Chapter 1

Introduction

1.1 Boron

Boron compounds have been known for hundreds of years, but the element itself was not discovered until 1808 by Davy, Guy-Lussac and Thénard.\(^1\) After producing metallic potassium by electrolysis, they used it to reduce borates to impure boron. It can also be obtained as a crude mixture by reduction of the oxide $\text{B}_2\text{O}_3$ by magnesium, or by reduction of $\text{BCl}_3$ by hydrogen on hot filaments to achieve the element in pure form. Boron is a relatively rare element in the earth’s crust, representing only 0.001%.

The element is found in a variety of similar minerals all related to borax, sodium tetraborate, $\text{Na}_2\text{B}_4\text{O}_7\cdot10\text{H}_2\text{O}$. Boron occurs naturally as 19.78% $^{10}\text{B}$ isotope and 80.22% $^{11}\text{B}$ isotope. The lighter isotope, $^{10}\text{B}$, has a high neutron capture cross section for thermal neutron absorption and is used as a control for nuclear reactors, as a shield for nuclear radiation and in instruments used for detecting neutrons. This property also makes the $^{10}\text{B}$ isotope a desirable component for Boron Neutron Capture Therapy (BNCT),\(^2,\ 3\) a promising experimental form of non-invasive treatment for cancer in humans. BNCT is based on initial targeting of tumour cells by an appropriate $^{10}\text{B}$-tagged compound, followed by irradiation of the cancer site with a neutron beam. The $^{10}\text{B}$ isotope absorbs a low energy neutron and splits into two highly charged particles, an $\alpha$-particle and a lithium ion (equation 1.1.1). The $\alpha$-particles release energy $E_k$ locally, within a range of about one cell diameter, killing the tumour cells containing high concentrations of boron without harming the normal tissue. BNCT is now well established and has been the subject of several clinical trials.

$$ ^{10}\text{B} + ^1\text{n} \rightarrow ^4\text{He} + ^7\text{Li} + E_k $$

*Equation 1.1.1* Radiative decay of $^{10}\text{B}$ following neutron capture.
1.2 Boranes

Boranes are compounds that are composed solely of boron and hydrogen and may be neutral or anionic. The chemistry of boranes was first studied systematically by Alfred Stock and his research group beginning in 1912 and continuing for almost 25 years.\(^4\) Stock developed the glass vacuum line and techniques for using it, which enabled him to synthesise and characterise these novel air sensitive compounds. This development permitted advances in a wide range of fields beyond boranes, as much of the inorganic chemistry done today involves oxygen- and moisture-sensitive compounds. A range of boranes from \(\text{B}_2\text{H}_6\) to \(\text{B}_{10}\text{H}_{14}\) was isolated and it was noted that they fell into two distinct homologous series: \(\text{B}_n\text{H}_{n+4}\) and \(\text{B}_n\text{H}_{n+6}\).

Various incorrect structures were proposed for these early small boron hydrides, because the bonding in boranes could not be directly compared with the bonding in alkanes due to the lower number of electrons involved. In the 1940s, Longuet-Higgins proposed the theory of 3-centre 2-electron (3c-2e) bonding,\(^5\) which allowed a more accurate picture to be developed.

The simplest of the boranes is diborane, \(\text{B}_2\text{H}_6\). \(\text{B}_2\text{H}_6\) has two fewer electrons available for bonding compared to its electron-precise \(\text{C}_2\text{H}_6\) analogue; therefore diborane has insufficient electrons present to allow for classical 2-centre 2-electron bonding. Boranes were consequently termed “electron deficient”. The idea of multicentre 2-electron bonding resulted in the realisation that \(\text{BH}_3\) actually existed in its dimeric form, \(\text{B}_2\text{H}_6\),\(^6,7\) a result later confirmed by the advent of X-ray diffraction techniques.

Each boron atom in the diborane structure is bound pseudo-tetrahedrally, with the four terminal hydrogen atoms each bound to the boron atoms with a standard 2-centre 2-electron bond. The two bridging B-H-B units seem unusual in that there does not appear to be enough electrons to form a bond between the two boron atoms and the bridging hydrogen. The bridging hydrogen atoms bind through a 3-centre 2-electron bond, where two boron \(sp^3\) hybrid orbitals overlap with the 1s orbital of the central hydrogen atom, effectively permitting each boron centre to achieve a stable octet (see figure 1.2.1).
Wade developed the most complete and refined method to predict the exact structure of a borane, and indeed those of other delocalised clusters, simply and quickly.\(^8\) This approach is commonly referred to as Wade’s rules and provided the basis of the Polyhedral Skeletal Electron Pair (PSEP) theory,\(^9\) which relates the number of electron pairs involved in skeletal bonding to the polyhedral geometry.

The basic principles of PSEP theory are as follows. The clusters are considered to be broken into fragments, which are denoted in the following manner: \{fragment\}. A certain number of skeletal electrons are employed by each fragment in cluster bonding.

For a main group vertex, for example \{BH\}

- \(v = \) number of valence electrons of the vertex atom
- \(x = \) number of electrons provided by groups attached to the main group element (for example, hydrogen)
- \(s = \) total number of skeletal electrons provided by the fragment

The following relationship is derived for a main group fragment:

\[
s = v + x - 2 \quad (\text{assuming an octet})
\]

The following analogous relationships apply for a transition metal vertex:

\[
s = v + x - 12 \quad (\text{for 18e species})
\]

\[
s = v + x - 10 \quad (\text{for 16e species})
\]

The number of skeletal electrons employed by each fragment is calculated. The total number of skeletal electrons for the cluster is determined by adding up all the contributions of the individual fragments, including bridging hydrogen atoms and any adjustment for charge. The total number of PSEPs is given by halving this value.
The number of PSEPs is related to the number of vertices (n) present in the cluster, which allows the structure to be predicted with the following rules:

(n+1) PSEPs  \textit{closo}  a closed, parent polyhedron
(n+2) PSEPs  \textit{nido}  an open polyhedron with one vertex removed
(n+3) PSEPs  \textit{arachno}  an open polyhedron with two adjacent vertices removed
(n+4) PSEPs  \textit{hypho}  an open polyhedron with three adjacent vertices removed

Williams was able to demonstrate the connection between the structures of many, often seemingly unrelated, boranes by successively removing the most highly connected vertices beginning with the closed parent polyhedron.\textsuperscript{10} In the closo species, the most highly connected vertex is removed, affording the nido fragment. The arachno fragment is then formed by removing the highest connected vertex in the open face of the nido fragment. This relationship is shown in what is commonly referred to as the Wade-Williams structural matrix (see figure 1.2.2).
Figure 1.2.2 Part of the Wade-Williams Structural Matrix, \( n \) defines the number of vertices.
1.3 Supraicosahedral Boron Hydrides

A considerable source of frustration for boron chemists comes from what has been termed the “icosahedral barrier”, which arises from the intrinsic stability of the $\text{B}_{12}$ icosahedron. It was Lipscomb\textsuperscript{11} who originally investigated supraicosahedral boranes theoretically and he identified a number of potentially stable synthetic targets based on the series of closo boranes $[\text{B}_n \text{H}_n]^2^-$ where $n \geq 13$. This seminal work was furthered over twenty years later by Schleyer,\textsuperscript{12} when he described a decreasing trend in cumulative BH addition energy as ‘$n$’ increases, with exceptions on going from $[\text{B}_{12}\text{H}_{12}]^2^-$ to $[\text{B}_{13}\text{H}_{13}]^2^-$ and, to a lesser degree, $[\text{B}_{14}\text{H}_{14}]^2^-$ to $[\text{B}_{15}\text{H}_{15}]^2^-$. The stabilities of the $[\text{B}_{12}\text{H}_{12}]^2^-$ and $[\text{B}_{13}\text{H}_{13}]^2^-$ boranes are such that this step is particularly unfavourable as it is endothermic. This 12-vertex to 13-vertex pathway is a clear synthetic bottleneck in boron chemistry.

As shown in figure 1.3.1, the formation of supraicosahedral boranes $[\text{B}_{13}\text{H}_{13}]^2^-$, $[\text{B}_{14}\text{H}_{14}]^2^-$ and $[\text{B}_{15}\text{H}_{15}]^2^-$, derived from addition of one, two or three $\{\text{BH}\}$ units to the icosahedral $[\text{B}_{12}\text{H}_{12}]^2^-$, are all endothermic processes which result in thermodynamically unstable products. On the other hand, formation of larger boranes such as $[\text{B}_{16}\text{H}_{16}]^2^-$ and $[\text{B}_{17}\text{H}_{17}]^2^-$ are exothermic processes, resulting in progressively more stable boranes.
Figure 1.3.1  Plot of cumulative BH addition energy (kcal/mol) vs. number of boron atoms for \([B_nH_n]^2\).
1.4 Carboranes

One of the most important classes of boron cluster compounds is that of the carboranes, which are defined by the presence of one or more carbon atoms within the cluster framework. The majority of studies on carboranes is based on the dicarbon species of general formula $\text{C}_2\text{B}_{n-2}\text{H}_n (n = 5\text{-}14)$. The \{CH\} fragment is isoelectronic and isolobal with \{BH\}; therefore members of this series of carboranes are neutral. The largest area of carborane research is concerned with the icosahedral heteroborane analogues of $[\text{B}_{12}\text{H}_{12}]^2$, namely $[\text{CB}_{11}\text{H}_{12}]^+$ and $\text{C}_2\text{B}_{10}\text{H}_{12}$.

There are three possible isomers of $\text{C}_2\text{B}_{10}\text{H}_{12}$ which are differentiated by increasing separation of cage carbon atoms. The first published rearrangement was reported\(^\text{13}\) soon after the synthesis of 1,2-$\text{C}_2\text{B}_{10}\text{H}_{12}$.\(^\text{14}\) This species undergoes rearrangement at 450°C to the 1,7-isomer and at still higher temperatures decomposes with partial conversion to the 1,12-isomer\(^\text{15}\) (figure 1.4.1). This last product has thermal stability extending well above 700°C, making it perhaps the most stable covalent neutral molecule known.

![Figure 1.4.1](image-url)

**Figure 1.4.1** Thermal isomerisation of carborane, 1,2-$\text{closo}$-$\text{C}_2\text{B}_{10}\text{H}_{12}$.

Study into the mechanism of these isomerisations is inhibited due to the high temperatures required for the processes. However, a number of theories have been postulated to rationalise the method of isomerisation. Several of these suggested mechanisms will now be briefly discussed, as some of the supraicosahedral compounds in this thesis undergo thermal isomerisation.
The first of these theories and perhaps the most renowned is Lipscomb’s diamond-square-diamond (DSD) mechanism. This consists of the lengthening and subsequent breaking of a common edge between the two triangular faces of a deltahedron. A single square is formed, which then closes via formation of a bond orthogonal to the original between the other two atoms, giving two triangular faces (figure 1.4.2).

![Figure 1.4.2](image)

**Figure 1.4.2** The DSD process at one diamond face of a polyhedron.

Lipscomb proposed a hextuple DSD process (six consecutive DSDs) for the method of isomerisation from $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$ to $1,7\text{-C}_2\text{B}_{10}\text{H}_{12}$. This proposed mechanism proceeds through a cuboctahedral intermediate, as illustrated in figure 1.4.3.

![Figure 1.4.3](image)

**Figure 1.4.3** Proposed hextuple diamond-square-diamond isomerisation process for $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$ proceeding via cuboctahedral intermediate.

Unfortunately, this isomerisation mechanism cannot be used to explain the subsequent transformation to $1,12\text{-C}_2\text{B}_{10}\text{H}_{12}$, starting from either the $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$ or $1,7\text{-C}_2\text{B}_{10}\text{H}_{12}$ isomers. In addition, Wales has calculated an unfeasibly high activation barrier for the formation of the cuboctahedral intermediate.

Triangular face rotation (TFR) is the simplest possible isomerisation mechanism and can account for many of the experimentally observed isomerisations. The mechanism
for one TFR involves the rotation of three triangularly-connected atoms by 120° (see figure 1.4.4).

Figure 1.4.4  An example of the triangular face rotation isomerisation mechanism.

The simplicity of the TFR process may be the reason why it is invoked so extensively, as all isomerisations that occur in deltahedral cages can be explained by several sequential TFR steps. However, one TFR can be considered as three consecutive DSD steps, giving the DSD mechanism greater generality in describing these isomerisations.\(^{19}\)

1.4.1 Reactivity

Protons on the 1,2-\textit{closo}-C\(_2\)B\(_{10}\)H\(_{12}\) cage carbon atoms are relatively acidic and facile removal of both can be achieved by treatment with two equivalents of an alkyl lithium reagent, such as butyl lithium. This results in the formation of a dilithium salt, which enables substitution by nucleophilic attack.

Boron atoms at positions 3 and 6 possess a weak positive charge. This leaves these borons vulnerable to nucleophilic attack and addition of a strong base (for example, KOH in an alcohol solution) affords a deboronated (decapitated) carborane (figure 1.4.1.1).\(^{20}\) There is an endo proton, situated on B10 on the resultant nido carborane,\(^{21}\) which can be removed by NaH or BuLi to yield a dicarbollide dianion, \([C_2B_9H_{11}]^{2-}\).
Two electron reduction of *closo*-carboranes is of paramount importance to this work as it is the foundation for the majority of new supraicosahedral species reported in this thesis. A dianionic nido carborane species results from the opening of the cage framework, but no vertices are lost in this process. Treatment of 1,2-*closo*-C_2B_{10}H_{12} with two equivalents of sodium metal in THF affords this type of reductive opening of a cluster, yielding the air-sensitive carbons-apart [7,9-*nido*-C_2B_{10}H_{12}]^{2-} (figure 1.4.1.2). This species cannot be isolated, but an air stable salt can be formed by protonation with H_2O to give the monoanion [nido-C_2B_{10}H_{13}]^{2-}.

The 12-vertex nido dianion can also be metallated with an \{M-L\} fragment to form a supraicosahedral metallacarborane. This will be discussed further in section 1.5.4.
1.5 Metallacarboranes

Metallacarboranes can be thought of as metal complexes incorporating carboranes as ligands or as heteroboranes with at least one metal atom present in or associated with the cage framework. The principle of isolobality is seen as the inspiration for the progress in metallacarborane chemistry. For instance, Hawthorne and co-workers first synthesised metallacarboranes in the mid-1960s when he recognised the apparent similarity between the open face of the dicarbollide dianion, $[\text{C}_2\text{B}_9\text{H}_{11}]^2-$, and the cyclopentadienide ion, $[\text{C}_5\text{H}_5]^-$ (see figure 1.5.1). This has since proven to be a useful guide for the syntheses of metallacarboranes that parallel those of metallocenes.

![Figure 1.5.1](image)

**Figure 1.5.1** Synthesis of first metallacarborane and orientation of the frontier orbitals in the dicarbollide dianion and the cyclopentadienide anion.

Many metallacarborane complexes have been synthesised since then with nearly all the metal and metalloid elements in the Periodic Table incorporated into the cluster framework. This area is dominated by the icosahedron, which is reflected in the fact
that there is an enormous number of known metallacaboranes based on this $MC_2B_9$ architecture. There are nine isomeric possibilities of this system, all of which are shown in figure 1.5.2.

![Figure 1.5.2](image)

Figure 1.5.2 The nine possible configurations for a 12-vertex $MC_2B_9$ icosahedral assembly.

Three numbers define these isomers, the first of which indicates the position of the metal atom whilst the remaining two identify the vertices occupied by the carbon atoms. The numbering begins at the highest-connected vertex which lies upon the principal axis of symmetry for closo species. Remaining positions are numbered in succession in a helical fashion crossing a vertex-vertex connectivity once each belt of atoms is
Heteroatoms should be assigned as low a number as possible, with the carbon atoms assuming highest priority (see figure 1.5.3).

![Figure 1.5.3](image_url)

**Figure 1.5.3** Numbering system for closo icosahedron.

Base removal of the most positive boron atom of the icosahedral carboranes 1,2-, 1,7- and 1,12-C$_2$B$_{10}$, followed by the addition of a metal fragment, results in the respective formation of the 3,1,2-, 2,1,7- and 2,1,12-MC$_2$B$_9$ cages. All of the nine possible isomers of the MC$_2$B$_9$ system have been described in the literature. Of these, the family of metallacarboranes having 3,1,2-MC$_2$B$_9$ geometry is the most widely studied.\(^{26}\) This is followed by the 2,1,7-MC$_2$B$_9$ type with around thirty known structures determined by X-ray crystallography,\(^{27,28}\) whilst there is only a handful of examples of metallacarborane complexes based on the 2,1,12-MC$_2$B$_9$ cage.\(^{27,29,30}\) The six remaining isomers of MC$_2$B$_9$ are synthesised via isomerisation of one of the previous icosahedral species. Of these, only compounds with 4,1,2-\(^{31}\) and 2,1,8-MC$_2$B$_9$\(^ {32}\) cage geometries have been crystallographically characterised. Table 1.5.1 summarises how widespread these different isomers are.
Table 1.5.1 A summary of the proportion of crystallographically characterised isomers within the $MC_2B_9$ system, where $x$ = number of structures in the Cambridge Structural Database (April, 2009).

<table>
<thead>
<tr>
<th>Isomer</th>
<th>$x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3,1,2-MC_2B_9$</td>
<td>628</td>
</tr>
<tr>
<td>$2,1,7-MC_2B_9$</td>
<td>39</td>
</tr>
<tr>
<td>$2,1,12-MC_2B_9$</td>
<td>1</td>
</tr>
<tr>
<td>$4,1,2-MC_2B_9$</td>
<td>9</td>
</tr>
<tr>
<td>$2,1,8-MC_2B_9$</td>
<td>36</td>
</tr>
<tr>
<td>$2,1,9-MC_2B_9$</td>
<td>0</td>
</tr>
<tr>
<td>$9,1,7-MC_2B_9$</td>
<td>0</td>
</tr>
<tr>
<td>$8,1,2-MC_2B_9$</td>
<td>0</td>
</tr>
<tr>
<td>$9,1,2-MC_2B_9$</td>
<td>0</td>
</tr>
</tbody>
</table>

1.5.1 Main group metallacarboranes

The insertion of both main group and transition metals into polyhedral carborane structures were first reported in the mid-1960s. However, the chemistry of transition metal carboranes has advanced much more rapidly than that of main group metal metallacarboranes.

The group 14 species are the most studied complexes among the main group metallacarboranes. The first group 14 metallacarboranes were prepared by Rudolph and co-workers when they treated $[7,8-nido-C_2B_9H_{11}]^2$ with $MX_2$ ($M = Ge$, Sn or Pb). These compounds, illustrated in figure 1.5.1.1, were perceived to have $3,1,2$-closo-$MC_2B_9H_{11}$ structures on the basis of NMR spectroscopy, with the cage carbon atoms occupying positions adjacent to the group 14 metal atom.
Three years later, this original study was expanded to include the carbons-apart germacarborane, $2,1,7$-$\text{GeC}_2\text{B}_9\text{H}_{11}$, which was characterised spectroscopically. Interestingly, when $\text{SnCl}_2$ was used instead of $\text{GeI}_2$ to prepare the analogous stannacarborane, the major products of the reaction were the oxidative-cage-closure species $2,3$-$\text{C}_2\text{B}_9\text{H}_{11}$ and tin metal. Unlike the carbons-adjacent isomer, the carbons-apart species apparently shows an increased tendency to undergo oxidative cage closure, which is surprising as this isomer is thought to be thermodynamically more stable. This also contradicts observations made in subicosahedral systems, where carbons-adjacent carboranes are more easily oxidised when compared to their carbons-apart analogues.

Chapter 2 presents an expansion on the work on $3,1,2$-$\text{MC}_2\text{B}_9$ main group metallacarboranes, together with a structural study of the adducts these species form with the classic Lewis base bipy.

In 1977, Wong and Grimes reported the synthesis of the smaller carborane homologues $\text{MC}_2\text{B}_4\text{H}_6$ ($M = \text{Ge, Sn and Pb}$). From NMR spectroscopic data, the group 14 heteroatom was proposed to occupy one of the apical positions in a pentagonal bipyramid (see figure 1.5.1.2).
A half-sandwich Sn(IV) carborane, 1,1-(Me)$_2$-1,2,3-*closo*-SnC$_2$B$_8$H$_{10}$, was reported by Kennedy and co-workers from the reaction of Me$_2$SnCl$_2$ with [6,9-*nido*-C$_2$B$_8$H$_{10}$]$^2$. Similarities were noted in the $^{11}$B NMR spectra between this compound and that of [µ-6,9-AlEt(OEt)$_2$-6,9-*nido*-C$_2$B$_8$H$_{10}$], in which the metal bridges the carborane through two cage C-Al bonds. This prompted the authors to describe the complex as a classically bridged *nido*-stannacarborane.

Following these inceptive reports, a considerable number of group 14 metallacarboranes have been synthesised, spectroscopically and structurally characterised, and their reaction chemistry has also been explored.

In 1986, the insertion of silicon was reported for both large and small cage carborane systems.$^{38, 39}$ The novel silicon sandwich complex 3,3'-Si-(1,2-*closo*-C$_2$B$_9$H$_{11}$)$_2$ (figure 1.5.1.3) was described by Hawthorne and co-workers and was prepared from the reaction of the dicarbolide dianion with SiCl$_4$ in refluxing benzene. X-ray structural characterisation of this complex showed that the silicon, in a formal 4+ oxidation state, is sandwiched between the planar and parallel C$_2$B$_3$ faces of the carborane ligands, with the cage carbon atoms occupying trans positions across the silicon.

![Figure 1.5.1.3](image)

*Figure 1.5.1.3* Structure of 3,3'-Si-(1,2-*closo*-C$_2$B$_9$H$_{11}$)$_2$.

A concurrent report by Hosmane and co-workers described the synthesis of the full-sandwich metallacarboranes of the SiC$_2$B$_4$ system.$^{40}$
There is an abundance of evidence in the literature that heavier group 14 metallacarborane half-sandwich complexes prefer the lower, 2+, oxidation state while the 4+ state is favoured in the full-sandwich complexes. The best example of this behaviour is found in the germacarboranes, where Hosmane\textsuperscript{41} reported that reaction of Li[2,3-(SiMe\textsubscript{3})\textsubscript{2}-2,3-C\textsubscript{2}B\textsubscript{4}H\textsubscript{5}] with GeCl\textsubscript{4} produced a mixture of the half-sandwich 2,3-(SiMe\textsubscript{3})\textsubscript{2}-1,2,3-closo-GeC\textsubscript{2}B\textsubscript{4}H\textsubscript{4} in 27\% yield and the full-sandwich 1,1′-Ge-[2,3-(SiMe\textsubscript{3})\textsubscript{2}-2,3-closo-C\textsubscript{2}B\textsubscript{4}H\textsubscript{4}]\textsubscript{2} in 20\% yield. In the latter compound, shown in figure 1.5.1.4, the Ge atom is sandwiched between two carborane ligands, resulting in the GeC\textsubscript{4}B\textsubscript{8} cluster having C\textsubscript{2h} symmetry. There is a greater slippage of the metal in the germacarboranes compared to their analogous silacarboranes. This is evidenced by the fact that the differences between the M-C distances and the M-B distances are greater in the germacarboranes.

\textbf{Figure 1.5.1.4} Structure of 1,1′-Ge-[2,3-(SiMe\textsubscript{3})\textsubscript{2}-2,3-closo-C\textsubscript{2}B\textsubscript{4}H\textsubscript{4}]\textsubscript{2}.

The occurrence of metallacarborane sandwich complexes with slipped geometries is not uncommon. This so-called \textit{slip distortion} - a pronounced lateral movement of the metal atom across the carborane ligand face, in a direction away from the cage carbon atoms - was first recognised in the 1960s.\textsuperscript{42-44} The distortion becomes especially significant in cases where a \textit{d}-block metal has a near-complete \textit{d}-electron configuration, for example, Ni\textsuperscript{2+}, Cu\textsuperscript{2+} or Au\textsuperscript{3+}. In addition to the total number of valence electrons, studies have shown that substituents on the open face of the carborane ligand may also influence the magnitude of this effect.\textsuperscript{45}
Slippage of the heteroatom with respect to the open face of a carborane ligand is commonly observed in single-cage metallacarboranes containing a main group atom. Throughout this thesis, slip distortion is assigned the symbol $\Delta$ and, for icosahedral species, is defined as the distance the metal atom is displaced from a position above the centroid of the lower pentagon of five B atoms. Another related parameter that should be introduced here is $z$, which is the perpendicular displacement of $M$ above the least-squares plane through the lower belt of B atoms (see figure 1.5.1.5).

![Figure 1.5.1.5](image)

**Figure 1.5.1.5** Pictorial representation of the derived structural parameters $\Delta$ and $z$.

Using methods similar to that described earlier by Rudolph and colleagues,$^{33,34}$ direct reaction of $\text{SnCl}_2$, $^{46,47} \text{SnCl}_4$ $^{48}$ or $\text{PbCl}_2$ $^{49}$ with the mono- or dianionic salts of the $\text{C}_2\text{B}_9$ and $\text{C}_2\text{B}_4$ nido carboranes resulted only in half-sandwich metallacarborane products. Only the subicosahedral compounds of this type have been characterised crystallographically. On attempting to synthesise heavier group 14 full-sandwich complexes by this direct carborane metal-halide reaction method, only reductive insertion of the metal occurs which yields the half-sandwich compound.$^{48}$ This can be explained on the basis that the heavier main group metals have a decreasing tendency to form high oxidation states. Despite this established disinclination of tin to form carborane complexes when it is in a 4+ oxidation state, there is one example in the literature of a full-sandwich $\text{Sn(IV)}$ carborane, $1,1'-\text{Sn-(2-SiMe}_3\text{-3-Me-2,3-closo-C}_2\text{B}_4\text{H}_4))_2$. $^{50}$ This compound, reported by Hosmane in 1992, was synthesised in 73%
yield by a redox reaction between 2-SiMe$_2$-3-Me-1,2,3-	extit{closo}-SnC$_2$B$_4$H$_4$ and TiCl$_4$, in a 1:1 molar ratio, in a solvent mixture of dry benzene and THF. The structure of this complex, illustrated in figure 1.5.1.6, differs from those of its silicon and germanium analogues in that the stannacarborane complex is bent, with a (ring centroid 1)-Sn-(ring centroid 2) angle of 142.5°.

![Figure 1.5.1.6](image) Bent structure of the full-sandwich Sn(IV) carborane, 1,1’-Sn-(2-SiMe$_3$-3-Me-2,3-	extit{closo}-C$_2$B$_4$H$_4$)$_2$.

Bending in the stannocenes and several other group 14 metallocones is well known and has been explained in terms of the stereochemical influence of the lone pair of electrons on the tin atom, which may be offset by the presence of large groups, such as C$_6$H$_5$ on the Cp ring.

The group 14 half-sandwich metallacarboranes have long been recognised as interesting molecules in that they show no tendency to function as Lewis bases, despite the presence of a lone pair of electrons on the M$^{2+}$ capping metals. In fact, quite the opposite is true, in that the chemistry of these complexes is dominated by Lewis acid behaviour. All the half-sandwich metallacarboranes of germanium, tin and lead have been reported to form donor-acceptor complexes with monodentate,\textsuperscript{49, 51-53} bidentate,\textsuperscript{46, 49, 54-57} bis(bidentate)\textsuperscript{58, 59} and tridentate bases.\textsuperscript{60} The structures of these complexes show that not only is the slip distortion more pronounced, but the plane of the donor bipy ligand is tilted with respect to the metallacarborane cage. These two features imply that although the lone pair of electrons on the M atom is chemically inert, it is fully stereochemically active. Inclination of terminal substituents or donor molecules is observed in many related metallacarboranes, such as 1-Me-1,2,3-	extit{closo}-GaC$_2$B$_4$H$_6$ and
1-Me-1,2,3-closo-InC$_2$B$_4$H$_6$.\textsuperscript{61} For the icosahedral systems in this thesis, the tilting of the ligand is quantified as $\theta$, the dihedral angle between the least-squares plane through the lower belt of five B atoms and the M3N1CCN2 plane (see figure 1.5.1.7).

