The icosahedral *closo*-{CuSeB₁₀} cage was identified in the structure of [(PPh₃)₂Cu₂SeB₁₀H₁₀], which has Cu and Se atoms adjacent; the *exo*-cage Cu(PPh₃) unit was bonded to one triangular {CuB₂} face *via* a Cu–Cu bond and two Cu–H–B interactions.¹¹¹



Scheme 5

The macropolyhedral compound **14** reacted with [PtMe₂(PMe₂Ph)₂] to give the [(PMe₂Ph)₂PtS₂B₁₅H₁₄(NHCOMe)]⁸⁸ and with [{RhCl₂Cp*]₂] yielded both *syn* and *anti* isomers of the macropolyhedral rhodathiaboranes [Rh₂Cp*₂S₂B₁₅H₁₄(OH)]; reaction with [NiBr₂(PPh₃)₂] in the presence of base afforded the 19-vertex cluster [(PPh₃)NiS₂B₁₆H₁₂(PPh₃)]. The latter consisted of a *nido*-shaped {1-NiB₈} sub-cluster and a *closo*-shaped {1,4-NiSB₁₀} sub-cluster fused with a {NiB₂} triangular face in common.^{75,76} Reaction of *syn*-[Cp*IrB₁₈H₂₀], obtained from [{IrCl₂Cp*]₂] with *syn*-B₁₈H₂₂ and base, with elemental sulfur afforded, by direct heteroatom insertion of the 20-vertex cluster anion, [Cp*IrSB₁₈H₁₉]⁻.¹¹²

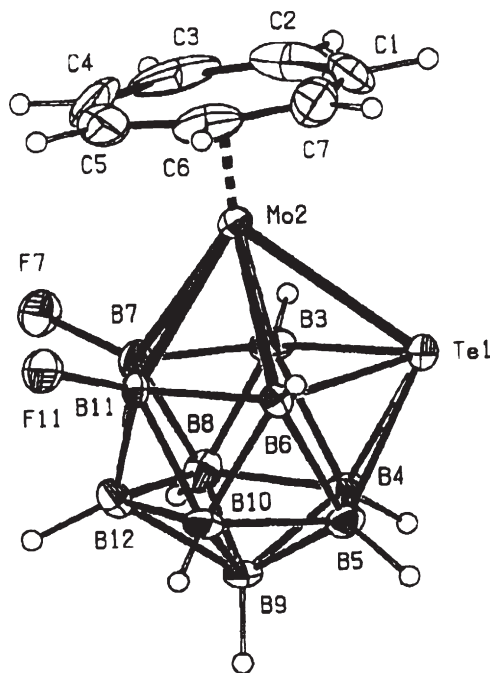
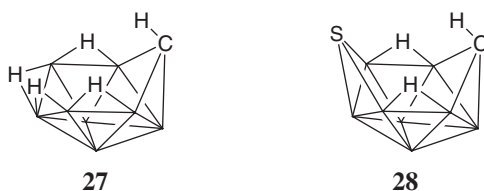


Figure 4 View of $[2-(\eta^7\text{-C}_7\text{H}_7)\text{-}7,11\text{-F}_2\text{-}2,1\text{-closo-MoTeB}_{10}\text{H}_8]$ (**25**)
(Reproduced with permission from J. Chem. Soc., Dalton Trans., 2001, 1521.)

1.3.2.3 Chalcogenoheteroboranes and Their Metallo Derivatives

Chalcogenoheteroboranes and their metallo derivatives are restricted to thio derivatives with no known examples in seleno- or telluraheteroborane chemistry. The six-boron thiacarborane anion *hypho*- $[7,8\text{-CSB}_6\text{H}_{11}]^-$ (**26**) has been prepared from *arachno*- $4\text{-CB}_8\text{H}_{14}$ (**27**).¹¹³ The first azathiaborane clusters, *hypho*- $7,8\text{-NSB}_6\text{H}_{11}$ and *arachno*- $6,9\text{-NSB}_8\text{H}_{11}$, were prepared by the reaction of *n*-butylnitrite with **13** in Et₂O or *nido*- $6\text{-SB}_9\text{H}_{11}$ in C₆H₆.¹¹⁴ The transformation of 3,4-*bis*(isopropylidene)-2,5-dichloro-1,2,5-dithiaborolane derivatives to the corresponding *nido*-4,5-diisopropyl-2,4,5-thiadicahexaboranes in low yield has been reported; the nine-vertex cluster *closo*- $5,6\text{-Pr}_2\text{-}4,5,6\text{-SC}_2\text{B}_6\text{H}_6$ was also detected by GC–MS and identified by the *ab initio*/IGLO/NMR method.¹¹⁵ A 4,5-dicarba-2-thia-*nido*-hexaborane was synthesized by the hydroboration reaction of 2,5-diduryl-1-thia-3,4-diisopropylidene-2,5-diborolane by BH₃.thf, with the product characterized by MS and multinuclear NMR spectroscopy.¹¹⁶ The structure of the nine-vertex *arachno*-thiadicahexaborane C₂SB₆H₁₀ was established by the *ab initio*/IGLO/NMR method as the 4,6,8-C₂SB₆H₁₀ isomer; the method also unambiguously ruled out the 4,6,5-C₂SB₆H₁₀ structural alternative.¹¹⁷ The nine-vertex *arachno*-5-Cp*-5,4,6-MCSB₆H₁₀ (M=Rh, Ir) clusters were prepared from the 10-vertex

