Studies of the synthesis and derivative chemistry of icosahedral carboranes

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STUDIES ON THE SYNTHESIS AND DERIVATIVE CHEMISTRY OF ICOSAHEDRAL CARBORANES

A Thesis Submitted to
The University of Durham

by

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(Hatfield College)

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To my parents

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I am indebted to the Ministry of Defence, Aldermaston for the maintenance grant and in particular to Mr. W.A. Fort for making the whole project possible and his close liaison.

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Finally my most sincere thanks go to Mrs. Margaret da Cunha for the many exasperating hours spent deciphering and typing this thesis.

MEMORANDUM

The work described in this thesis was carried out by me in the Chemistry Department of the University of Durham between October 1977 and September 1980. I declare that this work has not been submitted for any other degree. This thesis is my original work, except where indicated by reference to other work.

ABSTRACT

As part of the general study of icosahedral carborane chemistry a comprehensive literature survey is presented with references.

Investigations of the preparative routes to ortho-carborane, 1-methyl-o-carborane and some carborane polymers showed that improvements on existing literature methods could be made.

In the synthesis of possible carborane-polymer precursors, several coupled carborane systems were investigated. These included C-C', B-B' direct cage coupling reactions and coupling via short alkyl chains. Reactions of $Me\theta Li$ ($\theta = -CB_{10}H_{10}C-$) with boron chlorides produced the previously unreported boron coupled carboranes $(Me\theta)_2BR$, $(R = Cl, OH, Ph)$ and $Me\theta BPh_2$. Three carborane cages could not be bonded to a single boron atom. The previously unreported di-(3,3'-o-carboranyl)-N,N-piperazine was prepared from the $[H\theta H]^{2-}$ anion.

Studies were made of the reaction of $Me\theta Li$ with ICN and $(CN)_2$. An attempted ortho-metallation reaction with $SnCl_4$, $Me\theta Li$ and PhCN yielded an interesting dicyclic tin adduct, $SnCl_4 \cdot [(PhCN)_3]_2$.

The reactions of $C_2B_9H_{11}{}^{2-}$ with tin, germanium and silicon tetrachlorides produced a new class of dicarboranyl metal "sandwich" compounds for which a novel tilted cage structure was proposed. Zinc metallocarboranes could not be synthesised. Hot atom chemistry was employed in attempts to prepare main group metallocarboranes by polyhedral expansion.

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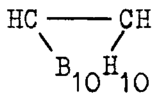
NOMENCLATURE

The nomenclature used throughout this thesis is based on that widely used in the current carborane literature with the exception of the Russian literature as indicated below.

Formula	Nomenclature
$1,2-C_2B_{10}H_{12}$	Ortho-carborane; 1,2-dicarbadodecaborane(12); (Rus:- barene)
$1,7-C_2B_{10}H_{12}$	Meta-carborane; 1,7-dicarbadodecaborane(12); (Rus:- neo-barene)
$1,12-C_2B_{10}H_{12}$	Para-carborane; 1,12-dicarbadodecaborane(12).
$C_2B_9H_{11}^{2-}$	Dicarbollide ion; dicarbaundecaborate(11) dianion.
$C_2B_9H_{12}^{-}$	Dicarbaundecaborate(12) anion.
$C_2B_9H_{13}$	Dicarbaundecaborane(13).
$C_2B_9H_{11}$	Dicarbaundecaborane(11).

The following symbols are used throughout this thesis to represent the carboranes.

Nomenclature	Symbols		
Ortho carborane	$H\theta H$;	$o-\underbrace{HCB_{10}H_{10}CH}$;	
Meta carborane	$H\theta'H$;	$m-\underbrace{HCB_{10}H_{10}CH}$	
Para carborane	$H'\theta'H$;	$p-\underbrace{HCB_{10}H_{10}CH}$	

NOTE: Care should be taken with the interpretation of diagrams containing exocyclic rings. For example a 4-membered ring containing the symbol θ in fact contains 5 atoms, and thus may be considered as a 5-membered ring.

CHAPTER 1

LITERATURE REVIEW

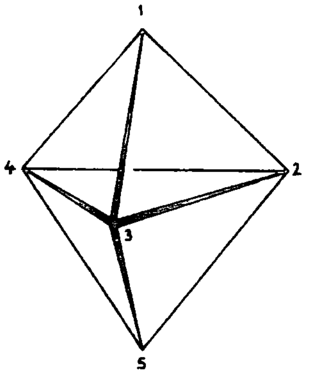
1.1 INTRODUCTION

This chapter surveys the published literature from the birth of the icosahedral carborane field in the early 60's to 1981. Whilst other reviews have been published concerning specific areas of carborane chemistry, no review has covered all the areas in one publication since Grimes's book "Carboranes" (68) in 1970. Although this review covers work described in "Carboranes", different interpretations have since been placed on some of the data presented in it, in the light of further work. It is therefore hoped that this review will be used as both a key to the literature and an introduction to the field for someone with no previous experience of carborane chemistry.

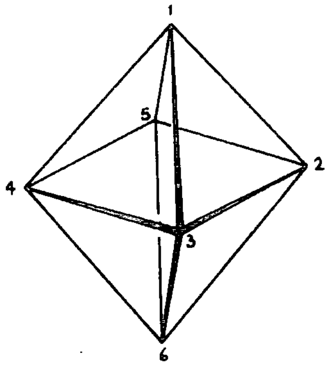
Structure and Bonding of Carboranes

Carboranes can be broadly described as a group of polyhedral compounds containing both carbon and boron atoms in the same molecule. The polyhedra can contain between 1 and 4 carbon atoms although those with two carbon atoms are more numerous. These dicarbaboranes can be divided into three distinct classes based on their formulae. The most synthetically important class the closo (closed) carboranes has the general molecular formula $C_2B_{n-2}H_n$ (n = 5 - 12), the nido- (nest like) carboranes have the general molecular formulae $C_2B_{n-4}H_n$ to $C_2B_{n-2}H_n^{2-}$, and the arachno- (web like) carboranes have the general formulae $C_2B_{n-6}H_n$ to $C_2B_{n-2}H_n^{4-}$.

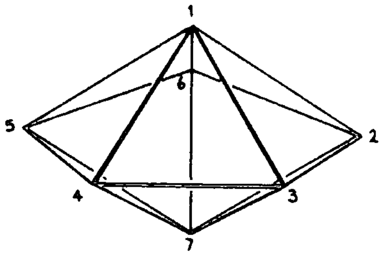
The closo dicarbadodecaboranes are the highest members of the closo carborane series (see Figure 1.1.1) and consist of two carbon atoms and ten boron atoms in an icosahedral arrangement, each of the atoms in the polyhedra possessing a terminal hydrogen. The presence of two carbon atoms



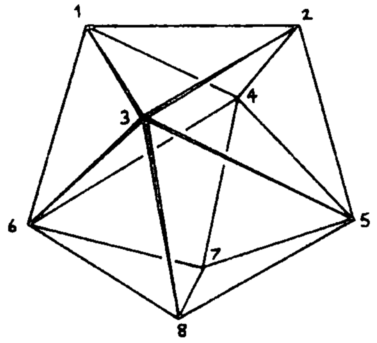
$C_2B_3H_5$



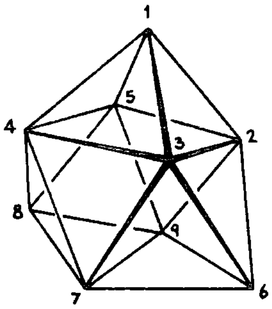
$C_2B_4H_6$



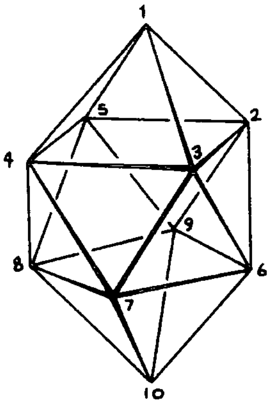
$C_2B_5H_7$



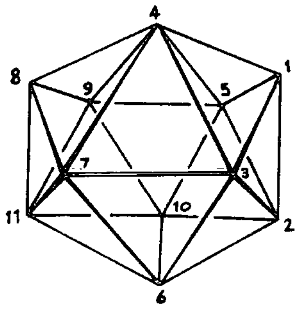
$C_2B_6H_8$



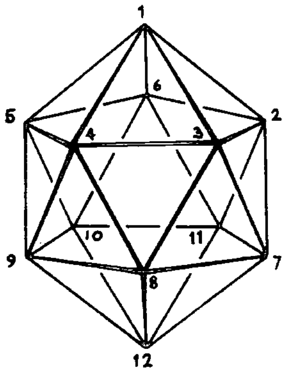
$C_2B_7H_9$



$C_2B_8H_{10}$



$C_2B_9H_{11}$



$C_2B_{10}H_{12}$

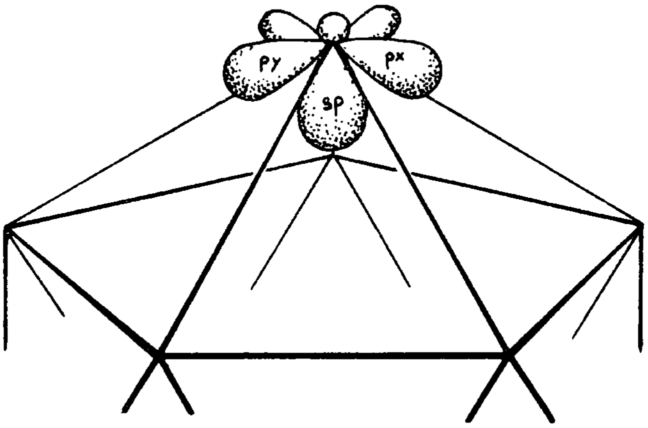
Figure 1.1.1. The Polyhedral Closo-Carborane Series

produces three possible isomers 1,2-dicarbadodecaborane (12) [or ortho-carborane], 1,7-dicarbadodecaborane (12) [meta-carborane] and 1,12-dicarbadodecaborane (12) [para-carborane].

The structures of the carboranes can be rationalised in terms of Wade's rules based on the total number of electron pairs available for skeletal bonding. (360,379)

Considering a B-H unit, if a single sp orbital is used to form the exo-B-H bond, then there remains one sp orbital pointing towards the centre of the polyhedron and two p orbitals available for skeletal bonding. (See Figure 1.1.2)

Figure 1.1.2.



Thus each B-H unit is capable of donating 2e$^-$ for skeletal bonding and by similar considerations, a C-H unit can donate 3e$^-$.

Wade's rules show that for a borane or carborane based on a polyhedron of n vertices a closo structure has n + 1 skeletal electron pairs, nido n + 2 and arachno n + 3. Thus for the dicarbadodecaboranes ($C_2B_{10}H_{12}$) there are 13 electron pairs available for skeletal bonding in a closo cage which must therefore have 12 vertices hence an icosahedral structure is adopted held together by three-centre bonds.

The electrons donated by the C-H and B-H units for skeletal bonding are delocalised throughout the entire polyhedron and have led to the description of carboranes as pseudo aromatic species. Indeed examples of aromatic behaviour have been noted and are discussed in later sections.

Preparation and Properties of Icosahedral Carboranes

Decaborane (14), $B_{10}H_{14}$, is attacked at the 6-and 9-positions by Lewis bases such as acetonitrile or diethyl sulphide with the loss of hydrogen and the formation of a bis-ligand, $B_{10}H_{12}L_2$. The reaction of this derivative with acetylene yields ortho-carborane (o-carborane).(3,4,380,445)

$$B_{10}H_{12}(CH_3CN)_2 + HC\equiv CH \longrightarrow H\Theta H + 2CH_3CN + H_2$$

The use of various substituted acetylenes leads to appropriately substituted ortho-carboranes with the exception of acetylenes containing alcohol or carboxylic acid groups as these cause degradation of the decaborane cage. C-C coupled ortho-carboranes are prepared by the reaction of diacetylene with bis(acetonitrile) decaborane. (18,19)

$$HC\equiv C-C\equiv CH + B_{10}H_{12}(CH_3CN)_2 \longrightarrow H\Theta\text{-}\Theta H + HC\equiv C-\Theta H$$

Ortho-carborane shows remarkable thermal stability in comparison to boranes and small closo carboranes. However, at 470° in an inert atmosphere it rearranges smoothly to 1,7-or meta-carborane (m-carborane) with near quantitative yields. (53,122,381, 382-384) Meta-carborane isomerises further at 620° to give 1,12-or para-carborane (p-carborane) although the yield is much smaller due to some cage degradation. (384,385) The isomerisation to meta carborane can be applied to ortho-carborane derivatives.

The mechanism for the rearrangement of ortho to meta-carborane has still to be conclusively proved but a "Diamond-Square-Diamond" rearrangement via a cubo-octahedral intermediate (see Figure 1.1.3) appears to be the most likely. (68, 386-388) Other workers (53,389) have suggested a mutual rotation of the two pentagonal bipyramidal halves of the cage. (Figure 1.1.4) Such a mechanism seems more unlikely yet it can be taken

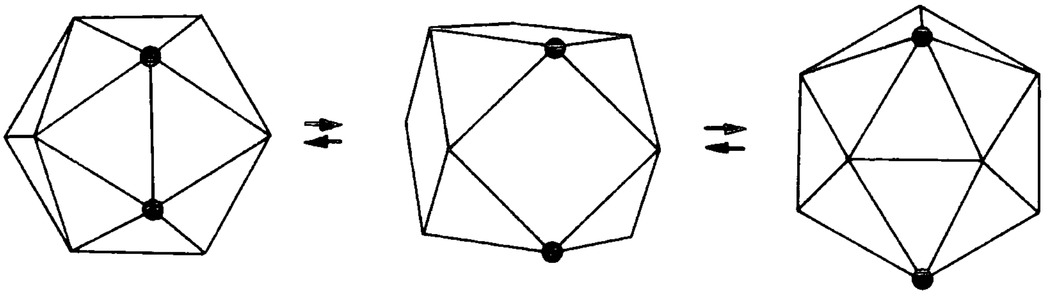


Figure 1.1.3. "Diamond-Square-Diamond" Rearrangement

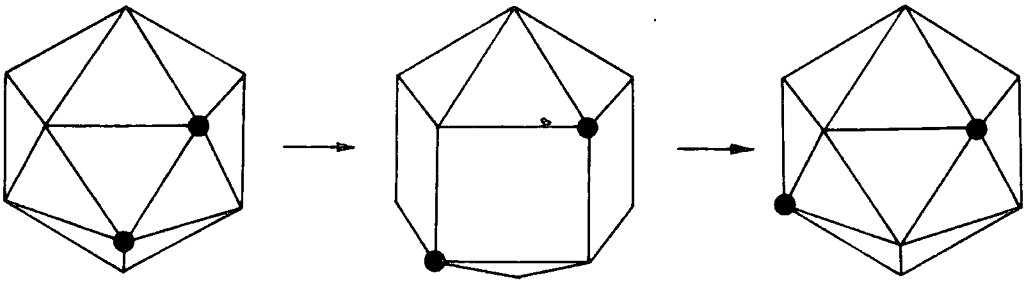
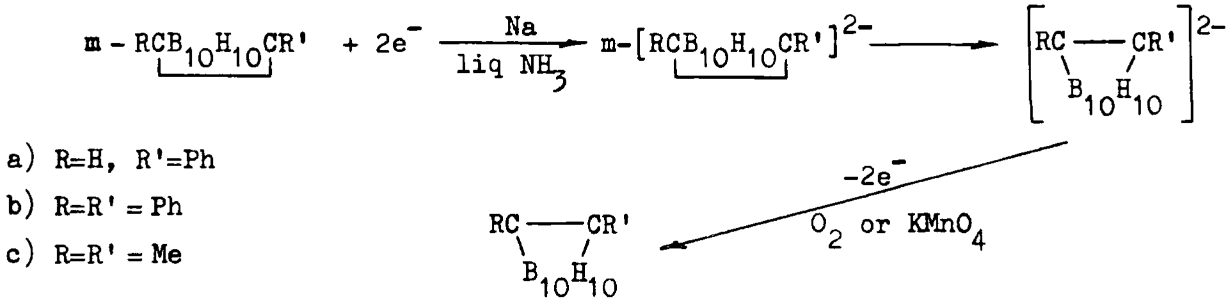


Figure 1.1.4. Mutual Rotation Rearrangement

one step further to explain the formation of para-carborane which the first mechanism cannot. However, a combination of the first mechanism followed by a rotation of a cubo-octahedral triangular face would give para-carborane and could explain why much more rigorous conditions are needed and why cage degradation occurs. (390)

The reverse isomerisations can be accomplished by treatment of para-carborane (391) or meta-carborane (392 - 394) with alkali metals in liquid ammonia.



a) R=H, R'=Ph
b) R=R' = Ph
c) R=R' = Me

The ortho-carborane cage is very stable to most forms of chemical attack, but is degraded by strong oxidizing agents such as nitric acid and by bases such as methoxide ion or alkyl amines. The chemical stability of the icosahedral carboranes allows a large amount of derivative chemistry to be performed at the carbon atoms or to a lesser extent at the boron atoms.

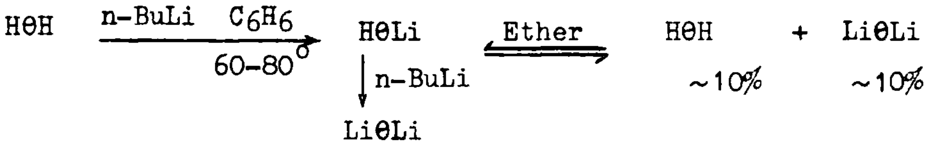
The charge distribution in the icosahedral carboranes has been studied by means of the position of electrophilic attack and also calculated theoretically (395 - 398) in terms of ground-state charge distributions. Both of these methods have shown that the highest negative charge is accumulated around the boron atoms furthest away from the carbon atoms in the cage. Thus for ortho-carborane the decrease of negative charge through the cage follows the order B(9,12) > B(8,10) > B(4,5,7,11) > B(3,6) > C(1,2). Tetrabromination of 1,2-dimethyl-o-carborane has shown that there is a net transfer of negative charge from C-bonded substituents into the cage. Indeed the cage carbon atoms themselves donate charge to the boron atoms.

This may appear to contradict basic electronegativity considerations but it must be remembered that the carbon atoms are not in their ground state valency. Other evidence for this inductive effect of the carboranes is shown by the relative pKa values of carboxylic acid derivatives. These are discussed in full in Section 1.6, but they show that the order of electron-withdrawal decreases in the order o-carborane > m-carborane > p-carborane, boron substituent.

1.2 ALKALI METAL AND MAGNESIUM DERIVATIVES

Alkali Metal Derivatives

The ortho carborane unit displays a strong electron-withdrawing character with regard to substituents on the carbon atoms. As a result the C-H bond is mildly acidic and so susceptible to attack by n-butyl lithium or phenyl lithium (12) to form the C-lithio derivative. In ether or in ether/benzene mixture an equilibrium exists between mono-lithio carborane and both di-lithio carborane and unsubstituted carborane, but in benzene alone, only the mono-C-lithio derivative is formed.



$$\begin{array}{ccccccc} H\theta H & \xrightarrow[60-80^{\circ}]{n\text{-}BuLi\quad C_6H_6} & H\theta Li & \overset{Ether}{\rightleftharpoons} & H\theta H & + & Li\theta Li \\ & & \big\downarrow{\scriptstyle n\text{-}BuLi} & & \sim 10\% & & \sim 10\% \\ & & Li\theta Li & & & & \end{array}$$

If an excess of n-butyl lithium is added to the mono-lithio derivative, the di-C-lithio derivative is formed. The equilibrium in ether can be conveniently shown by the reaction of carbon dioxide with mono-lithio carborane in ether, compared to the equivalent reaction in benzene. In ether, only the dicarboxylic acid ($HOOC\theta COOH$) is formed, showing that lithium exchange is taking place (12), whereas in benzene the mono-functional carboxylic acid ($H\theta COOH$) is formed. (225)

Meta-carborane undergoes similar reactions with n-butyl lithium. Again there is an equilibrium reaction in ether, but in this case the equilibrium is much further towards the left with only about 2% of the di-lithio-m-carborane being formed. The difference between the two equilibria can be explained by the weaker electron-withdrawing power of the meta-carborane giving rise to less polar C-H bonds, a slower rate of metallation and consequently a shifting of the equilibrium.

Metallation by sodium, potassium and calcium can be effected by addition of the metals to a solution of the carboranes in liquid ammonia, the reacting species being the alkali metal amides.

Magnesium Derivatives

Carboranyl Grignard reagents can be made by the action of magnesium on C-halo-carboranes or by the direct action of alkyl magnesium halides on the carborane cage.

$$H\theta Br + Mg \longrightarrow H\theta MgBr$$

$$H\theta H + EtMgBr \xrightarrow{THF} H\theta MgBr + EtH$$

In THF the reaction is complicated by an equilibrium analogous to that observed with the C-lithio carboranes in ether.

$$\underset{\sim 80\%}{2H\theta MgBr} \overset{THF}{\rightleftarrows} \underset{\sim 10\%}{H\theta H} + \underset{\sim 10\%}{BrMg\theta MgBr}$$

The 1-bromomagnesio-methyl carborane derivative also undergoes a similar equilibrium reaction as can be shown by the reaction of carbon dioxide with the Grignard reagent in THF and in ether. In THF, 1-bromomagnesio-methyl carborane rearranges to yield 1-methyl,2-bromomagnesio carborane, the reaction of carbon dioxide with which gives 1-methyl,2-carboxylic acid carborane. (52, 55, 158) A reaction scheme has been reported for this rearrangement. (159) The equivalent reaction in ether, in which very little rearrangement takes place, yields mostly carboranyl acetic acid.

$$\begin{tikzcd}
H\theta CH_2MgBr \arrow[r, "THF"] \arrow[d, "\substack{1.CO_2\\2.H_3O^+}"', "Ether"] & Me\text{-}\theta MgBr \arrow[d, "\substack{1.CO_2\\2.H_3O^+}"', "THF"] \\
H\theta CH_2COOH & Me\text{-}\theta COOH
\end{tikzcd}$$

The 1-chloromethyl carborane behaves differently from the 1-bromomethyl derivative on reaction with magnesium in ether, affording mostly the rearranged Grignard compound. Indeed, if 1-chloromethyl carborane is added to 1-bromo-magnesiomethyl carborane in ether, the net result is the metallation of the free cage C-H bond on the 1-chloromethyl carborane.

$$H\Theta CH_2Cl \; + \; H\Theta CH_2MgBr \xrightarrow{\text{Ether}} BrMg\Theta CH_2Cl \; + \; H\Theta CH_3$$

This reaction can be explained in terms of the higher electronegativity of chlorine, than bromine, which gives rise to a greater electron-withdrawal from the methylene group. This in turn makes the remaining C-attached hydrogen atom more acidic (227) and so more susceptible to metallation. Similarly, the reaction of n-butyl lithium with chloromethyl carborane yields mainly 1-lithio , 2-chloromethyl carborane, whereas bromomethyl carborane reacts via a lithium bromine exchange and isomerisation to give 1-lithio , 2-methyl carborane.

The isomerisation of the carboranyl Grignard reagents has been shown to take place via an intermolecular metal atom transfer.

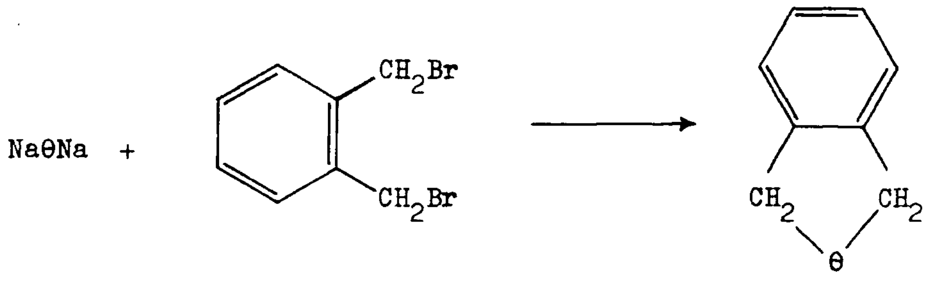
1.3 ALKYL AND HALOALKYL DERIVATIVES

Synthesis of Alkyl Derivatives

C-alkyl derivatives of the icosahedral carboranes can be prepared by several routes. The most frequently used route is the reaction of a primary alkyl halide (usually the bromide or iodide) with a C-lithio or C-Grignard carborane in ether, benzene or liquid ammonia. Secondary or tertiary alkyl halides do not react.

$$\mathrm{Ph\theta Li} + \mathrm{CH_3I} \longrightarrow \mathrm{Ph\theta CH_3} + \mathrm{LiI}$$

The method can be used for the preparation of exocyclic rings using di-C-metallo-o-carborane.

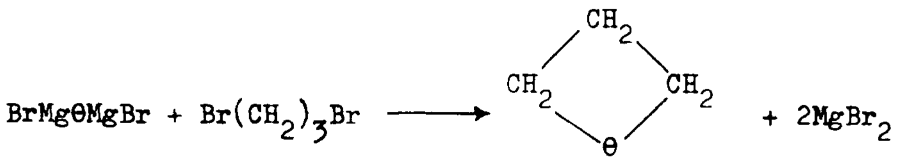


(See section 5). Alkyl derivatives can be synthesised by the reaction of carboranyl Grignards with primary alkyl bromides and iodides, and di-alkylsulphates. (36)

$$\mathrm{R\theta MgBr} + \mathrm{R'CH_2Br} \longrightarrow \mathrm{R\theta CH_2R'} + \mathrm{MgBr_2}$$

$$R = H,\ Me,\ Ph,\ CH = CH_2.$$

Here again the secondary and tertiary alkyl halides and the primary alkyl chlorides are unreactive. The adjacent carbon atoms in o-carborane allow the formation of small exo-cyclic ring systems by reactions with 1,3-di-bromo-propane.



Meta-carborane does not undergo this reaction because its carbon atoms are non-adjacent.

C-aryl and C-alkyl carboranes may also be prepared by the reaction of substituted acetylenes with bis-(acetonitrile) decaborane. (3, 4)

$$PhC \equiv CH + B_{10}H_{12}(CH_3CN)_2 \longrightarrow Ph\Theta H + H_2 + 2CH_3CN$$

Alkylation at the boron atoms can be achieved by the reaction of an alkyl boron dichloride with the dicarbollide anion. (See section 16)

$$(3)\text{-}1,2\text{-}C_2B_9H_{11}{}^{2-} + EtBCl_2 \xrightarrow[-40^\circ]{THF} \underbracket{HCB_{10}H_9(Et)CH} + 2Cl^-$$

This affords 3-alkylated products because the boron atom enters the cage adjacent to the two carbon atoms.

Electrophilic alkylation of the carborane nucleus (2) has been achieved in the presence of aluminium trichloride. The reaction takes place at the boron atoms in the order of decreasing electron density starting at the 9, 12 atoms in ortho carborane. The reactions are carried out in the refluxing alkyl halides and can lead in the case of ethyl bromide to the substitution of eight ethyl groups. Iso-propyl bromide only yields mono- and di-substituted o-carborane due to steric hindrance.

$$\underbracket{HCB_{10}H_{10}CH} + C_2H_5Br \xrightarrow[n = 1-8]{AlCl_3} \underbracket{HCB_{10}H_{10-n}(C_2H_5)_nCH}$$

Synthesis of Haloalkyl Derivatives

The preparation of haloalkyl carboranes is affected by the reaction of haloalkyl acetylenes with bis-(acetonitrile) decaborane, (5) or by the reaction of halogens with Grignard reagents as in the preparation of 1-iodomethyl - o-carborane. (173)

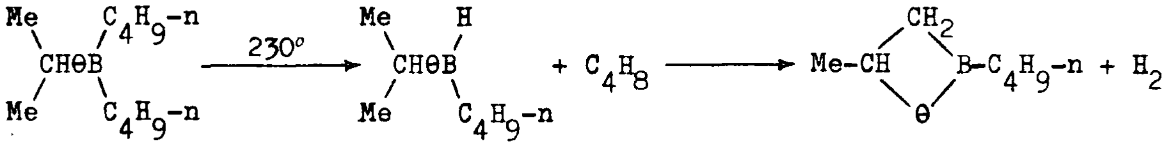
$$R\Theta CH_2MgBr \xrightarrow{I_2} R\Theta CH_2I \qquad R = H, CH_3$$

1-Fluoromethyl o-carborane can be prepared by the action of sulphur tetrafluoride on 1-hydroxymethyl-o-carborane. (6)

$$H\Theta CH_2OH + SF_4 \xrightarrow[80^{\circ}]{CH_2Cl_2} H\Theta CH_2F$$

Reactions of Alkyl and Haloalkyl Derivatives

The alkyl o-carboranes are mostly stable, crystalline solids that share the same inertness to degradation and chemical attack as ortho-, meta- and para-carborane. However, the action of heat on 1-isopropyl,2-di-n-butylboranyl-o-carborane has been shown to yield a cyclic compound involving the alkyl substituents. (7, 8)



The 1-haloalkyl carboranes show a much greater reactivity than the 1-alkyl derivatives, the β-haloethyl and γ-halopropyl carboranes being susceptible to nucleophilic attack at the halogenated carbon atom, (226)

$$H\Theta CH_2CH_2Cl + NaI \xrightarrow[\text{acetone}]{58^{\circ},\ 4hr.} H\Theta CH_2CH_2I + NaCl$$

and to Friedel Crafts attack on benzene with aluminium trichloride.

$$H\Theta CH_2CH_2X + C_6H_6 \xrightarrow{AlX_3} H\Theta CH_2CH_2C_6H_5 \qquad X = Cl, Br.$$

The halomethyl carboranes are very unreactive to both of these reactions.

$$H\Theta CH_2Cl + NaI \xrightarrow[\text{acetone}]{20h,\ 170^{\circ}} H\Theta CH_2I + NaCl \qquad \text{very slow}$$

$$75\%$$

Whilst treatment with a much stronger base results in cleavage of the cage, some di-alkyl amines, such as diethylamine, react smoothly to give good yields of the 1-(diethylamino) methyl carborane. (9, 10, 157)

$$H\Theta CH_2X + Et_2NH \xrightarrow[C_6H_6]{20^{\circ}} H\Theta CH_2N(Et)_2 + HC_2B_9H_{10}CH_2^{-}\ \overset{+}{N}H(Et)_2$$

$$70-75\%$$

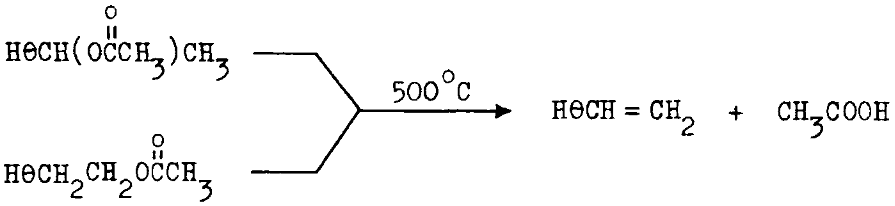
As expected, the 1-halomethyl carboranes react with magnesium to form Grignard reagents, (59) although again the rate of reaction is less than for the longer alkyl chain halides.

1.4 ALKENYL AND ALKYNYL DERIVATIVES

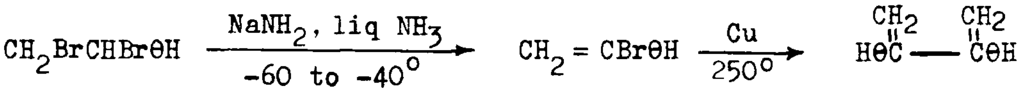
Synthesis of C-Alkenyl Derivatives

C-Alkenyl derivatives have been prepared by the reaction of a suitable alkenylacetylene with bis-(acetonitrile) decaborane, (3, 11) and by the reaction of primary bromoalkenes with C-metallo carboranes (12,13).

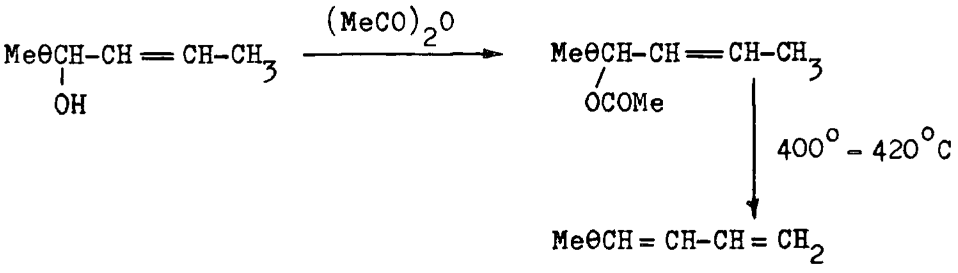
1-vinyl-o-carborane can be formed on pyrolysis of 1-(α-acetoxyethyl) or 1-(β-acetoxyethyl)-o-carborane.



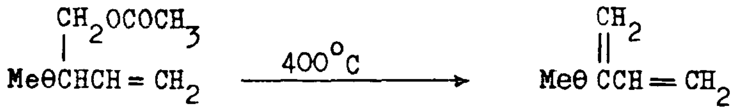
The action of sodamide in liquid ammonia on 1-(1,2-dibromoethyl) ortho-carborane yields 1-(1-bromovinyl) carborane which on heating with copper powder gives 2,3-di-(carboran-1-yl) – 1,3 butadiene (14).



1,3 -butadiene derivatives of ortho carborane can be synthesised by pyrolysis of 1-methyl, 2-(1-acetoxy but-2-enyl)-o-carborane in argon at 400° - 420°C. (29)

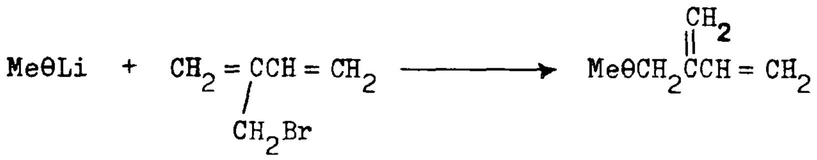


2-(2-methyl-o-carboran-1-yl)-1,3-butadiene is made by the pyrolysis of the appropriate ester by passing a solution of it in ethyl acetate through a tube at 400° C.



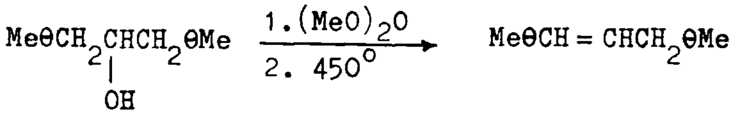
$$\mathrm{Me\theta\overset{CH_2OCOCH_3}{C}HCH=CH_2 \xrightarrow{400^{\circ}C} Me\theta\,\overset{CH_2}{\overset{\|}{C}}CH=CH_2}$$

Both of these butadiene derivatives are stable compounds which show no tendency to undergo polymerisation. In contrast, (2-methyl-o-carboran-1-yl) isopropene, which is prepared by the reaction scheme shown below, readily polymerises on standing, (60)

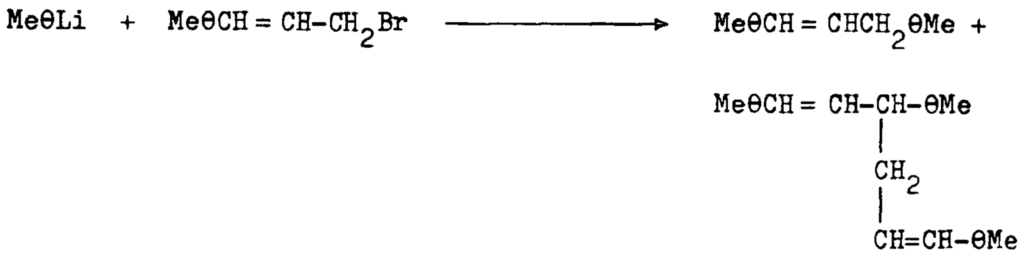


$$\mathrm{Me\theta Li + CH_2=\underset{CH_2Br}{C}CH=CH_2 \longrightarrow Me\theta CH_2\overset{CH_2}{\overset{\|}{C}}CH=CH_2}$$

1,3-bis-(2-methyl- o-carboranyl)propane has been prepared by two different methods:-



$$\mathrm{Me\theta CH_2\underset{OH}{C}HCH_2\theta Me \xrightarrow[2.\ 450^{\circ}]{1.(MeO)_2O} Me\theta CH=CHCH_2\theta Me} \qquad (13)$$



$$\mathrm{Me\theta Li + Me\theta CH=CH\text{-}CH_2Br \longrightarrow Me\theta CH=CHCH_2\theta Me + Me\theta CH=CH\text{-}\underset{\underset{CH=CH\text{-}\theta Me}{|}}{\underset{CH_2}{\underset{|}{C}}}H\text{-}\theta Me}$$

β-chloro vinyl-o-carborane derivatives can be synthesised by the reaction of acetylene with acyl chlorides, (16)

$$\mathrm{Me\Theta CH_2COCl} + \mathrm{HC \equiv CH} \xrightarrow[5^{\circ},\ \mathrm{ClCH_2CH_2Cl}]{\mathrm{AlCl_3}} \mathrm{Me\Theta CHCH=CHCl}$$

$$70.8\%$$

whilst some 1-(2-halovinyl) carboranes have recently been made by the reaction of C-copper carboranes with 1-iodo-2-haloethene. (15)

$$\mathrm{o,m - H\Theta Li} \xrightarrow{\mathrm{CuCl}} \mathrm{o,m - H\Theta Cu} \xrightarrow{\mathrm{ICH=CHX}} \mathrm{o,m - H\Theta CH=CHX}$$

$$X = \mathrm{Cl,Br,I.}$$

Boron alkenyl derivatives can be conveniently produced by the analogous reaction to the synthesis of B-alkyl derivatives, using vinyl boron dichloride and the dicarbollide ion.

$$\mathrm{C_2B_9H_{11}}^{2-} + \mathrm{CH_2=CHBCl_2} \longrightarrow \underbrace{\mathrm{HCB_{10}H_9(3\text{-}CH=CH_2)CH}} + 2\mathrm{Cl}^-$$

Synthesis of Alkynyl Derivatives

C-Alkynyl derivatives are prepared by the reaction of bis-(acetonitrile) decaborane and a di-alkyne. The simplest derivative is ethynyl o-carborane which is formed in about 30% yield together with some 5% of bis-1,1'-o-carborane,(17,18,19) by the reaction:-

$$\mathrm{B_{10}H_{12}(CH_3CN)_2} + \mathrm{HC\equiv C{-}C\equiv CH} \longrightarrow \mathrm{H\Theta{-}C\equiv CH} + \mathrm{H\Theta{-}\Theta H}$$

Some di-alkynes, however, react to give only the bis-carboranyl derivative, as in the case of 1,6-heptadiyne. (4,11) Ethynyl carboranes have also been synthesised from C-lithio carborane using 1-(trimethyl silyl)-2-bromoethyne, and an adaptation of this method allows the synthesis of aryl and alkyl alkynes. (20)

$$\text{o,m,p-H}\Theta\text{Li} \xrightarrow{\text{CuCl}_2} \text{o,m,p-H}\Theta\text{Cu} \xrightarrow{\text{BrC}\equiv\text{CR}} \text{o,m,p-H}\Theta\text{C}\equiv\text{CR}$$

$$\text{R} = \text{Me}_3\text{Si}, \text{C}_6\text{H}_5, \text{Alk.}$$

$$\text{o,m,p-H}\Theta\text{C}\equiv\text{CSiMe}_3 \xrightarrow{\text{KOH CH}_3\text{OH}} \text{o,m,p-H}\Theta\text{C}\equiv\text{CH}$$

1-aryl,2-ethynyl-o-carboranes can be prepared by the following reaction scheme; (34)

$$\begin{tikzcd}
\text{ArC}\equiv\text{C-CH}=\text{CHI} + \text{B}_{10}\text{H}_{14} \arrow[r, "\text{C}_6\text{H}_5\text{NMe}_2"] & \text{Ar}\Theta\text{CH}=\text{CHI} \arrow[dl, "\text{NaNH}_2\ \text{liq NH}_3"] \\
\text{Ar}\Theta\text{C}\equiv\text{CH} &
\end{tikzcd}$$

Non-terminal acetylenic derivatives have been synthesised as by-products of attempts to prepare 1-methyl,2-(prop-2-ynyl)-o-carborane, the other product being allenyl-o-carborane.(34)

$$\text{Me}\Theta\text{Na} \xrightarrow[\text{liq NH}_3]{\text{HC}\equiv\text{CCH}_2\text{Br}} \text{Me}\Theta\text{CH}=\text{C}=\text{CH}_2 + \text{Me}\Theta\text{C}\equiv\text{CCH}_3$$

Reactions of C-alkenyl Derivatives

Early workers in the carborane field noted the unreactivity of C-alkenyl carboranes towards many sorts of chemical attack. (4) Investigations did not show any reaction with bromine, although it has since been shown that in the case of 1-vinyl-o-carborane, (in CCl_4) 1 mole of bromine slowly adds across the double bond over 150 hr at 20°

or over 1.5 hrs at reflux in carbon tetrachloride. (21)

$$H\Theta CH=CH_2 \; + \; Br_2 \xrightarrow{\qquad\qquad} H\Theta CH(Br)CH_2Br$$

In the presence of aluminium trichloride, bromination is not confined to the C = C bond, resulting in bromination of the carborane cage and ultimately producing 1-(1,2 di-bromoethyl)-8,9,10,12-tetra-bromo-o-carborane. Subsequent reduction with zinc in ethanol reduces only the two carbon-bromine bonds generating 1-vinyl-8,9,10,12-tetrabromo-o-carborane. Addition of further bromine results in rebromination of the C = C bond at a much slower rate than that with 1-vinyl-o-carborane due to the marked increase in the electron-withdrawing power of the carborane cage when B-halo substitution is present.

$$\underline{HCB_{10}H_{10}C}CH(Br)CH_2Br \xrightarrow[AlCl_3]{Br_2} \underline{HCB_{10}H_6Br_4C}CH(Br)CH_2Br \xrightarrow[EtOH]{Zn} \underline{HCB_{10}H_6Br_4C}CH{=}CH_2$$

With 1-vinyl-o-carborane, chlorine adds to the double bond and substitutes the cage B - H groups. (21) In the presence of aluminium trichloride, the equivalent chlorination can be achieved merely by the use of a chlorocarbon. (23)

$$\underline{HCB_{10}H_{10}C}CH=CH_2 \xrightarrow[AlCl_3]{CCl_4 \text{ or } CHCl_3} \underset{79\%}{\underline{HCB_{10}H_8Cl_2C}CH(Cl)CH_2Cl}$$

The action of iodine on 1-vinyl-o-carborane in carbon tetrachloride with aluminium trichloride leads only to successive electrophilic iodination of the carborane cage. (21) (See Section 9)

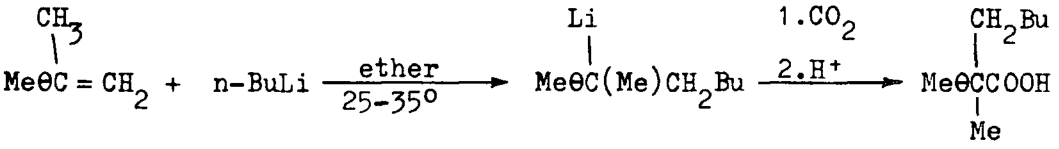
$$\underline{HCB_{10}H_{10}C}CH=CH_2 + I_2 \xrightarrow[80^{\circ}]{AlCl_3} \underline{HCB_{10}H_{10-n}I_nC}CH=CH_2$$

$$n = 1\text{–}4$$

In carbon disulphide, hydrogen chloride and bromide add across the double bond in the presence of aluminium trichloride to give 1-(1-haloethyl)-o-carborane, placing halogen on the terminal carbon atom in accordance with Markovnikov's rule.

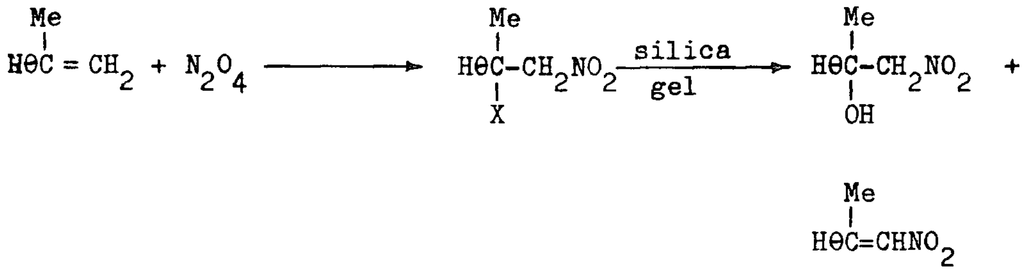
In contrast to 1-vinyl-o-carborane, 1-isopropenyl-o-carborane is rapidly dibrominated by bromine in carbon tetrachloride under ultraviolet light, whereas in the dark no reaction takes place. (22)

The isopropenyl group is stabilised to such an extent by the carborane nucleus that treatment with n-butyl lithium followed by carbon dioxide and hydrochloric acid results in the formation of 1-isopropenyl, 2-carboxylic acid o-carborane. (12) However, if the free carboranyl C-H is blocked by a methyl group in either 1-vinyl or 1-isopropenyl-o-carborane, lithiation by n-butyl lithium in ether takes place at the ∝ carbon atom. (24) Further reaction with carbon dioxide and acid yields the appropriate carboxylic acid.



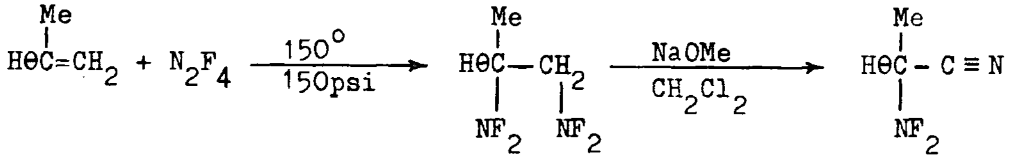
$$\mathrm{Me}\theta\overset{CH_3}{C}=CH_2 + n\text{-}BuLi \xrightarrow[25\text{-}35^{\circ}]{ether} \mathrm{Me}\theta\overset{Li}{C}(Me)CH_2Bu \xrightarrow{\substack{1.CO_2\\ 2.H^+}} \mathrm{Me}\theta\overset{CH_2Bu}{\underset{Me}{C}}COOH$$

Despite the apparent unreactivity of 1-isopropenyl-o-carborane compared with normal alkenes, it is susceptible to attack by oxidising agents such as ozone, and alkaline potassium permanganate. (4) 1-Isopropenyl-o-carborane undergoes attack by radicals such as dinitrogen tetroxide, and tetrafluorohydrazine. (22) Reaction with dinitrogen tetroxide gives a mixture of the nitro-nitrate and dinitro adduct. Attempted silica gel chromatography of these products led to their conversion to a nitro-alcohol and nitro-olefin respectively, with elimination of HNO_2.



