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REVIEW

Recent Studies of Group 14 Derivatives of Small *nido*-Boranes

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This article briefly reviews this area, describes some of our own recent work and also presents some new data. The preparation and characterization of a series of triphenyltin-substituted penta- and hexaboranes is described. The species 1-(SnPh$_3$)B$_5$H$_8$ (1) and 2,3-μ-(SnPh$_3$)B$_5$H$_8$ (3) are prepared from SnPh$_3$Cl and K[B$_5$H$_8$] by careful selection of solvent and conditions, and the intermediacy of 2-(SnPh$_3$)B$_5$H$_8$ (2), in the formation of 1 from 3, was demonstrated by NMR spectroscopy. The species 1, 2 and 3 were characterized by ^{11}B, ^{1}H and ^{119}Sn NMR spectra and ^{11}B–^{119}Sn coupling was observed for the first time in a polyhedral borane. Crystal structures were determined for 3 and the chloro-derivative of 1, 1-(SnClPh$_2$)B$_5$H$_8$ (4). Using similar techniques, three of the six possible linkage isomers of SnPh$_2$(B$_5$H$_8$)$_2$ namely μ,μ'-SnPh$_2$(B$_5$H$_8$)$_2$ (10), $\mu,2'$-SnPh$_2$(B$_5$H$_8$)$_2$ (11) and $\mu,1'$-SnPh$_2$(B$_5$H$_8$)$_2$ (12) were isolated and completely characterized including crystal structure determinations. The use of non-basic solvents such as CH$_2$Cl$_2$ allows the isolation of the bridging species 3 and 10 whereas basic solvents such as Et$_2$O or THF catalyse the rearrangement to species with the substituent in the 1-position, namely the 1 and 12 isomers. Isomer 11 is prepared by carrying out reactions in EtO$_2$ and 12 is also prepared by the reaction between 4 and K[B$_5$H$_8$] in CH$_2$Cl$_2$. The hexaborane derivatives 2,3-μ-(SnPh$_3$)B$_6$H$_9$, 2,3-μ-(SnMe$_3$)B$_6$H$_9$ and 2,3-μ-(SiPh$_3$)B$_6$H$_9$ were also prepared and characterized although all three species were too unstable to afford crystals suitable for X-ray analysis. Finally, attempts to prepare pentaboranyl derivatives containing two SnPh$_3$ substituents provided evidence for the formation of μ,1-(SnPh$_3$)$_2$B$_5$H$_7$ and 1,2-(SnPh$_3$)$_2$B$_5$H$_7$.

Keywords: boranes; pentaborane; hexaborane; stannylboranes; ^{119}Sn NMR spectroscopy

1 INTRODUCTION

The small *nido*-pyramidal boranes such as B$_5$H$_9$ and B$_6$H$_{10}$ contain bridging hydrogen atoms which are acidic and may be removed with strong bases.[1] The resulting anions are susceptible to electrophilic attack. There are many examples of systems in which the hydrogen has been replaced by both main-group[2] and transition-metal[3] moieties. For B$_5$H$_9$ the main-group Lewis acids range from very simple species such as a deuteron[1b,c] and borane(3)[4] through more complex[2a,5] species and those containing bulky substituents.[6] The main-group species thus introduced into the cluster include elements from *p*-block Groups 2,[7] 12,[8] 13,[9] 14[6,10] and 15.[11] For B$_6$H$_{10}$ there are fewer examples and they also include the deuteron[12] and Group 2,[13] 12[14] and 13[15] elements. There are several examples of Group 14 derivatives of pentaborane(9); they include species containing an MR$_3$ moiety (M = Si and R$_3$ = H$_3$,[10b] H$_2$Cl,[10d], Me$_3$,[10a,b]Et$_3$,[10b] F$_3$;[10e] or M = Ge and R$_3$ = H$_3$, Me$_3$, Et$_3$; or M = Sn and R$_3$ = Me$_3$,[10b] Ph$_3$;[6] or M = Pb and R$_3$ = Me$_3$[10b]) replacing a bridging proton. Before our own recent work there were no known examples of similar derivatives of hexaborane(10).[6c] Reaction between salts of either [2-Me$_3$MB$_5$H$_7$]$^-$ or [1-Me$_3$MB$_5$H$_7$]$^-$ (M = Si, Ge) with H$_2$BCl affords the 1-Me$_3$MB$_6$H$_9$ species,[16a] and the species 2-(Me$_3$Si)-μ-(Me$_2$B)B$_5$H$_7$[16b] is also known but this latter formal hexaboranyl Group 14 species is really a B$_5$H$_9$ derivative.

This review presents an introduction to the chemistry of Group 14-substituted *nido*-pentaboranyl(9) and -hexaboranyl(10) species

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and summarizes the work that has taken place recently in our laboratories.

2 FORMATION AND ISOMERIZATION OF GROUP 14 DERIVATIVES OF PENTABORANE(9)

Group 14 metal derivatives of B_5H_9 were prepared and characterized many years ago, principally by Gaines and co-workers, and also by others.[10] Removal of a bridging proton by a strong base such as MH (M = Na, K) or LiR (R = Me, Bu) affords the anion, as indicated in Scheme 1. Treatment of the anion with, for example, MR_3Cl (M = Si, Ge; R = H, Me, Et) affords 2,3,-μ-$(MR_3)B_5H_8$, also indicated in Scheme 1.[17]

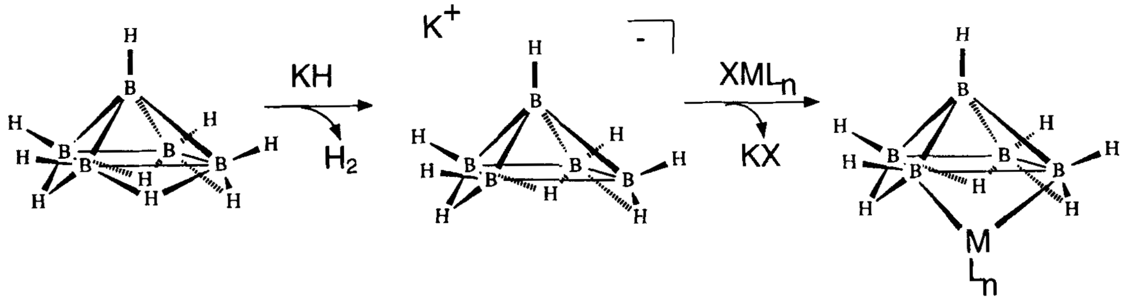
The resulting bridge-substituted pentaborane(9) is found to isomerize in the presence of Lewis bases. Thus treatment of 2,3-μ-$(MR_3)B_5H_8$ with diethyl ether affords the 2-isomer, 2-$(MR_3)B_5H_8$, and treatment of the latter with a stronger base such as 2,6-lutidine or hexamethylenetetramine (HMTA) affords the 1-isomer 1-$(MR_3)B_5H_8$.[17] These rearrangements are dependent on the base strength and on the nature of the substituent. This review deals only with Group 14 substituents. Treatment of either 2,3-μ-$(MR_3)B_5H_8$ or 2-$(MR_3)B_5H_8$ (M = Si, Ge) with HMTA results in a 4:1 equilibrium mixture of the 1- and 2- isomers respectively.[18] Species containing the substituents $SnMe_3$ or $PbMe_3$ do not rearrange.[10b] The former is quite stable but addition of base results in degradation, whereas for the latter species thermal instability rendered isomerization experiments very difficult.

Detailed isotopic substitution experiments by Gaines *et al.* have led to a much better understanding of these arrangement processes.[17] Only the conclusions of those studies are given here. The rearrangement of the 2,3-μ-isomer to the 2-isomer is considered to take place as indicated in Scheme 2. Addition of base to 2,3-μ-$(MR_3)B_5H_8$ results in coordination of a molar equivalent of base to the most electropositive center in the molecule,[19] a basal boron atom. This results in the addition of an electron pair to the cluster and according to the Polyhedral Skeletal Electron Pair Theory, the *nido*-cluster should open up to an *arachno*-system, as indicated in the scheme.[20] Loss of base would afford either the starting material or the less sterically crowded 2-isomer. Formation of the latter is illustrated in Scheme 2.

