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Account

# Heteroboranes of the p-block elements

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**Abstract**

The syntheses, structures and reactivities of the heteroboranes in which p-block elements have replaced one or more vertices in the parent borane cages have been reviewed. The purpose is to provide an overview of this field, rather than give a detailed history of its development. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Heteroboranes; Cage bonding; Electron pair; Metallaboranes; p-Block elements

## 1. Introduction

This review will cover some important aspects of the syntheses, structures and reactivity of the p-block (Groups 13–18) heteroboranes, with the exception of the carboranes [1]. In visualizing the bonding in these electron deficient cage compounds it is convenient to think of each boron atom as being sp hybridized with one hybrid orbital directed towards the center of the cage and the two unhybridized p-orbital oriented tangentially. The other sp hybrid is directed away from the cage and is used for a two-center-two-electron (2c–2e) bond with a 'terminal' hydrogen atom, leaving the other three orbitals and two electrons for cage bonding. Most of the cages are composed of fused deltahedra, as shown in Fig. 1. For such cages, there is a simple set of rules that have been developed to relate the cage structure to the number of cage electron pairs [2]. Accordingly, those clusters that have $n$ vertices and $n+1$ electron pairs involved in cage bonding will have a completely closed polyhedral structure, and are referred to as *closo*-boranes, structures *i*, *iv* and *vii* in Fig. 1 are examples. Cages having $n+2$ electron pairs are referred to as *nido*-boranes and have structures that are derived by the removal of one B–H vertex form the next higher *closo*-cage, in Fig. 1, *ii*, *v* and *viii* are nido-structures. In the same way, an $n$-vertex *arachno*-borane has $n+3$ cage electron pairs and structures with two missing vertices, as depicted in structures *iii*, *vi* and *ix* in Fig. 1. Therefore, the *closo*-boranes have the general formula $[B_nH_n]^{2-}$, the *nido*-boranes, $[B_nH_n]^{4-}$, and the

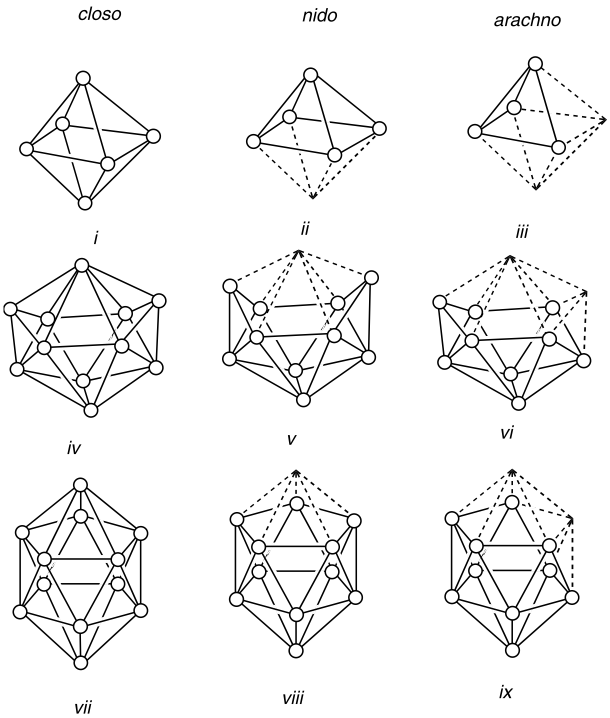

Fig. 1. Some idealized deltahedra and deltahedral fragments. The dashed lines delineate the positions of missing vertices.

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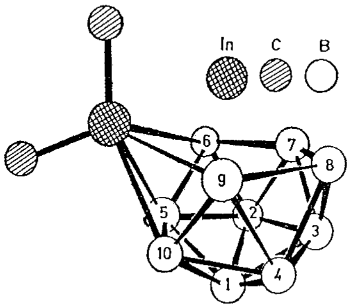


Fig. 2. Proposed heavy-atom structure of the $[B_{10}H_{12}InMe]^-$ ion. Reprinted with permission from [6].

*arachno*-boranes, $[B_nH_n]^{6-}$. In most cases charge compensation is accomplished with bridge hydrogens that are located on the open faces of the boranes. For example, pentaborane(9), $B_5H_9$, has the structure of *ii* with four hydrogens occupying bridging positions between the four borons on the open $B_4$ face. In the same way, *nido*-$B_{10}H_{14}$ (decaborane(14)), has the structure of *v* in Fig. 1 with four bridging hydrogens on its open face. The structures of the heteroboranes can be understood by noting that the substitution of a B–H vertex with an atom or group that can furnish one radially directed and two tangentially oriented orbitals and two electrons should not materially change the cage geometry. The structures of the heteroboranes having more electron rich isolobal groups can be rationalized by assuming that of all of the normal valence shell electrons associated with the vertex atom, one pair is *exo*-polyhedral (equivalent to the B–H 2c–2e pair) and the rest involved in cage bonding. In this way, both the N atom and the C–H group are three electron donors, while H–N and S donate four electrons to cage bonding. The electron counting rules have been extended to fused cages as well as single cage structures [2d]. It should also be pointed out that the above arguments still hold when other groups that bond to the vertex atoms by 2c–2e bonds replace one or more terminal hydrogens.

The literature on the main group heteroboranes is extensive, therefore, of necessity, this review will be limited. Specifically it will cover only those compounds in which a p-block element is incorporated into the actual cage structure. Compounds in which the element is involved in an exopolyhedral group bonded to the cage by standard 2c–2e bonds will not generally be included. This restriction precludes a discussion of the Group 17 element chemistry, so that, practically, only Groups 13–16 will be discussed. In addition, because of space limitations, the compounds in which carbons replace boron vertices to give the carboranes will not be included. Even with these restrictions, an exhaustive review would be the subject of a monograph rather than a review article. Our purpose is to engender interest in this field by highlighting some of the typical and/or unusual compounds formed when p-block elements are incorporated into borane cages.

## 2. Metallaboranes of p-block elements

### 2.1. Group 13

The compounds considered in this section will be heteroboranes containing Al, Ga, In and Tl. Since these elements are the heavier members of the boron group, the substitution of an M–R (M = Al, Ga, In and Tl) for a B–H unit in a borane should not drastically alter the cage geometry, once size differences are taken into account. However, a review of the literature shows that making such substitutions are not straightforward endeavors. For example, the observation that $Et_3NBH_3$ reacts with decaborane(14), $B_{10}H_{14}$, in a cage expansion reaction to give $[Et_3NH]_2^+$ [*closo*-$B_{12}H_{12}]^{2-}$ or, under milder conditions, $[Et_3NH]^+[B_{11}H_{14}]^-$, prompted Greenwood and co-workers to carry out a series of studies of the reaction of decaborane with different Group 13 trialkyls or trihydrides [3–6]. They found that $B_{10}H_{14}$ reacts with $Me_3NAlH_3$ in $Et_2O$ to give $[Me_3NH^+][B_{10}H_{12}AlH_2^-]\cdot n Et_2O$ and $H_2$ [3,4]. The structure of the $B_{10}H_{12}AlH_2^-$ is that of a $[B_{10}H_{14}]^{2-}$ cage in which an $AlH_2^+$ group bridges the 6, 9 positions by replacing a hydrogen on each boron atom (see Fig. 2 for the general boron cage structure and atom numbering system). On the other hand, $Me_3NGaH_3$ was found to react with decaborane without the elimination of $H_2$ to give $[Me_3NH]^+[B_{10}GaH_{16}]^-$ in which a $GaH_2^+$ was thought to bridge the 6, 9 positions of a the $[B_{10}H_{16}]^{2-}$ by replacing hydrogens on B(6) and B(9) [3]. A more extensive metal coordination was found for $[B_{10}H_{12}InMe_2]^-$, where all NMR spectral data were consistent with a structure in which the borane is $\eta^4$-bonded to an $In(Me_2)^+$ moiety, as shown in Fig. 2 [6]. However, the corresponding $[B_{10}H_{12}TlMe_2]^-$ gave a more complex $^{11}$B-NMR spectrum, suggestive of a less symmetric complex where the $TlMe_2^+$ was bridged only to B(6) and B(5) [6]. It is an open question as to how best to describe the bonding in the above compounds. While the indium atom is thought to occupy a facial position, and thus be 'fully' incorporated in the borane cage, the thallium-cage bonding in $[B_{10}H_{12}TlMe_2]^-$ is a bit more ambiguous. On the other hand, the aluminum and gallium atoms in $[B_{10}GaH_{16}]^-$ and $[B_{10}AlH_{14}]^-$ could be described as being tetrahedrally coordinated by two $H^-$ groups and a borane fragment acting as a classical bidentate ligand. It is important to note that in no case was an analogue of [*closo*-$B_{12}H_{12}]^{2-}$ found among the products in any of the above reactions. However, such a compound was produced in the reaction of trimethyl aluminum, $AlMe_3$ and $Na_2[B_{11}H_{13}]$ in diglyme, which gave $Na_2\{closo\text{-}[B_{11}H_{11}AlMe]\}$ in 90% yield [7]. The structure of the $[As(C_6H_5)_4]^+$ salt of the aluminaborane, shown in Fig. 3, is that of a classic *closo*-cage in which a valence shell isoelectronic and isolobal Al–Me group replaces a B–H vertex in $[B_{12}H_{12}]^{2-}$. Isolobal arguments can also be used to rationalize the structures of the metallatriboranes, $R_2MB_3H_8$ (R = Me, M = Al or Ga; R = H, M = Ga) [8]. Fig. 4 shows that $H_2GaB_3H_8$ has a tetraborane(10)-type structure, in which a $GaH_2$ group replaces one of the $BH_2$ vertices in $B_4H_{10}$ [9]. Similarities among the spectral properties of the $R_2MB_3H_8$ compounds indicate that they all have structures similar to that shown in Fig. 4.

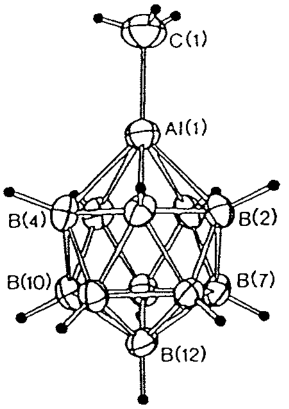


Fig. 3. Perspective view of the *closo*-$[B_{11}H_{11}AlCH_3]^{2-}$ ion. Reprinted with permission from [7].

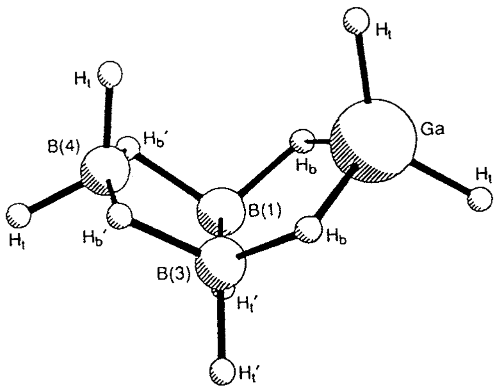


Fig. 4. Perspective view of 2-gallatetraborane(10) from electron diffraction analysis. Reprinted with permission from Ref. [9].