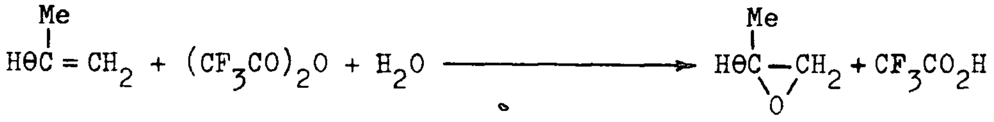
$$\overset{Me}{H\Theta C}=CH_2 + N_2O_4 \longrightarrow \underset{X}{\overset{Me}{H\Theta C}}-CH_2NO_2 \xrightarrow[\text{gel}]{\text{silica}} \underset{OH}{\overset{Me}{H\Theta C}}-CH_2NO_2 + \overset{Me}{H\Theta C}=CHNO_2$$

Hot tetrafluorohydrazine reacts to give the bis-difluoroamino derivative. This reaction is similar to known alkene reactions.



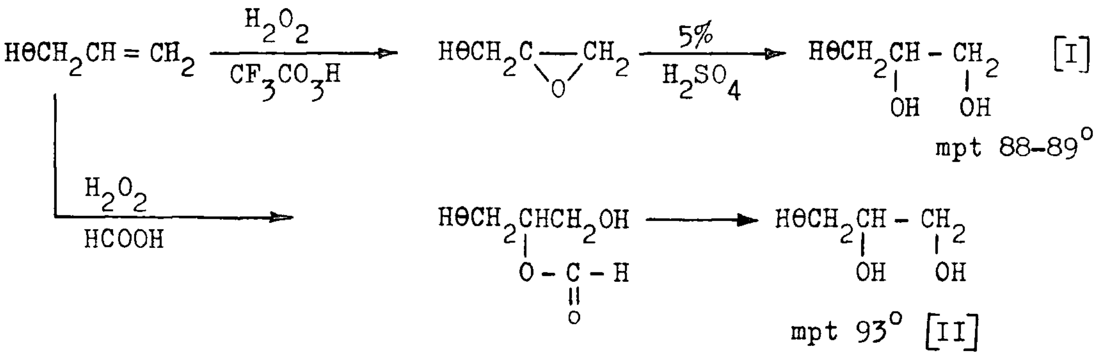
$$\overset{Me}{H\Theta C}=CH_2 + N_2F_4 \xrightarrow[150\text{psi}]{150^{\circ}} \underset{NF_2}{\overset{Me}{H\Theta C}}-\underset{NF_2}{CH_2} \xrightarrow[CH_2Cl_2]{\text{NaOMe}} \underset{NF_2}{\overset{Me}{H\Theta C}}-C\equiv N$$

Hydrogenation can be achieved by Raney nickel catalysis to yield 1-isopropyl-o-carborane. 1-Isopropenyl-o-carborane is readily oxidised by trifluoroperacetic acid to form an epoxide. (4)

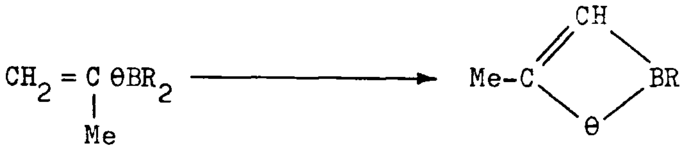


$$\overset{Me}{H\Theta C}=CH_2 + (CF_3CO)_2O + H_2O \longrightarrow \overset{Me}{H\Theta C}\underset{O}{-}CH_2 + CF_3CO_2H$$

1-Allyl-o-carborane undergoes similar epoxide ring formation. However, subsequent reactions have shown that the epoxide ring can be opened by the action of dilute acid to yield 1-(2,3 di-hydroxypropyl)-o-carborane [I]. A stereoisomer [II] of this compound has been prepared by conversion of 1-allyl-o-carborane into the hydroxyformyl derivative followed by hydrolysis. Both have identical analyses and infra red spectra, but different melting points.



This epoxide ring opening is inhibited when the ring is adjacent to the carborane cage. 1-Vinyl and 1-isopropenyl o-carborane derivatives can undergo cyclisation reactions when the 2-position substituent is a di-alkyl boron. (8)

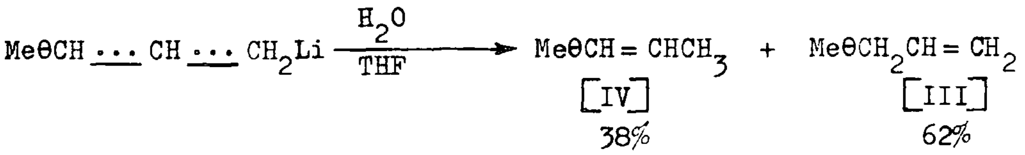


R = n - Bu, iso - Bu.

1-Allyl-o-carboranes have been the subject of much research since their first synthesis by reaction of C-lithio carborane with 1-bromo-prop-2-ene(12). The allyl derivatives are readily lithiated at room temperature by n-butyl lithium in benzene or ether benzene mixture. (25)

$$R\theta CH_2CH=CH_2 + n\text{-}BuLi \xrightarrow{\text{ether}} R\theta CH \underline{\cdots} CH \underline{\cdots} CH_2Li + C_4H_{10}$$

1-lithio-allyl-o-carborane reacts with water in THF to give a mixture of allyl [III] and trans propenyl [IV] derivatives.



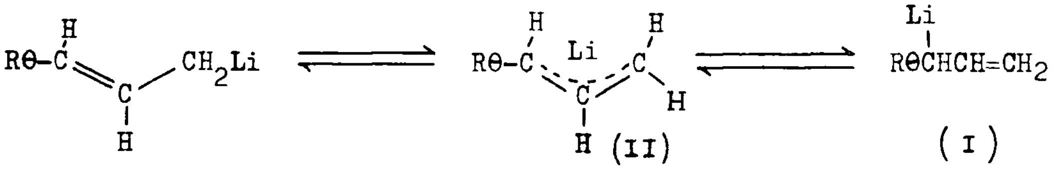
$$Me\theta CH \underline{\cdots} CH \underline{\cdots} CH_2Li \xrightarrow[\text{THF}]{H_2O} \underset{\substack{[IV] \\ 38\%}}{Me\theta CH=CHCH_3} + \underset{\substack{[III] \\ 62\%}}{Me\theta CH_2CH=CH_2}$$

The trans propenyl derivative is thermodynamically more stable than the allyl derivative, the latter being almost completely isomerised into the former when heated in the presence of a strong base. (26,27) This higher stability is apparently caused by the stabilising effect of the terminal methyl group, the effect predominating over the destabilisation caused by the 1-o-carboranyl group.

$$R\Theta CH_2CH=CH_2 \xrightarrow[Me_3COH]{Me_3COK} R\Theta\text{-}CH=CHCH_3$$

$$R = Me,\ i\text{-}C_3H_7,\ Ph,\qquad CH_2=C(Me)_2$$

Protonation of 1-lithio-allyl-o-carboranes can also be achieved with phenyl acetylene, acetic acid, ethyl and tert-butyl alcohols, in benzene/ether, benzene/THF, or liquid ammonia solutions, (excepting acetic acid in the latter medium). (28) The allyl derivative was found to be the major product except for protonation by tert-butyl alcohol in liquid NH_3 where the 1-isopropyl derivative predominated. Steric and solvent effects were shown to affect the yields; a greater solvation producing less covalent forms (I) and more ion pairs (II).



This can be shown by the reaction of 1-lithio-allyl o-carboranes with bromine in water, (26) to give almost entirely the trans propenyl derivatives.

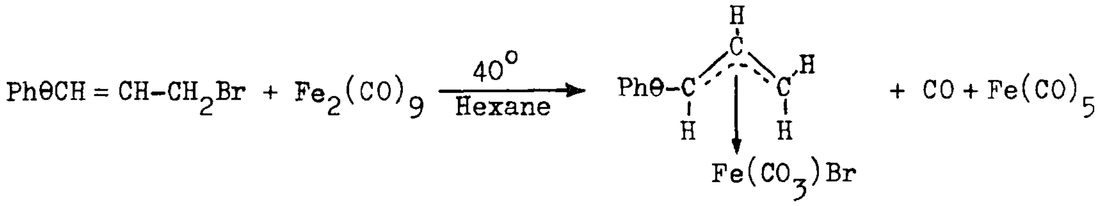
1-lithio-allyl-o-carborane reacts with carbon dioxide to give carboxylic acids and formaldehyde to give alcohols. (See sections 6 and 7)

Alkylation of the allyl group can be accomplished by the reaction of 1-lithioallyl,2-alkyl-o-carborane with an alkyl halide in ether/benzene solution giving a mixture of allyl and trans-propenyl compounds. (60)

The action of CuCl on 1-lithio-allyl-o-carborane leads to the dimerisation of the compound to give two isomers, the predominant one being the bis-(propenyl) derivative.

$$Me\theta CH\cdots CH\cdots CH_2Li \xrightarrow{CuCl} Me\theta CH=CHCH_2CH_2CH=CH\theta Me + \text{isomer}$$

Allyl iron compounds have been synthesised from iron carbonyls and 1-phenyl, 2-(1-bromo-prop-2-enyl)-o-carborane. (29)



$$Ph\theta CH=CH\text{-}CH_2Br + Fe_2(CO)_9 \xrightarrow[\text{Hexane}]{40^{\circ}} Ph\theta\text{-}CH\cdots CH\cdots CH_2 \to Fe(CO_3)Br + CO + Fe(CO)_5$$

A similar reaction occurs between iron pentacarbonyl and 1-methyl,2-(1,3-butadienyl)-o-carborane. This π-complex is readily decomposed by iodine in dichloromethane.

Fluroalkene derivatives can be made by direct reaction of fluoroalkenes with 1-methyl,2-lithio o-carborane. (30) Similar fluoro-olefins are susceptible to nucleophilic attack. Attack by alkoxides is found to take place at the β-atom of the double bond, (31,32) however, secondary amines attack the 3(6) position boron atom.

Reaction of Alkynyl Carboranes

Treatment of 1-ethynyl-o-carborane with n-butyl lithium or a Grignard reagent leads to metallation at the terminal acetylenic C-H bond rather than the cage. (33,34)

The reaction of the 1-lithio-ethynyl derivatives with copper chloride or methyl mercury bromide yields respectively the 1-cupro-and 1-methylmercurio-ethynyl carborane.

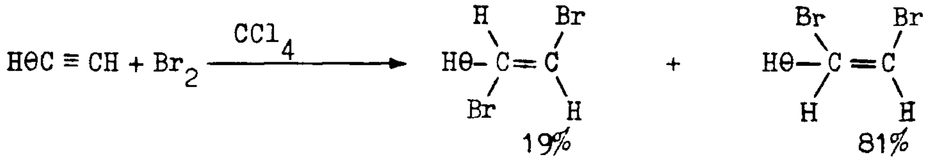
$$H\Theta C \equiv CH \xrightarrow{n\text{-}BuLi} H\Theta C \equiv CLi \xrightarrow{MeHgBr} H\Theta C \equiv CHgMe$$

The metallo derivatives react with iodine to give the expected 1-iodoethynyl product, and with carbon dioxide and dilute acid to give carboxylic acids. (33)

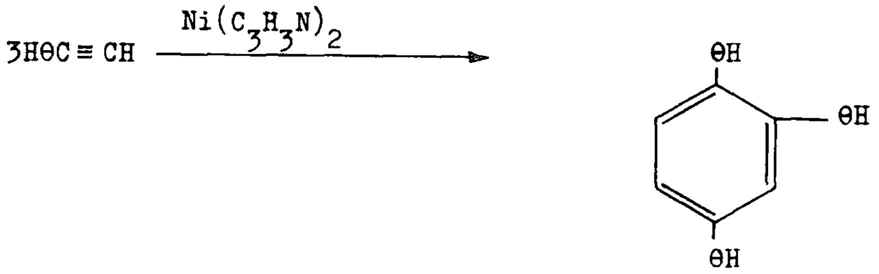
$$H\Theta C \equiv CCu \xrightarrow{I_2} H\Theta C \equiv CI$$

$$H\Theta\text{-}C \equiv CMgBr \xrightarrow[2.H^+]{1.CO_2} H\Theta C \equiv CCOOH$$

Although the presence of the carborane has been shown to greatly reduce the ability of the double bond to undergo electrophilic addition reactions (21), the carborane nucleus appears to have little effect on the triple bond in the ethynyl-derivatives. Bromine readily adds across the bond at room temperature to give cis and trans dibromo-derivatives. (34)



The triple bond has been shown to undergo cyclisation reactions in the presence of the acetylene cyclo trimerization catalyst, bis-(acrylonitrile) nickel [0]. (35)



The cyclic product was found not to be susceptible to electrophilic attack. Ethynyl-o-carborane reacts with $Co_2(CO)_8$ to give a tetrahedral $C_2Co_2(CO)_6H$ carboranyl substituent, whilst the reaction of a catalytic amount of CuCl with oxygen and ethynyl carborane yields a linear dimer in about 60% yield. The dimer's triple bonds do not react with bis-(acetonitrile) decaborane or bromine in dichloromethane, unlike ethynyl o-carborane.

$$2H\Theta C \equiv CH \xrightarrow{O_2,\ CuCl} H\Theta C \equiv C{-}C \equiv C\Theta H$$

1.5 ARYL DERIVATIVES

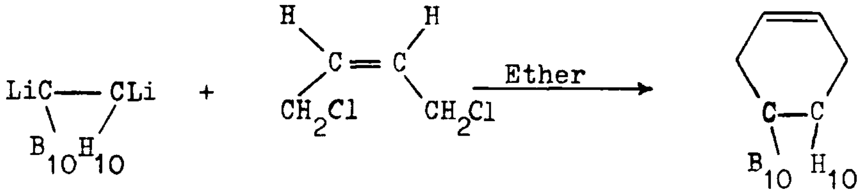
Synthesis

Carboranyl aryl derivatives can be made in an analogous manner to C-alkyl derivatives, namely either by reaction of bis-(acetonitrile) decaborane with an aryl acetylene, (3,4) or by reaction of a C-metallo-carborane with primary aryl halides. (36) Again, secondary and tertiary aryl chlorides are unreactive. More recently, a new method of synthesising aryl derivatives has been found, using aryldiazonium fluoroborates and C-copper carboranyls with about 50% yields. (37)

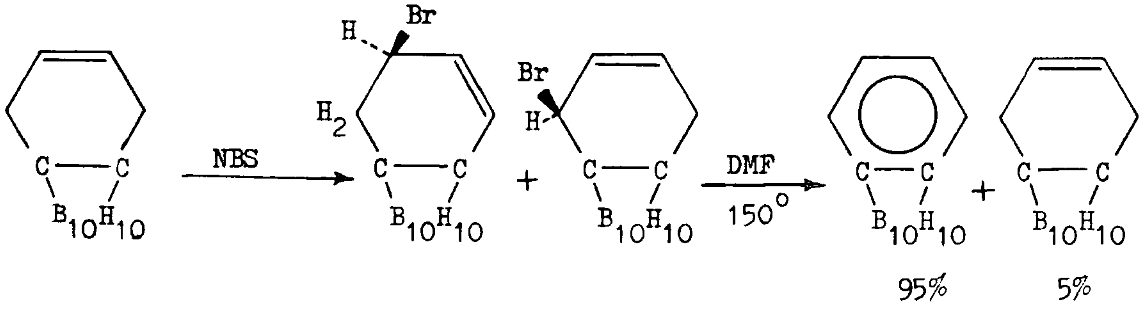
$$\mathrm{Ar\overset{+}{N}\equiv N\overset{-}{B}F_4} + \mathrm{o,m,p-H\Theta Cu} \longrightarrow \mathrm{o,m,p-H\Theta{-}Ar} + \mathrm{Cu\overset{+}{N}\equiv N\overset{-}{B}F_4}$$

This same method can also be used for the synthesis of biaryl, biarylazo and arylazo carboranes.

A range of aryl-o-carboranes has been synthesised, in which the two o-carboranyl carbon atoms are fused into the aryl ring. The smallest member of the group, benzocarborane, is formed by the reaction of 1,4-dichlorobut-2-ene with 1,2-dilitho-o-carborane.

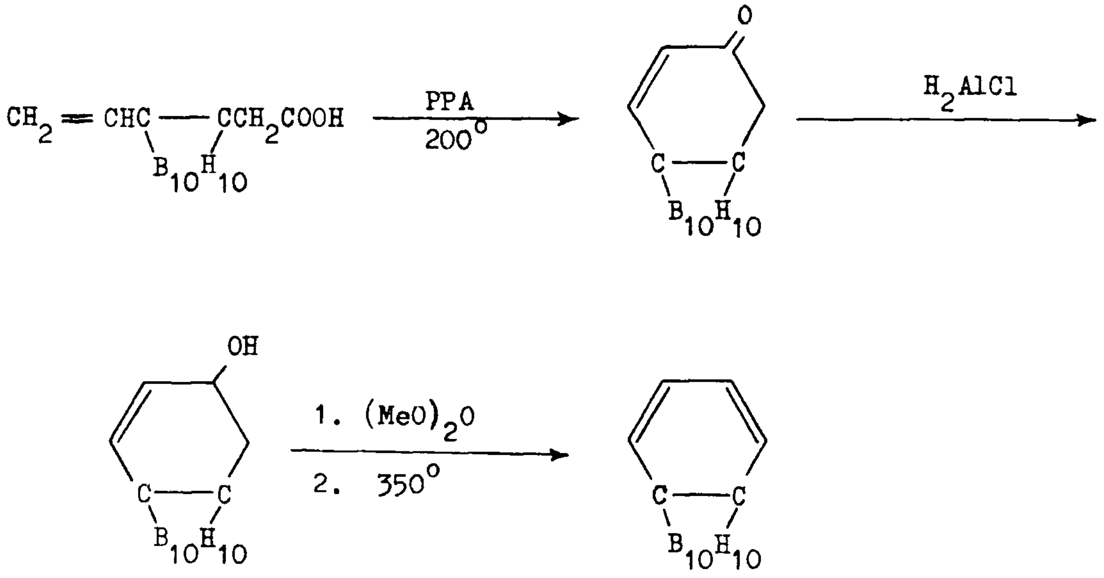


Reaction of this 1,2-carboranyl cyclohexene with N-bromo-succinimide does not as reported give only benzocarborane, (38) but gives a mixture of monobromo-1,2-carboranyl-cyclohexene derivatives and a trace of benzocarborane.



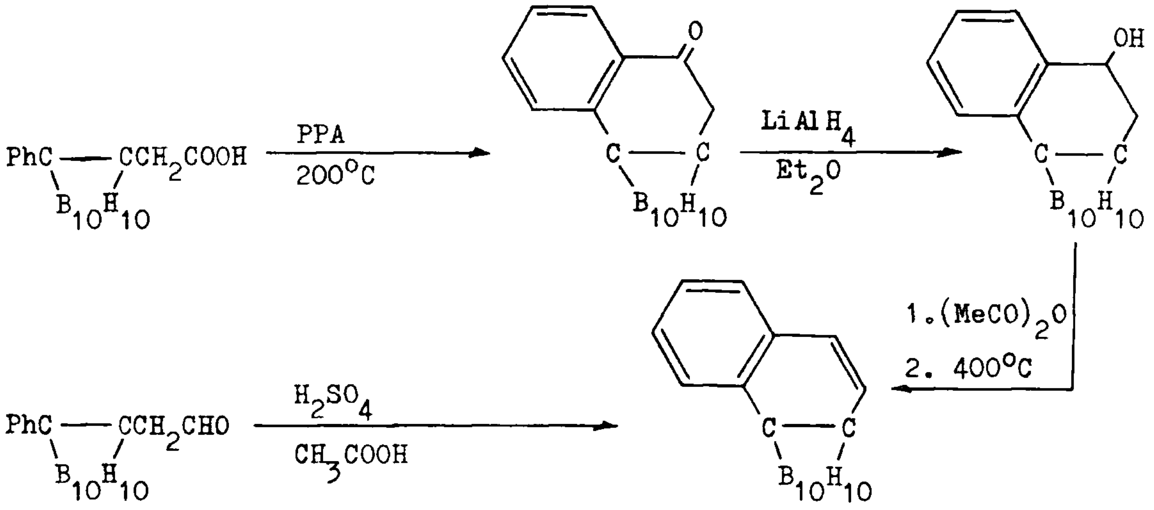
Benzocarborane is synthesised in 95% yield from this mixture by heating in D.M.F. causing dehydrobromination. (44)

Benzocarborane has also been prepared by cyclisation reaction as indicated by the following scheme; (42)

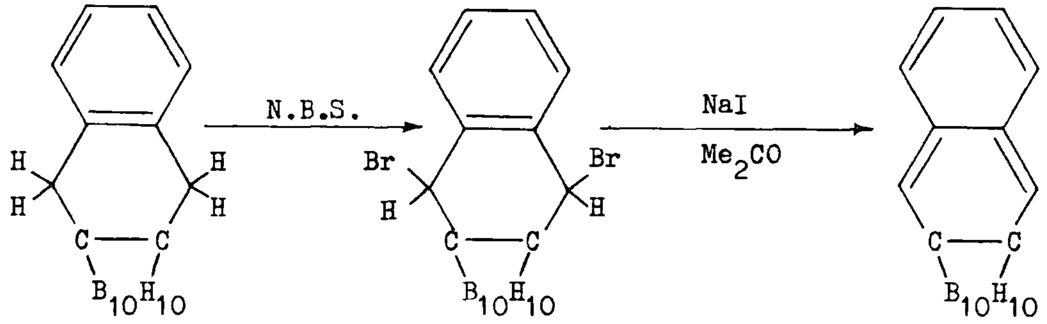


Although the carborane system has highly delocalised electrons, there is no evidence of conjugation between the π-system and the cage. Again contrary to early reports, (38) the ring of benzocarborane is susceptible to electrophilic attack by bromine; decolourisation taking one hour in carbon tetrachloride, but only two minutes in dichloromethane. (44) The resulting two isomers, 1,4-dibromo-and 1,4-dihydrobenzocarborane lose bromine above their melting points to regenerate benzocarborane.

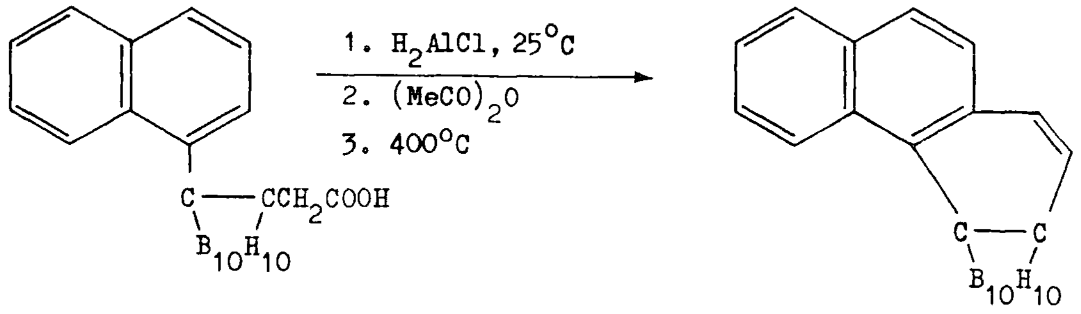
The equivalent naphtho derivatives have been prepared by the dehydration of l-phenyl-o-carboran-2-yl acetic acid with poly phosphoric acid at 200° (39) followed by hydrogenation and dehydration with acetic anhydride and pyrolysis to give naphtho- [1,2]-o-carborane. (40)



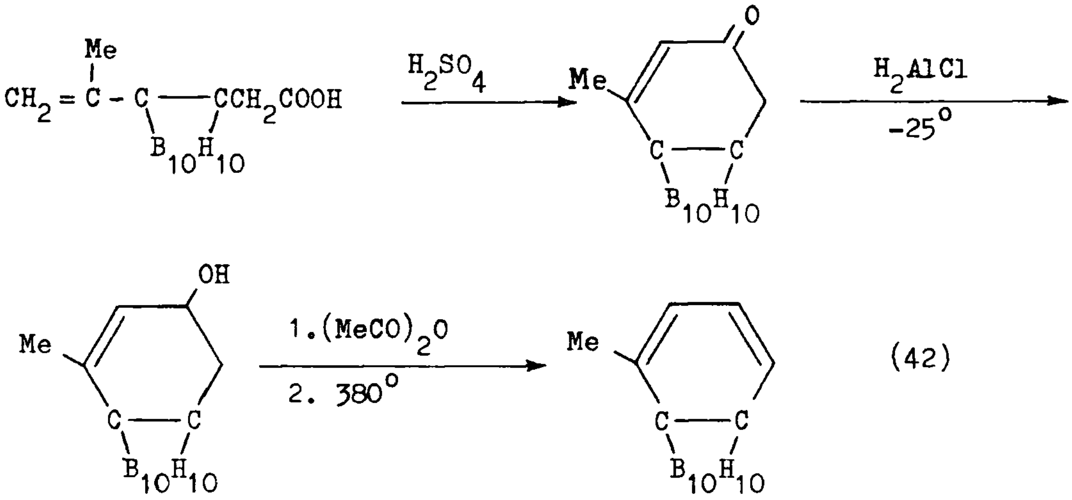
The same compound can also be made by a condensation reaction using 1-phenyl o-carboran-2-yl acetaldehyde. The preparation of naphtho - [2,3] - o-carborane can be achieved by bromination of 1,4-dihydronaphtho - [2,3] - o-carborane (see section 3) followed by treatment with sodium iodide in acetone.



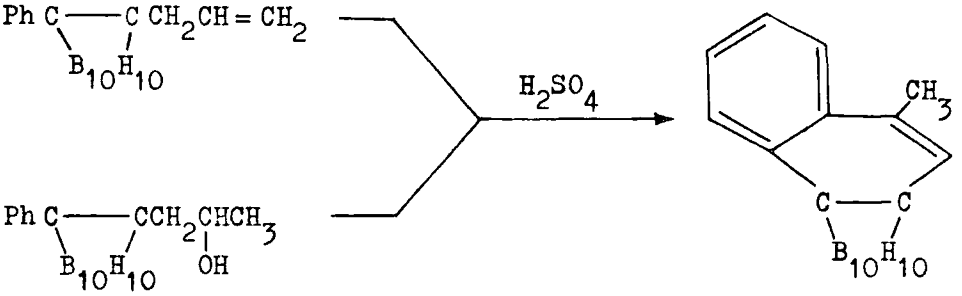
Phenanthreno - [3,4] -o-carborane can be synthesised by similar method to naphtho - [1,2] -o-carborane, (41) starting from 1-naphthyl-carboran-2-yl acetic acid.



Derivatives of all these fused ring systems have been made, mainly by the cyclisation of appropriately substituted carborane carboxylic acids, alkenes, alcohols and esters.

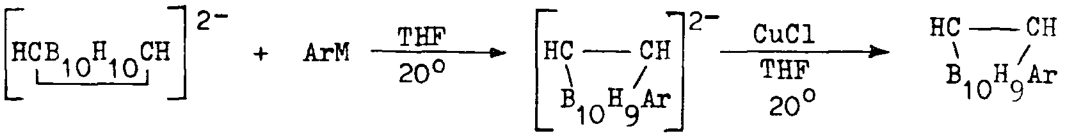


(42)



(43)

Boron-substituted aryl groups can be prepared either by the reaction of the dicarbollide ion $C_2B_9H_{11}^{2-}$ with an aryl boron dichloride to give cage closure and the 3(6) position aryl derivative, or by the reaction of the o-carboranyl di-anion with organo-magnesium and lithium compounds in THF. (47, 48) (See Section 16)



M = Li, MgX

This reaction is non-selective, and oxidation renders a mixture of 3-,4-,8- and 9-B-aryl-o-carboranes. Use of excess aryl magnesium halide leads to the formation of poly-aryl-o-carboranes.

Reactions of Aryl Carborane Derivatives

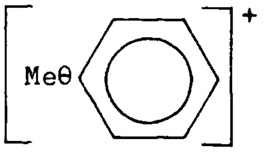
The electronic interactions and distributions present in aryl carborane species has been the subject of many studies.

1-phenyl-o-carborane reacts with potassium in THF or dimethoxyethane to give paramagnetic solutions, with no evolution of hydrogen. These air and moisture sensitive solutions are postulated to contain a stable phenyl carborane radical anion.

$$\mathrm{Ph\Theta H} + e^- \longrightarrow \left[\mathrm{Ph\Theta H}\right]^{\overline{\cdot}}$$

EPR spectra of these solutions have been interpreted as showing a delocalisation of the lone electron in the phenyl carborane anion. (45, 46)

Strong electron withdrawal effects have been noted in tropenylliumyl-substituted o-carboranyl cation [I]. These derivatives are made by the reaction of 1-lithio,2-methyl-o-carborane with tropenyl-methyl ether and heating at 165° to give the 1-methyl,2-(3-cyclohepta-1,3,5-trienyl) derivative. Reaction of this with triphenyl carbonium ion gives the desired cation.

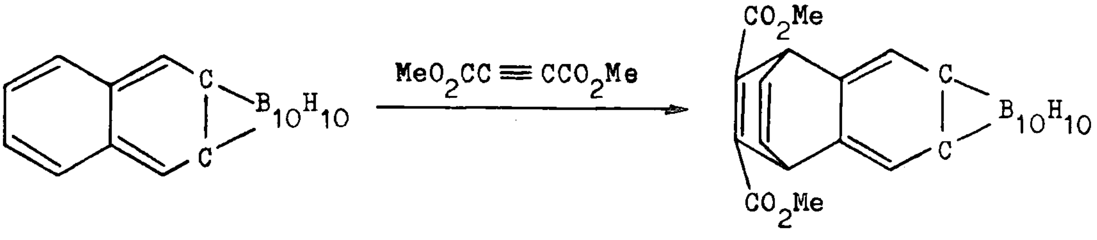


SbF_6^- [I]

The ultraviolet and proton NMR spectra indicate that there is an inductive effect produced by the carborane cage on the ring and virtually no electron transfer from the cage to the ring system. It is interesting to note that in the equivalent borane species $B_{10}H_9(C_7H_6)^-$ and $B_{12}H_{11}(C_7H_6)^-$ there is evidence of cage to ring donation in different energy states, indicating that most of the carboranyl inductive effect is caused by the relatively positive carbon atoms. Concurrent with this, m-carborane, which has less positive carbon atoms, shows a much weaker inductive effect. (49)

Whilst conjugation of the phenyl ring and the cage for o-carborane is absent, there is evidence of conjugation with species such as the 1-phenyl dicarbaundecaborane(13) anion. (50) Despite the electron-withdrawing effects of the carboranyl group, 1-phenyl-o-,m-carborane and 3-phenyl-o-carborane are nitrated largely at the ortho and para positions. This ortho, para directing effect might be explained by the high polarizability of the carboranes. (51) Electrophilic attack on 1-phenyl-o-carborane by halogens will be discussed in context with other carborane species in Section 9.

Naphtho-[2,3]-o-carborane is susceptible to attack by bromine to give dibromination at the inner ring, and atmospheric oxygen will react with solutions to yield a peroxide polymer. Steric hindrance prevents dienophiles from attacking the inner ring, but not the outer ring.



1.6 CARBOXYLIC ACID AND ACID HALIDE DERIVATIVES

Synthesis of Carboranyl Carboxylic Acids

Unlike the C-alkyl and aryl derivatives, carboranyl carboxylic acids cannot be synthesised directly from an acetylenic carboxylic acid and bis-(acetonitrile) decaborane, since acid groups destroy the borane cage. However, carboxylic acid derivatives have been prepared by a number of alternative means.

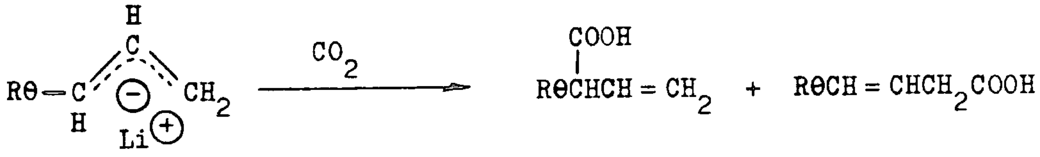
Lithio and dilithio-o-carborane react readily with carbon dioxide and then dilute acid to give good yields of mono and dicarboxylic acids. (12,52,53)

$$\mathrm{Li\theta Li} \xrightarrow[2.H^+]{1.CO_2} \mathrm{HOOC\theta COOH}$$

The reaction of monolithio-o-carborane with carbon dioxide in ether gives only the dicarboxylic acid derivative, whilst in benzene the mono carboxylic acid is the only product. (See section 2) The synthesis of specifically mono carboxylic acids is usually accomplished by using C-mono alkylated carborane so that only one carboranyl C-H bond can be lithiated. Acid derivatives can be prepared by this method from species such as bis-(1-o-carboranyl methyl ether) (54)

$$(\mathrm{H\theta CH_2})_2\mathrm{O} \xrightarrow{n\text{-BuLi}} (\mathrm{Li\theta CH_2})_2\mathrm{O} \xrightarrow[2.H^+]{1.CO_2} (\mathrm{HOOC\theta CH_2})_2\mathrm{O}$$

The reaction of 1-lithioallyl-o-carborane with carbon dioxide and acid gives a mixture of isomeric carboxylic acids.

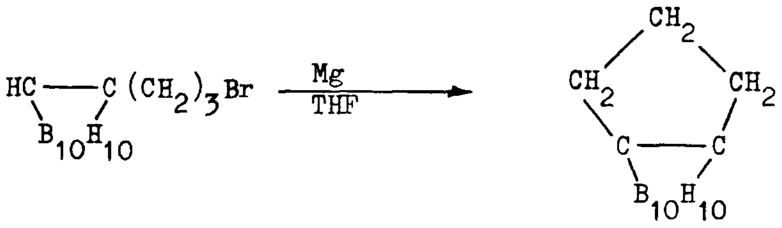


Grignard reagents react in a similar manner but are particularly suited to forming long chain acids. (55)

$$H\theta(CH_2)_nBr \xrightarrow[\text{Ether}]{\text{Mg}} H\theta(CH_2)_nMgBr \xrightarrow[2.H^+]{1.CO_2} H\theta(CH_2)_nCOOH$$

$$n = 1\text{–}4$$

Where n=1, the preparation of the Grignard reagent and subsequent exposure to carbon dioxide and then acid in THF leads to the formation of 1-methyl-carboran-2-yl carboxylic acid (see section 2) by a rearrangement, where the halide is bromine or chlorine. In ether, the bromo-derivative does not rearrange, but the chloro derivative does. With 1-alkyl,2-halomethyl-o-carboranes, no such rearrangements can occur; therefore the expected acid derivative is easily formed. Attempts to utilise this rearrangement with other haloalkyl groups have been unsuccessful, due to an intra-molecular attack at the lone carborane C-H bond, by the resulting Grignard reagent producing a cyclisation.



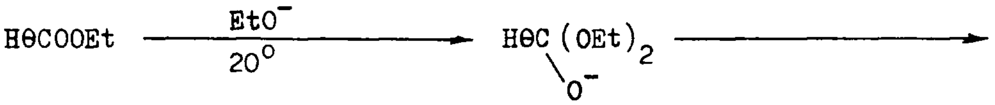
Ester hydrolysis reactions have been used to synthesise carboranyl carboxylic acids. The esters, unlike the acids, can be synthesised directly from acetylenic esters and bis-(acetonitrile) decaborane. (3,11,12,52,56) Hydrolysis of carboran-1-yl methylcarboxylate gives the free carboxylic acid. (12)

$$B_{10}H_{12}(CH_3CN)_2 + HC \equiv CCOOMe \longrightarrow H\theta COOMe \xrightarrow{H^+} H\theta COOH$$

Some of the esters, however, do not readily undergo hydrolysis. Di-methyl-1,2-o-carboranyl di-carboxylate was found to be stable to attack by refluxing concentrated hydrochloric acid, glacial acetic acid and trifluoroacetic acid. Saponification of the ester does occur with cold 50% aqueous potassium hydroxide, but the reaction gives poor yields. (52) Carboranyl methylmalonates also display strong resistance to attack although a similar saponification is slowly accomplished with 50% aqueous potassium hydroxide. Ethyl-o-carborane-acetate has been shown to resist the action of 96% sulphuric acid at 100°C, but is hydrolised under the action of 8N H_2SO_4 in aqueous dioxane. (57) In some cases, attempted alkaline ester hydrolysis leads to decarboxylation yielding the parent carborane.

$$R\theta COOEt \xrightarrow[Et\,OH]{KOH} R\theta H$$

An ionic mechanism has been proposed for such reactions which are catalysed by a small amount of sodium ethoxide in ethanol. (58)



$$H\theta COOEt \xrightarrow[20^{\circ}]{EtO^{-}} H\theta \underset{\setminus O^{-}}{C}(OEt)_2 \longrightarrow$$

$$(EtO)_2O + H\theta^{-} \xrightarrow{EtOH} H\theta H + EtO^{-}$$

These reactions are influenced by the strong electron-withdrawing power of the carborane cage, as the further the ester group is removed from the cage, the less prone it is to decarboxylation. When n=2, the carboxylic acid derivative is the only product. (58)

$$H\theta(CH_2)_nCOOEt \xrightarrow{KOH,EtOH} H\theta(CH_2)_nCOOH + H\theta(CH_2)_nH$$

$n=0,1,2,3.$ $\qquad n=0,1,2,3.$ $\qquad n=0,1.$

Carboranyl esters are more prone to decarboxylation when there is a substituent attached at the second cage carbon atom. For example, 1-phenyl carboran-2-yl carboxylate is converted quantitatively by 98% ethanol to 1-phenyl-o-carborane. (59)

$$\mathrm{Ph\theta COOK} \xrightarrow[20^{\circ}]{\mathrm{EtOH}} \mathrm{Ph\theta H} + \mathrm{KHCO_3}$$

The cleavage of ester can also be achieved by using organometallic reagents such as n-butyl lithium. This cleaves the ester at the carborane cage to give a lithio-carborane which can be converted back to a carboxylic acid with carbon dioxide and dilute acid. (82)

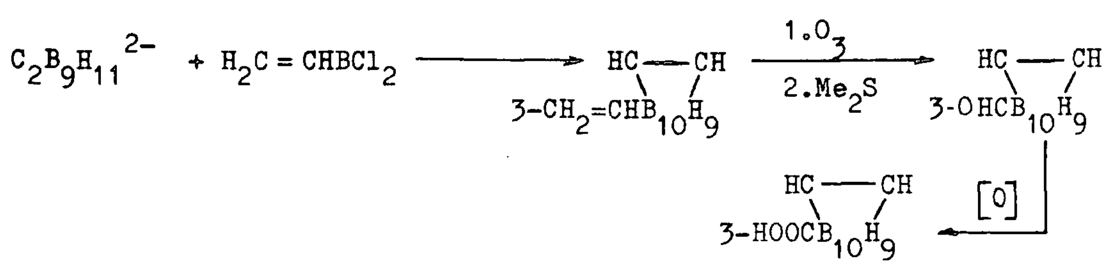
Carboranyl carboxylic acids may be synthesised from carboranyl alcohols by oxidation reactions using chromium trioxide, potassium dichromate or alkaline potassium permanganate. (12,54,57)

$$\mathrm{H\theta(CH_2)_nCH_2OH} \xrightarrow[\mathrm{H_2SO_4}]{\mathrm{CrO_3}} \mathrm{H\theta(CH_2)_nCOOH} \qquad n = 0,1,2.$$

$$\mathrm{(HOCH_2CH_2\theta CH_2)_2O} \xrightarrow[\mathrm{H^+\ acetone}]{\mathrm{K_2Cr_2O_7}} \mathrm{(HOOCCH_2\theta CH_2)_2O}$$

Di-acids can be prepared from diols. (12)

The preparation of boron substituted carboranyl carboxylic acids can be achieved by ozonolysis followed by oxidation of 3-vinyl-o-carborane, which is prepared from the dicarbollide ion (see section 16) and vinyl boron dichloride. (64)



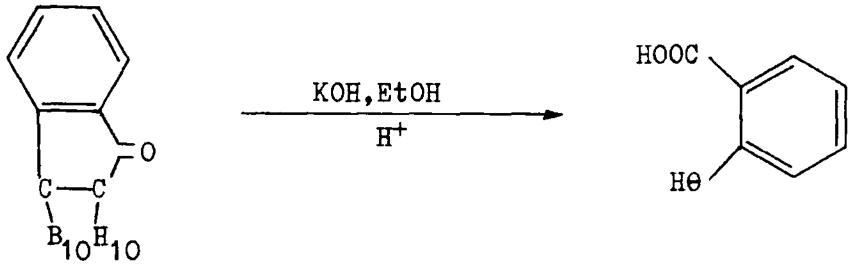
Alternatively, the 3-vinyl-m-carborane can be oxidised directly with chromium trioxide in sulphuric and acetic acid at room temperature. (65)

Mono-and di- boron substituted carboranyl carboxylic acids are accessible by a different route, which involves the oxidation of B-mono and bis-[2-(trimethylsilyl)ethyl] carborane. (66)

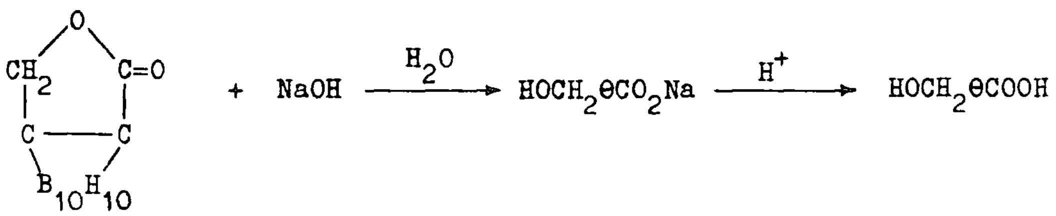
$$\underline{HCB_{10}H_{10-n}(CH_2CH_2SiMe_3)_nCH} \xrightarrow[H_2SO_4,\,CH_3COOH]{CrO_3} \underline{HCB_{10}H_{10-n}(COOH)_nCH}$$

Oxidation by alkaline potassium permanganate of primary ethyl and propyl alcohols gives the acid salts; however, reaction with hydroxymethyl or di-hydroxymethyl-o-carborane causes decarboxylation to give the parent carborane. (52)

Acid chlorides can be converted into carboxylic acid derivatives by hydrolysis with water. (12,57) Ortho carboranyl benzoic acid has been prepared by cleavage of an exocyclic ketone by ethanolic potassium hydroxide. (63)



Other exocyclic ring systems may be opened by alkalis to give carboxylic acid derivative as in the case of carboranyl lactone. (54)



Reactions of Carborane Carboxylic Acids

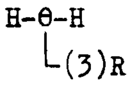
The strong electron withdrawing power of the carborane cage is clearly demonstrated by the lower pKa values and higher acid strength of carborane carboxylic acids in comparison to the pKa values of the free acids. The electron-withdrawal is also shown by ^{35}Cl NQR results for o-carboranyl acid chlorides. It is notable that the C-substituted acids of o-carborane are stronger than those of meta- and para-carborane, owing to the greater positive charge on the more localised carbon atoms in o-carborane. The 3-position substituted o-carborane acids are weaker than the C-substituted acids, owing to the lesser positive charge at the 3-position in the cage.

The acid strengths of 1-o-carboranyl carboxylic acids decrease when substituents which give a +I effect are bonded to the cage at the 2-position carbon, (69) and it has been noted that the greater the +I effect, the greater the increase in the pKa, or the lower the ionisation constant. When electron-withdrawing groups such as vinyl or phenyl are bonded to the cage, there is a great increase in the pKa, whereas an alkyl group causes only a mild increase in pKa. Later work, however, suggests that these apparently clear trends do not necessarily follow. (70) For example, investigations into the effects of 2-position substituents on 1-meta and 1-para benzoic acids show conflicting results. Substitution of a methyl group on the cage gives an increase in acid strength over the unsubstituted carboranyl benzoic acid. Acetyl and methoxy-carbonyl groups which are fairly strong electron acceptors cause a rise in acid strengths. The strongest acids are 2-methylmercury derivatives, but although methylmercury is a strong electron donor, it is thought that here an intramolecular co-ordination with the electrons of the benzene ring is taking place reducing the electron density in the ring, and thereby raising the acid strength. Similar anomalous results have been noted for o-carboran-1-yl formic and acetic acids.

TABLE 1

pKa VALUES OF CARBORANE CARBOXYLIC ACIDS

R	R'	pKa	Solvent
	R-θ-R'		
H	COOH	2.48	A
H	COOH	2.61	B
CH_3	COOH	2.74	B
H	CH_2COOH	4.06	A
H	CH_2COOH	3.83	C
H	$(CH_2)_2COOH$	4.58	C
H	m-C_6H_4COOH	6.57	D
H	p-C_6H_4COOH	6.55	D
	R-θ'-R'		
H	COOH	3.34	B
CH_3	COOH	3.14	B
H	m-C_6H_4COOH	6.96	D
H	p-C_6H_4COOH	6.79	D
	R-'θ'-R'		
H	COOH	3.64	B



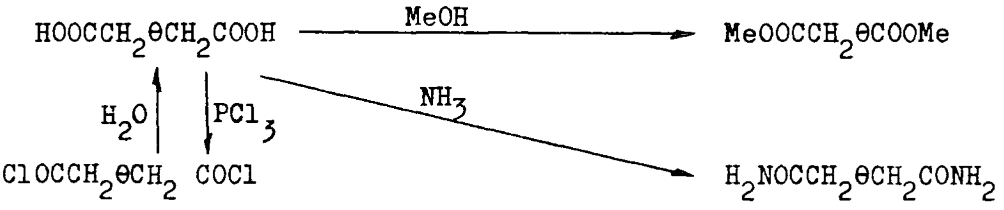
$\underset{\llcorner(3)R}{H\text{-}\theta\text{-}H}$

R	R'	pKa	Solvent
COOH		5.38	B
m-C_6H_4COOH		7.05	D
p-C_6H_4COOH		6.99	D

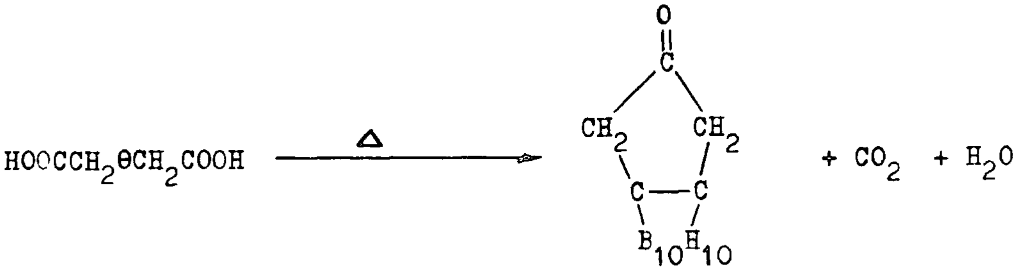
Solvents:- A = H_2O, B = 50% EtOH in H_2O, C = 20% EtOH in H_2O,
D = 70% Dioxane in H_2O.