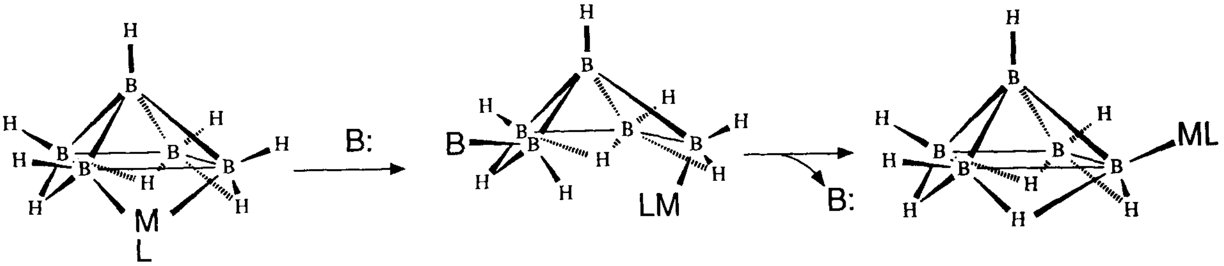
The rearrangement of 2-$(MR_3)B_5H_8$ to 1-$(MR_3)B_5H_8$ in the presence of stronger bases was shown to proceed without cleavage of the boron-substituent bond.[17] Two plausible mechanisms were suggested but we prefer the one also favored by the investigators. The two mechanisms are the 'base-swing' mechanism and the 'diamond–square–diamond' mechanism. The latter is favored by the investigators, Gaines *et al.*[17d] This mechanism invokes a series of diamond–square–diamond (dsd) rearrangements following the opening-up of the cage by coordination of base. The dsd rearrangement was first suggested by Lipscomb to explain rearrangements in boranes and carboranes[21] but it has since been used to explain rearrangements in a range of cluster systems. It is illustrated in Scheme 3 and the suggested overall process is given in Scheme 4.

3 TRIORGANYLSTANNYL DERIVATIVES OF PENTABORANE(9)

The reaction between $K[B_5H_8]$ and $SnClPh_3$ in THF at 0°C for 3 h affords a mixture of isomers.[6a,b] This is best illustrated by the ^{119}Sn NMR spectrum, which exhibits two 1:1:1:1 quartets and a broad single resonance. The quartets



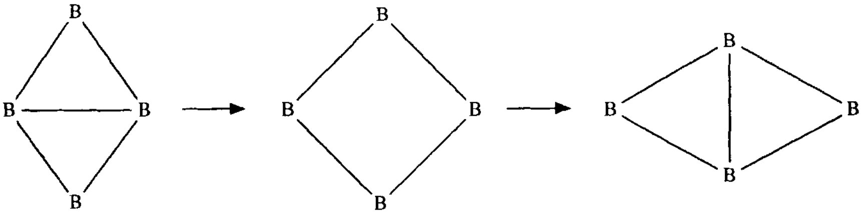
Scheme 1 Deprotonation of B_5H_9 and formation of 2,3-μ-$(ML_n)B_5H_8$.



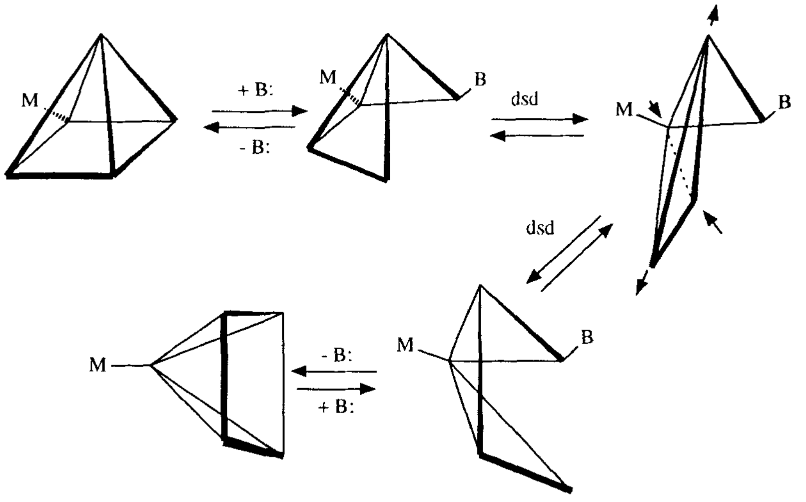
Scheme 2 Isomeric rearrangement of 2,3-μ-(ML_n)B_5H_8 to 2-(ML_n)B_5H_8.

arise from the 1-($SnPh_3$)B_5H_8 (**1**) and 2-($SnPh_3$)B_5H_8 (**2**) isomers, with the Sn atoms coupling to a σ-bonded ^{11}B atom ($I = 3/2$), and the single broad resonance is due to a bridging Sn atom in 2,3-μ-($SnPh_3$)B_5H_8 (**3**) coupling to two basal ^{11}B atoms. The ^1H and ^{11}B NMR spectra are quite overlapped. If the reaction mixture described above is stirred at 25°C for 12 h in THF, NMR spectra of the product mixture indicate the presence of only one species, 1-($SnPh_3$)B_5H_8 (**1**) in 61% yield. We will provide details of the identification of this species as an illustration of the way in which the other species described herein were identified. NMR spectra for **1** are illustrated in Fig. 1. The ^{11}B NMR spectrum clearly indicates that the $SnPh_3$ moiety is bonded to the apical 1-position, since the resonance which falls in the position expected for the apical B atom is a singlet, whereas the basal B atoms are seen as a doublet, due to coupling to the terminal H atom, with $J(^{11}B–^1H) = 164$ Hz. As expected the doublet collapses to a singlet on ^1H decoupling, as seen in Fig. 1. Also visible in the figure are the ^{119}Sn satellites on the B(1) resonances with $J(^{11}B–^{119}Sn) = 1123$ Hz. ^{119}Sn is the important NMR-active isotope of tin ($I = 1/2$) and it has a natural abundance of 8.58%. The ^{119}Sn NMR spectrum confirms that the species includes an Sn-containing moiety σ-bonded to a boron atom. This spectrum is also given in Fig. 1 and it clearly shows a 1:1:1:1 quartet with $J(^{11}B–^{119}Sn) = 1117$ Hz, and a weaker 1:1:1:1:1:1:1 septet due to coupling of the ^{119}Sn atom to the ^{10}B nucleus ($I = 3$) with $J(^{10}B–^{119}Sn) = 391$ Hz. The ^1H NMR spectrum is also consistent with the formulation as the 1-isomer. It exhibits a single broad resonance at $\delta = -2.30$ ppm assigned to the four bridging hydrogens and a single 1:1:1:1 quartet, $J(^{11}B–^1H) = 160$ Hz, at $\delta = 2.61$ ppm, assigned to the four basal terminal H atoms. There is no resonance where an apical H atom would appear and the resonances arising from the phenyl hydrogen atoms are observed at $\delta = 7.24 - 7.48$ ppm. **1** was not amenable to a crystal structure determination but the 1-chloro-derivative, 1-($SnClPh_2$)B_5H_8 (**4**), prepared from the reaction between K[B_5H_8] and $SnCl_2Ph_2$ in THF in 56% yield, afforded crystals suitable for X-ray analysis. The structure of **4** is given in Fig. 2. The unit cell contains two crystallographically unique molecules, each with a mirror plane containing Sn, Cl, B(1) and two of the bridging H atoms. The plane bisects the B_5 cage and lies on the midpoint of two opposite B–B bonds in the basal plane. The geometry of the cage is essentially that of B_5H_9,[22] with apex-to-base distances slightly shorter than in B_5H_9, but the B–B distances in the basal plane essentially the same. The B–Sn distances in the two molecules, 2.182 and 2.189 Å respectively, are shorter than the sum of the covalent radii of Sn (1.40) and B (0.88).[23] These distances are also slightly shorter than those in the only comparable systems, μ,2′-$SnPh_2(B_5H_8)_2$ (**10**) and μ,1′-$SnPh_2(B_5H_8)_2$ (**11**), which are described in Section 6.

If the reaction between K[B_5H_8] and $SnClPh_3$ is



Scheme 3 Diamond–square–diamond rearrangement.