arachno-6,9-CSB₈H₁₂ (**28**) (Scheme 6) or 9-vertex *arachno*-4,6-CSB₇H₁₁ (**29**) by site-specific metal centre additions with directed elimination of specific boron sites.¹¹⁸ The reaction of $[[\text{IrCl}_2\text{Cp}^*]_2]$ with **26** afforded $[2,7\text{-Cp}^*_2\text{-nido-2,7,8,6-Ir}_2\text{CSB}_6\text{H}_8]$ and $[2,7\text{-Cp}^*_2\text{-nido-2,7,8,6-Ir}_2\text{CSB}_6\text{H}_7\text{-9-Cl}]$.¹¹⁹



Scheme 6

The seven-boron thiacarborane **29** was prepared from **28**.¹¹³ The *arachno* cluster $[9,9\text{-(PMe}_2\text{Ph)}_2\text{-9,6,8-PtCSB}_7\text{H}_9]$, obtained in moderate yield from **29**, $[\text{PtCl}_2(\text{PMe}_2\text{Ph})_2]$, and proton sponge, underwent *ortho*-cycloboronation upon thermolysis to $[9,9\text{-(PMe}_2\text{Ph)}_2(\text{PMe}_2\text{C}_6\text{H}_4)\text{-arachno-9,6,8-PtCSB}_7\text{H}_8\text{-10}]$.¹²⁰

The nine-vertex monocarborane **27** reacted with S₈ in the presence of Et₃N to yield **28**.¹²¹ The UV–PES spectra of the thiaboranes *closo*-1-SB₁₁H₁₁ and *nido*-7-SB₁₀H₁₂ have been compared with spectra from more open thiacarboranes *nido*-7,8,10-C₂SB₈H₁₀ and **28**, with the main conclusion being that there was a significant contribution of the bridge hydrogen atoms to the cluster-bonding HOMO and the implication that the bridge H atoms were involved in cluster bonding.⁷¹ An extended series of thiacarborane clusters (**26**, **29**, *arachno*-[6,9-CSB₈H₁₁][−], *nido*-7,9-CSB₉H₁₁, and *nido*-[6,9-CSB₈H₉][−]) have been prepared from **27**.¹¹³ The thiacarborane **28** reacted with $[\text{RhCl}(\text{PPh}_3)_3]$ in ethanol solution at room temperature and produced the *nido* species $[8,8,8\text{-H}(\text{PPh}_3)_2\text{-8,9,7-RhCSB}_8\text{H}_{10}]$ in high yield.¹²² The 11-vertex thiacarborane anion $[1,6,7\text{-C}_2\text{SB}_8\text{H}_{11}]^{\text{−}}$, obtained from the addition of S₈ to the 10-vertex $[6,9\text{-C}_2\text{B}_8\text{H}_{10}]^{2\text{−}}$ anion, was characterized using the *ab initio*/GIAO/NMR method.¹²³

Nido-7,9-CSB₉H₁₁ has been prepared from **28**.¹¹³ A *nido*-11-vertex thiacarborane, 7,10,11-SC₂B₈H₁₀, and the first thiaphosphaborane, *nido*-10-Ph-7,10-SPB₉H₉, were produced by synthetic sequences involving the reaction of an organophosphorus dihalide and/or sulfur dihalide with borane clusters followed by *in situ* dehydrohalogenation reactions initiated by ‘proton-sponge’.⁷⁰

1.4 Binary, Ternary, and Quarternary Chalcogenoborates

Rapid progress in recent years has been made in the understanding of ternary and quarternary chalcogenoborates due to improvements in crystallographic

and solid-state preparative methods. However, the chemistry of known chalcogenoborate derivatives is limited to thio- and selenoborates with no known telluraborates. Despite this, a wide variety of compounds have been synthesized and structurally characterized over the period of this survey. As noted in Section 1.2, this topic has been reviewed recently.¹²