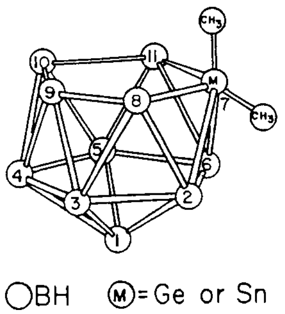


Fig. 5. Proposed structure of $(CH_3)_2MB_{10}H_{12}$. Reprinted with permission from Ref. [10].

## 2.2. Group 14

The general structural trends in the Group 14 heteroboranes can be understood in terms of a substitution of a $[B–H]^-$ group in a borane cage with the isoelectronic and isolobal M–R moiety (M = Group 14 element, R = H or an exopolyhedral group). The net result of such a substitution in a borane would be a cage of similar structure but with one less negative charge. For example, while the *closo*-boranes have the general formula of $[B_nH_n]^{2-}$, the corresponding *closo*-dicarbaborane would be $C_2B_{n-2}H_n$. The lower charged cages are generally more stable and are easier to work with than are the corresponding boranes. For this reason, there are probably more reports in the literature on the chemistry of the carboranes than on the boranes, or any of the other heteroboranes. Thus the carboranes are usually considered separately from the other heteroboranes.

Some 30 years ago, Loffredo and Norman [10] reported the low yield preparation of $(CH_3)_2MB_{10}H_{12}$ (M = Ge, Sn) from the reaction of $NaB_{10}H_{13}$ with the particular alkyl halide, $(CH_3)_2MCl_2$. Somewhat later the corresponding silicon compound, $(CH_3)_2SiB_{10}H_{12}$ was reported by the same authors [11]. The silaborane was found to be less susceptible to $(CH_3)_2M$ removal than either the Ge or the Sn analogues. The $^{11}$B-NMR spectra of the compounds were consistent with a structure in which a $(CH_3)_2M$ moiety occupies a position on the open face of an 11-vertex *nido* structure, as shown in Fig. 5. The structure is similar to that proposed for the Group 3 metallaborane, $[B_{10}H_{12}InMe_2]^-$, shown in Fig. 2. Since the Group 14 $(CH_3)_2M$ group is isoelectronic and isolobal with the $(CH_3)_2In^-$ moiety, similar structures would be expected. $(CH_3)_2SnB_{10}H_{12}$ was found to undergo cleavage reactions with halogens to give $(CH_3)_2SnX_2$ and $B_{10}H_{12}X_2$ ($X = Br_2$ and $I_2$) [12]. Greenwood and Youll reported the synthesis of the corresponding dihalostannaborate, $[B_{10}H_{12}SnCl_2]^{2-}$ from the reaction of either the $[Ph_4As]^+$ or the $[Ph_3MeP]^+$ salt of $[B_{10}H_{12}]^{2-}$ with $SnCl_2$ [13]. The reaction of $SnCl_2$ with $Na_2[B_{10}H_{12}]$ proved ineffective, but the larger cations, such as the tetraphenylarsonium or methyltriphenylphosphonium gave rise to reactivity. The $^{119}$Sn Mössbauer spectrum of the resulting $[B_{10}H_{12}SnCl_2]^{2-}$ was consistent with a Sn(II) coordination and a *nido*-geometry similar to that of $[B_{10}H_{12}InMe_2]^-$, shown in Fig. 2. Reaction of either the quaternary arsonium or phosphonium salt of $[B_{10}H_{12}]^{2-}$ with $R_2SnCl_2$ (R = Me, Et) produced a number of different products, among which was found

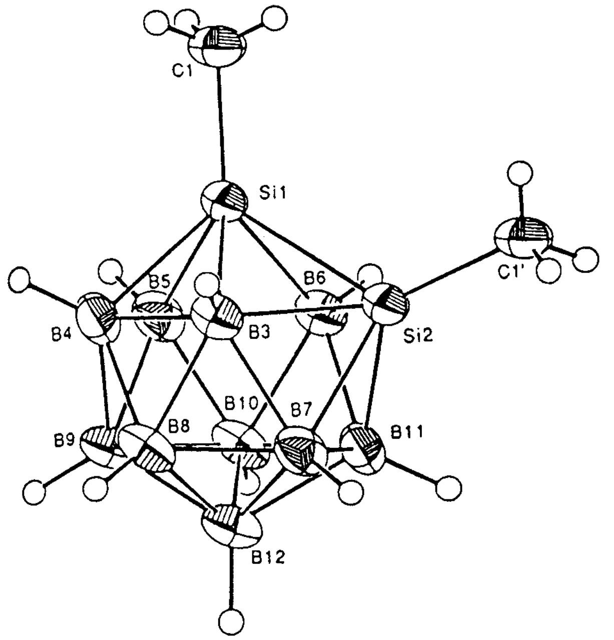
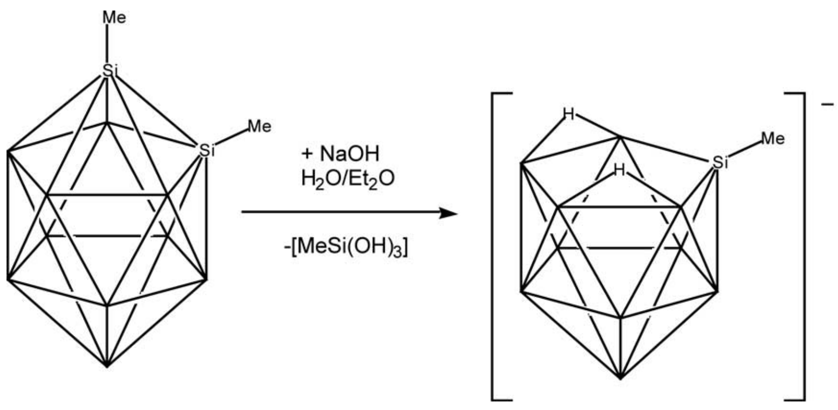
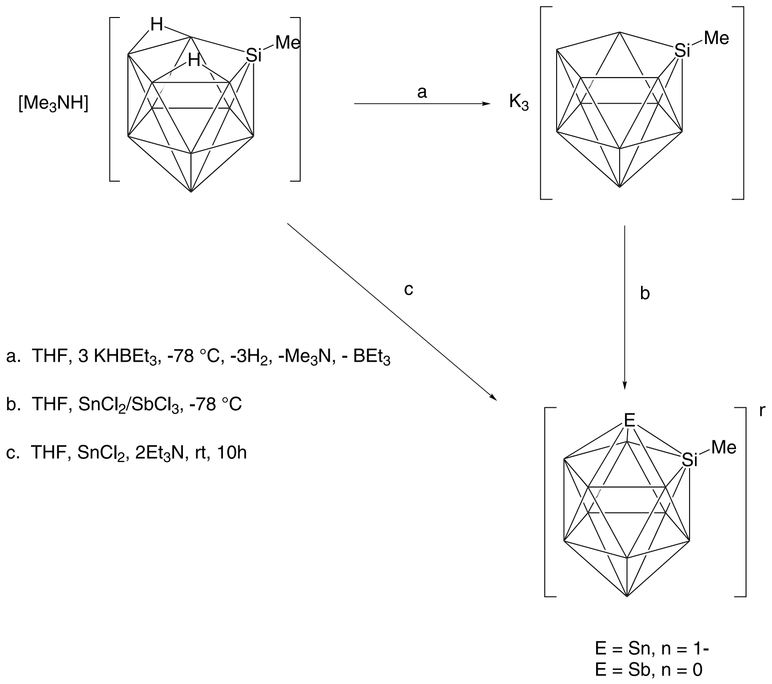


Fig. 6. ORTEP representation of 1,2-dimethyl-1,2-disila-*closo*-dodecaborane(12) showing the 35% probability ellipsoids. Reprinted with permission from Ref. [15].

the unusual $[B_{10}H_{12}R_2SnCl_2]^{2-}$ ion, whose Mössbauer and IR spectra were consistent with the presence of a Sn(IV) atom having a *cis*-$Cl_2$ and *trans*-$R_2$ linkages, with the $B_{10}H_{12}$ moiety involved in $\eta^2$-bonding to the metal [13]. By contrast, the routes to the silaboranes and silaborates were much more circuitous. Seyferth, and co-workers, reported the synthesis of the disilaborane, 1,2-$Me_2$-*closo*-1,2-$Si_2B_{10}H_{10}$, in 15% yield, from the reaction of $B_{10}H_{14}$ and $CH_3(H)Si[N(CH_3)_2]_2$ in refluxing toluene [14,15]. This disilaborane was an unexpected co-product in the synthesis of borane-amine polymers. The structure, shown in Fig. 6, is that of a distorted icosahedron in which the two silicon atoms occupy adjacent positions. The Si–Si bond distance is 2.308 Å which is only slightly less than the normal Si($sp^3$)–Si($sp^3$) distance and the Si–B bonds are very close to the sum of the covalent radii of the two atoms. Controlled nucleophilic degradation of the disilaborane resulted in the removal of a Si vertex to give the resulting *nido*-silaborate, $[CH_3SiB_{10}H_{12}]^-$, as shown in Eq. (1) [16,17]. The synthesis required the immediate precipitation of the silaborate by the presence of the precipitating agent, $[NMe_4]Cl$, in the reaction medium. If the monoanion remains in water for only a few minutes, further degradation occurs resulting in the complete removal of silicon [16]. As with other *nido*-boranes and carboranes the two bridged hydrogens can be removed to give a silaborate that can react with metal halides to give metal insertion. Scheme 1 shows such a reaction with either $SnCl_2$ or $SbI_3$ [18], to give the corresponding metallaborane. The *closo*-structures of the products were confirmed by the solid state structure of the stannasilaborane product, shown in Fig. 7 [18]. Transition metal insertion has also been observed with the formation of more complex structures in which the metal is both $\eta^5$-bonded to the cage and involved in additional bridge bonding through either hydrogens or amide groups, as shown in Figs. 8 and 9 [17]. It should be noted that the degradation reaction of the disilaborane, 1,2-$Me_2$-*closo*-1,2-$Si_2B_{10}H_{10}$, shown in Eq. (1) is quite different from its corresponding carborane analogue, *closo*-1,2-$(CR)_2B_{10}H_{10}$, which, under base hydrolysis, loses a B–H vertex to give the corresponding *nido*-7,8-$(CR)_2B_9H_{11}$ [19]. Both theoretical calculations and photoelectron spectroscopy studies on the silaboranes indicate that the $B_{10}H_{10}$ moiety is extremely electron rich, leaving the two adjacent silicon atoms highly positive. In addition, the LUMOs of the silaboranes are essentially concentrated on the two silicon atoms, so that they can serve as the sites of nucleophilic attack [15,20]. These observations not only explain the course of Eq. (1), but also help rationalize several other unusual reactions of the *o*-silaborane, 1,2-$(Me)_2$-*closo*-1,2-$Si_2B_{10}H_{10}$. For example, the reaction of the *o*-silaborane with $Et_2NLi$ gave a product whose $^{11}$B-NMR spectra was consistent with an adduct in which the ethylamido group bridged the two silicon atoms [21]. This structure was confirmed by the X-ray analysis of $[Zr(NEt_2)_3THF)_2]^+[(Et_2N)(MeSi)_2B_{10}H_{10}]^-$, that was formed, in 85% yield, from



(1)



Scheme 1.