![Figure 1.5.1.7](image)

**Figure 1.5.1.7** Pictorial representation of the derived structural parameter $\theta$.

Even in the base-SnCp system, these same observations are found. In the [($\eta$-C$_5$Me$_5$)Sn]$^+$ half-sandwich complex\textsuperscript{62}, the tin is centred over the pentagonal face of the Cp$^*$ ligand, whereas in the [(bipy)Sn(C$_5$Me$_5$)]$^+$ complex, the tin atom is slip distorted and the bipy ligand is oriented over one side of the Cp$^*$ ring.\textsuperscript{63}

While the majority of structural studies have been performed on the carbons-adjacent metallacarboranes, there have been several reports on the structures of carbons-apart base-stannacarborane adducts.\textsuperscript{53} Their structures bear the same relationship to their carbons-adjacent analogues, in that the base molecules are oriented opposite the cage carbon atoms and the tin atom is displaced in the direction of base orientation (see figure 1.5.1.8).
The most striking difference in these compounds is that the extent of slippage is less when compared to that found in the corresponding gallacarboranes and also the matching carbons-adjacent analogues. In addition, the dihedral angle between the molecular plane of the ligand and the C₂B₃ carborane face is larger than the value reported for their carbons-adjacent analogues. The Sn-N bond distances are also longer than those found in their respective carbons-adjacent isomers, which is indicative of weaker base-metallacarborane bonding. The longer Sn-N bonds, coupled with the larger base-carborane dihedral angle, suggest weaker base-tin bonding in the carbons-apart species.

Interest in icosahedral stannacarboranes has recently been enhanced by work conducted on the related stannaborate, [\textit{closo}-SnB₁₁H₁₁]²⁻, as described in the next section.

### 1.5.2 Stanna-\textit{closo}-dodecaborate chemistry

The monocarborate anion [CB₁₁H₁₂]⁻ and its derivatives have outstanding properties as weakly coordinating anions and have consequently received a great deal of attention. The coordination of the tin homologue, [SnB₁₁H₁₁]²⁻ (shown in figure 1.5.2.1), has been comprehensively studied by Wesemann and colleagues. Their seminal work has indicated that this dianionic group 14 heteroborate is a versatile ligand in coordination chemistry and can take up an assortment of coordination modes.
The original synthesis of \([\text{SnB}_{11}\text{H}_{11}]^{2-}\), together with the germanium and lead analogues, was first performed by Todd and co-workers in 1992.\(^6\) This consisted of deprotonation of \([\text{Me}_3\text{NH}][\text{B}_{11}\text{H}_{14}]\) in THF with four equivalents of \(n\)-BuLi, followed by addition of one equivalent of \(\text{SnCl}_2\) in THF at -78°C. Depending on which counterion was utilised, a variety of different stanna-\(\text{closo}\)-dodecaborate salts were afforded after precipitation from an aqueous solution. The solid state structure of the lithium salt revealed that the tin atom is positioned above the centre of the pentagonal \(\text{B}_5\) face, with \(\text{Sn-B}\) distances ranging from 2.381(4) – 2.389(3) Å.\(^6\)

As noted earlier, the neutral closo stannacarboranes \(\text{Sn(CR)}_2\text{B}_4\text{H}_4\) and \(\text{Sn(CMe)}_2\text{B}_9\text{H}_9\) behave as Lewis acids, giving rise to adducts with classic Lewis bases. However, the isolobal stannaborate \([\text{SnB}_{11}\text{H}_{11}]^{2-}\) shows no tendency to react with Lewis bases but instead itself behaves as an excellent Lewis base to a wide variety of transition metal fragments.

In 1999, the first coordination compounds of \([\text{SnB}_{11}\text{H}_{11}]^{2-}\) were reported.\(^6\) In each case, upon addition of \([\text{Bu}_4\text{N}]_2[\text{SnB}_{11}\text{H}_{11}]\) to a series of transition metal halogen derivatives, the halide was substituted by the stannaborate (figure 1.5.2.2).
A plethora of transition metal complexes containing the stannaborate ligand have since been synthesised which demonstrate the variability of this fascinating dianion. The stannaborate leads to gold-tin cluster formation with Au(I) fragments, to homoleptic complexes with metal-tin bonds (Pd, Pt, Au), and to ambidentate coordination with iron and ruthenium fragments. New compounds are still being isolated with this ligand, each with its own surprising structure.

The synthesis and coordination chemistry of 1,2-carbastanna-closo-decaborate, [1,2-closo-SnCB_{10}H_{11}], was presented in 2007. While [SnB_{11}H_{11}]^{2-} and SnC_{2}B_{9}H_{11} have been established to show Lewis-basic and Lewis-acidic reaction behaviour respectively, this intermediate monocarbon species appears to have both \( \sigma \)-donor and \( \pi \)-acceptor properties.

Three equivalents of [SnCB_{10}H_{11}] treated with Wilkinson’s catalyst, [RhCl(PPh_{3})_{3}], resulted in the formation of the intriguing dianion [Rh(PPh_{3})_{2}(SnCB_{10}H_{11})]^{2-}, which has a trigonal bipyrmidal geometry with equatorial anionic SnCB_{10}H_{11} ligands and axial PPh_{3} ligands. It has long been established that in a d^{8}-ML_{5} trigonal bipyrmidal Rh\(^{+}\) complex, the strongest \( \pi \)-acceptors occupy equatorial positions and the strongest \( \sigma \)-
donors reside in axial positions.\textsuperscript{70} It can then be concluded that the anionic [SnCB\textsubscript{10}H\textsubscript{11}]\textsuperscript{-} ligand must be a reasonably strong $\pi$-acceptor. However, when the carbastannaborate coordinates at gold in the complex [Au\textsubscript{4}(PPh\textsubscript{3})\textsubscript{4}(SnCB\textsubscript{10}H\textsubscript{11})\textsubscript{2}], it is behaving exclusively as a Lewis base. These contrasting behaviours are illustrated in figure 1.5.2.3.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.5.2.3.png}
\caption{\textit{\sigma-donor and $\pi$-acceptor behaviour of [1,2-\textit{closo}-SnCB\textsubscript{10}H\textsubscript{11}]}.}
\end{figure}

Very recently, these systematic changes in the donor/acceptor properties in the series [\textit{closo}-SnB\textsubscript{11}H\textsubscript{11}])\textsuperscript{2-}, [1,2-\textit{closo}-SnCB\textsubscript{10}H\textsubscript{11}]\textsuperscript{-} and 3,1,2-\textit{closo}-SnC\textsubscript{2}B\textsubscript{9}H\textsubscript{11} have been confirmed by Fox, Marder and Wesemann using DFT calculations.\textsuperscript{71}
1.5.3 Applications of Metallacarboranes

There has been an increasing effort directed at exploiting the special properties of metallacarboranes in a host of different areas. The scope of the actual and physical applications of these compounds is remarkable, encompassing problems in biology and medicine, environmental science, industrial processes, materials and microelectronics, optics and many others. The main attributes that metallacarboranes have to offer are that they have a high thermal and chemical stability, excellent solubility properties (neutral metallacarboranes tend to dissolve readily in organic solvents; ionic ones in aqueous media), tailorability (via changes in metals, carborane ligands and substituents on the cage), electron-delocalised frameworks and the ability to incorporate most elements in the Periodic Table into the cage framework. This means that in theory it is possible to design a metallacarborane which has the precise combination of properties required for a specific application.

Interesting applications of metallacarboranes include extraction of radionuclides\textsuperscript{72, 73} and homogeneous catalysis.\textsuperscript{74, 75} Several of the current applications of metallacarboranes would be enhanced if larger species could be prepared.

1.5.4 Supraicosahedral Metallacarboranes

The first supraicosahedral metallacarborane to be isolated was 4-Cp-4,1,6-c\textit{closo}-CoC\textsubscript{3}B\textsubscript{10}H\textsubscript{12} by Hawthorne \textit{et al.} in 1971.\textsuperscript{76} They used the ‘polyhedral expansion’ method, employing Na reduction of 1,2-c\textit{closo}-C\textsubscript{2}B\textsubscript{10}H\textsubscript{12} to [7,9-n\textit{ido}-C\textsubscript{2}B\textsubscript{10}H\textsubscript{12}]\textsuperscript{2-}, followed by metallation with Co\textsuperscript{2+}, Cp\textsuperscript{-} and aerial oxidation (figure 1.5.4.1).
Figure 1.5.4.1 Synthesis of the first 13-vertex metallacarborane, 4-Cp-4,1,6-closo-CoC₂B₁₀H₁₂, by polyhedral expansion.

This reduction/metallation or RedMet approach to synthesising supraicosahedral metallacarboranes is now well established. Since 1971, similar 13-vertex 4,1,6-MC₂B₁₀ species have been reported incorporating a wide range of early, mid and late transition metals, group 1 metals, group 2 metals, lanthanides and actinides.

For the majority of 13-vertex clusters, the polyhedron predicted and experimentally observed is the triangulated docosahedron. This structural framework consists of two degree-six vertices, one degree-four vertex and the remaining ten vertices are degree-five. The two most common views of this docosahedron, together with a numbering scheme, are shown in figure 1.5.4.2.

Figure 1.5.4.2 Numbering system for closo docosahedral clusters.

It is universally accepted that metal fragments prefer to occupy high-connected sites due to the relatively larger and more diffuse orbitals of the metal. The more electronegative
carbon atoms favour the lower connected sites as their orbitals are more contracted.\textsuperscript{10,89,90}

The seven potential isomers of the 13-vertex \textit{4,1,x-MC}_{2}B_{10} system are shown in figure 1.5.4.3.

![Diagram of potential isomers of \textit{4,1,x-MC}_{2}B_{10} system.]

\textbf{Figure 1.5.4.3} Potential isomers of \textit{MC}_{2}B_{10} assuming fixed positions for \textit{M} and one carbon atom.

Of these isomers, the 4,1,5-species is unlikely to ever be synthesised as it requires a carbon atom to occupy the degree-six site at position five. The 4,1,10-species results from reduction of the icosahedral carborane \textit{1,12-MC}_{2}B_{10}, followed by the addition of a metal fragment.\textsuperscript{91} A C,C-tether, required to keep the carbon atoms together upon reduction, is employed in order to synthesise 4,1,2-species.\textsuperscript{92} These compounds may adopt either docosahedral or henicosahedral structures depending on the metal fragment at position four. Isomerisation of the kinetic 4,1,6-product results in rearrangement to the 4,1,8-isomer, which itself can undergo further isomerisation to afford the thermodynamically most stable 4,1,12-isomer.\textsuperscript{93-95} The 4,1,12-species can also be achieved by isomerisation of the 4,1,10-analogue.\textsuperscript{91} Very recently, the first example of a 4,1,11-\textit{MC}_{2}B_{10} species was reported.\textsuperscript{96} This isomer was isolated as a minor product from reduction and subsequent metallation of 1,12-\textit{Ph}_{2}-1,12-\textit{closo-C}_{2}B_{10}H_{10}. 
A bicapped hexagonal antiprism is the polyhedron predicted for 14-vertex heteroboranes\textsuperscript{11, 12} (see figure 1.5.4.4 for structure and numbering scheme). It is expected that for bimetallacarboranes, the two metal atoms will occupy the two high coordinated vertices, 1 and 14, at opposite ends of the molecule.

Figure 1.5.4.4  Bicapped hexagonal antiprismatic geometry and numbering system of 14-vertex clusters.

Hawthorne reported the first examples of 14-vertex bimetallacarboranes in 1974.\textsuperscript{97} He described the preparation of \((\text{CpCo})_2\text{C}_2\text{B}_{10}\text{H}_{12}\) in two isomeric forms, but these species were only partially characterised. In 2005, Welch \textit{et al.} presented the synthesis and full characterisation of both homo and heterobimetallic 14-vertex \(M_2\text{C}_2\text{B}_{10}\) species.\textsuperscript{98} In this report, the bicapped hexagonal antiprismatic geometries (figure 1.5.4.4) of these compounds were validated.

The first example of a 15-vertex heteroborane, \(1-(\text{p-cymene})-8,14-\mu-(\text{CH}_2)_3-1,8,14\text{-closo-RuC}_2\text{B}_{12}\text{H}_{12}\), was reported by Welch \textit{et al.} in 2006.\textsuperscript{99} X-ray crystallography confirmed that the polyhedral architecture of this species is a 15-vertex polyhedron with only two degree-six vertices, differing slightly to that predicted\textsuperscript{97} for the \(D_{3h}\)-symmetric hexacosahedron (26 faces) borane dianion \([\text{B}_{15}\text{H}_{15}]^{2-}\). The 15-vertex heteroborane is instead not fully triangulated and an open quadrilateral face is generated from the absence of a B-C connectivity.

There is one other known isomer of a 15-vertex heteroborane in the literature, \(1,4-(\text{CH}_2)_3-7-(\text{p-cymene})-7,1,4\text{-closo-RuC}_2\text{B}_{12}\text{H}_{12}\).\textsuperscript{100} In this case, the structure matches the
hexacosahedron predicted for the parent borane dianion, with 26 fully triangulated faces and three degree-six vertices (figure 1.5.4.5).

\[ \text{Figure 1.5.4.5} \quad \text{The degree-six vertices in 14- and 15-vertex polyhedra.} \]

As the predicted size of the cluster increases, the number of degree-six vertices in the structure also increases. Transition metals stabilise these degree-six vertices in supraicosahedral clusters. Metal atoms prefer high connected sites in the cage, which offers the possibility of replacing these transition metals with main group metals, as main group metals have properties between those of transition metals and boron.

### 1.5.5 Supraicosahedral Main Group Metallacarboranes

In 2002, Welch et al. reported the first $p$-block 13-vertex heterocarboranes, $4,1,6$-$\text{closos}$-$\text{SnC}_2\text{B}_{10}\text{H}_{12}$ and $1,6$-$\text{Me}_2$-$4,1,6$-$\text{closos}$-$\text{SnC}_2\text{B}_{10}\text{H}_{10}$. Both these compounds were made by employing the RedMet methodology. Reduction of $1,2$-$\text{closos}$-$\text{C}_2\text{B}_{10}\text{H}_{12}$ and its C,C-dimethyl analogue, followed by reaction with SnCl$_2$, affords $4,1,6$-$\text{closos}$-$\text{SnC}_2\text{B}_{10}\text{H}_{12}$ and $1,6$-$\text{Me}_2$-$4,1,6$-$\text{closos}$-$\text{SnC}_2\text{B}_{10}\text{H}_{10}$ respectively in reasonable yields (see figure 1.5.5.1).
Figure 1.5.5.1  Synthesis of the first reported example of a supraicosahedral $p$-block metallacarborane.

This work was followed by reports of the first example of a carbons-adjacent supraicosahedral stannacarborane, $1,2-\mu-[o-C_6H_4(CH_2)_2]-4,1,2-closo$-$SnC_2B_{10}H_{10}$, and its adducts with MeCN, THF and DME (see figure 1.5.5.2).

Figure 1.5.5.2  Synthesis of the first reported example of a carbons-adjacent supraicosahedral stannacarborane.

Thus far, these were the only two examples of supraicosahedral main group heteroboranes. While the area of supraicosahedral transition metal chemistry has advanced extremely quickly, the area of supraicosahedral main group metallacarborane chemistry remains relatively unexplored. The aim of this work is to develop the area of supraicosahedral main group metallacarborane chemistry.
1.6 Analytical Techniques

A wide variety of modern analytical techniques has been applied in order to fully characterise the compounds reported in this thesis. An overview of these techniques will now be presented.

Boron NMR Spectroscopy

Boron NMR studies enable us to obtain structural information about carboranes and metallacarboranes in solution and can give details regarding molecular dynamics, such as fluxionality. Boron has two naturally occurring NMR-active nuclei, \(^{11}\)B and \(^{10}\)B, both of which are quadrupolar, have spins of \(\frac{3}{2}\) and 3 respectively. Both nuclei have the same broad chemical shift range. The greater abundance of \(^{11}\)B, along with it being more sensitive, makes it the boron nuclide of choice for NMR spectroscopy.

Despite the relatively large chemical shift range for heteroboranes, signal overlap is not uncommon. This is due to the similar chemical environments for many boron atoms. Main group metallacarboranes generally produce larger chemical shift ranges compared to carboranes, as main group metals have different properties to those of boron and carbon.

Correlation studies can also be used in order to establish BNH and BNB connectivities and aid signal assignment.

Mass Spectrometry

Mass spectrometry is an analytical tool used for measuring the molecular mass of a sample. For heteroboranes, the mass spectrum exhibits a characteristic base-peak envelope corresponding to the isotopes in the boron cluster. It should be noted that the parent ion peak is absent for the main group metallacarborane adducts reported in this
thesis. This is due to the weak main group metal-N bonds being ruptured during the ionisation process.

**Infrared Spectroscopy**

Infrared spectroscopy is useful for identifying certain functional groups in a compound. The most significant vibrational band observed in heteroboranes is a broad B-H stretch around 2500 cm\(^{-1}\). This broadening arises from many boron atoms residing in similar chemical environments.

**X-ray Diffraction**

Single-crystal X-ray diffraction is an analytical technique which establishes the molecular structure of compounds in the solid state. It allows the determination of precise atomic positions and therefore bond lengths and angles of molecules within a single crystal. The pattern produced by the diffraction of X-rays through the closely spaced lattice of atoms in the crystal is recorded and then interpreted and refined to obtain the crystal structure. This is the definitive method for the characterisation of heteroboranes as, unlike the other techniques, this method unequivocally determines the structure of the compound.

The pseudospherical nature of these cage compounds can sometimes lead to boron-carbon disorder in the structure. In order to prevent this from occurring, methyl groups have been attached to the carbon atoms in the cage for the majority of the compounds reported. This disrupts the symmetry of the molecule and allows the carbon and boron atoms to be correctly assigned.
1.7 Scope of Thesis

The background to heteroborane chemistry was described in chapter one in order to provide the reader with a synopsis of the relevant literature associated with the work presented in this thesis. The area of main group metallacarboranes was covered in significant detail, as the running theme of this thesis is the investigation of the role of main group metals in supraicosahedral heteroboranes.

Main group metallacarboranes incorporating the heavy group 14 metals into the cage framework have long been regarded as interesting molecules for their propensity to form adducts with Lewis bases, despite the lone pair of electrons on the metal. The work in this thesis begins with the expansion of the field of icosahedral main group metallacarboranes to include bipy adducts of a 12-vertex germacarborane and plumbacarborane. The structures of these compounds are studied, with particular emphasis placed on the slip distortion of the metal and the orientation and inclination of the ligand. These findings are then referenced to studies conducted previously on adducts of the subicosahedral system.

Ever since the synthesis of the first supraicosahedral metallacarborane, the area of 13-vertex metallacarboranes of transition metals has expanded considerably, while to date there are only two examples of supraicosahedral main group metallacarborane systems in the literature. The behaviour of these 4,1,6- and 4,1,2-SnC\textsubscript{2}B\textsubscript{10} isomers has now been studied by their reactions with a series of Lewis bases. The structures of the two different systems are compared and contrasted and factors that influence the slipping of the Sn atom are explored.

A route to the previously unreported 4,1,10-SnC\textsubscript{2}B\textsubscript{10} isomer is presented for the first time. The synthesis of this compound provides access to another previously unknown supraicosahedral main group isomer, 4,1,12-SnC\textsubscript{2}B\textsubscript{10}. In order to facilitate a structural investigation, adducts of these two new isomers were prepared and the interesting features of each are discussed.
Evidence for the first example of the insertion of a main group metal into a reduced transition metal metallacarborane is also reported, together with a full discussion of the importance and relevance of this significant result.
1.8 References


Chapter 2
Icosahedral Main Group Metallacarboranes and their Adducts

2.1 Introduction

Icosahedral transition metal metallacarboranes of the type $MC_2B_9$ are well established, while in contrast there are many fewer examples in the literature that include main group metals in the cage framework. The first examples of metallacarboranes that incorporated heavy main group metals into the cage were synthesised by Rudolph and co-workers in 1970.¹ They were obtained by deprotonation of the trimethylammonium salt of orthocarborane with NaH in benzene, followed by addition of the metal fragment as a halide salt. For example, the synthesis of 3,1,2-closo-$SnC_2B_9H_{11}$ is shown in figure 2.1.1.

![Figure 2.1.1](image)

**Figure 2.1.1** Synthesis of 3,1,2-closo-$SnC_2B_9H_{11}$, by Rudolph et al.¹

These compounds were characterised on the basis of IR and NMR spectroscopies and mass spectrometry. From this analysis and knowledge of the structure of the carborane precursor, the cage carbon atoms were assigned to positions adjacent to the group 14 metal. Structural assignment by X-ray crystallography was not possible, presumably due to disorder in the solid-state structures of these almost spherically symmetric compounds.

In 1987, Jutzi et al.² noted similarities between the analogous dimethylated compound, 1,2-Me₂-3,1,2-closo-$SnC_2B_9H_9$, and the half sandwich complex, $[(\eta^3-C_5Me_3)Sn]^+$.³ Given that the latter behaves as a Lewis acid,⁴ they treated 1,2-Me₂-3,1,2-closo-$SnC_2B_9H_9$ with
mono- and bidentate Lewis bases in order to ascertain if the stannacarborane behaved in a similar fashion. These reactions resulted in a series of air-sensitive solid adducts, the structures of two of which were determined by X-ray crystallography. Of all the adducts synthesised, the most pertinent to the work in this chapter is compound A, 1,2-Me₂-3-(bipy)-3,1,2-closo-SnC₂B₉Hₙ, which is shown in figure 2.1.2.

![Figure 2.1.2](image_url)

**Figure 2.1.2** 1,2-Me₂-3-(bipy)-3,1,2-closo-SnC₂B₉Hₙ (A).

It is important to note that although the dimethylated stannacarborane can give rise to adducts with classic Lewis bases, despite the presence of a lone pair of electrons on the Sn atom, it is unreactive toward electrophiles such as CF₃SO₃Me, MeI, SiCl₄ and SnCl₄. The stannacarborane can however undergo facile degradation in methanolic KOH to selectively remove the metal atom.

The major effect of Lewis base complexation is that there is a substantial elongation of the Sn-C distances with the Sn atom displaced further across the carborane ligand face towards the unique boron atom. Although the precursor to A, 1,2-Me₂-3,1,2-closo-SnC₂B₉Hₙ, has not been crystallographically characterised, its structure has recently been computed in $C_s$ symmetry⁵ resulting in an average Sn-C distance of ca. 2.55 Å. This distance is considerably shorter than the measured Sn-C distances, 2.86 and 2.88 Å, in A. In addition to this increase in slip distortion, the bipy ligand adopts an orientation such that the N atoms are trans to the cage C atoms and an inclination such that it is bent away from the cage C atoms.
Similar structural changes have been reported in smaller metallacarborane systems. In the pentagonal bipyrimidal analogue 2,3-(SiMe$_3$)$_2$-1,2,3-closo-SnC$_2$B$_4$H$_4$, distances from Sn to cage C atoms are 2.50 and 2.48 Å. On moving to the adduct 1-(bipy)-2,3-(SiMe$_3$)$_2$-1,2,3-closo-SnC$_2$B$_4$H$_4$, the Sn-C distances increase to 2.75 and 2.70 Å. The bipy N atoms are again trans to the cage C atoms. The bipy ligand is also clearly inclined with respect to the polyhedron. These structures are shown in figure 2.1.3.

![Figure 2.1.3](image)

**Figure 2.1.3** Structures of the pentagonal bipyrimidal stannacarborane 2,3-(SiMe$_3$)$_2$-1,2,3-closo-SnC$_2$B$_4$H$_4$ and its bipy adduct.

In this chapter are described the syntheses and characterisation of new germacarboranes 1,2-Me$_2$-3,1,2-closo-GeC$_2$B$_9$H$_9$ and 1,2-µ-(CH$_2$)$_3$-3,1,2-closo-GeC$_2$B$_9$H$_9$. For the purposes of quantifying the effect that substituents on the cage carbon atoms have on molecular structure, the syntheses and complete characterisation of two analogous ruthenacarboranes, 1,2-Me$_2$-3-(p-cymene)-3,1,2-closo-RuC$_2$B$_9$H$_9$ and 1,2-µ-(CH$_2$)$_3$-3-(p-cymene)-3,1,2-closo-RuC$_2$B$_9$H$_9$, are included. The bipy adducts of 1,2-Me$_2$-3,1,2-closo-GeC$_2$B$_9$H$_9$ and 1,2-Me$_2$-3,1,2-closo-PbC$_2$B$_9$H$_9$ are also reported and the molecular structures of these metallacarboranes and adducts are compared in order to explore how the geometry of the cage framework differs upon adduct formation.
2.2 Synthesis of 1,2-Me$_2$-3,1,2-closo-GeC$_2$B$_9$H$_9$ (1)

Deprotonation$^8$ of HNMe$_3$[7,8-Me$_2$-7,8-nido-C$_2$B$_9$H$_{10}$]$^8$ with $n$-BuLi followed by treatment with GeI$_2$ yielded the half-sandwich compound 1,2-Me$_2$-3,1,2-closo-GeC$_2$B$_9$H$_9$ (1) in 42% isolated yield. The product was purified by sublimation at 80°C under dynamic Schlenk vacuum and fully characterised by mass spectrometry, microanalysis and IR and NMR spectroscopic studies. Unfortunately, the colourless crystals obtained by diffusion of a DCM solution of 1 and 40-60 petroleum ether at 5°C were not of sufficient quality for X-ray diffraction studies.

Analysis of 1 revealed a broad peak in the IR spectrum at $\nu_{\text{max}}$ 2587 cm$^{-1}$, characteristic of B-H stretch. Mass spectrometry shows the parent ion to have a mass of 232 with the ubiquitous heteroborane envelope from 224 to 239, consistent with the expected mass for C$_4$H$_{15}$B$_9$Ge of 233. Elemental analysis was in fair agreement with the values expected for C$_4$H$_{15}$B$_9$Ge.

The $^1$H NMR spectrum of 1 shows the six H atoms of the two methyl groups as a singlet at 2.15 ppm. $^{11}$B$^{[1]}$H NMR spectroscopy revealed four peaks in the relative ratio 2:1:4:2. However, to be consistent with the $C_s$ symmetry anticipated for this molecule, up to six signals could be expected in the ratio 2:2:1:1:1. A degree of signal overlap is therefore assumed in the $^{11}$B$^{[1]}$H NMR spectrum of 1.
2.3 Synthesis of 1,2-µ-(CH₂)₃-3,1,2-closo-GeC₂B₉H₉ (2)

HNMe₃[7,8-µ-(CH₂)₃-7,8-nido-C₂B₉H₁₀] was deprotonated with n-BuLi and GeI₂ was then added to afford the half-sandwich compound 1,2-µ-(CH₂)₃-3,1,2-closo-GeC₂B₉H₉ (2) in 46% yield. The product sublimed at 80°C under dynamic Schlenk vacuum and was characterised by IR and NMR spectroscopies, mass spectrometry and microanalysis. Colourless crystals of quality suitable for an X-ray diffraction analysis of 2 were grown by diffusion of a DCM solution and 40-60 petroleum ether.