Two new high-pressure phases of boron sulfide, B_2S_3 -II and B_2S_3 -III, have been synthesized at 3.0–6.3 GPa.¹²⁴ A new method of preparing *meta*-thioboric acid (*c*-HBS₂), by reaction of H₂S with B₂S₃ in the vapour phase, has been reported.¹²⁵ The IR spectra of a series of binary K₂S/B₂S₃ glasses has been reported with spectra similar to those of the corresponding sodium thioborate system.¹²⁶ The XPS spectra of vitreous and crystalline Li₂S/B₂S₃ compounds were obtained and analyzed by theoretical calculations.¹²⁷ A structural neutron diffraction study of Li₂S/B₂S₃ glasses has also been reported.¹²⁸ TIBS₃ was obtained as a glassy product from Tl₂S·2B₂S₃ after treatment for 7 h at 850 °C followed by annealing in a two-zone furnace for 400 h at 350–400 °C.¹²⁹ A new series of anhydrous protonated chalcogenide glasses, (H₂S)_x(B₂S₃)_{1-x}, analogous to alkali-modified glasses have been prepared; characterization showed that these materials were unique and did not exhibit the borate anomaly.¹³⁰ Mixing HBS₂ and B₂S₃ and GeS₂ yielded proton-containing glasses in which, except in the GeS₂-rich formulations, the borate coordination was found to be trigonal.¹³¹

The orthothioborates Na₃BS₃, K₃BS₃, and Rb₃BS₃ have been prepared in solid-state reactions of metal sulfide, amorphous boron, and sulfur at 600 °C and their crystal structures revealed that all three compounds contained isolated BS₃³⁻ anions.¹³² The orthothioborates Li₃BS₃, Cs₃BS₃, Sr₃(BS₃)₂, Li₂CsBS₃, LiBaBS₃, and LiSrBS₃ have also been prepared and their structures, determined by XRD studies, also contained isolated planar [BS₃]³⁻ anions.^{133–136} The crystal structure of Li₃BS₃, obtained by crystallizing the corresponding glass, exhibited higher symmetry than other M₃B(O,S)₃ structures and Li₃BS₃ was described as a new member of the M₃AX₃ group of compounds.¹³⁷

The structure of Cs₂B₂S₄ contained isolated B₂S₄²⁻ groups consisting of four-membered B₂S₂ rings with exocyclic S atoms on each B; this was the first reported example of edge-sharing BS₃ groups in isolated thioborate anions.¹³⁸ The four-membered B₂S₂ ring was found as a building block in the polymeric thioborate anion structures observed for TIBS₂ and SrB₂S₄.¹³⁹ The crystal structure of the barium metathiaborate, BaB₂S₄, showed the boron atoms in both trigonal and tetrahedral coordination in a 1:1 ratio, in infinite anionic chains¹⁴⁰ and a new crystalline phase of EuB₂S₄ has been prepared and its crystal structure revealed polymeric [(B₂S₄)²⁻]_n anions.¹⁴¹

The synthesis, crystal structures, and properties of LiSrB₃S₆ and M₃B₃S₆ (M=Na, K, Rb) have been reported.¹⁴² The ternary thioborate Sr₃(B₃S₆)₂ and the quarternary thioborate LiBaB₃S₆ both contained boron centres in trigonal planar coordination environments with isolated B₃S₆³⁻ anions consisting of six-membered B₃S₃ rings with three exocyclic S atoms.^{136,143}

The perthioborate, RbBS₃, and Th₃B₃S₁₀ were prepared at 600 and 850 °C, respectively, and both compounds contained tetrahedrally coordinated boron

and consisted of polymeric anionic chains.¹²⁹ The perselenoborates RbBSe_3 , TlBSe_3 , and CsBSe_3 have been prepared and all three compounds contained polymeric anionic chains with spirocyclically fused five-membered B_2Se_3 rings in which the B atoms were in a tetrahedral BSe_4 coordination.¹⁴⁴ The lithium perselenoborate $\text{Li}_2\text{B}_2\text{Se}_5$ had a novel three-dimensional anion network with B atoms in tetrahedral BSe_4 coordination.¹⁴⁵ LiBSe_3 has been synthesized and it also possessed a novel polymeric network.¹⁴⁶ The perthioborates $\text{Na}_2\text{B}_2\text{S}_5$ and $\text{Li}_2\text{B}_2\text{S}_5$ had structures containing planar $\text{B}_2\text{S}_5^{2-}$ groups consisting of five-membered B_2S_3 rings with one additional exocyclic S atoms on each B.¹³⁹ The first alkaline earth perselenoborates BaB_2Se_6 and $\text{BaB}_4\text{Se}_{13}$ were synthesized from appropriate amounts of barium selenide, boron, and selenium at high temperatures.¹⁴⁷ The synthesis of $\text{Na}_2\text{B}_2\text{Se}_7$, $\text{K}_2\text{B}_2\text{S}_7$, and $\text{K}_2\text{B}_2\text{Se}_7$ has been reported with their structures contained polymeric $\text{B}_2\text{E}_7^{2-}$ anion chains formed by spirocyclically connected five-membered B_2E_3 and six-membered B_2E_4 rings.¹⁴⁸ Heating, followed by annealing of stoichiometric quantities of Li_2S , B, and S_8 , afforded the thioborates $\text{Li}_5\text{B}_9\text{S}_{13}$ (730 °C) and $\text{Li}_9\text{B}_{19}\text{S}_{33}$ (700 °C) and their crystal structures displayed interpenetrating polymeric boron–sulfur anionic networks.¹⁴⁹ New isotopic crystalline phases of $\text{Sr}_{4.2}\text{Ba}_{2.8}(\text{BS}_3)_4\text{S}$ and $\text{Ba}_7(\text{BSe}_3)_4\text{Se}$ were obtained through systematic studies on quarternary thioborates and selenoborates containing the heavier alkaline earth metals.¹⁵⁰