the reaction of the *o*-silaborane with $Zr(NEt_2)_4$ in THF [21]. The structure of the $[(Et_2N)(MeSi)_2B_{10}H_{10}]^-$ ion, given in Fig. 10, clearly shows the Si–N–Si bridge structure. The most unusual aspect is that the Si-Si bond distance of 2.332(1) Å is essentially the same as the 2.308(2) Å found for the starting *o*-silaborane (see Fig. 6). This same similarity was found when comparing the B–B and B–Si bond distances in the adduct with those in the starting material. The major structural change was found in the C–Si–Si bond angle, which increased by 28° on complexation. The diphenyl derivative of the *o*-silaborane was also synthesized and structurally characterized (see Fig. 11) [22]. The Si–Si bond distance of 2.314(1) Å observed in this compound is very similar to those found in Figs. 6 and 10. The diphenyl-*o*-silaborane was found to undergo the same degradation and amido addition reaction as did the dimethyl derivative [22]. The *o*-silaboranes were also found to react with Grignard reagents of the form RMgBr (R = Me, Ph, benzyl, allyl, vinyl and ethynyl) [20]. All show that the R-group bonds to one of the silicons to form anionic adducts with the general formula $[B_{10}H_{10}(SiR')_2R]^-$ (R′ = Me or Ph; R = Me, Ph, benzyl, allyl, vinyl and ethynyl), with yields ranging from excellent ( ~ 90%) to moderate ( ~ 60%). The mixed Me–Ph-*o*-silaborane could be synthesized from the product of the diphenyl-*o*-silaborane and MeMgBr, as outlined in Scheme 2 [20]. The reaction of the *nido*-silaborate, $[CH_3SiB_{10}H_{12}]^-$, formed in Eq. (1) with $Et_3NBH_3$ produced the *closo*-monosilaborate, [1-Me-*closo*-1-$SiB_{11}H_{11}]^-$ [23], which is the only reported synthesis of a *closo*-monosilaborane. The [1-Me-*closo*-1-$SiB_{11}H_{11}]^-$ could also be formed by the two atom cage expansion of the siladecaborane, $MeSiB_9H_{12}$-($NHMe_2$), as shown in Scheme 3 [24,25]. The report on [1-Me-*closo*-1-$SiB_{11}H_{11}]^-$ completes the Group 14 *closo*-monoheteroborane series; the monocarbon carborane was described over 30 years ago [26], while the [*closo*-$B_{11}H_{11}E]^{2-}$ (E = Ge, Sn, Pb) borates have been synthesized more recently by Todd and co-workers [27]. The stanna- and germaboranes were found to react with MeI to give the [*closo*-$B_{11}H_{11}EMe]^-$ products, whose geometry was confirmed by the X-ray crystallographic determination of the structure of methylstannaborane, which is shown in Fig. 12 [27]. The methylation reactions are of interest in that, at least formally, the metal–Me bond was formed using the metal's lone pair of electrons. This is in marked contrast to the corresponding stannacarboranes, 1,2,3-

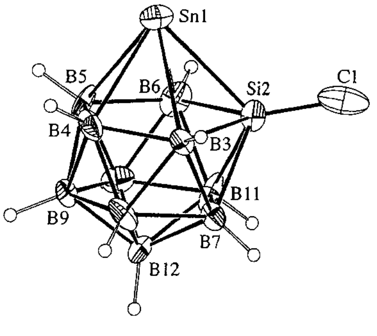


Fig. 7. Perspective of the [2-Me-*closo*-1,2-$SnSiB_{10}H_{10}]^-$ ion. Reprinted with permission from Ref. [18].

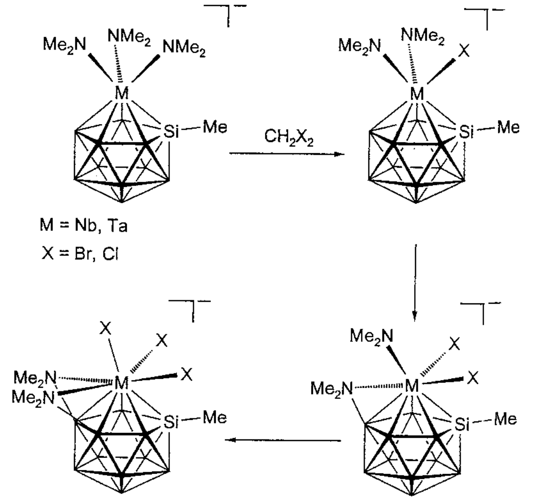


Fig. 8. Formation of M–N–B bridges in the silaboranes. Reprinted with permission from Ref. [17a].

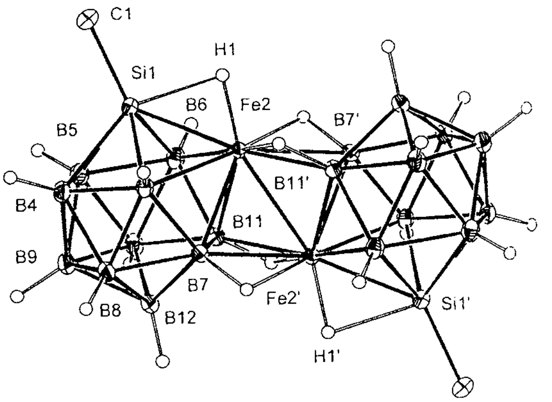


Fig. 9. Perspective of the $\{[HFe(MeSiB_{10}H_{10})]_2\}^{2-}$ anion. Reprinted with permission from Ref. [17b].

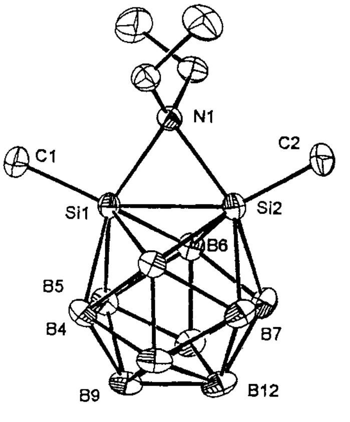


Fig. 10. Structure of the $[(Et_2N)(MeSi)_2B_{10}H_{10}]^-$ ion. Reprinted with permission from Ref. [21].

$Sn(CCH_3)_2B_9H_9$ and 1,2,3-$Sn(CSiMe_3)_2B_4H_4$, in which no evidence could be found for a chemically active metal lone pair [28,29]. The first reported *arachno*-silaborane, *arachno*-$MeSiB_9H_{12}(NHMe_2)$, shown in Fig. 13, was produced in 85% yield from the reaction of *arachno*-$B_9H_{13}(SMe_2)$ and $MeHSi(NMe_2)_2$ [24].

The reaction of the Group 14 metal alkyl halides with smaller borane cages, such as pentaborane(9), produced bridged complexes of the general form μ-$R_3MB_5H_8$ (R = H, $CH_3$, and $C_2H_5$; M = Si, Ge, Sn or Pb) [30,31]. These compounds were found to isomerize in the presence of mild Lewis bases to produce isomers in which the $R_3M$ is terminally bound to either the apical boron (1-$R_3MB_5H_8$) or to one of the basal borons (2-$R_3MB_5H_8$). In most cases the 2-isomer is the more stable and forms preferentially, with the 1-isomer being accessible only at elevated temperatures or in the presence of strong bases [32]. However, the stabilities can be reversed when bulky metal groups are present. For example, the 1-isomer seems to be the most stable product in the reaction of $K[B_5H_8]$ and $SnClPh_3$ [33], while the low temperature reaction of $K[B_5H_8]$ with $SnCl_2Ph_2$ (Ph = $C_6H_5$) in a 2:1 molar ratio produced the bridged intermediate, μ,μ′-$SnPh_2(B_5H_8)_2$, which rearranged on standing to give μ-2′-$SnPh_2(B_5H_8)_2$, a compound in which the Sn is bridged to one borane and is terminally bound to the other (see Fig. 14) [34].

### 2.3. Group 15

Although the Group 15 elements have been incorporated into borane or borate cages, the examples of such decrease as one goes down the group. As far as cage

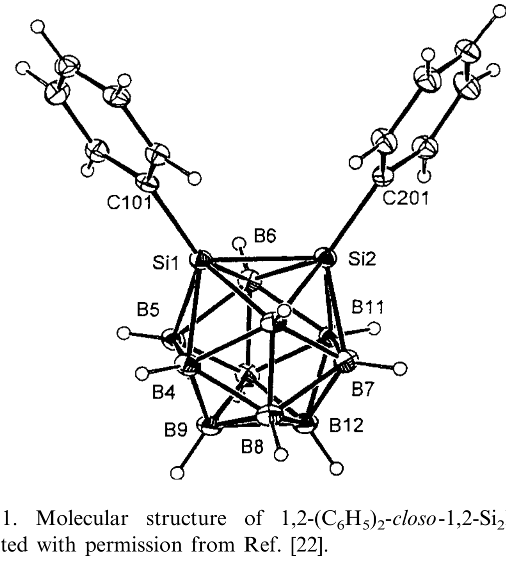
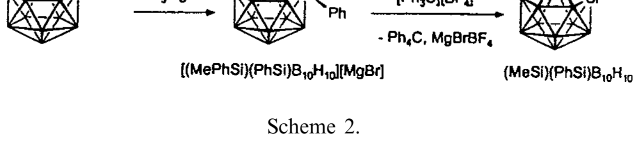
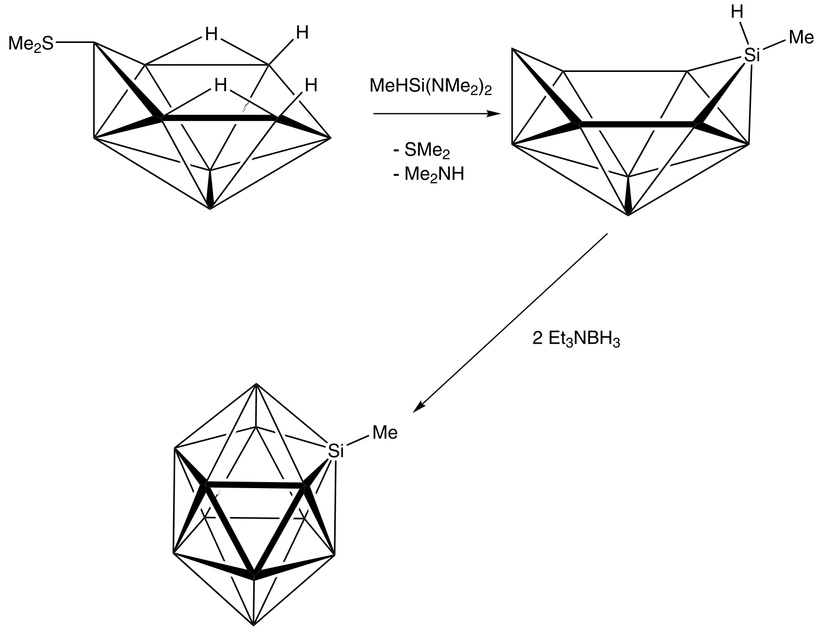


Fig. 11. Molecular structure of 1,2-$(C_6H_5)_2$-*closo*-1,2-$Si_2B_{10}H_{10}$. Reprinted with permission from Ref. [22].