Analysis of 2 revealed a broad peak in the IR spectrum at νₑₓₓ 2598 cm⁻¹, characteristic of B-H stretch. Mass spectrometry shows the parent ion to have a mass of 244 with a broad heteroborane envelope from 234 to 250 whilst elemental analysis was in good agreement with the values expected for C₅H₁₅B₉Ge.

The ¹H NMR spectrum of 2 shows the six H atoms of the tether as two multiplets centred on 2.55 and 2.35 ppm. ¹¹B{¹H} NMR spectroscopy revealed four peaks in the relative ratio 1:4:2:2. Theoretically, this molecule could display up to six signals as described for 1. This simplified spectrum of 2 presumably results from signal overlap.

The structure of 1,2-µ-(CH₂)₃-3,1,2-closo-GeC₂B₉H₉ (2) was established by single-crystal X-ray diffraction analysis. Four molecules of 2 crystallise in the orthorhombic space group Aba2.
Figure 2.3.1  Disorder in compound 2.

Consistent with this, and as shown in figure 2.3.1, the molecule exhibits crystallographic $C_2$ symmetry (the $C_2$ axis runs through C12 and the midpoint between B9 and B12) which necessitates structural disorder. Disordered component Ge3A, symmetrically equivalent to Ge3, sits above B6. Similarly, B6A sits underneath Ge3, with both sites being assigned 0.5 occupancy. These symmetry equivalent atoms have been removed in figure 2.3.2 and the molecule renumbered for consistency with other structures following.
The icosahedral structure of 2 is now clear, with all sites in the cage degree-five. The molecule has effective $C_5$ symmetry. The $C_3$ tether is in a planar conformation, instead of its usual envelope conformation, but this is a consequence of the crystallographically-imposed $C_2$ symmetry of the disordered structure. As noted previously, in figure 2.3.2 symmetry equivalent atoms have now been relabelled in order to mimic the numbering scheme of 12-vertex cages in general space.
2.4  Synthesis of 1,2-Me₂₃-(p-cymene)-3,1,2-closo-RuC₂B₉H₉ (3)

Deprotonation of HNMe₃[7,8-Me₂-7,8-nido-C₂B₉H₁₀] with n-BuLi, under THF reflux, followed by treatment with [Ru(p-cymene)Cl₂]₂ in THF produced a brown mixture. Column chromatography was carried out on the crude mixture to yield one major yellow compound, 1,2-Me₂₃-(p-cymene)-3,1,2-closo-RuC₂B₉H₉ (3). X-ray diffraction quality crystals were grown by diffusion of a CDCl₃ solution of 3 and 40-60 petroleum ether at room temperature.

Elemental analysis was in reasonable agreement with the expected values and the IR spectrum showed a broad peak centred on νmax 2534 cm⁻¹ consistent with B-H stretch.

The molecular ion was found in the mass spectrum at m/z 396, with a typical carborane envelope from 389 to 401. The confirmed the product as (C₁₀H₁₄)RuMe₂C₂B₉H₉.

¹H NMR spectroscopy revealed the fourteen protons of the p-cymene group; two doublets of total relative integral four at δ 5.85-5.70 corresponding to the protons on the cymene ring, a septet of integral one at δ 2.95 for the methyne proton of the isopropyl group, a singlet of integral three at δ 2.30 due to the methyl group para to the isopropyl group and doublet of integral six at δ 1.35 for the two equivalent methyl groups of the isopropyl group. In the NMR experiment, these methyl groups are effectively equivalent due to the free rotation of the p-cymene ring in solution at room temperature. This is a common feature for ruthenacarboranes that possess cage mirror symmetry. The cage CH₃ groups appear as one broad singlet of integral six at δ 2.15, indicating that they are equivalent.

¹¹B{¹H} NMR spectroscopy showed five peaks at δ 1.10, -0.28, -3.03, -9.67 and -14.48 in the ratio 1:1:2:2:3. This molecule would be expected to display up to six signals in a 2:2:2:1:1:1 ratio. The observed pattern must result from signal overlap.

An X-ray diffraction study confirmed the structure as 1,2-Me₂₃-(p-cymene)-3,1,2-closo-RuC₂B₉H₉. The asymmetric fraction of the unit cell contains two crystallographically independent molecules A and B. No pronounced differences exist between molecules A and B in the solid state. Molecule A is shown in figure 2.4.1.
Figure 2.4.1  Molecular structure of 1,2-Me₂-3-(p-cymene)-3,1,2-closo-RuC₂B₉H₉ (3).
2.5 Synthesis of 1,2-\(\mu\)-(CH\(_2\))\(_3\)-3-(p-cymene)-3,1,2-closo-RuC\(_2\)B\(_9\)H\(_9\) (4)

Deprotonation of HNMe\(_3\)[7,8-\(\mu\)-(CH\(_2\))\(_3\)-7,8-nido-C\(_2\)B\(_9\)H\(_{10}\)] with \(n\)-BuLi and subsequent addition of [Ru(p-cymene)Cl\(_2\)]\(_2\) in THF at 0°C, produced, on warming to room temperature, a cloudy, dark brown solution. Following column chromatography, the product 1,2-\(\mu\)-(CH\(_2\))\(_3\)-3-(p-cymene)-3,1,2-closo-RuC\(_2\)B\(_9\)H\(_9\) (4) was obtained as a yellow solid. Yellow crystals of quality suitable for an \(X\)-ray diffraction analysis of 4 were grown by diffusion of a CDCl\(_3\) solution and 40-60 petroleum ether at room temperature.

Compound 4 was fully characterised. Expected and found elemental analyses were in very good agreement and the IR spectrum revealed a broad peak at \(\nu_{\text{max}}\) 2535 cm\(^{-1}\) consistent with BNH stretch.

Mass spectrometry confirmed the molecular weight of (C\(_{10}\)H\(_{14}\))Ru(CH\(_2\))\(_3\)C\(_2\)B\(_9\)H\(_9\) to be 408, with a typical carborane envelope from 401 to 413.

The fourteen protons of the \(p\)-cymene group can be clearly identified in the \(^1\)H NMR spectrum; two doublets of relative integral four at \(\delta\) 5.77-5.65 due to the protons on the cymene ring, a septet of integral one at \(\delta\) 3.00 for the central proton of the isopropyl group, a singlet of integral three at \(\delta\) 2.36 corresponding to the methyl group \(para\) to the isopropyl group and a doublet of integral six at \(\delta\) 1.35 due to the two equivalent methyl groups on the isopropyl group. The protons from the tether appear as two 3H multiplets between 2.88-2.78 and 2.69-2.60 ppm.

The \(^{11}\)B\{\(^1\)H\} NMR spectrum contains five peaks in a 1:1:2:3:2 ratio, from high frequency to low frequency. The most logical explanation for the reduction in number of peaks found relative to the maximum number of resonances possible is overlapping of signals.

\(X\)-ray diffraction studies confirmed the structure as 1,2-\(\mu\)-(CH\(_2\))\(_3\)-3-(p-cymene)-3,1,2-closo-RuC\(_2\)B\(_9\)H\(_9\). The unit cell contained three crystallographically independent molecules A, B and C. These molecules are essentially the same, although there is disorder in the isopropyl group of molecule A. Molecule C is shown in figure 2.5.1.
Figure 2.5.1 Molecular structure of 1,2-µ-(CH$_2$)$_3$-3-(p-cymene)-3,1,2-closo-RuC$_2$B$_9$H$_9$ (4).
2.6 Synthesis of 1,2-Me₂-3-(bipy)-3,1,2-closo-GeC₂B₉H₉ (5)

A toluene solution of 1 was added with stirring to a toluene solution of bipy and a yellow precipitate formed instantly. After leaving to stir overnight, this solid was washed with petroleum ether and X-ray diffraction quality yellow crystals were grown by diffusion of 40-60 petroleum ether and a DCM solution of 5 at 25°C.

The mass spectrum of 5 did not exhibit the parent ion, but did show fragments at $m/z$ 231 and 154 corresponding to M-bipy and M-GeC₄B₉H₁₅, respectively. The absence of the parent ion, coupled with the presence of the bipy ion fragment with 100% relative intensity, indicate that the Ge-N bonds in 5 are very weak and were ruptured during the ionisation. Elemental analysis gave results in good agreement with the expected values for C₁₄H₂₃N₂B₉Ge.

The acquisition of NMR data for compound 5 was inhibited by experimental unavailability.

A suitable crystal of adduct 5 was selected for an X-ray diffraction study, which confirmed the structure as 1,2-Me₂-3-(bipy)-3,1,2-closo-GeC₂B₉H₉ (figure 2.6.1).
The icosahedral cage structure is still in place in compound 5, but it is slightly distorted due to the Ge atom having to make a further two connections to the N atoms of the bipy ligand. The Ge-C connections suffer the most, with G3-C1 and Ge3-C2 distances of 2.760(5) and 2.772(5) Å, respectively. The Ge-C1 and Ge-C2 distances are in fact so long that they exceed the sum of covalent radii for Ge and C and therefore these connectivities appear as dashed lines. The distances between the Ge atom and the boron atoms on the upper belt are all long – Ge3-B8 is 2.209(6) Å, Ge3-B4 is 2.420(6) Å and Ge3-B7 is 2.425(7) Å. Connectivities Ge3-N1 and Ge3-N2 measure 2.192(4) Å and 2.220(4) Å, respectively. The bipy ligand is inclined at an angle of 24.4° with respect to the cage framework and oriented so that its N atoms are trans to the cage C atoms.
2.7 Synthesis of $\text{1,2-Me}_2\text{-3-(bipy)-3,1,2-closo-PbC}_2\text{B}_9\text{H}_9$ (6)

To a stirring toluene solution of bipy was added slowly a toluene solution of $\text{1,2-Me}_2\text{-3,1,2-closo-PbC}_2\text{B}_9\text{H}_9$. The yellow adduct $\text{1,2-Me}_2\text{-3-(bipy)-3,1,2-closo-PbC}_2\text{B}_9\text{H}_9$ (6) was precipitated at once. After thorough washing with petroleum ether, crystals suitable for $X$-ray diffraction were grown by slow evaporation of a DCM solution of 6 at room temperature.

Full characterisation of compound 6 was restricted due to experimental unavailability.

An $X$-ray diffraction study confirmed the structure as $\text{1,2-Me}_2\text{-3-bipy-3,1,2-closo-PbC}_2\text{B}_9\text{H}_9$ (6), shown in figure 2.7.1.

![Molecular structure of 1,2-Me_2-3-(bipy)-3,1,2-closo-PbC_2B_9H_9 (6).](image)

**Figure 2.7.1** Molecular structure of $\text{1,2-Me}_2\text{-3-(bipy)-3,1,2-closo-PbC}_2\text{B}_9\text{H}_9$ (6).
A similar structure is observed for 6 as was reported for 5. The Pb3-C1 and Pb3-C2 bond distances are very long, at 3.005(7) Å and 2.975(7) Å, respectively, and for reasons discussed in section 2.6, appear as dashed lines. Long distances are also noted for Pb3-B8, Pb3-B4 and Pb3-B7 (2.454(9) Å, 2.701(9) Å and 2.627(9) Å), while the Pb3-N connectivities measure 2.483(6) Å for Pb3-N1 and 2.536(6) Å for Pb3-N2. As observed for compound 5, the N atoms on the bipy ligand are positioned trans to the cage C atoms and the bipy is tilted away from C1 and C2 by an angle of 11.4° with respect to the carborane.
2.8 Discussion

In a manner adapted from that originally described by Rudolph, the icosahedral
germacarborane 1,2-Me_2-3,1,2-closo-GeC_2B_9H_9 (1) was synthesised and characterised
by NMR and IR spectroscopies, mass spectrometry and elemental analysis. Unfortunately, it was not possible to obtain crystals of 1 suitable for X-ray diffraction
experiments. A subsequent bipy adduct of 1 was synthesised, 1,2-Me_2-3-(bipy)-3,1,2-
closo-GeC_2B_9H_9 (5). The instantaneous formation of the adduct upon addition of the
ligand was in contrast to the subicosahedral germacarboranes, which did not readily
form adducts and required constant stirring for 4-7 days at room temperature to
complete the complexation. Study into the structural changes in the polyhedral cage
induced by the bipy ligation in 5 was frustrated, as there was no reference structure of 1.
In order to overcome this obstacle, a C_3 tether alternative was synthesised, 1,2-μ-(CH_2)_3-3,1,2-GeC_2B_9H_9 (2). This compound was fully characterised and the crystal
structure of 2 is the first reported of a 12-vertex group 14 metallacarborane with a naked
metal atom.

2.8.1 Effect of adduct formation on the structure of germacarboranes

The structural differences between 1 and 2 must be established before comparisons
could be made between 2 and 5. To facilitate the investigation into dimethylated and
tethered metallacarboranes, two analogous ruthenacarboranes, 1,2-Me_2-3-(p-cymene)-
3,1,2-closo-RuC_2B_9H_9 (3) and 1,2-μ-(CH_2)_3-3-(p-cymene)-3,1,2-closo-RuC_2B_9H_9 (4),
were synthesised and completely characterised. For comparison, table 2.8.1.1 lists cage
connectivities and selected molecular parameters for 3 and 4. The slip distortion – the
distance the metal atom is displaced from a position above the centroid of the lower
pentagon of five B atoms – is assigned the symbol Δ and the perpendicular displacement
of the metal atom above the least-squares plane through the lower belt of B atoms is
given the symbol z.
The most significant difference between the dimethylated and tethered species is found in the CNC distance, which is on average 0.059(11) Å longer in 3 compared to 4. It is reasonable that the CNC bond could be shorter in the tethered species as it is constrained within a five-membered ring in this structure. Between 3 and 4 there are insignificant variations in connectivities between the Ru atom and the top belt of the cage, which suggests that the differing C\textsubscript{cage} substituents have no influence on the bonding of the
metal. There is no slip distortion in the dimethyl compound 3, whereas in the tethered ruthenacarborane 4 there is an average $\Delta$ value of 0.101 Å. It can therefore be concluded that the presence of a C$_3$ tether adds *ca.* 0.1 Å to the total slip of the metal.

The conclusions from the ruthenacarborane study now allow a confident comparison to be made between the structures of 1,2-$\mu$-(CH$_2$)$_3$-3,1,2-*closo*-GeC$_2$B$_9$H$_9$ (2) and the bipy adduct 1,2-Me$_2$-3-(bipy)-3,1,2-*closo*-GeC$_2$B$_9$H$_9$ (5), to determine what effect adduct formation has on the polyhedral geometry of the germacarborane in spite of the differing C$_{cage}$ substituents in 2 and 5. The lengths of the cage connectivities and selected derived structural parameters for 2 and 5 are listed in table 2.8.1.2.
The icosahedral structure of the germacarborane is retained in adduct 5, but there is some distortion of the polyhedron arising from the weakening of connectivities from the metal atom to the top C1C2B4B8B7 belt of atoms. This is caused by the two further connections Ge must make to the N atoms of the bipy ligand. The Ge3-C distances in the germacarborane, at 2.28 and 2.29 Å, are much shorter than those recorded in the

\[ \begin{array}{c|cc}
   & 2 & 5 \\
   \hline
   \text{Ge3-C1} & 2.277(3) & 2.760(5) \\
   \text{Ge3-C2} & 2.286(3) & 2.772(5) \\
   \text{Ge3-B4} & 2.220(4) & 2.420(6) \\
   \text{Ge3-B8} & 2.183(5) & 2.209(6) \\
   \text{Ge3-B7} & 2.228(4) & 2.425(6) \\
   \text{C1-C2} & 1.614(5) & 1.567(7) \\
   \text{C1-B4} & 1.704(5) & 1.645(8) \\
   \text{C1-B5} & 1.697(5) & 1.706(8) \\
   \text{C1-B6} & 1.713(9) & 1.725(8) \\
   \text{C2-B7} & 1.697(5) & 1.656(8) \\
   \text{C2-B11} & 1.704(5) & 1.724(8) \\
   \text{C2-B6} & 1.706(9) & 1.727(8) \\
   \text{B4-B9} & 1.756(6) & 1.760(9) \\
   \text{B4-B5} & 1.760(5) & 1.787(8) \\
   \text{B4-B8} & 1.800(5) & 1.794(9) \\
   \text{B5-B6} & 1.701(10) & 1.751(9) \\
   \text{B5-B10} & 1.797(5) & 1.762(9) \\
   \text{B5-B9} & 1.760(6) & 1.762(9) \\
   \text{B6-B11} & 1.700(9) & 1.751(9) \\
   \text{B6-B10} & 1.671(11) & 1.768(9) \\
   \text{B7-B12} & 1.760(6) & 1.762(9) \\
   \text{B7-B11} & 1.760(5) & 1.785(9) \\
   \text{B7-B8} & 1.797(5) & 1.807(8) \\
   \text{B8-B9} & 1.768(6) & 1.768(8) \\
   \text{B8-B12} & 1.774(6) & 1.780(8) \\
   \text{B9-B10} & 1.774(6) & 1.798(9) \\
   \text{B9-B12} & 1.797(9) & 1.807(9) \\
   \text{B10-B11} & 1.800(5) & 1.766(9) \\
   \text{B10-B12} & 1.768(6) & 1.779(9) \\
   \text{B11-B12} & 1.756(6) & 1.756(9) \\
   \hline
   \Delta & 0.159 & 0.676 \\
   \Delta_d & & 0.517 \\
   z & 3.175 & 3.483 \\
\end{array} \]

Table 2.8.2.1 Cage connectivities and selected derived structural parameters (Å) in 2 and 5.
bipy adduct at 2.76 and 2.77 Å. The Ge3-B connectivities are also found to be longer in
the adduct, but not to the same extent as observed for the Ge3-C distances. The weaker
Ge-C connections in adduct 5 compared to uncomplexed 2 mean that \( \Delta \) is greater in the
adduct with a value of 0.68 Å. The increase in slip in 5 with respect to that in 2 is
defined as \( \Delta_s \) and is calculated to be 0.52 Å. The slip distortion is so much greater in 5
than in 2 in spite of 2 having a C\(_3\) tether, which had previously shown to cause an
increase in \( \Delta \) of ca. 0.1 Å. The \( z \) value is ca. 0.3 Å greater in 5, which is expected as the
germanium atom is less tightly bound to the cage than in 2. The bipy ligand is clearly
tilted away from the cage C atoms in 5 and is oriented so that N2 is trans to C1 and N1
is trans to C2 (see figure 2.6.1). The ligand adopts this orientation so that the Sn-N
connectivities are opposite the weakest connectivities between the Sn and the top belt of
atoms.

2.8.2 Periodic trends in the structures of 1,2-Me\(_2\)-3-(bipy)-3,1,2-closo-MC\(_3\)B\(_9\)H\(_9\)
\((M = \text{Ge, Sn, Pb})\)

The Pb analogue of the Ge species 5 and the Sn species A, 1,2-Me\(_2\)-3-(bipy)-3,1,2-
closo-PbC\(_2\)B\(_3\)H\(_9\) (6), was synthesised in order to complete the set of group 14
compounds. Again, adduct formation was instant, unlike the slow synthesis observed
for the subicosahedral lead adducts.\(^{10}\) The formation of 6 allowed the structures of all
three adducts to be analysed and any structural trends as the group is descended to be
investigated.

Table 2.8.2.1 lists the cage connectivities for adducts 5, A and 6, together with the \( M-N \)
distances in each case.
Table 2.8.2.1 Cage connectivities and $M$-$N$ distances (Å) in adducts 5, A and 6.

The $M$-$C$ connectivities are the longest in each adduct and these distances increase on going from 5 (Ge) to A (Sn) to 6 (Pb). The $M$-$B$ distances also experience an increase but not as significantly as the $M$-$C$ distances. Of all the connections the metal makes to the top belt $M3$-$B8$ is, as expected, always the shortest, as the direction of slip is always towards the unique boron atom, B8. The distances between $M$ and N are longest in 6 and shortest in 5. In the pentagonal bipyramidal system 1-(bipy)-2,3-(SiMe$_3$)$_2$-1,2,3-closo-$MC_2B_4H_4$ ($M$ = Ge, Sn and Pb), one $M$-$N$ bond is significantly shorter than the
other when \( M = \text{Ge} \) and \( \text{Pb} \), causing a severe tilting of the ligand towards two adjacent boron atoms of the \( \text{C}_3\text{B}_3 \) face,\(^{11} \) while the \( M-N \) distances are equal when \( M = \text{Sn}. \)\(^{6} \) This preference for bidentate coordination in the stannacarborane is not reproduced here.

Selected derived molecular parameters for the three adducts \( 5, \ A \) and \( 6 \) are given in table 2.8.2.2. The inclination of the bipy ligand to the cage is quantified as \( \theta \), the dihedral angle between the least-squares plane through the lower belt of five B atoms and the \( \text{M}3\text{N}1\text{CCN}2 \) plane. The twisting of the bipy ligand about its central C-C bond is quantified as the dihedral angle between NC\(_5 \) planes, \( \chi \).

<table>
<thead>
<tr>
<th></th>
<th>( 5 ) (Ge)</th>
<th>( A ) (Sn)</th>
<th>( 6 ) (Pb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta )</td>
<td>0.676</td>
<td>0.629</td>
<td>0.659</td>
</tr>
<tr>
<td>( \theta )</td>
<td>24.4</td>
<td>22.5</td>
<td>11.4</td>
</tr>
<tr>
<td>( z )</td>
<td>3.483</td>
<td>3.642</td>
<td>3.776</td>
</tr>
<tr>
<td>( \chi )</td>
<td>9.0</td>
<td>10.1</td>
<td>3.0</td>
</tr>
</tbody>
</table>

**Table 2.8.2.2** Selected derived molecular parameters (Å, °) in adducts \( 5, \ A \) and \( 6 \) by crystallographic analysis.

The slip of the metal is greatest in the germanium species, \( 5 \), while it is smallest in the tin species, \( A \). In \( 5 \) and \( A \), the bipy ligand is significantly twisted, with \( \chi \) angles measuring 9.0° and 10.1°, respectively. Much less twisting is evident in the bipy ligand of \( 6 \); \( \chi \) here is only 3.0°. The \( z \) value increases on going from \( 5 \) to \( A \) to \( 6 \), as would be expected as we increase the size of the metal atom from Ge to Sn to Pb. As seen in table 2.8.4 and clearly visible from figures 2.6.1 and 2.7.1, \( \theta \) is much smaller in \( 6 \) than in \( 5 \) (and \( A \)). The smaller \( \theta \) value in \( 6 \) can be attributed to crystal packing effects. On examination of the unit cell shown in figure 2.8.2.1, it can be seen that the plane of the bipy ligand of one molecule is \( \pi-\pi \) stacked with the plane of the bipy ligand of the molecule related across the inversion centre at \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\). The perpendicular distance between these planes is 3.36 Å, well within the range normally associated with \( \pi-\pi \) stacking\(^{12} \) and close enough to influence the orientation of the ligand. It should be noted that the structures of \( 5, \ A \) and \( 6 \) are not isomorphous.
Figure 2.8.2.1  The unit cell of 6, which shows how the crystal packing influences the molecular geometry.

Figure 2.8.2.2 illustrates the structures of the pentagonal bipyramidal analogues of 5, A and 6; 1-(bipy)-2,3-(SiMe$_3$)$_2$-1,2,3-closo-GeC$_2$B$_4$H$_4$ (B)\(^{13}\), 1-(bipy)-2,3-(SiMe$_3$)$_2$-1,2,3-closo-SnC$_2$B$_4$H$_4$ (C)\(^{6}\) and 1-(bipy)-2,3-(SiMe$_3$)$_2$-1,2,3-closo-PbC$_2$B$_4$H$_4$ (D).\(^{14}\)
Figure 2.8.2.2  Structures of 1-(bipy)-2,3-(SiMe$_3$)$_2$-1,2,3-closo-GeC$_2$B$_4$H$_4$ (B)$_{13}$, 1-(bipy)-2,3-(SiMe$_3$)$_2$-1,2,3-closo-SnC$_2$B$_4$H$_4$ (C)$_6$ and 1-(bipy)-2,3-(SiMe$_3$)$_2$-1,2,3-closo-PbC$_2$B$_4$H$_4$ (D)$_{14}$.

Table 2.8.2.3 summarises the derived structural parameters of adducts B, C and D to determine if the same relationships exist in these species as were observed earlier for their icosahedral counterparts.

<table>
<thead>
<tr>
<th></th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta$</td>
<td>0.405</td>
<td>0.440</td>
<td>0.329</td>
</tr>
<tr>
<td>$\theta$</td>
<td>29.3</td>
<td>24.2</td>
<td>25.1</td>
</tr>
<tr>
<td>$z$</td>
<td>1.931</td>
<td>2.130</td>
<td>2.238</td>
</tr>
<tr>
<td>$\chi$</td>
<td>11.1</td>
<td>5.6</td>
<td>9.2</td>
</tr>
</tbody>
</table>

Table 2.8.2.3  Selected molecular parameters (Å, °) in adducts B, C and D.

The only common trend between the two sets of adducts is the increase in $z$ from the Ge to the Pb species. $\theta$ is quite similar for all the pentagonal bipyramidal adducts – there is no packing effect evident in D as there was for its icosahedral analogue. The greatest slip distortion is recorded in the tin species C; in the icosahedral system the tin species A showed the least slip. Once again, structures B, C and D are non-isomorphous.

The distances between $M$ and the top belt of atoms are longer and the $M$-N connectivities are shorter in the icosahedral species compared to their pentagonal bipyramidal analogues. The net result is that for main group metals, slip distortion is greater in the icosahedral species compared to the pentagonal bipyramidal species. It is interesting to note that this observation is reversed for platinacarboranes – a larger
slippage is noted in the 7-vertex 1,1-(PEt$_3$)$_2$-2,3-Me$_2$-1,2,3-closo-PtC$_2$B$_4$H$_4$ compared to the 12-vertex 3,3-(PEt$_3$)$_2$-1,2,3-closo-PtC$_2$B$_9$H$_{11}$.$^{15,16}$
2.9 Summary

The icosahedral germacarboranes 1 and 2 were synthesised in a manner similar to that described by Rudolph\(^1\) for the synthesis of the group 14 metallacarboranes \(3,1,2-MC_2B_{9}H_{11}\). The bipy adducts 5 and 6 were subsequently synthesised using the same technique adopted by Jutzi et al. for the preparation of the Sn analogue A.\(^2\) The structures of 5, A and 6 are illustrated in figure 2.9.1.

\[ \text{Figure 2.9.1 Adducts 5, A and 6.} \]

The same type of structural distortions observed in the smaller pentagonal bipyramidal analogues have been reproduced in these icosahedral systems. Adduct formation causes the \(M-C\) distances to lengthen as the metal atom slips further across the carborane ligand face. Also, there is a clear inclination of the bipy ligand with respect to the carborane cage framework and the bipy is oriented so that its N atoms are trans to the cage C atoms. By adopting this position, the bipy N atoms are opposite the weakest connectivities in the cage.