The thioborate $\text{Na}_6\text{B}_{10}\text{S}_{18}$, composed of $\text{B}_{10}\text{S}_{20}$ units linked through tetrahedral corners, was shown to be a highly polymeric macrotetrahedral 3d network.¹⁵¹ New polymeric-layered anion networks composed of corner-sharing super-adamantane-type $\text{B}_{10}\text{E}_{20}$ units, connected by Li and Cs cations were observed in $\text{Li}_{6-x}\text{Cs}_x\text{B}_{10}\text{E}_{18}$ ($x \sim 1$; $\text{E}=\text{S}, \text{Se}$) and $\text{Na}_6\text{B}_{10}\text{Se}_{18}$.¹⁵² Lithium selenoborates such as $\text{Li}_{6-2x}\text{Ba}_{1+x}\text{B}_{10}\text{Se}_{19}$ and $\text{Li}_{3+x}\text{Na}_{5-x}\text{B}_{10}\text{Se}_{19}$, which have severely disordered cations, were reported as excellent candidates for mechanistic analysis of ionic conductivity measurements.^{153,154} Similarly, $\text{Li}_{6-2x}\text{Sr}_{2+x}\text{B}_{10}\text{Se}_{20}$ ($x = 0.7$) has also been studied.¹⁵⁵

The selenoborate $\text{Cs}_8[\text{B}_{12}(\text{BSe}_3)_6]$ (**Cs₈30**) was obtained from the reaction of caesium selenide, boron, and selenium by means of a high-temperature solid-state synthesis (Figure 5).¹⁵⁶ The retention of the icosahedral boron network during this reaction has been noted as very unusual.¹⁵⁷ The three selenoborates **Rb₈30**, **Rb₄Hg₂30**, and **Cs₄Hg₂30**, prepared from the metal selenides, amorphous boron, and selenium in solid-state reactions at 700 °C, also contained the B_{12} icosahedral unit saturated with six trigonal-planar BSe_3 entities.¹⁵⁸ Systematic studies of icosahedral- B_{12} containing selenoborates with alkali metal cations have led to a new crystalline phase for $\text{Na}_6[\text{B}_{18}\text{Se}_{17}]$, which contained neighbouring $\{\text{B}_{12}\text{Se}_{18}\}$ cluster moieties connected in one direction *via* exocyclic Se atoms in an infinite-chain anion.¹⁵⁹ A new crystalline phase of **K₈30** has been obtained with the selenoborate anion showing three different substitution patterns.¹⁶⁰ New crystalline phases of **Rb₈30** and **Cs₈30** have been reported by reaction of amorphous boron with alkali metal sulfide and sulfur at ~600 °C in evacuated carbon-coated silica tubes.¹⁶¹

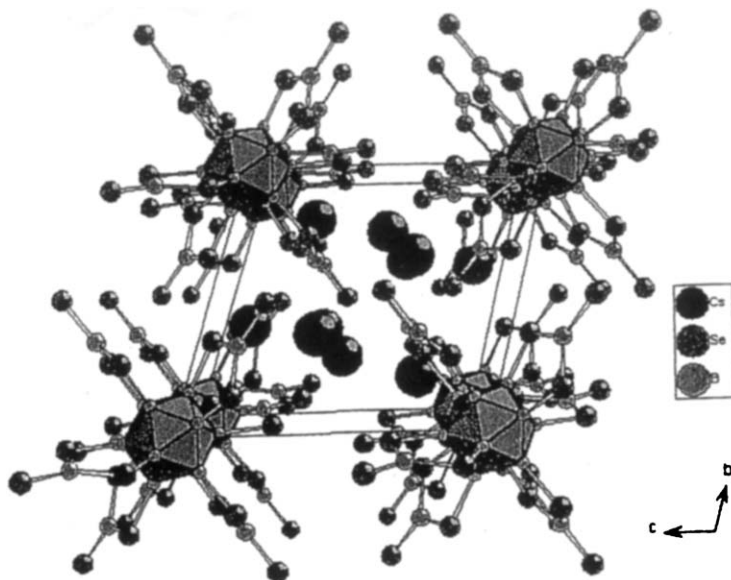


Figure 5 Unit cell of $Cs_8[B_{12}(BSe_3)_6]$, ($Cs_8\mathbf{30}$)
(Reproduced with permission from *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1903.)