It has been shown, however, that the ^{35}Cl NQR frequencies of carboxylic acid chlorides are linearly dependent on the induction constants of the substituents, an increase in electron-acceptor ability giving higher frequencies. (93) Shielding of the acid chloride group by CH_2 groups leads to lower frequencies. (94)

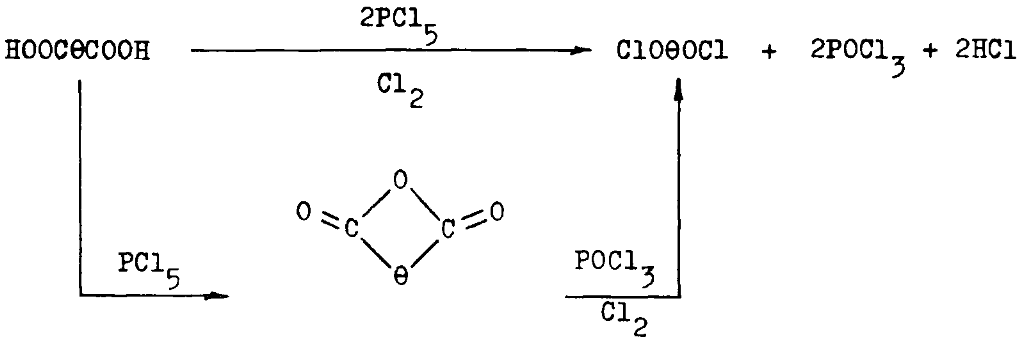
It has previously been mentioned that the inductive -I effect of the cage on an acid substituent is lessened by the interposition of CH_2 groups between the cage and the acid group. This is clearly shown by the increase in pKa values from the formic to acetic to propionic to benzoic acid derivatives. (68) Carboxylic acids which are shielded from the cage by CH_2 groups tend to behave as a normal acid, whilst those that are bonded directly to the cage will to some extent be influenced by the inductive and steric effects of the cage. This is true of o-carboranyl-(1,2-bis-(acetic acid) and o-carboranyl-1,2(dicarboxylic acid), the former showing many reactions of a carboxylic acid. (12)



The action of heat on the same acid gives a cyclic ketone which is similar to that formed by adipic acid upon heating.



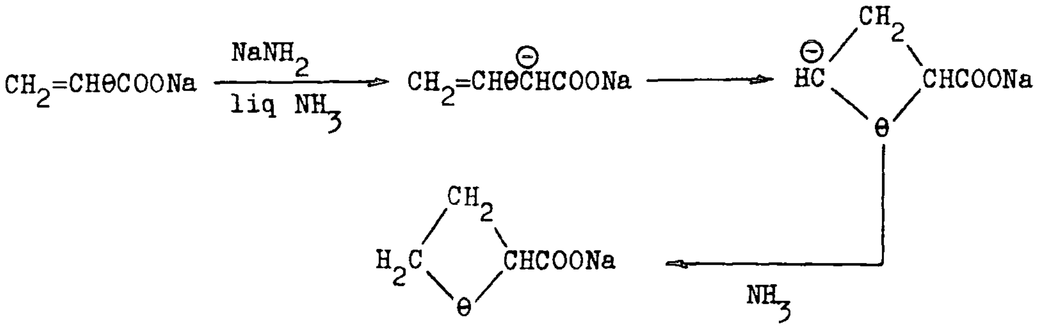
Carboranyl 1,2-(dicarboxylic acid) in comparison, does not react with ammonia or amines to form a di-amide, nor can it be esterified. Treatment with phosphorus pentachloride or thionyl chloride causes cyclisation instead of giving the acid chloride. However, reaction of the acid with chlorine and phosphorus pentachloride in chlorine gives the acid chloride. (13,52)



1-Phenyl-o-carboran-2-yl carboxylic acid can be converted to the acid chloride by treatment with phosphorus pentoxide although attempts to prepare it directly from the appropriate acetylene and bis-(acetonitrile) decaborane leads to cyclisation. (63) Related compounds which do not have shielding from the cage also show a reluctance to esterify or react with thionyl chloride.

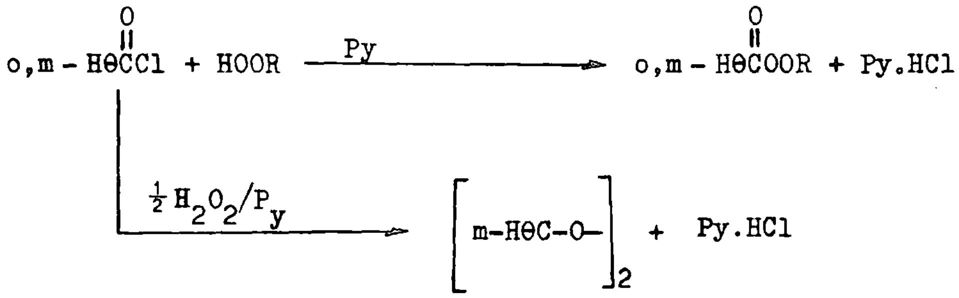
Decarboxylation of the carborane carboxylic acids occurs upon heating mercury di-(carboranyl carboxylates), (stabilised by electron donor ligands such as 1,10-phenanthroline) above their melting points, giving the corresponding bis-carboranyl mercury derivatives. (72) Quantitative decarboxylation has been reported in the presence of beryllium and zirconium acetylacetonates. (73)

The sodium salt of 1-vinyl-o-carboran-2-yl acetic acid has been shown to undergo cyclisation reactions under the influence of sodamide in liquid ammonia via an anionic intermediate. (74)



1-Isopropenyl-o-carboran-2-yl carboxylic acid also undergoes a cyclisation reaction in sulphuric acid at 150°C. (187) This cyclic acid behaves as a normal carboxylic acid, forming esters and acid chlorides.

Di-acyl peroxides and peroxyesters have been synthesised by the reactions of tert-butyl and tert-pentyl hydroperoxides with o-,m-carboran-1-yl carbonyl chlorides in the presence of pyridine inethanol, pentane or hexane. (75,76) Symmetric di-acyl peroxides were prepared by the action of hydrogen peroxide on m-carboran-1-yl carbonyl chloride with pyridine at -10°C. (76)



$$o,m-H\theta\overset{O}{\overset{\|}{C}}Cl + HOOR \xrightarrow{Py} o,m-H\theta\overset{O}{\overset{\|}{C}}OOR + Py.HCl$$

$$\xrightarrow{\frac{1}{2}H_2O_2/P_y} \left[m\text{-}H\theta C\text{-}O\text{-}\right]_2 + Py.HCl$$

Boron substituted peroxides have been made by an analogous method. (77)

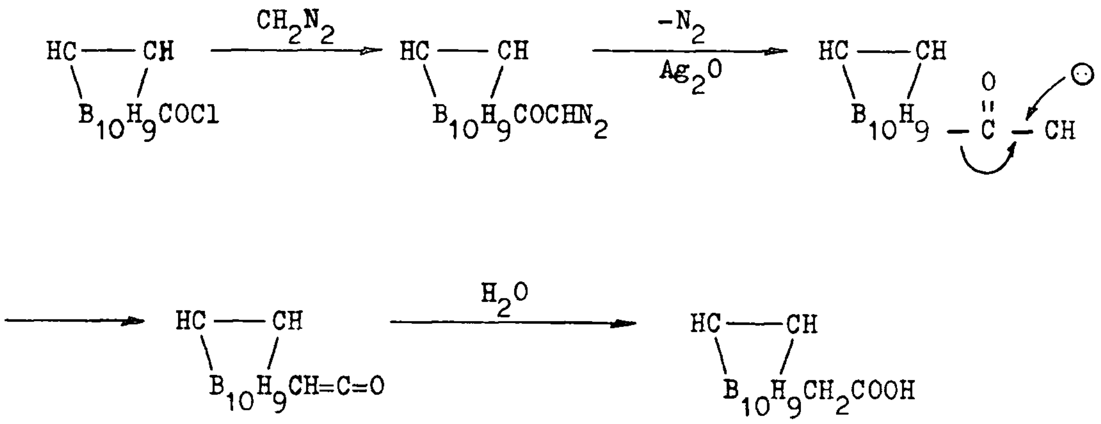
The chemistry of B-carboxylic acids is nearer that of the free acids owing to the reduced electron-withdrawal felt at the boron atoms. The formation of esters and acid chlorides proceeds normally. (65,66)

$$HCB_{10}H_{10-n}(COOH)_nCH \xrightarrow{MeOH} HCB_{10}H_{10-n}(COOMe)_nCH$$

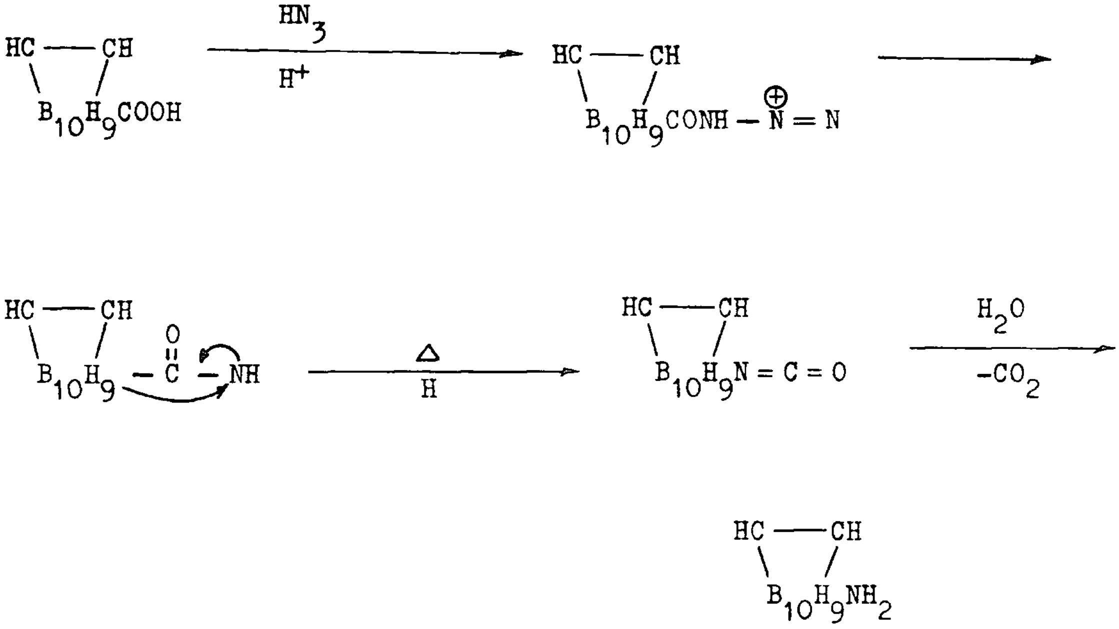
$$\xrightarrow[SOCl_2]{} HCB_{10}H_{10-n}(COCl)_nCH$$

Boron substituted carboxylic acid and carbonyl chlorides undergo Wolff, Beckmann, Curtius and Schmidt rearrangements, readily by B-C cleavage rather than the more normal C-C cleavage. (78)

Wolff Rearrangement



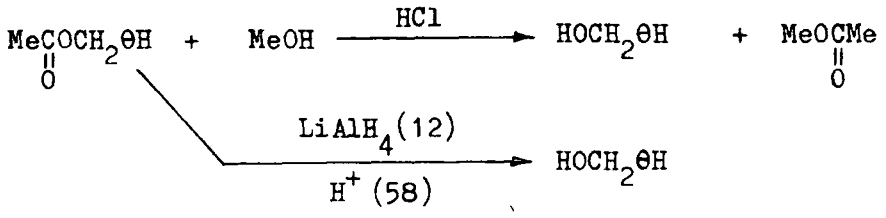
Schmidt Rearrangement



1.7 ALCOHOL, ETHER AND ESTER DERIVATIVES

Synthesis of Alcohols

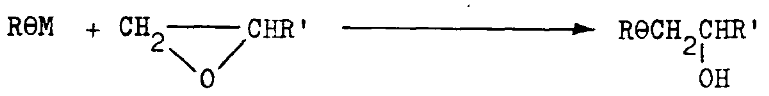
o-Carboranyl alcohols like the carboxylic acids, cannot be synthesised directly from acetylenic alcohols and bis-(acetonitrile) decaborane, since the decaborane cage is degraded by the alcohol groups. The usual alternative is to use an ester of the acetylenic alcohol. The carborane ester may then be converted back to the alcohol by hydrolysis (12,52,58) or by transesterification. (11)



$$\mathrm{Me\underset{O}{\underset{\|}{C}}OCH_2\theta H + MeOH \xrightarrow{HCl} HOCH_2\theta H + MeO\underset{O}{\underset{\|}{C}}Me}$$

$$\mathrm{Me\underset{O}{\underset{\|}{C}}OCH_2\theta H \xrightarrow[H^+\,(58)]{LiAlH_4\,(12)} HOCH_2\theta H}$$

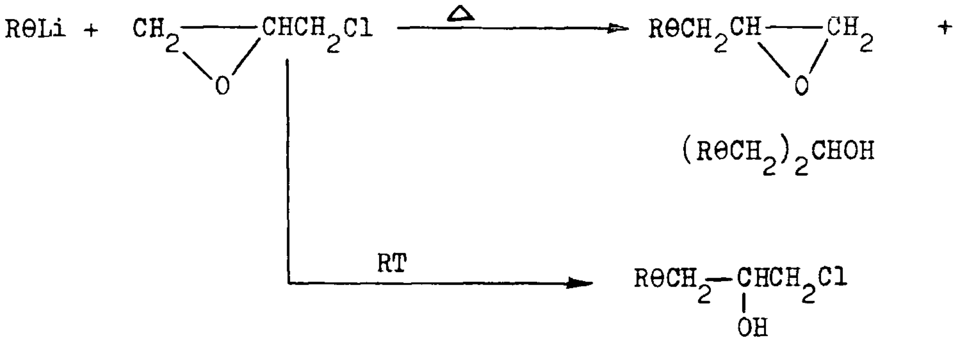
Alcohols may be prepared by reactions of C-alkali metal carborane derivatives with aldehydes, ketones, esters and epoxides. Di-lithio-o-carborane reacts with ethylene oxide to give bis-(β -hydroxymethyl)-o-carborane. (12,53,54) Similar reaction with epoxides gives secondary alcohols. (79)



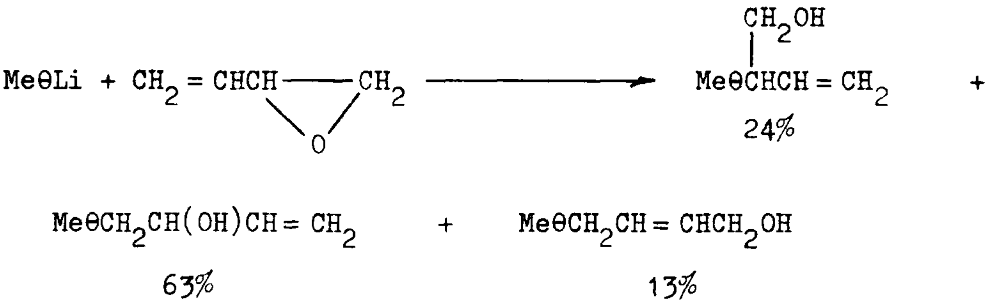
$$\mathrm{R\theta M + CH_2\!-\!CHR'\ (\text{O bridged}) \longrightarrow R\theta CH_2\underset{OH}{\underset{|}{C}}HR'}$$

M=Li, Na; R=H, Me, CH_2=CH, Ph; R' = H, Me, Ph, CH_2Cl

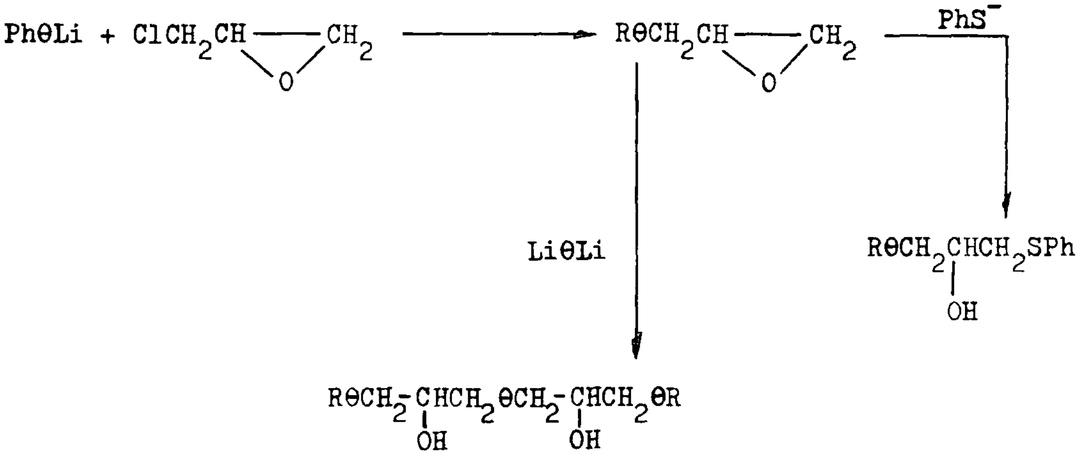
If, however, the reaction with epichlorhydrin is conducted at an elevated temperature, a mixture of an epoxide and a di-carboranyl alcohol result. At low temperature the expected chloro-alcohol is formed. (79)



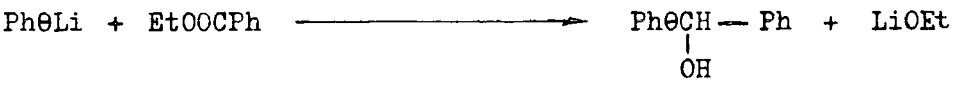
The reaction of 1-lithioallyl-o-carborane with ethylene oxide or formaldehyde leads to the formation of primary allyl and trans-propenyl alcohols, whilst the reaction with 3,4-epoxy-but-1-ene yields a mixture of primary and secondary alcohols. (60)



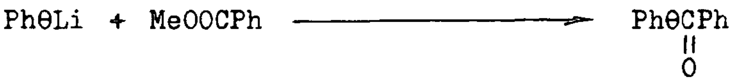
Secondary alcohols have been formed by the reaction of o-carboran-1-yl-1,2-epoxypropanes wih nucleophilic reagents such as alkoxides, thiophenolates, or lithio carboranes. (90)



1-phenyl, 2-lithio-o-carborane and ethyl benzoate react giving a secondary alcohol, (80,107) whilst the reaction with methyl benzoate gives a ketone.

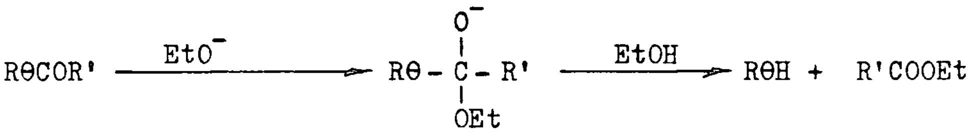


$$\mathrm{Ph\Theta Li} + \mathrm{EtOOCPh} \longrightarrow \mathrm{Ph\Theta}\underset{\mathrm{OH}}{\underset{|}{\mathrm{C}}}\mathrm{H}-\mathrm{Ph} + \mathrm{LiOEt}$$

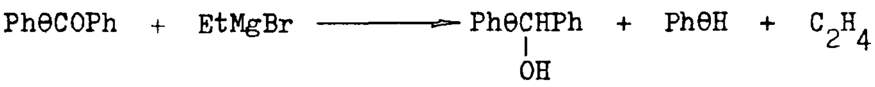


$$\mathrm{Ph\Theta Li} + \mathrm{MeOOCPh} \longrightarrow \mathrm{Ph\Theta}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{Ph}$$

Organolithium compounds or Grignard reagents would be expected to react with such carboranyl ketones followed by hydrolysis to give tertiary alcohols. Instead, secondary alcohols are formed, or cleavage of the ketone group from the cage occurs to give the parent carborane. Other nucleophiles such as ethoxide ion, NH_2^- ion or even small catalytic amounts of OH^- cause a similar cleavage of the C-C bond. (56,81,82)



$$\mathrm{R\Theta COR'} \xrightarrow{\mathrm{EtO^-}} \mathrm{R\Theta}-\overset{\mathrm{O^-}}{\overset{|}{\underset{\mathrm{OEt}}{\underset{|}{\mathrm{C}}}}}-\mathrm{R'} \xrightarrow{\mathrm{EtOH}} \mathrm{R\Theta H} + \mathrm{R'COOEt}$$



$$\mathrm{Ph\Theta COPh} + \mathrm{EtMgBr} \longrightarrow \mathrm{Ph\Theta}\underset{\mathrm{OH}}{\underset{|}{\mathrm{C}}}\mathrm{HPh} + \mathrm{Ph\Theta H} + \mathrm{C_2H_4}$$

The action of n-butyl lithium gives only the C-lithiated parent carborane. Secondary alcohols have also been prepared by the reaction of Grignard reagents with o-carboranyl aldehydes, (83) or by the reaction of o-carboranyl Grignard reagents or lithio-carborane (12,54,85) with aldehydes, excepting formaldehyde which gives primary alcohols. (84) The action of methyl magnesium iodide on m-carboranyl acid chlorides or 1-methyl, 7-benzoyl-m-carborane gives tertiary alcohols. (83)

Ketones such as bis-(phenyl-carboranyl) ketone are cleaved by Grignard reagents to a secondary alcohol and phenyl carborane (82), whilst 1,2-benzo-3,4-carboranyl cyclopentane ketone reacts with lithium aluminium hydride to yield an alcohol. (57)

1-Hydroxy o- and m-carboranes can be prepared by the action of air and dilute acid on lithio carboranes or by the action of benzoyl peroxide on 1-lithio, 2-methyl-o-carborane followed by hydrolysis. (87)

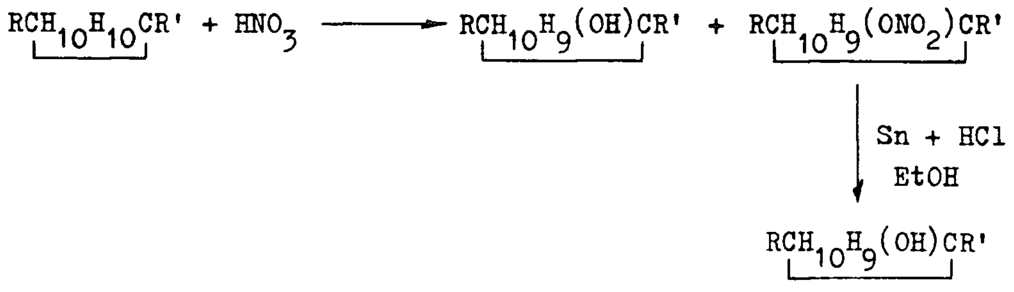
$$Me\Theta Li + (PhCOO)_2 \longrightarrow Me\Theta OLi + Me\Theta COPh + PhCOOLi$$

The reaction with air is fairly slow and yields only about 40% product. (87)

$$R\Theta Li \xrightarrow[(2)\ H_2O/H^+]{(1)\ O_2} R\Theta OH \qquad R = H,\ Me$$

CC-bis-p-hydroxybenzyl derivatives of carboranes have been synthesised as possible polymer precursors. (88)

B-hydroxy-o-carboranes have been reported to be formed by the action of concentrated nitric acid on o-carborane or its methyl and dimethyl derivatives in carbon tetrachloride. (89,96)



$$\begin{tikzcd} \underline{RCH_{10}H_{10}CR'} + HNO_3 \arrow[r] & \underline{RCH_{10}H_9(OH)CR'} + \underline{RCH_{10}H_9(ONO_2)CR'} \arrow[d, "Sn + HCl,\ EtOH"] \\ & \underline{RCH_{10}H_9(OH)CR'} \end{tikzcd}$$

o-and m-carborane undergo oxidation by potassium permanganate in acetic acid unselectively to give four isomers of B-hydroxy carborane. Oxidation by chromium trioxide gives more selectively substitution at the more negatively charged boron atoms. Para carborane only gives one product due to the equivalence of the boron atoms. (95) These B-hydroxy compounds are very susceptible to alkaline cleavage yielding dicarbaundecaborate (12) salts. (96)

$$\underline{HCB_{10}H_9(OH)CH} \xrightarrow{KOH} \left[\underline{HCB_{10}H_9(O)CH}\right]^- \xrightarrow{KOH} KC_2B_9H_{12} + B(OH)_3$$

Other B-substituted alcohols have been prepared by the reduction of B-substituted acid chlorides with lithium aluminium hydride in ether. (65)

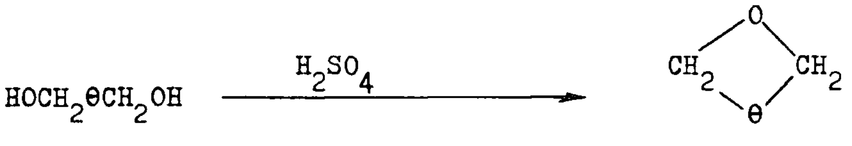
$$m\text{-}\underline{HCB_{10}H_9(2\text{-}COCl)CH} \xrightarrow{LiAlH_4} m\text{-}\underline{HCB_{10}H_9(2\text{-}CH_2OH)CH}$$

Synthesis of Ethers

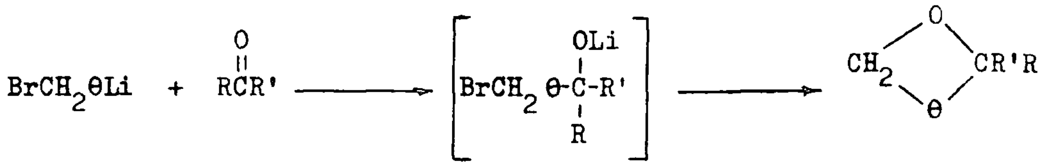
Aliphatic ethers are usually prepared by the reaction of acetylenic ethers with bis-(acetonitrile) decaborane, (54) for example bis-(carboranylmethyl) ether is synthesised from dipropargyl ether.

$$2B_{10}H_{12}(CH_3CN)_2 + (HC \equiv CCH_2)_2O \longrightarrow H\theta CH_2OCH_2\theta H + 4MeCN + 2H_2$$

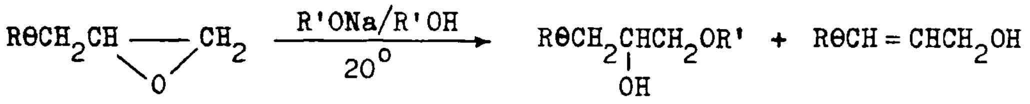
There are several reported cyclic ethers, formed by the dehydration or decarboxylation of other carboranyl ethers, alcohol or carboxylic acids. (12,54)



Bis-hydroxymethyl-o-carborane forms exocyclic ethers with formaldehyde, dibutoxymethane and 1-epoxyisopropyl-o-carborane. (59,91,92) Other cyclic ethers have been formed by reactions between aldehydes or ketones and 1-bromomethyl-o-carboranes. (85)



The reaction of alkoxides in alcohol with o-carboranyl-1,2-epoxypropane produces the respective hydroxyether and allyl alcohol. (90)



R=Me, i-Pr; R'=Me, Et.

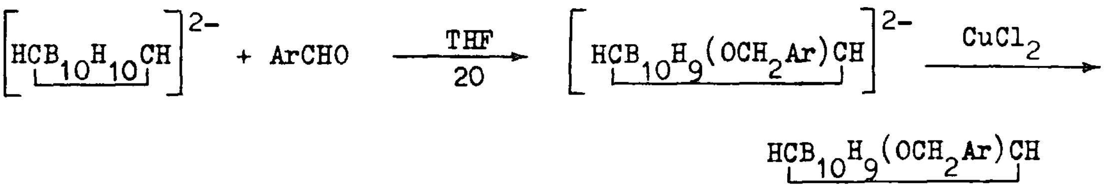
Addition of methoxy chloromethane to 1-lithioallyl-o-carborane gives practically only the allyl ether isomers, unlike other reactions of 1-lithioallyl-o-carborane.

Some cage-oxygen-alkyl bonded ethers have been prepared by the reaction of 1-hydroxy carboranes with di-azo methane. (87)

$$R\theta OH + CH_2N_2 \longrightarrow R\theta OMe$$

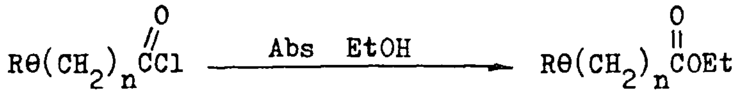
These directly bonded ethers appear to be more resistant to cleavage.

Some B-O-C pseudo ethers were synthesised by the action of benzaldehyde on the o-carboranyl di-anion in THF.



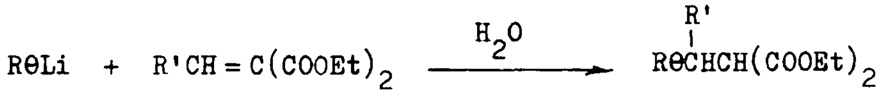
Synthesis of Esters

Carboranyl esters are usually prepared from either the reaction of acetylenic esters and bis-(acetonitrile) decarborane, (11,52,57,58) or by the reactions of alcohols with carboranyl carboxylic acids, carbocylic acids with carboranyl alcohols, (12) or the action of alcohols on carboranyl acid chlorides. (56)



$$R\Theta(CH_2)_n\overset{O}{C}Cl \xrightarrow{\text{Abs EtOH}} R\Theta(CH_2)_n\overset{O}{C}OEt$$

Other carboranyl esters have been synthesised from unsaturated esters on reaction with lithio o-carboranes. (99)

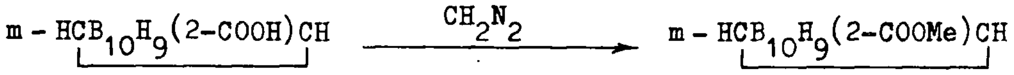


$$R\Theta Li + R'CH=C(COOEt)_2 \xrightarrow{H_2O} R\Theta\overset{R'}{C}HCH(COOEt)_2$$

$R = R' = Me, Ph.$

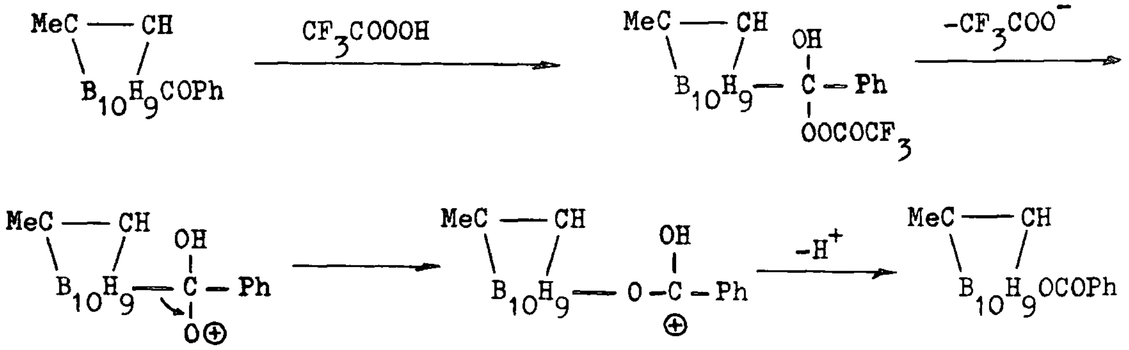
Alternatively, 1-hydroxy-o-carborane yields esters on reaction with acetyl chloride, as will the trimethyl ammonium salt with benzoyl chloride. (87)

B-substituted esters differ from the C-substituted analogues by their mode of preparation. Addition of alcohol to the acid appears not to be sufficient, instead, the B-carboxylic acid is reacted with di-azomethane to give the methyl ester. (65)



$$m-\underline{HCB_{10}H_9(2\text{-}COOH)CH} \xrightarrow{CH_2N_2} m-\underline{HCB_{10}H_9(2\text{-}COOMe)CH}$$

O-carboranyl B-esters can also be prepared by reacting 3-hydroxy-o-carborane with acetic anhydride, (11) or by the Bayer-Villigier reaction of pertrifluoroacetic acid on (1-methyl o-carboran-3-yl) phenyl ketone; (see section 8) the 3-o-carboranyl fragment being the migrating group. (78)



Reactions of Alcohols

The oxidation of primary alcohols to carboxylic acids has already been discussed in the previous section.

The electron withdrawal of the carborane cage is as apparent in the chemistry of alcohols as it is for the carboxylic acid derivatives. Again separation of the functional group from the cage produces more normal alcohol chemistry. This can be clearly shown by comparing the reactions of hydroxymethyl-o-carborane with hydroxyethyl- and hydroxypropyl-o-carboranes. Whilst alkaline potassium permanganate oxidises hydroxyethyl- and hydroxypropyl-o-carboranes to their acid salts, hydroxymethyl-o-carborane is converted directly to the parent carborane. (52) Hydroxymethyl-o-carborane also reacts with thionyl chloride in the presence of pyridine by replacement of the hydroxyl group with chlorine; it is unaffected by 48% hydrobromic acid in sulphuric or sodium bromide in concentrated sulphuric acid. (59)

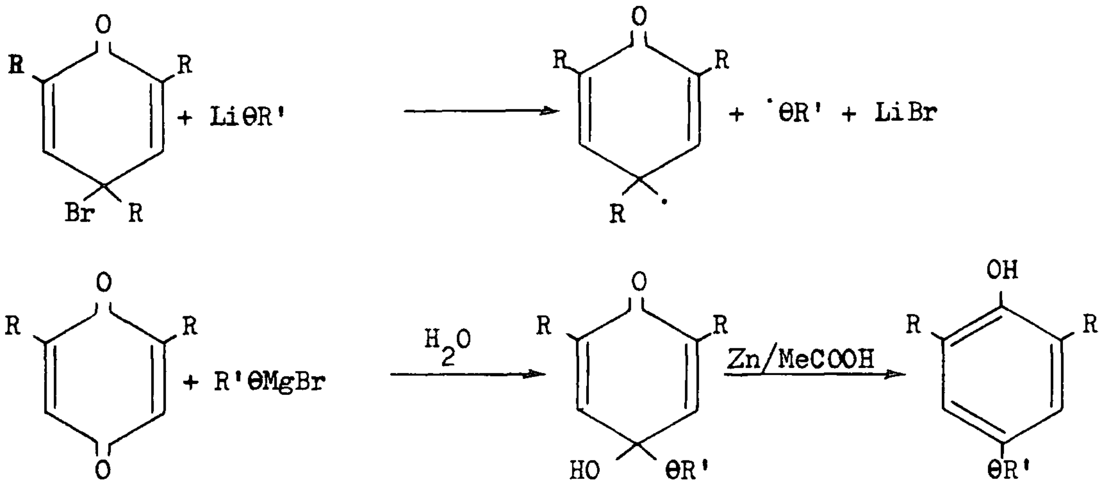
The action of sodium forms the dimetallo-alcoholate which was found to be unreactive except towards hydrolysis. (12) As already shown, bis-(hydroxymethyl)-o-carborane undergoes cyclisation reactions readily, although this could be due to more steric reasons.

Apart from the aforementioned reactions, carboranyl alcohols react normally, reacting with aliphatic acids, acid anhydrides, and acid chlorides to give esters. Cleavage of the tertiary alcohols occurs with catalytic amounts of OH^- in ethanol, breaking the cage alcohol C-C bonds to give the parent carborane. (83)

Clearly, hydroxyalkyl-o-carboranes would appear to be good polymer precursors, but owing to steric and possibly electronic effects, the attempts to prepare polymers from them has met with limited success. This has been due in some cases to the formation of exocyclic rings.

Meta-carborane derivatives have been used instead of the ortho hydroxyalkyls, owing to their inability to form small exocyclic rings on steric grounds. The formation of the polymers will be discussed more fully in section 15.

Sterically hindered C-phenol derivatives have undergone specific study because of their ability to form stable radicals. For example, the reaction of 1-lithio, 2-alkyl-o-carborane with a "quinobromide" leads to a radical pair formation. Grignard carboranes give only a stable phenol derivative. (97)



(I)

R = t-Bu R' = H,Me

Oxidation of (I) with lead dioxide gave a stable phenoxyl radical. With the meta-carborane derivative the ESR spectrum shows a rearrangement of the radical to the ortho-carborane derivative. (98)

Reactions of Esters

The esters of the carboranes, like the acids and alcohols, show chemistry which is dependent on the position of the ester group relative to the carborane cage. Carboranyl methyl acetate is easily cleaved by nucleophiles to give the parent carborane, whilst the interposition of one methylene group between the cage and the ester stops this reaction. (56,57) The products in the latter case are an acid or alkyl derivative.

$$H\theta(CH_2)_nCOOEt \xrightarrow{KOH,\ EtOH} H\theta(CH_2)_nCOOH + H\theta(CH_2)_nH$$

$$n=0,1,2,3 \qquad\qquad n=0,1,2,3 \qquad\qquad n=0,1$$

In dioxane, the hydrolysis of the ethyl acetate ester leads exclusively to the acid. (57)

Pyrolysis of 1-methyl, carboran-2-yl-(1-vinyl)-ethylacetate in ethylacetate leads to the formation of 2-(2-methyl-o-carboran-1-yl)-1,3-butadiene, (60) and pyrolysis of other esters similarly leads to alkene synthesis. (See section 4)

1.8 ALDEHYDE AND KETONE DERIVATIVES

Synthesis of Aldehydes

Aldehyde derivatives can be synthesised by the reduction of C-acid chlorides with hydrogen in boiling xylene in the presence of Pd/$BaSO_4$ or Pd/charcoal catalyst. (100,102,104)

$$\text{o,m,p-}\ H\Theta-(CH_2)_nCOCl \xrightarrow[n=0,1]{[H]} \text{o,m,p-}\ H\Theta-(CH_2)_nCHO$$

Ozonolysis of vinyl-o-carboranes forms aldehydes in almost quantitative yields. (64,101)

Whereas the oxidation of carboranyl alcohols with chromium trioxide gives carboranyl carboxylic acids, and with alkaline potassium permanganate gives the parent carborane, treatment of hydroxyethyl-o-carborane with DMSO in the presence of bicyclohexyl carbo-di-imide gives the carboranyl aldehyde in the form of the 2,4-dinitrophenyl hydrazone in low yields. (102) The oxidation of 3-(carboranyl) prop-l-en-3-ols with manganese dioxide in hexane proceeds to give the respective aldehydes in near quantitative yields. (103)

$$\text{o}-R\Theta CH=CHCH_2OH \xrightarrow[\text{Hexane}]{MnO_2} \text{o}-R\Theta CH=CHCHO$$

$$R = H, CH_3$$

Other methods of synthesis include the Sonn-Müller reaction on the anilides of o- and m-carboranes, (100,102) although yields are not high.

$$\text{o,m}-H\Theta CONHC_6H_5 \xrightarrow{PCl_5} \text{o,m}-H\Theta CCl=NC_6H_5 \xrightarrow[H_3O^+]{SnCl_2} \text{o,m}-H\Theta CHO$$

A convenient method of synthesis which gives a 40% yield of the C-aldehyde is by the hydrolysis of the methyl di-acetate with water. (102)

$$H\theta CH(OCOCH_3)_2 \; + \; H_2O \longrightarrow H\theta CHO$$

The hydrolysis of C-di-alkoxides with dilute acid in ether is reported to give good yields of aldehydes. (105)

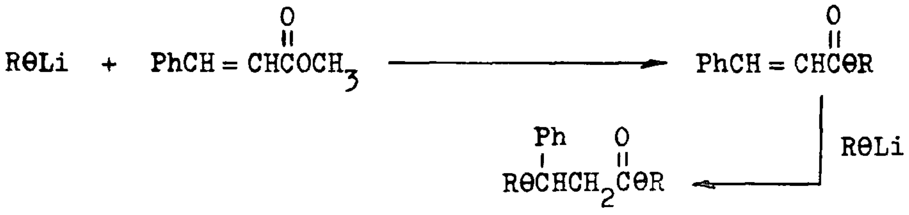
Di-aldehydes can be prepared by all of the above methods although an alternative route starting from dilithio-m-carborane has recently been published. (106)

$$Li\theta'Li \xrightarrow[2.)\ H^+]{1.)\ PhOCH(OEt)_2} OHC\theta'CHO$$

B-substituted aldehydes have been prepared by the ozonolysis of 3-vinyl-o-carborane, (64) and 2-vinyl-m-carborane. (65)

Synthesis of Ketones

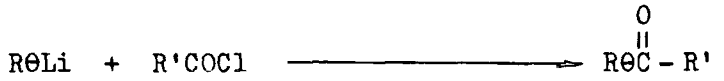
Carboranyl ketones are produced by a wide range of reactions. Secondary β- carboranyl alcohols are oxidised by chromic acid to the corresponding ketones. (79) Methyl esters react with lithio-o-carboranes to give ketones, whilst the reactions of methyl or ethyl formate or other ethyl esters lead to the formation of secondary alcohols (See section 7). (80,107) In contrast, the esters of α,β unsaturated acids are attacked by lithio carboranes at the carbonyl group to give an α,β unsaturated carboranyl ketone, which will further react with lithio carborane at the double bond to give a bis-(o-carboranyl) ketone.



$$R\theta Li + PhCH{=}CH\overset{O}{\overset{\|}{C}}OCH_3 \longrightarrow PhCH{=}CH\overset{O}{\overset{\|}{C}}\theta R \xrightarrow{R\theta Li} R\theta\overset{Ph}{\overset{|}{C}H}CH_2\overset{O}{\overset{\|}{C}}\theta R$$

A similar reaction of lithio-o-carborane occurs with unsaturated ketones again with terminal addition of a carborane cage. (107)

Lithio-carboranes will react with aliphatic, aromatic and even carboranyl acid chlorides to give ketones. (61,81)



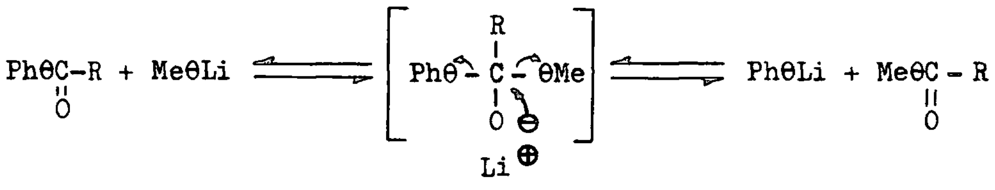
$$R\Theta Li + R'COCl \longrightarrow R\Theta\overset{O}{\overset{\|}{C}}-R'$$

$R = Me, Et, Ph;\ R' = Me, Ph, i\text{-}Pr, R\Theta-$

Di-ketones can be formed by action of oxalyl chloride on lithio carboranes, but under the action of phosgene, a cyclic di-carboranyl-di-ketone is formed. (108) Lithio-m-carborane cannot cyclise due to steric hindrance.

$$Ph\Theta Li + ClOC-COCl \longrightarrow Ph\Theta\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}\Theta Ph$$

During the reaction of lithio-carboranes with acid chlorides, no formation of the tertiary alcohols was observed due to the instability of the alcoholates of the carboranyl tertiary alcohols under the reaction conditions. However the formation of the tertiary alcoholates is confirmed by the action of 1-methyl, 2-lithio-o-carborane on 1-phenyl, 2-p-chlorobenzoyl o-carborane to give two ketones, 1-phenyl, 2-lithio-o-carborane andl-methyl, 2-lithio-o-carborane via a bis-o-carboranyl alcoholate intermediate. (61)

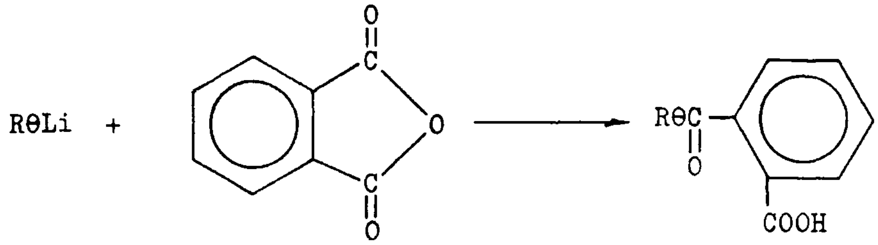


$R = -C_6H_4Cl$

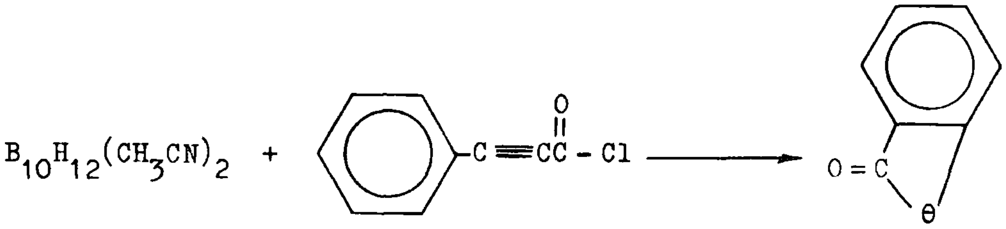
In the reaction between phenyl magnesium bromide and 1-phenyl o-carboran-2-yl acyl chloride, a mixture of bis-(1-phenyl carboran-2-yl) ketone and 1-phenyl, 2-benzoyl o-carborane is formed. (61) Acid chlorides also react with carboranyl Grignard reagents with the formation of ketone in the same manner as lithio carborane. (84)

1-Vinyl- and 1-phenyl-o-carboran-2-yl acyl chloride is capable of undergoing a condensation reaction in the presence of benzene and aluminium trichloride to yield the corresponding 2-benzoyl derivative. (61) An analogous reaction with acetylene has also been reported, with the formation of β-chlorovinyl ketones. (109)

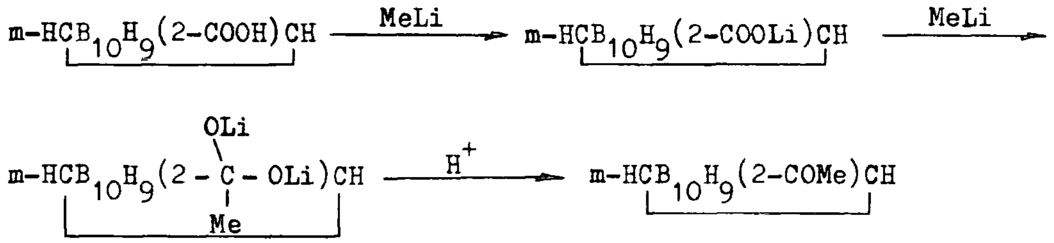
The reaction of lithio-carborane with acid anhydrides and cyclic anhydrides gives ketones and keto acids respectively. (107)



As already mentioned in section 5, cyclic carboranyl ketones can be formed by pyrolysis of carboranyl carboxylic acids. (12) They can also be formed by the dehydration of acids with polyphosphoric acid (110) or by the treatment of bis-(acetonitrile) decaborane with phenyl propiolyl chloride. (57)



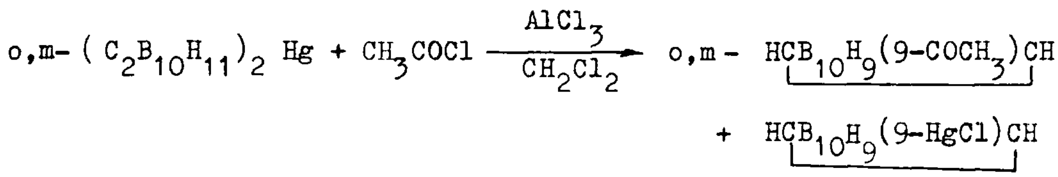
B-substituted ketones can be synthesised from B-carboxylic acids by the action of methyl lithium and acid, or by Friedel-Crafts reaction of the o- or m-carborane acid chloride with benzene in the presence of aluminium trichloride to give 2-benzoyl-m-carborane. (65,78)



$$m\text{-}\underline{HCB_{10}H_9(2\text{-}COOH)CH} \xrightarrow{MeLi} m\text{-}\underline{HCB_{10}H_9(2\text{-}COOLi)CH} \xrightarrow{MeLi}$$

$$m\text{-}\underline{HCB_{10}H_9(2-\overset{OLi}{\underset{Me}{C}}-OLi)CH} \xrightarrow{H^+} m\text{-}\underline{HCB_{10}H_9(2\text{-}COMe)CH}$$

Ortho-carboran-3-yl methyl ketone can be prepared by the methylation of the 3-substituted acid chloride by dimethyl cadmium. (78) Until recently, only the meta-2- or ortho-3-position ketones were known, however, a method of preparing ortho- and meta-9-position ketones has been devised, using bis-(o-, m-carboran-9-yl) mercury (II). (112,113) (see section 14)



$$o,m\text{-}(C_2B_{10}H_{11})_2\ Hg + CH_3COCl \xrightarrow[CH_2Cl_2]{AlCl_3} o,m\text{-}\ \underline{HCB_{10}H_9(9\text{-}COCH_3)CH} + \underline{HCB_{10}H_9(9\text{-}HgCl)CH}$$

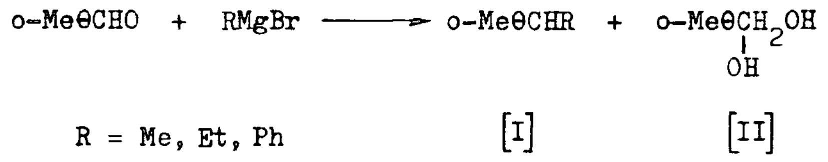
Reactions of Aldehydes

Carboranyl aldehydes are subject to alkaline cleavage at the C - C cage to aldehyde bond to give the parent carborane. (83,100,102,114,118) The kinetics of this cleavage for ortho, meta and para carborane have been investigated and the reaction is shown to proceed via a hemiacetal intermediate. (115) A similar reaction was found by Crampton with meta and para benzaldehyde derivatives on addition of methanol. (116)

Reactions with organo lithium compounds yield secondary alcohols. (83,101,102)

$$o\text{-}Me\theta CHO + o\text{-}Me\theta Li \longrightarrow (o\text{-}Me\theta)_2CHOH$$

The reaction of aldehydes with Grignard reagents in ether gives two products; one [I] via normal addition to the carbonyl group, the other [II] by reduction of the aldehyde to a primary alcohol. (83,102)

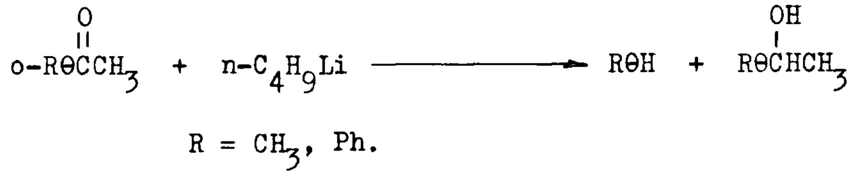


$$o\text{-}Me\theta CHO + RMgBr \longrightarrow o\text{-}Me\theta CHR + o\text{-}Me\theta \underset{OH}{C}H_2OH$$

$$R = Me,\ Et,\ Ph \qquad [I] \qquad [II]$$

Reactions of Ketones

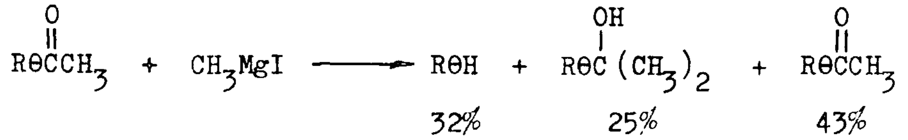
O-carboranyl ketones are cleaved by both alkalis and sodamide in liquid to give the parent carborane, (56,82,102,118,119) indeed presence of basic alumina used in thin layer chromatography is often enough to cause cleavage. (56,61,118) The action of organo-lithium compounds causes some cleavage of the C-C bond, but also produces secondary alcohols (83,118) of 1-acetyl o-carboranes.



$$o\text{-}R\theta\overset{O}{\overset{\|}{C}}CH_3 + n\text{-}C_4H_9Li \longrightarrow R\theta H + R\theta\overset{OH}{\overset{|}{C}}HCH_3$$

$$R = CH_3,\ Ph.$$

The nature of attack by Grignard reagents depends on the alkyl group attached to the magnesium atom. For example ethyl magnesium bromide almost completely reduces the carbonyl group of 1-methyl, 2-acetyl-o-carborane to give a secondary alcohol. (83,118) The equivalent reaction with methyl magnesium iodide in ether, however, gives methyl o-carborane a tertiary alcohol and unreacted ketone. The methyl carborane is formed as a result of the decomposition of the unstable carboranyl tertiary alcohol. The action of heat, or the use of THF leads to a great reduction in the amount of tertiary alcohol, the latter being due to the higher solubility of the tertiary alcoholate. (83)

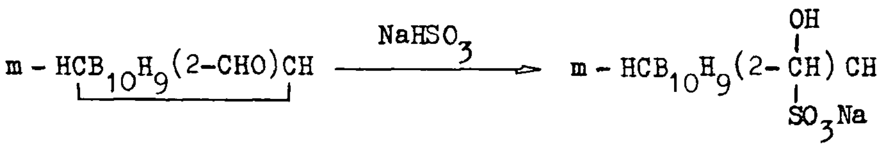


$$R\theta\overset{O}{\overset{\|}{C}}CH_3 + CH_3MgI \longrightarrow \underset{32\%}{R\theta H} + \underset{25\%}{R\theta\overset{OH}{\overset{|}{C}}(CH_3)_2} + \underset{43\%}{R\theta\overset{O}{\overset{\|}{C}}CH_3}$$

1-Methyl, 7-acetyl-m-carborane in ether yields tertiary alcohols by the action of methyl lithium, or methyl and ethyl magnesium halides. This is due to the greater stability of the m-carboranyl tertiary alcoholates; indeed, C–C cleavage does not occur even with sodium ethoxide and heating. Methyl magnesium iodide also gives the tertiary alcohol of 1-phenyl, 2-benzoyl-o-carborane, contrary to early literature reports, but only gives secondary alcohol on reaction with bis-(1-phenyl-carboran-2-yl) ketone.