Scheme 4 Isomeric rearrangement of 2-$(ML_n)B_5H_8$ to 1-$(ML_n)B_5H_8$.

carried out in the non-coordinating solvent CH_2Cl_2, the product formed is the bridging species 2,3-μ-$(SnPh_3)B_5H_8$ (**3**), in 53% yield. In this case the ^{119}Sn NMR spectrum gives a single broad resonance and the ^{1}H and ^{11}B NMR spectra are completely consistent with a species in which a bridging H atom has been replaced with an $SnPh_3$ moiety. The crystal structure determination confirms the NMR data. ^{1}H NMR spectra and a projection of the crystal structure are given in Fig. 3. The $SnPh_3$ moiety occupies a bridging site between B(2) and B(3) and may be considered as a pseudohydrogen since it replaces a proton, thus bonding to the cage by a three-center two-electron bond. The structure is similar to that for 1-Br-2,3-μ-$(SiMe_3)B_5H_7$.[24] The much larger central bridging atom (covalent radii: Sn 1.40 Å, Si 1.17 Å) has little effect on the dimensions of the boron cage. The B(2)–B(3) distance, 1.757(6) Å, is shortened from the basal B–B bond distance in B_5H_9, 1.803(5) Å, and it is shorter than the hydrogen-bridged B–B distances in **3**. This is also

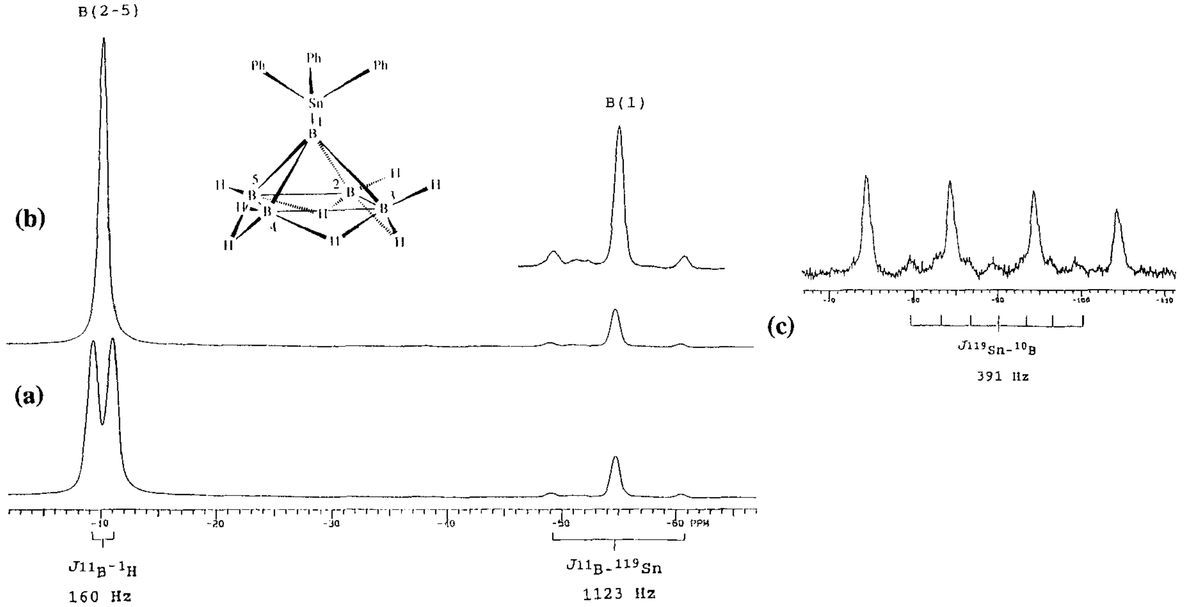


Figure 1 ^{11}B and ^{119}Sn NMR spectra and proposed structure of 1-$SnPh_3B_5H_8$ (**1**).

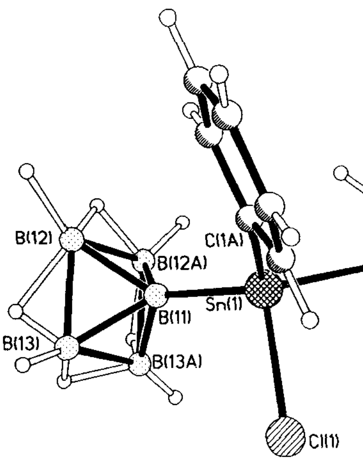


Figure 2 Structure of 1-$SnClPh_2B_5H_8$ (**4**).

observed for silicon-,[24] beryllium-[7b] and boron-bridged[25] pentaborane derivatives for which X-ray structures have been determined. The B_{apex}-B_{base} distances are shorter on the side containing the Sn bridge, that is B(1)–B(2 or 3), than they are on the other side of the pyramid, B(1)–B(4 or 5), and the H atom bonded to B(1) is tilted slightly towards the edge containing the Sn atom, as has been noted for 2,3-μ-(9-BBN)B_5H_8[25] and 2,3-μ-(BeCp)B_5H_8[7b] (BBN = 9-borabicyclo [3.3.1]nonyl; Cp = η^5 = cyclopentadienyl). The only real analogue of **3** before our subsequent work, 1-Br-2,3-μ-($SiMe_3$)B_5H_7, contains a plane of symmetry through B(1), the $SiMe_3$ moiety and the bisector of B(2)–B(3), and B(4)–B(5).[24] This is not the case for **3** since, for steric reasons, the phenyl groups cannot be oriented so as to render two of them equivalent, and the third one either exactly on or perpendicular to the plane. Several other analogous systems have been characterized structurally. They include the B, Be and Si species mentioned previously, and also the coinage-metal derivatives 2,3-μ-[$(PPh_3)_2Cu$]B_5H_8[26] and 2,3-μ-(PPh_3Au)B_5H_8.[27] The dihedral angle between the B(2–5) basal plane of the cage and the B(2)–B(3)–Sn plane for **3** is 53.0°, comparable with the corresponding angles in the B, Be, Si, Cu and Au systems, which are 52°, 56.18°, 51.7°, 52° and 54.2° respectively, and with our own systems, the isomers of $SnPh_2(B_5H_8)_2$, described later. The external dihedral angles between the B(1)–B(2)–B(3) face and the B(2)–B(3)–M face in **3** are all close to 180°. On the other hand the analogous angles for *arachno*-2,3-μ-(PPh_2)B_5H_8, which has been structurally characterized,[11e] are 22.5° and 148° respectively, as expected since the P atom is a three-electron donor and thus forms normal 2e$^-$ bonds with the adjacent boron atoms.

We presume that the reaction between K[B_5H_8] and $SnClPh_3$ proceeds via the initial formation of the bridge-substituted species 2,3-μ-($SnPh_3$)B_5H_8 (**3**) as described in Section 2. This bridge-substituted isomer rearranges, in the presence of base to form the 2-substituted species (**2**), which is thermodynamically much more stable.[5a, 17] However, in the presence of THF, the rearrangement continues to form the 1-isomer as the sole product after stirring for extended periods, rather than an equilibrium being reached between the 2- and 1-substituted species containing a 4:1 ratio of 1-(MR_3)B_5H_8 and 2-(MR_3)B_5H_8 respectively, as observed by Gaines and Iorns.[18] In the case of the $SnPh_3$-substituted species, the $SnPh_3$ moiety is apparently sufficiently sterically hindered to render the 2-isomer much less stable than the 1-isomer. Thus initial formation of the bridging isomer is followed by isomerization to the 2-isomer, and after 12 h, the product is exclusively 1-($SnPh_3$)B_5H_8, the thermodynamically more stable isomer. Thus we observe a mixture of all three isomers if the ^{119}Sn NMR spectrum of the product mixture is examined after stirring at 0°C in THF for 3 h. The quartets arise from Sn bonded terminally to ^{11}B ($I = 3/2$), and although one might ideally expect a septet from an Sn atom bridging two borons, experience indicates that resolution of the septet is typically missing for boranes and that broad resonances are observed.[28] This observation of a mixture of two terminally bonded Sn derivatives and a single bridge-bonded one supports our conclusion that the process proceeds as 2,3,-μ-($SnPh_3$)B_5H_8 $\rightarrow$ 2-($SnPh_3$)B_5H_8. The amount of 2-($SnPh_3$)B_5H_8 present is quite small and our surmise is that this species is the least thermodynamically stable species and that it only forms when there is a kinetic pathway provided by the Lewis base. Electronic effects on the relative stabilities of the three isomers of $SiH_3B_5H_8$ have been studied by theoretical calculations and also photoelectron spectroscopy.[29] The conclusions were that the 2-isomer is favored for highly electronegative substituents, while the 1-isomer is favored by substituents with low electronegativities that are π-acceptors or π-donors. Tin certainly fits this category although the *d*-orbitals may be too diffuse to participate in such bonding. In this case, steric effects probably contribute substantially so that the equilibrium mixture contains almost exclusively the 1-isomer.