1.5 Heterocycles Containing B–E Linkages

The first stable disulfanylboration (Tbt)B(SH)₂ (**31**) was prepared by reaction of the overcrowded lithium hydroborate, (Tbt)BH₃Li(thf)₃ with S₈.¹⁶² Dilithiation of **31** followed by treatment with electrophiles such as Cp₂TiCl₂, (mes)₂GeBr₂, PhSnCl₂, and (Tbt)SbBr₂ resulted in the isolation of novel four-membered 1,3-dithiaboretane rings $\overline{S}\{B(Tbt)\}S\{ER_n\}$ ($ER_n = TiCp_2, Ge(mes)_2, SnPh_2$ (**32**, Figure 6), or Sb{ Tbt }); the structures of these ring systems were confirmed in all cases by single-crystal XRD studies.^{162,163}

B₂H₆ was shown to react with H₂S₂, H₂S₃, or crude sulfane oil to form the 1,2,4,3,5-trithiadiborolane, H₂B₂S₃.¹⁶⁴ The reaction of ¹Bu₂S₂ with ArBBr₂ (Ar=Ph, 2-MeC₆H₄, 3-MeC₆H₄, 4-MeC₆H₄, 4-EtC₆H₄, 3,5-Me₂C₆H₃) in refluxing toluene gave the thermally stable, moisture-sensitive 1,2,4,3,5-trithiadiborolanes, Ar₂B₂S₃.¹⁶⁵ The reaction of ArBBr₂ with HgS in benzene at reflux produced a series of 1,3,5-triarylborthiins (Ar₃B₃S₃), which were found to be less stable than Ph₃B₃S₃ and were significantly decomposed to mixed B/O/S rings (*e.g.* Ar₃B₃S₂O, Ar₃B₃SO₂) within minutes in air.¹⁶⁶ Reaction of the ArBBr₂ species with (Me₃Si)₂S in benzene at room temperature afforded the corresponding 1,3,5-triarylborthiins, and not the expected 1,3,2,4-dithiadiboretanes (Ar₂B₂S₂), while the reaction of S₈ with PhBBr₂ or

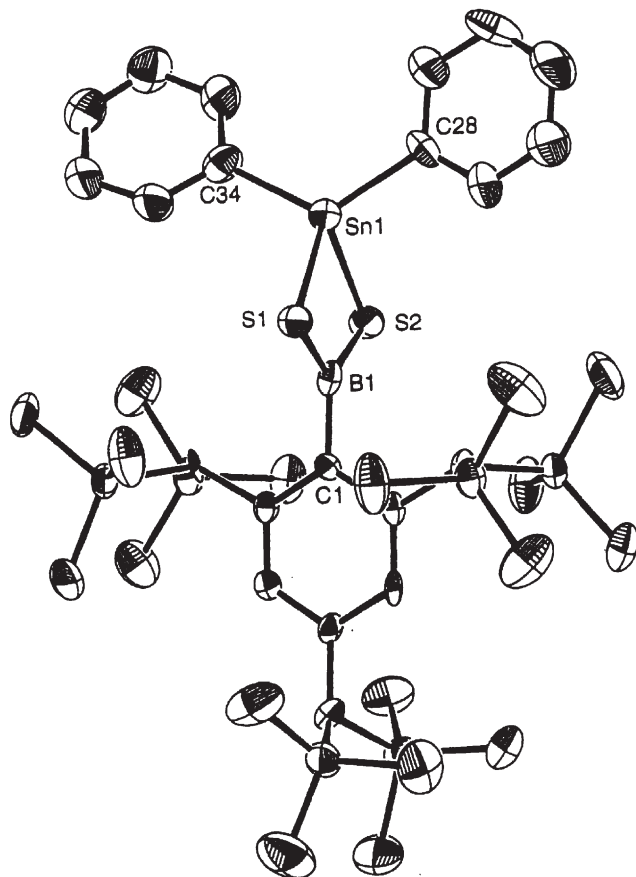
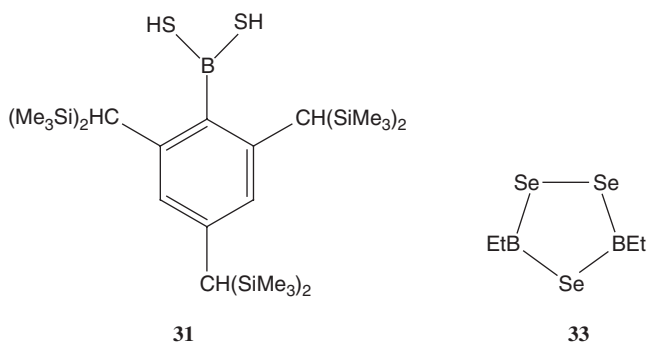