Bromination studies on o-carboranyl ketones have shown that the α-hydrogen is not very prone to attack by bromine in carbon tetrachloride even when the carbonyl group is separated from the cage by a CH_2 unit. Bromination does, however, occur in acetic acid at 115° without attack on the cage.

Previous reviewers have reported (68) that steric hindrance in the carboranyl ketones is shown by the slow rates of reaction with 2,4-dinitrophenyl hydrazones (118) and by the lack of formation of bisulphite derivatives in comparison to β-(o-carboranyl) aldehydes. (117) This seems unlikely to be the main cause of unreactivity, as Zakharkin et al (65) have reported the formation of both of these derivatives by 2-formyl-m-carborane.



$$m-\underline{HCB_{10}H_9(2\text{-}CHO)CH} \xrightarrow{NaHSO_3} m-HCB_{10}H_9(2\text{-}\overset{OH}{\underset{SO_3Na}{CH}})\,CH$$

1.9 HALOGEN DERIVATIVES

The halogen derivatives of the three icosahedral carboranesdiffer from the derivatives discussed in other sections in that their chemistry is largely that of B-substituted derivatives.

Electrophilic Substitution

There have been many studies made of the effect of direct attack on the cage by chlorine, bromine and iodine, and these have revealed that there is little variation in the position of substitution. In general, substitution starts at the most negative boron atoms, that is, those furthest away from the carbon atoms, and proceeds towards the carbons. The carbon atoms and those boron atoms directly attached to them do not appear to be susceptible to electrophilic halogenation in ortho-and meta-carborane. (121 - 125) Para-carborane, however, in which all the boron atoms are equivalent and are bonded to a carbon atom, does undergo electrophilic chlorination in refluxing carbon tetrachloride over aluminium trichloride giving up to a tetrachloro species. Bromine and iodine only give the mono-halo p-carborane derivative. (126,127) Treatment of o-carborane with chlorine over $FeCl_3$, $AlBr_3$ or $AlCl_3$ gives mainly the mono-di-and tri-chloro derivatives with a smaller amount of B-tetrachloro o-carborane, (122 - 124, 128 - 130) and a trace of mono-8-chloro-o-carborane. (130) There is also evidence that the choice of catalyst can effect the selectivity and rate of halogenation. (128)

Electrophilic halogenation of m-carborane was at first thought only to give 9, 10-dihalo-m-carborane. Later work, however, showed that in fact further halogenation of 9-halo-m-carborane gave a mixture of 9,10-; 3,9-; and 5,9-dihalo-m-carborane. Further chlorination of 9,10-dichloro-m-carborane proceeds via 3,9,10- and 4,9,10- trihalo isomers to a mixture of four tetrachloro isomers. Bromination gives the equivalent isomers, though in different proportions.

There have been reports that exhaustive chlorination over $AlCl_3$ at 80° gives tri-and tetrachloro-m-carboranes, (8,12,131) whilst under the same conditions, bromination gives up to the hexabromo-species. (131) m-carborane substitution appears also to have a catalyst dependence. (128)

Studies of the effects of halogen substitution on the cage have revealed much about carborane polarisabilities. A comparison of the dipole moments of 1,2-dibromo-o-carborane and 9,12-dibromo-o-carborane has shown that the cage is made more polar by 9,12-dibromination and less polar by 1,2-dibromination. This agrees with the assumption that the carbon atoms are the positive centres of the cage. (132) Electrophilic bromination and iodination of o-carborane (124,128,129,131) proceeds in the same manner as chlorination, except that higher temperatures are required for reaction with iodine. Tribomination of o-carborane can also be achieved by this method, although 1,2-dimethyl-o-carborane can be tetrabrominated. (125) This indicates that the methyl group is undergoing a transfer of negative charge to the cage, making it more susceptible to electrophilic attack. Tribromo-o-carborane will undergo further electrophilic attack by chlorine to give tribromo, pentachloro-o-carborane, whilst dibromo-o-carborane gives ultimately dibromo,-octachloro-o-carborane. Dibromo-m-carborane also undergoes the latter reaction. (125) This increased reactivity is probably due to the B-substituted bromine atoms causing an increase in the polarity of the cage, thereby making even the carbon bonded boron atoms liable to electrophilic attack.

Electrophilic bromination and iodination can be accomplished in aqueous media by bromine and bromate ions, iodine and iodate ions respectively.

$$5\,o-\underline{HCB_{10}H_{10}CH} + 2I_2 + IO_3^- \xrightarrow[H_2SO_4,\ 100^\circ]{CH_3COOH} 5\,o-\underline{HCB_{10}H_9ICH} + 3H_2O$$

Addition of two or three times the amount of iodinating material gives di- and triiodo-o-carborane. With bromine, only the mono-and dibromo-species can be prepared, as bromination of the acetic acid occurs. Workers appear not to have tried using bromoacetic acid to overcome this difficulty. (121)

Freidel-Crafts halogenation of 1-phenyl-o-carborane has shown that in the presence of $AlCl_3$ or iron filings, attack by the first molecule of chlorine takes place preferentially at the benzene ring with only minor attack at the cage. The second molecule attacks both the cage and the ring. (133) This is in direct contradiction to earlier findings (124) quoted in some reviews. (68) Bromine, however, preferentially attacks the cage, but successive additions of molecular amounts of bromine cause ring substitution. Iodine also preferentially attacks the cage. Exhaustive chlorination leads to 8,9,10,12-tetrachloro-1-(pentachlorophenyl)-o-carborane, whereas exhaustive bromination leads to 8,9,10,12-tetrabromo-1-(tribromophenyl) - o-carborane, the difference being caused by steric hindrance of the ring ortho positions by bromine. (124,131,133) Electrophilic bromination of 1-phenyl-m-carborane and 3-phenyl-o-carborane showed that in both cases, there was preferential bromination of the benzene ring. (133) This is probably due to the decreased electron-withdrawal felt by the ring, rendering it more liable to electrophilic attack.

Electrophilic chlorination and bromination of 1-vinyl-o-carborane occurs with initial attack taking place at the vinyl group. Iodination occurs only at the cage. (21)

Halogenation can also occur in refluxing halomethanes, thus o-carborane is chlorinated by chloroform or carbon tetrachloride. (128,134) 8 and 9 position iodination takes place with o-carborane and iodo-benzene at 300°. (135)

Photochemical Halogenation

Photochemical halogenation of o-carborane by chlorine takes place under ultraviolet light with the attack starting at the most negative boron atoms and continuing until all ten boron atoms have been substituted, (21,124,136,137) the most positive 3 and 6 position boron atoms being the last to react. The intermediate B-chloro derivatives have been isolated by varying the conditions and reaction times. (124,136)

Unlike chlorination, bromination under ultraviolet light goes with difficulty, but in the presence of iron in carbon tetrachloride at 120° - 140°C it proceeds readily to give tetrabromo-o-carborane. (124) No further substitution has been achieved.

Meta-carborane (124) and para-carborane (126) also ultimately give a decachloro species or photochemical chlorination. Photo bromination of meta carborane however yields only mono-9-bromo-m-carborane (124)

1-Phenyl-o-carborane reacts with chlorine and bromine under ultraviolet light with attack taking place only at the cage, (unlike the electrophilic attack by chlorine), the final product for chlorine being 1-phenyl, B-decachloro-o-carborane, whilst the major product for bromine is 1-phenyl, 12-bromo-o-carborane. (124) The ring of 1-phenyl-m-carborane is also unreactive under these conditions.

Fluorination

Fluorination of o-, m- and p-carborane occurs on their exposure to fluorine in liquid hydrogen fluoride at 0°C. The attack is largely non-selective, although there is some indication that the site of first substitution effects the position of secondary substitution, (138) the ultimate products are perfluoro o-, m-, p-carboranes.

$$\underline{HCB_{10}H_{10}CH} \; + \; 10F_2 \xrightarrow[0^{\circ}]{HF(liq)} \underline{HCB_{10}F_{10}CH} \; + \; 10HF$$

The reactions of the carboranes with fluorine monochloride give the respective decachloro carboranes.

Synthesis from Halo-Decaborane [14]

The reaction of monohalo-deca-borane [14] with acetylene leads to the formation of B-monohalo-o-carborane with the halogen remaining on the same boron atom. (139,140) Thus 1-halo-decaborane gives only 9, (12)-halo-o-carborane, but if an alkyl acetylene is used, then the two possible isomers of monohalo-o-carborane are recovered as the 9 and 12 positions are no longer equivalent. In this way, monohalo-o-carboranes can be synthesised in higher yields than with other methods.

Synthesis of 3-Halo-o-Carborane

Specifically 3-halo-o-carboranes can be synthesised by reacting boron trihalides with the (3)-1,2-dicarbaundecaborate [11] ion. (141) Alternatively, 3-diazonium salts may be converted to 3-halo-salts by cuprous halide. (See section 10)

C-Halo Derivatives

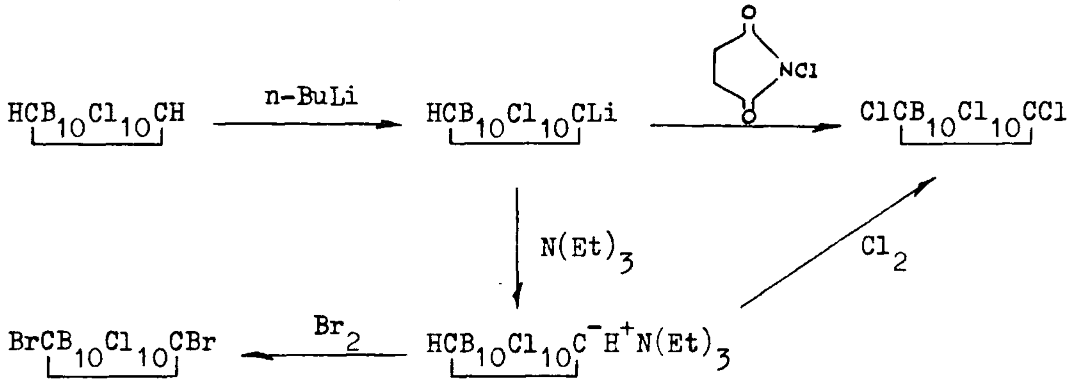
As previously mentioned, electrophilic and photochemical halogenation methods do not give C-carboranyl halides, owing to the positive nature of the carbon atoms. However, organo-lithium or Grignard derivatives of carboranes react with halogens to give C-halo-derivatives.

$$R\Theta H \xrightarrow{n\text{-}BuLi} R\Theta Li \xrightarrow{X_2} R\Theta X + LiX$$

$$R = Ph, Me; \quad X = Cl, Br, I$$

With Grignard reagents, the presence of a halomethane can be enough to halogenate the carbon atoms, although halogen is usually used as well. (12, 143-145) In the presence of ethyl magnesium bromide, the carboranyl Grignard reagent is attacked at both the carbon and boron atoms by carbon tetrachloride or chlorine. (144) This reaction also occurs in THF although with o- and m-carboran-1-yl magnesium iodide and carbon tetrachloride in THF a mixture of C-iodo-and chloro-species results. (149)

Decachloro o- and m-carboranes can be C-dihalogenated by the following reactions. (146-147)



Another but less common method of preparing C-substituted halo-o-carborane is by the use of a mono- or di-halo acetylene in the reaction with bis-(acetonitrile) decaborane. (3,148)

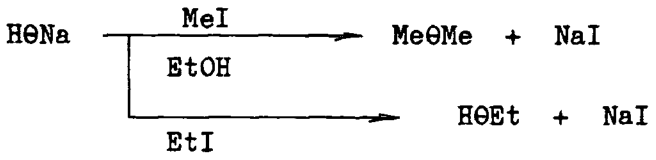
Reactions of Halogen Derivatives

The B-halo-carboranes, especially the B-chloro-carboranes are extremely stable, the stability appearing to increase with the number of halogens substituted onto the cage. The most stable is B-decachloro-o-carborane, the B-Cl bond of which is resistant to hydrolysis by hot aqueous NaOH. (124) Attempts to invoke nucleophilic attack with sodium thiophenolate in ethanol on iodo o-,m-,p-carborane failed to replace the iodine although it proved a strong enough base to degrade the carborane cage. (151)

50% aqueous potassium hydroxide in hydrogen peroxide leads to the removal of all of the chlorine atoms in this and other B-chloro-compounds. (136)

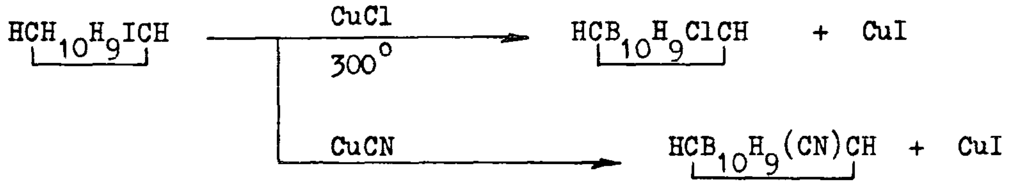
Unlike the B-decachloro-o-carborane, the B-decafluoro-derivative is very susceptible to nucleophilic attack, and is easily hydrolysed by water. (138)

The replacement of B-H bonds by B-Cl bonds causes the acidic character of the C-H bonds to be enhanced. (124,136,146,147) The greater the substitution the more the acid strength of the C-H group increases, until in the case of B-decachloro o-carborane, the strength is comparable to that of carboxylic acids. The pKa values have been measured and compared with common acids, indeed B-decachloro-o-carborane titrates as a monoprotic acid, (147) on reaction with methyl magnesium iodide, <u>two</u> moles of methane are evolved with Grignard formation. (124) B-decachloro-m-carborane dissolves in basic media, and B-decachloro-o-carborane forms salts in sodium or potassium hydroxide (168) which will react with alkyl halides in alcohol with C-alkyl substitution. The mono sodium salt reacts with methyl iodide to give di-methyl substitution, whereas ethyl iodide gives only the mono-ethyl derivative. (150)



The higher B-bromo-o-carboranes undergo similar reaction to those above.

There are few examples of nucleophilic substitution reaction involving B-chloro,- bromo-and iodo-species. Attempts at such reactions with some alkalis have already been mentioned. Substitution can, however, be accomplished by heating monobromo-or monoiodo-o,m-carboranes with cuprous chloride (151,152,153) or 9-iodo-o-carborane with cuprous cyanide. (154) This is the analogous carborane reaction to the Sandmeyer reaction.



$$HC\underbrace{H_{10}H_9I}CH \xrightarrow[300^\circ]{CuCl} HC\underbrace{B_{10}H_9Cl}CH + CuI$$

$$\xrightarrow{CuCN} HC\underbrace{B_{10}H_9(CN)}CH + CuI$$

The reaction proceeds more slowly with di- and tri-halo-substituted starting-material. (151)

Early reports that 9-iodo-o-carborane undergoes an Ullmann coupling reaction with copper powder (155) are thought to be doubtful by later workers. (151)

The boron-halogen bond can be hydrogenated by the action of alkali metals in liquid ammonia. The reaction proceeds more rapidly with iodo derivatives than bromo or chloro derivatives. (156)

There have been various studies made of the electronic effects in C- and B-halo-o-, m- and p-carboranes (137,157,160,163) some of which were based on the observed substitution orientation patterns in C-methyl-carboranes and C-methyl-B-halo-carboranes during electrophilic halogenation. (161,162,163) It has been shown from PMR, "B NMR and IR spectra that whatever the atom the substituent is on, the influence of the substituent is shown on the atoms directly linked to the substituted boron and at the directly opposite apex of the cage. The change of electron density at the substituted atom is related to the electron density it had before substitution. (163)

The electron-withdrawing effects felt by C-bonded bromine and iodine have been shown to give the halogen atoms positive character by the dehalogenation of C-bromo-and iodo-o-, m- carboranes by alcoholic alkali. (164,165) The C-chloro-carboranes undergo cage cleavage, showing that

C-bonded -I effect substituents destabilise the cage, and that chlorine has little positive character. C-bromo-and iodo-compounds also readily undergo metal exchange reactions with n-butyl lithium and ethyl magnesium bromide. (165)

The action of heat on C-bromo-and chloro-o-carboranes or, 1-chloromethyl and 1-bromomethyl o-carboranes causes an intermolecular reactions yielding B-halogenated species. (135)

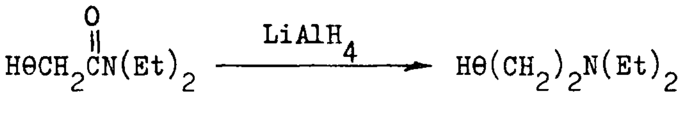
9-chloro-m- and p- carboranes can be rearranged by the action of sodium in liquid ammonia followed by oxidation with potassium permanganate to give 9-chloro-o-carborane and 2-, 4-,5-, 9-monochloro-m-carboranes respectively. (178,179) Mechanisms have been proposed for the rearrangement. (178)

1.10 NITROGEN DERIVATIVES

Synthesis of Amines

C-amino-o-carboranes can be prepared from amino-acetylenes and bis-(acetonitrile) decaborane, (3) or by the reduction of o-carboranyl-cyanides and some amides with lithium aluminium hydride. (60,176,169)

$$Ph\theta CN \xrightarrow{LiAlH_4} Ph\theta CH_2NH_2 \quad + \quad Ph\theta H$$



$$H\theta CH_2\overset{\overset{O}{\|}}{C}N(Et)_2 \xrightarrow{LiAlH_4} H\theta(CH_2)_2N(Et)_2$$

Ortho-and meta-carboranyl amines can be synthesised from C-acyl-chlorides by the action of sodium azide and sulphuric acid. (170,171)

$$\begin{tikzcd}
o,m - R\theta COCl \arrow[r, "NaN_3"] & R\theta CON_3 \arrow[r, "H_2SO_4"] & R\theta NCO \arrow[d, dash] \\
{} & R\theta NH_2 & {} \arrow[l, "H_2SO_4"']
\end{tikzcd}$$

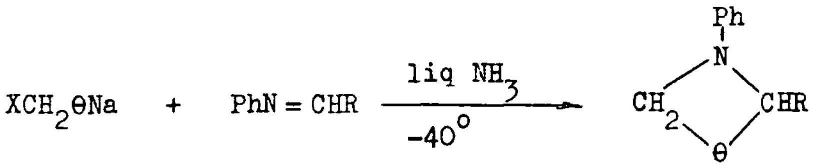
C-amines have also been prepared by reduction of C-nitroso-o- and m-carboranes with chloro-aluminium hydride, n-butyl-lithium or phenyl-thiol in xylene. The latter two producing some hydroxyamino-carborane as well. (172) The reduction of meta and para nitrophenyl-o-, m-carborane with tin and hydrochloric acid gives a mixture of the amino-phenyl-o-, m-carboranes. (180,181)

Amines where the amino group is separated from the cage can be formed by other methods than cyanide reduction, the reaction of C-halomethyl o-carborane with diethylamine in benzene being an example, (173,174) and by this weakbase method even fluoromethyl-o-carborane undergoes nucleophilic attack.

$$H\theta CH_2X \; + \; (Et)_2NH \; \xrightarrow[C_6H_6]{20^o} \; \underset{70\text{–}75\%}{H\theta CH_2N(Et)_2} \; + \; H\theta CH_2{}^{-}\overset{+}{N}H(Et)_2$$

$X = Cl, Br, I$

Weaker bases than diethylamine are not strong enough nucleophiles to replace the halogen; stronger bases lead entirely to cage degradation, Whilst use of di-methyl-amine as a reagent leads to cage degradation, but the di-methyl-aminomethyl-o-carborane can be prepared by the reaction of di-methyl-(chloromethyl) amine with lithio-o-carboranes or by the reduction of di-methyl amide by aluminium chloro-hydride. Lithium aluminium hydride leads to C-C cleavage. (175) Some interesting cyclic amines have been produced in reactions between 1-halomethyl,2-sodio-o-carborane and Schiffs bases in liquid ammonia. (201)

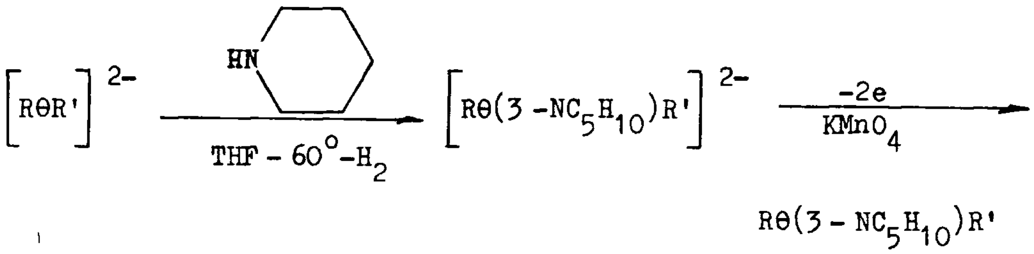


$R = Ph, \; 2\text{-}C_4H_5O; \quad X = Cl, Br$

B-amino carboranes have received much more attention than the C-amino-derivatives. They have been prepared in high yields by the action of sodium in liquid ammonia. (176,177,178)

$$R\theta R' \xrightarrow[liqNH_3]{2Na} \left[R\theta R'\right]^{2-} \xrightarrow{liq\,NH_3} \left[R\theta(3\text{-}NH_2)R'\right]^{2-} \xrightarrow[KMnO_4]{-2e} R\theta(3\text{-}NH_2)R'$$

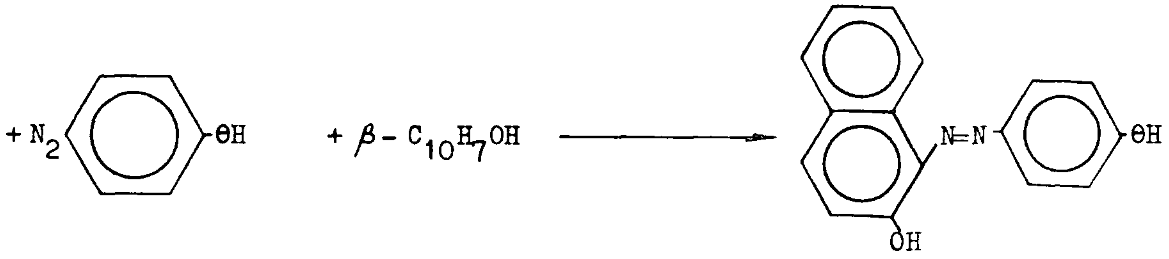
Only o-carborane derivatives can be prepared by this means, as the use of m-carborane gives o-carborane derivatives. (See section 1). Substantial 1, 2-position substituent effects are noted for the reaction, electron-releasing groups speeding-up the reaction, bulky groups slowing it down, such as in di-phenyl-o-carborane which is unreactive. (177) 9-Halo-o-carboranes are dehalogenated by the above reaction and isopropenyl-o-carboranes hydrogenated. 1,2-bis-(o-carboranyl) ethane and 1,2-bis-(o-carboranyl) benzene can also be aminated in liquid ammonia at the 3-position, both cages being substituted. (182) In some cases secondary amines will react with the carboranyl anion in THF. (111)



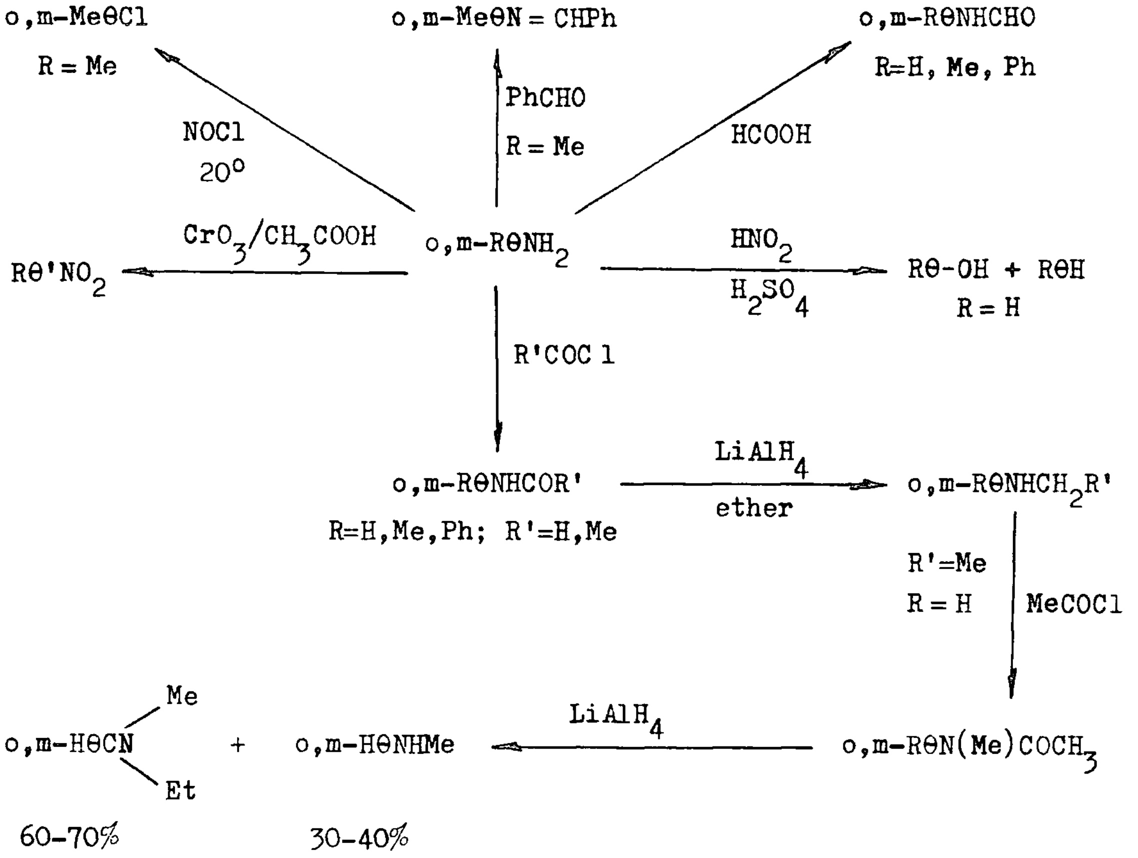
3-position amines can also be synthesised from B-amides by the Hoffmann rearrangement or from B-acyl-chlorides or B-carboxylic acids by the Curtius and Schmidt rearrangements respectively. (78) (See section 6.)

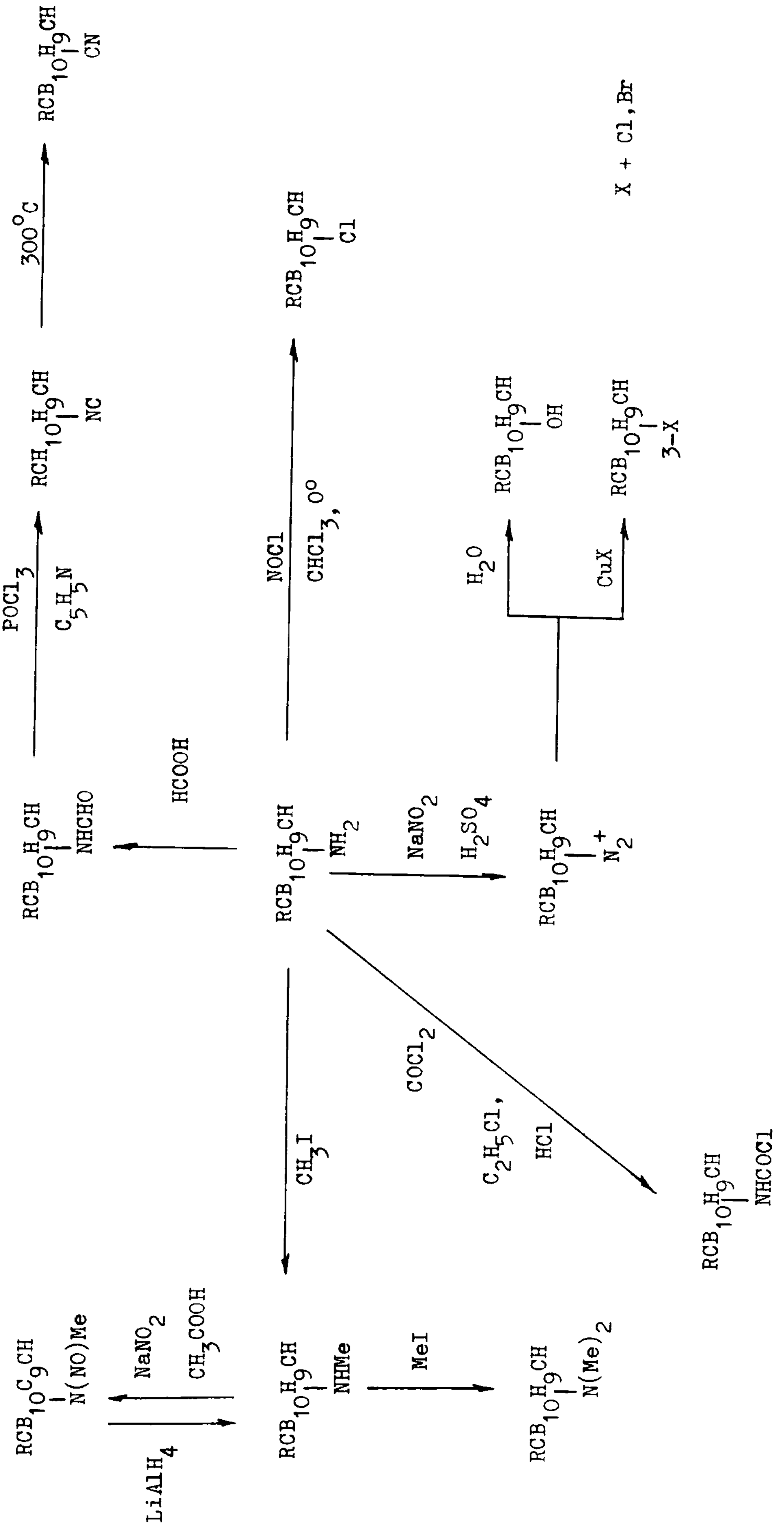
Reactions of Amino Derivatives

C-amino o-carboranes are very weak bases, soluble in concentrated sulphuric acid but not in dilute. (170,171,180,181) Amines such as m-aminophenyl-o-carborane can be oxidised to the nitrophenyl derivative by the action of 90% hydrogen peroxide and trifluoracetic acid. (180) Phenyl amines are easily di-azotised by nitrosyl sulphuric acid in glacial acetic acid. The salts react normally with potassium iodide, copper chloride and bromide, giving iodo-, chloro- and bromo-substituted phenyl carboranes. Azo combination has been observed with β-naphthol in alkaline medium. (181)

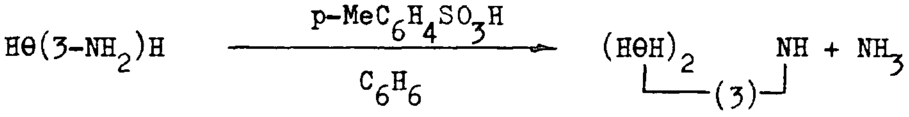


The reactions of C-amino-carboranes have not been explored as fully as the B-aminos have. The reactions of the C-amines and B-amino-carboranes are summarised on the following pages. (172,177,178,183,184)




RCB10H9CH NHCHO
HCOOH
POCl3
C5H5N
RCH10H9CH NC
300°C
RCB10H9CH CN
NOCl
CHCl3, 0°
RCB10H9CH Cl
RCB10H9CH NH2
NaNO2
H2SO4
RCB10H9CH N2+
H2O
CuX
RCB10H9CH OH
RCB10H9CH 3-X
X + Cl,Br
CH3I
COCl2
C2H5Cl,
HCl
RCB10H9CH NHCOCl
RCB10C9CH N(NO)Me
NaNO2
CH3COOH
LiAlH4
RCB10H9CH NHMe
MeI
RCB10H9CH N(Me)2

More recently, 3-amino-o-carborane has been shown to undergo coupling reactions in benzene with a catalytic amount of p-toluene sulphonic acid. (186)

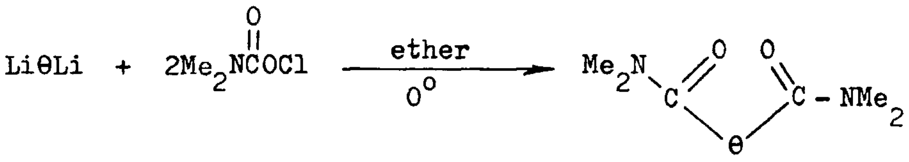


$$H\theta(3\text{-}NH_2)H \xrightarrow[C_6H_6]{p\text{-}MeC_6H_4SO_3H} \underbrace{(H\theta H)_2 \quad NH}_{(3)} + NH_3$$

Coupling also occurs with aniline in the presence of the same catalyst.(186)

Synthesis of Amides

C-carboranyl amides can be prepared by the direct combination of a carboranyl acid chloride with ammonia or an amine, (12,56,59,185) or by the reaction of bis-(acetonitrile) decaborane with acetylenic amides. Anilides can be formed by the reaction of phenyl isocyanate or isothiocyanate with lithio carboranes. (190) The reaction of di-lithio-o-carborane with N,N dimethyl-carbamoyl-chloride gives sterically hindered di-amide. (193)



$$Li\theta Li + 2Me_2N\overset{O}{\overset{\|}{C}}OCl \xrightarrow[0^o]{ether}$$

Ortho carboranyl amides are more stable towards C-C cleavage by sodium ethoxide in ethanol than the o-carboranyl esters and acyl-o-carboranes. The C-C bond in o-carboran-1-yl amides resist attack by cold sodium ethoxide and only the cage is degraded to the dicarbaundecaborate anion by boiling ethoxide in ethanol. (188) Cleavage of the C-C bond does occur with 1-phenyl-o-carboran-2-yl amide and ethoxide ion, although there is still some cage degradation. Separation of the amide group from the cage by CH_2 groups prevents alkoxide cleavage.

Lithium aluminium hydride cleaves amides directly bonded to the cage, and the interposition of CH_2 groups results only in hydrogenation. (169)

Cleavage of the C-C bond also occurs with sodium in liquid ammonia.(189)

Cyano Derivatives

Ortho-carboranyl C-cyano-derivatives were first prepared by the action of cyanogen chloride on lithio-o-carboranes in ether/benzene mixture. (167)

$$2\mathrm{Ph\theta Li} \xrightarrow{\mathrm{ClCN}} \underset{\sim 50\%}{\mathrm{Ph\theta Cl}} + \underset{\sim 50\%}{\mathrm{Ph\theta CN}}$$

The separation of the above mixture proved to be quite complex, however, an adaptation of an organic preparative route cyanides using aromatic cyanates and Grignard reagents or organolithiums leads to a more convenient synthesis. (191)

$$\text{o,m-}\mathrm{R\theta Li} + \mathrm{PhOCN} \xrightarrow[\text{ether/benzene}]{25^{\circ}} \text{o,m-}\mathrm{R\theta CN} + \mathrm{PhOLi}$$

$$\mathrm{R = Me, Ph}$$

Lithium aluminium hydride reduces the cyanide group to an amine whilst the action of water and iso-butyl aluminium hydride gives an aldehyde. (167) Alcohols cleave the cyanides to give a carboranyl anion, (167,191) which can form methyl pyridinium salts. The preparation of some fluoro-amino-cyanides was shown in section 4.

Cyanides separated from the cage by a CH_2 group can be prepared either by reaction of an alkyl carboranyl Grignard reagent with aromatic cyanates (19) or by reacting chlorocyano-methane with sodio carborane in liquid ammonia. (194) Cyanoethyl-o-carborane is prepared by the direct interaction of acrylonitrile on o-carborane in the presence of triton-B. (195)

B-substituted cyanides can be made by the pyrolysis of isocyanides or by heating B-iodo derivatives with copper (I) cyanide. (154)

Cyanates can be synthesised by the low-temperature (-10° to 0° C) condensation of carboranyl diols with cyanogen chloride in acetone solution. (192) Reaction of bis-(hydroxymethyl) -o,m-carborane with cyanogen chloride and triethylamine has yielded cyanate esters ($-CH_2OCN$ derivatives). (230) Cyanate esters are usually unstable or very difficult to make, the stability of the carboranyl esters is probably due to steric protection by the cage.

Nitrates and Related Derivatives

The action of 100% nitric acid on o-carborane or methyl-o-carboranes in carbon tetrachloride at room temperature leads to the formation of B-hydroxy and B-nitrate derivatives. The reaction is liable to detonate however, without warning. (89,196)(See section 7.) Attack is thought to occur at the 9(12) boron atom. Cold nitric acid attacks bis-(hydroxymethyl)-o-carborane to give the highly explosive C,C -dinitrate of o-carborane. (58) 1-phenyl-o-carborane reacts with 100% nitric acid or a nitric/sulphuric acid mixture to give a mixture of 1-(m-nitrophenyl) and 1-(p-nitrophenyl)-o-carboranes. (180,181,197) The mixed acid nitration of B-3-phenyl-o-carborane leads to the formation of 3-(o-,m- and p-nitrophenyl)-o-carborane. (198)

As mentioned earlier, 1-nitrophenyl-o-carborane can also be made by oxidation of 1-aminophenyl-o-carborane. Other nitrates have been synthesised from lithio carborane and p-nitrobenzoyl chloride. (61)

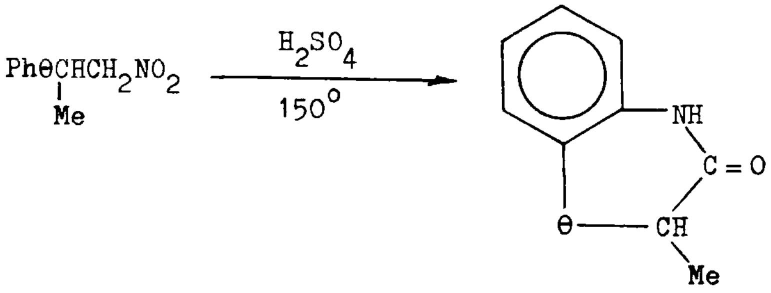
Nitroso-derivatives of o-carborane can be made from lithio-carboranes and nitrosyl chloride at about -100°C. These derivatives are easily hydrogenated. (180,183)

$$R\Theta Li \xrightarrow[-75 \text{ to } -125^{\circ}]{NOCl} R\Theta NO \qquad R = H,Me,Ph$$

Oxidation of C-amino-m-carborane with chromium trioxide in acetic acid gives the m-carboranyl nitroso-derivative. Further oxidation in this medium gives 1-nitro-m-carborane. (183)

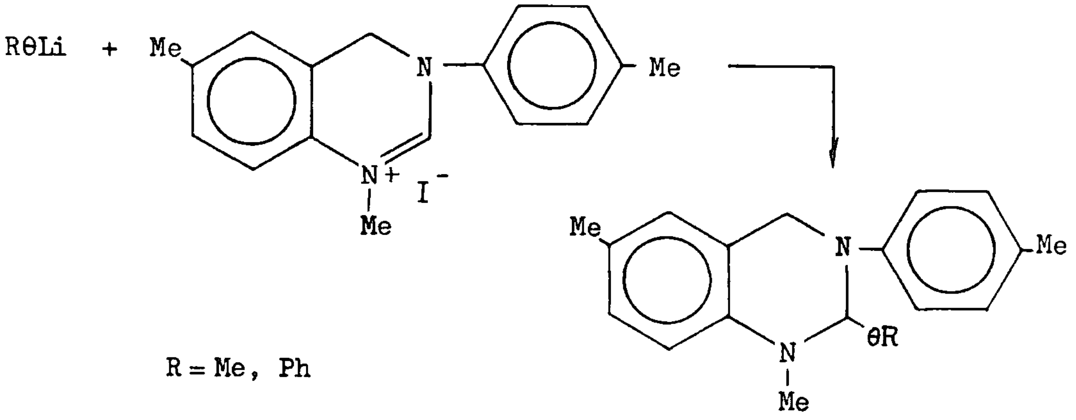
Some nitro derivatives have been made by the reaction of 1-lithio or 1-bromomagnesio,2-alkyl-o-carborane with unsaturated nitro alkenes via a 1,4 addition. Alkenes such as, 1-nitro-2-phenyl ethene have been used. (203)

The action of sulphuric acid on 1-methyl,2-(1-methyl-2-nitroethyl)-o-carborane gave previously unknown proprionic acid derivative. However, when 1-(1-methyl-2-nitroethyl),2-phenyl-o-carborane was heated to 150° in sulphuric acid, a cyclisation reaction occurred. (199)



Other Nitrogen Derivatives

The effect of lithio-carboranes on quaternary ammonium salts has been studied with a view to their use for neutron-absorption therapy of cancer. 1-Alkyl quinoline, 1-methyl pyridine, 9,10-di-hydroacridine and 1,2,3,4-tetra hydro-1,2-dimethyl-3-p-tolylquiazoline derivatives have been prepared by such reactions. (200,201)



Pyridyl-o-carborane alcohols have been synthesised from metallo carboranes and β and γ -pyridyl aldehydes. (84)

Tricarboranyl borazine compounds in which three o-carborane cages are bonded to an N-tri-methyl borazine ring can be prepared from lithio-o-carborane and N-tri-methyl-B-tri-chloro-borazine.