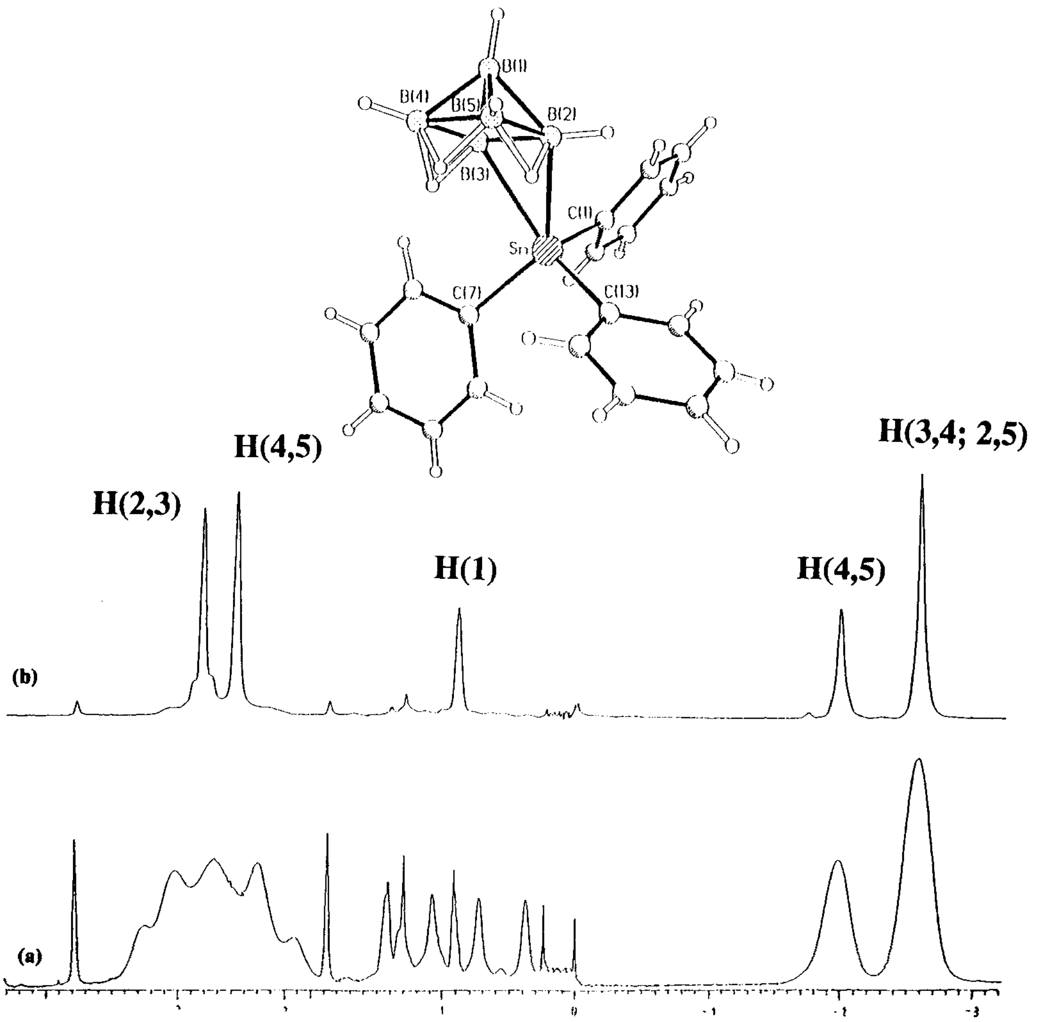


Figure 3 ^{1}H NMR spectra and structure of 2,3-μ-(SnPh$_3$)B$_5$H$_8$ (3). (a) Coupled spectrum. (b) ^{1}H{^{11}B} spectrum.

These results demonstrated the utility of ^{119}Sn–^{11}B coupling for the identification of tin atoms bonded to a pyramidal borane. There are several other reports in the literature of ^{119}Sn NMR spectra of tin bonded to boron[30,31] and our data for $J\,^{11}$B–^{119}Sn, 1117 Hz for **1** and 1272 Hz for **4**, fall at the upper end of the range of previously observed values. These couplings and the values for $J\,^{11}$B–^{119}Sn were confirmed by our observation of ^{119}Sn satellites in the ^{11}B NMR spectra which give values of 1123 and 1270 Hz for **1** and **4** respectively. It is well established that resonances involving nuclei with quadrupole moments are substantially broadened due to quadrupolar relaxation.[32] For pyramidal boranes, the more highly symmetrical apical borons provide the least favorable environment for such relaxation and the relaxation times are the longest.[33] Thus it is not unexpected that we were able to observe ^{119}Sn–^{11}B coupling only for the apical resonance.

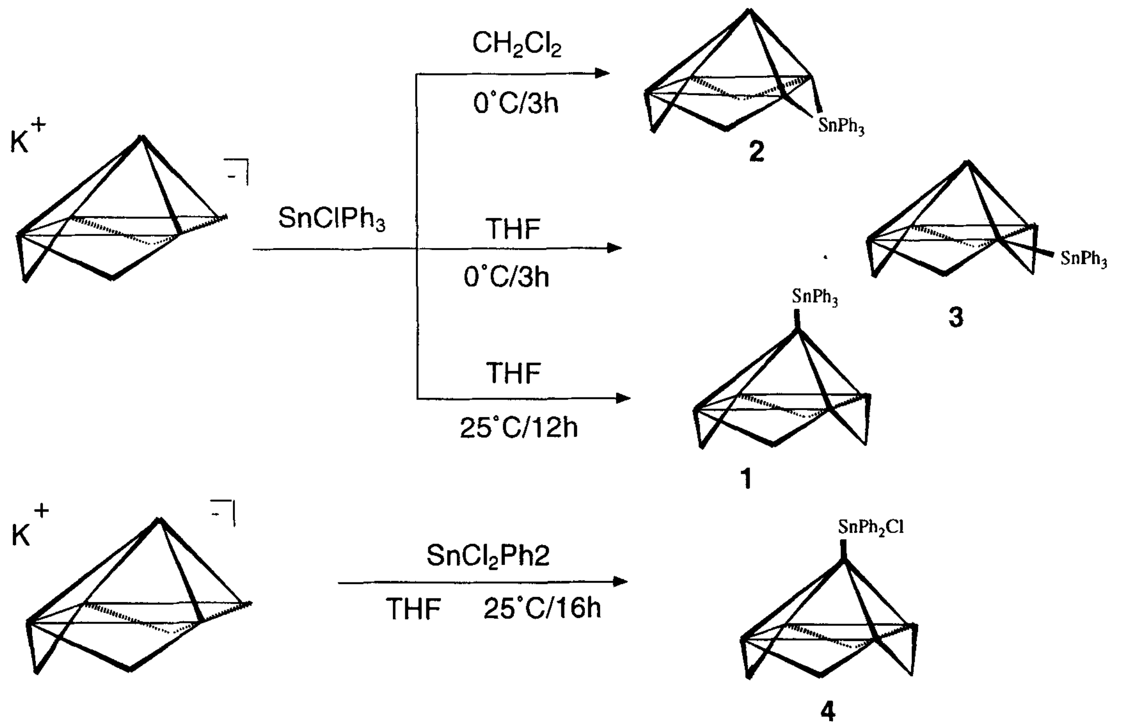
The formation of the isomers of Sn(Ph$_3$)B$_5$H$_8$ is summarized in Scheme 5.

4 DISUBSTITUTED GROUP 14 DERIVATIVES OF PENTABORANE(9)

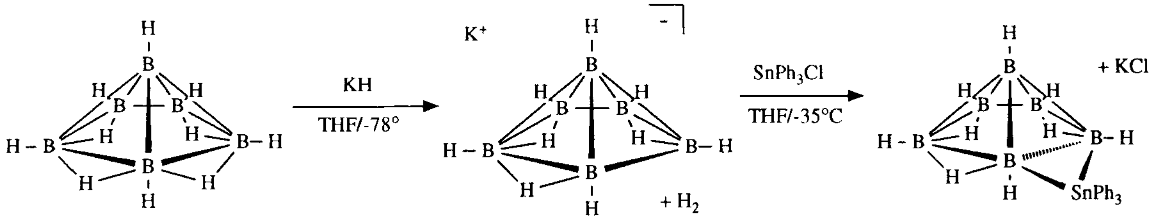
Pentaborane(9) cages in which two hydrogen atoms are replaced by Group 14 moieties have been known for many years. Onak and co-workers[34] prepared the species μ,1-(SiH$_3$)$_2$B$_5$H$_7$, 1,2-(SiH$_3$)$_2$B$_5$H$_7$, μ,1-(SiMe$_3$)$_2$B$_5$H$_8$ and 1,2-(SiMe$_3$)$_2$B$_5$H$_8$ from the starting mterials 1-(SiH$_3$)$_2$B$_5$H$_8$ and 1-(SiMe$_3$)$_2$B$_5$H$_8$ by insertion of the appropriate group and careful selection of base catalyst for the rearrangement process. These species are volatile and are collected and purified on the vacuum line.