Figure 6 ORTEP drawing of $(Tbt)BS_2SnPh_2$ (**32**)
(Reproduced with permission from *Organometallics*, 1997, **16**, 4316.)

4-MeC₆H₄BBr₂ was investigated by ¹¹B NMR and mass spectrometry and cyclic RBS_n species were identified.¹⁶⁶ A theoretical study of the structures and energetics and magnetic properties of H₃B₃E₃ (E=O, S, Se) has been reported with the discussion centred on the relative aromaticity of these rings compared to those of related group 15 boron heterocycles.¹⁶⁷

The triselenadiborolanes 3,5-R₂-1,2,4,3,5-Se₃B₂ {R=Et (**33**), Pr} readily formed coordination adducts with two equivalents of pyridine, 3,5-dimethylpyridine, and 3-chloropyridine.¹⁶⁸ With one equivalent of base, only one of the B atoms became coordinated, and surprisingly, the system was not fluxional at room temperature.¹⁶⁸ The addition of two equivalents of pyrazole to **33** (Scheme 7) resulted in a brown suspension and a yellow solution. Crystals of a B₂N₄Se₂-bicyclo[2.2.2]octane were formed upon cooling this solution to -80 °C. With bulkier pyrazole derivatives (*e.g.* 3-methylpyrazole, 3-phenylpyrazole), the B₂N₄Se-bicyclo[2.2.1]heptanes were formed.¹⁶⁹



Scheme 7

Elimination of hydrogen halides from dihalogenoorganylboranes by reaction with ferrocene-1,1'-dithiol resulted in 1,3-dithia-2-boryl[3]ferrocenophanes.¹⁷⁰ These borylferrocenophanes were air sensitive, but were characterized by NMR, MS, and elemental analysis.¹⁷⁰ A series of 1,3-dibora-2-X-[3]ferrocenophanes (X=S, Se, Te) were prepared and characterized and the crystal structure of [Se{NⁱPr₂}BC₅H₄]₂Fe] has been reported.¹⁷¹

The first organoborontellurium compound was prepared from the reaction of 9-Cl-9-BBN with Na₂Te₂ and Na₂Te. The product, (9-BBN)₂Te, reacted with water to give elemental Te, (9-BBN)₂O and (9-H-9-BBN)₂.¹⁷²

The 1,2-benzothiaborolidine, a heteroaromatic analogue of indenyl, has been prepared and shown to form a η⁵-complex with RuCp*.¹⁷³ The related anion, 2-(diisopropylamino)-1,2-thiaborolide(1-) has also been prepared and coordinated to Ru in [{{(ⁱPr₂N)BSC₃H₃}RuCp*}] (**34**, Figure 7) and Zr in [{{(ⁱPr₂N)BSC₃H₃}ZrCl₂Cp*}].¹⁷⁴

1.6 Miscellaneous Boron–Chalcogen Compounds and Reagents

The use of bulky aryl substituents allowed the structural characterization of the monomeric B–S compounds, mes₂BSPh and (2,4,6-Pr^t₃C₆H₂) B(SPh)₂, showing short B–S distances (180 pm) consistent with B–S π-interaction. Barriers to rotation of 18.4 and 12 kcal mol⁻¹ were determined by variable temperature NMR studies.¹⁷⁵ A thioxoborane (Tbt)BS, with a B=S bond and the very bulky aryl group on the B atom was obtained from the thermolysis of an overcrowded four-membered boracycle, 1,3,2,-dithiastannaboretane.¹⁷⁶ The barrier to rotation about B=E bonds of coordinatively unsaturated borates and thiaborates has also been discussed with the lower rotational barrier in the O derivatives attributed to greater stabilization of the transition state.¹⁷⁷ The rotational barriers did not reflect the relative strengths of the B=E π bonds.¹⁷⁷