1.11 GROUP IV DERIVATIVES

Silicon Derivatives

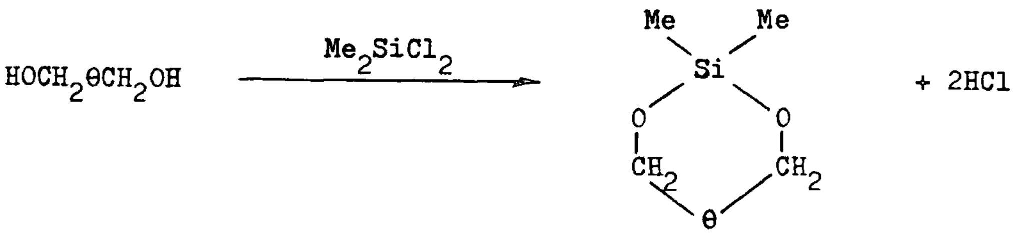
C-Silicon derivatives have been mainly prepared by the reaction of chlorosilyl-and alkyl-chlorosilyl compounds with lithio-carboranes (12,205,206,207,235) or carboranyl Grignard reagents. (208)

$$R\theta Li + R'_nSiCl_{4-n} \longrightarrow R\theta Si\begin{matrix} R'_n \\ Cl_{3-n}\end{matrix} + LiCl$$

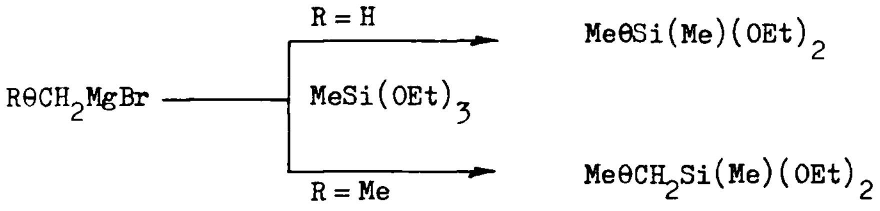
Two 1-lithio-o-carborane species can react with a dichloride or higher chloride of silicon. The reactions of dilithio-carboranes are the same, except that dialkyl-dichloromethyl silicon compounds can form exocyclic rings with dilithio-o-carborane. The formation of exocyclic rings is one of the main features of ortho-carboranyl silicon chemistry. Silyl-allyl-carboranes can be made by the reaction of 1-lithioallyl-o-carborane with trimethyl silicon chloride yielding only the trans-propenyl derivative, unlike other organic reagents. (60)

The hydrolysis of 1,2-bis-(chlorodimethylsilyl)-o-carborane with water, or treatment with an amine leads to the formation of five-membered exocyclic rings containing an oxygen or substituted nitrogen atom respectively. (205,209) Reaction of the same compound with dilithio-o-carborane or the reaction of dilithiated silicon coupled carboranes with other dichloro-silanes produces ring systems containing two o-carborane cages. (205,209)

Alkoxysilanes are made by the reaction of C-hydroxymethyl-carboranes with alkyl-chlorosilanes. (208) Again, the use of dichlorosilanes forms exocyclic rings.



Dilithio-o-carborane will break-up alkyl chlorosiloxane chains with the formation of five- and seven-membered rings. (68) Reactions of o-carboranyl methyl magnesium bromide with alkoxysilanes results in a rearrangement, which 1-methyl,2-bromomagnesiomethyl-o-carborane does not undergo. (208)



Diethoxy-methylsilane will, in the presence of platinised carbon, add across the double bond of carboranyl alkenes with the exception of vinyl carborane; trichloro-methylsilane will add across the vinyl group at elevated temperature. In all cases, the silicon adds onto the carbon atom furthest from the cage. (68,208)

One of the most convenient methods for preparing dialkoxysilyl-o- and m-carboranes is by the reaction of dilithio-o-,m-carborane with chloroethoxydialkylsilane. Early workers found that yields were only about 50%, and this was later shown to be due to the formation of oligomers, owing to the presence of lithium alkoxide. The use of hydrocarbon solvents alone suppressed lithium alkoxide formation and improved yields. (210) The formation of oligomers also reduces the yields of products from dilithio-o-carborane and dichloro-dialkyl silane. (211)

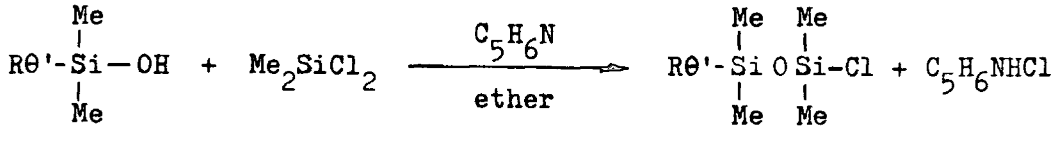
Alkyl-silyl-m-carboranes are prepared like the ortho derivatives by the reaction of alkyl-chlorosilanes with 1-lithio or 1,2-dilithio-m-carborane. (211,213)

The chlorosilanes of ortho-carborane are cleaved at the cage-silicon bond by the action of acid or alkali and they react with aliphatic alcohols to give alkoxides. (208) The meta-carborane derivatives also react to form silyl alkoxides with alcohols, but form silyl hydroxides with water as exocyclic ring formation is not possible with the meta species. (211,213) Whilst traces of alkoxide ions in the alcohols can cause some cage-silicon cleavage, stronger solutions of alkoxides cause total cleavage for which mechanisms have been proposed. (211 — 213) The action of hydroxide, heptafluoro-butoxide or poly dimethyl- siloxanolate ions in catalytic amounts on monosilyl-o-, m-carboranes can cause a rearrangement via an equilibrium reaction (215,216) to disilyl-o-carborane and m-carborane, depending on the cation. The equilibrium for o-carborane derivatives is displaced almost entirely towards the left, whereas the m-carborane derivatives lie towards the right. (216)

$$\text{o,m} - \mathrm{H\theta SiR_2R'} \xrightleftharpoons{\mathrm{KOH}} \mathrm{R'R_2Si\theta SiR_2R'} + \mathrm{H\theta H}$$

Hydrosilyl containing o- and m-carboranes may be chlorinated by the electrophilic attack of chlorine in a carbon tetrachloride with replacement of the Si-H bond by Si-Cl. (219)

Meta-carboranyl compounds containing one or more linked siloxy groups have been made by reacting hydroxysilanes with chlorosilanes or dichloro-tetramethyl-disiloxane with lithio carborane. Both are capable of further reaction with lithio carborane. (213)



$$\mathrm{R\theta'{-}Si(Me)_2{-}OH} + \mathrm{Me_2SiCl_2} \xrightarrow[\text{ether}]{\mathrm{C_5H_6N}} \mathrm{R\theta'{-}Si(Me)_2\,O\,Si(Me)_2{-}Cl} + \mathrm{C_5H_6NHCl}$$

Other siloxy compounds have bee prepared by using carboranyl lithoxysilanes in reactions with alkyl chlorosilanes. (214) Some methoxyalkyl-silyl-m-carboranes can be coupled by the action of water at 80°C. (214)

Boron-substituted silicon derivatives have resulted from the direct attack by chlorovinyl-silanes or alkyl-chlorovinylsilanes on ortho-, meta- or para-carborane in the presence of $AlCl_3$. (217,218)

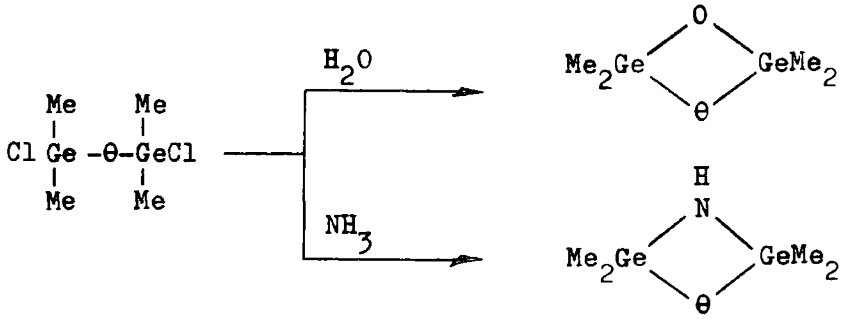
$$\text{o,m,p-}\underline{HCB_{10}H_{10}CH} + H_2C=CHSiCl_3 \xrightarrow[80-120^{\circ}]{AlCl_3} \underline{HCB_{10}H_{10-n}(CH_2CH_2SiCl_3)_nCH}$$

$$n = 1,2,3$$

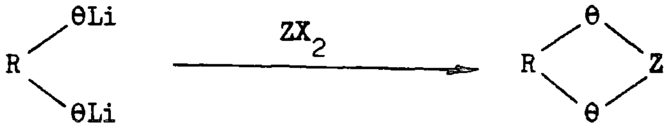
Most of the derivative chemistry of the silicon derivatives is aimed towards polymer formation due to the high thermal stability of silyl and siloxyl derivatives, indeed, many meta-carborane derivatives are prepared by the thermal isomerisation of ortho compounds. Further silicon chemistry will be found in section 15 relating to polymers.

Germanium, Tin and Lead Derivatives

The chemistry of the germanium and tin derivatives of ortho-carborane bears a striking similarity to that of the silicon derivatives; both elements can form exocyclic rings systems with o-carborane. Most of the derivatives are made by the reaction of mono- or di-lithio-o-carborane with alkyl metal chlorides. For example, the reaction of dimethyl-dichloro-germane with dilithio-o-carborane yields 1,2-bis-(dimethyl-chlorogermyl)-o-carborane, which on reaction with water or ammonia forms five-membered ring analogues of the silicon derivatives. (220)



Dialkyl-dichloro tin compounds form six-membered rings on reaction with dilithio-o-carborane. (220,221) Diphenyl-dichloro-tin cannot form such rings, owing to the steric hinderance of the phenyl rings. Other ring-forming reactions are given below.



$R = MeOCH$, $Z = SiMe_2$, $GeMe_2$, $SnMe_2$. (222,229)
$R = -CH_2CH_2-$, $Z = SiMe_2$, $GeMe_2$. (223)
$R = -CH_2$, $Z = SiMe_2$, $GeMe_2$, $SnMe_2$, $SnPh_2$.(224)
$R = SiMe_2$, $Z = GeMe_2$, $SnMe_2$. (228)
$R = GeMe_2$, $Z = SnMe_2$ (228), PPh (229)
$R = SnMe_2$, $Z = SnMe_2$. (220)

The structures of many of these have been resolved by X-ray studies. (229)

The reaction of tin (IV) chloride with 1-phenyl, 2-lithio-o-carborane gives both di- and tri-carboranyl tin chloride compounds. (207) The equivalent silicon and germanium reactions only produced the dicarboranyl compounds, the central metal atom not allowing tri-substitution on steric grounds. (207) X-ray studies on bis-(o-carboranyl)-dimethyl-germane have been made. (233)

Dilithio m- and p-carboranes react quite differently with dialkyl-dichloro group (IV) metals. Small exocyclic ring formation is not sterically possible, and so polymers tend to be formed. The use of a mixture of dilithio m- and p-carboranes leads to formation of co-polymers as does use of a mixture of dialkyl-dichloro-germanium and tin. The reaction of dimethyl-dichloro germane with dilithio-m-carborane gives 80% of polymeric material and 20% of 1,2-bis-(dimethyl-chloro-germyl)-o-carborane. The latter compound reacts with ammonia, as does the ortho analogue, but differs in that a carborane-metal-amino-bonded polymer is formed. (220) Polymers containing lead (68) and non-polymeric lead derivatives (230) have been synthesised in lesser amounts than the above metals, but nevertheless by analogous reactions.

PMR studies of the effect of cage substituents and solvent solvating power on the Sn-C-H and Pb-C-H coupling constants have been made. (230) Other studies have revealed that the influence of trimethyl C-bonded group (IV) elements on the cage boron chemical shifts is equal for all the borons and not position-dependent. (231)

Unlike the mercury-carborane Hg-C bond, the tin carborane Sn-C bond is susceptible to nucleophilic attack. The action of potassium hydroxide and water in benzene on bis-(1-phenyl-o-carboran-2-yl) tin dichloride gave a mixture of bis-(1-phenyl-o-carboran-2-yl) tin oxide and 1-phenyl-o-carborane in 62%:30% yields respectively. Treatment with ethanolic potassium hydroxide gave the parent carborane in quantitative yields. Sn-C and Ge-C bonds are cleaved by basic alumina, whilst Si-C bonds resist attack. (232)

Ge-B bonded compounds have been prepared by the reaction of germanium chloride and o,m-bis-(carboran-9-yl)-mercury. (246)

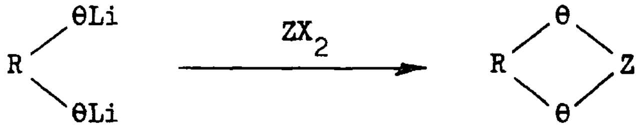
Further derivatives of group (IV) elements in which they form part of the icosahedral cage are discussed in section 16.

1.12 GROUP V DERIVATIVES

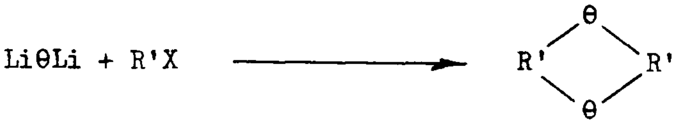
The chemistry of the nitrogen-containing carboranes has been discussed in section 10.

In many ways, the chemistry of phosphorus and arsenic derivatives closely parallels that of the group (IV) elements. Monochloro-dialkyl-phosphorus compounds react smoothly with mono- or dilithio-o-carborane to give mono- and di-substituted dialkylphosphino-o-carborane. (207,234-238) Identical reactions are noted for arsenic. (239,240)

As with silicon and germanium, 5-membered exocyclic rings can be formed by the reaction of dilithio-o-carborane with dichloro-phosphines followed by treatment with ammonia. Arsenic, like tin, cannot form such rings with two carboranes on steric grounds. Some of these reactions are summarised below with phosphorus cyclisation reactions.

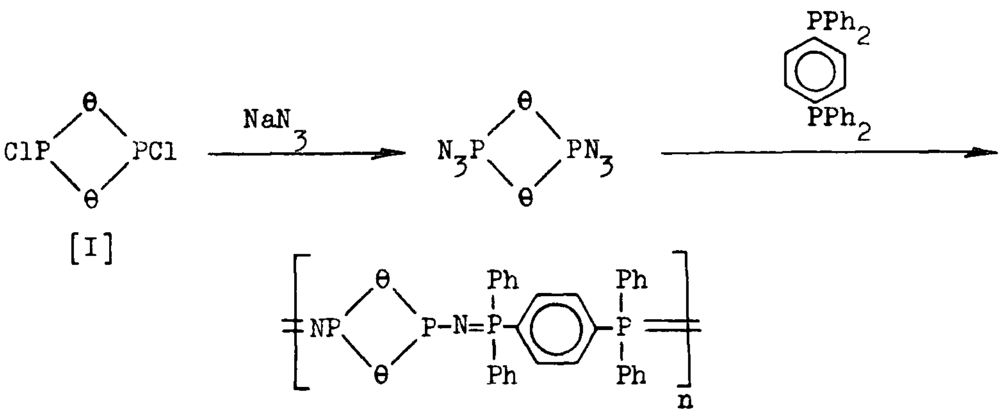


R = -	Z=PPh, X=Cl; Z=AsMe, X=I.	(223)
R = $GeMe_2$	Z=PPh, X=Cl.	(229)
R = MeOCH	Z=PPh, X=Cl; Z=AsMe, X=I	(222)
R = $SiMe_2$, $GeMe_2$	Z=PPh, X=Cl; Z=AsMe, X=I	(228)
R = CH_2	Z=PPh, PMe; X=Cl; Z=AsMe, X=I	(224)
R = $-CH_2CH_2-$	Z=AsMe X=I	(223)



R' = PCl, X=Cl_2 (234).	R' = AsMe, X=Br_2 (240)
R' = PF, X=FBr (248).	R' = PPh, X=Cl_2 (234)

Some of the phosphorus cyclic compounds can be polymerised. (234)



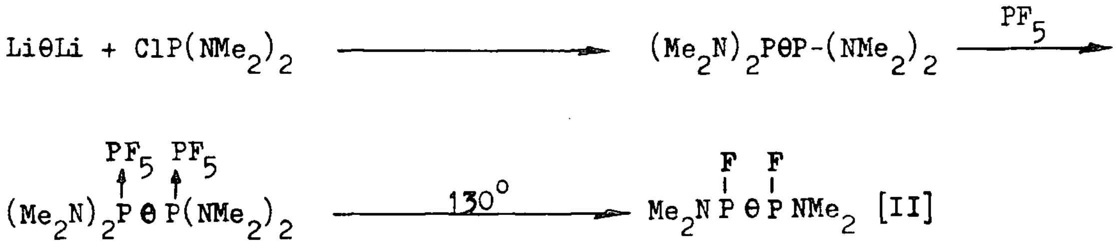
[I]

M.Wt 2,400 - 10,000

Treatment of [I] with ammonia yields a phosphine amino derivative, (234) whilst treatment with lithium aluminium hydride reduces the P-Cl bonds. (241) Bis-(phenyl-chlorophosphino)-o-carborane forms an unstable di-azide on treatment with sodium azide, which readily polymerises at 40°C with loss of nitrogen.

Early reviews (68,242) suggested that the small size of the phosphorus atom did not allow more than two carborane cages to bond to it, however, the work of Zakharkin et al (236) has shown that prolonged heating of 1-phenyl, 2-lithio-o-carborane with phosphorus oxychloride can force three cages around a central phosphorus-forming tri-(1-phenyl-o-carboran-2-yl)-phosphorus oxide.

Dimethylamino-phosphino-o-carborane has been synthesised from dilithio-o-carborane and bis-(dimethylamino)-chlorophosphine. Addition of a fourfold excess of PF_5 to the product produced an adduct which on heating gave bis-[(dimethylamino) fluorophosphino]-o-carborane. [II](248)



$$LiΘLi + ClP(NMe_2)_2 \longrightarrow (Me_2N)_2PΘP\text{-}(NMe_2)_2 \xrightarrow{PF_5}$$

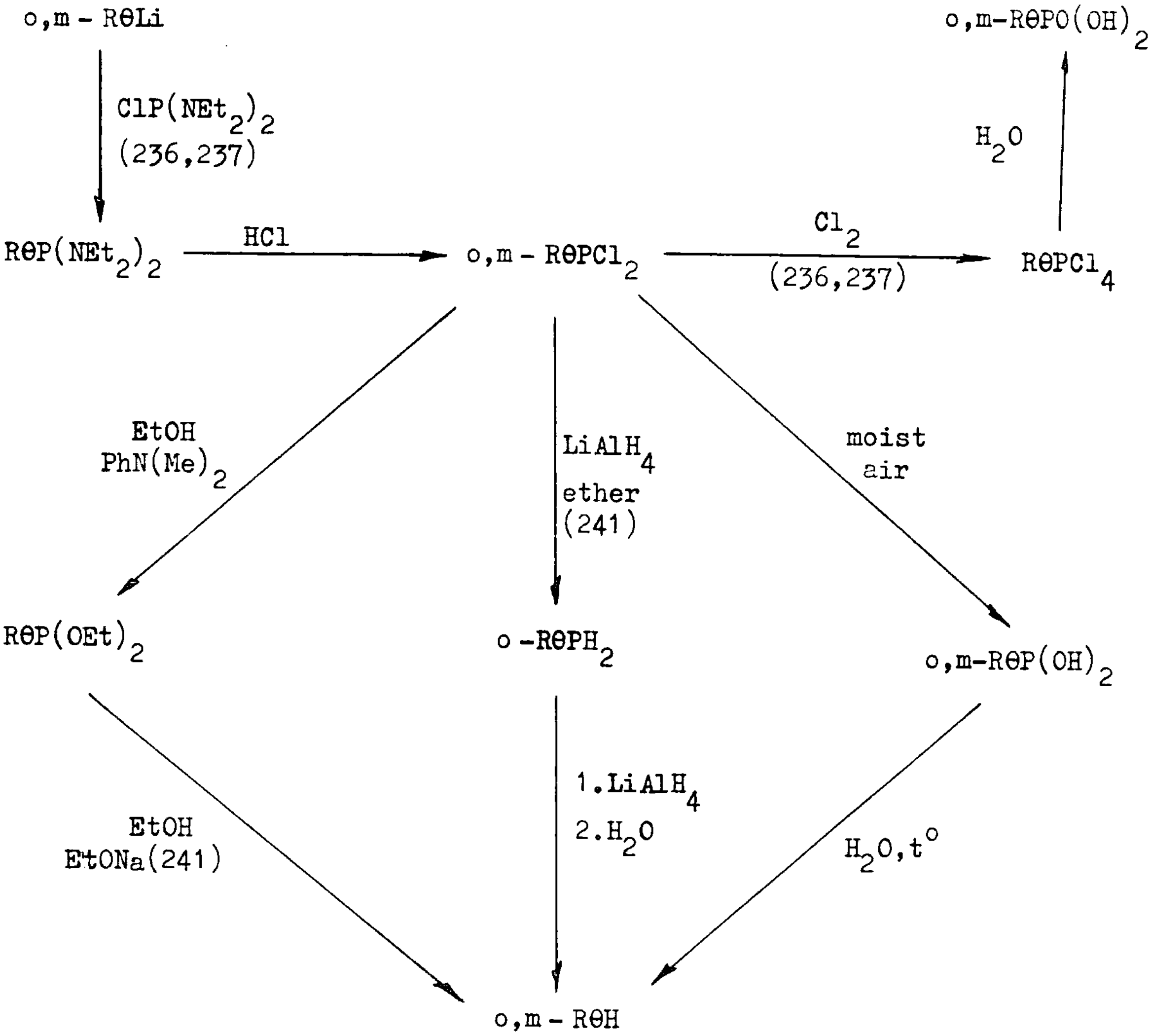
$$(Me_2N)_2\overset{PF_5}{\overset{\uparrow}{P}}\,Θ\,\overset{PF_5}{\overset{\uparrow}{P}}(NMe_2)_2 \xrightarrow{130^{\circ}} Me_2N\overset{F}{\overset{|}{P}}\,Θ\,\overset{F}{\overset{|}{P}}NMe_2 \quad [II]$$

Addition of further PF_5 to compound [II]produced only a PF_6^- adduct and not replacement of the other dimethylamino-group. (248) The equivalent arsenic and antimony reactions all yield tricarboranyl species. (207) The reactions of some carboranyl phosphines are summarised on the following page with references.

Phenyl-chlorophosphino, diphenylphosphino and 1-(diphenylphosphino), 2-methyl-o-carboranes all react with sulphur upon heating to give P-S derivatives with a pentavalent phosphorus atom. (238,241) Diphenylphosphino-o-carboranes can be oxidised to o-carboranyl phosphine oxides by chromium trioxide in acetic acid. (239) Trivalent chlorophosphines are hydrolised by moist air to phosphorous acids, whilst pentavalent tetrachlorophosphines are hydrolysed to phosphonic acids. (236,237) The P-Cl bonds can be reduced by $LiAlH_4$ tc phosphines and in the case of di-(1-isopropenyl)-o-carboran-2-yl) phosphorus chloride, without effecting the carbon-carbon double bond, (241) however excess reducing agent can cleave the cage-P bond. Bis-(phenyl-o-carboranyl) phosphorus chloride is unaffected by $LiAlH_4$.

As with carboranyl esters, carboranyl-phosphorus esters are cleaved at the cage by catalytic amounts of alkoxide ion. (241)

Bis-phosphino and bis-arsino derivatives of o-carborane readily form complexes with transition metals. Nickel (II) chloride combines with bis-(diphenylphosphino)-o-carborane in methanol or ethyl acetate at room temperature to give a 1:1, nickel:phosphino-carborane complex. (243) On heating, the complex gives a 1:2 compound which is diamagnetic. This, electronic, spectral and conductance data suggests a square planar configuration. (243) Other 1:1 complexes of nickel and iron can be prepared from the respective metal carbonyls whilst a palladium complex can be prepared by reacting dibenzonitrile palladium (IV) chloride with bis-(diphenylphosphino)-o-carborane (244) or its B-halo derivatives. (245) Bis-(dimethylarsino)-o-carborane reacts with nickel, iron and molybdenum


o,m - RθLi
ClP(NEt$_2$)$_2$
(236,237)
RθP(NEt$_2$)$_2$
HCl
o,m - RθPCl$_2$
Cl$_2$
(236,237)
RθPCl$_4$
H$_2$O
o,m-RθPO(OH)$_2$
EtOH
PhN(Me)$_2$
LiAlH$_4$
ether
(241)
moist
air
RθP(OEt)$_2$
o -RθPH$_2$
o,m-RθP(OH)$_2$
EtOH
EtONa(241)
1.LiAlH$_4$
2.H$_2$O
H$_2$O,t°
o,m - RθH

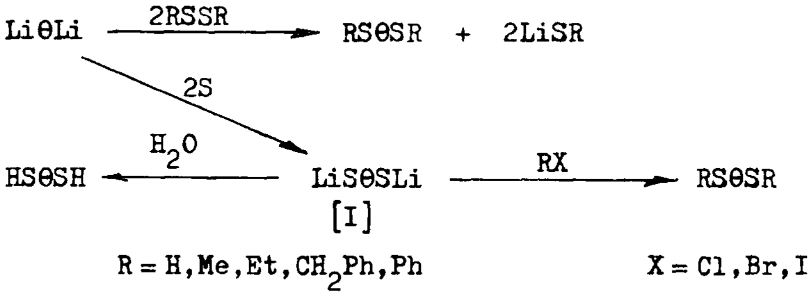
carbonyls to form 1:1 complexes with the loss of two moles of carbon monoxide. (240) Bis-(diphenylarsino)-o-carborane forms complexes with palladium (II) chloride and iodide. (239)

Derivatives of ortho- and meta-carborane containing B-group(V)element bonds have been prepared from o- or m-bis-(9-carboranyl) mercury on reaction with phosphorus, arsenic or antimony trichlorides in dichloroethane or benzene. (246,247) Treatment of the 9-B-arsenic and antimony compounds with bromine gave 9-bromo-o- and m-carboranes. (247)

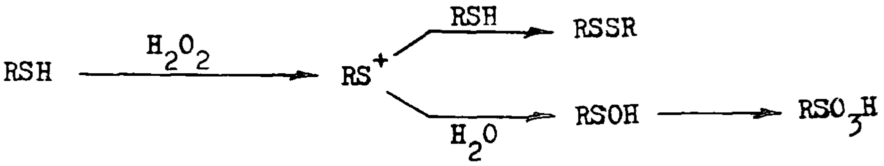
An interesting class of icosahedral carboranes has been discovered in which group(V)elements replace one carbon atom in the icosahedron. These will be discussed in section 16.

1.13 GROUP VI DERIVATIVES

Sulphur derivatives of the carboranes can be prepared by the action of organic disulphides on dilithio-o-, m-carboranes. Alternatively, treatment of the dilithio-carboranes by sulphur followed by alkyl halides or water gives bis-(thioether) and bis-thiol derivatives respectively. (249) The reaction of lithio-o-carboranes with stoichiometric amounts of carbon disulphide at 0° C gives interesting dithiocarboxylato- (-CSSLi) o-carboranyl derivatives capable of co-ordinating with transition metals. (282) (See section 14)



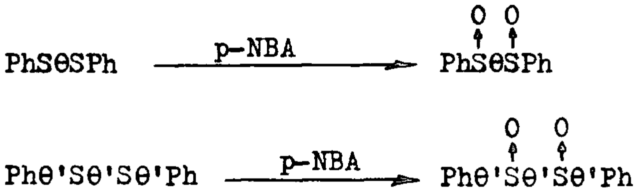
Mono- or bis-C-thiol carboranes can both be prepared by the action of sulphur on lithio- sodio-or potassio-carboranes in liquid ammonia, followed by acid hydrolysis. The reaction of methyl iodide with the resulting liquid ammonia solution of carboranyl lithio sulphides [I] yields thio ethers, whilst iodine causes the formation of dicarboranyl disulphides. (250,251) Oxidation of monothiol o-, m-carboranes by hydrogen peroxide in acetic acid yields a mixture of disulphides and sulphonic acids, showing that the oxidation goes via an RS^+ intermediate. (251)



The same reaction performed on 1-phenyl-o-carboran-2-yl methyl sulphide leads to the complete cleavage of the cage to boric acid, (250) although in formic acid no reaction was noted. (253) In contrast, m-, p-carboranyl methyl sulphides form sulphones. (252,253)

$$\text{m,p-R}\theta\text{SMe} \xrightarrow[CH_3COOH]{H_2O_2} \text{R}\theta\text{SO}_2\text{Me}$$

Ortho-carboranyl bis-(phenylthioether) is oxidised by p-nitrobenzoic acid to a bis-sulphoxide, whilst the meta and para ethers give sulphones. Meta-carboranyl sulphoxides can be formed from di- and tri-(carboranyl) thioethers. (253)



$$\text{PhS}\theta\text{SPh} \xrightarrow{\text{p-NBA}} \text{Ph}\overset{O}{\overset{\uparrow}{S}}\theta\overset{O}{\overset{\uparrow}{S}}\text{Ph}$$

$$\text{Ph}\theta\text{'S}\theta\text{'S}\theta\text{'Ph} \xrightarrow{\text{p-NBA}} \text{Ph}\theta\text{'}\overset{O}{\overset{\uparrow}{S}}\theta\text{'}\overset{O}{\overset{\uparrow}{S}}\theta\text{'Ph}$$

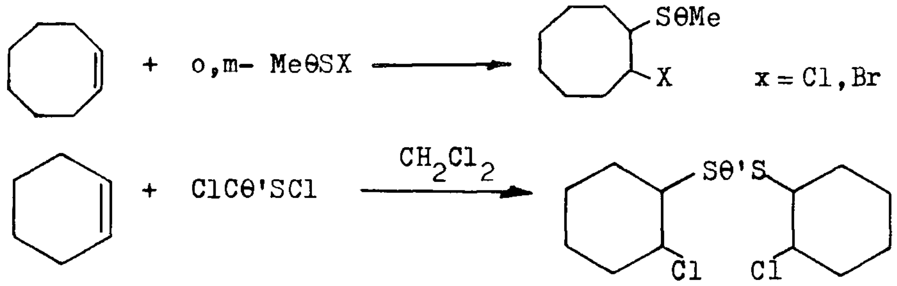
Ortho- and meta-carboranyl sulphinic acids can be prepared by reacting sulphur dioxide with lithio-carboranes (250-252) or carboranyl Grignard reagents. (252)

$$\text{o,m - R}\theta\text{Li} + SO_2 \xrightarrow{H_2O/H^+} \text{R}\theta\text{SO}_2\text{H}$$

Both ortho and meta acids are readily oxidised in aqueous solution by potassium permanganate to the respective sulphonic acids. (251,252) The sulphinic acids form sulphonyl halides on treatment with chlorine or bromine. Reaction with aniline gives anilides. (251,252) n-Butyl lithium does not cleave o- and m-carboranyl thiols but forms lithiosulphides which on heating in benzene at 80° generate 1-lithio-o- and m-carboranes. (251)

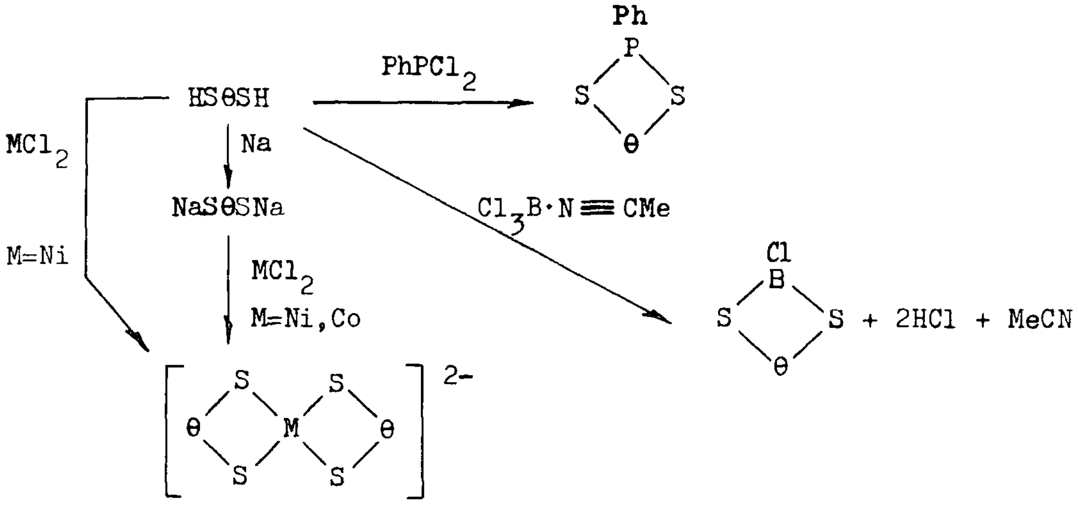
The action of chlorine or bromine on o-,m-, or p-carboranyl thiols produces sulphenyl halides. (251,254) The presence of aluminium oxide in a solution of the o- and m-carboranyl sulphenyl chlorides and bromides produces disulphides, although on standing the crystalline chloride slowly reverts by itself to the disulphide. (251) The S-S bond in the disulphide is very resistant to attack by hot acid, hydrogen peroxide or halogens, due either to the strong electron-withdrawal of the carboranyl cage or steric effects. (251) Meta- and para-carboranyl sulphenyl chlorides are oxidised to sulphonyl halides by aqueous sodium hypochlorite. (254)

One interesting feature of the chloro- and bromo-sulphenyl halides is their ability to add across olefinic double bonds as in cyclo-octene, 1,4-cyclo-octodiene (251), 1,3-cyclo-octadiene, and cyclohexene. (254)

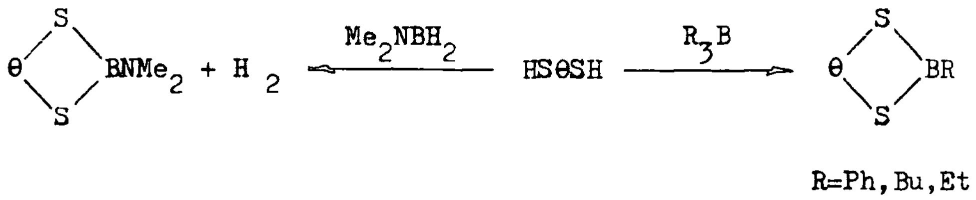


Carboranyl sulphenyl chlorides are susceptible to attack by nucleophiles such as cyanide ion, ammonia, and ethanol (in the presence of trimethylamine) with the replacement of the sulphur bonded chlorine by CN, NH_2, and OEt respectively. (254)

1,2-bis-(thiol)-o-carborane can form five-membered exocyclic rings by reaction with dichlorides of phosphorus (249,255), boron (255), nickel and cobalt (249,256,257) or boron hydrides and boron alkyls. (255)

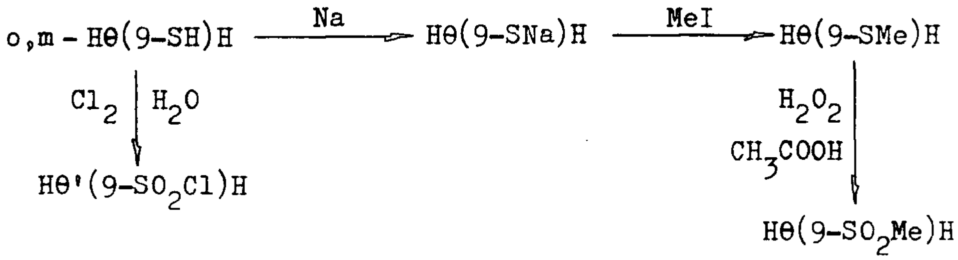


square planar



The boron-sulphur exocyclic rings are readily hydrolysed in air to a carboranyl bis-thiol and boric acid. Boron trichloride only forms such ring systems in the presence of acetonitrile.

Cage boron bonded sulphur derivatives have only been prepared in recent years, the thiol derivatives of o-,m- and p-carboranes being synthesised by the reaction of sulphur on the parent carboranes in the presence of aluminium trichloride at about 130° C. The reaction also forms an appreciable amount of disulphide which can be reduced to the thiol by zinc dust in acetic acid. (258) The attack is electrophilic with the 9-position hydrogen atom being substituted by SH in o- and m-carboranes. The B-thiols can be oxidised to B-sulphonic acids by hydrogen peroxide in acetic acid. (259) On reaction with iodine in ethanol they form disulphides. These sulphides, in contrast to C-bonded disulphides, are also oxidised by hydrogen peroxide on acetic acid to B-sulphonic acids. (259) They form sodiosulphides with sodium, which can be converted to thioethers with alkyl halide, the oxidation of which gives sulphones. Chlorine in water converts the thiols to sulphonyl chlorides. (259)



1.14 SIGMA-BONDED TRANSITION METAL DERIVATIVES

Mercury Derivatives

A large number of mercury derivatives have been prepared owing partly to the difference in their chemistry from that of organo-mercury compounds. C-carboranyl mercury compounds are formed by the reaction of mercury halides with lithio-o-,m-carboranes. The reaction of 1-lithio-o-,m-carboranes with mercury (II) chloride gives a good yield of a symmetric bis-(carboranyl) derivative. (235,207,260-262,264)

$$o,m - 2R\theta Li + HgX_2 \longrightarrow o,m - R\theta - Hg - \theta R$$

$$X = Cl,Br \qquad R = H,Me,Ph,CH_2 = CH$$

The use of an organo-mercury halide leads only to a mono-carboranyl species. In the reaction of phenyl mercury chloride with 1-lithio,7-phenyl-m-carborane, a small amount of bis-(phenyl-m-carboran-1-yl)-mercury and diphenyl mercury is also formed due to an exchange reaction. (261)

$$Ph\theta'Li + PhHgCl \longrightarrow \underset{[I]}{Ph\theta'HgCl} + PhLi$$

Mixed bis-(carboranyl)-mercury compounds can be made by the reactions of phenyl-m-carboranyl-mercury chloride [I] and phenyl-lithio-o-carborane. Methyl-m-carboranyl-mercury bromide undergoes a similar reaction. (261) The action ofnaphthalene anion-radicals on o-carboranyl-mercury chloride derivatives forms bis-(o-carboranyl)-mercury in near quantitative yield. (270,271)

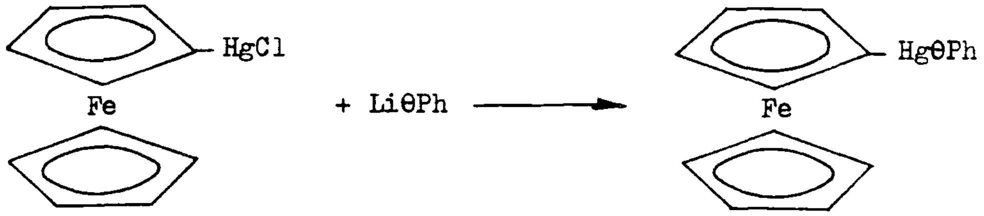
Direct mercuration of o-carborane has been accomplished by the use of organo-mercury hydroxides, the reaction taking place more readily with B-halo-o-carboranes. (263)

Ortho and meta-carboranyl asymmetric mercury compounds are susceptible to electrophilic attack by agents such as HCl in alcohol, mercury (II) chloride, and bromine, (260,261,264) or chlorine. (271)

Chlorine gas causes Hg-C cleavage of (1-phenyl-o-carboranyl)-ethyl-mercury in near quantitative yield. (271) Bis-(phenyl-o-carboranyl)-mercury is practically inert to prolonged boiling with HCl in ethanol, (260) whilst bis-(methyl-m-carboranyl) or bis-(phenyl-m-carboranyl)-mercury are slowly cleaved to give the parent carborane and m-carboranyl mercury chloride. (261) The same compound does not react with bromine in refluxing solvent, (264) but does react with dimethyl mercury to give methyl-(phenyl-m-carboranyl) mercury in 70% yield. (267) The cage-Hg bonds are also cleaved by lithium aluminium hydride, n-butyl lithium, or lithium in 1,2-dimethoxyethane. (267)

Studies of the preparation and properties of B-decachloro-o-carboranyl-mercury compounds have been made. (265) They are prepared by either direct mercuration of the B-decachloro-o-carborane by organo-mercury hydroxides or acetates of mercury, or by the reaction of sodio-carboranes with methyl-mercury bromide. Di-(o-carboranyl)-mercurys are made in the same manner as above. The greater electron-withdrawal of the decachloro-o-carborane is shown by the cleavage of the cage-Hg bond of (1-methyl B-decachloro-o-carboranyl) methyl mercury by bromine in benzene compared with the normal Hg-C cleavage.

Ferrocene derivatives have been prepared by the reaction between 1-phenyl,2-lithio-o-carborane and ferrocenyl-mercury chloride. (264)



The reaction of 1-lithioallyl-o-carborane with mercury (II) chloride gives, as does trimethylchlorosilane, only the trans propenyl derivative. (60) Complexes of carboranyl mercurys with o-phenanthroline have been reported. (277)

Boron-mercury derivatives of o- and m-carborane have been synthesised by the reaction of mercury trifluoroacetate in trifluoroacetic acid on the parent carboranes. (268,269) This method is capable of giving up to penta-mercuric substitution by successive electrophilic attack. The carboran-9-yl mercury trifluoroacetate formed by the reaction can be converted to the 9-mercury chloride or iodide by aqueous sodium halide in acetone, or can be brominated by bromine in carbon tetrachloride. (268,272) The action of methyl magnesium iodide on the 9-mercury chloride derivative gives 9-methylmercury, whilst HCl in ethanol regenerates the chloride and methane is evolved. (269) The trifluoroacetate can be converted to bis-(carboran-9-yl)-mercury by naphthalene anion-radical, cadmium amalgam in acetone, (272) lithium aluminium hydride, (112) or by heating 9-ethyl mercury at 1 mm Hg at 100°. (272) These B-symmetric compounds are not as stable to heat or attack by electrophiles (272) as the C-symmetric derivatives. Boron-mercury compounds have been used to prepare B-organic derivatives as mentioned in previous sections.

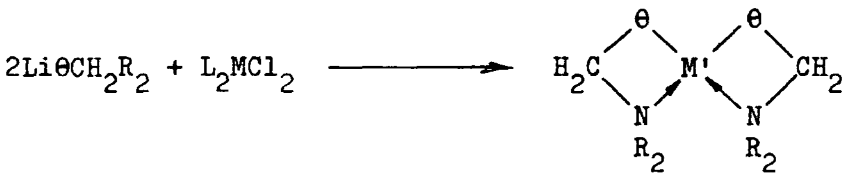
Investigations of C-methyl-mercury derivatives of o-, m- and p-carboranes by PMR methods have shown a dependence of spin-spin interaction constants $J\,^{199}\text{Hg-C-}^{1}\text{H}$ on the nature of the other C-carboranyl C-substituent and the solvent. (273)

A number of derivatives have been reported where a carborane cage is σ-bonded to a transition metal compound. In general, these compounds are prepared by the reaction of a halo transition metal and its bonded ligands with a C-metallo carborane or by reaction of a chloro carborane derivative with an alkali metal-transition metal derivative. The former is the more common and examples of this route exist for Fe (274,279,286), Pd (275,276, 278,288), Pt (276,278,280*,288*), Ti (262), Cu (276), Mn (279, Au (281), Rh (287*)

* (Both ortho and meta-carborane derivatives reported)

A number of co-ordination compounds of dilithio-o-carborane and transition metals have also been reported; Ni (283,285), Cu (283,285), Co (283,285), Zn (283).

The Cu^{II}, Ni^{II}, and Co^{I} anionic complexes were shown to be remarkably stable and have a square planar configuration about the metal atom with a carborane cage at each corner. (283) Other transition metal derivatives with two separate carborane cages bonded to a transition have also been prepared, Ti (262), Pt (276,284), Pd, Cu (276). 1-lithio, 2-methyl-o-carborane reacts with cis-dichloroplatino-phosphines to give a dimethyl-o-carboranyl-diphosphino-platinum species. (284) Some interesting co-ordination complexes have recently been prepared by the reaction of 1-lithio,2-N,N-diethylaminomethyl-o-carborane and 1-lithio,2-N,N-dimethylaminomethyl-o-carborane with copper, palladium and platinum chlorides. (276)

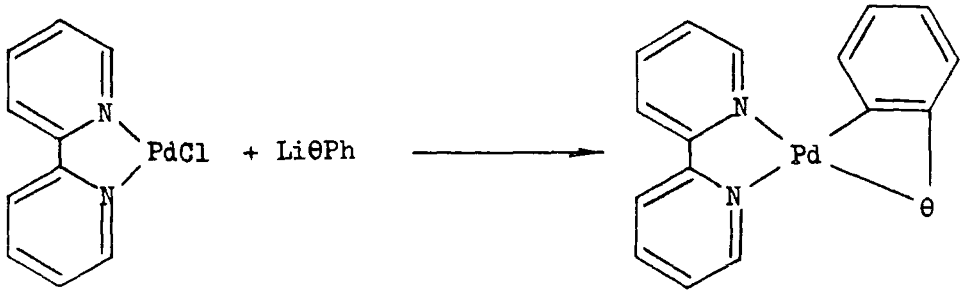


M = Pd, M' = Pd, Li = Ph, R = Et cis & trans isomers
M = Pt, M' = Pt(PhCN), L = PhCN, R = Et. cis isomers only

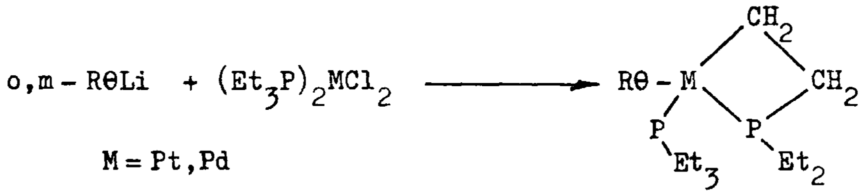
The reaction with CuCl only gives a dicarborane trans product when R = Me. (276)

Di-(triphenylphosphino)-platinum and palladium dichlorides react with dilithio-o-carborane to form an unusual three membered ring with the metal atom bridging the two carboranyl carbons. (278)

Whereas for most of the above reactions, the ligands are usually tri-organo phosphines, carbonyl groups, π-cyclopentadienes or mixtures thereof, a palladium complex using 2,2-bipyridinyl-palladium dichloride as a starting material has been made by a ring-closure procedure. (275)



Another cyclisation reaction has been reported. (288,289)



M = Pt,Pd

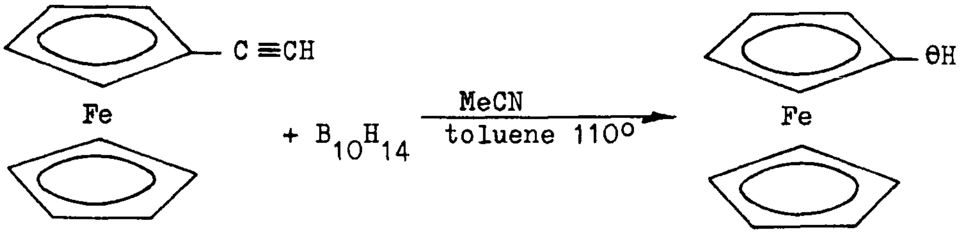
Another method of preparing cage-transition metal σ-bonded compounds is by reacting carboranyl acyl chlorides with alkali metal transition metal compounds. Fe (290,291), and Re (292)

$$\begin{tikzcd} R\text{-}\theta'COCl \ + \ NaFe(CO)_2\pi\text{-}Cp \arrow[r] & R\theta'COFe(CO)_2\pi\text{-}Cp \arrow[dl, "t^{o}"] \\ CO + R\theta'Fe(CO)_2\pi\text{-}Cp & \end{tikzcd}$$

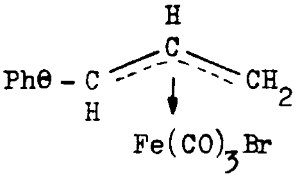
The o-carboranyl iron derivative rearranges to give a C-cyclopentadienyl-iron tricarbonyl compound for which considerable derivative chemistry has been reported. (290) The same reaction scheme has been used to prepare stable o-carboran-3-yl-iron (292,300) and rhenium (293) derivatives from o-carboran-3-yl acyl chlorides. 9-Position platinum compounds can be prepared by the reaction of m-carboran-9-yl-mercury chloride and triphosphinoplatinum in benzene forming 9-platino-diphosphino chloride. Similar reaction occurs with C-HgCl derivatives giving C-HgP-L_2Br compounds. (301)

Some dicarboranyl iridium compounds can be synthesised by an addition reaction between 1-ethynyl-o-carborane and chlorodi-(triphenylphosphino)-iridium carbonyl. The product contains a carboranyl acetylide and a carboanyl vinyl substituent. (296) Some iridium compounds react with C-phosphino-o-carboranes with oxidative addition across a B-H bond. (302,303)

Some transition metal compounds have been prepared in which the carborane cage is σ-bonded to transition metal σ-bonded compound. For example, σ-bonded ferrocene derivatives are synthesised by either the following reaction;



or by the action of a chloromethyl ferrocene on a lithio-carborane. (294) Oxidation and reduction potentials of both of these compounds have been reported. (294) A π - allyl complex is formed on the reaction of 1-phenyl, 2-(3-bromoprop-1-enyl)-o-carborane with diiron mono-carbonyl giving compound [I].