Our efforts to prepare analogues containing the bulky substituent SnPh$_3$ have not been entirely conclusive. Preparation and isolation of 1-(SnPh$_3$)B$_5$H$_8$, followed by treatment with KH in THF, affords the salt K[1-(SnPh$_3$)B$_5$H$_7$] in essentially quantitative yield on the basis of the volume of H$_2$ evolved in the reaction, and NMR spectra. The ^{11}B NMR spectrum consists of a very broad singlet resonance at $\delta = -14.9$ ppm of area 4, assigned to B(2–5), and a sharper singlet at $\delta = -56.2$ ppm of area 1, assigned to B(1). Decoupling has little effect on the spectrum. The proton spectrum consists of a broad quartet at $\delta = 1.64$ ppm and a broad singlet at $\delta = -3.42$ ppm, assigned to the terminal and bridging H atoms respectively.

Treatment of K[1-(SnPh$_3$)B$_5$H$_7$] with SnClPh$_3$ in CH$_2$Cl$_2$ affords a species which we tentatively identify as μ,1-(SnPh$_3$)$_2$B$_5$H$_7$ (**5**).[35] The ^{119}Sn NMR spectrum gives a 1:1:1:1 quartet at $\delta = -88$ ppm and a broad singlet as $\delta = -84$ ppm, of equal intensity, with J^{11}B–^{119}Sn = 771 Hz. The ^{11}B NMR spectrum gives a broad doublet which on ^{1}H-decoupling affords a singlet at –8.0 ppm (J^{11}B–^{1}H = 166 Hz) and a singlet at –52.5 ppm. These data are consistent with the formulation but attempts to isolate the product from solution were unsuccessful as were attempts to isomerize it by adding base. The latter afforded complex mixtures which were very difficult to interpret. It was noteworthy that the coupling constant J^{11}B–^{119}Sn was much lower (771 vs. 1120 Hz) than those observed for the mono-substituted stannylboranes. If the reaction is carried out in THF followed by stirring for one day at 25°C, the NMR spectra suggest the presence of 1,2-(SnPh$_3$)$_2$B$_5$H$_7$ (**6**).[35] The ^{11}B NMR spectrum gave a doublet with a shoulder at low field and a singlet at $\delta = -55.7$ ppm assigned to B(1). On proton-decoupling, the low-field resonance appears as two overlapped single peaks at –13.9 and –11.7 ppm. The former is about three times as intense as the latter and they are assigned to B(2, 3, 5) and B(4), respectively. The ^{11}B–^{1}H coupling constants appear to be about 170 Hz. Presumably the B(3, 5) resonance and that for B(2) are overlapped. The ^{119}Sn NMR spectrum gives two quartets at $\delta = -85.5$ and 72.8 ppm with J^{11}B–^{119}Sn = 756 and 863 Hz, respectively. On the basis of comparisons with the



Scheme 5 Formation of isomers of SnPh$_3$B$_5$H$_8$.



Scheme 6 Structure of B_6H_{10} and formation of 2,3-μ-$(SnPh_3)B_6H_9$.

monostannyl pentaboranes, we assign these resonances to Sn(2) and Sn(1), respectively. A B_5 cage with Sn moieties at the 1- and 2-positions would be expected to exhibit an upfield singlet and a 1:2:1 pattern at low field in its ^{11}B NMR spectrum, consisting of overlapped doublets and a singlet. Also the ^{119}Sn spectrum would be expected to exhibit two 1:1:1:1 quartets.

The data described are clearly consistent with the formation of **5** and **6** but they are not conclusive and further work is required before definitive conclusions may be reached.

5 GROUP 14 DERIVATIVES OF HEXABORANE(10)

The Group IV derivatives of B_6H_{10} are similar to those for B_5H_9, with some important differences. Hexaborane(10) is much less thermally stable than B_5H_9 and it has been studied much less than the latter.[36] The structure, given in Scheme 6, provides some clues to these differences. There is a basal B–B bond which renders the system fluxional on the NMR time scale[27] and may also be the reason for its increased reactivity. The bridging H atoms are considered to exchange by migration into and out of the basal B–B bond. There are many fewer derivatives of B_6H_{10} than B_5H_9, although the major difference between the two species leads to a different mode of reaction for the former. As noted above, deprotonation of B_5H_9 affords an anion containing a basal B–B bond. This bond is susceptible to insertion by electrophiles, especially Lewis acids and cationic metal reagents. The B–B bond in neutral B_6H_{10} similarly is prone to attack by electrophiles,[38] and some work has been done to exploit this property.[39] Deprotonation of B_6H_{10} produces an anion containing two B–B bonds and thus it is more susceptible to reaction chemistry than the $[B_5H_8]^-$ anion.

The Group 6 derivatives of B_6H_{10}—2,3-μ-$(SnPh_3)B_6H_9$ (**7**), 2,3-μ-$(SnMe_3)B_6H_9$ (**8**) and 2,3-(μ-$SiPh_3)B_6H_9$ (**9**)—are prepared according to Scheme 6, with minor modifications for **8** and **9**.

Insertion of the $SnPh_3$ moiety into a basal B–B bond, by the reaction of $SnClPh_3$ with $K[B_6H_9]$ in CH_2Cl_2, results in the formation of 2,3-μ-$(SnPh_3)B_6H_9$ (**7**) and in 48% yield. The species is identified by elemental analysis, by ^{11}B, ^{119}Sn and ^1H NMR spectra, and by mass and infrared spectra. Compound **7** forms B_6H_{10} on protonation, suggesting that the Sn group occupies a bridging position. The ^{11}B NMR spectrum is given in Fig. 4. Low-temperature NMR spectra suggest a pyramidal structure with four different boron environments. The ^{11}B-decoupled proton spectrum gives two resonances for the bridging H atoms and four for the terminal ones at –105°C, but at room temperature only a single resonance is observed for the basal terminal H atoms (see Fig. 5). To account for these observations, we assume that the bridging H atoms in **7** are fluxional on both the ^{11}B and ^1H NMR time scales but that the motion of the bridging hydrogen atoms is partially quenched, as observed for other 2,3-μ-metalladerivatives of hexaboranes.[40] At temperatures above about –10°C, some simple motion of the cage relative to the SnR_3 group is invoked to account for the spectra of **7**. Processes equivalent to those given in Fig. 6 are considered to account for the observed spectra. The stannylhexaborane, **7**, is much less stable than its pentaboranyl congeners. Rearrangement does not happen in the presence of bases; rather, degradation of the cage occurs.

Two other base-substituted hexaboranyl species are also clearly identified but they are quite unstable. The species 2,3-μ-$(SnMe_3)B_6H_9$ (**8**) is clearly unstable at temperatures above –35°C. It appears to melt just below –35°C. Analytical data on the solid isolated at or just below ambient temperature indicate that the species decomposes to something which loses the characteristics of a borane, perhaps due to reduction of the Sn moiety by the borane. The mass spectrum of **8**, prepared and stored at –35°C prior to running spectra of the sample as it warmed to ambient temperature, exhibited spectra identical to those expected for B_6H_{10} and also peaks corresponding to $SnMe_3^+$, $SnMe_2^+$ and $SnMe^+$, suggesting that decomposition was occurring in the ion source. NMR spectra suggest that 2,3-μ-($SnMe_3$)B_6H_9 is stable at low temperatures. The ^{11}B spectrum at –40°C is very similar to that given in Fig. 4. It contains resonances indicative of trace impurities of B_6H_{10} and 2,3-μ-($SnMe_3$)B_5H_8. The region in which basal B atoms are expected to be observed shows two broad resonances in area ratio 2:3, with the larger resonance containing a shoulder, and a sharp doublet upfield of area 1. This suggests an arrangement of six boron atoms in a pentagonal pyramidal arrangement with a plane of symmetry. This would occur if the bridging hydrogen atoms were fluxional. The ^1H NMR spectrum is consistent with this conclusion. A single broad resonance of area 5 in the region where basal terminal H atoms are expected, presumably due to partially thermally decoupled signals which overlap, and a single broad resonance of area 3 in the bridging hydrogen region, along with a quartet arising from the apical H atom, is expected for a 2,3-μ-hexaboranyl derivative. The ^{119}Sn NMR spectrum gives a single broad resonance at –20.33 ppm and is what is expected for a system containing an Sn moiety in a basal bridging position. The Si derivative, 2,3-μ-($SiPh_3$)B_6H_9 (**9**), is also unstable at room temperature but less so than **8**.[41] The species, obtained in 55% yield, exists as a waxy white solid which soon loses infrared spectral bands due to $\nu_{B\text{-}Ht}$ on standing for a few minutes. The NMR sample prepared from the solid at room temperature indicated the absence of B—H groups but a sample carefully prepared at –78°C, and maintained at or below that temperature, indicated the presence of 2,3-μ-($SiPh_3$)B_6H_9. The spectra are quite similar to those obtained for **7** and **8** and the structures of all three species are assumed to be of the same type.