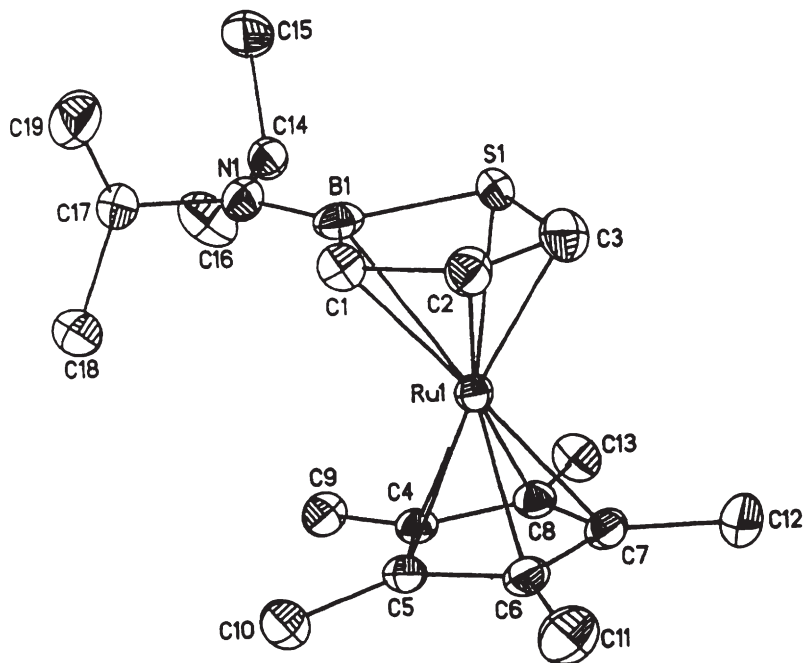


Figure 7 Solid-state structure of $[(i\text{-Pr}_2\text{N})\text{BSC}_3\text{H}_3]\text{RuCp}^*$ (**34**)
(Reproduced with permission from *Organometallics*, 2000, **19**, 4937.)

n-Octadecanethiol was found to react with $\text{B}(\text{C}_6\text{F}_5)_3$ to yield an equilibrium mixture of reactants and the 1:1 adduct, and the adduct was deprotonated by ‘proton-sponge’ to yield the salt $[\text{C}_{10}\text{H}_6(\text{NMe}_2)_2\text{H}][(\text{n-C}_{18}\text{H}_{37}\text{S})\text{B}(\text{C}_6\text{F}_5)_3]$.¹⁷⁸ Reaction with Cp^*MMe_3 ($\text{M}=\text{Ti}, \text{Hf}$) yielded $[\text{Cp}^*\text{MMe}_2][(\text{n-C}_{18}\text{H}_{37}\text{S})\text{B}(\text{C}_6\text{F}_5)_3]$, which was a good initiator for the copolymerization of isobutene with isoprene in high conversions to high molecular weight copolymers.¹⁷⁹ The crystal structure of the tetrathiophene adduct of tris(pentafluorophenyl)borane, $(\text{C}_4\text{H}_8\text{S})\text{B}(\text{C}_6\text{F}_5)_3$, was reported and it showed a comparatively long BS distance of 2.0843 Å.¹⁸⁰ Metal-catalyzed additions of B–X ($\text{X}=\text{H}, \text{B}$) bonds to thiocarbonyl compounds and vinyl sulfides afforded α -thioboronate esters.¹⁸¹

The reaction of $\text{BH}_3\cdot\text{thf}$ with NaSH or anhydrous Na_2S , or the reaction of $\text{BH}_3\cdot\text{thf}/\text{Na}[\text{BH}_4]$ (2:1) with excess H_2S , produced the adamantane-like compound $\text{Na}_2[(\text{BH}_2)_6\text{S}_4]$.¹⁸² The analogous selenium compound was obtained from the reaction of elemental Se with $\text{Na}[\text{BH}_4]$ (1:1) in diglyme. The X-ray structures of both of these cage anions were determined.¹⁸² The reaction of $\text{Na}[\text{BH}_4]/\text{BH}_3\cdot\text{thf}$ with S_8 proceeded with elimination of H_2 and gave $\text{Na}[(\text{BH}_2)_5\text{S}_4]$ with a noradamanatane-like $\{\text{B}_5\text{S}_4\}$ skeleton.¹⁸³ The salt $[\text{Na}(\text{triglyme})]_2[\text{S}(\text{BH}_3)_4]$, which contained an anion isoelectronic with $[\text{SO}_4]^{2-}$, was obtained from the reaction of $\text{Na}[\text{BH}_4]$ with $\text{Na}[\text{H}_3\text{B}-\mu_2\text{-S}(\text{B}_2\text{H}_5)]$ in triglyme.¹⁸⁴