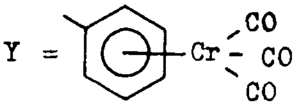


[I]

A diene co-ordination complex is formed with carboranyl-1,3-butadiene and iron pentacarbonyl. (295)

The reaction of chromium hexacarbonyl with aryl-o-,m-carboranes produces carboranyl aryl π-chromium tricarbonyl compounds in low yields. (297)

$$o,m - PhCH_2\theta CH_2Ph + 3Cr(CO)_6 \longrightarrow YCH_2\theta CH_2Ph + YCH_2\theta CH_2Y$$



Five-coordinate Ni^{II} complexes of 1,2-bis-(diphenylphosphino)-o-carborane have been made on reflux of di-(tetraethylamino)-nickel tetrahalide with the aforementioned carborane in acetonitrile with the loss of tetraethylammonium chloride, although the adduct has not been fully characterised. (298)

Some of the σ-bonded transition metal compounds have been used in the preparation of other carborane derivatives. For example, carboranyl acetic acid can be prepared from o-carboranyl iron cyclopentadienyl-dicarbonyl. (274,299)

$$\pi\text{-CpFe(CO)}_2\text{Br} + \text{H}\theta\text{CH}_2\text{MgBr} \longrightarrow \text{H}\theta\text{CH}_2\text{Fe(CO)}_2\pi\text{-Cp} \xrightarrow{X_2}$$

$$\text{H}\theta\text{CH}_2\text{COFe(X)}_2\text{(CO)}\pi\text{-Cp} \xrightarrow[2.H_2O]{1.X_2} \text{H}\theta\text{CH}_2\text{COOH} \qquad X = \text{Cl,Br,I.}$$

Di-(triphenylphosphino)-o-carboranyl rhodium has the ability to reversibly exchange triphenylphosphine for two carbonyls, and this and other rhodium-metallo-carboranes have been studied for their catalytic properties. (278)

1.15 POLYMER DERIVATIVES

The formation of polymers containing icosahedral carboranes has become one of largest areas of active research. The incorporation of carboranes has been found to greatly improve the thermal stability of such polymers compared to their organic counterparts. This stability is thought to arise from the electron withdrawal effects of the cage although in some cases steric effects may be dominant.

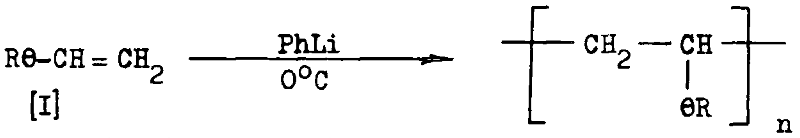
Commercial backing has resulted in restrictions on literature publications, many of which contain mainly physical and mechanical data and little chemistry. This section will deal mainly with the chemistry of the publications.

Many specialised reviews have been published on carborane polymers (399-404); therefore this section will serve only as an introduction to the field.

Carborane polymers can be broadly divided into two groups; those with pendant carborane units, and those in which the cage forms part of the polymer backbone.

Pendant Carborane Polymers

Polymerisation of 1-vinyl-o-carborane [I] can be achieved by treatment with phenyl lithium in ether at 0°C



$$R\Theta\text{-}CH=CH_2 \xrightarrow[0^{\circ}C]{PhLi} \left[CH_2 - \underset{\Theta R}{CH} \right]_n$$

[I]

R = H, (405); Et (412)

The resulting polyvinyl-o-carborane has molecular weights between 50,000-140,000 and a softening point of about 250°C (405) whilst the ethyl derivative is air stable up to 360°C. (411)

Direct polymerisation by exposure to γ radiation (413-415) or X-rays

(415) has been achieved but molecular weights were no higher than 25,000. Copolymerisation of [I] with vinyl-benzene (416) 1-prop-2-enyl-o-carborane (417), ethylene (418), and 1,3-butadiene (406) have been reported.

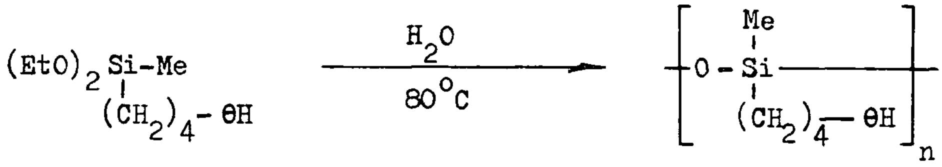
Some polyesters can be prepared although steric factors can cause difficulty in polymerisation (407).

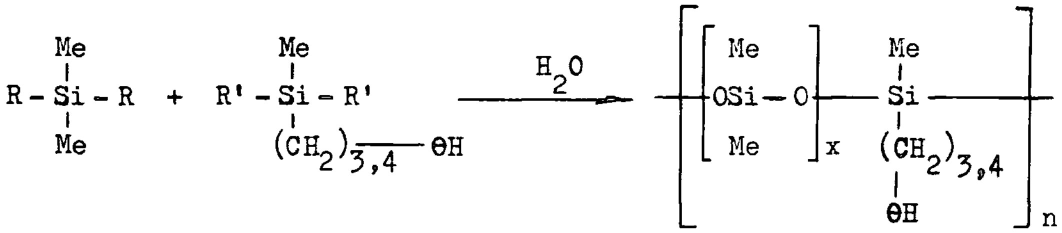
Polymethacrylates are formed by free radical-catalysed polymerisation of 1-methacryloyloxymethyl-o-carborane or its derivatives.

R = H, Me; R' = H,Me

The properties of these polymers appear to depend largely on the R and R' substituents. (408,409)

Polysiloxane-o-carborane polymers have shown very high thermal stabilities and have been prepared by hydrolysis of o-carboranyl chloro-and ethoxysilanes (408,410) or by their copolymerisation. (408,411)



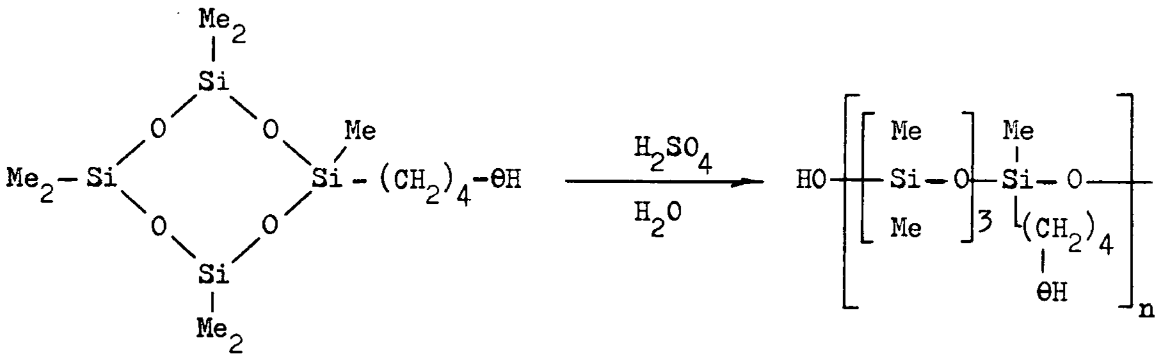


R = Cl, OEt; R' = Cl, OEt

Polymers prepared from alkyl- and aryl-(o-carboranylisopropyl)-chlorosilanes have a liquid range from -108°C to 350°C at which they decompose. (68)

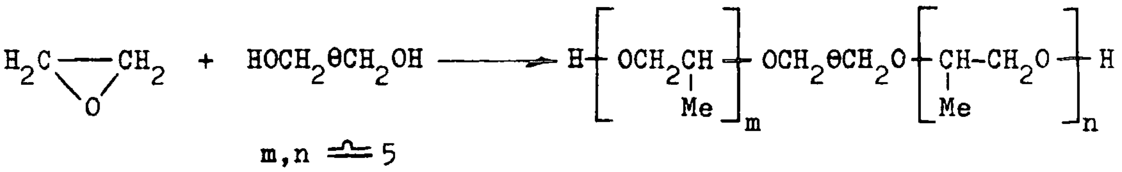
Isopropenyl-o-carborane can be linked into existing polyalkylhydro-siloxanes by heating the two reactants at 200 - 300°C. The stability of the resulting polymer increases with the number of carborane units. (419)

Other siloxypolymers can be prepared by the opening of cyclic rings. (420)



Chain Linking Carborane Polymers

Ortho-carboranyl polyformyls can be made despite the tendency for o-carboranyl diols to form small exocyclic rings. Reaction of bis-hydroxymethyl-o-carborane with propylene oxide yields a polymer which is stable up to 200°C. (421)

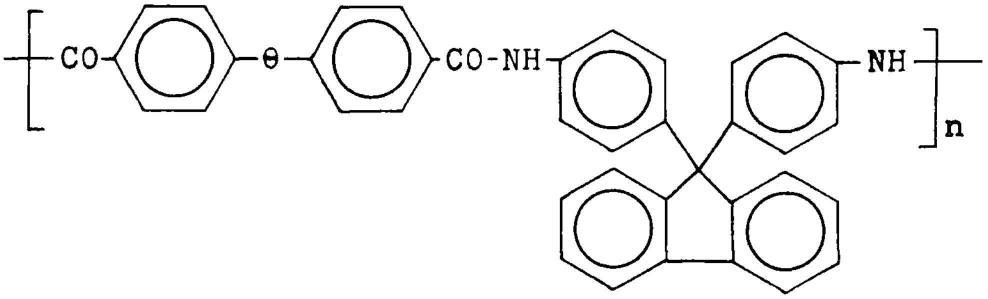


Carboranyl polyesters can be synthesised by a number of means:-
By the reaction of carboranyl diacids with organic diols, (422); the reaction of carboranyl diols with organic diacids (407, 423) or organic diacid chlorides, (407, 423, 424) or by the reaction of carboranyl diacid chlorides with organic diols (425, 426) or carboranyl diols. (399)

Other polyesters have been made by the reaction of carborane diols or epoxides with boric acid. (427)

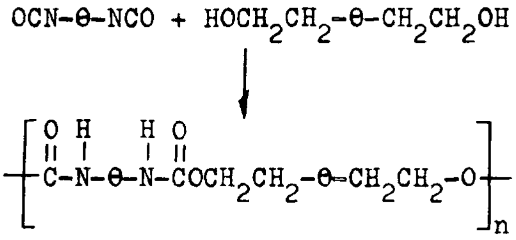
$$HOCH_2\theta CH_2OH + H_3BO_3 \longrightarrow \left[OCH_2\theta CH_2\text{-}OB(OH) \right]_n$$

o-carboranyl polyamides are formed by the reaction between diacid chlorides and diamines where either or both of the reactants may contain carborane units. The reaction between 1,2-diamino-o-carborane and phenyl diacid chlorides yields carboranyl polyamides which in inert atmosphere can withstand 900°C without weight loss. (428) The use of organic diamines allows the incorporation bulky groups into the polymer chain, and cross linking with tri-and tetramino-monomers.



(429)

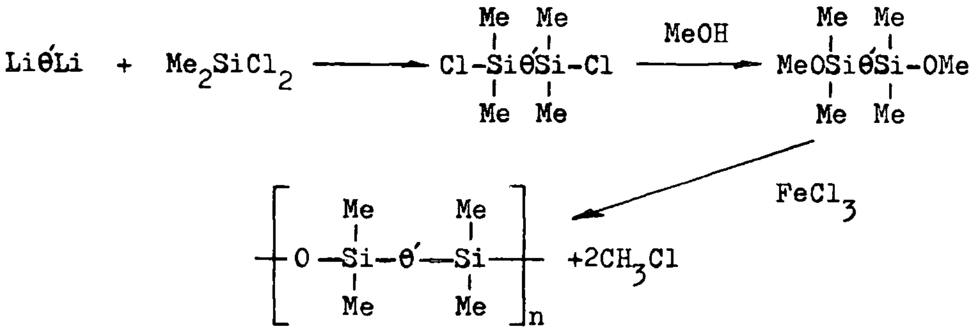
Carboranyl polyamides can also be synthesised from bis-isocyanata-o-carborane and o-carboranyl diols, (430) although molecular weights of only 5000 can be achieved.



Unlike other carborane polymers, the hydrolytic degradation of polyamides can lead ultimately to the degradation of the carborane cage most likely due to attack by alkyl amines in moist conditions.

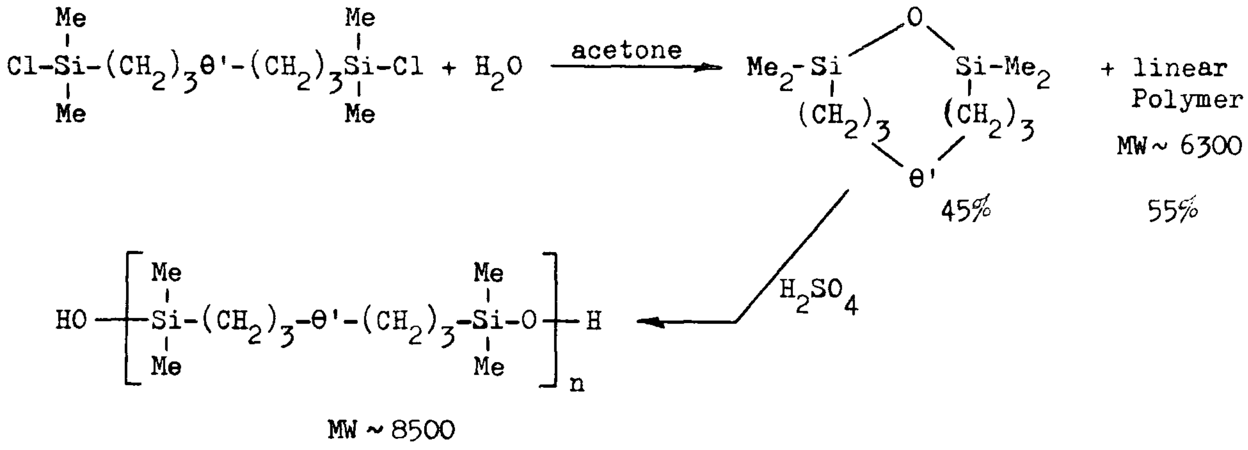
Carboranyl polysiloxanes are by far the biggest group of carborane polymers due to commercial interests. The vast majority are based on m-carborane as the positioning of the carbon atoms prevent exocyclic ring formation which is the characteristic of o-carborane silicon chemistry. (431) The polysiloxanes are exceptionally heat resistant elastomers and are widely known as the Dexsil polymers.

The first carboranyl polysiloxanes were prepared by the following reaction scheme:- (432)



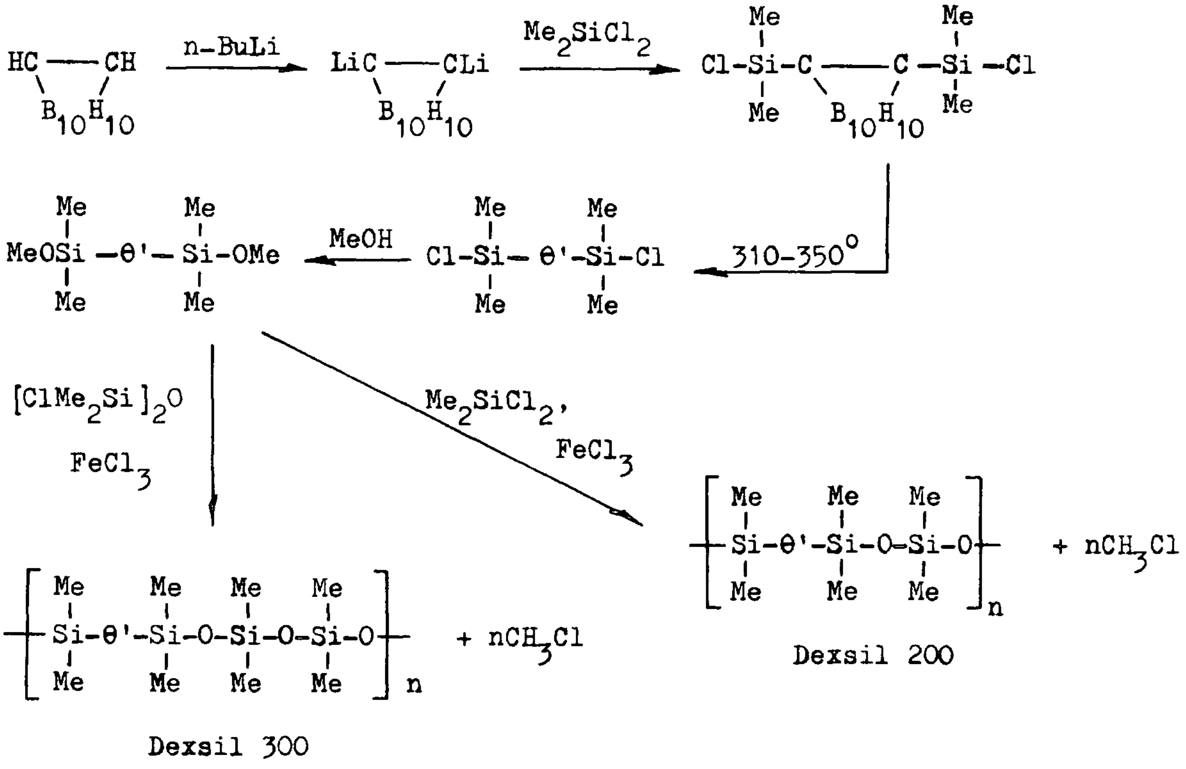
Dexsil 100

Attempted hydrolysis of the Si - Cl bond with water only gave a very stable hydroxy species which could not be polymerised. However, the insertion of three CH_2 groups between the cage and the silicon atoms allows aqueous hydrolysis to occur. (420)



It is likely that the removal of the influence of the carborane cage that permits polymerisation in the latter case.

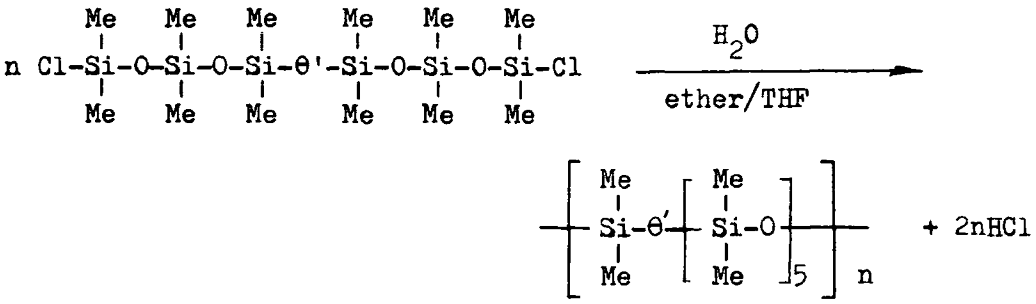
A series of other Dexsils up to Dexsil 400 have been prepared by similar means although many workers have started from ortho-carborane rather than meta carborane. (432-436)



Dexsil 200

Dexsil 300

The Dexsils are usually polymerised along with about 1% of a vinyl carborane to promote crosslinking. Dexsil 300 and 500 have been prepared by hydrolytic polycondensation in water/ether/THF solutions at 0°C. (437)



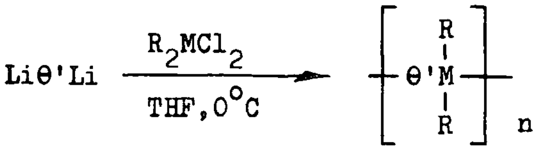
Dexsil 500

The first digit in the Dexsil number represents the number of siloxy repeating groups.

The high thermal stability of the Dexsils is directly attributable to the electron-withdrawing effect of the meta-carborane cage. This is evident in the observed reduction in thermal stability as the number of siloxy groups increases. Air oxidation of the polymers with temperature follows the trend:- Dexsil 100, $> 450^{\circ}$C; Dexsil 200 + 300, $\approx 335^{\circ}$C and Dexsil 400, $\approx 325^{\circ}$C. It has been suggested that the oxidation begins at silicon bonded methyl groups. (432)

Different methods of curing and use of fillers have produced composite materials with improved stability and elastomeric properties. Thermo gravimetric and mechanical tests have been carried out on these composites and the Dexsil polymers, and the results published in a review by Ditter. (399)

Polymers containing Group IV, V and VI atoms have been prepared. In general, Group IV polymers are synthesised by the reaction of a dialkyl metal dichloride with dilithio-m-carborane in THF. (220,438,439)



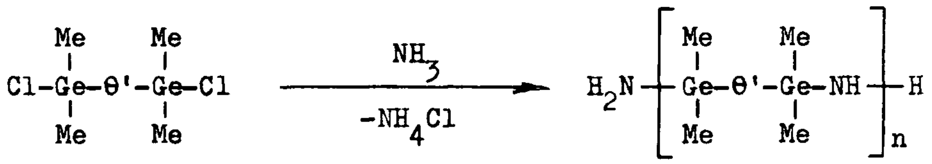
M = Si,Ge,Sn,Pb

R = Me,Et,n-Bu,Ph

Para carborane forms slightly longer chain polymers than m-carborane with

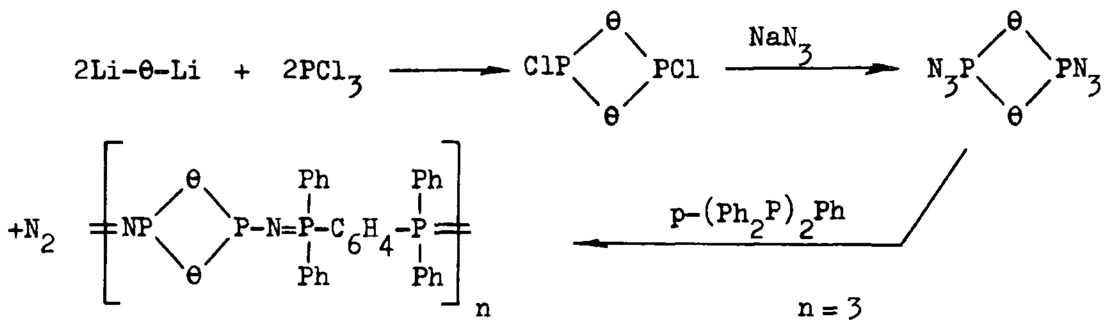
with up to eleven repeat tin units being formed with diphenyl tin dichloride. The reaction of dilithio-p-carborane and dimethyl tin dichloride in ether and xylene produced a polymer with a softening point of 420°C. (220) Related germanium species have melting points upto 480°C. (220)

Carborane-germanium-imino bonded polymers have been prepared containing about 7 repeat units.

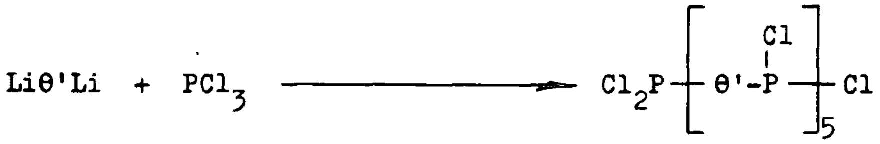


$$\mathrm{Cl{-}Ge(Me)_2{-}\theta'{-}Ge(Me)_2{-}Cl} \xrightarrow[-NH_4Cl]{NH_3} \mathrm{H_2N}\left[\mathrm{Ge(Me)_2{-}\theta'{-}Ge(Me)_2{-}NH}\right]_n\mathrm{H}$$

Group V element containing polymers can be prepared using o-carborane units. These polymers make use of the tendency of ortho-carborane to cyclise. (234)

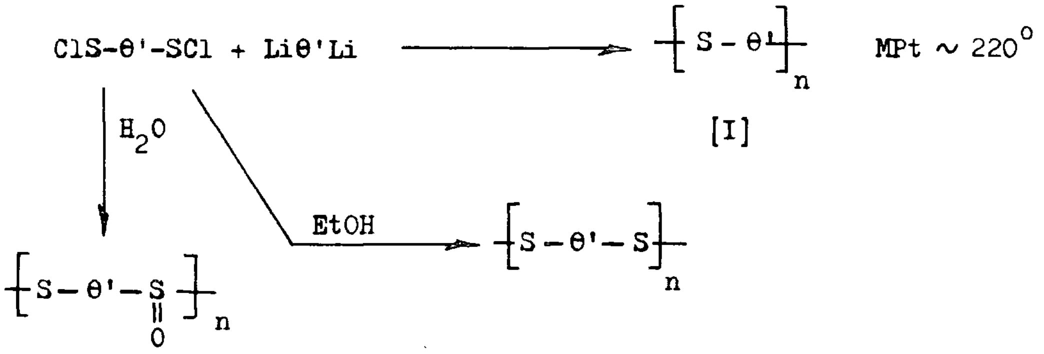


The polymer is a solid with a melting point of 225 to 250°C with good hydrolytic stability. The reaction of dilithio-m-carborane with phosphorus trichloride produced a low molecular weight polymer containing 5 carboranyl repeat units. (440)



$$\mathrm{Li\theta'Li} + \mathrm{PCl_3} \longrightarrow \mathrm{Cl_2P}\left[\mathrm{\theta'{-}P(Cl)}\right]_5\mathrm{Cl}$$

Group VI element polymers have been prepared from carboranyl sulphur derivatives. (254)



The equivalent para-carborane product to [I] exhibited a softening point above 420°C; no molecular weight is reported due to its insolubility in common organic solvents. (254)

1.16 CARBORANYL ANIONS AND ICOSAHEDRAL HETEROATOM CAGES

In this section, the preparation and reactions of some carboranes which include one or more heteroatoms in an icosahedron will be discussed, with the synthesis of some of the anionic precursors. The reactions and preparations of some transition metal icosahedral carboranes will only briefly be discussed as unlike many other areas of carborane chemistry, there are many reviews of this now vast field. A detailed survey of this topic would be outside the scope of this review, however a list of detailed reviews by other authors is given at the end of this section.

Synthesis of Carboranyl Anions

Ortho- and meta-carboranes but not para-carborane are selectively degraded by strong bases in the presence of a protic solvent, with the removal of the most positive 3 position boron atom from the cage. (68,304) The resulting nido 1,2-and 1,7-dicarbaundecaborate (12) anions have essentially an icosahedral structure with one missing vertex. This gives rise to an open five-membered face above which sits the twelfth hydrogen atom (Figure 1.16.1). Retaining the original numbering, the anions are written as (3)-1,2-$C_2B_9H_{12}^-$ and (3)-1,7-$C_2B_9H_{12}^-$ where (3) refers to the position of the removed boron atom. A six centre bond has been proposed to retain the lone hydrogen atom. (305)

The dicarbaundecaborate (12) anions are colourless, air stable compounds inert to aqueous bases and non-oxidising acids. (305) On heating to 300°, however, the (3)-1,2-$C_2B_9H_{12}^-$ anion quantitatively rearranges to (3)-1,7-$C_2B_9H_{12}^-$. (306) Bromine (307) and ferric chloride (308) in aqueous media cause complete cage degradation whilst iodine in aqueous ethanol undergoes electrophilic attack at a boron atom adjacent to a carbon on the open face. (309)

1,2-$C_2B_9H_{12}^-$ and 1,7-$C_2B_9H_{12}^-$ can be protonated at room temperature to yield the respective neutral nido dicarbaundecaborane (13) compounds. (304)

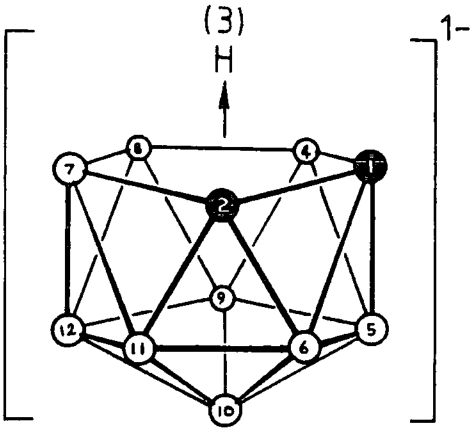


Figure 1.16.1.

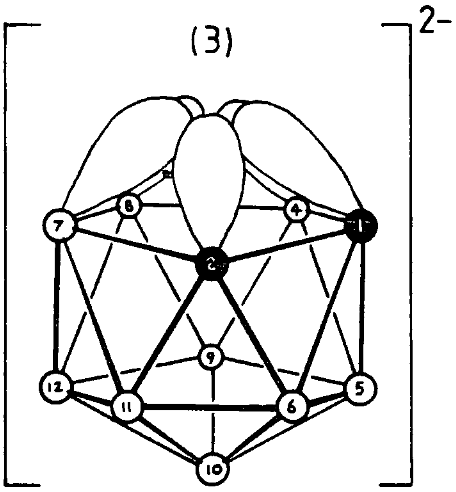


Figure 1.16.2.

At 75 - 100° the neutral $C_2B_9H_{13}$ species loses hydrogen to give closo-1,8-$C_2B_9H_{11}$. (306,310)

Treatment of 1,2-$C_2B_9H_{12}^-$ and 1,7-$C_2B_9H_{12}^-$ anions with sodium metal, sodium hydride (311-313) or n-butyl lithium (314) in ethereal solvents produces the dicarbollide ion, with the evolution of hydrogen. The dicarbollide ion (Figure 1.16.2) has an open two carbon, three boron atom face with five approximately sp^3 orbitals directed towards the vacant (3)-position vertex of the icosahedron. The ion is hydrolysed by water back to the dicarbaundecaborate (12) anion. (311) The dicarbollide ion is also produced in low concentration by the action of hot concentrated aqueous sodium hydroxide on the mono anion. (315)

The dicarbollide ion has synthetic importance by the formation of 3-position organo derivatives of ortho and meta carborane (see previous sections) on reaction with organo boron dichlorides. (316,317,332)

$$(3)\text{-}1,2\ C_2B_9H_{11}^{2-} + RBCl_2 \xrightarrow[-40^\circ]{THF} o\text{-}\underbrace{HCB_{10}H_9RCH}_{} + 2Cl^-$$

R = Me, Et, Ph; $CH=CH_2$, -OH, $N(Et)_2$, OEt.

3-substituted o-carborane prepared in this manner can be treated with ethoxide ion to give a (6)-1,2-$C_2B_9H_{11}R^-$ species. This can be converted into the equivalent dicarbollide ion where the 6-position is vacant, and will react with further $R'BX_2$ compounds to give 3,6-disubstituted o-carboranes. (317) 1,4-bis-(3-o-carboranyl) butane has been prepared by utilising the basic insertion reaction. (333)

$$2\ (3)\text{-}1,2\text{-}C_2B_9H_{11}^{2-} + Cl_2B(CH_2)_4BCl_2 \longrightarrow \underbrace{HCB_{10}H_9CH \qquad HCB_{10}H_9CH}_{(CH_2)_4}$$

The nido $C_2B_{10}H_{12}^{2-}$ anion is prepared by the reduction of o- or m-carboranes with sodium in THF.

The meta isomer undergoes rearrangement to the ortho isomer. (See section 10)

$$\text{o,m-}H\underline{CB_{10}H_{10}C}H \xrightarrow{NaTHF} \text{o-}\left[H\underline{CB_{10}H_{10}C}H\right]^{2-}$$

Mono-carbon Carborane Anions

Mono-carbon carborane anions of the formulae $CH_{10}H_{13}^-$, $CB_{10}H_{11}^-$, $CB_9H_{10}^-$ and $CB_{11}H_{12}^-$ can be prepared not from o- or m- carboranes but from deca-borane. The synthesis of the anions will be dealt with in the above order.

The reaction of deca-borane (14) with alkyl isocyanides give C-amino derivatives of $CB_{10}H_{13}^-$ which on treatment with sodium hydride followed by dimethyl sulphate gives an alkyldimethylamino derivative. (334,335)

$$B_{10}H_{14} + RN\equiv C: \longrightarrow RH_2NCB_{10}H_{12} \xrightarrow[2.(Me)_2SO_4]{1.H^-} R(Me)_2NCB_{10}H_{12}$$

$$R = Me,\ Et,\ n\text{-}Pr,\ t\text{-}Bu$$

The C-trimethylamino derivative has also been produced by the protonation of $Na_2B_{10}H_{13}CN$ on ion exchange columns. (335,336) The C-trimethyl amino derivative can be deaminated by treatment with sodium in THF followed by water to yield $NaB_{10}H_{12}CH$. (335) Deamination with sodium in THF proceeds via $Na_3CB_{10}H_{11}(THF)_2$ and can be used in this form for insertion reactions.

High yields of the $CB_{10}H_{11}^-$ ion have been achieved by the oxidation of the above THF adduct with iodine. (337)

$$Na_3CB_{10}H_{11}(THF)_2 + I_2 \longrightarrow NaCB_{10}H_{11} + 2NaI + 2THF$$

$CB_9H_{10}^-$ and $CH_{11}H_{12}^-$ are conveniently prepared by the action of heat on $CsCB_{10}H_{13}$ during which hydrogen is evolved and the caesium salt of both anions is formed. (335) $CsCB_{11}H_{12}$ can also be prepared by heating the same starting material with triethylamino-borontrihydride. The smaller mono-carbon cage can be prepared as follows:

$$NaB_{10}H_{12}CN.S(Me)_2 \xrightarrow[\text{ion exchange}]{H_3O^+} B_{10}H_{11}(OH)CNH_3 \xrightarrow[NaOH]{(Me)_2SO_4}$$

$$B_{10}H_{11}(OH)CN(Me)_3 \xrightarrow[THF]{OH^-} B_9H_{11}CN(Me)_3 \xrightarrow[2.(Me)_4N^+,\ H_2O]{1.Na,THF}$$

$$(Me)_4N^+CB_9H_{10}^- + H_2$$

Icosahedral Mono-carbon Heteroatom Cages

Phosphorus, (338,339) arsenic and antimony (340) heteroatoms have been incorporated into mono-carbon cages, completing the icosahedron by the reaction of $Na_3CB_{10}H_{11}(THF)_2$ with phosphorus trichloride, arsenic trichloride and antimony tri-iodide respectively in refluxing THF. Germanium derivatives have been made from methyl germanium dichloride by an analogous method. (340) In each case the heteroatom enters the cage at the ortho-(2)-position relative to the lone carbon atom.

$$Na_3CB_{10}H_{11}(THF)_2 + PCl_3 \longrightarrow 1,2\text{-}CPB_{10}H_{11} + 3NaCl + 2THF$$

The Group V derivatives rearrange at elevated temperature to give the 1,7 or meta derivative although in the case of antimony there is extensive cage degradation. (340) Exposure of the phosphorus and arsenic compounds to higher temperatures produce a 1,12 or para isomers, which as expected are less polar than the ortho and meta isomers. (339,340) As with the carborane series, para-carbaphospha and arsaboranes undergo reverse isomerisation in THF with sodium followed by oxidation with $CuCl_2$ to the respective meta isomers. (352)

Carbaphosphaboranes like carboranes undergo electrophilic photochemical, and exchange halogenation with polyhalomethanes at the boron atoms of the cage. (341) Electrophilic and exchange halogenation for the ortho-derivative takes place mainly at 8,9,10,12-atoms, the meta-at 9-and 10-atoms whilst the para-derivative is halogenated mostly at 7,8,9,10,11-atoms. Unlike the ortho-and meta-carbaphosphaboranes, the para-derivative is halogenated easier than its dicarba-analogue. Photo-chemical halogenation is non selective with all three isomers. (341) The halogenation rates for the carba-arsaboranes are higher than for the corresponding carborane and carbaphosphaborane isomers. (353)

The o-carbaphospha-and arsaboranes are degraded by boiling piperidine solutions (342,343), piperidine in benzene at 20^{o}, alkoxide ion, n-butyllithium, and Grignard reagents. (348)

$$\text{o-CPB}_{10}\text{H}_{11} + 3\text{RM} \longrightarrow \text{M}_3\text{B}_{10}\text{H}_{10}\text{CH} + \text{R}_3\text{P}$$

$$\text{RM} = \text{n-Buli}, \quad \text{EtMgBr}$$

$$\text{o-CPB}_{10}\text{H}_{11} + 4\text{KOH} \xrightarrow{\text{EtOH}} \text{KCB}_{10}\text{H}_{13} + \text{P(OH)}_3 + \text{H}_2\text{O}$$

The meta-isomer is unaffected by cold alcoholic ethoxide ion or KOH but prolonged boiling gives a mixture of two salts.

$$\text{m-CPB}_{10}\text{H}_{11} + \text{C}_2\text{H}_5\text{OH} + \text{KOH} \longrightarrow \underset{90\%}{\text{m-KCPB}_9\text{H}_{11}} + \underset{10\%}{\text{m-KCPB}_{10}\text{H}_{13}}$$

Treatment of arsenic and antimony derivatives with piperidine in benzene results, as with carbaphosphaboranes, in the removal of a boron atom. (340)

Meta-and para-carba phospha- and arsa-boranes can be lithiated at the carbon atom by phenyl lithium, (344,345) the meta products reacting with carbon dioxide and dilute acid to give carboxylic acid derivatives. The pKa value of carbaphosphaborane carboxylic acid (3.16) show it to be weaker than o-carborane carboxylic acid (2.61) but stronger than m-carboranecarboxylic acid (3.34) in 50% ethanol. (344) These results and those of polargraphic reduction studies show that in each case the replacement of a CH group by a P or As atom in o, m- or p- carborane leads to an increase in the electron acceptor effect of the cage. (346) Other evidence has come from the alcoholic alkaline cleavage of some mixed ketones. (345,347) The cleavage with m-carborane

$$\text{m-}B_{10}H_{10}ECCO\phi Me \xrightarrow[EtOH]{NaOH} \text{m-}B_{10}H_{10}ECH \quad + \quad \text{m-}Me\phi COONa$$

$$E = P, As$$

substituents occurring at the heteroatom cage, whereas with o-carborane substituents on the m-heteroatom cage the C-C cleavage occurs at the o-carboranyl unit. The PMR spin-spin interaction constants for meta-isomers show that J and the electron acceptor effect increases with m-carborane $<$ m-carbaarsa, $<$ m-carbaphosaboranes. Hence As and P atoms are more electronegative than a CH group. (348) This helps to explain the position of electrophilic halogenation in p-carbaphosphaboranes.

As NQR studies (349) and the vibrational spectra of carbaphospha- and arsa-boranes (350) have been made.

The organic chemistry of carbaphospha- and arsa-boranes has been shown to be very similar to that of the icosahedral carboranes, (344,345,347) with the formation of acids, ketones and acyl chlorides. Organo-mercury derivatives can be prepared by the reaction of m and p- C-lithio-carbaboranes with methyl mercury bromide. (348)

$$\text{m,p-}B_{10}H_{10}ECLi \xrightarrow{MeHgBr} \text{m,p-}B_{10}H_{10}ECHgCH_3 \qquad E = P, As$$

Transition metal carbonyl derivatives of the related $B_9H_{11}CE^-$ ($E = P$, As) ion have been reported. (340,342,351) Reaction of the $CEB_9H_{10}^-$ ions ($E = P$, As) with germanium (II) iodide yields an icosahedron containing 3 heteroatoms which gives three different isomers on heating under vacuum. (354)

Dicarbon Heteroatom Icosahedra

This group of derivatives is dominated by a vast number of transition metal compounds to which only an introduction can be given in this review.

A simple orbital description of the open face of the dicarbollide ion approximates it to five nearly sp^3 atomic orbitals containing 6 delocalized electrons in three bonding and two antibonding orbitals. This array is equivalent to the cyclopentadienide ion $C_5H_5^-$ and so chemistry similar to this ion would be expected. (311,68) Recognising this, workers prepared analogues of ferrocene (311,312), the resulting complex being easily air oxidised to Fe^{3+}, reduction reversing the process.

$$2\ (3)\text{-}1,2\text{-}C_2B_9H_{11}^{\ 2-} + FeCl_2 \xrightarrow{THF} \left[\pi\text{-}(3)\text{-}1,2\text{-}C_2B_9H_{11}\right]_2 Fe^{2-} + 2Cl^-$$

X-ray studies of these and related cobalt meta dicarbollide compounds showed them to have a "sandwich" structure. (311,356,357). "Sandwich" structures with a mixture of dicarbollide and cyclopentadienide ions were also prepared. (356,313) (Fig. 1.16.3)

$$C_5H_5^- + (3)\text{-}1,2\text{-}C_2B_9H_{11}^{\ 2-} + CoCl_2 \xrightarrow{THF} \left[\pi\text{-}C_5H_5\right]Co\left[\pi\text{-}(3)\text{-}1,2\text{-}C_2B_9H_{11}\right]^- + 2Cl$$

Some of these species were shown to be surprisingly stable towards chemical attack, bromine in acetic acid for example brominating only the cage in cobalt sandwich compounds. (311)

The preparation of d^9Cu^{2+} and d^8Cu^{3+} (358,359) di-cage sandwich compounds led to species that were shown by X-ray diffraction to have a slipped structure. (Fig. 1.16.4) The reason for the formation of the slipped configuration has been explained by Wade. (360)

Photochemical reaction of dicarbollide ion with chromium, molybdenum and tungsten hexacarbonyls led to formation of metal tricarbonyl capped cages. (361) Some of these will react further with other hexacarbonyls to

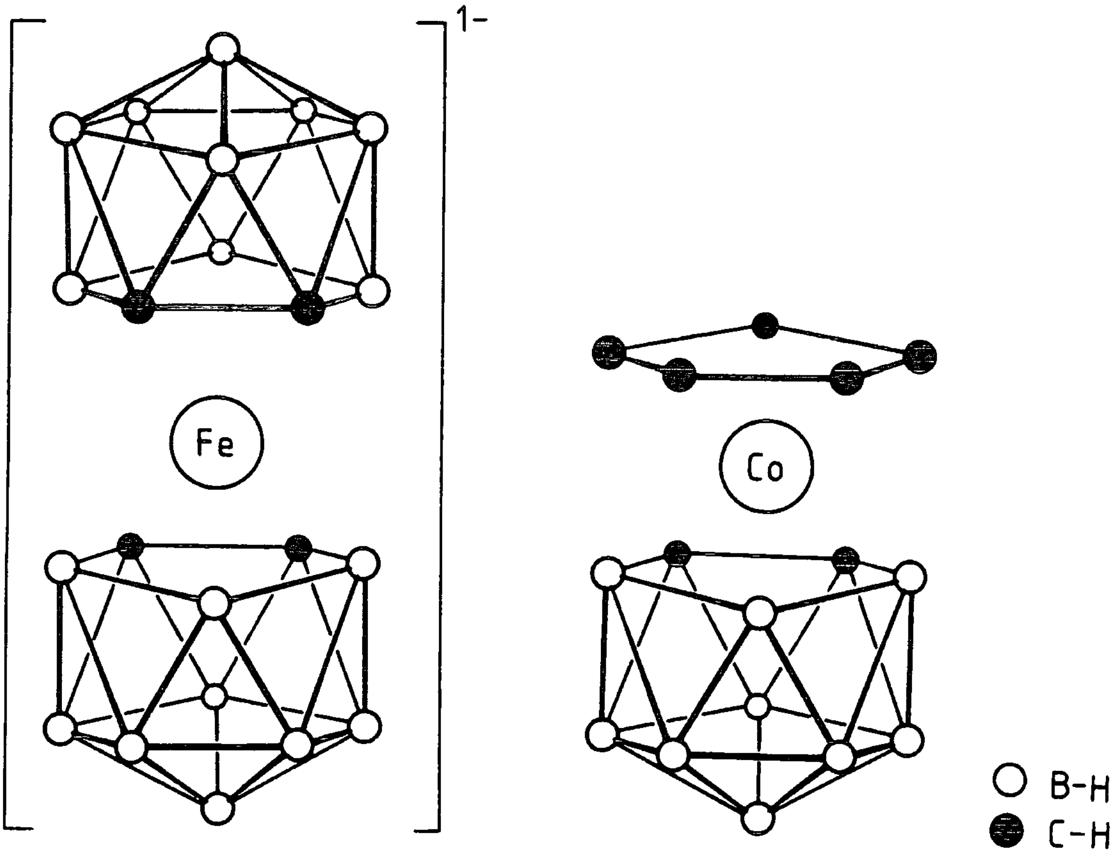


Figure 1.16.3.