Analysis of the molecular structures of adducts 5, A and 6 revealed little difference in the \(\Delta\) values, with the greatest slippage reported in the germanium species. The dihedral angle \(\theta\) in the Pb species was much smaller than those recorded in 5 and A. This observation can be rationalised by crystal packing effects.
2.10 References


Chapter 3  
Adducts of the Supraicosahedral Stannacarborane  
1,6-Me₂-4,1,6-closο-SnC₂B₁₀H₁₀

3.1 Introduction

A wide range of supraicosahedral metallacarboranes have resulted from the two electron reduction of 1,2-closο-C₂B₁₀H₁₂ (or its C-dimethyl derivatives) and subsequent addition of a metal fragment. The first example, 4-Cp-4,1,6-closο-CoC₂B₁₀H₁₂, was reported in 1971¹ and since then many 13-vertex metallacarboranes have been synthesised incorporating metals from all over the Periodic Table. However, notable by its absence has been literature documenting supraicosahedral metallacarboranes of the p-block elements. In 2002, two such species, 4,1,6-closο-SnC₂B₁₀H₁₂ and 1,6-Me₂-4,1,6-closο-SnC₂B₁₀H₁₀(E), were reported by Welch and co-workers.²

Reaction of a THF solution of Na₂[7,9-nido-C₂B₁₀H₁₂] (prepared by Na reduction of 1,2-closο-C₂B₁₀H₁₂) with one equivalent of SnCl₂ at 0°C afforded the colourless stannacarborane 4,1,6-closο-SnC₂B₁₀H₁₂ in 44% yield after work-up. An analogous reaction starting with Na₂[7,9-Me₂-7,9-nido-C₂B₁₀H₁₀] produced E in 31% yield (see figure 3.1.1).

![Figure 3.1.1](image)

Figure 3.1.1 Synthesis of the first reported examples of supraicosahedral p-block metallacarboranes.

These compounds represent the first 13-vertex metallacarboranes involving p-block metals. They were characterised by mass spectrometry and ¹H, ¹¹B and ¹³C NMR
spectroscopies. A single-crystal X-ray diffraction study of the C-dimethyl analogue (figure 3.1.2) showed that the molecule shares the same basic polyhedral docosahedral geometry observed in earlier 13-vertex metallacarboranes. With respect to the polyhedron, the Sn4 and B5 vertices are both degree-six, while only C1 is degree-four. When compared to distances observed in smaller stannacarboranes,\textsuperscript{3, 4} connectivities between Sn4 and adjacent boron atoms are somewhat longer. Also, the Sn4-C6, B5-B2 and B5-B3 distances are considerably long, fully consistent with results from prior studies on 13-vertex $MC_2B_{10}$ species.\textsuperscript{5, 6}

![Figure 3.1.2](image)

**Figure 3.1.2** Perspective view of 1,6-Me\textsubscript{2}-4,1,6-closo-SnC\textsubscript{2}B\textsubscript{10}H\textsubscript{10} (E).

These supraicosahedral stannacarboranes are extremely air sensitive. They decompose after only a few minutes in air with formation of a black solid, suggesting that tin metal is extruded from the cage.

The fluxional nature of 4,1,6-$MC_2B_{10}$ metallacarboranes has been recognised for many years and has been discussed in terms of a $C_1$ transition state related to the ground state molecule by a double diamond-square-diamond rearrangement.\textsuperscript{7} These supraicosahedral stannacarboranes are fluxional in solution, with the room temperature $^{11}$B NMR spectra of both species clearly indicating time-averaged $C_s$ molecular symmetry, although the crystallographic studies reveal asymmetric molecules. However, the fluxionality of these species cannot be arrested by cooling to -90°C.
Consistent with the implication from this fact that the energetic barrier to fluxionality is low, DFT calculation shows that $E_{\text{act}}$ for 4,1,6-\textit{closo}-SnC$_2$B$_{10}$H$_{12}$ is only 25.4 kJ mol$^{-1}$ (see figure 3.1.3).$^2$

![Figure 3.1.3](image1)

\textbf{Figure 3.1.3} The double DSD process involved in the fluxionality of 4,1,6-\textit{closo}-SnC$_2$B$_{10}$H$_{12}$. The calculated activation energy is 25.4 kJ mol$^{-1}$.

Predictably, this flexibility of the kinetic 4,1,6- isomer makes it susceptible to thermal rearrangement. When transition metal 4,1,6-MC$_2$B$_{10}$ metallacarboranes are heated to reflux overnight in THF, the 4,1,8- isomer is produced. The 4,1,8- isomer can undergo further thermal isomerisation when heated to reflux in toluene, resulting in the thermodynamically more stable 4,1,12- isomer (see figure 3.1.4).$^8,9$

![Figure 3.1.4](image2)

\textbf{Figure 3.1.4} Thermal isomerisation of 4,1,6-\textit{closo}-CoC$_2$B$_{10}$H$_{12}$ to 4,1,12-\textit{closo}-CoC$_2$B$_{10}$H$_{12}$ via 4,1,8-\textit{closo}-CoC$_2$B$_{10}$H$_{12}$. 
The separation of the relatively electronegative carbon atoms is seen as the driving force for this process. The 4,1,12-MC\textsubscript{2}B\textsubscript{10} isomer is widely accepted as the thermodynamically most stable as it features the greatest possible carbon atom separation. This process is yet to be investigated for supraicosahedral main group metallacarboranes.

The reactions of 1,6-Me\textsubscript{2}-4,1,6-\textit{closo}-SnC\textsubscript{2}B\textsubscript{10}H\textsubscript{10} (E) with a series of Lewis bases were studied in order to discover if the Lewis acid behaviour of the smaller stannacarboranes extended to this 13-vertex system. In this chapter are presented the syntheses and structures of the adducts 1,6-Me\textsubscript{2}-4-(L\textsubscript{2})-4,1,6-\textit{closo}-SnC\textsubscript{2}B\textsubscript{10}H\textsubscript{10} for L\textsubscript{2} = bipy, o-phen, Me\textsubscript{2}bipy and Ph\textsubscript{2}bipy.
3.2 Synthesis of 1,6-Me₂-4-(bipy)-4,1,6-closo-SnC₂B₁₀H₁₀ (7)

A toluene solution of E was added to a stirring toluene solution of bipy and a yellow precipitate of 7 formed immediately. This solid was washed with petroleum ether and X-ray diffraction quality crystals were grown by diffusion of 40-60 petroleum ether and a THF solution of 7 at 5°C.

Compound 7 is analytically pure by C, H and N microanalysis without the need for chromatography. The B-H stretching frequency at $\nu_{\text{max}}$ 2524 cm$^{-1}$ and the shape of the peak in the IR spectrum are typical for metallacarboranes.

The mass spectrum of 7 did not yield the molecular ion but simply showed envelopes centred on 291 and 171 corresponding to M-L₂ and M-{SnL₂} respectively, as well as a peak for the bipy ligand at 154 (i.e. M-{SnMe₂C₂B₁₀H₁₀}).

$^1$H NMR spectroscopy showed unique resonances for the bipy ligand appearing as a doublet of relative integral two at $\delta$ 8.95, a doublet of integral two at $\delta$ 8.30, a doublet of doublets of integral two at $\delta$ 8.20 and a doublet of doublets of integral two at $\delta$ 7.70. A single resonance at $\delta$ 2.50 was assigned to the cage-bound CH₃ groups.

$^{11}$B{$^1$H} NMR spectroscopy showed five peaks at $\delta$ 6.89, 4.50, -0.74, -4.33 and -8.35 in a 2:1:3:1:3 pattern (all resonances becoming doublets on retention of proton coupling).

The structure of adduct 7 was established by an X-ray diffraction study (figure 3.2.1).
The adduct adopts a docosahedral geometry, albeit with some distortion from what may be regarded as regular. The C atoms are located at positions 1 and 6, which are degree-four and degree-five sites respectively. The Sn atom resides in the degree-six vertex at position 4, while the other degree-six site is occupied by B5. The Sn4-C1, Sn4-B2 and Sn4-C6 cage connectivities are considerably long, at distances of 2.717(3), 3.033(4) and 3.173(4) Å respectively. For these reasons, the Sn4-C1,B2,C6 connectivities in this chapter henceforth appear as dashed lines only. The Sn-N distances are very similar, with values of 2.389(3) Å for Sn4-N41 and 2.384(3) Å for Sn4-N42. The bipy ligand is significantly twisted about its central C-C bond, with a dihedral angle between the NC₅ planes of 15.2°.
Polyhedral distances involving the degree-six B5 are long, particularly its connection with B2. This is a typical feature of 4,1,6-SnC\textsubscript{2}B\textsubscript{10} heteroboranes.\textsuperscript{9,10} B2-B5, B3-B5, B5-B8 and B5-B9 are relatively very long, at 2.065(16), 1.896(6), 1.885(6) and 1.904(6) Å, respectively. The C1-B5 distance, at 1.769(6) Å, is not as long as the four previous connectivities involving B5. In this case, the degree-six B5 is connected to a degree-four atom and the effects of these different connectivities are averaged, as is evident in the intermediate distance between the atoms. The B5-B11 connectivity is quite normal at 1.810(6) Å. The short C1-B2 and C1-B3 distances, 1.512(6) and 1.541(6) Å, are also emblematic of MC\textsubscript{2}B\textsubscript{10} compounds.
3.3 Synthesis of 1,6-Me₂-4-(o-phen)-4,1,6-closo-SnC₂B₁₀H₁₀ (8)

A toluene solution of E was added slowly with stirring to a toluene solution of o-phen. The bright yellow adduct 1,6-Me₂-4-(o-phen)-4,1,6-closo-SnC₂B₁₀H₁₀ (8) was precipitated instantaneously. After thorough washing with petroleum ether, crystals suitable for X-ray diffraction were grown by slow diffusion of 40-60 petroleum ether and a THF solution of 8 at 5°C.

Elemental analysis was in good agreement with the expected values for C₁₆H₂₄B₁₀N₂Sn and IR spectroscopy indicated the presence of B-H with a broad signal at ν_max 2528 cm⁻¹.

The molecular ion was not observed in the mass spectrum but two characteristic carborane envelopes were found centred on 291 (M-L₂) and 171 (M-{SnL₂}).

¹H NMR spectroscopy showed eight protons of the o-phen ligand; a doublet of relative integral two at δ 9.30, a doublet of integral two at δ 8.65, a singlet of integral two at δ 8.10 and a doublet of doublets of integral two at δ 8.00. The cage CH₃ groups appear as one singlet of integral six at δ 2.55, indicating they are equivalent in solution at room temperature.

¹¹B{¹H} NMR spectroscopy showed five peaks at δ 7.25, 4.57, -0.80, -4.57 and -8.38 in the ratio 2:1:3:1:3.

An X-ray diffraction study confirmed the structure as 1,6-Me₂-4-(o-phen)-4,1,6-closo-SnC₂B₁₀H₁₀, 8, shown in figure 3.3.1. This adduct crystallised with one molecule of THF of solvation.
The docosahedral geometry of the 1,6-Me$_2$-4-(o-phen)-4,1,6-closo-SnC$_2$B$_{10}$H$_{10}$ cage is retained upon forming the adduct, but there is some polyhedral distortion arising from the long Sn-C and Sn-B2 distances. The Sn$_4$-C$_1$,B$_2$,C$_6$ connectivities measure 2.725(3) Å, 3.027(3) Å and 3.064(3) Å, respectively. The cage is characterised by short C$_1$-B$_2$ and C$_1$-B$_3$ distances (1.515(5) and 1.540(4) Å), very long B$_2$-B$_5$ and B$_3$-B$_5$ distances (2.059(5) and 1.936(5) Å) and long B$_5$-B$_8$ and B$_5$-B$_9$ connections (1.895(4) and 1.874(6) Å). The C$_1$-B$_5$ distance of 1.790(4) Å is not as long, for reasons discussed earlier. The Sn$_4$-N$_{42}$ distance of 2.397(2) Å is shorter than that between Sn$_4$ and N$_{41}$ which measures 2.425(2) Å.
3.4 Synthesis of 1,6-Me₂-4-(Me₂bipy)-4,1,6-closo-SnC₂B₁₀H₁₀ (9)

Treatment of a toluene solution of Me₂bipy with E in toluene gave a yellow precipitate of 9 that was washed with petroleum ether and dried *in vacuo*. The product was crystallised by slow evaporation of a CD₂Cl₂ solution at room temperature.

Elemental analysis was in good agreement with the values predicted for C₁₆H₂₈B₁₀N₂Sn. IR spectroscopy confirmed the presence of B-H with a broad absorption at \( \nu \text{max} \) 2523 cm\(^{-1}\). Mass spectrometry showed an envelope centred on 291 corresponding to M-L₂ and another at 182 from M-{SnMe₂C₂B₁₀H₁₀}.

Resonances in the \(^1\text{H} \) NMR spectrum for the Me₂bipy ligand were found as follows; a doublet of relative integral two at \( \delta \) 8.75, a singlet of integral two at \( \delta \) 8.08 and a doublet of relative integral two at \( \delta \) 7.48. There are two singlets, each integrating for six protons, at \( \delta \) 2.59 and \( \delta \) 2.49. However, it is unclear which of these CH₃ resonances is due to the Me₂bipy ligand and which to the cage methyl groups.

The \(^{11}\text{B}\{^1\text{H}\} \) NMR spectrum can be interpreted as five peaks at \( \delta \) 6.91, 4.20, -1.07, -4.54 and -8.64 in a 2:1:3:1:3 ratio (high frequency to low frequency).

An X-ray diffraction study of the yellow crystals confirmed compound 9 to be 1,6-Me₂-4-(Me₂bipy)-4,1,6-closo-SnC₂B₁₀H₁₀ (figure 3.4.1). In 9, there is one molecule of CD₂Cl₂ of solvation.
As described for the previous two adducts, the structure of compound 9 is a slightly distorted docosahedron. The significantly long Sn4-C1, Sn4-B2 and Sn4-C6 connectivities measure 2.6502(14) Å, 3.0642(17) Å and 3.1182(15) Å, respectively. The distance from Sn4 to N41 of 2.3854(12) Å is longer than that to N42 of 2.3611(13) Å. Compared to 7, there is much less twist evident here in the Me₂bipy ligand; the dihedral angle between the NC₅ planes is only 0.3°. The high connectivity of B5 is reflected in the B2-B5 and B3-B5 distances (2.086(3) and 1.920(2) Å), which are relatively very long. The B5-B8 and B5-B9 connectivities are long at 1.887(3) and 1.886(2) Å respectively, while C1-B5 is not as long (1.780(2) Å) for reasons discussed earlier. There are short distances observed between C1-B2 and C1-B3 (1.518(2) and 1.540(2) Å).
3.5  Synthesis of 1,6-Me₂-4-(Ph₂bipy)-4,1,6-closo-SnC₂B₁₀H₁₀ (10)

A solution of E in toluene was stirred with a toluene solution of Ph₂bipy, affording 10 as a yellow precipitate. The product was washed with petroleum ether and crystals suitable for X-ray diffraction studies were grown by slow evaporation of a CD₂Cl₂ solution of 10 at room temperature.

IR spectroscopy showed a broad absorption at $\nu_{\text{max}}$ 2530 cm⁻¹ indicative of B-H stretch. Compound 10 is less stable than the previous three adducts and reliable microanalysis could not be obtained. Equally, NMR spectra of solutions of 10 always contained evidence of significant decomposition. Nevertheless, the structural identity of 10 was unequivocally established by a crystallographic study (figure 3.5.1). There is one molecule of CD₂Cl₂ of solvation in 10.

![Figure 3.5.1](image)

**Figure 3.5.1**  Molecular structure of 1,6-Me₂-4-(Ph₂bipy)-4,1,6-closo-SnC₂B₁₀H₁₀ (10).

The cage structure of 10 is essentially docosahedral. This adduct features short C1-B2 and C1-B3 distances (1.539(11) and 1.529(11) Å) and long B2-B5 and B3-B5 distances (2.059(11) and 1.933(11) Å). The especially long polyhedral distances between Sn4
and C1, B2 and C6 cause a distortion of the cage geometry. The connectivities between these atoms measure 2.692(7) Å, 3.008(8) Å and 3.025(7) Å, respectively. The Sn4-N41 distance is again longer than that for Sn4-N42, with a value of 2.374(6) Å for the former and 2.347(7) Å for the latter. The dihedral angle between the NC₅ planes of the Ph₂bipy ligand is 4.5°, which is considerably less than the degree of twisting observed for 7.
3.6 Attempts to isomerise 4,1,6-SnC₂B₁₀ species

1,6-Me₂-4,1,6-*closo*-SnC₂B₁₀H₁₀ (E) and its bipy adduct 7 were each heated to reflux in degassed THF in an effort to obtain the respective 4,1,8- isomer (see figure 3.6.1). Unfortunately, these 4,1,6-SnC₂B₁₀ species simply decomposed upon thermolysis, resulting in the decomposition products 1,2-Me₂-1,2-*closo*-C₂B₁₀H₁₂ (identified by $^{11}$B{¹H} NMR spectroscopy) and Sn metal.

![Diagram of E and 7 isomerisation](image)

**Figure 3.6.1** Unsuccessful isomerisation of E and 7.
3.7 Attempts to synthesise 1,6-Me₂-4,1,6-closo-GeC₂B₁₀H₁₀ and 1,6-Me₂-4,1,6-closo-PbC₂B₁₀H₁₀

Attempts were made to synthesise the analogous germanium and lead compounds of 13-vertex 1,6-Me₂-4,1,6-closo-SnC₂B₁₀H₁₀ (illustrated in figure 3.7.1). The same procedure was used in each case, with germanium(II) iodide and lead(II) chloride employed for the metallation steps. The appropriate parent ion was found in the mass spectrum of the crude mixture for each supraicosahe dral main group metallacarborane. For 1,6-Me₂-4,1,6-closo-GeC₂B₁₀H₁₀ (MW 245), the boron envelope appeared from 239 to 250 and for 1,6-Me₂-4,1,6-closo-PbC₂B₁₀H₁₀ (MW 379), the typical metallacarborane envelope was centred on 386.

![Structures of 1,6-Me₂-4,1,6-closo-GeC₂B₁₀H₁₀ and 1,6-Me₂-4,1,6-closo-PbC₂B₁₀H₁₀.](image)

**Figure 3.7.1** Structures of 1,6-Me₂-4,1,6-closo-GeC₂B₁₀H₁₀ and 1,6-Me₂-4,1,6-closo-PbC₂B₁₀H₁₀.

However, it was not possible to isolate these compounds due to the air sensitivity of each. Efforts to grow crystals of each species were unsuccessful.
3.8 Discussion

3.8.1 Synthesis and Spectroscopy

The 13-vertex stannacarborane $1,6$-$\text{Me}_2$-$4,1,6$-$\text{closo}$-$\text{SnC}_2$-$\text{B}_{10}$-$\text{H}_{10}$ (E) readily reacts with bipy, $\text{o}$-phen, $\text{Me}_2$-bipy and $\text{Ph}_2$-bipy, in toluene, to precipitate the bright yellow adducts $1,6$-$\text{Me}_2$-$4$-(bipy)-$4,1,6$-$\text{closo}$-$\text{SnC}_2$-$\text{B}_{10}$-$\text{H}_{10}$ (7), $1,6$-$\text{Me}_2$-$4$-($\text{o}$-phen)-$4,1,6$-$\text{closo}$-$\text{SnC}_2$-$\text{B}_{10}$-$\text{H}_{10}$ (8), $1,6$-$\text{Me}_2$-$4$-($\text{Me}_2$-bipy)-$4,1,6$-$\text{closo}$-$\text{SnC}_2$-$\text{B}_{10}$-$\text{H}_{10}$ (9) and $1,6$-$\text{Me}_2$-$4$-($\text{Ph}_2$-bipy)-$4,1,6$-$\text{closo}$-$\text{SnC}_2$-$\text{B}_{10}$-$\text{H}_{10}$ (10) in good yield (57-80%). The numbering scheme for these compounds is shown in figure 3.8.1.1.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{numbering.png}
\caption{Line diagrams for numbering.}
\end{figure}

$^1$H and $^{11}$B NMR spectra of 7-9 in CD$_2$Cl$_2$ provide confirmation for an intramolecular fluxional process, given the asymmetric structures revealed by crystallographic study (vide supra). As a result, the $^{11}$B{$^1$H} spectra show a 2:1:3:1:3 ratio of resonances (high frequency to low frequency) between δ +8 and -9 (all resonances becoming doublets on retention of proton coupling, $^1J_{\text{BH}}$ 117-156 Hz). Only a single resonance integrating for six protons is observed for the cage-bound CH$_3$ groups (δ 2.5-3.0) in the $^1$H spectra, in addition to unique resonances for only half the $L_2$ ligand. It can therefore be assumed that, in solution at room temperature, 7-9 are $C_s$-symmetric on the NMR timescale, presumably via the same double diamond-square-diamond isomerisation process that
was previously proposed for $4,1,6$-closo-SnC$_2$B$_{10}$H$_{12}$.$^2$ This gives an idealised 2:2:1:1:1:1:1 ratio of resonances in the $^{11}$B{$_1^1$H} spectra, which can be simply related to two 2+1 co-incidences in the observed patterns for 7-9.

In the $^1$H NMR spectrum of 8, all of the resonances in the aromatic region are shifted to low frequency by $ca.$ 0.3 ppm compared to those of the free $o$-phen ligand, as this ligand is conformationally predisposed to chelation.

### 3.8.2 Molecular structures

Table 3.8.2.1 lists the lengths of cage connectivites and the Sn-N distances in the structures of compound E and adducts 7-10, which were all established by single-crystal X-ray diffraction studies.
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Table 3.8.2.1 Cage connectivities and Sn-N distances (Å) in E and adducts 7-10.

In each case, the basic docosahedral cage structure of E is preserved upon coordination of the $L_2$ ligand, albeit with some distortion. Increased Sn-cage distances are the consequence of addition of the bipy, o-phen, Me$_2$bipy and Ph$_2$bipy ligands, most dramatically Sn4-C1 (2.41 to 2.69-2.75 Å), Sn4-B2 (2.64 to 3.00-3.06 Å) and Sn4-C6 (2.67 to 3.02-3.17 Å). The only apparent exception to this trend is found in 9, where the
Sn4-B7 connectivity is actually shorter (2.14 compared to 2.45 Å). Whilst increases in Sn4-B10 and Sn4-B3 are smaller (ca. 0.15 Å), Sn4-B7 remains, for all intents and purposes, unaffected for the series as a whole.

Long cage connectivities from the six-connected B5 atom are typical of 4,1,6-MC2B10 systems9,10 and are observed in adducts 7-10. This feature can be explained in terms of electronegativities and connectivity numbers of the atoms involved. Evidently, the bonding of B5 to boron atoms which are themselves adjacent to cage carbon atoms is severely weakened. This is the apparent outcome of low electron density associated with the high connection of B5 coupled with the relatively high electronegativity of carbon. Therefore, the B2-B5 (2.06-2.09 Å) and B3-B5 (1.90-1.94 Å) distances are particularly long. The B5-B8 (1.88–1.90 Å), B5-B9 (1.87–1.90 Å) and C1-B5 (1.77-1.79 Å) distances are also long, but not to the same extent.

The above explanation has been used to rationalise why B2-B5 > B3-B5 and B5-B9 > B5-B8 in 4,1,6-MC2B10 heteroboranes.10 However, whilst the first is true also for 7-10, the B5-B8 distance is longer than the B5-B9 distance in 8, while in 9 these distances are almost equal.

<table>
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<th></th>
<th>E</th>
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<th>8</th>
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<th>10</th>
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<td>0.582</td>
<td>0.665</td>
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</tr>
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<td>0.308</td>
<td>0.391</td>
<td>0.275</td>
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<td>20.6</td>
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<tr>
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<td>15.2</td>
<td>0.0</td>
<td>0.3</td>
<td>4.5</td>
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**Table 3.8.2.2** Selected derived molecular parameters (Å, °) in E and compounds 7-10 by crystallographic analysis.

In the icosahedral main group metallacarboranes and adducts described in Chapter 2, slip distortion Δ was defined with respect to the centroid of the lower belt of five boron atoms. For the supraicosahedral stannacarborane E and adducts 7-10, it is the B5B9B12B13B8 pentagon that is employed as the appropriate analogous reference plane. In Table 3.8.2.2 (see also figure 3.8.2.1) it is evident that the Sn atom in E is not
positioned directly above this centroid, but is actually displaced with $\Delta = 0.27$ Å. This slip distortion increases to between 0.55 and 0.67 Å on forming adducts 7-10.

Increase in slip with respect to $E$ is defined as $\Delta \Delta$. The greatest increased slippage is recorded in the Me$_2$bipy adduct 9 at 0.39 Å, whilst the least is found in the Ph$_2$bipy adduct 10 at 0.28 Å. The trend here seems to be that the Sn-cage interactions appear to weaken when a stronger Lewis base is used. A stronger Lewis base will form stronger Sn-N connectivities with the stannacarborane and as a result, the Sn-cage atom connections will weaken, causing the Sn atom to slip further. On the other hand, Sn-N connectivities between the stannacarborane and a weaker Lewis base will not be as strong, so the Sn-cage atom connections will not be weakened to the same extent and the Sn atom will be held more strongly to the cage, prohibiting it from slipping as much.

**Figure 3.8.2.1** View of $E$ perpendicular to the best plane through atoms B5, B9, B12, B13 and B8.
Figures 3.8.2.1 and 3.8.2.2 are projections onto the best (least-squares) plane through the lower pentagon of E and 7 (similar views for 8-10 are essentially equivalent to that for 7). These figures clearly show that the increase in slip is in the direction towards a position above B7. The substantial increases in Sn4-C1, Sn4-B2 and Sn4-C6 distances are fully consistent with this observation. However, since there is also a (smaller) increase in the Sn4-B10 and Sn4-B3 connectivities on adduct formation, and Sn4-B7 is effectively unchanged, an alternative description of the structural change accompanying $L_2$ addition to E would be a hinge distortion (pivoting about an axis parallel to B3---B10 and passing through B7) rather than a slip distortion. With increased hinging the Sn atom is located further above the B5 reference plane. The parameter $z$ is defined as the perpendicular displacement of Sn above the least-squares plane through atoms B5B9B12B13B8. It should be noted that $z$ increases from 3.40 Å in E to 3.65-3.69 Å in 7-10.

The trend of the ligand orientation with its N atoms opposite the weakest connections in the cage, observed in the icosahedral main group metallacarborane adducts described in
chapter 2, is reproduced here in the supraicosahedral 4,1,6-SnC₂B₁₀ system. In each adduct 7-10, the N atoms of the ligand are opposite the Sn₄-C₁, Sn₄-B₃ and Sn₄-C₆ connections, all of which undergo a significant increase upon adduct formation.

As described earlier, the Sn₄-N4₁ distance in 7 is longer than that for Sn₄-N4₂ in adducts 8, 9 and 10. In 7, the Sn-N distances are nearly identical. The fact that Sn₄-N4₂ is shorter than Sn₄-N4₁ can be explained in terms of the relative trans influences of B and C atoms in carborane ligands and the well-known localisation of the frontier orbitals of nido carboranes away from the cage C atoms of the open face.¹¹ N4₂ is almost exactly trans to C₆ and this results in a shortening of the Sn₄-N4₂ distance. Conversely, N4₁ is trans to the C₁-B₂ edge, so the Sn₄-N4₁ distance is longer. These arguments were originally established for icosahedral metallacarboranes and have since been extended to supraicosahedral species.¹⁰,¹²,¹³ The significant twisting of the bipy ligand (χ in table 3.8.2.2) in 7 is presumably linked to the Sn-N distances measuring approximately the same length.