Perhaps the most important feature of the hexaboranyl derivatives, which distinguish them from their pentaboranyl congeners, is their fluxionality. This is a consequence of the basal B–B bond,[31] which may also be the reason for the decreased stability of the hexaboranes. There is clearly a remarkable difference in the stability of the main-group borane derivatives 2,3-μ-(MR_3)B_5H_8 and 2,3-μ-(MR_3)B_6H_9. As noted above, the former retain their integrity at room temperature and may be isomerized to the 2- and 1-isomers. On the other hand, the hexaboranyl derivatives are much less stable than their pentaboranyl congeners and are quite difficult to work with. Isomerization of such species has not been observed; rather, decomposition occurs in the

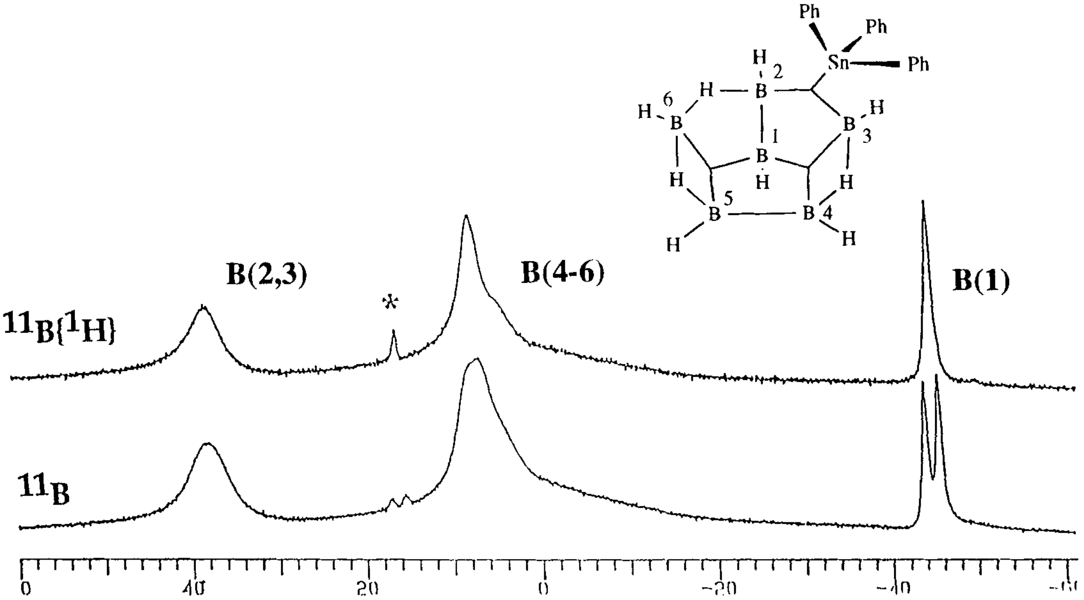


Figure 4 ^{11}B NMR spectrum of 2,3-μ-($SnPh_3$)B_6H_9 (**7**).

presence of bases. Thus hexaborane(10) derivatives are quite rare and present a challenge to chemists.

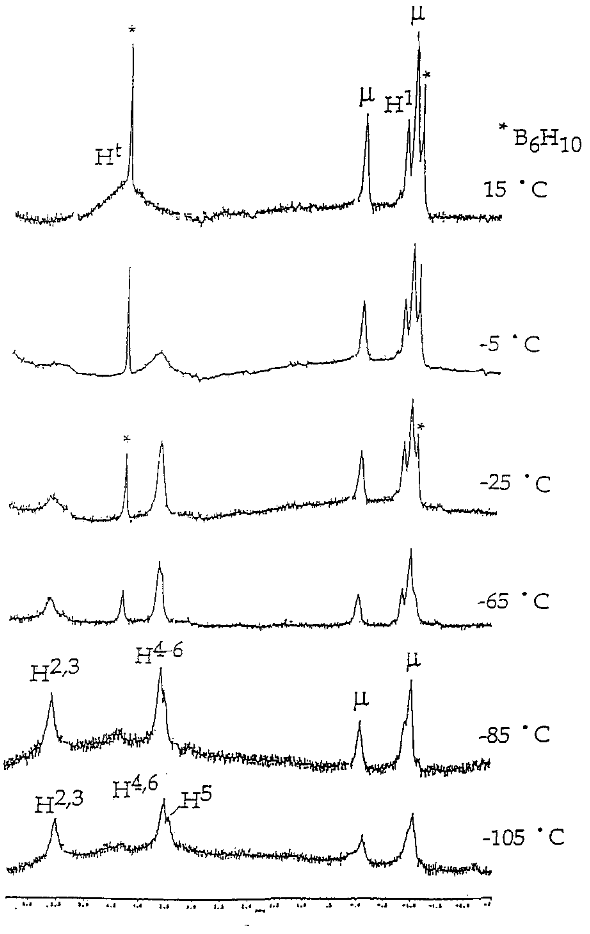


Figure 5 250 MHz $^1H\{^{11}B\}$ NMR spectra of 2,3-μ-$(SnPh_3)B_6H_9$ (7) at various temperatures.

6 ISOMERS OF DIPHENYLSTANNYLPENTABORANE(9)

Our previous work led us to consider whether it would be possible to prepare similar systems in which the Sn moiety bridged B_5 cages. Examples of borane clusters linked by single heteroatoms are quite rare. The large cage systems $[Cu(1\text{-}B_{10}H_9N_2)_2]^-$,[42] $[Pd(B_{10}H_{12})_2]^{2-}$,[43a] $[Pt(B_{10}H_{12})_2]^{2-}$,[43b] $[Au(B_{10}H_{13})_2]^{2-}$,[44] $[Au(B_{10}H_{12})_2]^-$,[44] $[Zn(B_{10}H_{12})_2]^{2-}$[45a] and $(B_{10}H_{13})_2O$[45b] have all been characterized by crystal structure determinations. Three systems based on hexaborane(10) are known. They include $Mg(B_6H_9)_2(THF)_2$[40] and $Pt(B_6H_{10})_2Cl_2$,[39g] for which structures are also available, and $Cd(B_6H_9)_2$,[40a] which was identified spectroscopically. There are two reports for pentaboranyl(9) cages, one involving Hg(II)[46a] and the other involving Si and Ge.[10c] In both cases, the species were characterized by low-field NMR spectroscopy although a somewhat related Hg-bridged cobaltacarborane system was structurally characterized.[46b] We were able to show that careful selection of solvent and conditions allows individual isolation of three of the six possible linkage isomers of $SnPh_2(B_5H_8)_2$.

Two B_5H_8 cages may be coupled via an $SnPh_2$

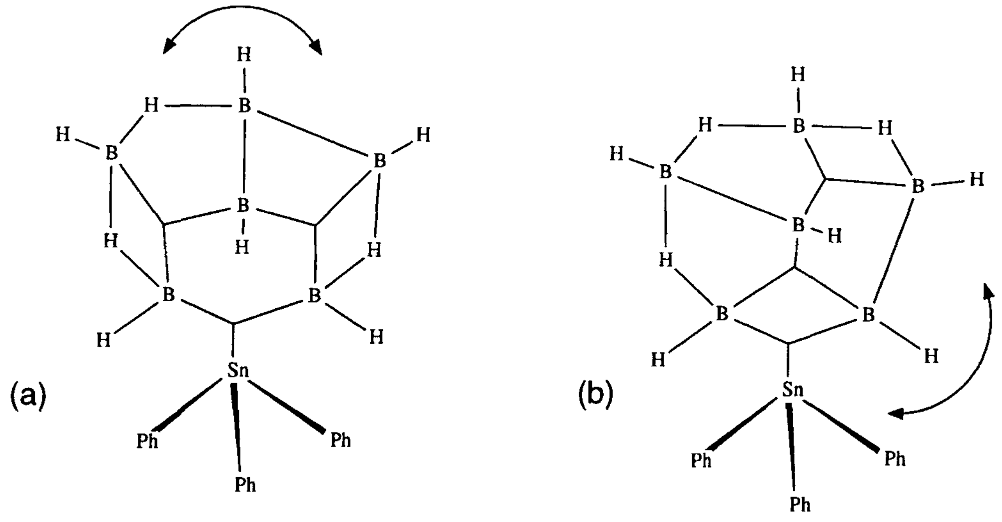


Figure 6 Proposed fluxional luxional motion of 7.