Scheme 2.



Scheme 3.

bonding is concerned, an isolated Group 15 element, E, is a three electron donor that is isoelectronic and isolobal with an R–C or a [B–H]$^-$ group, while the R–E group is considered a four electron donor. In general the lighter Group 15 elements (N and P) are usually present as members of an R–E group, while the heavier congeners are often incorporated as individual atoms. Using this electron counting scheme, in conjunction with Wade's rules [2,35], it is easy to rationalize the geometries of azaboranes such as *closo*-1-$(PhCH_2)NB_{11}H_{11}$ (Fig. 15) and *arachno*-4-$NB_8H_{13}$ (Fig. 16), with $n+1$ and $n+3$ cage electron pairs, respectively [36,37]. Scheme 4 shows that the 4-$NB_8H_{13}$ was the azaborane product obtained from the reaction of decaborane(14) with $NaNO_2$ followed by treatment with dilute HCl; when concentrated $H_2SO_4$ was used instead, *nido*-6-$NB_9H_{12}$ was the major product [38]. 6-$NB_9H_{12}$ can also be obtained from the thermolysis of *arachno*-$B_9H_{13}(NH_3)$ or *arachno*-$B_{10}H_{12}(N_3)(NH_2)$ [39]. However, thermolysis of *arachno*-$B_9H_{11}(NRH_2)$ afforded the corresponding *nido*-$RNB_9H_{11}$ [40]. Both 4-$NB_8H_{13}$ and 6-$NB_9H_{12}$ have proven to be versatile precursors in the syntheses of other azaheteroboranes. $NB_9H_{12}$ can add Lewis bases to the B(9) atom causing a shift of the bridged hydrogens to span the B(5)–B(10) and B(7)–B(8) bonds (Scheme 4 shows the atom numbering system and Fig. 17 the structure of the one such addition product) [38,39,41]. It is also possible to derivatize the N by reaction with Lewis acid containing compounds, such as $Et_3NBH_3$ [39]. $RNB_9H_{11}$ can act as a hydroborating agent with certain alkynes and substituted ethenes [42]; they can also be metallated to give the corresponding *closo*-metalla-azaboranes, such as 1-$(\eta^5\text{-}C_5H_5)$-1,2-$CoNHB_9H_9$, whose structure is shown in Fig. 18 [43]. *Arachno*-4-$NB_8H_{13}$ reacts with $[PtCl_2(PMe_2Ph)_2]$ to give $[(PMe_2Ph)_2PtNB_8H_{11}]$, which has an *arachno*-$PtNB_8$ cage, as shown in Fig. 19 [44]. A number of *closo*- and *commo*-complexes in the icosahedral

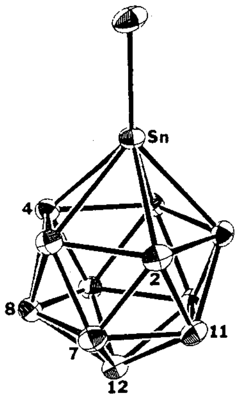


Fig. 12. Molecular structure of *arachno*-$MeSiB_2H_{12}(NHMe_2)$. Reprinted with permission from Ref. [24].

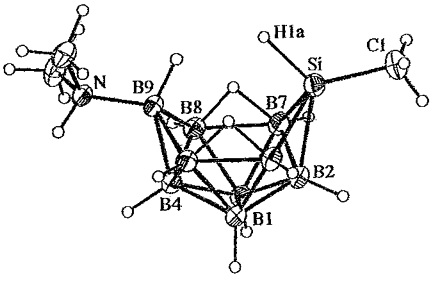


Fig. 13. ORTEP drawing of the [1-Me-*closo*-1-$SnB_{11}H_{11}$]$^-$ ion. Hydrogens omitted for clairty. Reprinted with permission from Ref. [27].

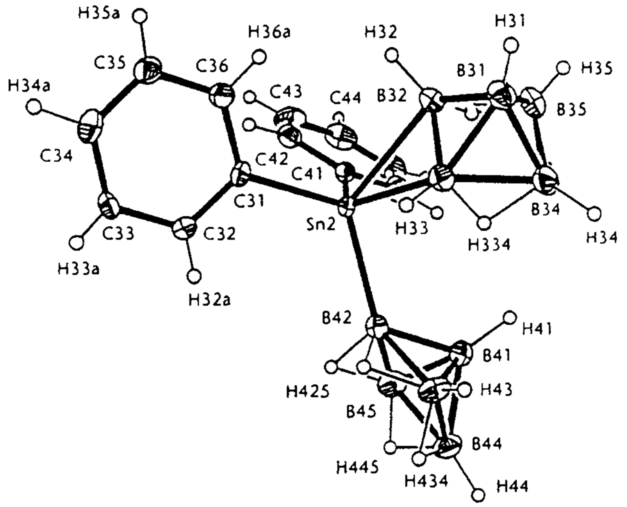


Fig. 14. Structure of $\mu$,2′-$SnPh_2(B_5H_8)_2$. Reprinted with permission from Ref. [34].

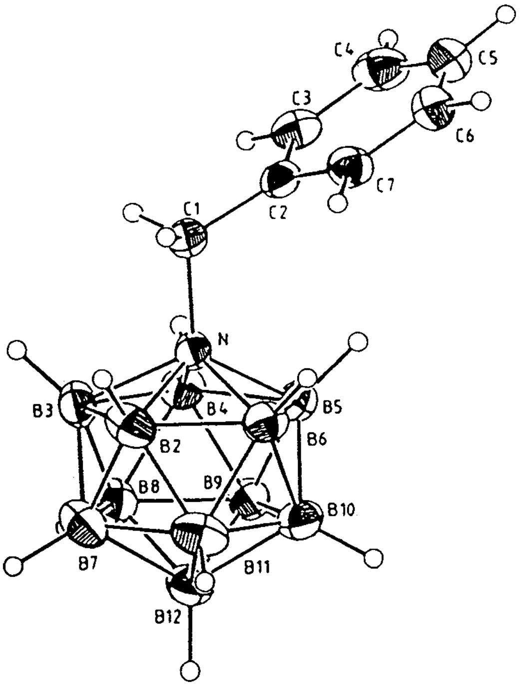


Fig. 15. Molecular structure of 1-($PhCH_2$)-*closo*-1-$NB_{11}H_{11}$ with 30% probability ellipsoids. Reprinted with permission from Ref. [36].

system have been reported from the metallation of [*nido*-$NB_{10}H_{11}$]$^{2-}$, which is isoelectronic with the well-known dicarbollide, [*nido*-$C_2B_9H_{11}$]$^{2-}$ [45]. Fig. 20 shows the structure of the *closo*-1-($C_6Me_6$)-1,2-$RuNB_{10}H_{11}$. It is of interest to note that the metal is essentially symmetrically bonded to the atoms in the $NB_4$ face; the relevant distances are: Ru–B(3) = 220.4(3), Ru–B(7) = 224.2(3), Ru–B(11) = 223.2(3), Ru–B(6) = 219.2(3) and Ru–N = 218.9(2) pm [45]. In addition, diazaboranes [46] and macropolyhedral azaboranes have been described [47]. The reader is referred to several recent reviews for further discussions of the azaboranes [48].

As with N, the heavier Group 15 elements have all been incorporated into borane cages either as isolated atoms (P, As, Sb and Bi) or as having derivative groups attached (P). The *closo*-structures of 2-$Me_3N$-1-$PB_{11}H_{10}$, shown in Fig. 21 [49] and 6-$(C_2H_5)_3N$-2-$PB_9H_8$, shown in Fig. 22 [50], are consistent with the P acting as a three electron donor to the cage giving electron-pair counts of 13 and 11, respectively. In the same way, the four cage electron-pair donor R–P group

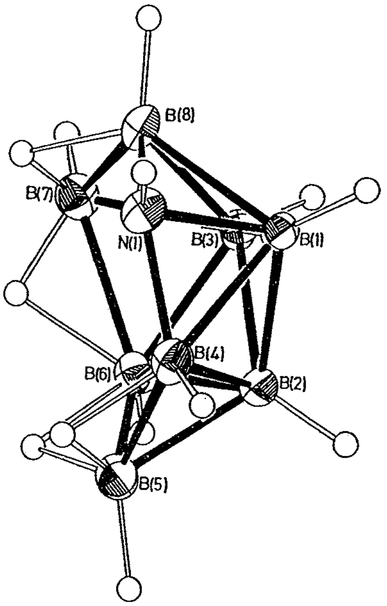
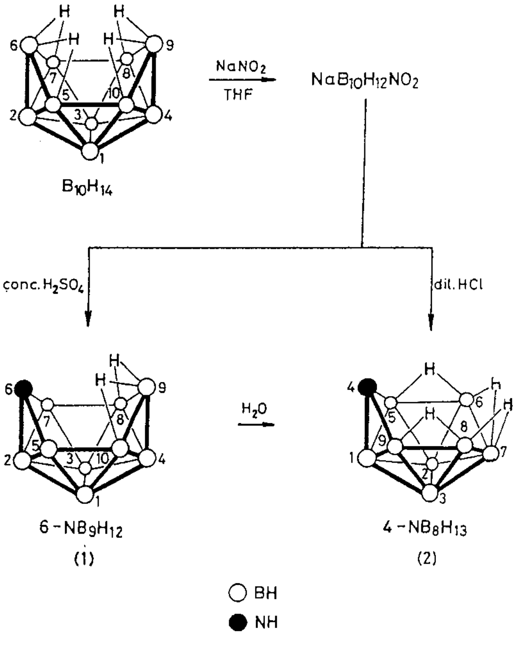


Fig. 16. Structure of 4-azanonaborane(13). Reprinted with permission from Ref. [37].



Scheme 4.