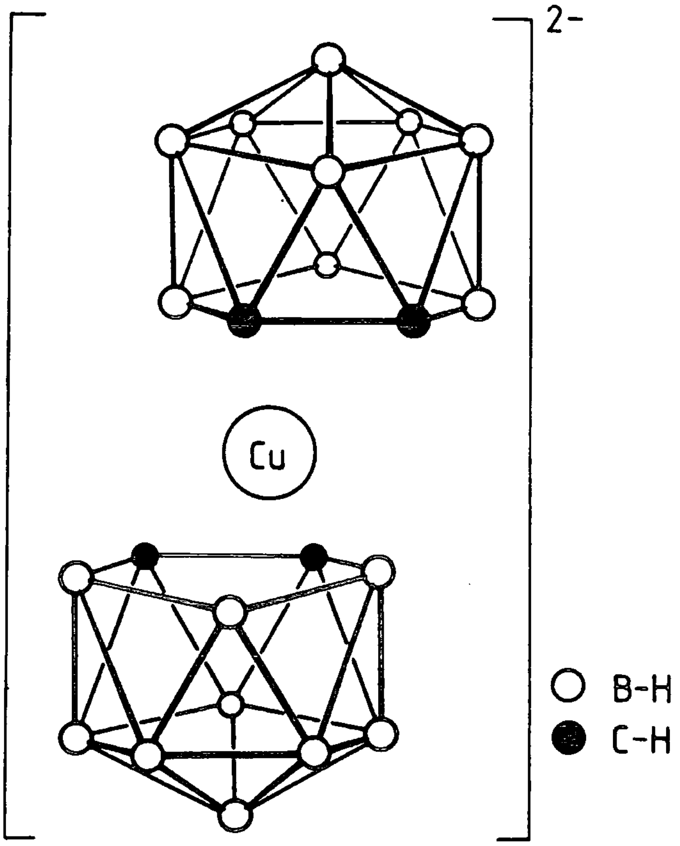


Figure 1.16.4.

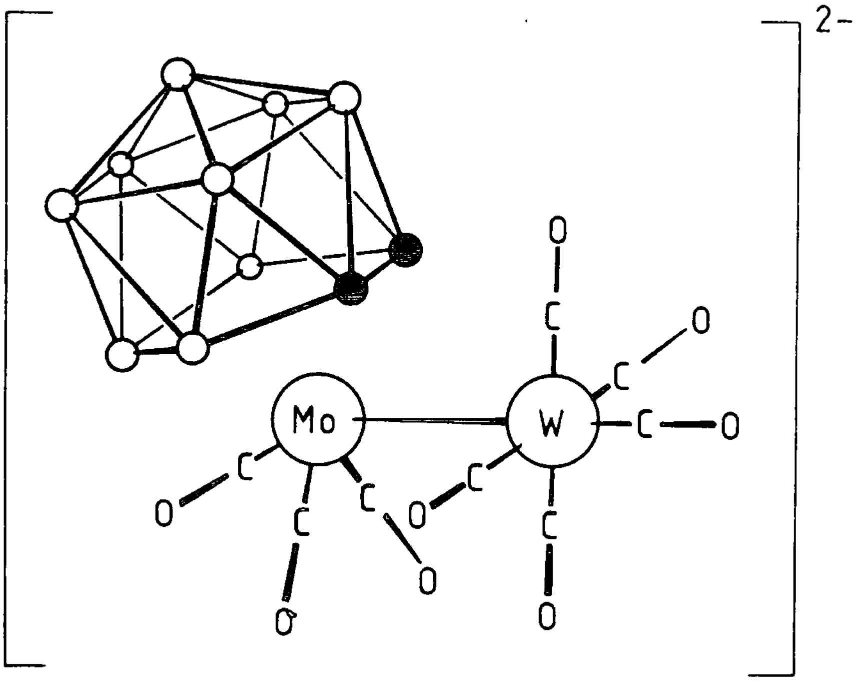


Figure 1.16.5.

form compounds of the structure shown. (Fig. 1.16.5)(311)

$$(1,2\text{-}C_2B_9H_{11})M(CO)_3^{2-} + M'(CO)_6 \longrightarrow CO + 1,2\text{-}C_2B_9H_{11}M(CO)_3M'(CO)_5^{2-}$$

M and M' = Mo or W

The preparation of some cobalt species in protonic solvents such as ethanol or water led to the formation of some interesting triple and quadruple decker sandwich compounds containing two cobalt and one $C_2B_8H_{10}^{4-}$ ion, and three cobalt atoms and two $C_2B_8H_{10}^{4-}$ respectively, (362,363,364) the $C_2B_8H_{10}^{4-}$ or dicarbacanastide ion π-bridging between two cobalt atoms.

Other methods of preparing icosahedral metallocarboranes have been employed by direct-insertion techniques. The reaction of ortho carborane with $(\pi\text{-}C_5H_5)Co(CO)_2$ at 300 °C in an evacuated ampule gave the previously reported $(\pi\text{-}C_5H_5)CoC_2B_9H_{11}$. (365)

Other transition metal compounds have been prepared by reaction of the metal dichloride with the thallium species $Tl_2C_2B_9H_{11}$ or its C-alkyl derivatives in THF. (322)

Icosahedral metallocarboranes are known in which there is more than one metal atom in the cage. (366,367)

$$(\pi\text{-}C_5H_5)CoC_2B_7H_9 \xrightarrow[C_{10}H_8]{Na} \xrightarrow[Na^+C_5H_5^-]{CoCl_2} \underset{22\%}{(\pi\text{-}C_5H_5)_2Co_2C_2B_7H_9} + \underset{\sim 3\%}{(\pi\text{-}C_5H_5)_3Co_3C_2B_7H_9}$$

Dicobalt icosahedra have been prepared by thermal isomerisation of $C_5H_5CoC_2B_8H_{10}$, giving a mixture of six isomers of $(C_5H_5)_2Co_2C_2B_8H_{10}$, (368, 369) some of which can also be prepared from $C_2B_8H_{10}$ and $CoCl_2$. (370)

As already mentioned the number of icosahedral metallocarboranes prepared to date is vast, with derivatives of most of the transition elements being formed. Amongst these the rhodium derivatives are worthy of note for their catalytic properties. Treatment of tri-(triphenylphosphino)-rhodium-chloride with dicarbaundecaborate (12) in methanol at 60° gave an icosahedral rhodio-carborane with two triphenyl phosphine and one hydrogen as rhodium ligands. The compound was found to be air/water stable in solid phase but not in solution. Benzene solutions under inert atmosphere catalysed the isomerisation of benzene to 5 hexene isomers. Under hydrogen atmosphere the same isomerisations occurred but the products were hydrogenated to n-hexane. The metallocarborane also catalyses deuterium exchange at borane B-H bonds. (371,372) The utility of the hydrogenation catalyst has been increased by its incorporation into a polymer such as polymethyl styrene. (373,374) Hydrorhodium carboranes are catalysts, for the hydrosilation of ketones (371,375,376) and acetylenes. (377) Reaction of the compound with sulphuric acid gives hydrogen and di-(triphenylphosphino)-rhodium-carborane hydrogen sulphate with the hydrogen sulphate oxygen bonded to the rhodium. Addition of hydrogen regenates the catalyst. (378)

In comparison to the number of transition metal metallocarboranes, the number of main group element derivatives is small. An introduction to these derivatives is given in Chapter 6, on main group element metallocarboranes.

Further information on metallocarboranes can be found in some of the following detailed reviews.

R.N. Grimes, Carboranes. Academic Press (1970)
Journal of Organometallic Chemistry Annual Reviews
Organo metallic Chemistry Vol. 1-8
M.F. Hawthorne, Acc. Chem. Res. 1,281 (1968)
L.J.Todd, Advances. Orgmetal. Chem 8, 87 (1970)
K.P. Callahan and M.F. Hawthorne, Advances Orgmetal. Chem 14,145 (1976)
R.N. Grimes, Orgmetal. Reac and Synth. 6, 63 (1977)

CHAPTER 2

PREPARATION OF ORTHO CARBORANE AND 1-METHYL ORTHO CARBORANE

2.1 Introduction

There are three distinct methods of preparing an unsubstituted icosahedral carborane cage of the formula $C_2B_{10}H_{12}$ from non-icosahedral starting materials. (See Chapter 1.1) These are by:-

1. The reaction of acetylene gas with bis-(acetonitrile) decaborane $B_{10}H_{12}(MeCN)_2$ to give unsubstituted ortho-carborane in 70% yield. (445)

2. The reaction of a substituted acetylene with bis-(acetonitrile) decaborane to give a substituted ortho-carborane, and the subsequent reduction of this compound to ortho-carborane by chemical means in about 45% yield. (319)

3. The pyrolysis of nido-2-CB_5H_9 to give meta-carborane in 16% yield. (447)

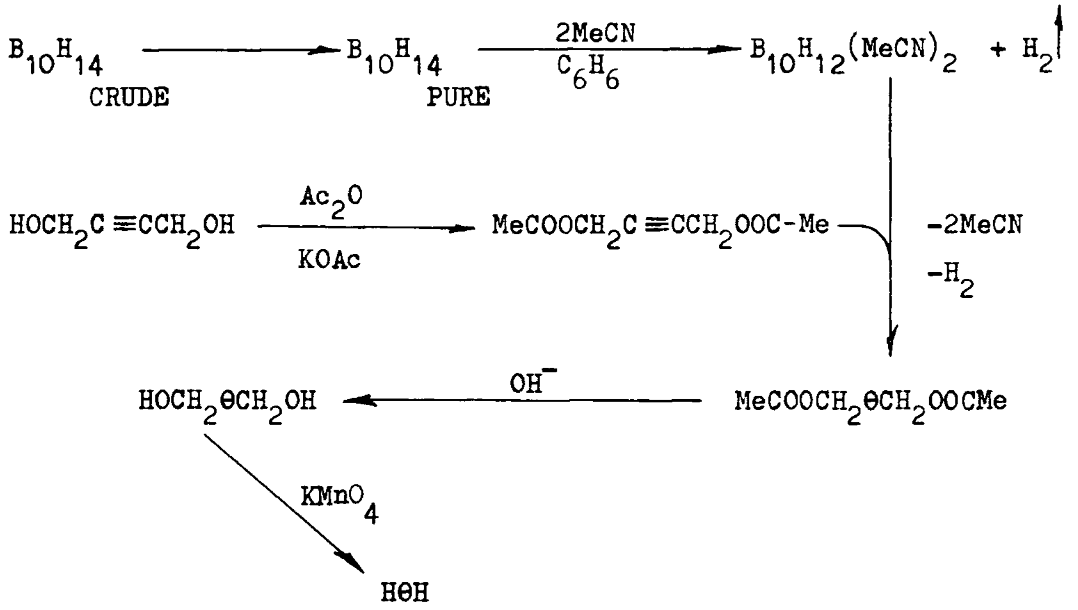
For the purposes of routine preparation of ortho-carborane the latter method is not practical. Although the first reaction directly with acetylene gas gives good yields of ortho-carborane, it requires the use of a complicated purification train for the acetylene gas and the main reaction takes 40 hours to complete. The use of acetylene produces a fire hazard requiring constant supervision during the run, and the work up procedure can cause inflammation due to by products.

The second method whilst producing a lower yield of ortho-carborane is safer and simpler being based on the oxidative degradation of 1,2-bis(hydroxymethyl)-o-carborane and involving short steps which require no overnight supervision.

The following section describes investigations made into this second method of preparing ortho-carborane and shows improvements made to the method outlined in the literature. (319)

2.1.1 Reaction Scheme

The following reaction scheme outlines the steps described in this section.



2.1.2 Purification of Decaborane (14)

Some commercial decaborane, or decaborane that has been stored for a length of time contains a proportion of yellow polymeric material which lowers the yields of ortho-carborane and in the direct reaction with acetylene produces unstable side products. The literature reports favour a purification of the decaborane by sublimation (319,445) in preference to recrystallisation from heptane. In my opinion, both methods have disadvantages. Purification by sublimation involves heating crude decaborane and sand to 80°C under high vacuum. Both authors warn that at temperatures approaching 100°C crude decaborane can decompose violently, and private communications have suggested that the yellow polymeric material is the cause of such reactions. Sublimation only serves to concentrate this material at elevated temperature. In addition, contact with air at sublimation temperatures leads to violent oxidative decomposition of decaborane. I regard that these facts make the method unnecessarily hazardous.

The purification of decaborane by recrystallisation from heptane whilst avoiding the heating of solid crude decaborane was found to be a slow and unwieldy technique if appreciable quantities of decaborane were required.

I have found that purification of decaborane by Soxhlet extraction with benzene using the apparatus shown in Fig. 2.1.1. to be a fast and safe method of producing pure decaborane in large quantities.

(i) Experimental

The apparatus was flushed with dry nitrogen and assembled as in Fig. 2.1.1. and the benzene heated to about 50°C with stirring. The connection to the vacuum pump (fitted with a liquid nitrogen cold trap) was slowly opened until the benzene was running freely from the condenser into the Soxhlet thimble. Keeping a constant pressure in the apparatus, the extraction was continued until the level of decaborane was seen (by shining a light through the thimble) to be about 2cm. The apparatus was then let down to nitrogen through the main flask and the heat source removed.

Refilling of the thimble was accomplished using a lengthened powder funnel until the decaborane was about 3 cms from the top of the thimble. The apparatus was then reassembled and the connection to the vacuum pump reopened to purge nitrogen through the apparatus for 3 minutes. The nitrogen inlet on the flask was then closed and the heat restored.

This process was continued until a saturated solution was formed in the main flask at which point the apparatus was let down to nitrogen, the heat removed and the Soxhlet assembly replaced by the Rotaflo apparatus

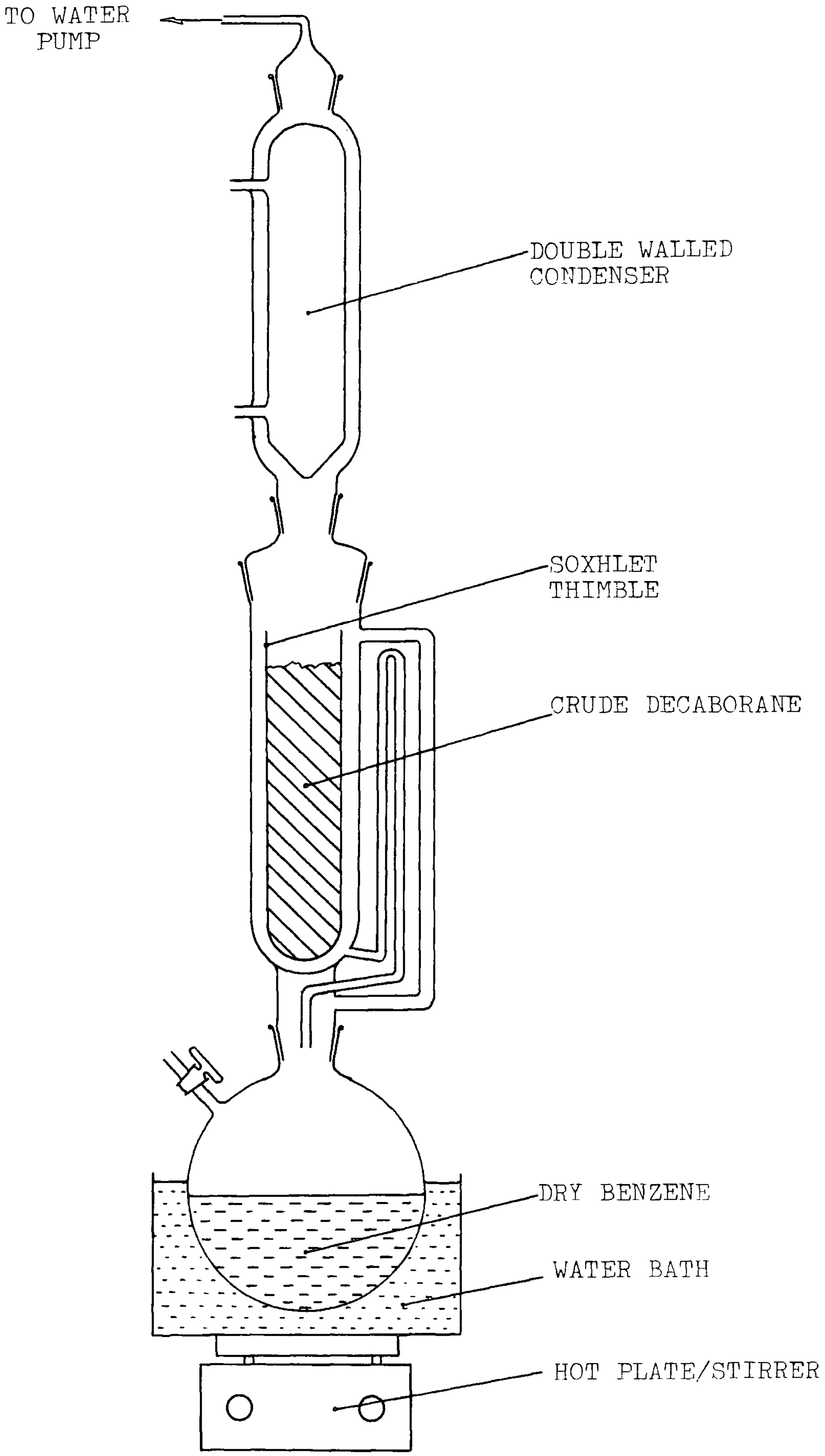


Figure 2.1.1. Soxhlet Apparatus.

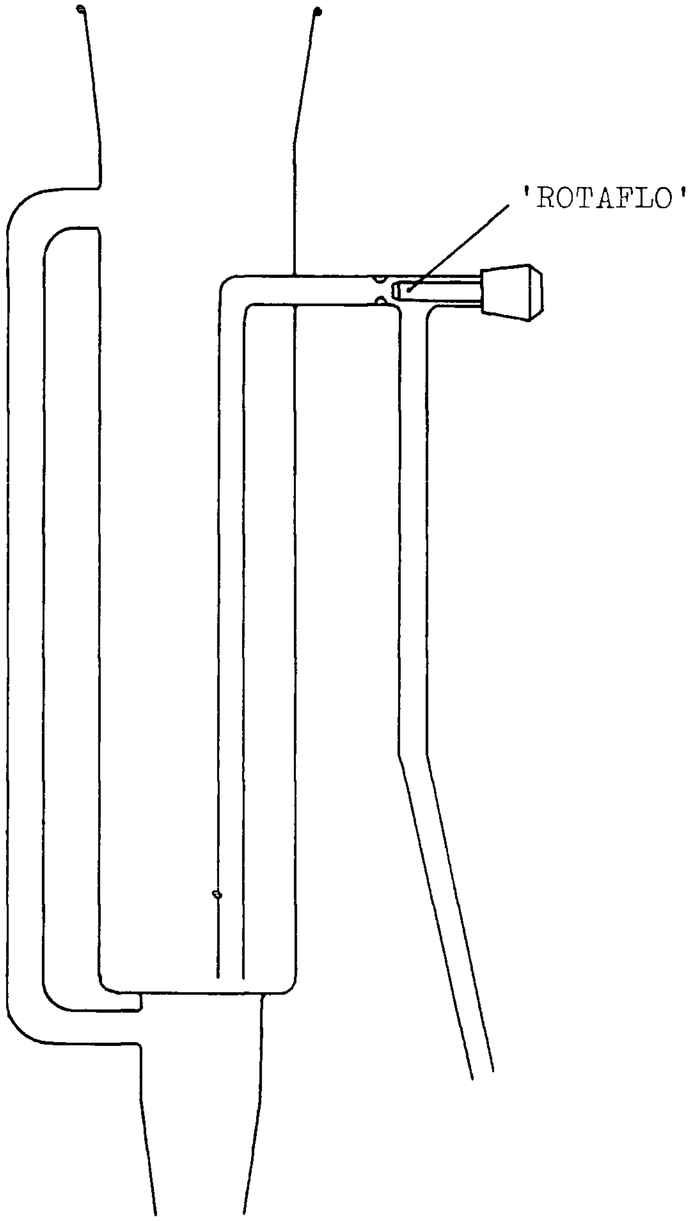


Figure 2.1.2. Rotaflo Apparatus.

shown in Fig. 2.1.2. The heat and vacuum were then restored and the benzene collected in Rotaflo apparatus until it was level with the Rotaflo seal (~ 400 mls). The benzene was then run off at atmospheric pressure into a flask for reuse, the heat removed from the main Soxhlet flask and the nitrogen inlet opened. The Soxhlet flask was allowed to cool to room temperature, when it was connected to the vacuum pump and the remaining benzene removed under high vacuum with heating sufficient only to maintain the flask at room temperature. The flask was then let down to nitrogen and the purified decaborane removed ready for use.

Using this technique, 179.7g of decaborane was recovered from 500 mls of benzene in 2-3 hours. The quoted yield for the sublimation technique is about 20g per hour.

Examination of the residue in the Soxhlet thimble showed it to contain a large amount of yellow/orange polymeric material, (The amount varied with the age and source of the crude decaborane) which was carefully destroyed by adding methanol to a suspension of the residue in hexane.

(ii) Results

Analysis

	B	H
% Found	88.2	11.61
$B_{10}H_{14}$ requires	88.53	11.47

Mass Spectrum

The mass spectrum showed a highest mass peak at m/e 124, $^{11}B_{10}\,^{1}H_{14}$. Below this peak was an isotope pattern due the various combinations of ten atoms of ^{10}B and ^{11}B. (Figure 2.1.3). The pattern is characteristic of species containing a large number of boron atoms. Boranes and carboranes

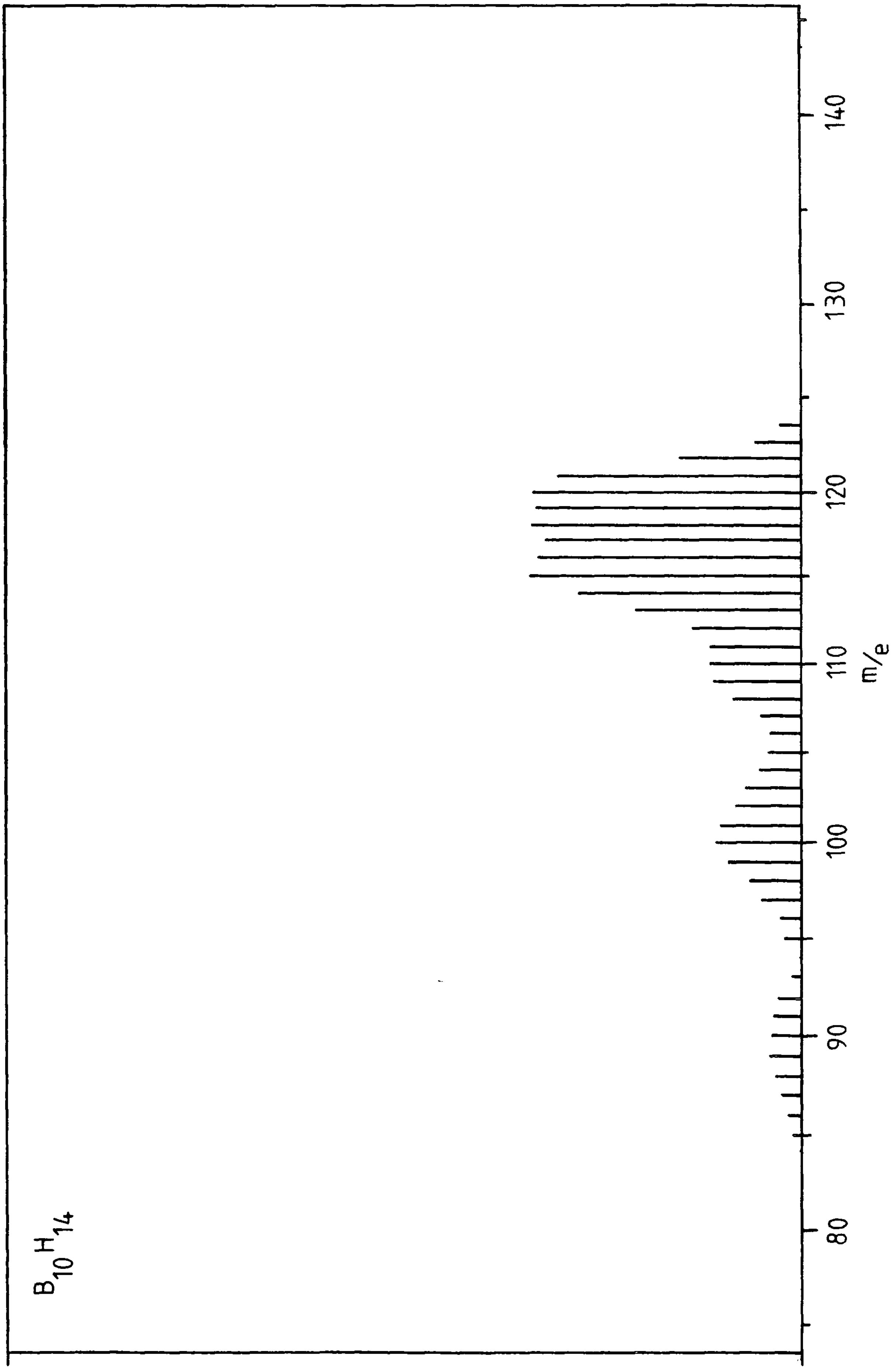


Figure 2.1.3.

quite often show half mass peaks due to doubly charged parent ions and for decaborane these are seen at m/e 57 - 62 (ie. m/2e 114 - 124).

I.R.

The infra-red spectrum showed the following peaks:-

ν max, KBr disc(cm^{-2}) 2619 (s), 2590 (s), 2575 (s), 2540 (s),
1934 (w), 1891 , 1556 , 1516 (s), 1465 ,
1104 , 1038 , 1008 , 973 , 967 ,
939 , 921 , 904 , 860 , 815 ,
767 , 750 , 723 , 710 (sh), 702 (sh),
652 (w), 622 , 438 (w), 390 ,

The following vibrations could be assigned:- B-H stretch (2619-2540 cm^{-1}); B-H deformation (1516 cm^{-1}); B-H skeletal vibration (1008 cm^{-1}); skeletal vibration (725 cm^{-1}).

The above infra-red spectrum is of solid decaborane. Nujol mulls of decaborane only show a single B-H stretch at 2580 cm^{-1}.

Melting Point 99°C [Lit 99.7°C (446)]

2.1.3 Important Safety Note

Decaborane is an extremely toxic, cumulative poison attacking the central nervous system. The maximum allowable concentration is 3 p.p.m. but the minimum detectable level by smell is $>$ 5 p.p.m.

Decaborane should only be used in a fume cupboard and disposable gloves worn. Oxidising agents such as nitric acid should not be kept in the same fume cupboard as these will cause violent explosions on contact with decaborane. Apparatus and spillages should be decontaminated with 50/50 methanol/water mixture. Apparatus should be immersed in the mixture for a minimum of

3 days after use.

Solvents for decaborane must be chosen with care. Halogenated solvents, such as carbon tetrachloride, and ethers such as dioxane form solutions which which may be detonated by shock.

2.1.4 Preparation of Bis-(acetonitrile)-Decaborane

(i) Experimental

$$B_{10}H_{14} + 2MeCN \xrightarrow{C_6H_6} B_{10}H_{12}(MeCN)_2 + H_2\uparrow$$

25g(0.205 moles) of purified decaborane was dissolved in 100 mls of dry benzene with stirring under dry nitrogen, and 21.4 mls of freshly dried acetonitrile added. The mixture was refluxed for 6 hours during which a precipitate was formed. The mixture was allowed to cool and the bis-(acetonitrile) decaborane removed on a grade 3 sinter, washed with 20 mls of dry benzene and dried under vacuum.

Removal of the solvent and acetonitrile from the filtrate recovered the unreacted decaborane which could be purified and reused.

(ii) Results

% Yield from decaborane = 78.17 (32.35g)

Analysis

	C	H	B	N
% Found	24.21	9.07	-	13.6
$B_{10}H_{12}(MeCN)_2$ requires	23.75	8.91	53.49	13.85

Mass Spectrum

The mass spectrum showed a highest mass peak at m/e 206 with an associated borane isotope pattern. This is attributed to bis(acetonitrile) decaborane, $^{11}B_{10}\ ^{12}C_4\ ^{15}N_2\ ^{1}H_{18}$. Below this was a group of peaks at about m/e 164 due to the loss of a MeCN unit. Both of these groups of peaks had equivalent m/2e peaks.

I.R.

The infra-red spectrum showed the following peaks:-

νmax, CsI disc (cm^{-1}) 2986 (s), 2980 (s), 2918 (s) , 2525 (s),
2480 (s), 2372 (w), 2335 (w), 1460 (sh), 1495 ,
1355 (w), 1122 , 1080 , 1032 , 1020 (sh),
998 (s), 974 , 950 , 940 , 930 ,
875 (w), 795 , 777 , 750 , 675 ,
653 (w), 490 , 440 , 400 , 308 ,

The following vibrations can be assigned:- Aliphatic C-H stretch (2986 - 2918 cm^{-1}); B-H stretch (2525 - 2480 cm^{-1}); C-H bend (1460 - 1405 cm^{-1}); B-H cage vibration (1020 - 998 cm^{-1})

The spectrum does not show any C≡N stretch from acetonitrile (2247 cm^{-1} in MeCN) showing that the acetonitrile is bonded through the CN group.

2.1.5 Preparation of 2-Butyne-1,4-diacetate

$$HOCH_2C \equiv CCH_2OH \xrightarrow[KOAc \quad 98^{\circ}C]{Ac_2O} MeCOOCH_2C \equiv CCH_2OOCMe$$

2-Butyne-1,4-diacetate is not readily available from chemical suppliers but it can be easily synthesised from 2-butyne-1,4-diol by the method given below.

(i) Experimental

2-Butyne-1,4-diol (100g, 1.16m.moles), 300 mls of acetic anhydride and 10g of potassium acetate were refluxed at 98°C for 13 hours with constant stirring under dry nitrogen. The reaction mixture was allowed to cool to room temperature and an excess of sodium bicarbonate slowly added to neutralize the remaining acid. The product was then extracted with 250mls of diethyl ether and shaken with 200 mls of water to extract unreacted diol. The washing was repeated twice more and the ether layer run off and dried over anhydrous chloride. The solution was filtered through a grade 4 sinter to remove the calcium chloride, and the solvent removed under vacuum to yield a pale brown crystalline product. A routine infra-red spectrum was then run to look specifically for a diol absorption at 3472 cm^{-1}. If this peak was visible then the product was dissolved in ether and shaken with water three more times, and the product worked up and checked again. (Subsequent tests using slightly impure diacetate showed that the ultimate carborane yield was significantly reduced due to degradation of bis-(acetonitrile) decaborane by the diol).

(ii) Results

Melting Point 30 - 31°C (Lit 30 - 31°C, (319))

Analysis

	C	H	O
% Found	56.31	6.02	-
$MeOOCCH_2C{\equiv}CCH_2COOMe$ requires	56.47	5.88	37.65

I.R.

The infra-red spectrum showed the following peaks:-

νmax, contact film (cm^{-1}) 2942 , 1745 (s), 1435 ,
1382 (s), 1360 , 1240 (s) , 1156 , 1027 (s),
967 , 915 , 830 , 800 (w), 630 (w),
604 , 542 (w), 496 (w).

The following vibrations could be assigned:- Aliphatic C-H stretch (2942 cm^{-1}); C=O stretch (1745 cm^{-1}); δ_{as}C-H (1435 cm^{-1}); δ_s C-H (1382 cm^{-1}); Acetate CC(=O)-O stretch (1240 cm^{-1})

2.1.6 Preparation of 1,2-Bis(Acetoxymethyl)-o-Carborane

(i) Experimental

$$MeCOOCH_2C{\equiv}CCH_2OOCMe \xrightarrow[-2MeCN,\,-H_2]{B_{10}H_{12}(MeCN)_2} MeCOOCH_2\theta CH_2OOCMe$$

35.51g (0.1757 moles) of bis-(acetonitrile) decaborane was added to a solution of 29.87g (0.176 moles) of 2-butyne-1,4-diacetate in 100 mls of dry benzene and after the initial exothermic reaction had subsided, refluxed with stirring for 7-8 hours under dry nitrogen.

The excess acetonitrile and benzene were then removed under vacuum and the residue stirred overnight with 150mls of dry methanol to destroy any remaining bis-(acetonitrile) decaborane. The volume was then reduced to 50mls under vacuum and the solution cooled to about -10°C to induce crystallisation. The crystals were removed on a grade 2 sinter and water slowly added to the filtrate to produce a yellow/orange oil (On larger scales, careful addition of water may yield further product). Additional product was extracted from the oil with hexane from which it could be recrystallised as a white air-stable crystalline solid and dried over anhydrous calcium chloride.

In the work up procedure, the literature (319) recommends the slow addition of water to the filtrate after initial crystallisation as a means of recovering further product. This was found not to work on the scale used in this preparation and was difficult to achieve even on larger scales. Extraction with hexane was found to be a simpler method of recovery and yielded pure product.

(ii) Results

Yield	69.6% with respect to decaborane
Melting Point	42 - 43°C

Analysis

	C	H	B	O
% Found	33.54	7.15	37.1	-
$(MeCOOCH_2)_2\theta$ requires	33.32	6.94	37.52	22.21

Mass Spectrum

The mass spectrum showed a parent ion with a carboranyl isotope pattern at m/e 282-290 corresponding to 1,2-bis(acetoxymethyl)o-carborane. A series of other lower mass groups of peaks due to breakdown products of 1,2-bis-(acetoxymethyl)-o-carborane were seen at m/e 287 - 268; 248 - 240; 234 - 225; 218 - 209; 189 - 180; 160 - 146; and 146 - 133. All of these showed a distinct carboranyl isotope pattern and the latter group was assigned to an ortho carborane ion itself. Below this mass was a series of sharp individual peaks attributable to the breakdown of acetoxymethyl groups. The most abundant of these peaks at m/e 43 was assigned to $CH_3C^+{=}O$.

I.R.

The infra-red spectrum showed the following peaks:-

ν max, KBr disc (cm^{-1}) 2955 , 2920 , 2850 ,
2580, 1750 (s), 1655 (w), 1433 , 1376 (s),
1360, 1257 (s), 1218 (s), 1155 (s), 1025 (s),
967, 914 , 863 , 825 , 801 ,
700, 685 , 660 , 630 , 603 ,
540, 493 , 410 (sh).

The following vibrations could be assigned:- Aliphatic C-H stretch (2955 - 2850 cm^{-1}); B-H stretch (2580 cm^{-1}); C=O stretch (1750 cm^{-1}); C-H bend (1433 - 1360 cm^{-1}); Acetate CC(=O)O stretch (1255 cm^{-1}).

2.1.7 Preparation of Ortho Carborane from 1,2-bis(acetoxymethyl) carborane

$$3(MeCOOCH_2)_2\theta + 10KOH + 8KMnO_4 \longrightarrow 3H\theta H + 6MeCOOK + 8MnO_2 + 6K_2CO_3 + 8H_2O$$

(i) Experimental

1,2-Bis-(acetoxymethyl)-o-carborane (11.07g, 38.4 m.moles) was stirred with 170 mls of 20% aqueous potassium hydroxide until the immiscible layer disappeared (about 5 hours). The reaction mixture was then cooled to 0°C and 40g of finely powdered potassium permanganate was slowly added over 8 hours at 0°C with vigorous stirring. Slow addition was necessary at the beginning of the oxidation to prevent coagulation of the potassium permanganate resulting in incomplete oxidation to carborane. At the end of the addition, the liquid phase should be green due to the presence of MnO_4^{2-} ions which show completion of the oxidation. The mixture was then transferred to a 400 ml beaker (for different scales the beaker should be capable of holding at least twice the reaction mixture volume) and, keeping the temperature at 0°C - 5°C, about 35g of potassium metabisulphite was added, immediately followed by 60 mls of ice-cold 35% aqueous sulphuric acid. Addition of the sulphuric acid caused a large amount of effervescence on top of which the crude greyish ortho-carborane floated where it was scraped off, mixed with anhydrous calcium chloride and placed into a Soxhlet thimble. The ortho-carborane was Soxhlet extracted with dry n-pentane for 28 hours, the solvent removed under vacuum and the ortho-carborane residue further purified by sublimation at 45°C and 0.01 m.m.Hg.

(ii) Results

Yield	5.13g (46.7% with respect to $B_{10}H_{14}$)
Melting Point	300°C sealed tube [Lit. 287-288° (52); 295°, 285-287° (4); 320° (319)]

Kutal et al (319) report that ortho-carborane of analytical purity showed depressions in melting point of up to 25°C. Repeated recrystallisation from n-pentane produces ortho-carborane with a melting point of 320°C.

Analysis

	C	H	B
% Found	16.41	8.52	74.6
$C_2B_{10}H_{12}$ requires	16.66	8.33	75.01

Mass Spectrum

The mass spectrum of the product (Fig.2.1.4) showed a high mass group of peaks with a carboranyl isotope pattern with the highest mass peak at m/e 146 attributable to $^{12}C_2\ ^{11}B_{10}\ ^{1}H_{12}$. Below this group was a number of lower mass groups also showing carborane isotope patterns the most notable of which appeared at m/e 66 – 73 due to m/2e 132 – 146 .

I.R.

The infra-red spectrum showed the following peaks:-

ν max, KBr disc (cm^{-1}) 3070 (s), 2590 (s), 1213 ,
1148 , 1139 , 1080 (w), 1046 , 1034 ,
1015 , 984 , 940 , 917 , 885 (w),
787 , 716 (s), 580 (w).

The following vibrations could be assigned:- Carboranyl C-H stretch (3070 cm^{-1}); B-H stretch (2590 cm^{-1}); cage vibration (716 cm^{-1})

^{11}B n.m.r.

19MHz ^{11}B n.m.r. was run on the product and compared with the n.m.r. of known pure ortho-carborane. The spectra were found to be identical. A typical trace of the "B n.m.r. is shown in Figure 2.1.5.

2.1.8 Discussion

The method of preparation given above whilst being based on that used by Kutal et al (319) contains significant improvements on that method.

The purification of decaborane has been improved in both safety and yield over the sublimation method.

The isolation of bis-(acetonitrile) decaborane before use to prepare 1,2-bis-(acetoxymethyl)-o-carborane means that the unreacted decaborane which by Kutal's method was destroyed later, is now recovered for reuse,

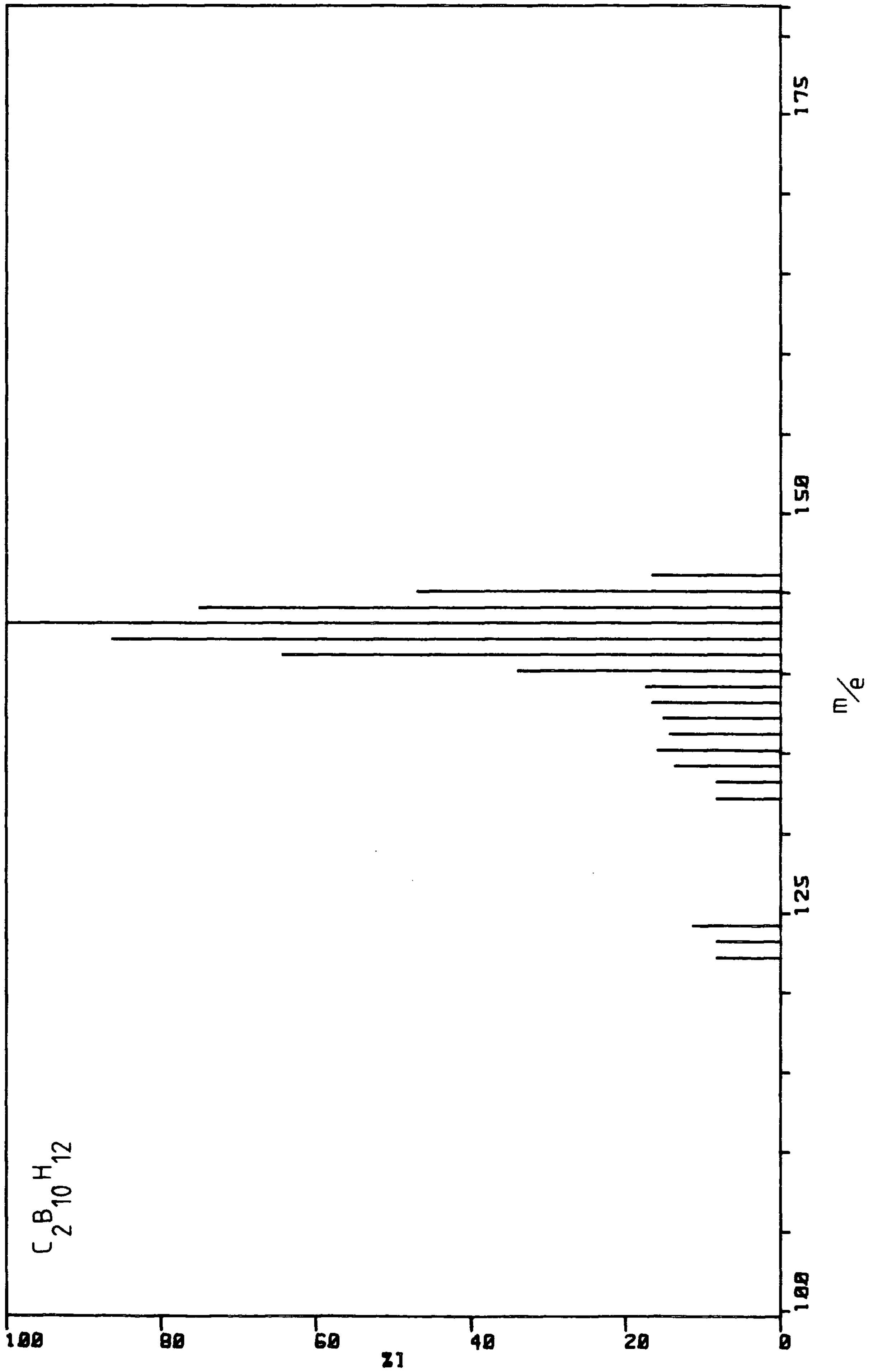


Figure 2.1.4.

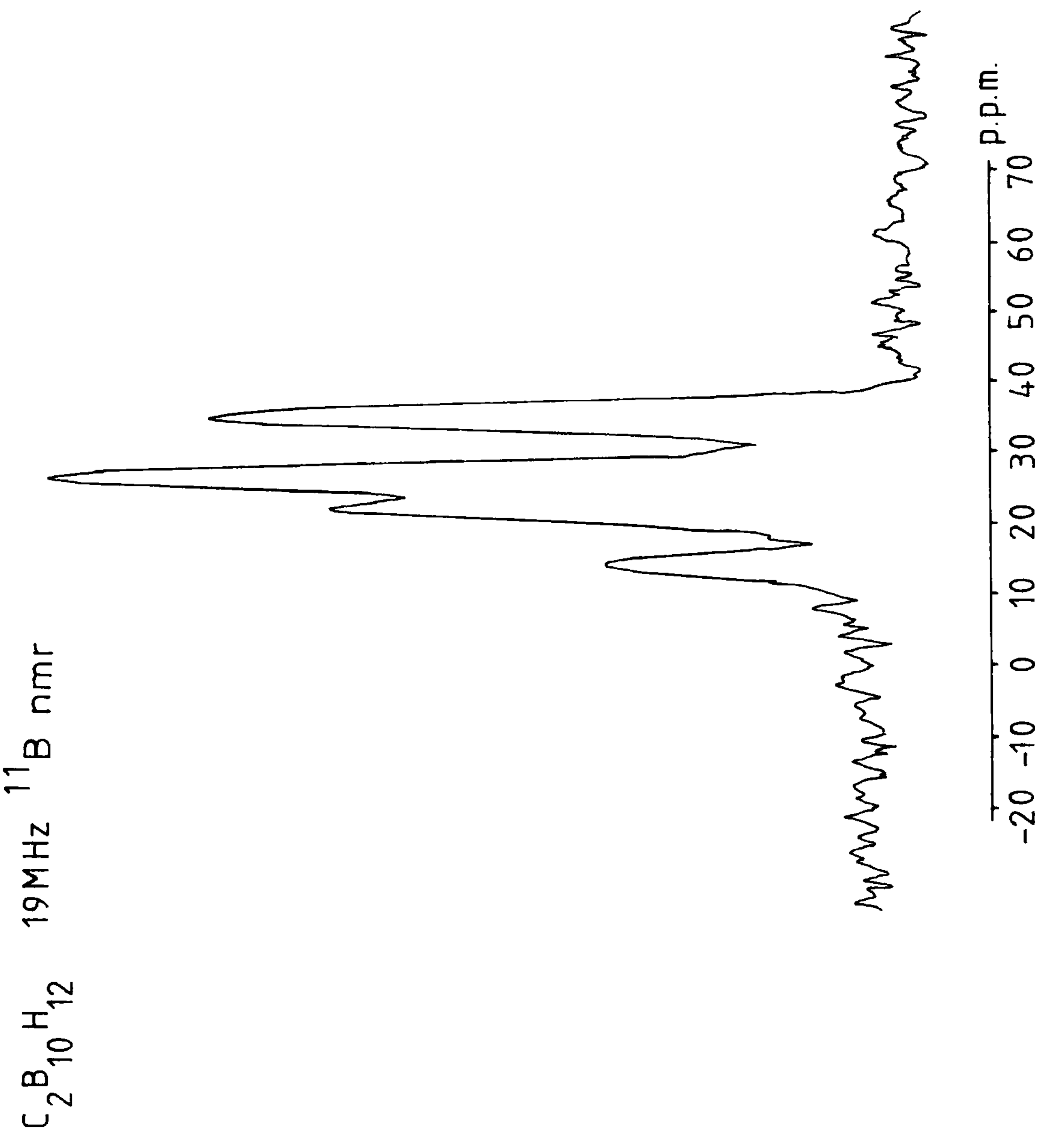


Figure 2.1.5.

thereby saving valuable starting material and giving an effective yield from decaborane of 51.22% in terms of decaborane loss.

The method shows that careful elimination of all traces of diol from 2-butyne-1,4-diacetate is essential to obtain good yields of ortho-carborane.

The work up procedure for the recovery of 1,2-bis-(acetoxymethyl)-o-carborane has been improved to make the method more flexible on different scales.

2.2 Preparation of 1-Methyl Ortho-Carborane

1-Methyl Ortho-Carborane was prepared by the method used by Hawthorne et al. (445)

$$B_{10}H_{12}(MeCN)_2 + HC\equiv CCH_2Br \longrightarrow H\theta CH_2Br + H_2 + 2MeCN$$

$$H\theta CH_2Br + Mg \xrightarrow{Et_2O} H\theta CH_2MgBr$$

$$H\theta CH_2MgBr + H_2O \xrightarrow{Et_2O} H\theta Me + Mg(OH)Br$$

(i) Results

Yield 91% (literature yield 93%)

Melting Point 211° (literature 211 - 213°)

Analysis	C	H	B
% Found	22.58	8.91	69.0
MeθH requires	22.77	8.86	68.37

Mass Spectrum

The mass spectrum showed an M+1 peak at m/e 161, where M = $^{12}C_3\,^{11}B_{10}\,^{1}H_{14}$ with a corresponding carborane isotope pattern from m/e 147 - 160. At lower masses there was a series of less intense peaks due to cage fragmentation with a carborane pattern and a group of half mass peaks at m/e 73.5 - 80 (m/2e 147-160)

I.R.

The infra-red spectrum showed the following peaks:-

max, KBr disc (cm^{-1}) 3058 (s), 2995 (w), 2940,
2868, 2610-2530 (s), 2050 (w), 1990 (w), 1947,
1925, 1848, 1490 (sh), 1475 (sh), 1460 (sh),
1445, 1391, 1228, 1130, 1092,
1085 (sh), 1031 (s), 1015 (s), 995 (s), 975,
935, 917, 883, 787, 769,
720 (s), 675, 653, 498, 462,
433.