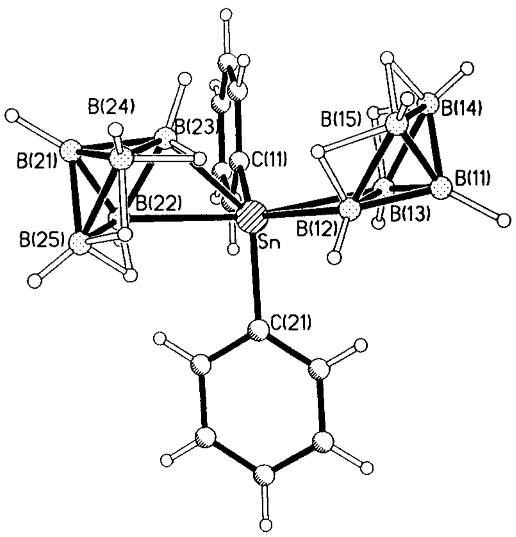


Figure 7 Structure of μ,μ'-$SnPh_2(B_5H_8)_2$ (**10**).

moiety by treatment of $K[B_5H_8]$ with $SnCl_2Ph_2$ in 2:1 molar ratio in CH_2Cl_2 at –35°C. Stirring the reaction mixture for 4 h and then at 25°C for 1 h allows the isolation of μ,μ'-$SnPh_2(B_5H_8)_2$ (**10**) as a white solid in 59% yield. Compound **10** decomposes above 98°C and is very soluble in THF, CH_2Cl_2 and $CHCl_3$ and moderately soluble in C_5H_{12}, C_6H_{14} and Me_2O. NMR spectra are valuable in identifying **10** as the μ,μ'-isomer. The ^{119}Sn spectrum gives a single broad resonance at $\delta =$ –40.1 ppm, fwhm = 187 Hz, and it is useful to compare this with the analogous data for 2,3-μ-$(SnPh_3)B_5H_8$, which are $\delta = -98.3$ ppm and fwhm = 108 Hz.[6b] ^{11}B and ^1H NMR, IR and mass-spectral data are completely consistent with the formulation. The X-ray structure determination of **10**, as illustrated in Fig. 7, confirms that it consists of two B_5H_8 cages linked by an $SnPh_2$ group so that the Sn atom replaces a bridging proton in each cage and thus the cages share a bridging Sn atom. The Sn lies at the center of a distorted tetrahedron which comprises the two phenyl groups and the two B_5H_8 cages. The largest of the angles around Sn is that involving cage(1)–Sn–cage(2), measured at the centroids (X) of the bridged B–B bonds (121.6°), and the smallest angles are those between the centroids and the *ipso*-C atom which is away from the open face of the cage. These angles, 98.5° and 98.9° for X–Sn–C(21) and X′–Sn–C(11), respectively, suggest that the open face of the cage is the more sterically hindered side. The two interplanar angles between the B(2)–B(3)–Sn and the basal B(2)–B(3)–B(4)–B(5) planes of the cage are smaller than those in all the other known 2,3-μ-substituted pentaboranes(9), including **11** and **12** which are described below. This interplanar angle for the two cages averages 49.7°, compared with those for species with B,[24] Be,[7] Si,[24] Sn,[6b] Cu[26] and Au[27] atoms bridging a single cage for which the reported angles are 52°, 56.18°, 51.7°, 53°, 52° and 54.7°, respectively. The angles in **10** are low, presumably due to steric hindrance. The open faces of the B_5 cages do not point away from each other but are twisted so that the B(2)–B(3)–Sn planes in the two cages are at 117.5° to each other.

If **10** is stored in $CDCl_3$ at 25°C for several weeks, changes are observed in the NMR spectra which are interpreted to indicate the formation of the μ,2′-isomer after about one month and the μ,1′-isomer after about four months. After one month the ^{119}Sn NMR spectrum shows diminution of the single resonance at −40.1 ppm and a single 1:1:1:1 quartet appears at –138.5 ppm which we assign to μ,2′-$SnPh_2(B_5H_8)_2$ (**11**). Compound **11** is also formed if the initial reaction between $K[B_5H_8]$ with $SnCl_2Ph_2$ in 2:1 mole ratio is carried out in Et_2O. Work-up affords a white solid in 64% yield, which melts at 74–75°C. NMR spectra and a crystal structure determination confirm the identity of **11**. The ^{11}B NMR spectrum of the basal boron atoms shows a 1:2:1 pattern which overlaps a 2:2 pattern, easily interpreted in terms of the μ,2′-structure, and at 500 MHz the apical H atoms are clearly observed in the ^1H spectrum as two distinct overlapping 1:1:1:1 quartets. Compound **11** is very soluble in THF, CH_2Cl_2 and $CHCl_3$, and less soluble in C_6H_{14}, C_5H_{12} and Me_2O. Recrystallization of **11** from hexane affords colorless rectangular crystals which allowed a crystal structure determination. The structure of **11** is given in Fig. 8 along with some structural parameters: it clearly consists of an $SnPh_2$ group coupled to one B_5H_8 cage at the basal boron B(22) and to the other cage by bridging the basal boron atoms B(12)–B(13). The Sn atom lies well below the basal plane of the cage to which it occupies a bridging position; the average interplanar angles between planes Sn–B(2)–B(3) and B(2, 3, 4, 5) in the two molecules is 52.9°, comparable with the value of 53° observed for the corresponding angle in 2,3-μ-$(SnPh_3)B_5H_8$.[6b] The B(22)–Sn σ-bond distance is 2.230(5) Å, a little longer than that in the species 1-$(SnClPh_2)B_5H_8$ which is 2.182(7) Å.

If the NMR spectrum of the solution of **10** in

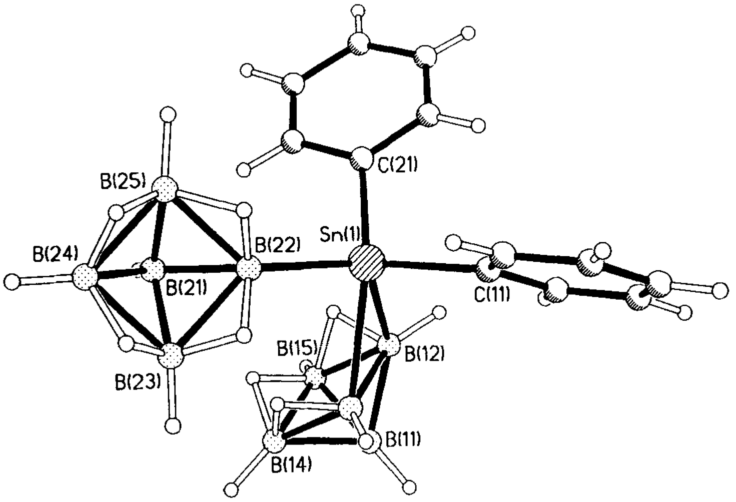


Figure 8 Structure of μ,2'-$SnPh_2(B_5H_8)_2$ (**11**).

$CDCl_3$ is observed after standing for four months, a second 1:1:1:1 quartet at −80.1 ppm, assigned to a third isomer, μ,1'-$SnPh_2)(B_5H_8)_2$ (**12**) is observed. Traces of a second quartet under the major one, assigned to a second isomer and discussed later, are just visible at $\delta = -75.8$ ppm, as seen in Fig. 10 below. Alternatively, **12** is prepared in the reaction between 1-$(SnClPh_2)B_5H_8$ (**4**) and $K[B_5H_8]$ in CH_2Cl_2 at −35°C. Work-up allows isolation of **12** in 52% yield as an off-white solid. Slow evaporation of a solution in hexane allows colorless rectangular crystals, suitable for X-ray study, to be isolated. Compound **12** melts at 86–88°C. It is much more air-sensitive than **10** and **11**, and has similar solubility properties to **1**. Spectral data are consistent with the assignment of **12**. In addition to the ^{119}Sn spectrum, which shows the expected quartet arising from coupling to the directly bonded ^{11}B atom ($I = 3/2$), the ^{11}B NMR spectrum exhibits two resonances in the high-field region where the apical B atom resonance is normally observed in B_5H_9. These are a doublet at −48.2 ppm which collapses to a singlet on ^1H decoupling, and a singlet at −51.6 ppm which is unaffected by decoupling. The ^{119}Sn satellites are just discernible for the peak at −51.6 ppm. The latter is assigned to the apical B atom on the B_5H_8 cage which is directly bonded to Sn, and the former is assigned to the apical boron on the other B_5H_8 cage, which still bears a terminal H atom. The structure of **12** is shown in Fig. 9. The B_5 cage which is bonded to the Sn via a bridging site has its open face pointing away from the other B_5 cage. Presumably this position is favored for steric reasons over the alternative structure in and a Cd[40a] system was identified spectroscopically. The Cd species is analogous to the previously reported $Hg(B_5H_8)_2$[46a] and to the recently described $Cd(B_5H_8)_2$.[47] Only three other examples of structures for 2-substituted pentaboranyl cages are known. They are *trans*-$(PMe_3)_2Br_2(CO)IrB_5H_8$,[48a] [$\mu$-$(Ph_2P)B_5H_7FeCp(CO)_2$][48b] and 2,3-$Me_2B_5H_7$, determined many years ago.[48c] There are only three other fully characterized systems with a heteroatom in the 1-position of B_5H_9. They are 1-$(SnPh_2Cl)B_5H_8$,[6b] 1-Br-2,3-μ-$(SiMe_3)B_5H_8$[24] and 1-IB_5H_8.[49]