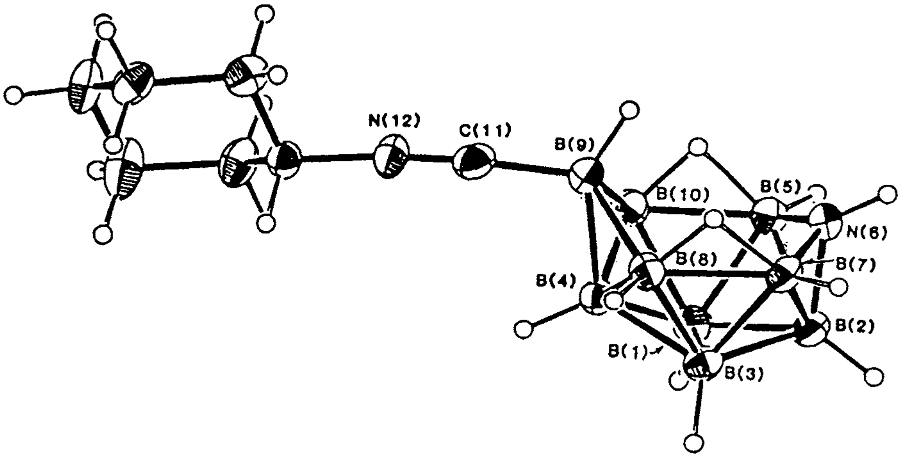


Fig. 17. ORTEP diagram of 9-[($C_6H_{11}$)NC]-6-$NHB_9H_{11}$. Reprinted with permission from Ref. [41].

gives rise to a *closo*-structure of $B_{11}H_{11}PCH_3$ (Fig. 23) [51]. It is of interest that while *closo*-$B_{11}H_{11}PCH_3$ was the product of the reaction of $Na_2[B_{11}H_{13}]$ and $P(CH_3)Cl_2$ in THF, the same two reactants gave *nido*-$B_{10}H_{12}PCH_3$ in $Et_2O$ (see Fig. 24) [51]. Both structures are consistent with the $CH_3$–P group acting as a four-cage electron donor. On the other hand, the $R_2P$ group, rather than functioning as a five-cage electron donor, bonds to a borane fragment quite differently. There have been a number of reports of the incorporation of such groups into both small and large borane cages, in all cases, the $R_2P$ group was found to bridge a pair of boron atoms with two 2c–2e bonds. Thus the reaction of $Na[B_5H_8]$ with $(C_6H_5)_2PCl$ in THF produced the bridged compound, $[(\mu\text{-}(C_6H_5)_2P]B_5H_8$, in 29% yield. While this compound was an oil, it could be converted into a solid suitable for X-ray analysis by reaction of its sodium salt, $Na\{[\mu\text{-}(C_6H_5)_2P]B_5H_8\}$ with $Fe(\eta^5\text{-}C_5H_5)(CO)_2I$, to form 4-$[Fe(\eta^5\text{-}C_5H_5)(CO)_2]B_5H_7(2\text{-}\mu\text{-}P(C_6H_5)_2)$, whose structure is shown in Fig. 25 [52]. In this compound it is quite clear that the immediate bonding environment about the phosphorus atom is that of a distorted tetrahedron. Furthermore, the B(2)–B(3) interatomic distance of 2.68 Å is significantly longer than of the B(2)–B(5) (1.790 Å), B(3)–B(4) (1.802 Å) and B(4)–B(5) (1.759 Å) distances giving rise to a cage structure that is similar to that of *arachno*-$B_5H_{11}$ [53] with the bridging phosphorus atom replacing the two *endo*-hydrogens on the $B_5H_{11}$ equivalents to B(2) and B(3), shown in Fig. 25. Similarly, the structure of the *arachno*-$[B_{10}H_{12}P(C_6H_5)_2]^-$ anion, shown in Fig. 26, is that of [*arachno*-$B_{10}H_{14}]^{2-}$ [54] with the bridging phosphorus replacing its *endo*-hydrogens on B(6) and B(9) [55]. It is of interest that the neutral phosphinoborane, 5,6-$\mu$-$[P(C_6H_5)_2]B_{10}H_{13}$, which is the conjugate acid of *arachno*-$[B_{10}H_{12}P(C_6H_5)_2]^-$, exhibits some *nido*-structural characteristics, as shown in Fig. 27 [56]. The structure of the conjugate acid is similar to that of *nido*-$B_{10}H_{14}$ with a $P(C_6H_5)_2$ moiety replacing a bridged hydrogen. However, an inspection of the intracage boron distances shows that the B(5)–B(6) distance is 2.69 Å, which is significantly longer than the B(6)–B(7) distance of 1.70 Å. Thus the adjacent borons that are

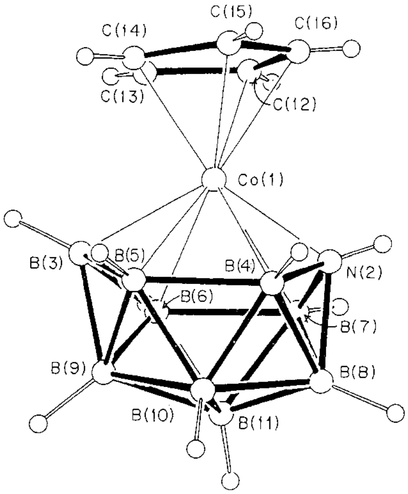


Fig. 18. Crystal structure of 1-($\eta^5$-$C_5H_5$)-1,2-$CoNB_9H_9$. Reprinted with permission from Ref. [43].

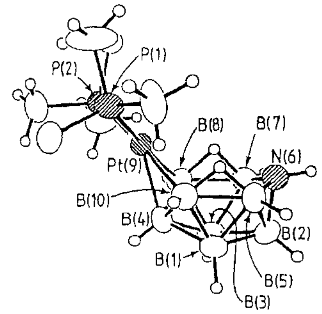


Fig. 19. Molecular structure of 9,9-$(PMe_2Ph)_2$-*arachno*-9,6-$PtNB_8H_{11}$ with the P-phenyl atoms omitted for clarity. Reprinted with permission from Ref. [44].

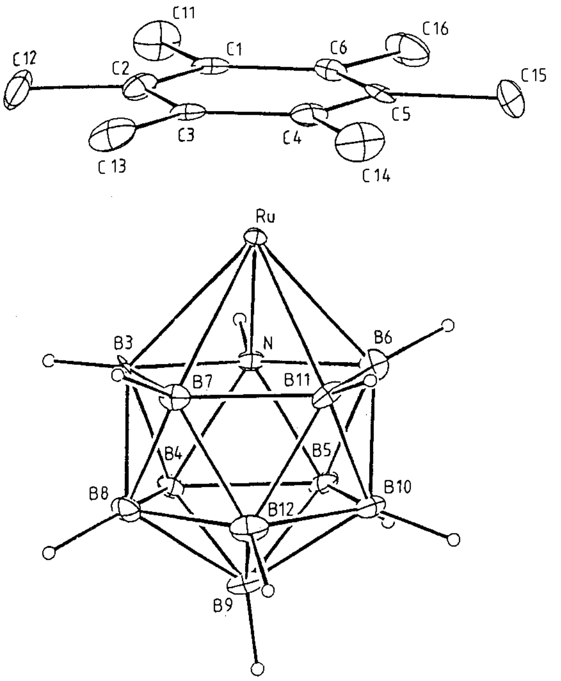


Fig. 20. Molecular structure of 1-($\eta^6$-$C_6Me_6$)-*closo*-1,2-$RuNB_{10}H_{10}$ with 30% probability ellipsoids drawn for the nonhydrogens. Methyl hydrogens omitted for clarity. Reprinted with permission from Ref. [45].

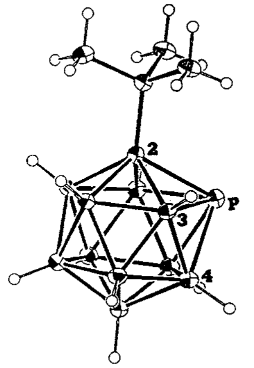


Fig. 21. Crystal structure of 2-($Me_3N$)-*closo*-1-$PB_{11}H_{10}$. Reprinted with permission from Ref. [49].

spanned by the phosphino group are not bonded to one another, but instead form two 2c–2e bonds with the phosphorus atom. Deprotonation of this compound induces both a hydrogen and a phosphino shift to give the structure shown in Fig. 26.

There have been reports of a large number of Group 15 diheteroboranes whose structures conform to the electron counting rules. Thus, the heteroboranes, 1,2-$E_2B_{10}H_{10}$ (E = P [50], As [57], Sb [58], Bi [59]) all have *closo*-structures analogous to the well-known *o*-carborane, *closo*-1,2-$C_2B_{10}H_{12}$. As with its *o*-carborane analogue, 1,2-$P_2B_{10}H_{10}$ was found to undergo thermal rearrangement to its 1,7-isomer [50]. In addition to the homonuclear 1,2-$E_2B_{10}H_{10}$, mixed Group 15 heteroboranes have also been reported [58,59]. Both the mono- and di-Group 15 heteroboranes could be metallated to their respective metallaheteroboranes. For example, decaborane in the presence of a base was found to react with $AsCl_3$ to give [*nido*-7-$B_{10}H_{12}As$]$^-$, which, in turn reacts with metal halides to give both full- and half-sandwich metallaarsaboranes [57,60]. A number of other Group 15 metallaheteroboranes have been pre-

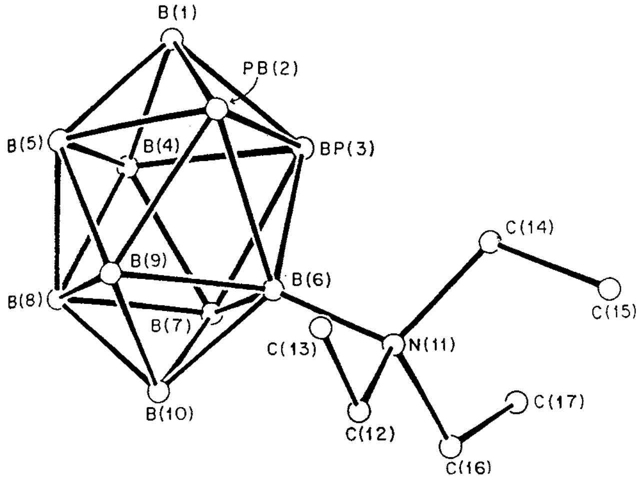


Fig. 22. Molecular srtucture of the heavy atom of 6-($Et_3N$)-*closo*-2-$NB_9H_8$. Reprinted with permission from Ref. [50].

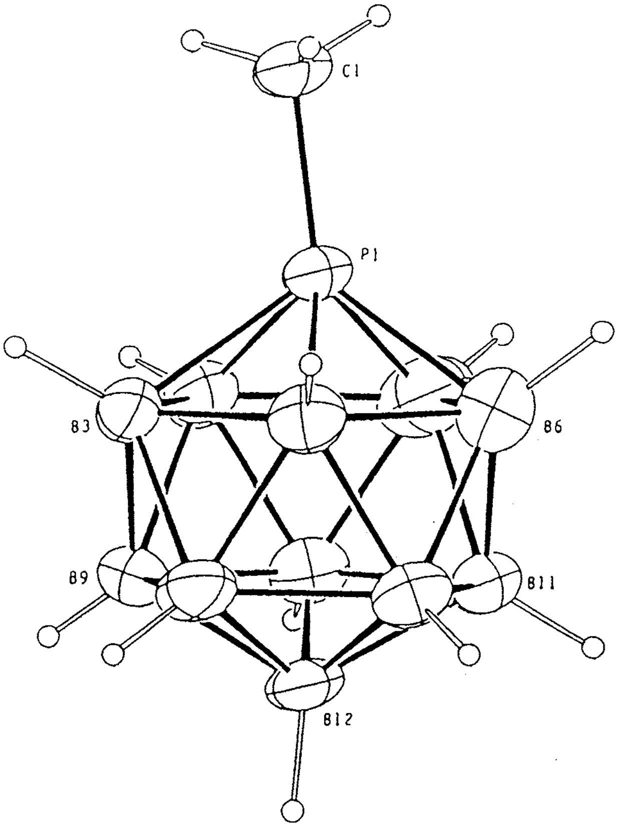


Fig. 23. Crystal structure of 1-Me-*closo*-1-$PB_{11}H_{11}$. Reprinted with permission from Ref. [51].