In the series of icosahedral main group metallacarborane adducts (Chapter 2), the ligand was clearly inclined at an angle θ with respect to the carborane cage. In these supraicosahedral cases, θ is quantified as the dihedral angle between the least-squares plane through B₅B₉B₁₂B₁₃B₈ and Sn₄N₄₁CCN₄₂, the values of which are given in table 3.8.2.2. The orientation of ligating atoms again implies that the Sn lone pair is fully stereochemically active yet chemically inert, since E shows no Lewis base properties when in the presence of classic acceptors such as BH₃. θ is greatest for 9 (26.4°), least for 10 (19.0°) and intermediate for 7 and 8 (21.2 and 20.6°, respectively). There appears to be a direct correlation between θ and Δ, in that as Δ increases, so too does θ.

3.8.3 Computational studies¹⁴

DFT calculations conducted on adducts 7, 9 and 10 by D. McKay successfully reproduce the structural distortion that accompanies adduct formation. These computational studies help rationalise both the orientation and inclination of the chelating ligand. The calculated structures were in excellent agreement with the
experimental values in terms of Sn-cage distances and the related parameters $\Delta$ and $z$. There were however some discrepancies in the Sn-N distances as the strength of the Sn-$L_2$ bonding appeared to be underestimated in the calculations. Testing of the computational method ruled out these small differences as an artefact of the calculations. The difficulty in reproducing the Sn-N distances is explained by differences between the gas- and solid-phase structures, which was verified by reoptimising the structures with Sn-N distances taken from the experimental data.

The orbital energy of the HOMO of 4,1,6-SnC$_2$B$_{10}$H$_{12}$ matches that calculated previously$^{15}$ and can be considered in effect as a lone pair of electrons on the Sn atom pointing outward over B2. The Sn lone pair is retained as the HOMO of 7 and confirms that there is no lone pair interaction with the ligand. Orientation of the $L_2$ ligands in adducts 7-10 is rationalised from the form and direction of LUMO and LUMO+2, which point in the same direction that the ligand orientates itself. This therefore gives maximum overlap between the N lone pairs and the unoccupied Sn orbitals.
3.9 Summary

These studies have shown that the supraicosahedral stannacarborane 1,6-Me₂-4,1,6-
closo-SnC₂B₁₀H₁₀ functions as a Lewis acid towards bipy, o-phen and substituted bipy
in a manner similar to related icosahedral and sub-icosahedral species. In all cases
adduct formation results in significantly increased slipping or hinging of the Sn atom,
resulting in dramatic increases in Sn–C and Sn–B₂ distances, and there appears to be a
correlation between the Lewis base strength of the ligand and the extent of the
molecular distortion. DFT calculations on model compounds successfully reproduce
the general structural features of these adducts.

Adducts 7, 8 and 9 show similar fluxionality in solution at room temperature as that
reported for 4,1,6-closo-SnC₂B₁₀H₁₂. However, due to the thermal instability of 4,1,6-
Sn compounds, thermolysis of these species results only in decomposition.
3.10 References


Chapter 4
Adducts of the Supraicosahedral Stannacarborane System

4,1,2-\textit{closo}-SnC_2B_{10}H_{10}

4.1 Introduction

The general synthetic route to 13-vertex metallacarboranes is reduction of a \textit{closo} C_2B_{10} carborane followed by metallation. Reduction of 1,2-\textit{closo}-C_2B_{10}H_{12} and its derivatives results in spontaneous C atom separation,\textsuperscript{1} with subsequent metallation affording 4,1,6-MC_2B_{10} species.\textsuperscript{2}

In order to prepare the C-adjacent isomer 4,1,2-MC_2B_{10}, it is necessary to first tether the cage C atoms of the 1,2-\textit{closo}-C_2B_{10} icosahedra using a short exopolyhedral strap. This strategy was previously employed in the synthesis of the first supraicosahedral carborane\textsuperscript{3} and prevents the separation of the cage C atoms during the initial reduction step. It is imperative for the tether to be stable enough to withstand the harsh conditions of this step for it to be considered synthetically useful.

4,1,2-MC_2B_{10} compounds can exist in the solid state with either docosahedral or henicosahedral structures, the topological difference between them being the formal absence of a 2-5 connectivity in the latter. In the docosahedron, the C1C2B9B5 unit is a diamond, with a measureable difference in C1-C2-B9 and C2-C1-B5 angles and also a measureable difference in C2-B9-B5 and B9-B5-C1 angles, whereas in the henicosahedron the C1C2B9B5 unit is trapezoidal and the C1-C2-B9 and C2-C1-B5 angles are equal, as are the C2-B9-B5 and B9-B5-C1 angles (see figure 4.1.1).
Soon after the 4,1,6-SnC\textsubscript{2}B\textsubscript{10} species was reported,\textsuperscript{4} Xie described the synthesis of the first example of a carbons-adjacent supraicosahedral stannacarborane, \textit{1,2-\(\mu\)}-{\textsubscript{4}}C\textsubscript{6}H\textsubscript{4}(CH\textsubscript{2})\textsubscript{2}-4,1,2-closo-SnC\textsubscript{2}B\textsubscript{10}H\textsubscript{10} (F).\textsuperscript{5} Here, an exopolyhedral \(\alpha,\alpha\)-\(\alpha\)-xylylene bridge between the cage C atoms was utilised to prevent their separation during the reduction step (figure 4.1.2).

Figure 4.1.1 The docosahedron (left) and henicosahedron (right) and their numbering schemes.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure411}
\caption{The docosahedron (left) and henicosahedron (right) and their numbering schemes.}
\end{figure}

Although no crystal structure was obtained for the ligand-free species, structures of its adducts with MeCN, THF and DME were determined by X-ray crystallography. These
structures showed a slip distortion of the Sn atom away from the cage C atoms, as previously observed in stannacarboranes of the C$_2$B$_4$, C$_2$B$_9$, and C$_2$B$_{10}$ systems.

Studies conducted by Hosmane and co-workers on the structures of the subicosahedral stannacarborane adduct 1-(bipy)-2,3-(SiMe$_3$)$_2$-1,2,3-closo-SnC$_2$B$_4$H$_4$, B, and its carbons-apart analogue, 1-(bipy)-2,4-(SiMe$_3$)$_2$-1,2,4-closo-SnC$_2$B$_4$H$_4$, G (see figure 4.1.3), revealed that slip distortion is smaller in the carbons-apart species; $\Delta$ was calculated to be 0.44 Å in the carbons-adjacent species and 0.34 Å in the carbons-apart species. This smaller $\Delta$ value is accompanied by relatively longer Sn-N connectivities and a shorter z distance. In the carbons-apart species, the Sn atom is slipped and the bipy ligand inclined away from the unique boron atom in the C$_2$B$_3$ face, B$_3$, resulting in a noticeably longer Sn-B$_3$ distance (2.683(6) Å) compared to Sn-B$_5$B$_6$ (2.405(6) Å, 2.393(5) Å). In G, the $\theta$ value at 28.3° is greater than in B at 24.2°.

![Figure 4.1.3](image)

Figure 4.1.3 Structures of 1-(bipy)-2,3-(SiMe$_3$)$_2$-1,2,3-closo-SnC$_2$B$_4$H$_4$ (B) and 1-(bipy)-2,4-(SiMe$_3$)$_2$-1,2,4-closo-SnC$_2$B$_4$H$_4$ (G).

The trend in $\Delta$ for subicosahedral compounds is reproduced in icosahedral \{L$_2$M\}C$_2$B$_9$ compounds ($M$ = Pt or Pd, L = typically phosphine), where the slip distortion is greater in 3,1,2-MC$_2$B$_9$ species (cage C atoms adjacent) than in 2,1,7-MC$_2$B$_9$ species (cage C atoms separated).

There is a superficial similarity that exists in the relationship between 4,1,6-SnC$_2$B$_{10}$ and 4,1,2-SnC$_2$B$_{10}$ and between 2,1,7-MC$_2$B$_9$ and 3,1,2-MC$_2$B$_9$. In this chapter, a number of adducts of 4,1,2-SnC$_2$B$_{10}$ stannacarboranes using exclusively bidentate L$_2$
bases have been prepared to establish if these compounds would also display increased slip distortions relative to their 4,1,6-SnC₄B₁₀ cousins.
4.2 Synthesis of 1,2-µ-(CH$_2$)$_3$-4,1,2-closo-SnC$_2$B$_{10}$H$_{10}$ (11)

A solution of 1,2-µ-(CH$_2$)$_3$-1,2-closo-C$_2$B$_{10}$H$_{10}$ in degassed THF was reduced with sodium pieces in the presence of naphthalene. The resulting dark-green solution was added to a THF solution of SnCl$_2$ at -196°C producing, on warming to 0°C, a dark brown suspension. Following evaporation of solvent, the brown solid was suspended in DCM and filtered to afford, after work-up, the colourless stannacarborane 1,2-µ-(CH$_2$)$_3$-4,1,2-closo-SnC$_2$B$_{10}$H$_{10}$ (11) in 25% yield. Pale-yellow X-ray diffraction quality crystals of 11 were grown by diffusion of a DCM solution and 40-60 petroleum ether at 5°C. Much like its 4,1,6-SnC$_2$B$_{10}$ analogue E, compound 11 decomposes in air after a short period of time.

Compound 11 was fully characterised. IR spectroscopy confirmed the presence of B-H with a broad absorption at $\nu_{\text{max}}$ 2547 cm$^{-1}$ and elemental analysis was in excellent agreement with the predicted values for C$_5$H$_{16}$B$_{10}$Sn. Mass spectrometry showed the highest mass signal to range from 298 to 308 with the most intense signal at 302, corresponding to the parent ion (303).

$^1$H NMR spectroscopy shows three multiplets, each integrating for two protons, at 3.20-3.10, 2.85-2.75 and 2.05-1.90 ppm, corresponding to the six tether protons. The $^{11}$B{$^1$H} NMR spectrum consists of five resonances in a 2:4:1:1:2 ratio. For a molecule with $C_s$ symmetry, we could expect six resonances in the ratio 2:2:1:1:2:2, so the observed pattern can be explained by two coincident signals of integral two.

An X-ray diffraction study confirmed the compound to be 1,2-µ-(CH$_2$)$_3$-4,1,2-closo-SnC$_2$B$_{10}$H$_{10}$ (figure 4.2.1).
The structure of stannacarborane 11 is an asymmetric docosahedron and thus the cage geometry observed is inconsistent with the $C_5$ symmetry implied by the NMR spectra. This disparity can be accounted for by the same fluxional process described for 1,2-$\mu$-(CH$_2$)$_3$-4,1,2-closo-NiC$_2$B$_{10}$H$_{10}$, which interconverts enantiomeric docosahedral structures via a henicosahedral intermediate (figure 4.2.2). This process is rapid on the NMR timescale and yields an apparent averaged $C_5$ symmetric structure for compound 11.
C1 occupies the only degree-four site in the cage structure, while C2 resides in a degree-five site and B5 is in a degree-six site. The distance between C1 and C2 is 1.445(3) Å, typical for 4,1,2-MC2B10 metallacarboranes. The C2-B5 distance measures 2.056(4) Å, almost identical to the corresponding distance in the docosahedral species 1,2-$\mu$-(CH2)$_3$-4,4-(PMe2Ph)$_2$-4,1,2-closo-PtC2B10H10. The tether lies in an envelope conformation, with the C4 methylene group of the tether pointing upwards.

The Sn vertex occupies the remaining degree-six site in the structural framework. The cage is defined by particularly long Sn4-C1, C2, B6, B3 distances (2.545(2), 2.727(3), 2.582(3) and 2.692(3) Å, respectively). The Sn4-B7, B10 connectivities are relatively shorter (2.492(3) and 2.375(3) Å), suggesting that the metal is dislocated in a direction away from the cage C atoms, as in 1,6-Me2-4,1,6-closo-SnC2B10H10 (E). However, Sn-cage atom distances in 11 vary somewhat from the corresponding distances in E, with connectivities to vertex atoms 1, 2, 3 and 6 longer whilst those to 7 and 10 are shorter.
4.3 Synthesis of 1,2-µ-(CH$_2$)$_3$-4-(bipy)-4,1,2-closo-SnC$_2$B$_{10}$H$_{10}$ (12)

A toluene solution of 11 was added to a toluene solution of bipy, yielding an immediate yellow precipitate of adduct 12. Small crystals of 12 were grown by vapour diffusion of a DCM solution and 40-60 petroleum ether at 5°C.

IR spectroscopy showed a broad absorption at $\nu_{\text{max}}$ 2518 cm$^{-1}$, indicative of B-H stretch. The $^{11}\text{B}\{^{1}\text{H}\}$ NMR spectrum contains five peaks in a 3:2:2:2:1 ratio, from high frequency to low frequency. Presumably, the first signal is the result of a 2+1 coincidence.

$^{1}\text{H}$ NMR spectroscopy displayed unique resonances for the bipy ligand appearing as a doublet of relative integral two at $\delta$ 8.99, a doublet of integral two at $\delta$ 8.22, a doublet of doublets of integral two at $\delta$ 8.13 and a doublet of doublets of integral two at $\delta$ 7.69. Signals for the tether are observed as a multiplet of relative integral two at 3.05-2.95 ppm, a multiplet of integral two at 2.77-2.68 ppm, a multiplet of integral one at 1.99-1.90 ppm and a multiplet of integral one at 1.78-1.66 ppm.

The yellow crystals of 12 were subjected to an X-ray diffraction study which determined the compound to be 1,2-µ-(CH$_2$)$_3$-4-(bipy)-4,1,2-closo-SnC$_2$B$_{10}$H$_{10}$. The study revealed two crystallographically independent molecules A and B in the asymmetric fraction of the unit cell. Molecule A is shown in figure 4.3.1.
The adduct 12 adopts a henicosahedral geometry, which, as discussed earlier, differs from the docosahedral geometry only by the absence of the C2-B5 connectivity. As a consequence of this missing connectivity, the two C vertices are now both degree-four, while B5 is in a degree-five site and the Sn atom remains in the only degree-six site. The tether lies in an envelope conformation with C4 bending downwards. Molecule B is essentially identical to molecule A.

As observed in adducts of the 4,1,6-Sn system, the ligand in 12 is tilted with respect to the plane of the lower pentagon of boron atoms. The bipy ligand is oriented so that N41 and N42 are opposite C2 and C1. The inclination of the bipy relative to the carborane can be quantitatively defined as θ, the dihedral angle between the B5B9B12B13B8 and Sn4N41CCN42 planes.

Crystallisation of compound 12 revealed two different crystallographic habits – small yellow plates of 12 and also colourless lathe-like crystals. The colourless crystals were
determined to be a complex that was obtained as a minor co-product from this reaction (see figure 4.3.2).

**Figure 4.3.2** Molecular structure of the Na(bipy) co-product.

The stoichiometry of this co-product is \([\text{Na(bipy)}][7,8-\mu-(\text{CH}_2)_3-7,8-nido-\text{C}_2\text{B}_9\text{H}_{10}]\) and in the crystal it features an \(\{\text{Na(bipy)}\}\)\(^+\) fragment co-ordinated to three \([7,8-\mu-(\text{CH}_2)_3-7,8-nido-\text{C}_2\text{B}_9\text{H}_{10}]\)\(^+\) cages. There is directional B-H…Na bonding from the Na\(^+\) ion to two H atoms on the top belt of cage A, one B-H…Na\(^+\) interaction with one H atom on the open face of cage B and two B-H…Na interactions with two H atoms on the lower belt of atoms on cage C. The Na atom is also co-ordinated to the bipy ligand.

The origin of this co-product appears to be that the unstable nature of stannacarborane 11 prohibits a purification step before addition of the ligand. Examination of the \(^{11}\text{B}\{^1\text{H}\}\) NMR spectrum of the sample prepared for X-ray crystallography showed an
additional six signals not due to adduct 12 at δ 0.32, -2.63, -11.65, -16.07, -22.16 and -24.63.
4.4 Synthesis of 1,2-µ-(CH₂)₃-4-(o-phen)-4,1,2-closo-SnC₂B₁₀H₁₀ (13)

A solution of 11 in degassed toluene was introduced slowly to a toluene solution of o-phen. The yellow adduct 13 was precipitated immediately. Yellow crystals were grown by solvent diffusion of 40-60 petroleum ether and a DCM solution of 13 at 5°C.

The broad stretch in the IR spectrum at ν_{max} 2540 cm⁻¹ is indicative of B-H stretch. As in 12, five peaks appear in the {¹²B}⁺{¹H} NMR spectrum in a 3:2:2:2:1 ratio.

Signals for the o-phen ligand are found in the {¹H} NMR spectrum as a doublet of relative integral two at δ 9.34, a doublet of integral two at δ 8.59, a singlet of integral two at δ 8.05 and a doublet of doublets of integral two at δ 8.00. The six protons of the tether appear as a multiplet of relative integral two at 3.15-3.05 ppm, a multiplet of integral two at 2.82-2.72 ppm, a multiplet of integral one at 2.05-1.95 ppm and a multiplet of integral one at 1.80-1.70 ppm.

An X-ray diffraction study confirmed compound 13 to be 1,2-µ-(CH₂)₃-4-(o-phen)-4,1,2-closo-SnC₂B₁₀H₁₀ (figure 4.4.1).
The structure of 13 is a henicosahedron, as described for 12. The C2-B5 distance across the open, trapezoidal face is calculated to be 2.503(3) Å, while that from C1 to B9 is 2.410(3) Å. The cage features long Sn-C connectivities (2.803(2) Å for Sn4-C1 and 2.820(2) Å for Sn4-C2) and also long distances from Sn4 to B6 and B3 (2.899(3) and 2.755(2) Å), which provides evidence that Δ is in a direction away from the cage C atoms. The Sn-N distances are almost identical, with Sn4-N41 measuring 2.4481(17) Å and Sn4-N42 measuring 2.4460(18) Å. When compared with the o-phen adduct of 1,6-Me2-4,1,6-closo-SnC2B10H10 (8), the connectivity from Sn to vertex 1 is longer in 13, those to 2 and 6 are shorter and those to 10, 7 and 3 are similar (the length of the connectivity from Sn to vertex 3 is, in fact, almost identical). The Sn-N distances are longer in 13, which, coupled with the fact that most of the Sn-cage connectivities are shorter, suggests that the Sn atom is more tightly held to the cage in the C-adjacent isomer 13.
As in 12, the carbon backbone of the tether adopts an envelope-like conformation in 13 and the methylene group at C4 is folded downwards. The distance between C1 and C2 is 1.433(3) Å. The $\alpha$-phen ligand is oriented so that the N atoms are opposite the cage carbon atoms and the ligand is clearly inclined with $\theta = 30.2^\circ$ to the B5B9B12B13B8 plane.
4.5 **Synthesis of 1,2-µ-(CH$_2$)$_3$-4-(Ph$_2$bipy)-4,1,2-closo-SnC$_2$B$_{10}$H$_{10}$ (14)**

To a stirring toluene solution of Ph$_2$bipy was added a degassed toluene solution of 11. The resulting yellow precipitate of adduct 14 was formed in 82% yield. Compound 14 was crystallised as yellow blocks by solvent diffusion of 40-60 petroleum ether and a DCM solution of 14 at -5°C.

The IR spectrum of 14 revealed a broad single band at $\nu_{\text{max}}$ 2522 cm$^{-1}$, due to B-H stretch. $^{11}$B$^1$H) NMR spectroscopy revealed four peaks in a ratio of 3:2:4:1 (high frequency to low frequency).

In the $^1$H spectrum, signals attributed to the sixteen protons of the Ph$_2$bipy ligand were found as a doublet of relative integral two at $\delta$ 9.03, a doublet of integral two at $\delta$ 8.45, a doublet of integral two at $\delta$ 7.91, a multiplet of integral four at $\delta$ 7.82-7.73 and a multiplet of integral six at $\delta$ 7.64-7.55. The signals relating to the tether appear as a multiplet of relative integral two at 3.05-2.99 ppm, a multiplet of integral two at 2.80-2.70 ppm, a multiplet of integral one at 2.01-1.92 ppm and a multiplet of integral one at 1.78-1.69 ppm.

An X-ray diffraction study on the yellow crystals of 14 confirmed the adduct to be 1,2-µ-(CH$_2$)$_3$-4-(Ph$_2$bipy)-4,1,2-closo-SnC$_2$B$_{10}$H$_{10}$. Compound 14 crystallises with two independent molecules in the asymmetric fraction of the unit cell and only molecule A is shown in figure 4.5.1.
Figure 4.5.1 Molecular structure of molecule A of $1,2$-$\mu$-(CH$_2$)$_3$-4-(Ph$_2$bipy)-4,1,2$-closo$-$SnC$_2$B$_{10}$H$_{10}$ (14).

The cage of 14 adopts a henicosahedral geometry, as reported for the previous two adducts. The C2-B5 and C1-B9 distances across the trapezoidal face are 2.513(7) Å and 2.378(7) Å, respectively. The slip of the Sn atom is in a direction away from the cage C atoms, illustrated by the long Sn-C connectivities (2.782(4) Å for Sn4-C1 and 2.864(5) Å for Sn4-C2). On comparison with the Ph$_2$bipy adduct of the 4,1,6$-$SnC$_2$B$_{10}$ system (10), the distance from Sn to vertex 1 is longer in 14, while the connectivities to vertices 2 and 6 are shorter and those to vertices 3, 10 and 7 are very similar. This observation, along with the longer Sn-N connectivities in 10, is evidence for the Sn atom being more strongly bound to the cage in 14.

The N atoms of the Ph$_2$bipy ligand are oriented such that they are opposite C1 and C2. The ligand is clearly inclined with respect to the cage, in a direction away from the cage C atoms. The $\theta$ angle is $27.1^\circ$ in molecule A and $16.0^\circ$ in molecule B. Molecules A and B are virtually the same, except the methylene group of the tether points upwards in A and downwards in B.
4.6 Synthesis of 1,2-µ-{C₆H₄(CH₂)₂}-4-(bipy)-4,1,2-closo-SnC₂B₁₀H₁₀ (15)

A solution of 1,2-µ-{C₆H₄(CH₂)₂}-4,1,2-closo-SnC₂B₁₀H₁₀ in degassed toluene was added to a stirring toluene solution of bipy, affording adduct 15 as a bright yellow solid. Diffraction quality yellow crystals were grown by slow evaporation of a DCM solution of 15 at room temperature.

IR spectroscopy showed a broad absorption at ν max 2521 cm⁻¹ indicative of B-H stretch. The ¹¹B{¹H} NMR spectrum was broad but could nevertheless be interpreted as six resonances in the relative ratio 2:2:2:1:1:2, exactly the pattern which could be predicted for a thirteen-vertex C₅ symmetric structure.

The eight hydrogen positions of the bipy ligand gave signals in the ¹H NMR spectrum as follows; a doublet of relative integral two at δ 8.87, a doublet of integral two at δ 8.24, a doublet of doublets of integral two at δ 8.04 and a doublet of doublets of integral two at δ 7.60. The protons from the α,α-xylylene tether appear as a 4H multiplet at 7.27-7.10 ppm and two doublets of relative integral two at 3.98 and 3.82 ppm.

The heicosahedral structure of 1,2-µ-{C₆H₄(CH₂)₂}-4-(bipy)-4,1,2-closo-SnC₂B₁₀H₁₀ (15) was confirmed by X-ray diffraction studies and is shown in figure 4.6.1. Compound 15 crystallises with ½ molecule of hexane.
The distance between C2 and B5 measures 2.516(6) Å, while that from C1 to B9 is recorded at 2.399(6) Å. There are long connectivities from Sn4 to C1, C2, B6 and B3 (2.849(4), 2.852(4), 2.871(4) and 2.775(5) Å, respectively), implying that the direction of slip of the Sn atom is away from the cage C atoms. The Sn4-N42 distance of 2.418(3) Å is slightly longer than that from Sn4 to N41 of 2.382(3) Å.

A comparison between the molecular structures of the bipy adducts of the 4,1,2-SnC\(_2\)B\(_{10}\) system (15) and the 4,1,6-SnC\(_2\)B\(_{10}\) system (7) reveals that the connectivity from Sn4 to vertex 1 is longer in 15, while distances from the metal to vertices 2 and 6 are shorter. The distance from Sn4 to vertex 3 is slightly longer in 15 and that to vertex 10 is a little longer in 7. Connectivities from Sn4 to vertex 7 are very similar in both adducts. The Sn4-N41 connectivities are almost identical in length, whereas the Sn4-N42 distance is slightly longer in 15 when compared to that in 7.

The N atoms of the bipy ligand are oriented such that they lie opposite the cage C atoms and the bipy is tilted at an angle of 29.5° with respect to the plane of the bottom belt of five B atoms.
4.7 Discussion

4.7.1 Synthesis and Spectroscopy

Using a procedure similar to that employed for the preparation of supraicosahedral transition metal $4,1,2$-$MC_2B_{10}$ species, sodium naphthalenide reduction of $1,2$-$\mu$-($CH_2)_3$-1,2-$closo$-$C_2B_{10}H_{10}$ in THF followed by metallation with SnCl$_2$ affords $1,2$-$\mu$-($CH_2)_3$-4,1,2-$closo$-$SnC_2B_{10}H_{10}$ (11). This compound was fully characterised using elemental analyses, infrared spectroscopy, mass spectrometry, NMR spectroscopy and X-ray crystallography and constitutes the first time a ligand-free $4,1,2$-$MC_2B_{10}$ species ($M = p$-block element) has been structurally characterised.

Compound 11 was treated with a series of bidentate $L_2$ bases to produce the following adducts:

$1,2$-$\mu$-($CH_2)_3$-4-(bipy)-4,1,2-$closo$-$SnC_2B_{10}H_{10}$ (12);

$1,2$-$\mu$-($CH_2)_3$-4-(o-phen)-4,1,2-$closo$-$SnC_2B_{10}H_{10}$ (13) and

$1,2$-$\mu$-($CH_2)_3$-4-(Ph$_2$bipy)-4,1,2-$closo$-$SnC_2B_{10}H_{10}$ (14).

In order to provide a link between these supraicosahedral $4,1,2$-$SnC_2B_{10}$ adducts and those reported by Xie, a $4,1,2$-$SnC_2B_{10}$ bipy adduct was synthesised using a $\mu$-{$C_6H_4(CH_2)_2$} tether $(1,2$-$\mu$-{$C_6H_4(CH_2)_2$}-4-(bipy)-4,1,2-$closo$-$SnC_2B_{10}H_{10}$, compound 15) instead of a $\mu$-($CH_2)_3$- tether. Adducts 12-15 were characterised by IR spectroscopy and NMR spectroscopy and in all cases structures were determined by X-ray crystallography. This facilitated a structural comparison between the adducts of $4,1,2$-$SnC_2B_{10}$ and $4,1,6$-$SnC_2B_{10}$ compounds, as well as a study to establish if using a different tether has an effect on molecular structure.

The $^{11}$B{$^{1}$H} NMR spectrum of 11 suggests a molecule with $C_s$ symmetry. However, crystallographic studies reveal that compound 11 adopts an asymmetric docosahedral structure in the solid state. In contrast, adducts 12-15 adopt henicosahedral cage structures and these adducts are found to be $C_s$ symmetric both in solution and (effectively) in the solid state. A facile diamond-trapezium-diamond fluxional process by which the enantiomers of a docosahedral molecule interconvert was reported by
Welch for $4,1,2$-$MC_2B_{10}$ transition metal metallacarboranes$^{12}$ and also accounts for this observation in 11.