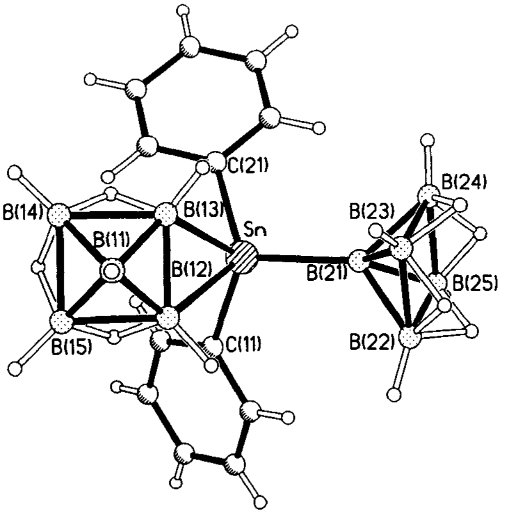


Figure 9 Structure of μ,1'-$SnPh_2(B_5H_8)_2$ (**12**).

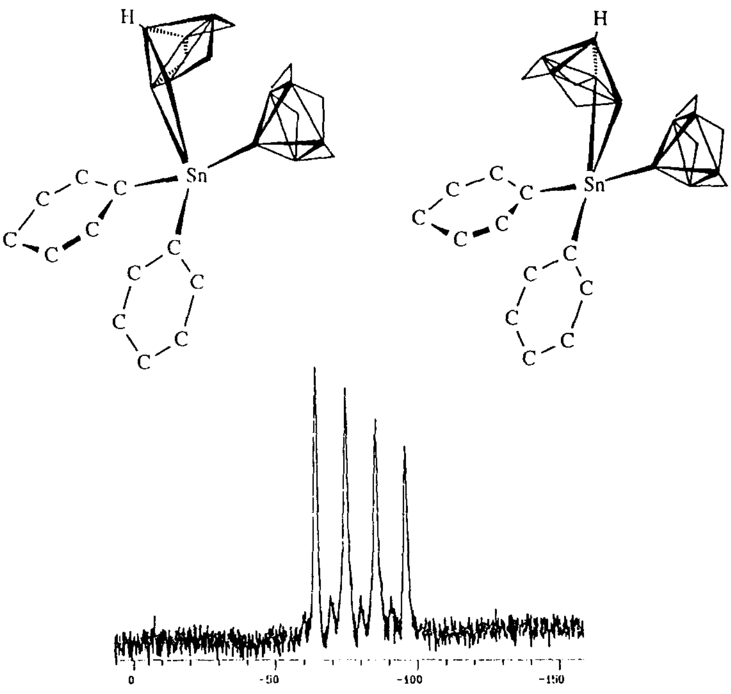
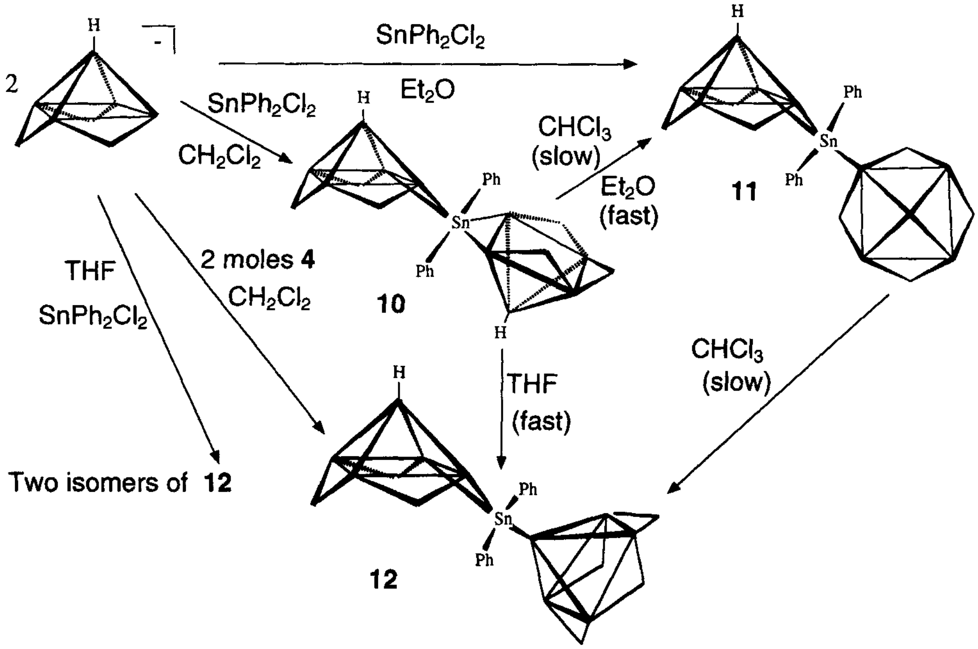


Figure 10 Two isomers of **12** and the ^{119}Sn NMR spectrum of **12** prepared by the slow isomerization of **10** in $CHCl_3$.



Scheme 7 Formation of isomers of $SnPh_2(B_5H_8)_2$.

which the open face of the cage points towards the second B_5 cage. The B–Sn distances in the bridging moiety, 2.504(3) Å and 2.532(3) Å, are on average longer than the corresponding distances in 2,3-μ-$(SnPh_3)B_5H_8$, which are 2.467(4) Å and 2.512(5) Å. Similarly the bond distance Sn–B(21), i.e. the Sn–B_{apex} distance, is 2.197(2) Å, which is longer by *ca* 0.01 Å than the corresponding distance in 1-$(SnClPh_2)B_5H_8$, 2.186(6) Å. These observations are presumably attributable to the greater steric requirements of the B_5H_8 cage in **12** relative to those of the flat C_6H_5 groups in 2,3-μ-$(SnPh_3)B_5H_8$. The product of the reaction between $SnPh_2Cl_2$ and $K[B_5H_8]^-$, in 1:2 mole ratio in THF, gives equal amounts of species with ^{119}Sn quartets at $\delta = -75.8$ and -80.1 ppm. These are the positions of the major and minor quartets shown in Fig. 10. The formation of two isomers in THF is not completely understood, but two isomers of **12** can exist. Figure 10 illustrates this point. The two isomers differ only in the way the open face of the B_5 cage, which is bonded to the Sn via a bridging site, is directed. The open face may point towards or away from the other B_5 cage. It appears that the latter orientation, which is observed in the crystal structure determination, may be favored for steric reasons. Interestingly, different isomers are formed depending on the conditions used. The formation and interconversion of the isomers of $SnPh_2(B_5H_8)_2$ are summarized in Scheme 7.

Compounds **10** – **12** represent the first structurally characterized small borane cages linked by a single atom, although examples involving hexaboranyl cages linked by Mg[40] and Pt[39g] are known

7 CURRENT AND FUTURE DIRECTIONS

We are continuing these studies and our results suggest that careful selection of solvent and conditions should allow the preparation of the three other linkage isomers of $SnPh_2(B_5H_8)_2$ and of higher oligomers containing the $SnPh(B_5H_8)$ moiety and also of related bridged pentaboranes(9). Thus we have prepared a series of Group 12 metal-bridged systems and are applying our methods to transition-metal species such as Pd and Pt. As yet we have not prepared chains of B_5 cages containing more than two cages, but our methods are certainly amenable to such studies. Formation of larger chains of B_5 cages, which are bonded to organic groups, may provide possible routes to boron carbide and related technologically attractive materials. Large molecules containing boron may have other applications, including possible sources of ^{10}B for boron neutron capture studies. We are not currently undertaking studies on these latter two areas but there is clearly potential.

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