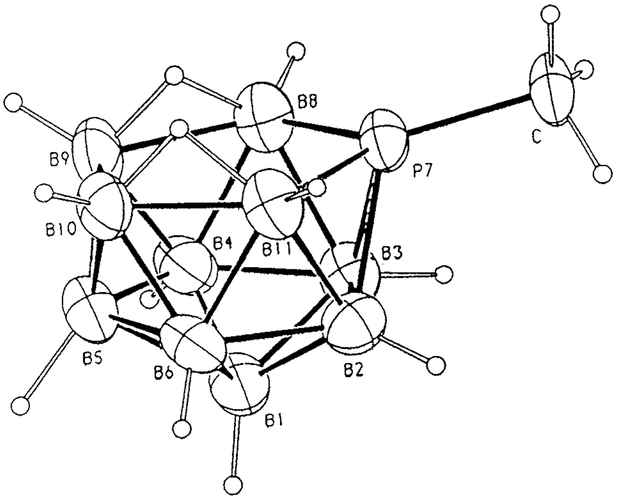


Fig. 24. Molecular structure of 7-Me-*nido*-7-$PB_{10}H_{12}$ with 50% probability ellipsoids. Reprinted with permission from Ref. [51].

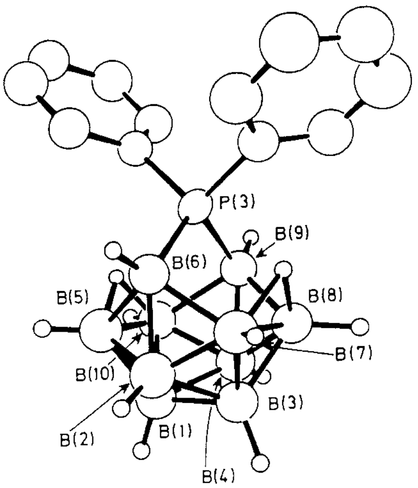


Fig. 26. ORTEP drawing of the $[B_{10}H_{12}(PPh_2)]^-$ ion. Phenyl hydrogens omitted for clarity. Reprinted with permission from Ref. [55].

pared and characterized. Their behavior generally parallels that of the corresponding metallacarboranes. Fig. 28 shows the structure of the [3,3-$(PMe_2Ph)_2$-*closo*-3,1,2-$PtAs_2B_9H_9$] [61] in which the Pt coordinates to the $As_2B_3$ pentagonal face of the arsaborane to give $PtAs_2B_9$ cage with a distorted icosahedral geometry. The Pt is not symmetrically bound to the arsaborane, but is slightly displaced, or slipped, away from the arsenic atoms towards the unique boron [B(8) in Fig. 28]. Stone and coworkers have described a similar slip distortion in the platinacarboranes [62]. In both complexes the other ligands on the Pt are oriented so that the R–Pt–R plane is parallel to the hetero-cage atom bond (in Fig. 28, the As(1)–As(2) bond). However, in solution the [3,3-$(PMe_2Ph)$-*closo*-3,1,2-$PtAs_2B_9H_9$] has been shown to be fluxional in that there seems to be free rotation of the [Pt$(PMe_2Ph)_2$] moiety about the Pt–B(10) axis. Similar fluxionality has been observed in the platinacarboranes as well as in [$(PMe_2Ph)_2$-$PdAs_2B_9H_9$] and [$(PPh_3)_2PtAs_2B_9H_9$] [61,62].

There have been several reports of the derivatization of the boron atoms in the Group 15 heteroboranes, many of which were obtained as unexpected co-products in the usual metallation reaction of the heterobo-

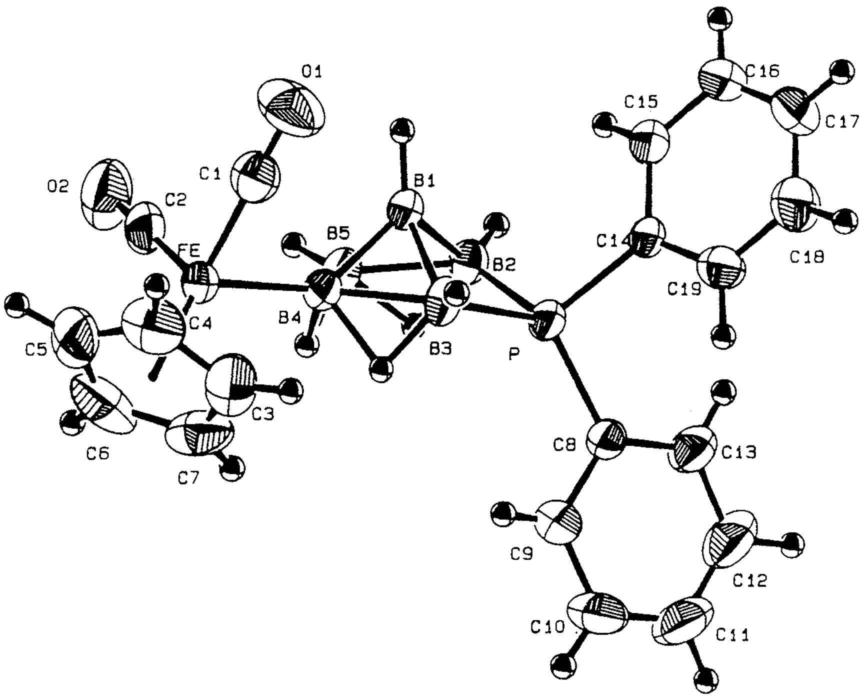


Fig. 25. ORTEP drawing of [μ-$(C_6H_5)_2P$]$B_5H_7Fe(\eta^5$-$C_5H_5)(CO)_2$ with 50% probability ellipsoids. Reprinted with permission from Ref. [52].

ranes [61]. Todd and coworkers have described the palladium assisted ligand substitution reactions leading to metallaheteroboranes in which one or more of the terminal hydrogens on the borane cage were substituted for a Cl or CN ligand [63]. Unfortunately, the yields in these reactions were low to modest (6–30%). A more extensive substitution pattern was described by Haubold and coworkers who synthesized and structurally characterized the perchlorinated diphosphaboranes, 1,7-$P_2B_{10}Cl_{10}$ [64], 1,2-$P_2B_4Cl_4$ [65a] and 1,2-$As_2B_4Cl_4$ [65b]. These were prepared, in low yield, by the pyrolysis reactions of $B_2Cl_4$ and $PCl_3$ or $AsCl_3$, respectively. Their structures, shown in Figs. 29–31, clearly show *closo*-geometries and verify the P–(C–H) and As–(C–H) equivalency. However, it is of interest to note that the *closo*-1,2-$P_2B_4Cl_4$ as well as the *closo*-1,2-$As_2B_4Cl_4$ rather than their 1,6-isomers were the major products. This is in contrast to the results found in the carborane system where the 1,6-$(CR)_2B_4H_4$ isomer is the thermodynamically more stable one and is obtained by heating 1,2-$(CR)_2B_4H_4$ (R = H [66], $SiMe_3$ [67]) to temperatures of 200–250 °C. The presence of only the 1,2-$X_2B_4Cl_4$ (X = P or As) isomers from 300–330 °C pyrolysis reactions [65] could indicate a reversal in stability or a much higher activation energy for the rearrangement process.

### 2.4. Group 16

All of the Group 16 elements (other than Po) have been incorporated into a borane or metallaborane cage. In all cases when the four-electron donor Group 16 atom replaces a B–H vertex, other changes, such as the loss of two bridged hydrogens or cage oxidation, must accompany these substitutions. For example, one of the few reports of oxygen being incorporated into a borane cage was that of 2-[$\eta^6$-$C_6(CH_3)_3H_3$]Fe-6-$OB_8H_{10}$, shown in Fig. 32(a). The structure of this compound, and the isoelectronic ferraborane, 5-[$\eta^6$-$C_6(CH_3)_3H_3$]$FeB_9H_{13}$, shown in Fig. 32(b), is derived from that of decaborane(14) with a [$\eta^6$-$C_6(CH_3)_3H_3$]Fe moiety replacing a B–H vertex and, in the case of 2-[$\eta^6$-$C_6(CH_3)_3H_3$]Fe-6-$OB_8H_{10}$, an oxygen occupying an adjacent position [68]. The ferraborane and the ferraoxaborane are related to one another by the substitution of the O for a B–H and two bridged hydrogens, which results in a 10-vertex, 12 cage electron-pair ($n+2$) *nido*-clusters. In addition, the 11-vertex *nido*-[($\eta^5$-$C_5(CH_3)_5$)$RhB_{10}H_{11}Cl${$P(CH_3)_2$-

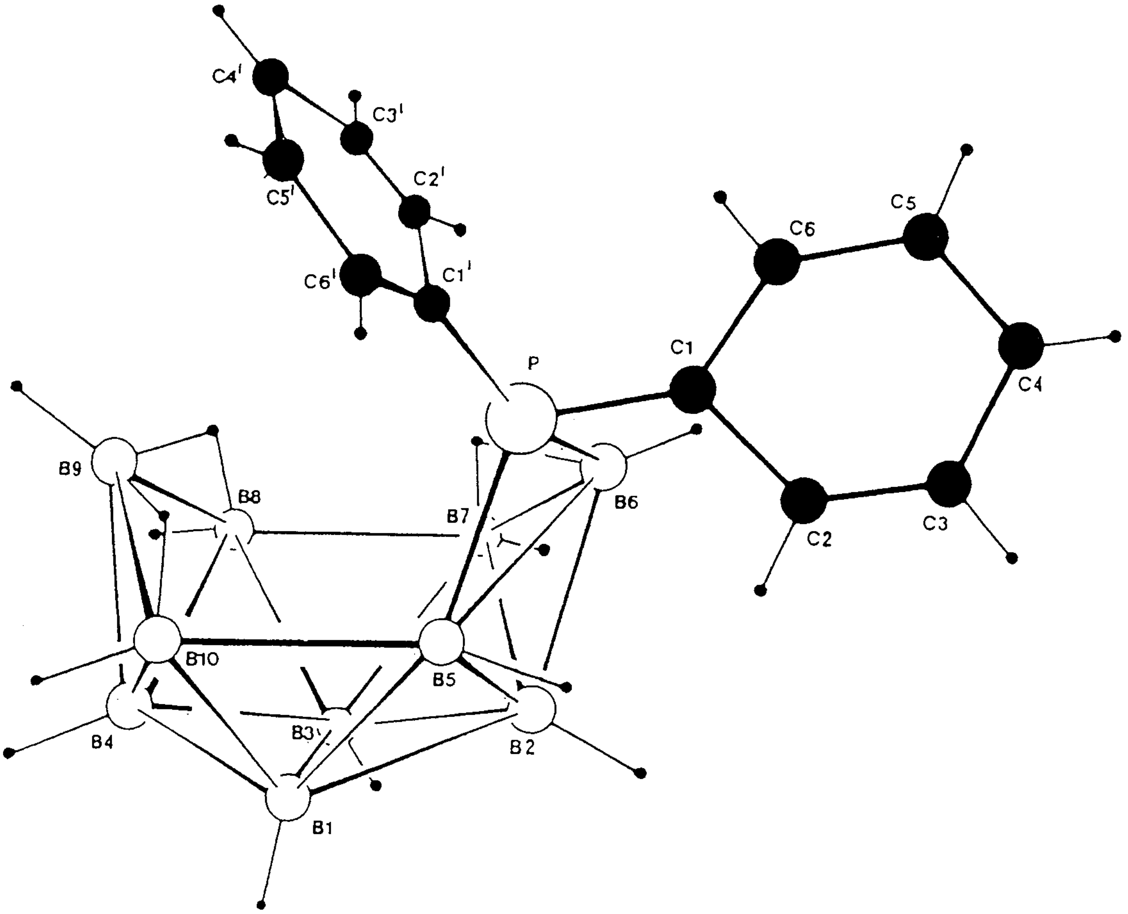


Fig. 27. Molecular structure and numbering system for 5,6-μ-[$P(C_6H_5)_2$]$B_{10}H_{13}$, atoms drawn with arbitrary radii. Reprinted with permission from Ref. [56].