4.7.2 Molecular structures

As noted previously, the crucial difference between a docosahedron and a henicosahedron is the formal absence of a C2-B5 connectivity in the latter. A structural study of compounds 11-15 clearly reveals that the cage of the ligand-free stannacarborane 11 appears to be best described as docosahedral, whilst those of adducts 12-15 are best described as henicosahedral. For the series of metallacarboranes $1,2$-$\mu$-(CH$_2$)$_3$-$4$-$L$-$4,1,2$-$closo$-MC_2B_{10}H_{10},$ $^{12}$ Welch reported a progression of structural type from henicosahedral ($ML =$ CoCp, Ru{p-cymene}), through intermediate ($ML =$ Pt{PMe$_2$Ph}$_2$) to essentially docosahedral ($ML =$ Ni{dppe}).

In order to place all known structurally characterised 13-vertex 1,2-$C_2B_{11}$ carboranes and analogous heterocarboranes in this sequence, the angle $\phi$ is defined as the average of the differences between angles C1-C2-B9 and C2-C1-B5 and angles C2-B9-B5 and B9-B5-C1 (see figure 4.7.2.1), i.e.

$$\phi = \frac{(| C1-C2-B9 - C2-C1-B5 | + | C2-B9-B5 - B9-B5-C1 |)}{2}$$

For a $C_s$-symmetric henicosahedron, the value of $\phi$ is 0. As the C2-B5 distance shortens, $\phi$ increases and the structure becomes docosahedral. The species defined as “most docosahedral” is $1,2$-$\mu$-(CH$_2$)$_3$-$4$-dppe-$4,1,2$-$closo$-NiC$_2B_{10}H_{10}$, with $\phi = 41.55^\circ$. It is now possible to define $x$, the “percentage docosahedral character”, as $x = (\phi/41.55)$.
× 100%. Hence, a species with a high \( x \) value will have an essentially docosahedral cage structure, whilst species with a low \( x \) value can be considered henicosahedral. This enables the percentage docosahedral character of all 1,2-C\(_2\)B\(_{11}\) carboranes and analogous heteroboranes to be assessed on a common scale. It should be noted however that the model docosahedral nickelcarborane was chosen expeditiously and it is feasible that future species will be “more docosahedral” with \( x \) values greater than 100%.

Table 4.7.2.1 hosts \( \phi \) and \( x \) values for all structurally characterised 13-vertex carbons-adjacent carboranes and metallacarboranes reported in the literature.
Table 4.7.2.1 Structural analysis of the cages of 13-vertex 1,2-C2 heteroboranes.

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<th>$\chi$</th>
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| I | 1,2-$\mu$-(CH$_2$)$_3$-4-Cp-4,1,2-closo-CoC$_2$B$_{10}$H$_{10}$ |
| II | 1,2-$\mu$-(CH$_2$)$_3$-4-(p-cymene)-4,1,2-closo-RuC$_2$B$_{10}$H$_{10}$ |
| III | 1,2-$\mu$-(CH$_2$)$_3$-4-(PMe$_2$Ph)$_2$-4,1,2-closo-PtC$_2$B$_{10}$H$_{10}$ |
| IV | 1,2-$\mu$-(CH$_2$)$_3$-4-dppe-4,1,2-closo-NiC$_2$B$_{10}$H$_{10}$ |
| V | 1-Me-4-(PEt$_3$)-4,6/7-$\mu$-{Co(PEt$_3$)2-$\mu$-(H)$_2$}4,1,2-closo-CoC$_2$B$_{10}$H$_{10}$ |
| VI | 1,2-$\mu$-{C$_6$H$_4$(CH$_2$)$_2$}4-(MeCN)-4,1,2-closo-SnC$_2$B$_{10}$H$_{10}$ |
| VII | 1,2-$\mu$-{C$_6$H$_4$(CH$_2$)$_2$}4-(THF)-4,1,2-closo-SnC$_2$B$_{10}$H$_{10}$ |
| VIII | 1,2-$\mu$-{C$_6$H$_4$(CH$_2$)$_2$}4-(DME)-4,1,2-closo-SnC$_2$B$_{10}$H$_{10}$ |
| IX | 1-CN-4-Cp-4,1,2-closo-CoC$_2$B$_{10}$H$_{11}$ |
| X | [[1,2-$\mu$-{C$_6$H$_4$(CH$_2$)$_2$}]4-(THF)4,1,2-closo-NaC$_2$B$_{10}$H$_{10}$,Na(THF)$_2$]$_n$ |
| XI | [4,4'-Cl]$_2$-4,4'-Zr(1,2-$\mu$-{C$_6$H$_4$(CH$_2$)$_2$}1,2-closo-C$_2$B$_{10}$H$_{10}$)$_2$ (monoclinic) |
| XII | [4,4'-Cl]$_2$-4,4'-Zr(1,2-$\mu$-{C$_6$H$_4$(CH$_2$)$_2$}1,2-closo-C$_2$B$_{10}$H$_{10}$)$_2$ (triclinic) |
| XIII | 1,2-$\mu$-{C$_6$H$_4$(CH$_2$)$_2$}3-Ph-1,2-closo-C$_2$B$_{11}$H$_{10}$ |
| XIV | 1,2-Me$_2$-1,2-closo-C$_2$B$_{11}$H$_{11}$ |
| XV | 1,2-$\mu$-{Me$_2$Si(CH$_2$)$_2$}1,2-closo-C$_2$B$_{11}$H$_{11}$ |
| XVI | 1,2-$\mu$-{C$_6$H$_4$(CH$_2$)$_2$}1,2-closo-C$_2$B$_{11}$H$_{11}$ |

$^a$ C2 disordered over vertices 2 and 3.
$^b$ Crystallographically-imposed $C_s$ symmetry.
$^c$ This paper reports four further, similar, species, two of which have multiple crystallographically-independent molecules, but all are essentially docosahedral, with C1-B9 and C2-B5 distances ranging from 2.139(3) to 2.629(3) Å.
$^d$ Two crystallographically-independent molecules.
4,1,2-MC_2B_{10} metallacarboranes may appear anywhere on this continuum, while the 1,2-C_2B_{11} carboranes are all essentially henicosahedral. The ligand-free stanncarborane 11 has $x = 80.3\%$, which verifies its essentially docosahedral cage structure. Adducts 12-15 have $x$ values between 11.3 and 21.6\%, making them fundamentally henicosahedral.

Table 4.7.2.2 lists the cage connectivities and Sn-N distances for compounds 11-15, while selected derived molecular parameters for these compounds are given in table 4.7.2.3.
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Table 4.7.2.2 Cage connectivities and Sn-N distances (Å) for compounds 11-15.
Structurally, adduct formation induces a change in the cage framework from the docosahedron of the ligand-free stannacarborane 11 to an essentially henicosahedral structure of the adducts 12-14. There is also an increase in slip distortion of the Sn atom on forming each adduct, with $\Delta$ increasing from 0.14 Å in 11 to between 0.32 and 0.45 Å in adducts 12-14.

Since adducts 12-14 are essentially henicosahedral with local mirror symmetry passing through the cage, for the purposes of this discussion it is instructive to average connectivities Sn-NC1 and Sn-NC2, Sn-NB3 and Sn-NB6, and Sn-NB7 and Sn-NB10. The average Sn-C distance increases significantly on going from 11 to 12-14, with a value of 2.64 Å in 11 and 2.84 Å for 12-14. The average Sn-B3,B6 distance also undergoes a substantial elongation, increasing from 2.64 Å in 11 to 2.85 Å in 12-14. This suggests that the slip of the Sn atom is in a direction away from the adjacent cage C atoms, but the overall structural change is not that simple as there is also a small increase in the average Sn-B7,B10 distance, which measures 2.43 Å in 11 and 2.49 Å in 12-14. A more complicated structural variation is confirmed by the $z$ values, as the Sn atom is displaced further from the B5 reference plane in adducts 12-14 (average distance 3.65 Å) than it is in 11 (3.46 Å).

As expected, the bipy, o-phen and Ph$_2$bipy ligands in 12-14 are oriented such that their N atoms lie opposite the cage C atoms. In addition, they are tilted at $\theta$ angles ranging from 16-30° to the B5 reference plane. The smallest $\theta$ angle is found in 14B, but in 14 there is clear evidence of intermolecular $\pi-\pi$ interactions in the crystal. This inclination of the ligand reflects the stereochemical influence of the lone pair of electrons on the Sn atom.

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Table 4.7.2.3 Selected derived molecular parameters (Å, °) for compounds 11-15.
There is a variation of some extent between the Sn-cage atom distances in compound 11 and the corresponding distances in 1,6-Me₂-4,1,6-closo-SnC₂B₁₀H₁₀, E. Table 4.7.2.4 lists the Sn-cage connectivities and selected derived molecular parameters of these two stannacarboranes for comparison. The connectivities from Sn to vertices 1, 2, 3 and 7 are 0.04-0.13 Å longer in E, whilst those to 6 and 10 are shorter by 0.09 and 0.05 Å, respectively. Furthermore, the difference between the longest and shortest Sn-cage distances in 11 is greater (0.35 Å) than that in E (0.26 Å). Despite this observation, the Sn atom is less slipped in 11 with \( \Delta = 0.14 \) Å, compared to 0.27 Å in E. This is contrary to the observations found in studies of the isomeric icosahedral platinacarboranes where the greater slip distortion was found when the two cage C atoms were adjacent.\(^{10}\) This measurement of a smaller slip in the carbons-adjacent 13-vertex SnC₂B₁₀ species compared to that in the carbons-apart isomer is noteworthy.

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Table 4.7.2.4 Sn-cage atom distances and selected derived molecular parameters (Å) for the 13-vertex carbons-apart stannacarborane E and the carbons-adjacent analogue 11.

Adduct formation of 1,6-Me₂-4,1,6-closo-SnC₂B₁₀H₁₀ resulted in a similar occurrence as that observed in 12-14, in which the Sn atom was slipped further away from the cage C atoms and was displaced further from the B5B9B12B13B8 plane. However, the increase in slipping is 0.19-0.26 Å in 12-14, less than that calculated for the isomeric 4,1,6-SnC₂B₁₀ species of 0.28-0.39 Å. Since they both start from a smaller base and
change by less, overall, therefore, the slipping parameters in the carbons-adjacent compounds 12-14, 0.33-0.40 Å, are ca. 0.20-0.25 Å smaller than those in the analogous 4,1,6 species. This is an unexpected result because, as noted previously, a greater slip was observed in the carbons-adjacent isomer of the subicosahedral stannacarborane system than in the carbons-apart species.⁶⁹ The unpredicted origin of the greater slip for the carbons-separated species is currently being investigated computationally by D. McKay.¹⁹

For example, Sn-N connectivities, Sn-cage atom connectivites and selected derived molecular parameters for the o-phen adducts of the 4,1,2- (13) and 4,1,6-systems (8) are given in table 4.7.2.5 to illustrate these points. The o-phen adducts were chosen arbitrarily – the same trend is reproduced in the bipy (7 and 12) and Ph₂bipy (10 and 14) adducts.
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Table 4.7.2.5 Sn-cage atom and Sn-N distances and selected derived molecular parameters (Å, °) for the o-phen adducts of 4,1,6- (8) and 4,1,2-SnC₂B₁₀ (13).

There are minor differences between the z values of the 4,1,2- and 4,1,6-SnC₂B₁₀ species. On average, the value of θ in the 4,1,6-SnC₂B₁₀ adducts (21.8°) is smaller than that in 12-14 (24.5°). The Sn-N distances in 12-14 are 2.42-2.46 Å, somewhat longer than the corresponding distances in the related 4,1,6-SnC₂B₁₀ adducts which measure 2.35-2.43 Å. This observation may be associated with the smaller slipping distortions in the carbons-adjacent compounds.
4.7.3 Effect of different tethers

A comparison of the two bipy adducts of the 4,1,2SnC$_2$B$_{10}$ system, 12 (with the $\mu$-(CH$_2$)$_3$- tether) and 15 (with the $\mu$-{C$_6$H$_4$(CH$_2$)$_2$}- tether) reveals little dissimilarity in the structures, with an insignificant difference in C1-C2 distances and comparable $\Delta$ values. It can therefore be concluded that tether type has minimal effect on the molecular structure. However, now that the structure of 15 has been determined, it can be compared with the three existing adducts of the 1,2-$\mu$-{C$_6$H$_4$(CH$_2$)$_2$}-4,1,2-SnC$_2$B$_{10}$ system, synthesised by Xie and co-workers,$^5$ which are shown in figure 4.7.3.1.

![Figure 4.7.3.1](image_url)  

**Figure 4.7.3.1** MeCN (VI), THF (VII) and DME (VIII) adducts of the 1,2-$\mu$-{C$_6$H$_4$(CH$_2$)$_2$}-4,1,2-SnC$_2$B$_{10}$ system.$^5$

Table 4.7.3.1 hosts the Sn-cage atom connectivities and selected derived molecular parameters for adduct 15 and those of Xie, VI, VII and VIII.
Based solely on the measured Sn-cage atom distances, Xie postulated that a stronger base leads to an increased slip distortion of the Sn atom from the centre of the C$_2$B$_4$ bonding face, despite the use of a mixture of mono- and bidentate Lewis bases in his study. However, Xie did not actually calculate the slip distortions of these adducts. The $\Delta$ values have now been determined (see table 4.7.3.1) and they do not corroborate Xie’s proposition. It is in fact the THF adduct that exhibits the greatest slippage, while the adduct with the strongest base, VIII, gives an intermediate $\Delta$ value. Nevertheless, the differences in slip distance are not very significant.

On comparison of 15 with VIII, the only adduct Xie synthesised using a bidentate Lewis base, the Sn-C1,C2,B6,B10 distances are all longer in 15, while the Sn-B3 and Sn-B7 connectivities are of similar length. The net result is that the Sn atom is further slipped in 15 by approximately 0.1 Å and a slightly greater $z$ value is also observed in the bipy adduct. It is no surprise that the slip distortion is greater in 15 than in both VI and VII, as monodentate Lewis bases are employed in the latter two adducts.

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Table 4.7.3.1  Sn-cage atom connectivities and selected derived molecular parameters for adducts 15, VI, VII and VIII (Å).
4.8 Summary

The supraicosahedral stannacarborane $1,2-\mu-(CH_2)_3-4,1,2$-closo-$SnC_2B_{10}H_{10}$ (11) was synthesised and fully characterised. This represents the first time a ligand-free carbons-adjacent supraicosahedral main group element metallacarborane has been structurally characterised. It enabled a structural comparison to be undertaken between 11 and four adducts of the 4,1,2-$SnC_2B_{10}$ system, which were also synthesised and characterised.

The henicosahedral adducts of the 4,1,2-$SnC_2B_{10}$ system 12-15 possess effective $C_s$ symmetry, both in the solid state and in solution. The docosahedral stannacarborane 11 has no symmetry in the solid state, but is found to be $C_s$ symmetric in solution on the NMR timescale. A fluxional process which interconverts two enantiomeric docosahedral structures via a henicosahedral intermediate accounts for this observation.

Similar structural features were found in the 4,1,2-$SnC_2B_{10}$ species as those reported for the 4,1,6-$SnC_2B_{10}$ system. The direction of slip of the Sn atom is away from the cage C atoms and was found to increase on forming the adducts. Adduct formation also resulted in an increase in the perpendicular displacement of the Sn atom from the B5B9B12B13B8 least-squares plane. In adducts 12-15, the ligands are oriented so that their N atoms are opposite the cage C atoms, symbolising that the Sn-C connectivities are the weakest in the cage structure. The ligands are also inclined with respect to the carborane, which demonstrates that the Sn lone pair of electrons is stereochemically active.

However, slip distortion is less in the 4,1,2-$SnC_2B_{10}$ species than in their respective 4,1,6-counterparts and there are longer connectivities from the Sn atom to the ligand N atoms in the adducts. This is the first time that a smaller slip has been reported in carbons-adjacent species relative to carbons-apart isomers, and further research to understand the origins of this observation is ongoing.
4.9 References


Chapter 5
New 13-vertex Stannacarboranes

5.1 Introduction

Following the synthesis of the first supraicosahedral heteroborane, 4-Cp-4,1,6-closo-CoC₂B₁₀H₁₂, in 1971,¹ more than two hundred or so 13-vertex metallacarboranes have been reported. The vast majority of these have 4,1,6-MC₂B₁₀ docosahedral architectures. However, the 4,1,6-MC₂B₁₀ arrangement is only the initial kinetically formed product and for some metal fragments, in particular {CpCo}, thermolysis successively yields the 4,1,8- and 4,1,12- isomers.²,³

Welch recently reported the first examples of 13-vertex 4,1,10-MC₂B₁₀ species, which can undergo facile isomerisation to the corresponding 4,1,12-isomer.⁴ Reduction of 1,12-closo-C₂B₁₀H₁₂ or its C,C-dimethyl analogue with sodium in liquid ammonia, followed by mettallation with {CpCo}²⁺, {(arene)Ru}²⁺ or {(dppe)Ni}²⁺ fragments, afforded 4,1,10-MC₂B₁₀ species after work up involving TLC. Thermolysis of these compounds yielded the appropriate 4,1,12-MC₂B₁₀ isomers by a new reliable, high-yielding route (see figure 5.1.1).

![Figure 5.1.1](image)

**Figure 5.1.1** General synthetic route to 4,1,10- and 4,1,12-MC₂B₁₀ species.

While the 4,1,10- and 4,1,12-MC₂B₁₀ isomers are known for 13-vertex transition metal metallacarboranes, there are no reported examples in the literature of these structures incorporating a main group metal into the cluster framework.
The 4,1,12-\(MC_2B_{10}\) species have been shown to undergo a two electron reduction when treated with sodium metal.\(^5\)\(^6\) Capping the open face of the nido species thus produced with a suitable metal fragment results in the formation of a 14-vertex metallacarborane, in a manner first reported by Hawthorne.\(^5\) The 4,1,12-\(MC_2B_{10}\) isomer is a very attractive precursor for polyhedral expansion to form 14-vertex metallacarboranes, as the single carbon atom in the lower belt will stabilise the open face of the nido species afforded upon reduction (figure 5.1.2).

![General synthetic route to 1,14,2,10-\(MM'C_2B_{10}\) species.](image)

**Figure 5.1.2** General synthetic route to 1,14,2,10-\(MM'C_2B_{10}\) species.

The first fully characterised 14-vertex metalladicarboranes were reported in 2005.\(^6\) The bicapped hexagonal antiprismatic cage structures of these complexes were confirmed (figure 5.1.3), with the metal atoms antipodal and occupying the sites of highest connectivity.

![The first fully characterised 14-vertex metalladicarborane, with bicapped hexagonal antiprismatic cage structure, 1,14-(\(p\)-cymene)-1,14,2,10-\(Ru_2C_2B_{10}H_{12}\).](image)

**Figure 5.1.3** The first fully characterised 14-vertex metalladicarborane, with bicapped hexagonal antiprismatic cage structure, 1,14-(\(p\)-cymene)-1,14,2,10-\(Ru_2C_2B_{10}H_{12}\).\(^6\)
Reduction and metallation of $3,1,2-MC_2B_9$ icosahedra has been shown to result in symmetric $4,5,2,3$-$closo-M_2C_2B_9$ 13-vertex bimetallacarboranes (figure 5.1.4), where $M$ represents the common late transition metal fragments $\{\text{CpCo}\}$ or $\{(p$-cyrene$)$Ru$\}$.\(^7\) The symmetric species can be converted to their asymmetric $4,5,1,6-M_2C_2B_9$ isomers by heat or by thermolysis of the reduced species prior to metallation.

![Reduction and metallation of 3,1,2-MC2B9 icosahedra to 4,5,2,3-closo-M2C2B9 13-vertex bimetallacarboranes](image)

**Figure 5.1.4** Synthesis of 13-vertex bimetallacarboranes by polyhedral expansion.

It should be noted that 13-vertex bimetallacarboranes can also be prepared by polyhedral subrogation\(^8\) or by direct insertion of a metal fragment into a 12-vertex metallacarborane.\(^9\) These bimetallic products can contain the same or different metals. However, there is yet to be an example published in the literature of a 13-vertex bimetallacarborane that incorporates any main group metals into the cage structure.

The synthesis and characterisation of the first example of a $4,1,10-MC_2B_{10}$ main group metallacarborane, $1,10$-$\text{Me}_2$-$4,1,10$-$closo$-$SnC_2B_{10}$H$_{10}$, is reported in this chapter. This species undergoes thermolysis in refluxing toluene and converts smoothly to the $4,1,12$-isomer in good yield. Also included are the structures of an adduct of each of these new isomers of supraicosahedral $p$-block metallacarboranes. Evidence is also presented for the formation of a unique 13-vertex bimetallacarborane including both a Ru and a Sn atom in the structure.
5.2 Synthesis of 1,10-Me₂-4,1,10-closo-SnC₂B₁₀H₁₀ (16)

Sodium reduction of 1,12-Me₂-1,12-closo-C₂B₁₀H₁₀ in liquid ammonia and subsequent evaporation of the ammonia yielded the dry residue of the sodium salt of the carborane dianion. This was extracted into degassed THF and treated with one equivalent of SnCl₂ at -196°C. After warming and work-up, the colourless stannacarborane 1,10-Me₂-4,1,10-closo-SnC₂B₁₀H₁₀ (16) was afforded in modest yield. Diffraction quality colourless block crystals were grown by solvent diffusion of a DCM solution of 16 and petroleum ether at -30°C.

Compound 16 was fully characterised. Mass spectrometry found the mass of the stannacarborane to be 289 (MW 291) and results from elemental analysis were in excellent agreement with the expected values. IR spectroscopy shows a broad absorption at ν_{max} 2552 cm⁻¹ which is indicative of B-H stretch.

A pattern of 2:2:2:1:1 could be predicted for the resonances in the \(^{11}\text{B}\{^{1}\text{H}\}\) NMR spectrum of 16 due to its C₅ symmetry yet a ratio of 4:5:1, from high frequency to low frequency, is observed experimentally. This reduction in the number of peaks found in the \(^{11}\text{B}\{^{1}\text{H}\}\) NMR spectrum must result from signal overlap.

\(^{1}\text{H}\) NMR spectroscopy showed one singlet at δ 1.70, corresponding to the methyl groups on the cage carbon atoms. This must be a coincidence, as in the analogous Ru compound 1,10-Me₂-4-(p-cymene)-4,1,10-closo-RuC₂B₁₀H₁₀, four broad singlets ca. 0.8 ppm apart are observed for the cage methyl groups in the \(^{1}\text{H}\) NMR spectrum, each with relative integral three. The cage methyl groups in 16 are not equivalent and there is no fluxional process that can occur in solution to make them equivalent on the NMR timescale, so it must be concluded that the one singlet observed in the \(^{1}\text{H}\) spectrum results from two coincident singlets of integral three.

One of the colourless block crystals was selected for an X-ray diffraction study and this confirmed compound 16 to be 1,10-Me₂-4,1,10-closo-SnC₂B₁₀H₁₀ (figure 5.2.1).
The stannacarborane 16 adopts a docosahedral structure, with the Sn atom residing at the degree-six vertex 4 and the C atoms located at positions 1 and 10, which are degree-four and degree-five sites, respectively. This gives the cage effective $C_s$ symmetry, which was confirmed by the $^{11}$B{$^1$H} NMR spectrum. The cage features long connectivities around the degree-six B atom B5, ranging from 1.7374(19) to 2.007(2) Å, reflecting the high connectivity of B5. The longest such connections are those which involve the boron atoms which are adjacent to C1 (B3 and B2). The metal-cage connectivities in 16 are longer than those reported for 4,1,10-MC$_2$B$_{10}$ transition metal species.\textsuperscript{6}
5.3 Synthesis of 1,10-Me₂-4-(Me₂bipy)-4,1,10-closo-SnC₂B₁₀H₁₀ (17)

To a stirring toluene solution of Me₂bipy was added a solution of 16 in toluene. The resulting bright yellow precipitate was stirred within the mixture overnight and then washed with petroleum ether. Yellow block crystals were grown by vapour diffusion of 40-60 petroleum ether and a DCM solution of 17 at 5°C.

Full characterisation of 17 was undertaken. IR spectroscopy revealed a broad absorption at $\nu_{\text{max}}$ 2521 cm⁻¹ indicative of B-H stretch, while elemental analysis correlated well with the expected values for C₁₆H₂₈N₂B₁₀Sn.

The $^{11}$B{¹H} NMR spectrum of 17 consists of six signals in a 2:1:1:2:2:2 ratio, consistent with the $C_s$ symmetry of the adduct. In the $^1$H NMR spectrum, resonances for the Me₂bipy ligand were found as follows; a doublet of relative integral two at $\delta$ 8.60, a singlet of integral two at $\delta$ 8.15, a doublet of relative integral two at $\delta$ 7.55 and a singlet of integral six at $\delta$ 2.60 which corresponds to the methyl groups on the bipy ligand. There are two singlets, each integrating for three protons, at $\delta$ 1.33 and $\delta$ 1.30, due to the cage methyl groups.

An X-ray diffraction study was conducted on one of the yellow block crystals of 17, which confirmed the adduct to be 1,10-Me₂-4-(Me₂bipy)-4,1,10-closo-SnC₂B₁₀H₁₀ (figure 5.3.1). Compound 17 crystallised with one molecule of DCM of solvation.
As previously observed for the 4,1,6-SnC$_2$B$_{10}$ system in chapter 3, the docosahedral cage structure of 16 is retained on forming the adduct 17, but there is some distortion due to lengthening of Sn-cage atom distances. The Me$_2$bipy ligand is oriented with its N atoms trans to the degree-five C10 atom, with $\theta = 38.6^\circ$ to the B5B9B12B13B8 reference plane. This is accompanied by the fact that the Sn4-B7 and Sn4-C10 connectivities suffer the most severe elongation, increasing from 2.5066(16) and 2.4760(12) Å in 16 to distances of 2.747(6) and 2.742(5) Å in 17, respectively. For that reason these connectivities appear as dashed lines in figure 5.3.1. The Sn-N distances

Figure 5.3.1 Molecular structure of 1,10-Me$_2$-4-(Me$_2$bipy)-4,1,10-cloo-so-SnC$_2$B$_{10}$H$_{10}$ (17).
can be considered equal, with Sn4-N41 measuring 2.455(4) Å and Sn4-N42 measuring 2.451(4) Å.
5.4  Synthesis of 1,12-Me$_2$-4,1,12-closo-SnC$_2$B$_{10}$H$_{10}$ (18)

Thermolysis of the stannacarborane 16 in refluxing toluene yielded 1,12-Me$_2$-4,1,12-closo-SnC$_2$B$_{10}$H$_{10}$ (18) after three hours. However, this process was accompanied by some decomposition. Unfortunately, no crystals of 18 were obtained for X-ray diffraction studies.

A strong absorption peak with $\nu_{\text{max}}$ at 2544 cm$^{-1}$ consistent with B-H stretch was found in the IR spectrum. The mass spectrum of 18 was analogous to that of the 4,1,10-isomer, but also included a typical carborane envelope centred on $m/z$ 171 corresponding to the decomposition product C$_4$B$_{10}$H$_{16}$.