Potentially chelating $[\text{H}_2\text{B}(\text{SPh})_2]^-$, $[\text{HB}(\text{SPh})_3]^-$, and $[\text{B}(\text{SPh})_4]^-$ ligands have been prepared and their reactions with 3d transition-metal complexes were investigated.¹⁸⁵ The synthesis, characterization, and reactivity of the S-rich tridentate ligand tetrakis(2-thienyl)borate anion was reported; unlike $[(\text{MeS})_4\text{B}]^-$, it did not coordinate to $\{\text{Mo}(\text{CO})_3\}$ when reacted with $[(\text{C}_7\text{H}_8)\text{Mo}(\text{CO})_3]$.¹⁸⁶ Stabilization of the tetrathioborato ligand has been achieved in novel sulfido niobium clusters. Thus, the neutral diamagnetic complex, $[\text{Nb}_3\text{Cp}_3\text{S}_3(\text{S}_3\text{BSH})]$ (**35**, Figure 8), was obtained in yields of up to 28% by reaction of S_8 with $[\text{Nb}_2\text{Cp}_2(\text{B}_2\text{H}_6)_2]$ in decane at 170°C .¹⁸⁷

Finally, this section reports on a few unusual reactions of B–E-containing compounds in which they serve as reagents, with loss of chalcogen. A novel route for the synthesis of icosahedral *closo*- $\text{RNB}_{11}\text{H}_{11}$ ($\text{R} = {}^t\text{BuCH}_2, \text{Ph}$) clusters involving the use of $\text{BH}_3\cdot\text{SMe}_2$ and *nido*- $\text{RNB}_9\text{H}_{11}$ in decalin at 170°C has been reported.¹⁸⁴ The reaction of $\text{ClBH}_2\cdot\text{SMe}_2$ and proton sponge and NaH with *nido*- $\text{B}_{10}\text{H}_{14}$ leads to the formation of $[\text{B}_{11}\text{H}_{14}]^-$.¹⁸⁸ The synthesis and characterization of the first example of a three-membered borocyclopropane ring coordinated to a trimetal fragment, $[\text{Fe}_3(\text{CO})_9(\eta^3\text{-BHCHCMe})]$, has been reported; it was obtained in low yield from the reaction of $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ with $[\text{Fepy}_6][\text{Fe}_4(\text{CO})_{13}]$.¹⁸⁹ The two metallaboranes $[\text{Co}_2(\text{CO})_6\text{B}_2\text{H}_4]$ and $[\text{Co}_5(\text{CO})_{13}(\mu\text{-CO})\text{B}_2\text{H}]$ were prepared in low yield by reaction of $[\text{Co}_2(\text{CO})_8]$ with $\text{BH}_3\cdot\text{SMe}_2$; both compounds were characterized by XRD and the former compound was isoelectronic with $[\text{Fe}_2(\text{CO})_6\text{B}_2\text{H}_6]$ and $[\text{Co}_2(\text{CO})_6\text{C}_2\text{H}_2]$.¹⁹⁰

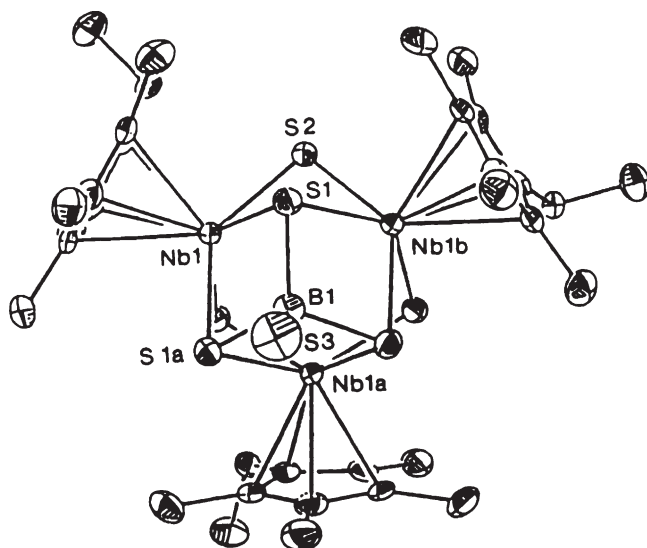


Figure 8 Structure of $[\text{Nb}_3\text{Cp}_3\text{S}_3(\text{S}_3\text{BSH})]$ (**35**)

(Reproduced with permission from *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1022.)

$\text{BH}_3\cdot\text{SMe}_2$ readily reacted with P_4O_6 and formed the adduct $\text{P}_4\text{O}_6\cdot\text{BH}_3$, which was shown to dimerize spontaneously at $-30\text{ }^\circ\text{C}$ to $\text{P}_8\text{O}_{12}(\text{BH}_3)_2$.¹⁹¹

Abbreviations

Arene	any derivative of C_6H_6
Aryl	any derivative of C_6H_5
9-BBN	9-borabicyclo[3.3.1]nonane
Cp	C_5H_5^-
Cp*	C_5Me_5^-
Tbt	2,4,6- $[\text{Me}_3\text{Si}_2\text{HC}]_3\text{C}_6\text{H}_2$
Thf	tetrahydrofuran

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