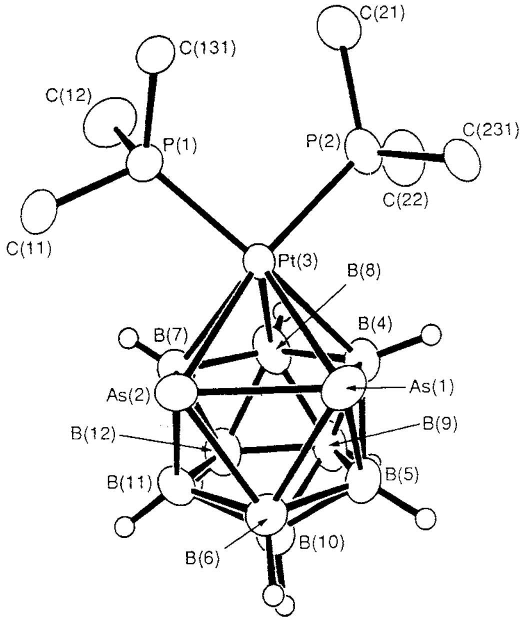


Fig. 28. ORTEP diagram of [3,3-$(PPh_3)_2$-*closo*-3,1,2-$PtAs_2B_9H_8$] with P-organyl atoms other than those attached to phosphorus omitted for clarity. Reprinted with permission from Ref. [61].

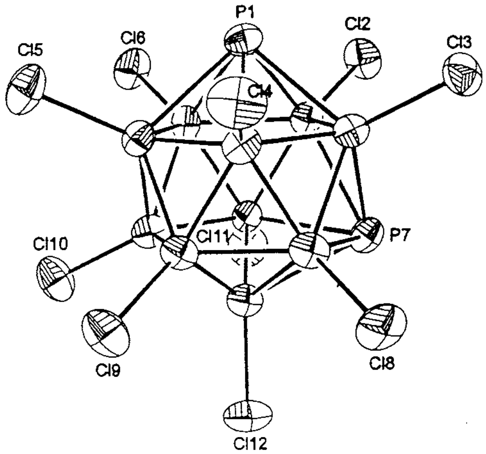


Fig. 29. Molecular structure of *closo*-1,7-$P_2B_{10}Cl_{10}$. Reprinted with permission from Ref. [64].

$(C_6H_5)\}]$ was found to react with $H_2O$ in $CH_2Cl_2$ to give *nido*-$[(\eta^5\text{-}C_5(CH_3)_5)RhOB_{10}H_9Cl\{P(CH_3)_2(C_6H_5)\}]$ as outlined in Eq. (2) [69]. The structures of the reactant and product compounds are shown in Fig. 33. At least formally, the two compounds

$$\begin{aligned}&nido\text{-}[(\eta^5\text{-}C_5(CH_3)_5)RhB_{10}H_{11}Cl\{P(CH_3)_2(C_6H_5)\}]\\&\quad + H_2O \rightarrow nido\text{-}[(\eta^5\text{-}C_5(CH_3)_5)RhOB_{10}H_9Cl\\&\quad \{P(CH_3)_2(C_6H_5)\}] + 2H_2 \qquad (2)\end{aligned}$$

are related to one another in that the rhodaoxaborane results from the replacement of two bridged hydrogens and two electrons by a four electron donor oxygen atom. There have been several reports of metal free oxaboranes. The biphasic reaction of $Et_4NB_{11}H_{14}$ with $As_2O_3$ and NaOH in a $CH_2Cl_2$–$H_2O$ reaction mixture produced a small amount of an oxaborane, later identified as $Et_4N[OB_{11}H_{12}]$, along with the expected $(Et_3NH)B_{11}H_{11}As$ product [70]. NMR evidence suggests that the compound is a *nido*-12-vertex 14-electron pair oxaborane. While this geometry could not be verified by X-ray diffraction, another oxaborane anion, $[OB_{18}H_{21}]^-$, could be structurally characterized. Fig. 34 shows that the compound has an *anti*-$B_{18}H_{22}$ structure with an oxygen atom substituted for the μ-8,9 bridging hydrogen. The B(8)–B(9) bond distance of 186.4 pm is not too different from the 182.4 pm found for B(9)–B(10) distance, indicating that the oxygen is incorporated directly into the borane cage structure [71]. The resulting 23 cage electron pair is consistent with the structure shown in Fig. 34.

In contrast to the paucity of reports on the oxaboranes, the literature contains a great deal of information on the heavier, less electronegative Group 16

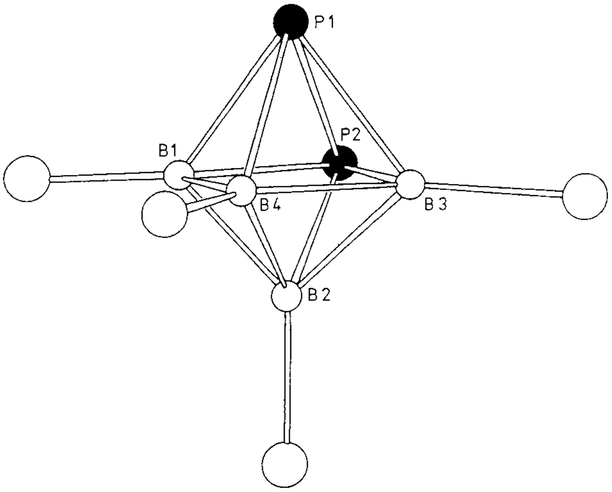


Fig. 30. Molecular structure of *closo*-1,2-$P_2B_4Cl_4$. Reprinted with permission from Ref. [65a].

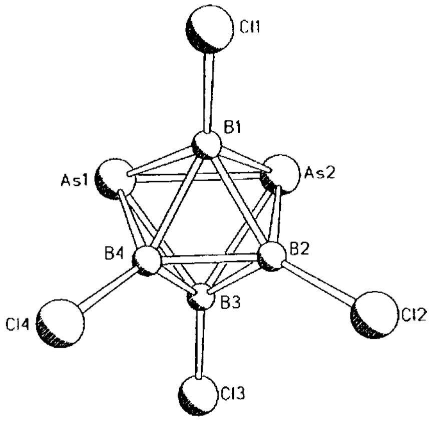


Fig. 31. Molecular structure of *closo*-1,2-$As_2B_4Cl_4$. Reprinted with permission from Ref. [65b]

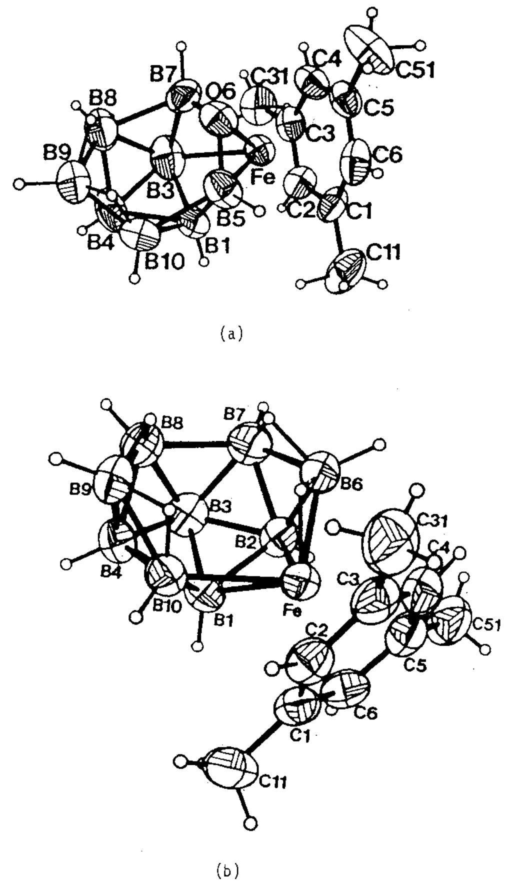


Fig. 32. ORTEP drawings of: (a) 2-[$\eta^6$-$C_6Me_3H_3$]-Fe-6-$OB_8H_{10}$; and (b) 5-[$\eta^6$-$C_6Me_3H_3$]-$FeB_9H_{13}$ with nonhydrogen atoms drawn with 50% probability ellipsoids. Reprinted with permission from Ref. [68].

heteroboranes, especially the thiaboranes. All act as four cage electron donors and the structures of the resulting heteroboranes are those predicted by the electron counting rules. Hertler et al. reported the synthesis of the first thiaborane, Cs[*arachno*-6-$SB_9H_{12}$], which was obtained in 90% yield from the reaction of $B_{10}H_{14}$ and ammonium sulfide, followed by precipitation with CsF [72]. The structure of its $\{[(C_6H_5)_3P]_3Au\}^+$ salt was determined by X-ray crystallography[73] and is shown in Fig. 35. The $[SB_9H_{12}]^-$ is a useful precursor for the formation of other thiaboranes, as shown in Scheme 5. As can be seen, it reacts directly with metal halides in the presence of BuLi to give metallathiaboranes of the form $[(SB_9H_{11})_2M]^{2-}$, in which the commo-metal is thought to be bound directly to the sulfur in the open $MSB_3$ pentagonal faces of 11-vertex nido-structures (*viii* in Fig. 1) [74]. In addition, the reaction of $[SB_9H_{12}]^-$ with either $K_2Se_x$ [75] or $AsCl_3$ [76] produced the 11-vertex nido-products, $B_9H_9SSe$ and $As_2SB_8H_8$, respectively. In all of these compounds the hetero atoms occupy adjacent positions on their open pentagonal faces. A number of other thiaboranes can be obtained from the controlled pyrolysis of the [*arachno*-6-$SB_9H_{12}$]$^-$ or its oxidation products (see Scheme 5). Specifically, Pretzer and Rudolph reported that Cs[*arachno*-6-$SB_9H_{12}$] could be oxidized by $I_2$ in benzene to give *nido*-6-$SB_9H_{11}$ in 85% yield, which could then be pyrolyzed at ~375 °C to give *closo*-1-$SB_9H_9$ in 50% purified yield [77]. The $^{11}$B-NMR of the product was consistent with a structure in which the sulfur occupied an axial position in a bicapped Archimedian antiprism [77b]; this was verified by the crystal structure analysis of its dimer, 2,2′-*bis*[1-thia-*closo*-decaborane(8)], shown in Fig. 36 [78]. The *closo*-thiaborane could be degraded by alcoholic KOH to give [*nido*-4-$SB_8H_9$]$^-$ [77a]. In addition to cage closure, the *nido*-6-$SB_9H_{11}$ was also found to undergo a cage expansion reaction with $Et_3NBH_3$ to give [*nido*-7-$SB_{10}H_{11}$]$^-$ [72]. However, the [*nido*-7-$SB_{10}H_{11}$]$^-$ could more conveniently be obtained directly from the 200 °C pyrolysis of Cs[*arachno*-6-$SB_9H_{12}$] [72]. Scheme 5 shows that the [*nido*-7-$SB_{10}H_{11}$]$^-$ could in turn be used to prepare a number of full- and mixed-sandwich metallathiaboranes [72], or, after acidification to give neutral *nido*-7-