$^{11}$B{$^{1}$H} NMR spectroscopy displayed five signals in the ratio 1:1:4:3:1, from high to low frequency, spread across ca. 21 ppm. Although there is some overlap of signals, this pattern shows that the new isomer has lost symmetry. The $^1$H NMR spectrum revealed a singlet at $\delta$ 1.25 tentatively assigned to the methyl groups on the cage. The cage methyl groups are not equivalent, so as in 16 it must again be concluded that the one singlet observed is the result of two coincident singlets which each have relative integral three. Two broad singlets, each with relative integral three and ca. 0.3 ppm apart, are observed in the $^1$H NMR spectrum of the analogous Ru species, 1,12-Me$_2$-4-(\(\eta\)-C$_6$H$_6$)-4,1,12-closo-RuC$_2$B$_{10}$H$_{10}$.\textsuperscript{4}
5.5  **Synthesis of 1,12-Me$_2$-4-(bipy)-4,1,12-*closo*-SnC$_2$B$_{10}$H$_{10}$ (19)**

A solution of 18 in degassed toluene was added slowly to a stirred toluene solution of bipy. The yellow adduct 1,12-Me$_2$-4-(bipy)-4,1,12-*closo*-SnC$_2$B$_{10}$H$_{10}$ (19) was afforded immediately. After washing with petroleum ether, yellow block crystals were grown with difficulty by vapour diffusion of 40-60 petroleum ether and a DCM solution of 19 at room temperature.

Due to the considerable instability of compound 19, full characterisation could not be completed. However, an X-ray diffraction study of 19 indisputably determined its structure as 1,12-Me$_2$-4-(bipy)-4,1,12-*closo*-SnC$_2$B$_{10}$H$_{10}$ (figure 5.5.1).

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**Figure 5.5.1**  Molecular structure of 1,12-Me$_2$-4-(bipy)-4,1,12-*closo*-SnC$_2$B$_{10}$H$_{10}$ (19).
The cage structure of 19 is a slightly distorted docosahedron, with the structural changes once again induced by adduct formation. As in 16 and 17, C1 remains degree-four and Sn4 degree-six but the second carbon atom, unambiguously identified by its methyl label, has moved from vertex 10 to the adjacent (but still degree-five) vertex 12. The longest B-B distances are again B2-B5 and B3-B5, at 2.018(6) Å and 2.013(6) Å respectively. The connectivities from Sn4 to B2, C1 and B3 (2.758(5), 2.713(4) and 2.870(5) Å) are the longest between the metal and the atoms in the upper belt. The Sn metal is therefore slipped in a direction away from C1. The bipy ligand is oriented opposite C1 and inclined at an angle of 27.5° to the plane of the B5B8B9B13C12 pentagon. The Sn4-N41 distance of 2.568(3) Å is marginally longer than the Sn4-N42 distance, which measures 2.552(3) Å.
5.6 Synthesis of 4-(p-cymene)-4,5,2,3-closo-RuSnC$_2$B$_9$H$_{11}$ (20)

Sodium reduction of the icosahedral ruthenacarborane 3-(p-cymene)-3,1,2-closo-RuC$_2$B$_9$H$_{11}$ followed by treatment with one equivalent of SnCl$_2$ at low temperature affords a 13-vertex bimetallacarborane, tentatively assigned as 4-(p-cymene)-4,5,2,3-closo-RuSnC$_2$B$_9$H$_{11}$ (20) in reasonable yield. Unfortunately, crystals of 20 suitable for X-ray diffraction studies could not be obtained.

Mass spectrometry of compound 20 revealed the molecular ion at $m/z$ 485, with a typical carborane envelope from 480 to 492 which confirmed the presence of (p-cymene)RuSnC$_2$B$_9$H$_{11}$ (MW 486). A fragment ion at 365 represents the loss of Sn.

$^{11}$B{$^1$H} NMR spectroscopy of the crude product showed many signals, but none matched those of the 3-(p-cymene)-3,1,2-closo-RuC$_2$B$_9$H$_{11}$ starting material. Compound 20 also formed a precipitate when treated with bipy, providing further proof of formation of the “mixed metal” species.

Sodium reduction of the icosahedral ruthenacarborane 3-(p-cymene)-3,1,2-closo-RuC$_2$B$_9$H$_{11}$ followed by treatment with 0.5 equivalents of [Ru(p-cymene)Cl$_2$]$_2$ affords 4,5-(p-cymene)$_2$-4,5,2,3-closo-Ru$_2$C$_2$B$_9$H$_{11}$. This structural geometry was confirmed by X-ray crystallography. On the basis of this precedent, 20 is assigned as 4-(p-cymene)-4,5,2,3-closo-RuSnC$_2$B$_9$H$_{11}$ (figure 5.6.1), the first reported example of a metallacarborane with both a transition metal and a main group metal occupying vertices in the same cluster framework.

![Figure 5.6.1](image-url) Proposed structure of compound 20.
5.7 Discussion

5.7.1 A structural study of the 4,1,10-SnC$_2$B$_{10}$ system

When a THF solution of Na$_2$[Me$_2$C$_2$B$_{10}$H$_{10}$] (prepared by Na reduction of 1,12-Me$_2$-1,12-closo-C$_2$B$_{10}$H$_{10}$ in NH$_3$)$_{10}$ is treated with SnCl$_2$, the colourless stannacarborane 1,10-Me$_2$-4,1,10-closo-SnC$_2$B$_{10}$H$_{10}$ (16) is formed in 21% yield after work-up. Compound 16 was characterised by mass spectrometry, IR spectroscopy, $^1$H and $^{11}$B NMR spectroscopies and a single-crystal X-ray diffraction study. 16 is the first reported example of a 4,1,10-MC$_2$B$_{10}$ species incorporating a main group metal into the cage framework.

In chapters 3 and 4, the 4,1,6- and 4,1,2-SnC$_2$B$_{10}$ systems have been shown to exhibit Lewis acid behaviour when treated with a series of Lewis bases. The 4,1,10- isomer is no exception and forms a bright yellow adduct 17 when reacted with Me$_2$bipy. In the previous systems studied, the ligand would orientate itself so that the N atoms were trans to the weakest $M$-cage atom connectivities – usually between $M$ and the cage C atoms. However, in the 4,1,10- system, the carbon atoms are positioned at opposite ends of the top face of atoms, prohibiting the ligand from tilting away from both carbons. An X-ray diffraction study of compound 17 revealed that the N atoms of the Me$_2$bipy ligand are situated trans to the degree-five C10 atom (illustrated in figure 5.7.1.1). This suggests that for 4,1,10-MC$_2$B$_{10}$ systems in general, connections between $M$ and the degree-five C are weaker than those between $M$ and the degree-four C, C1, which is eminently sensible. The slip distortion of the Sn atom is also in the direction of C1. Slippage of the $M$ atom away from C10 and towards C1 has been noted in 4,1,10-MC$_2$B$_{10}$ transition metal sandwich complexes.$^{11}$
Figure 5.7.1.1 View of 17 perpendicular to the best plane through atoms B5, B9, B12, B13 and B8.

Table 5.7.1.1 lists the cage connectivities in the structures of compound 16 and its Me₂bipy adduct 17, along with Sn-N distances for 17, which were determined by X-ray diffraction studies.
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Table 5.7.1.1 Cage connectivities and Sn-N distances (Å) in 16 and adduct 17.

The $M$-cage atom connectivities recorded in the stannacarborane 16 are on average longer than the corresponding distances in transition metal 4,1,10-MC$_2$B$_{10}$ species. The average $M$-cage atom distance in 16 is 2.511 Å, significantly greater than those in 4-Cp-4,1,10-closo-CoC$_2$B$_{10}$H$_{12}$ (2.147 Å), 4-(p-cymene)-4,1,10-closo-RuC$_2$B$_{10}$H$_{12}$ (2.258 Å) and 4-(dppe)-4,1,10-closo-NiC$_2$B$_{10}$H$_{12}$ (2.183 Å). However, the relative
order of $M$-cage atom connectivities is consistent through all these species, with the $M$-C distances the shortest (and $M$-C10 always longer than $M$-C1) and with the longest connectivities found from $M$ to B2 and B3.

In the 4,1,10-SnC$_2$B$_{10}$ system, the Sn-cage atom distances once again all increase upon adduct formation. The greatest difference on going from 16 to 17 is found in the Sn4-C10 distance, which provides further confirmation that the direction of slip in 17 is away from C1. Sn-C10 increases by almost 0.3 Å, making it the longest connectivity in the cage structure of 17 along with Sn-B7. In 17, the Sn-C1 connectivity remains the shortest in the cage, while there is a substantial elongation of Sn-B6 and Sn-B3. The rest of the cage framework remains relatively unchanged, although there is notable shortening of B-C connectivities involving C10, clearly to compensate for the weakening of the Sn-C10 bonding.

Table 5.7.1.2 hosts selected derived structural parameters for compounds 16 and 17.

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**Table 5.7.1.2** Selected derived molecular parameters (Å, °) in 16 and 17 determined crystallographically.

The slip distortion increases by 0.17 Å on going from 16 to 17. The increase in $z$ is a direct result of the weakening of the Sn-cage connectivities induced by adduct formation. The tilting of the ligand is the largest reported for adducts of supraicosahedral main group metallacarboranes, with a dihedral angle of $38.6^\circ$. 
5.7.2 A structural study of the 4,1,12-SnC\textsubscript{2}B\textsubscript{10} system

It was reported in chapter 3 that when 4,1,6-SnC\textsubscript{2}B\textsubscript{10} species were heated to reflux in an attempt to promote rearrangement to the 4,1,8- isomer, the stannacarborane simply fell apart and Sn metal was extruded from the cage. In spite of this finding, 1,10-Me\textsubscript{2}-4,1,10-c\textit{closo}-SnC\textsubscript{2}B\textsubscript{10}H\textsubscript{10} (16) was heated to reflux in toluene and the \textsuperscript{11}B\{\textsuperscript{1}H\} NMR spectrum was recorded after each hour of heating. After one hour, five new resonances attributed to the 4,1,12- isomer had appeared in the spectrum, while a significant amount of 4,1,10- isomer remained. The 4,1,12- isomer was in the majority following two hours of heating. After three hours, \textsuperscript{11}B\{\textsuperscript{1}H\} NMR spectroscopy revealed that only a small amount of 4,1,10- isomer remained, with the spectrum dominated by signals for the 4,1,12- isomer, 1,12-Me\textsubscript{2}-4,1,12-c\textit{closo}-SnC\textsubscript{2}B\textsubscript{10}H\textsubscript{10} (18), the first example of a 4,1,12-MC\textsubscript{2}B\textsubscript{10} main group metallacarborane. Unfortunately, structural analysis was thwarted as diffraction quality crystals of the 4,1,12- isomer could not be grown.

To facilitate obtaining a structure of a 4,1,12- main group species, the bipy adduct of 1,12-Me\textsubscript{2}-4,1,12-c\textit{closo}-SnC\textsubscript{2}B\textsubscript{10}H\textsubscript{10} (19) was synthesised. Thankfully, X-ray diffraction quality yellow block crystals were obtained of this adduct and the structure was determined to be that of the 4,1,12- isomer. The cage connectivities, Sn-N distances and selected derived structural parameters of this adduct are listed in table 5.7.2.1.
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**Table 5.7.2.1** Cage connectivities, Sn-N distances and selected derived molecular parameters (Å, °) in 19.
A comparison of the $M$-cage atom connectivities in 19 with the corresponding distances in the 4,1,12- transition metal metallacarborane, 1,12-Me$_2$-4-(η-C$_6$H$_6$)-4,1,12-closo-RuC$_2$B$_{10}$H$_{10}$, reveals that the distances in 19 are extensively longer. It should be noted that 19 is an adduct and its $M$-cage atom connectivities would experience an increase upon complexation with the ligand. However, studies conducted on the 4,1,10-SnC$_2$B$_{10}$ system suggest that longer connectivities from the metal to the cage would be expected in the Sn species compared to the Ru species, regardless of the presence of a Lewis base on the stannacarborane. $M$-B3 and $M$-B2 are found to be the longest $M$-cage atom connectivities in both 19 and 1,12-Me$_2$-4-(η-C$_6$H$_6$)-4,1,12-closo-RuC$_2$B$_{10}$H$_{10}$, while the shortest connectivity is between $M$ and C1 in the Ru species and between $M$ and B10 in 19 (it is plausible that the shortest distance in 18, the ligand-free 4,1,12 stannacarborane, would also be between $M$ and C1, but this connectivity will unquestionably experience considerable lengthening upon adduct formation in 19).

It is important to note that in 19, the reference plane used to calculate $\Delta$, $\theta$ and $z$ now contains a carbon atom at position 12, i.e. B5B8B9B13C12. The slip distortion of 0.12 Å is the smallest recorded for all of the adducts observed in this thesis. This is to be expected however as there is now only one carbon atom in the top belt of atoms for the metal atom to move away from, whereas in each previous case there have been two. This also suggests that $\Delta$ would be extremely small in the parent 1,12-Me$_2$-4,1,12-closo-SnC$_2$B$_{10}$H$_{10}$ stannacarborane, 18. There is also a significant twisting of the bipy ligand, with an angle between the NC$_5$ planes ($\chi$) of 13.5°.

A structural comparison of adducts 17 and 19 shows that the ligand can be considered to have “flipped over” on going from the 4,1,10-SnC$_2$B$_{10}$ species, 17, to the 4,1,12-SnC$_2$B$_{10}$ species, 19 (see figure 5.7.2.1). The ligand always orientates itself so that its N atoms are opposite the weakest connections in the cage. Judging from the orientation of the ligand in the 4,1,10-SnC$_2$B$_{10}$ system, the weakest connectivity in 17 must be between Sn and C10. However, on moving to the 4,1,12-SnC$_2$B$_{10}$ system, the N atoms of the ligand in 19 are now trans to B3 and C1, implying that the Sn-B3 and Sn-C1 connectivities are the weakest in this structure. In assuming this orientation, the ligand in 19 has adopted the opposite location to that in 17, causing this effect of the ligand “flipping over”. 
The ready formation of the 4,1,12-SnC₂B₁₀ species by thermal rearrangement is significant because the corresponding 4,1,6- compounds decomposed when thermolysis was attempted. The 13-vertex 4-Cp-4,1,12-closos-CoC₂B₁₀H₁₂ has been shown to be the precursor, following reduction and subsequent metallation, to 14-vertex bimetallic $M₂C₂B₁₀$ supraicosahedra. The potential of these 4,1,12 main group stannacarboranes is currently being explored in the hope of synthesising 14-vertex metallacarboranes from them.
5.7.3 The first “mixed metal” metallacarborane and potential routes to larger species

Reduction of the icosahedral ruthenacarborane \(3-(p\text{-cymene})-3,1,2\text{-closo-RuC}_2\text{B}_9\text{H}_{11}\) followed by treatment with SnCl\(_2\) yields a 13-vertex bimetallacarborane. From mass spectral analysis, this species is proposed to be \(\left(p\text{-cymene}\right)\text{RuSnC}_2\text{B}_9\text{H}_{11}\) (20) and represents the first example of a metallacarborane incorporating both a \(d\)-block and a \(p\)-block metal into the cage framework. On the basis of precedent,\(^7\) compound 20 is drawn as the 4,5,2,3-RuSnC\(_2\)B\(_{9}\) isomer in figure 5.7.3.1.

![Figure 5.7.3.1 Synthesis of compound 20.](image)

Supraicosahedral expansion of 13-vertex bimetallacarboranes has proved unsuccessful due to the inherent stability of the precursor.\(^{12}\) These compounds have transition metal fragments occupying both degree-six vertices and the reduction step necessitates one of the metal fragments to occupy a lower connected site in the open face on forming the nido species (figure 5.7.3.2). This process is highly unfavourable and is thought to be the reason behind the failure of this synthesis.

![Figure 5.7.3.2 Unsuccessful reduction of 4,5,2,3-closo-\(M_2\)C\(_2\)B\(_9\)H\(_{11}\).](image)
Similarly, attempts to expand 14-vertex bimetallacarboranes yielded only starting material upon reduction and metallation. The great stability of these compounds, which also have two transition metal fragments in two degree-six vertices (for example, see figure 5.1.3), appears to prohibit the molecule from experiencing rearrangement to form a stable nido species in the reduction step.

A potential solution to both these problems is to replace one (or both) of the transition metal fragments in the cage framework with a main group metal. The extremely stable structures of the transition metal bimetallacarboranes may not be reproduced if a main group metal occupied one of the degree-six sites in the cage, as main group metals possess properties between those of transition metals and boron. This work has shown that this type of “mixed metal” species can exist and could potentially undergo polyhedral expansion to afford larger supraicosahedral metallacarboranes.
5.8 Summary

In an attempt to expand supraicosahedral main group metallacarborane chemistry beyond the 4,1,6- and 4,1,2-SnC₂B₁₀ species already known, two new isomers were synthesised and characterised.

The first example of a 4,1,10 $p$-block metallacarborane, 1,10-Me₂-4,1,10-closo-SnC₂B₁₀H₁₀ (16), was prepared by sodium/liquid ammonia reduction of 1,12-Me₂-1,12-closo-C₂B₁₀H₁₀ to produce the C-separated [7,10-Me₂-7,10-nido-C₂B₁₀H₁₀]$^{2-}$ dianion. This species was then treated with SnCl₂ to afford 16 in 21% yield. When treated with the Lewis base Me₂bipy, 16 forms the adduct 1,10-Me₂-4-(Me₂bipy)-4,1,10-closo-SnC₂B₁₀H₁₀ (17). A structural study of 17 revealed that the Sn atom slips away from the degree-five C₁₀ and towards the degree-four C₁, with the N atoms of the ligand trans to C₁₀.

A second new isomer of the SnC₂B₁₀ system, 1,12-Me₂-4,1,12-closo-SnC₂B₁₀H₁₀ (18), was prepared by thermolysis of 16 in refluxing toluene. Unusually for a main group metallacarborane, the 4,1,10- isomer converted smoothly to the 4,1,12-isomer in good yield without significant decomposition upon thermal rearrangement. The bipy adduct of 18, 1,12-Me₂-4-(bipy)-4,1,12-closo-SnC₂B₁₀H₁₀ (19), was prepared to confirm the structure of the 4,1,12-species. This adduct displayed the least metal slip distortion of all the supraicosahedral compounds reported in this thesis.

As a result of this successful formation of a 4,1,12-SnC₂B₁₀ species, the possibility of synthesising novel 14-vertex bimetallacarboranes now arises. This could proceed via reduction of compound 18 followed by capitation with a main group metal or a transition metal fragment. (see figure 5.8.1).
Figure 5.8.1 Potential reduction and metallation of 18.

The idea of reducing a transition metal metallacarborane and inserting a main group metal has been shown to be possible by mass spectrometry. 4-(p-cymene)-4,5,2,3-closo-RuSnC₂B₉H₁₁, compound 20, is the first reported example of a “mixed metal” metallacarborane, i.e. a main group metal and a transition metal are both present in the cage framework. This unique species offers the possibility to succeed where the transition metal bimetallacarboranes failed, in that it may be possible to reduce this compound, with metallation of the nido species affording the very first supraicosahedral trimetallacarborane.

These exciting results provide a basis on which to cultivate new synthetic pathways to larger species and stimulate the full development of supraicosahedral metallacarborane chemistry.
5.9 References


Chapter 6
Experimental Section

6.1 General Experimental

Syntheses

All experiments were carried out under a dry, oxygen-free, nitrogen atmosphere, using Schlenk-line techniques, with some subsequent manipulation being completed in the open laboratory. Most of the ultimate compounds reported are stable in air both as solids and as solutions. All solvents were dried with the appropriate drying agents under nitrogen immediately before use [DCM and MeCN, CaH$_2$; THF and diethyl ether, sodium wire-benzophenone; toluene and light petroleum (b.p. 40-60ºC), sodium-wire] and were degassed (3 × freeze-pump-thaw cycles) before use, or were stored over 4 Å molecular sieves.

Analyses

NMR spectra were recorded on a Bruker AC200 spectrometer for [HNMe$_3$][7,8-$\mu$-(CH$_2$)$_3$-7,8-nido-C$_2$B$_9$H$_{10}$] ($^1$H spectra at 200.1 MHz, $^{11}$B spectra at 64.2 MHz) or a DPX400 spectrometer for compounds 1-20 ($^1$H spectra at 400.1 MHz, $^{11}$B spectra at 128.4 MHz). Unless stated otherwise, NMR spectra were obtained from CD$_2$Cl$_2$ solutions at 298K; proton chemical shifts are reported in ppm relative to external SiMe$_4$ and boron chemical shifts in ppm relative to external BF$_3$.OEt$_2$. IR spectra were recorded on a Perkin Elmer Spectrum RX FT spectrophotometer from DCM solutions. El mass spectrometry was carried out using a Kratos Concept mass spectrometer with the parent ion taken as the most abundant component in the heteroborane envelope. Elemental analyses were determined by the departmental service.
Hazards

Standard principles of safe handling and good general laboratory practice were followed, including the wearing of protective clothing and safety glasses. Extra care and attention was employed when handling flammable solvents, sodium and toxic carboranes.

Standard Preparations

The compounds: [HNMe$_3$][7,8-Me$_2$-7,8-nido-C$_2$B$_9$H$_{10}]$, $^1$ [Ru(p-cymene)Cl$_2$]$_2$, $^2$ 1,2-Me$_2$-3,1,2-closo-PbC$_2$B$_9$H$_9$, $^3$ 3-(p-cymene)-3,1,2-closo-RuC$_2$B$_9$H$_{11}$, $^4$ 1,6-Me$_2$-4,1,6-closo-SnC$_2$B$_{10}$H$_{10}$, $^5$ 1,2-µ-(CH$_2$)$_3$-1,2-closo-C$_2$B$_{10}$H$_{10}$, $^6$ 1,2-µ-{C$_6$H$_4$(CH$_2$)$_2$}-4,1,2-closo-SnC$_2$B$_{10}$H$_{10}$ $^7$ and 1,12-Me$_2$-1,12-closo-C$_2$B$_{10}$H$_{10}$ $^8$ were prepared by literature methods or slight variants thereof. All other reagents and solvents were supplied commercially and were used as received.

Crystallographic Data Collection

Single crystals suitable for X-ray diffraction were mounted in inert oil on a glass fibre and cooled to 100K by an Oxford Cryosystems Cryostream. Data were collected on a Bruker X8 APEX2 diffractometer, $^9$ employing graphite-monochromated Mo-K$_\alpha$ X-radiation ($\lambda = 0.71069$ Å) and were corrected for absorption semi-empirically from symmetry-equivalent and repeated reflections. Structures were solved by direct and difference Fourier methods and refined by full-matrix least-squares against $F^2$ using the SHELXTL program suite. $^{10}$ Refinement was completed with all non-hydrogen atoms assigned anisotropic displacement parameters. Geometry measurements were made using the Mercury program. $^{11}$
6.1.1 Synthesis of [HNMe$_3$][7,8-µ-(CH$_2$)$_3$-7,8-nido-C$_2$B$_9$H$_{10}$]

An EtOH solution (25 mL) of 1,2-µ-(CH$_2$)$_3$-1,2-closo-C$_2$B$_{10}$H$_{10}$ (502 mg, 2.73 mmol) and KOH (388 mg, 6.82 mmol) was heated to reflux for 72 h under a nitrogen atmosphere. After cooling to room temperature, CO$_2$ was bubbled through and the excess KOH was removed by filtration of the resulting K$_2$CO$_3$ formed as a white precipitate. The remaining solvent was removed in vacuo to yield a white solid. This solid was dissolved in deionised water resulting in a milky suspension, which was then filtered through Celite® filter aid. To the clear aqueous solution of K[7,8-µ-(CH$_2$)$_3$-7,8-nido-C$_2$B$_9$H$_{10}$] was added [HNMe$_3$]Cl (273 mg, 2.78 mmol) dissolved in deionised water (15 mL) to precipitate [HNMe$_3$][7,8-µ-(CH$_2$)$_3$-7,8-nido-C$_2$B$_9$H$_{10}$] as a fine white solid.

**Yield**
408 mg, 64%

$^{11}$B$^1$H NMR C$_2$D$_6$CO, δ -10.13 (2B), -14.45 (1B), -18.92 (4B), -31.71 (1B), -35.43 (1B).

$^1$H NMR C$_2$D$_6$CO, δ 3.15 (s, 9H, HNMe$_3$), 1.70-1.30 (m, 6H, (CH$_2$)$_3$).
6.2 Chapter 2. Icosahedral Main Group Metallacarboranes and their Adducts

6.2.1 Synthesis of 1,2-Me$_2$-3,1,2-$\text{closo}$-GeC$_2$B$_9$H$_9$ (1)

Dry [HNMe$_3$][7,8-Me$_2$-7,8-$\text{nido}$-C$_2$B$_9$H$_{10}$] (260 mg, 1.15 mmol) was treated with a 2.5 M solution of $n$-BuLi (0.85 mL, 2.12 mmol) in dry THF (25 mL) at 0°C under a nitrogen atmosphere. The solution was heated for 30 minutes at 40°C. After cooling to room temperature, GeI$_2$ (173 mg, 0.53 mmol) was added to the solution and the mixture was heated to reflux for 4 h. The mixture was cooled to room temperature and the clear solution was decanted from the precipitated LiI via cannula. After filtration through a Celite® filter aid, solvent was removed in vacuo and the pure product was obtained as a white solid after sublimation.

Yield 52 mg, 42%
CHN $C_4$$C_{15}$$B_9$$Ge$ requires C, 20.62; H, 6.49. Found: C, 22.77; H, 7.05%.
IR $\nu_{\text{max}}$ 2587 cm$^{-1}$ (B–H).
$^1$$B$$^1$$H$ NMR CDCl$_3$, $\delta$ -2.62 (2B), -3.51 (1B), -4.65 (4B), -6.80 (2B).
$^1$$H$ NMR CDCl$_3$, $\delta$ 2.15 (s, 6H, $(CH_3)_2$).
MS $m/z$ 232 (M$^+$).
6.2.2 Synthesis of 1,2-\(\mu-(\text{CH}_2)_3\)-3,1,2-closo-\(\text{GeC}_2\text{B}_9\text{H}_9\) (2)

A 2.5 M solution of \(n\)-BuLi (1.10 mL, 2.82 mmol) was added slowly under nitrogen to a suspension of 330 mg (1.41 mmol) of dry \([\text{HNMe}_3][\text{7,8-\(\mu-(\text{CH}_2)_3\text{-7,8-nido-C}_2\text{B}_9\text{H}_{10})]}\) in 25 mL of dry THF at 0°C. The solution was stirred for 30 minutes at 40°C and then allowed to cool to room temperature. GeI\(_2\) (238 mg, 0.73 mmol) was added to the suspension and the mixture was heated to reflux for 4 h. The mixture was cooled to room temperature and a cannula was used to separate the clear solution from the LiI precipitate. The solution was filtered through Celite® and solvent was removed \textit{in vacuo}. The pure product was then obtained as a white solid after sublimation. X-ray diffraction quality colourless block crystals of 2 were grown by diffusion of a DCM solution and 40-60 petroleum ether at room temperature.

**Yield**

82 mg, 46%

**CHN**

\(\text{C}_3\text{H}_{15}\text{B}_9\text{Ge}\) requires C, 24.51; H, 6.17. Found: C, 24.40; H, 6.48%.

**IR**

\(\nu_{\text{max}}\) 2598 cm\(^{-1}\) (B–H).

**\(^{11}\text{B}\{^1\text{H}\}\text{ NMR}\)**

CDCl\(_3\), \(\delta -2.93\) (1B), -4.22 (4B), -7.18 (2B), -9.04 (2B).

**\(^1\text{H}\text{ NMR}\)**

CDCl\(_3\), \(\delta 2.55\) (mH, \(\mu-(\text{CH}_2)_3\)), 2.35 (m, 2H, \(\mu-(\text{CH}_2)_3\)).

**MS**

\(m/z\) 244 (M\(^+\)).
6.2.3 Synthesis of 3-(p-cymene)-1,2-(CH$_3$)$_2$-3,1,2-closo-RuC$_2$B$_9$H$_9$ (3)

[HNMe$_3$][7,8-Me$_2$-7,8-nido-C$_2$B$_9$H$_{10}$] (200 mg, 0.91 mmol) was deprotonated with a 2.5 M solution of $n$-BuLi (0.72 mL, 1.81 mmol) in dry, degassed THF (20 mL). To this was added a THF solution (20 mL) of [Ru(p-cymene)Cl$_2$]$_2$ (282 mg, 0.46 mmol) at 0°C. The reaction mixture was stirred and warmed to room temperature overnight. Volatiles were removed *in vacuo* to give an oily brown solid. The crude product was dissolved in the minimum amount of DCM and passed through a silica column, using as eluent a mixture of 2:1 DCM:40-60 petroleum ether. The mobile pale yellow band was collected and the volatiles were removed *in vacuo* to yield a yellow solid 3. Yellow crystals suitable for $X$-ray diffraction were grown by diffusion of 40-60 petroleum ether and a CDCl$_3$ solution of 3 at room temperature.

| Yield       | 48 mg, 13% |
| CHN         | C$_{14}$H$_{29}$B$_9$Ru requires C, 42.49; H, 7.39. Found: C, 40.70; H, 7.22%.
| IR          | $\nu_{\text{max}}$ 2534 cm$^{-1}$ (B–H). |
| $^{11}$B{$^1$H} NMR | $\delta$ 1.10 (1B), 0.28 (1B), -3.03 (2B), -9.67 (2B), -14.48 (3B). |
| $^1$H NMR   | $\delta$ 5.85-5.70 (2d, 4H, CH$_3$C$_6$H$_4$CH(CH$_3$)$_2$), 2.95 (septet, 1H, CH$_3$C$_6$H$_4$CH(CH$_3$)$_2$), 2.30 (s, 3H, CH$_3$C$_6$H$_4$CH(CH$_3$)$_2$), 2.15 (s, 6H, (CH$_3$)$_2$), 1.35 (d, 6H, CH$_3$C$_6$H$_4$CH(CH$_3$)$_2$). |
| MS          | $m/z$ 396 (M$^+$). |
6.2.4 Synthesis of 3-(p-cymene)-1,2-µ-(CH₂)₃-3,1,2-closo-RuC₂B₉H₉ (4)

Deprotonation of [HNMe₃][7,8-µ-(CH₂)₃-7,8-nido-C₂B₉H₁₀] (260 mg, 1.12 mmol) was achieved by treating it with a 2.5 M solution of n-BuLi (0.88 mL, 2.24 mmol) in dry, degassed THF (20 mL). A solution of [Ru(p-cymene)Cl₂]₂ (343 mg, 0.56 mmol) in THF was added to the solution of Li₂[7,8-µ-(CH₂)₃-7,8-nido-C₂B₉H₁₀] thus formed at 0°C. The mixture was stirred and allowed to warm slowly, stirring overnight. The volatiles were then removed in vacuo and the resulting brown solid was dissolved in the minimum amount of DCM and passed through a silica column, eluting with 2:1 DCM:40-60 petroleum ether. The mobile pale yellow band was collected and volatiles were removed in vacuo, giving a yellow solid, 4. X-ray diffraction quality yellow crystals were grown by diffusion of 40-60 petroleum ether and a CDCl₃ solution of 4 at 25°C.

Yield  87 mg, 19%

CHN  C₁₅H₂₉B₉Ru requires C, 44.18; H, 7.17. Found: C, 43.93; H, 7.28%.

IR  ν max 2535 cm⁻¹ (B–H).

¹¹B{¹H} NMR  δ 2.82 (1B), 1.93 (1B), -5.37 (2B), -10.70 (3B), -15.38 (2B).

¹H NMR  δ  5.77-5.65 (2d, 4H, CH₃C₆H₄CH(CH₃)₂), 3.00 (septet, 1H, CH₃C₆H₄CH(CH₃)₂), 2.88-2.78 (m, 3H, (CH₂)₃), 2.69-2.60 (m, 3H, (CH₂)₃), 2.36 (s, 3H, CH₃C₆H₄CH(CH₃)₂), 1.35 (d, 6H, CH₃C₆H₄CH(CH₃)₂).

MS  m/z 408 (M⁺).
6.2.5 Synthesis of 1,2-Me$_2$-3-(bipy)-3,1,2-closo-GeC$_2$B$_9$H$_9$ (5)

A solution of 1,2-Me$_2$-3,1,2-closo-GeC$_2$B$_9$H$_9$ (100 mg, 0.43 mmol) in dry, degassed toluene (10 mL) was transferred via filter stick to a dry, degassed toluene solution (10 mL) of bipy (80 mg, 0.50 mmol). The resulting bright yellow suspension was stirred for 24 h. The toluene was removed using a gas-tight syringe, leaving a yellow solid. This solid was washed with petroleum ether (2 × 10 mL) and any remaining solvent was removed in vacuo. X-ray diffraction quality yellow block crystals of 5 were grown by diffusion of a DCM solution and 40-60 petroleum ether at room temperature.

Yield  130 mg, 79%

CHN  

C$_{14}$H$_{23}$N$_2$B$_9$Ge requires C, 43.20; H, 5.96; N, 7.20. Found: C, 41.57; H, 5.34; N, 6.50%.

MS  
m/z 231 (M – bipy), 154 (M – GeC$_4$B$_9$H$_{15}$).
6.2.6 Synthesis of 1,2-Me$_2$-3-(bipy)-3,1,2-$closo$-PbC$_2$B$_9$H$_9$ (6)

To a dry, degassed toluene solution (10 mL) of bipy (100 mg, 0.64 mmol) was added a yellow toluene solution of 1,2-Me$_2$-3,1,2-$closo$-PbC$_2$B$_9$H$_9$ (125 mg, 0.34 mmol) via filter stick and Celite® filter aid. A yellow precipitate formed immediately. The mixture was constantly stirred for 24 h at room temperature. After removal of all solvent, the yellow solid was washed with petroleum ether ($2 \times 20 \text{ mL}$). Yellow block crystals were grown by slow evaporation of a DCM solution of 6 at 25°C.

Yield 118 mg, 66%
6.3 Chapter 3. Adducts of the Supraicosahedral Stannacarborane

1,6-Me₂-4,1,6-closo-SnC₂B₁₀H₁₀

6.3.1 Synthesis of 1,6-Me₂-4-(bipy)-4,1,6-closo-SnC₂B₁₀H₁₀ (7)

A clear, colourless solution of 1,6-Me₂-4,1,6-closo-SnC₂B₁₀H₁₀ (72 mg, 0.25 mmol) in dry, degassed toluene (10 mL) was added to a Schlenk tube containing bipy (47 mg, 0.30 mmol) in dry, degassed toluene (10 mL). A bright yellow suspension formed immediately and was stirred for 24 h. A yellow solid remained after removal of the toluene via syringe. This solid was washed thoroughly with petroleum ether (2 × 10 mL) and any remaining solvent was removed in vacuo. X-ray diffraction quality crystals were grown by diffusion of 40-60 petroleum ether and a THF solution of 7 at 5°C.

Yield 86 mg, 77%

CHN C₁₄H₂₄B₁₀N₂Sn requires C, 37.61; H, 5.41; N, 6.26. Found: C, 37.19; H, 5.37; N, 6.24%.

IR νₘₐₓ 2524 cm⁻¹ (B–H).

¹¹B{¹H} NMR δ 6.89 (2B), 4.50 (1B), -0.74 (3B), -4.33 (1B), -8.35 (3B).

¹¹H NMR δ 8.95 (d, 2H, bipy), 8.30 (d, 2H, bipy), 8.20 (d of d, 2H, bipy), 7.70 (d of d, 2H, bipy), 2.50 (s, 6H, (CH₃)₂).

MS m/z 291 (M – bipy), 171 (M – Sn{bipy}), 154 (M – SnMe₂C₂B₁₀H₁₀).
6.3.2 Synthesis of 1,6-Me$_2$-4-(o-phen)-4,1,6-closo-SnC$_2$B$_{10}$H$_{10}$ (8)

A dry, degassed toluene solution (10 mL) of 1,6-Me$_2$-4,1,6-closo-SnC$_2$B$_{10}$H$_{10}$ (80 mg, 0.27 mmol) was added to a dry, degassed toluene solution (10 mL) of o-phen (54 mg, 0.30 mmol) and the resulting yellow precipitate was constantly stirred for 24 h. After removal of the solvent, the yellow solid was washed with petroleum ether (2 × 10 mL) and dried in vacuo. Crystals suitable for X-ray diffraction were grown by slow diffusion of 40-60 petroleum ether and a THF solution of 8 at 5°C.

**Yield**

94 mg, 74%

**CHN**

C$_{16}$H$_{24}$B$_{10}$N$_2$Sn requires C, 40.79; H, 5.13; N, 5.95.

Found: C, 40.04; H, 5.32; N, 5.70%.

**IR**

$\nu_{\text{max}}$ 2528 cm$^{-1}$ (B–H).

**$^{11}$B{$_1$H} NMR**

δ 7.25 (2B), 4.57 (1B), -0.80 (3B), -4.57 (1B), -8.38 (3B).

**$^1$H NMR**

δ 9.30 (d, 2H, o-phen), 8.65 (d, 2H, o-phen), 8.10 (s, 2H, o-phen), 8.00 (d of d, 2H, o-phen), 2.55 (s, 6H, (CH$_3$)$_2$).

**MS**

$m/z$ 291 (M – o-phen), 171 (M – Sn{o-phen}), 179 (M – SnMe$_2$C$_2$B$_{10}$H$_{10}$).
6.3.3 Synthesis of 1,6-Me₂-4-(Me₂bipy)-4,1,6-closo-SnC₂B₁₀H₁₀ (9)

To a dry, degassed toluene (10 mL) solution of Me₂bipy (25 mg, 0.14 mmol) was added slowly a solution of 1,6-Me₂-4,1,6-closo-SnC₂B₁₀H₁₀ (40 mg, 0.137 mmol) in dry, degassed toluene (10 mL) with stirring. A yellow precipitate instantly formed and was stirred overnight. Toluene was removed from the yellow solid using a gas-tight syringe, before the product was washed with petroleum ether (2 × 10 mL) and dried under vacuum. Crystals were grown by slow evaporation of a CD₂Cl₂ solution of 9 at room temperature.

**Yield**
53 mg, 80%

**CHN**
C₁₆H₂₈B₁₀N₂Sn requires C, 40.44; H, 5.94; N, 5.89.
Found: C, 40.52; H, 6.06; N, 5.85%.

**IR**
νmax 2523 cm⁻¹ (B–H).

**¹¹B{¹H} NMR**
δ 6.91 (2B), 4.20 (1B), -1.07 (3B), -4.54 (1B), -8.64 (3B).

**¹H NMR**
δ 8.75 (d, 2H, Me₂bipy), 8.08 (s, 2H, Me₂bipy), 7.48 (d, 2H, Me₂bipy), 2.59 (s, 6H, (CΗ₃)₂), 2.49 (s, 6H, (CΗ₃)₂).

**MS**
m/z 291 (M – Me₂bipy), 182 (M – SnMe₂C₂B₁₀H₁₀).
6.3.4 Synthesis of 1,6-Me₂-4-(Ph₂bipy)-4,1,6-closo-SnC₂B₁₀H₁₀ (10)

A solution of 1,6-Me₂-4,1,6-closo-SnC₂B₁₀H₁₀ (30 mg, 0.10 mmol) in dry, degassed toluene (10 mL) was introduced with stirring to a dry, degassed toluene (10 mL) solution of Ph₂bipy (32 mg, 0.10 mmol), which resulted in the instantaneous formation of a yellow precipitate. After stirring for 24 h, the solvent was removed leaving a bright yellow solid. This solid was washed with petroleum ether (2 × 10 mL) and dried in vacuo. The product was recrystallised from slow evaporation of a CD₂Cl₂ solution of 10 at room temperature.

Yield 33 mg, 57%
IR \( \nu_{\text{max}} \) 2530 cm\(^{-1}\) (B–H).
6.4 Chapter 4. Adducts of the Supraicosahedral Stannacarborane 4,1,2-\textit{closo}-SnC\textsubscript{2}B\textsubscript{10}H\textsubscript{10}

6.4.1 Synthesis of 1,2-\(\mu\)-(CH\textsubscript{2})\textsubscript{3}-4,1,2-\textit{closo}-SnC\textsubscript{2}B\textsubscript{10}H\textsubscript{10} (11)

A solution of 1,2-\(\mu\)-(CH\textsubscript{2})\textsubscript{3}-1,2-\textit{closo}-C\textsubscript{2}B\textsubscript{10}H\textsubscript{10} (150 mg, 0.81 mmol) in dry, degassed THF (20 mL) was stirred with sodium pieces (130 mg, 5.7 mmol) and naphthalene (\textit{ca.} 10 mg) at room temperature for 48 h. The resulting dark green solution of the reduced carborane was transferred \textit{via} cannula to a dry, degassed THF solution (10 mL) of SnCl\textsubscript{2} (153 mg, 0.81 mmol) at -196°C, then allowed to warm to 0°C with stirring. The crude, dark brown reaction mixture was evaporated to dryness and then suspended in DCM (40 mL). The mixture was filtered and all volatiles were removed \textit{in vacuo}, yielding a white solid. Recrystallisation by diffusion of a DCM solution and 40-60 petroleum ether at 5°C afforded pale yellow block crystals of the product.

\textbf{Yield} \quad 60 mg, 25%

\textbf{CHN} \quad C\textsubscript{5}H\textsubscript{16}B\textsubscript{10}Sn requires C, 19.8; H, 5.32. Found: C, 19.9; H, 5.44%.

\textbf{IR} \quad \nu_{\text{max}} 2547 \text{ cm}^{-1} (B–H).

\textbf{\textit{^1}B\{\textit{^1}H\} NMR} \quad \delta 7.73 (2B), 6.45 (4B), 4.12 (1B), 1.06 (1B), -0.27 (2B).

\textbf{\textit{^1}H NMR} \quad \delta 3.20-3.10 (m, 2H, (CH\textsubscript{2})\textsubscript{3}), 2.85-2.75 (m, 2H, (CH\textsubscript{2})\textsubscript{3}), 2.05-1.90 (m, 2H, (CH\textsubscript{2})\textsubscript{3}).

\textbf{MS:} \quad m/z 302 (M\textsuperscript{+}), 119 (M − C\textsubscript{5}H\textsubscript{16}B\textsubscript{10}).
6.4.2 Synthesis of 1,2-µ-(CH$_2$)$_3$-4-(bipy)-4,1,2-closo-SnC$_2$B$_{10}$H$_{10}$ (12)

A solution of 1,2-µ-(CH$_2$)$_3$-4,1,2-closo-SnC$_2$B$_{10}$H$_{10}$ (10 mg, 0.03 mmol) in dry, degassed toluene (5 mL) was added to a dry, degassed toluene solution (3 mL) of bipy (6 mg, 0.04 mmol) and the resulting yellow suspension was stirred for 24 h. On settling, the toluene was removed using a gas-tight syringe, leaving a yellow solid which was washed with petroleum ether (2 × 10 mL) and dried in vacuo to afford 12 as a yellow solid. Small crystals were grown by vapour diffusion of 40-60 petroleum ether and a DCM solution of 12 at 5°C.

**Yield**  
10 mg, 73%

**IR**  
$\nu_{\text{max}}$ 2518 cm$^{-1}$ (B–H).

**$^{11}$B{$^1$H} NMR**  
$\delta$ 3.35 (3B), 2.30 (2B), -4.05 (2B), -5.16 (2B), -10.78 (1B).

**$^1$H NMR**  
$\delta$ 8.99 (d, 2H, bipy), 8.22 (d, 2H, bipy), 8.13 (d of d, 2H, bipy), 7.69 (d of d, 2H, bipy), 3.05-2.95 (m, 2H, (CH$_2$)$_3$), 2.77-2.68 (m, 2H, (CH$_2$)$_3$), 2.19-1.66 (m, 1H, (CH$_2$)$_3$).
6.4.3 Synthesis of 1,2-µ-(CH$_2$)$_3$-4-(o-phen)-4,1,2-closo-SnC$_2$B$_{10}$H$_{10}$ (13)

A solution of 1,2-µ-(CH$_2$)$_3$-4,1,2-closo-SnC$_2$B$_{10}$H$_{10}$ (30 mg, 0.10 mmol) in dry, degassed toluene (10 mL) was stirred with a dry, degassed toluene solution (10 mL) of o-phen (20 mg, 0.11 mmol) and a yellow precipitate formed immediately. The precipitate was stirred for 24 h. After solvent removal, the yellow solid 13 was washed with petroleum ether (2 × 10 mL) and dried in vacuo. Crystals by solvent diffusion of 40-60 petroleum ether and a DCM solution of 13 at 5°C.

**Yield**  
31 mg, 64%

**IR**  
ν$_{\text{max}}$ 2540 cm$^{-1}$ (B–H).

**$^{11}$B{$^1$H} NMR**  
δ 3.73 (3B), 2.36 (2B), -4.25 (2B), -5.07 (2B), -10.69 (1B).

**$^1$H NMR**  
δ 9.34 (d, 2H, phen), 8.59 (d, 2H, phen), 8.05 (s, 2H, phen), 8.00 (d of d, 2H, phen), 3.15-3.05 (m, 2H, (CH$_2$)$_3$), 2.82-2.72 (m, 2H, (CH$_2$)$_3$), 2.05-1.95 (m, 1H, (CH$_2$)$_3$), 1.80-1.70 (m, 1H, (CH$_2$)$_3$).
6.4.4 Synthesis of 1,2-µ-(CH\textsubscript{2})\textsubscript{3}-4-(Ph\textsubscript{2}bipy)-4,1,2-closo-SnC\textsubscript{2}B\textsubscript{10}H\textsubscript{10} (14)

A solution of 1,2-µ-(CH\textsubscript{2})\textsubscript{3}-4,1,2-closo-SnC\textsubscript{2}B\textsubscript{10}H\textsubscript{10} (10 mg, 0.03 mmol) in dry, degassed toluene (10 mL) was allowed to react with a dry, degassed toluene solution (10 mL) of Ph\textsubscript{2}bipy (12 mg, 0.04 mmol). A yellow solid was precipitated instantaneously. Following overnight stirring, the toluene was removed using a gastight syringe and the remaining yellow solid of 14 was washed with petroleum ether (2 × 10 mL) and dried in vacuo. The product was crystallised by solvent diffusion of 40-60 petroleum ether and a DCM solution of 14 at -5°C.

**Yield** 15 mg, 82%

**IR** 2522 cm\textsuperscript{-1} (B–H).

**\textsuperscript{11}B{\textsuperscript{1}H} NMR**

δ 3.70 (3B), 2.41 (2B), -4.13 (4B), -10.79 (1B).

**\textsuperscript{1}H NMR**

δ 9.03 (d, 2H, Ph\textsubscript{2}bipy), 8.45 (d, 2H, Ph\textsubscript{2}bipy), 7.91 (d, 2H, Ph\textsubscript{2}bipy), 7.82-7.73 (m, 4H, Ph\textsubscript{2}bipy), 7.64-7.55 (m, 6H, Ph\textsubscript{2}bipy), 3.05-2.99 (m, 2H, (CH\textsubscript{2})\textsubscript{3}), 2.80-2.70 (m, 2H, (CH\textsubscript{2})\textsubscript{3}), 2.01-1.92 (m, 1H, (CH\textsubscript{2})\textsubscript{3}), 1.78-1.69 (m, 1H, (CH\textsubscript{2})\textsubscript{3}).
6.4.5 Synthesis of 1,2-µ-\{C₆H₄(CH₂)₂\}-4-(bipy)-4,1,2-closo-SnC₂B₁₀H₁₀ (15)

A solution of 1,2-µ-\{C₆H₄(CH₂)₂\}-4,1,2-closo-SnC₂B₁₀H₁₀ (70 mg, 0.192 mmol) in dry, degassed toluene (10 mL) was added to a dry, degassed toluene solution (10 mL) of bipy (90 mg, 0.575 mmol). The resulting yellow suspension was stirred for 24 h. After settling, the toluene was removed using a gas-tight syringe, leaving a yellow solid which was subsequently washed with petroleum ether (2 × 10 mL). Any remaining solvent was removed \textit{in vacuo} to afford 15 as a yellow solid. Diffraction-quality crystals were grown by slow evaporation of a DCM solution of 15 at room temperature.

**Yield**

61 mg, 61%

**IR**

\(\nu_{\text{max}}\) 2521 cm\(^{-1}\) (B–H).

**\(^{11}\text{B}\{^{1}\text{H}\} \text{NMR}\)**

\(\delta\) 7.19 (br, 2B), 4.16 (br, 2B), 2.92 (br, 2B), -3.65 (br, 1B), -5.62 (br, 1B), -10.48 (br, 2B).

**\(^{1}\text{H} \text{NMR}\)**

\(\delta\) 8.87 (d, 2H, bipy), 8.24 (d, 2H, bipy), 8.04 (d of d, 2H, bipy), 7.60 (d of d, 2H, bipy), 7.27-7.10 (m, 4H, C₆H₄(CH₂)₂), 3.98 (d, 2H, C₆H₄(CH₂)₂), 3.82 (d, 2H, C₆H₄(CH₂)₂).
6.5 Chapter 5. New 13-vertex Stannacarboranes

6.5.1 Synthesis of 1,10-Me₂-4,1,10-closo-SnC₂B₁₀H₁₀ (16)

Sodium (0.19 g, 8.13 mmol) reduction of 1,12-NMe₂-N₁,12-N₁₂-closo-C₂B₁₀H₁₀ (0.20 g, 1.16 mmol) in liquid ammonia (ca. 20 mL) at -78°C for 4 h yielded a dark blue solution. Removal of ammonia upon warming the reaction mixture allowed the dry residue to be extracted into degassed THF (20 mL). The grey suspension was filtered into a Schlenk tube under nitrogen giving a clear solution. Following addition via cannula to a THF (20 mL) solution of SnCl₂ (0.22 g, 1.16 mmol) at -196°C, the reaction mixture was cooled to -196°C before slowly warming to room temperature with stirring. A dark brown solid remained after removal of solvent, which was suspended in DCM and filtered. All volatiles were then removed in vacuo, leaving a white solid. Recrystallisation of the product by diffusion of a DCM solution and 40-60 petroleum ether at -30°C afforded colourless block crystals of the product.

Yield: 71 mg, 21%

CHN: C₄H₁₆B₁₀Sn requires C, 16.51; H, 5.54. Found: C, 16.30; H, 5.64%.

IR: ν_max 2552 cm⁻¹ (B–H).

¹¹B{¹H} NMR: δ 4.89 (4B), -0.24 (5B), -3.25 (1B).

¹H NMR: δ 1.70 (s, 6H, (CH₃)₂).

MS: m/z 289 (M⁺), 171 (M – Sn), 119 (M – C₄H₁₆B₁₀).
6.5.2 Synthesis of 1,10-Me₂-4-(Me₂bipy)-4,1,10-closo-SnC₂B₁₀H₁₀ (17)

A stirring degassed toluene solution (5 mL) of Me₂bipy (20 mg, 0.11 mmol) was treated with a toluene solution (5 mL) of 1,10-Me₂-4,1,10-closo-SnC₂B₁₀H₁₀ (30 mg, 0.10 mmol) at room temperature. A bright yellow precipitate formed instantaneously. The yellow suspension was stirred overnight, after which time the toluene was removed using a gas-tight syringe. The resulting yellow solid was washed with petroleum ether (2 × 10 mL) and dried in vacuo. X-ray diffraction quality crystals were grown by vapour diffusion of 40-60 petroleum ether and a DCM solution of 17 at 5°C.

Yield 20 mg, 42%

CHN C₁₆H₂₈N₂B₁₀Sn requires C, 40.44; H, 5.94; N, 5.89. Found: C, 39.85; H, 5.76; N, 5.72%.

IR νₘₐₓ 2521 cm⁻¹ (B–H).

¹¹B{¹H} NMR δ 16.62 (2B), 4.01 (1B), -2.00 (1B), -6.48 (2B), -13.53 (2B), -21.99 (2B).

¹H NMR δ 8.60 (d, 2H, Me₂bipy), 8.15 (s, 2H, Me₂bipy), 7.55 (d, 2H, Me₂bipy), 2.60 (s, 6H, Me₂bipy), 1.33 (s, 3H, CH₃), 1.30 (s, 3H, CH₃).
6.5.3 Synthesis of 1,12-Me₂-4,1,12-*closo*-SnC₂B₁₀H₁₀ (18)

A degassed toluene solution (20 mL) of 1,10-Me₂-4,1,10-*closo*-SnC₂B₁₀H₁₀ (438 mg, 1.51 mmol) was heated to reflux for 3 h. After cooling to room temperature, the solution was filtered and solvent was removed. Following washing with petroleum ether (2 × 20 mL) and drying *in vacuo*, compound 18 was afforded as a white solid.

Yield 288 mg, 66%
IR \( v_{\text{max}} 2544 \text{ cm}^{-1} \) (B–H).
\(^{11}\text{B}\{^{1}\text{H}\} \text{ NMR} \) C\(\text{T}\)D₈, \( \delta \) 17.13 (1B), 11.15 (1B), 1.98 (4B), -0.90 (3B), -3.67 (1B).
\(^{1}\text{H} \text{ NMR} \) C\(\text{T}\)D₈, \( \delta \) 1.25 (s, 6H, (CH₃)₂).
MS \( m/z \) 289 (M⁺), 171 (M – Sn), 119 (M – C₄H₁₆B₁₀).
6.5.4 Synthesis of 1,12-Me\textsubscript{2}-4-(bipy)-4,1,12-closo-SnC\textsubscript{2}B\textsubscript{10}H\textsubscript{10} (19)

A solution of 1,12-Me\textsubscript{2}-4,1,12-closo-SnC\textsubscript{2}B\textsubscript{10}H\textsubscript{10} (10 mg, 0.03 mmol) in degassed toluene (3 mL) was added dropwise to a stirring degassed toluene (3 mL) solution of bipy (6 mg, 0.04 mmol). The resulting pale yellow suspension was stirred for 24 h. Solvent was removed using a gas-tight syringe and a yellow solid remained. This solid was washed with petroleum ether (2 × 10 mL) and any remaining solvent was removed \textit{in vacuo}. X-ray diffraction quality crystals were grown by vapour diffusion of 40-60 petroleum ether and a DCM solution of 19 at 25°C.

Yield 4 mg, 30%
6.5.5 Synthesis of 4-(p-cymene)-4,5,2,3-closo-RuSnC₂B₉H₁₁ (20)

A solution of 3-(p-cymene)-3,1,2-closo-RuC₂B₉H₁₁ (150 mg, 0.41 mmol) in dry, degassed THF (20 mL) was stirred overnight with finely cut sodium pieces (94 mg, 4.10 mmol). The resulting dark red solution of Na₂[(p-cymene)RuC₂B₉H₁₁] was transferred via cannula to a second Schlenk tube containing a dry, degassed frozen THF solution (10 mL) of SnCl₂ (85 mg, 0.45 mmol). The mixture was re-frozen and then warmed slowly to 0°C, before stirring the brown suspension overnight at room temperature. Volatiles were removed in vacuo, leaving an oily brown solid. This solid was suspended in DCM and filtered through Celite® producing a clear yellow solution. Solvent was removed in vacuo to yield a yellow solid.

Yield 89 mg, 45%

MS m/z 485 (M⁺), 365 (M – Sn).
6.6 References