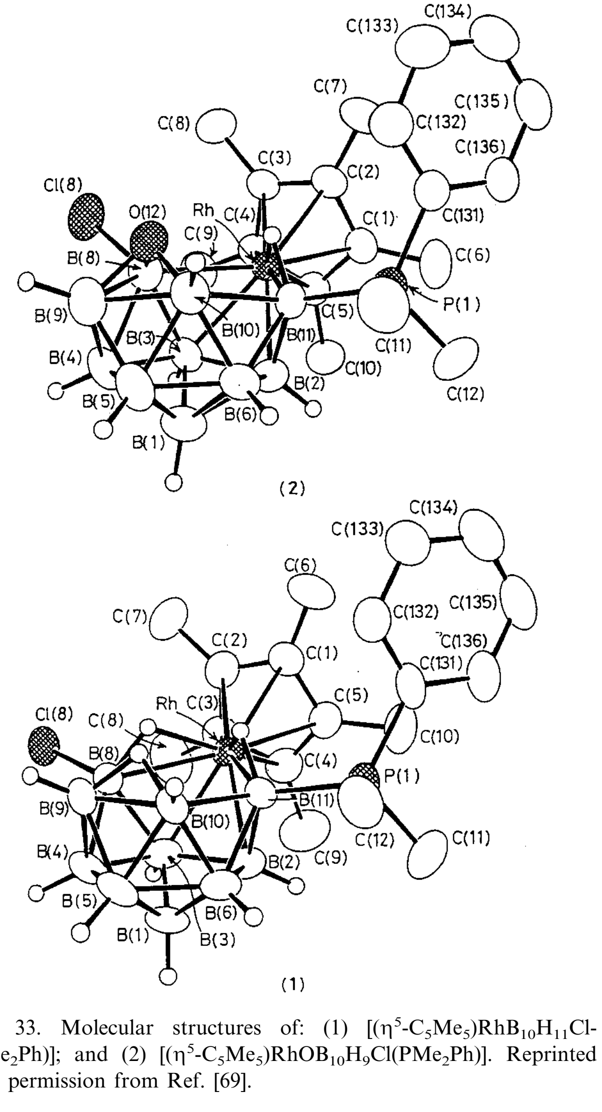


Fig. 33. Molecular structures of: (1) [($\eta^5$-$C_5Me_5$)$RhB_{10}H_{11}Cl$-($PMe_2Ph$)]; and (2) [($\eta^5$-$C_5Me_5$)$RhOB_{10}H_9Cl$($PMe_2Ph$)]. Reprinted with permission from Ref. [69].

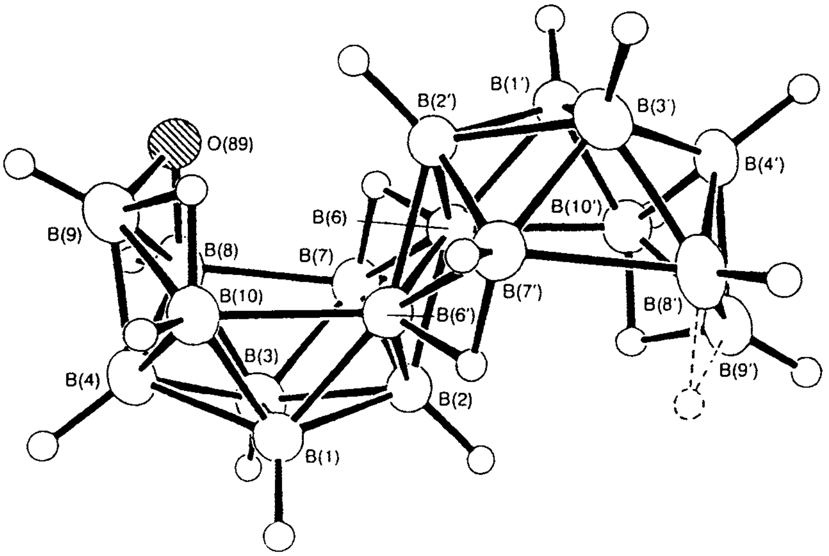


Fig. 34. ORTEP drawing of the [μ-8,9-O-*anti*-$B_{18}H_{21}$]$^-$ ion. H(8′,9′) shown by hatched lines not crystallography located. Reprinted with permission from Ref. [71].

$SB_{10}H_{12}$, further pyrolyzed to give the icosahedral thiaborane, *closo*-1-$SB_{11}H_{11}$. As with the *closo*-1-$SB_9H_9$, the *closo*-1-$SB_{11}H_{11}$ could undergo cage degradation in alcoholic KOH, to give [*nido*-7-$SB_{10}H_{11}$]$^-$ [77a]. Similar, though less extensive, studies have been carried out on the insertion of Se and Te in borane cages. These expansion reactions are usually accomplished by the reaction of a borane with either sodium polyselenide or polytelluride, as in the preparation of [*nido*-7-$XB_{10}H_{11}$]$^-$ (X = Se, Te) from decaborane(14) [79] or in the preparation of [$XB_9H_{12}$]$^-$ from $B_9H_{13}\cdot S(CH_3)_2$ [80]. The heteroboranes, $B_{11}H_{11}Se$ and $B_{11}H_{11}Te$, have also been synthesized in moderate yield (18–25%) from the reaction of [$B_{11}H_{14}$]$^-$ with $NaHSeO_3$ or $TeO_2$, respectively, in heptane–water mixtures [81]. As with their thiaborane analogue, both [$SeB_{10}H_{11}$]$^-$ and [$TeB_{10}H_{11}$]$^-$ react with metal halides under basic conditions to give the corresponding full- and mixed-sandwich metallaheterocarboranes [79].

## 3. Conclusions

From the above discussion, it is apparent that the main-group heteroboranes are a source of many interesting compounds. The structures of these heteroboranes can be reliably predicted from current electron counting rules. Therefore, by adjusting the heteroatom and the cage size of targeted heteroboranes, it should be possible to design a series of molecules that mimic the behavior of the more popular carboranes and cyclopentadienyl organometallic ligands, but may not suffer from the complications introduced by unwanted ionic charge. It is an area that needs further exploiting.

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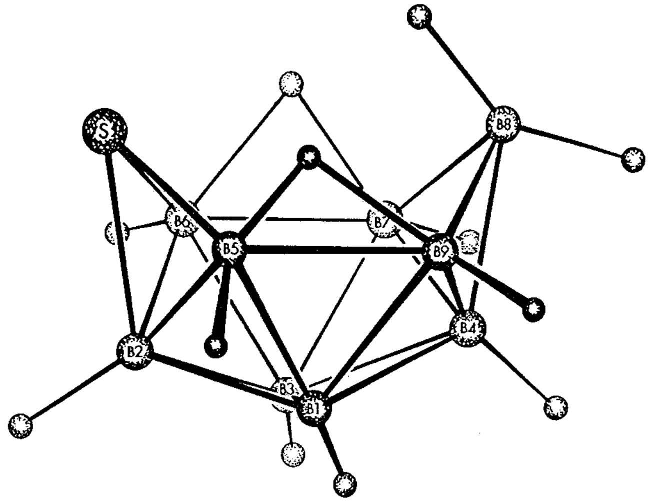
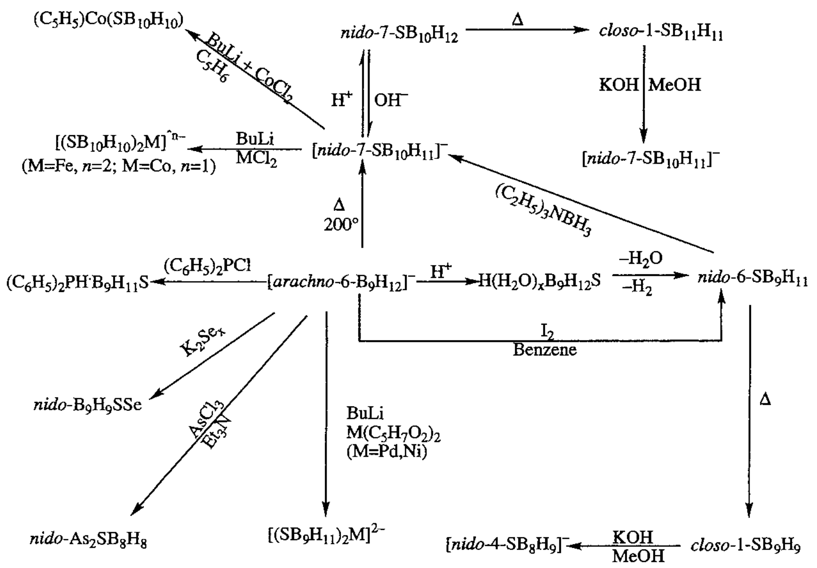


Fig. 35. Structure of the [*arachno*-6-$B_9H_{12}$]$^-$ ion. Reprinted with permission from Ref. [73].



Scheme 5.

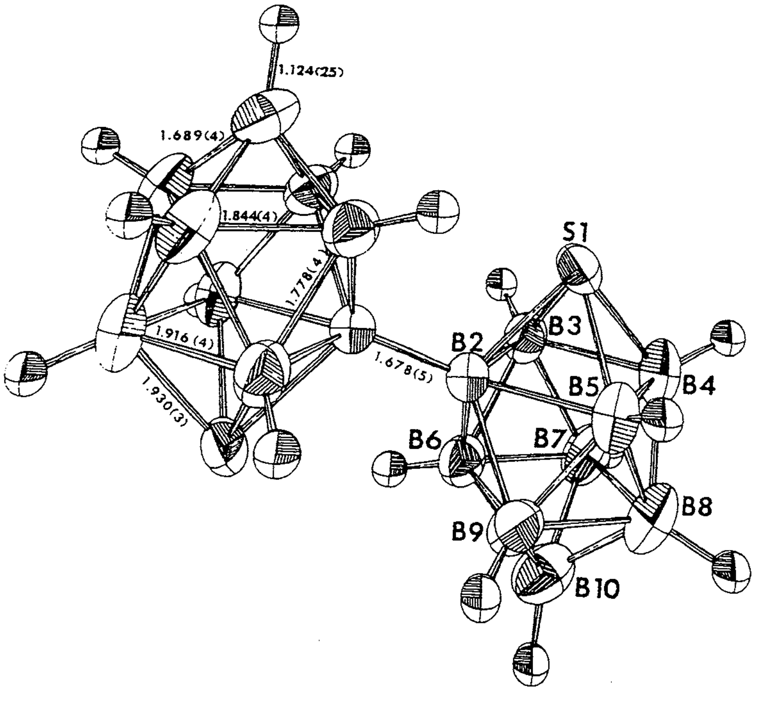


Fig. 36. ORTEP drawing of $2,2'(closo\text{-}1\text{-}SB_9H_8)_2$. Reprinted with permission from Ref. [78].

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