The following vibrations can be assigned:- Carboranyl C-H stretch (3058 cm^{-1}); Aliphatic C-H stretch (2940 cm^{-1}); B-H stretch (2610-2530 cm^{-1}); δ as CH_3 (1445 cm^{-1}); δ s CH_3 (1391 cm^{-1}); Cage vibration (720 cm^{-1}).

(ii) Discussion

The method used to prepare 1-methyl ortho carborane was found to work well and gave very high yields of product. No improvements were found to be necessary to the literature method.

CHAPTER 3

COUPLED CARBORANE SYSTEMS

3.1 Introduction

The majority of the published literature concerned with the synthesis of carborane polymers deals with the initial synthesis of a monomer containing a carborane cage. This gives rise to essentially a conventional polymer containing one cage per repeat unit, however this cage is generally sufficient to endow the polymer with improved thermal stability as well as altering other physical properties. These features are attributed to the electron withdrawing power and physical size of the cage.

The literature contains little work concerned with the use of monomers that contain more than one carborane cage. This chapter describes the investigation of methods of bonding two or more carborane cages directly together or through short linking units for use as possible monomer precursors. Clearly there are several ways of coupling carboranes as either the carbon atoms or the boron atoms of the cage may be used. The latter method of coupling is particularly appealing to polymer use as boron coupled carboranes would leave more cage C-H units available for conventional organic reactions.

3.2 CARBON-CARBON COUPLED 1,1'-BIS-CARBORANES

3.2.1 Introduction

Carbon-Carbon coupled 1,1'-bis-carboranes have been reported to be formed by the reaction of bis-(acetonitrile) decaborane with butadiyne in a two-stage reaction. (19)

$$B_{10}H_{12}(MeCN)_2 + HC{\equiv}C-C{\equiv}CH \longrightarrow H\theta-C{\equiv}CH + H_2 + 2MeCN$$

$$H\theta-C{\equiv}CH + B_{10}B_{12}(MeCN)_2 \longrightarrow H\theta-\theta H + H_2 + 2MeCN$$

Zakharkin has reported that bis-carborane may be lithiated and then reacted with copper (II) chloride to give a tetramer. (448)

$$2H\theta-\theta H + 2BuLi \longrightarrow 2H\theta-\theta Li \longrightarrow H\theta-\theta-\theta-\theta H$$

In this section is described the investigation of the formation of bis-carborane from butadiyne in a two step reaction and a single step process.

3.2.2 Preparation of Butadiyne

(i) Experimental

Butadiyne was prepared by the method used by Reppe. (449)

$$\begin{tikzcd}
HOCH_2C{\equiv}CCH_2OH + SOCl_2 \arrow[r, "RT"] & ClCH_2C{\equiv}CCH_2Cl \arrow[d, "40\%\ KOH" right, "75^{\circ}C" ' right] \\
& HC{\equiv}C-C{\equiv}CH
\end{tikzcd}$$

The butadiyne thus prepared was stored at ~ $-25^{\circ}C$ to prevent polymerisation. It should be noted that in the above preparation, the 1,4-dichloro-but-2-yne is distilled prior to the addition of KOH. This distillation must be carried out at 16mm Hg and 65-6°C as the compound explodes above 100°C.

(ii) Results

Yield 21,84% (from 1,4-dichloro-but-2-yne)

3.2.3 Preparation of Bis-carborane by Two stage Synthesis

(i) Experimental

1,3-Butadiyne (0.659g, 13.2 m.moles) was dissolved in 2.1 mls of dry acetonitrile by vacuum transfer and was then slowly added by a micro-syringe over 45 minutes to a refluxing solution of 2.62g (13.2 m.moles) of bis-(acetonitrile) decaborane in 10.5 mls of dry acetonitrile under dry nitrogen. The mixture was refluxed for 4 hours and then the solvent removed under vacuum. The resulting syrup was treated with 3.5 mls of 10% NaOH. The product was extracted with n-pentane dried over anhydrous magnesium sulphate, filtered and evaporated to yield a white solid. The product was purified by vacuum sublimation.

(ii) Results

Melting Point 164°C (biscarborane 309°, Ethynyl-carborane 63-70°)

Mass Spectrum

The mass spectrum showed two distinct species with a carboranyl isotope pattern. The higher of these appeared at m/e 270 - 290 and was attributable to bis-carborane ($^{12}C_4\ ^{11}B_{20}\ ^{1}H_{22}$, m/e 290) whilst the other species had a mass of m/e 171 - 160 and was attributable to ethynyl-o-carborane ($^{12}C_4\ ^{11}B_{10}\ ^{1}H_{12}$, m/e 170).

I.R.

The infra-red spectrum showed the following peaks:-

ν max, KBr disc (cm^{-1}) 3290 (s), 3065 (s), 2640 (sh),
2610 (s) , 2595 (s), 1120 , 1068 , 1015 ,
1002 (sh), 915 , 730 , 720 , 688 ,
663 , 420 , 393.

The following vibrations can be assigned:- Acetylenic C-H stretch (3290 cm^{-1}); Carboranyl C-H stretch (3065 cm^{-1}); B-H stretch (2640-2595 cm^{-1}); Cage vibrations (730, 720 cm^{-1}); =C-H bend (663 cm^{-1}).

(iii) Discussion

The results after the first stage of the reaction show that there is a mixture of two species present namely ethynyl-o-carborane and bis-carborane, this is consistent with the literature results.

(iv) Experimental

0.257g of the mixture from the first stage of the reaction was refluxed for 16 hours with about 7 mls of dry acetonitrile and an excess of bis(acetonitrile) decaborane. The excess acetonitrile was removed under vacuum and the residue stirred overnight with dry methanol to destroy any unreacted bis(acetonitrile) decaborane and the methanol removed under vacuum to yield a white powder which was purified by vacuum sublimation.

(v) Results

Melting Point 307°C (literature 309 - 310°C)

Analysis

	C	H	B
% Found	16.85	7.90	73
HΘ—ΘH requires	16.77	7.69	75.54

Mass Spectrum

The mass spectrum of the product showed only peaks attributable to bis carborane m/e 270 - 290 with a corresponding half mass group at m/e 119 - 145. The large number of half mass peaks suggests that even loss of small fragments from the parent ion still yields relatively stable species. Other low abundance peaks were observed throughout the mass range and were due to cage fragmentation, the largest of these being at m/e 135-145 due to intercage C-C bond cleavage.

I.R.

The infra-red spectrum showed the following peaks:-

ν max, KBr disc (cm^{-1}) 3061 (s), 2680, 2650 (s),
2600 (s), 2580 (s), 2550 (sh), 1265 (w), 1240 (w),
1177, 1118, 1070, 1020, 1004,
940 (w), 920 (w), 910 (w), 785, 730,
716.

The following vibrations could be assigned:- Carboranyl C-H stretch (3061 cm^{-1}); B-H stretch (2680 - 2550 cm^{-1}); Cage vibration (730, 716 cm^{-1}).

(vi) Discussion

The results show that bis-carborane has been successfully prepared by the two step method given in the literature. It is notable that the infra-red spectrum shows a splitting of the cage vibration frequency and this feature is characteristic of C-C bonded bis-carborane.

It was not clear why bis-carborane is prepared by a two stage reaction when the product of the first stage shows that bis-carborane is formed to some amount in the initial reaction. To investigate this further, a single step preparation was attempted.

3.2.4 Preparation of Bis-carborane by a Single Stage Synthesis

(i) Experimental

Butadiyne (0.294g, 5.88 m.moles) was dissolved in 1 ml of dry acetonitrile and added by syringe over 45 minutes to a stirred solution of 2.40g (12.0 m.moles) of bis(acetonitrile) decaborane in 5 mls of dry acetonitrile at -10°C under dry nitrogen. The mixture was then stirred at -10°C for a further 30 minutes and allowed to warm up to room temperature. The reaction mixture was then slowly heated to reflux and maintained at that temperature for 16 hours then allowed to cool. The excess solvent was then removed under vacuum, replaced by 40 mls of dry methanol and stirred overnight. The methanol was then slowly removed under vacuum to yield a white solid which was purified by two vacuum sublimations.

(ii) Results

Yield 0.653g, 19% based on bis(acetonitrile) decaborane
(literature ~ 20% for 2 step process)

Melting Point 310 - 311°C (literature 309 - 310°)

Analysis

	C	H	B
% Found	16.91	7.52	73.5
HΘ—ΘH requires	16.77	7.69	75.54

Mass Spectrum

The mass spectrum of the product was identical to the product of the two stage synthesis.

I.R.

The infra-red spectrum of the product was indistinguishable from that of the two stage synthesis product.

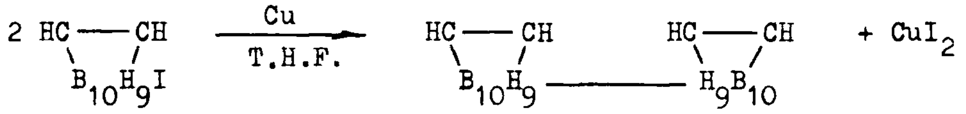
(iii) Discussion

The results of the above reaction have shown that it is unnecessary to adopt a two stage synthesis of bis-carborane as equivalent yields can be achieved by a more convenient single stage method. This seems to be a significant improvement over the literature method.

3.3 BORON-BORON COUPLED BIS-CARBORANES

3.3.1 Introduction

Boron-Boron linked ortho-carborane cages have been reported to be formed by an Ullmann coupling reaction. (155)



Later workers however questioned the accuracy of this reported coupling reaction. (151)

The following section describes investigations carried out to determine whether ortho-carborane cages could be coupled by the reported method.

3.3.2 Preparation of 9-Iodo Ortho Carborane

(i) Experimental

9-Iodo ortho carborane was prepared by the method outlined by Stanko. (121)

$$5\ o\text{-}HCB_{10}H_{10}CH + 2I_2 + IO_3^- \xrightarrow[H_2SO_4,\,100^\circ]{MeCOOH} 5\ o\text{-}HCB_{10}H_9ICH + 3H_2O$$

(ii) Results

Yield 89.6% (Lit 82%, Radio chemical 92-96%)

Analysis

	C	H	B	I
% Found	8.62	4.31	38.7	47.6
$C_2B_{10}H_{11}I$ requires	8.88	4.07	40.04	47.0

Mass Spectrum

A highest mass group of peaks showing a carboranyl isotope pattern was seen at m/e 261 - 272 the highest of these attributable to $^{12}C_2\ ^{11}B_{10}\ ^{1}H_{11}\ ^{127}I$ with a small M + 1 peak at m/e 273. At lower mass was a group of peaks due to loss of iodine from the parent ion, at m/e 130 - 146.

I.R.

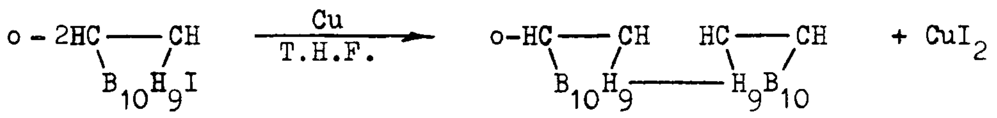
The infra-red spectrum showed the following peaks:-

ν max, KBr disc (cm^{-1}) 3067 (s), 3043 (s) , 2637 (s),
2609 (s), 2580 (s) , 1207 , 1150 (sh) , 1138 ,
1048 (w), 1030 , 1000 , 982 , 970 ,
950 , 925 (sh), 916 (w), 910 (sh) , 890 (w),
853 , 833 (s) , 820 (s), 780 (sh) , 767 ,
757 , 725 (s) , 678 (w), 620 , 593.

The following vibrations can be assigned:- Carboranyl C-H stretch (3067 - 3043 cm^{-1}); B-H stretch (2637 - 2580 cm^{-1}); Cage Vibrations (725 cm^{-1}).

The infra-red spectrum shows some distinct changes from that of ortho-carborane. The two C-H bonds have now become non-equivalent causing splitting of the C-H stretch. Similarly the B-H stretching mode is also split by the iodine atoms influence. There are two groups of new peaks at 853-820 cm^{-1} and 620 cm^{-1}, these are probably B-I stretch and bending vibrations.

3.3.3 Reaction between 9-Iodo-O-Carborane and Cu in T H F



$$o - 2\underset{B_{10}H_9I}{HC\!-\!CH} \xrightarrow[\text{T.H.F.}]{Cu} o\text{-}\underset{B_{10}H_9}{HC\!-\!CH}\!-\!\!-\!\underset{H_9B_{10}}{HC\!-\!CH} + CuI_2$$

(i) Experimental

9-Iodo ortho-carborane (0.4086g, 1.513 m.moles) was dissolved in 4 mls of dry THF and the mixture refluxed for 14 hours with 0.1g of copper powder under dry nitrogen. The THF was then removed under vacuum and the residue treated with aqueous sodium thiosulphate to remove some free iodine that had been formed during the reaction . The solution was filtered through a grade 4 sinter and the solid recovered washed with 10 mls of water and dried over anhydrous calcium chloride.

(ii) Results

Analysis

	C	H	B	I
% Found	8.37	4.46	-	46.4
$C_4B_{20}H_{18}$ requires	17.01	6.38	76.61	0.0
$C_2B_{10}H_9I$ requires	8.88	4.07	40.04	47.0

Mass Spectrum

The mass spectrum of the product did not show a high mass group of peaks due to 9,9'-bis-carborane at m/e 276 - 286. The observed peaks at m/e 261 - 272 and m/e 130 - 146 were assigned to 9-iodo-o-carborane and ortho carborane respectively.

I.R.

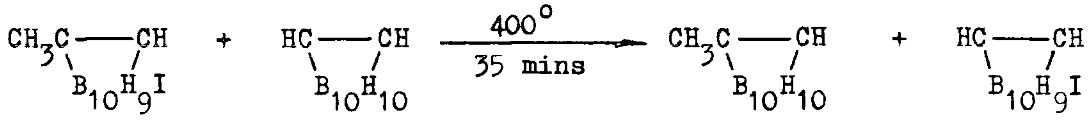
The infra-red spectrum was identical to that of 9-iodo-o-carborane.

(iii) Discussion

The reaction described by Stanko (155) was repeated several times with no evidence of any coupling reaction having taken place. Impurities such as Cu^{2+}, I^- and technical grade copper powder were deliberately introduced into other reactions in case they acted as catalyst yet still no coupling was observed. A more forceful technique was used to try and initiate coupling in which 9-iodo-o-carborane was reacted with copper powder in a sealed ampoule at 300°C. At this temperature it is known that 9-iodo-o-carborane will react with copper (I) chloride to give a 9-chloro-derivative.

$$\mathrm{H\underline{CB_{10}H_9IC}H} + \mathrm{CuCl} \xrightarrow{250 - 350^{\circ}\mathrm{C}} \mathrm{H\underline{CB_{10}H_9ClC}H} + \mathrm{CuI}$$

Intermolecular iodine exchange has been shown to take place at elevated temperature by Zakharkin et al.



thus an Ullmann coupling reaction may be expected to take place at these temperatures.

3.3.4 Reaction between 9-Iodo-o-carborane and Cu Powder at High Temperature

(i) Experimental

9-Iodo ortho carborane (0.863, 3.20 m.moles) and copper powder (0.5g) were intimately mixed and sealed at atmospheric pressure under dry nitrogen in a 1cm wide silica ampoule. The ampoule was then placed inside a steel tube with one end sealed and glass wool packed tightly around the ampoule. A 0-400°C thermometer was then pushed down between the steel tube and the ampoule and the whole assembly inserted into an isojacket heater. A temperature controller was then connected to the thermometer and the power supply to the isojacket adjusted such that it would keep the temperature inside the jacket at 300°C ± 5°C. The isojacket was switched on and the system checked for correct control of the temperature at 300°C and then left for 12 hours behind protective screens, followed by a 40 minute hold at 400°C. The apparatus was then switched off, allowed to cool to room temperature the ampoule removed and opened in a dry nitrogen glove box. The soluble contents were extracted with 10 mls of dry n-pentane and worked up to yield a white powder. The residue in the ampoule was extracted as a slurry in n-pentane and dried to yield a copper coloured powder.

(ii) Results

Analysis

(white powder)	C	H	B	I
% Found	8.43	4.26	-	47.3
$C_4B_{20}H_{18}$ required	17.01	6.38	76.61	0.0

	C	H	B	I
$C_2B_{10}H_9I$ requires	8.88	4.07	40.04	47.0

(Copper coloured powder)

	Cu	I
% Found	99.93	0

Mass Spectrum

The mass spectrum of the white solid showed only peaks consistent with 9-iodo-o-carborane.

I.R.

The infra-red spectrum of the white powder was identical to 9-Iodo-ortho carborane.

(iii) Discussion

Clearly the high temperature reaction of 9-iodo-o-carborane with copper powder was unsuccessful. It appeared that copper was not a reactive enough metal to bring about B-B carboranyl coupling under the conditions used and so a further reaction was attempted in which lithium amalgam was used in place of copper.

3.3.5 Reaction between 9-Iodo-o-carborane and Lithium Amalgam

(i) Experimental

3g of lithium metal was cut into small pieces and slowly added to about 10 mls of redistilled mercury under dry nitrogen with stirring. A solution of 9-iodo-o-carborane (0.742g, 2.75 m.moles) in 10 mls of dry THF was then added to the amalgam and the mixture stirred under dry nitrogen for 3 days. The organic layer was then syringed off and the THF removed under vacuum to yield a white solid.

(ii) Results

Analysis

	C	H	B	I
% Found	8.58	3.82	-	47.41

		C	H	B	I
$C_4B_{20}H_{18}$	requires	17.01	6.38	76.61	0.0
$C_2B_{10}H_9I$	requires	8.88	4.07	40.04	47.0

Mass Spectrum

The mass spectrum only showed peaks attributable to 9-iodo-o-carborane.

I.R.

The infra-red spectrum was identical to that of 9-iodo-o-carborane.

(iii) Discussion

Like other workers in the field of carboranes, I have been unsuccessful in repeating the Ullmann coupling reaction reported by Stanko (155). The evidence suggests that this reaction does not take place under normal circumstances, and I can only conclude that the conditions used by Stanko differed from those used by other workers, possibly in the form of a catalytic amount of some trace impurity.

3.4 ALKYL CHAIN COUPLED CARBORANES

3.4.1 Introduction

This section describes investigations carried out to determine whether two or more carborane cages can be coupled via short alkyl chains by the reaction of lithiated carboranes with primary alkyl dibromides. Meta-carborane was used initially instead of ortho-carborane to reduce the possibility of exocyclic ring formation. (see Chapter 1.3) Primary alkyl bromides were used as primary alkyl chlorides and secondary and tertiary alkyl halides are unreactive towards lithiated carboranes.

3.4.2 Reaction between Dilithio-m-Carborane and Dibromo-ethane

(i) Experimental

$$\mathrm{Li\theta'Li} + \mathrm{BrCH_2CH_2Br} \xrightarrow{\text{ether}} \left[\theta'\text{-CH}_2\text{-CH}_2\right]_n + 2n\mathrm{LiBr}$$

To 20 mls of dry diethyl ether was added 0.92g (6.385 m.moles) of m-carborane with stirring under dry nitrogen. The solution was cooled to $0^{\circ}C$ and 7.74 mls (12.77 m.moles) of 1.65M n-butyl lithium in hexane added by syringe. The mixture was stirred for 1 hour at $0^{\circ}C$ then allowed to warm to room temperature and left stirring to digest overnight under dry nitrogen.

In a second flask, a solution of 0.55 mls (6.385 m.moles) of dibromo-ethane in 10 mls dry diethyl ether was prepared and added with stirring over 30 minutes to the dilithio-carborane, producing a clear yellow solution. Stirring was continued for 2-3 hours, the solvent replaced by 30 mls of dry 40-60° pet. ether and refluxed for 1 hour. The mixture was filtered through a grade 4 sinter to remove a precipitate which was washed with 20 mls of dry pet. ether and dried. The solvent was then removed from the filtrate under vacuum to give an opaque yellow oil.

(ii) Results

Analysis

(Solid)

	Li	Br
% Found	7.63	92.8
LiBr requires	7.99	92.01

(Yellow oil)

	C	H	B
% Found	21.04	7.48	67
$\{\theta'\text{-}CH_2CH_2\}_n$ requires	28.2	8.2	63.5

Although these figures seem fairly close to those required it must be remembered that with the difference in MWt between a cage and $-CH_2-CH_2-$ units, a small difference in percentage can represent a large change in the ratio between the number of carborane and $-CH_2-CH_2-$ moles. Working from the carbon and hydrogen figures it can be shown that there are approximately 3 moles of carborane for every $-CH_2-CH_2-$ mole in the product. Clearly reaction had not gone to completion.

Mass Spectrum

The mass spectrum showed a number of peaks with carboranyl isotope patterns. These were identified as m/e 254 - 257 $^+\theta'CH_2CH_2Br$; m/e 226 - 216 $^+\theta'Br$; m/e 201 - 194 $CH_2CH_2\theta'CH_2CH_2^+$; m/e 173 - 163 $^+\theta'CH_2CH_2$; m/e 145 - 135 , $^+\theta'$.

These results show that the reaction has not gone to completion although it is interesting that despite the presence of peaks for $\overset{+}{C}H_2CH_2\theta'CH_2CH_2$ there were none for the brominated species. This suggests that some short chains of $\{\theta\text{-}CH_2CH_2\}_n$ may have been formed.

I.R.

The infra-red spectrum showed the following bands:-

ν max (cm^{-1}) 3060, 3023 (w), 2953, 2924, 2870, 2590 (s), 1635 (w), 1603 (w), 1493, 1450, 1408, 1386, 1305, 1259 (s), 1200 (w), 1160, 1132, 1085 (sh), 1068 (s), 1023 (s), 990 (s), 973, 935, 858, 842, 803 (s), 727 (s), 693 (w), 658 (w).

The following vibrations could be assigned:- Carboranyl C-H stretch (3060 cm^{-1}); aliphatic C-H stretch (2953 - 2870 cm^{-1}); B-H stretch (2590 cm^{-1}); δ_s CH_2 scissoring (1493 - 1408 cm^{-1}); cage vibrations (727 cm^{-1}).

In addition to these peaks there was at 1259 cm^{-1} a strong peak which is characteristic of meta-carborane. This is most likely a C-B-C stretch mode.

(iii) Discussion

Clearly these results did not give a clear indication of whether or not oligomeric or polymeric material had been prepared. The physical properties of the product suggested that some polymeric material might have been formed as low MWt. polymers are often liquids.

The crucial question was, had $-CH_2CH_2-$ bridges been formed between two carborane cages. To investigate this, the reaction was repeated using 1-methyl, 2-lithio-o-carborane and dibromo ethane so that any bridging of cages would lead to a fixed compound.

3.4.3 Reaction between 1-Methyl, 2-lithio-o-carborane and dibromo ethane

(i) Experimental

$$2\,Me\theta Li + BrCH_2CH_2Br \longrightarrow Me\theta{-}CH_2{-}CH_2{-}\theta Me + 2LiBr$$

1-Methyl-o-carborane (1.36g; 8.61 m.moles) was dissolved in 30 mls of dry hexane with stirring under dry nitrogen. To this was added 5.22 mls

(8.61 m.moles) of 1.65M n-butyl lithium in hexane and the mixture stirred for 2 hours at room temperature.

A solution of 0.37 mls of dibromo ethane (4.305 m.moles) and 10 mls of dry hexane was added to the lithio, methyl-o-carborane and stirred overnight at room temperature under dry nitrogen. A white precipitate was then removed on a grade 4 sinter, washed with 10 mls of dry hexane and dried under vacuum. The volume of the filtrate was then reduced to about 10 mls and the concentrated solution placed in a fridge overnight. The resulting oil was removed by syringe and the excess solvent removed under vacuum to give a very viscous yellow material.

(ii) Results

Analysis

(Precipitate)

	Li	Br
% Found	7.71	91.7
LiBr requires	7.99	92.01

(Yellow oil)

	C	H	B	Br
% Found	23.34	9.56	37.9	29.3
$\mathrm{Me\theta CH_2CH_2\theta Me}$ requires	21.04	8.77	63.2	0
$\mathrm{Me\theta CH_2CH_2Br}$ requires	22.64	6.41	40.79	30.15

Mass Spectrum

The mass spectrum showed no evidence for the formation of a bridged species, and all the species showing a carboranyl isotope pattern could be identified as follows:- m/e 268 - 258, $\mathrm{Me\theta CH_2CH_2Br}$; m/e 187 - 177, $\mathrm{Me\theta CH_2CH_2^+}$; m/e 173 - 163 $\mathrm{Me\theta CH_2^+}$; and m/e 160 - 150, $\mathrm{Me\theta^+}$.

I.R.

The infra-red spectrum showed the following peaks:-

ν max (cm^{-1}) 3062, 2946, 2870, 2595,
1445, 1390, 1262 (w), 1137, 1095,
1037, 1019, 1000, 940, 920,
787, 721 (s), 676, 656.

The following vibrations could be assigned:- Carboranyl C-H stretch (3062 cm^{-1}); Aliphatic C-H stretch (2946-2870 cm^{-1}); B-H stretch (2595 cm^{-1}); δ_s C-H bend or scissoring (1445-1390 cm^{-1}); cage vibrations (721 cm^{-1}).

Unfortunately, whilst the presence of the methyl group on the carborane simplifies the chemistry, it complicates the infra-red spectrum because it absorbs at a similar frequency to $-CH_2$ groups from the dibromo ethane. As a result, little difference can be seen between the product spectrum and that of 1-methyl-o-carborane except that the intensity of the B-H stretch is reduced.

(iii) Discussion

Whilst the infra-red is not very helpful, the elemental analysis and mass spectrum show that the bridged compound has not been synthesised, instead, 1-methyl , 2-bromoethyl-o-carborane is the major product.

In case the chain length was the factor preventing a second carborane substitution for bromine, the reaction was repeated using 1,3-dibromopropane to try and reduce the possible influence of the first carborane cage on the second substitution.

The reaction was divided into two parts so that different aspects of the substitution could be studied in one experiment. Firstly dilithio-m-carborane was reacted with 2 mole equivalents of 1,3-dibromopropane to see if m-carborane could be disubstituted by this technique. Secondly the product was reacted with 1-methyl,2-lithio-o-carborane to see if cage-cage chains could be formed.

3.4.4 Two Stage Alkyl Chain Coupling Reaction

(i) Experimental

(a) Reaction between Dilithio-m-Carborane and 1,3-Dibromopropane

$$Li\theta'Li + 2Br(CH_2)_3Br \longrightarrow Br(CH_2)_3\theta'(CH_2)_3Br + 2LiBr$$

Meta-carborane (0.69g, 4.79 m.mole) was dissolved in 20 mls of dry diethyl ether with stirring under dry nitrogen. To this was added 5.81 mls (9.58 m.moles) of 1.65M n-butyl lithium in hexane and the mixture left stirring under nitrogen overnight to digest.

A solution of 0.952 mls (9.58 m.moles) of 1,3-dibromopropane in 10 mls of dry diethyl ether was then added to the dilithio-m-carborane solution and the mixture stirred for 2 hours, then refluxed for 2 hours.

(b) Reaction of the Product of (a) with 1-Methyl,2-lithio-o-carborane

$$R\theta'CH_2CH_2Br + Li\theta Me \longrightarrow R\theta'CH_2CH_2\theta Me + LiBr$$

$R = Li$ or $BrCH_2CH_2-$.

1-Methyl-o-carborane (1.52g, 9.58 m.moles) was dissolved in 50 mls of dry diethyl ether with stirring under dry nitrogen. To the solution was added 5.81 mls (9.58 m.moles) of n-butyl lithium in hexane and the mixture stirred for 2 hours. This lithiated methyl-o-carborane was then added dropwise to the solution from the previous reaction. The reactants were refluxed for 3 hours then stirred overnight at room temperature. A precipitate was then removed on a grade 4 sinter, washed, and dried under vacuum. The solvent was removed from the filtrate under vacuum yielding an orange oil from which no crystals could be recovered.

(ii) Results

Analysis

(Precipitate)	Li	Br
% Found	7.61	91.9
LiBr requires	7.99	92.01

(Filtrate)

	C	H	B	Br
% Found	26.72	7.61	52	12.8
$\mathrm{Me\theta(CH_2)_3Br}$ requires	25.8	6.81	38.7	28.6
$\mathrm{Me\theta(CH_2)_3\theta(CH_2)_3Br}$ requires	28.5	7.56	46.7	17.25

Mass Spectrum

The mass spectrum showed a parent ion peak with a carborane isotope pattern at m/e 282. This is attributable to the species $\mathrm{Me\theta(CH_2)_3\ Br}$. Only two other carborane patterns were visible in the spectrum, m/e 201 - 190, $\mathrm{Me\theta(CH_2)_3}^+$; and m/e 187 - 177 $^+\mathrm{\theta(CH_2)_3}$ or $\mathrm{Me\theta CH_2CH_2}^+$.

I.R.

The infra-red spectrum showed very broad bands from which no structural information could be deduced.

(iii) Discussion

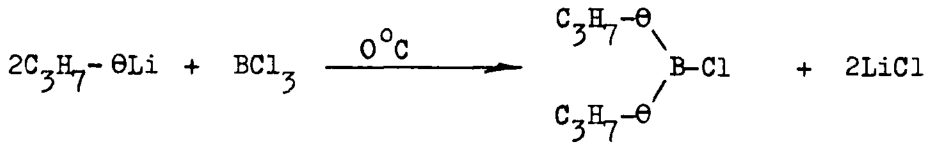
The results from this experiment show no conclusive evidence of cage-alkyl-cage coupling. The presence of bromine in the filtrate indicates that the coupling reaction has not gone to completion, but the ratio of the boron:bromine found (30:1) does suggest that some coupling has taken place.

Unfortunately, repeated attempts to promote crystal formation in the filtrate were unsuccessful and fractional distillation caused the products to decompose. Without further data, no firm conclusions can be drawn as to the nature of the reaction.

3.5 BORON-COUPLED CARBORANES

3.5.1 Introduction

Work on the coupling of 2 or more carborane cages by a boron atom was investigated for the potential of such a system as a provider of possible polymer precursors. The field has attracted little published work although Mikhailov (7) has prepared a di-(1-propyl-o-carboranyl) boron chloride species by the reaction of 1-propyl,2-lithio-o-carborane with boron trichloride in benzene/hexane at 0°C.



$$2C_3H_7\text{-}\theta Li + BCl_3 \xrightarrow{0^oC} (C_3H_7\text{-}\theta)_2B\text{-}Cl + 2LiCl$$

This compound raises the question of whether it is the steric hindrance of the carborane cage or the propyl groups which do not allow the third carboranyl substitution. If the carborane cages could be grouped around a central atom as with phosphorus (236) (See Chapter 1.12), using a monolithio carborane then possibly the use of a dilithio carborane could give rise to a cross linked polymeric material containing a very high percentage of carborane.

Initially the work was carried out using 1-lithio-o-carborane in order to minimize the steric effects of an alkyl substituent on the second carboranyl carbon atom.

3.5.2 Reaction of 1-Lithio-o-carborane with Boron Trichloride

(i) Experimental

1.165g of o-carborane (8.08 m.moles) was dissolved in 50 mls of dry toluene and cooled to 0°C. To this solution was added 4.9 mls of 1.65M n-butyl lithium in n-pentane and the mixture stirred for 2 hours. The resulting solution was then cooled to liquid nitrogen temperature, connected to a vacuum line and the flask evacuated. 2.84g of freshly distilled boron trichloride (2.1 mls) was then slowly condensed onto the frozen lithio-o-carborane solution, the flask let down to dry nitrogen and allowed to warm up to dry ice/acetone temperature with stirring. The reaction mixture was held at this temperature for 3 hours and then slowly warmed to room temperature and left stirring overnight. A whitish precipitate was clearly visible in the reaction flask and this was removed on a grade 4 sinter under dry nitrogen. The filtrate was gently warmed under vacuum to remove the solvent and this yielded a medium brown viscous liquid.

(ii) Results

Analysis

(Precipitate)	Li	Cl
% Found	16.1	82.8
LiCl requires	16.37	83.63

(Filtrate)	C	H	B	Cl
% Found	15.5	7.1	71.9	4.0
$(H\theta)_3B$ requires	16.36	7.50	76.14	0

Mass Spectrum

The mass spectrum of the filtrate showed a series of clearly carboranyl isotope patterns up to a parent ion at m/e 511. The spectrum (Figure 3.5.1) is quite complex and none of the expected m/e values for possible products fit either parent ion or breakdown pattern.

I.R.

The filtrate gave a very poorly resolved spectrum with only broad C-H stretch and B-H stretch peaks being dicipherable.

(iii) Discussion

Attempts to purify the filtrate by crystallisation failed due to its almost polymeric physical properties. Fractional distillation only caused

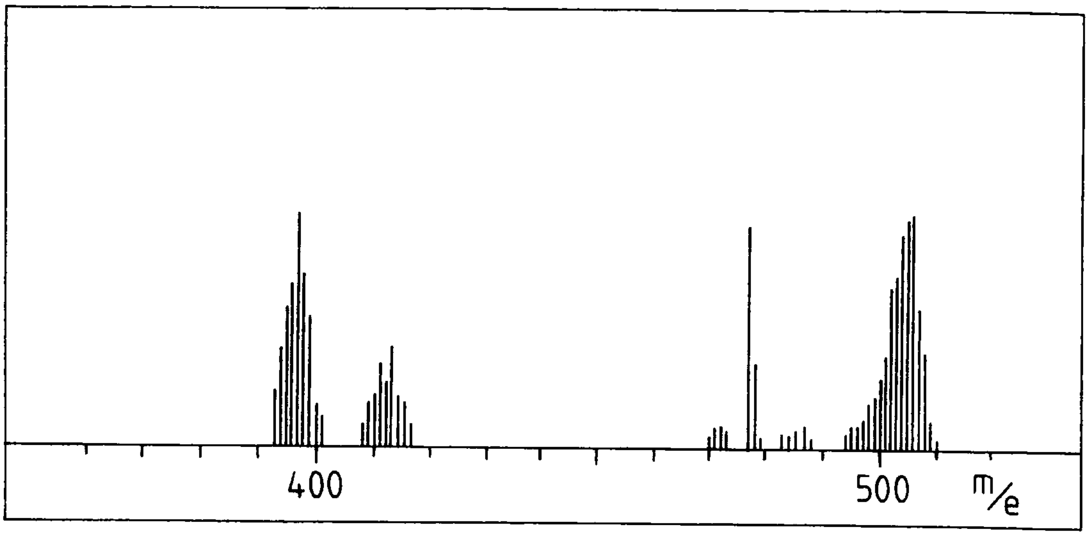


Figure 3.5.1.

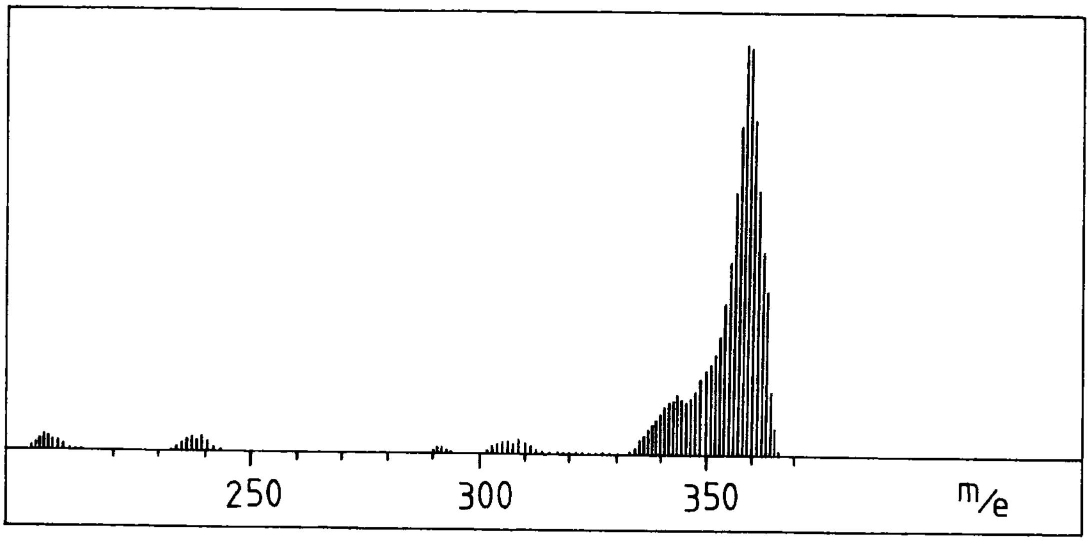


Figure 3.5.2.

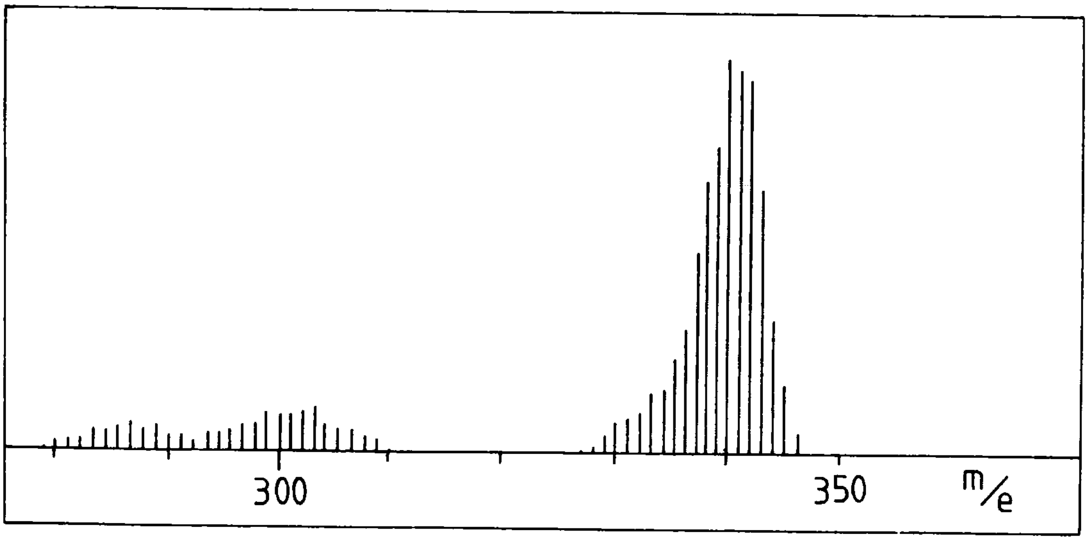


Figure 3.5.3.

degradation of the product to parent carborane.

The brown viscous product is most likely a polymeric substance formed by the presence of small amounts of dilithio-o-carborane as a result of localised excesses of n-butyl lithium during the preparation of the mono-lithiated compound. The presence of the dilithio-o-carborane would cause the formation of higher molecular weight species than the expected parent ion at m/e 446 by reaction with partially reacted and unreacted boron trichloride.

The presence of an involatile and thermally unstable product must cause one to view mass spectral data as not necessarily being representative of the true product.

In the light of the results obtained from the above reaction of lithio-o-carborane with boron trichloride, it was decided to restrict the lithiation of the carborane cage to a single carbon atom by using 1-methyl-o-carborane. It was hoped that the methyl group would have minimal steric hindrance in comparison to a propyl group and so would still allow tight packing of carborane cages around a single boron atom.

3.5.3 Reaction of 1-Methyl,2-Lithio-O-Carborane and Boron Trichloride

(i) Experimental

1-Methyl-o-carborane (1.56g, 9.87 m.moles) was added to a 100 ml two necked flask which was then evacuated and let down to dry nitrogen. The solid was dissolved in 30 mls of dry benzene and 5.98 mls (9.87 m.moles) of 1.65M n-butyl lithium in pentane added by syringe at room temperature. The reaction mixture was stirred for 3 hours to digest, then the flask was cooled in liquid nitrogen and 0.28 mls (3.29 m.moles) of freshly distilled boron trichloride was added using a previously cooled 1 ml glass syringe. The mixture was allowed to warm to room temperature over the course of 1 hour then left stirring overnight under dry nitrogen.

The reaction mixture was then filtered through a grade 3 sinter and the solid recovered washed with 10 mls of dry benzene and dried under vacuum. The benzene was removed from the filtrate by pumping leaving a pale brown viscous liquid which formed crystals on standing overnight.

(ii) Results

Analysis

(Filtrate)

	C	H	B	Cl
% Found	21.6	60.1	7.9	7.4
$(Me\theta)_3B$ requires	22.4	69.5	8.09	0
$(Me\theta)_2BCl$ requires	19.97	62.97	7.21	9.83

(Precipitate)

	Li	Cl
% Found	15.5	79.9
LiCl requires	16.37	83.63

Mass Spectrum

As with the previous reaction, the mass spectrum showed a large number of peaks with an apparent parent ion at m/e 387 - 401. However in some scans there appeared a higher group of peaks at m/e ~ 464 - 471. Neither these nor the lower mass peaks in the spectrum could be interpreted in terms of expected carboranyl species although carboranyl isotope patterns were clearly visible in many groups of peaks. Despite their high mass, they only contained a single carboranyl species, as shown by their narrow mass range ~ 11.

At higher temperatures the mass spectrum of the product changed dramatically to give three main groups of peaks with carboranyl isotope patterns. The parent ion peak was observed at m/e 366. The group of peaks ranged from m/e 329 - 366 although there was definite shoulder at about m/e 340 suggesting that possibly two groups of peaks are overlapping. If this is the case then the group culminating in the parent ion contains two carboranyl units. This would suggest that the parent species is $(\mathrm{Me\Theta})_2\mathrm{BCl}$ m/e 366. (Figure 3.5.2)

The two remaining lower mass groups of peaks were seen at m/e 164 - 183 and m/e 150 - 161. The former was due to doubly charged parent ion whilst the latter was due to 1-methyl-o-carborane.

The fact that the parent ion peaks were superimposed on a second species suggested that some $(\mathrm{Me\Theta})_2\mathrm{BOH}$ was present m/e 325 - 346. This would have been formed by the brief unavoidable contact with air on insertion of the sample into the mass spectrometer. To confirm this, the sample was removed and given a longer exposure to air, replaced and the mass spectrum rerun. The parent ion was now at m/e 346 with the range in value for the top group of peaks from 326 - 346. (Figure 3.5.3) Below this was a group at m/e 164 - 172 due to doubly charged parent ion showing half masses and a group at m/e 150 - 161 due to methyl carborane. Analysis of the air exposed sample showed there to be no chlorine present.

I.R.

The infra-red spectrum of the crystalline product showed the following peaks.

ν max.(nujol mull) $\mathrm{cm^{-1}}$ 2960-2850 (s) 2640 (s , 2590 (s) ,
1950 (w,br), 1855 (w,br), 1455 (s) , 1395 (sh), 1390
- 1364 (s) , 1300 , 1210 (sh), 1175 (s) , 1174 (s) ,
1135 (s) , 1071 , 1028 , 963 (sh), 955 ,
935 (sh) , 869 (w) , 839 , 797 , 730 ,
710 , 680 , 650 (w) , 570 , 550

The following vibrations could be assigned:- C-H stretch (2960 - 2850 $\mathrm{cm^{-1}}$); B-H stretch (2590 $\mathrm{cm^{-1}}$); C-B stretch (1210 - 1135 $\mathrm{cm^{-1}}$); cage vibrations (797 - 650 $\mathrm{cm^{-1}}$)

There is surprisingly no clear evidence in the i.r. for a B-Cl stretch mode. In compounds such as diphenyl boron chloride and phenyl boron dichloride these B-Cl stretch modes are evident in the region 880 - 950 cm^{-1} and are strong, sharp absorptions. In the product's spectrum there is a medium-broad absorption (963 - 935 cm^{-1}) which falls in this region although 1-methyl-o-carborane also has weak to medium absorptions in this area which complicates the spectrum. There is an absorption at 839 cm^{-1} in the product which has no equivalent in the 1-methyl-o-carborane i.r.

On exposure of the product to air and rerunning of the i.r. there is only one noticeable change in the spectrum, with the appearance of a strong absorption at 3540 cm^{-1}. This is most likely due to BO-H stretch.

(iii) Discussion

The reaction to produce a tri-carboranyl boron species appears to have been unsuccessful, with the evidence pointing towards the formation of dicarboranyl boron chloride. This previously unreported compound whilst not being able to react with a third lithio, methyl-o-carborane is clearly capable of reacting with water to give dicarboranyl boron hydroxide showing that B-Cl bond is still reactive. Steric factors alone seem to prevent the third boron-carborane bond formation.

As with the previous reaction using 1-lithio-o-carborane attempts to further purify the product by distillation, sublimation or fractional crystallisation were unsuccessful. The first two techniques led to decomposition of the product with the recovery of only 1-methyl-o-carborane. The product could only be crystallised in the presence of a viscous brown material and could not be preferentially redissolved in other solvents.

In the above reaction, the proportion of this viscous material was low and did not appear to affect the results much. However in other reactions using slightly different conditions or solvents, the proportion of the viscous material increased and varied from reaction to reaction. The nature of this material is unknown although the low temperature mass spectrum indicated that only a single carborane unit was present.

The results from the reaction of boron trichloride with 1-lithio,2-methyl-o-carborane indicate that under the conditions used, it is only possible to bond two carborane cages around a single boron atom. To investigate the steric effects in greater depth, reactions using 1-lithio,2-methyl-o-carborane and diphenyl boron chloride and phenyl boron dichloride were carried out. These would show if a phenyl group, although of comparable size to the cross-section of a cage, could relieve steric effects by rotation out of the cage-boron-cage plane.

3.5.4 Reaction of Diphenyl Boron Chloride with 1-Methyl,2-Lithio-O-Carborane

(i) Experimental

$$Ph_2BCl \; + \; Me\theta Li \xrightarrow{\text{Benzene}} Ph_2B\theta Me \; + \; LiCl$$

1-Methyl-o-carborane (2.12g, 13.4 m.moles) was added to a 100 ml two necked, round bottomed flask and purged for 30 minutes with dry nitrogen. The solid was dissolved with stirring in 30 mls of dry benzene and 8.12 mls (13.4 m.moles) of 1.65M n-butyl lithium in hexane added. The reaction mixture was stirred for 2 hours, cooled to $0^{o}C$ in an ice bath and 1.72 mls (13.4 m.moles) of freshly vacuum distilled diphenyl boron chloride added by syringe. Stirring was continued at $0^{o}C$ for a further 5 - 6 hours and then warmed to room temperature and left stirring under dry nitrogen overnight.

The reaction mixture was then refluxed in a water bath for 2 hours and filtered under nitrogen through a grade 4 sinter. The solid collected was washed with 10 mls of dry benzene and pumped dry.

The solvent was removed from the filtrate to leave a clear, pale yellow, viscous liquid, which could not be crystallised at room temperature.

(ii) Results

Analysis

(Filtrate)

	C	H	B	Cl
% Found	50.2	8.06	35 ± 3	0
$Ph_2B\Theta Me$ requires	55.92	7.14	36.9	0

(Solid)

	Li	Cl
% Found	12.57	67.9
LiCl requires	16.37	83.63

The results from the filtrate suggest that the expected compound had been prepared. The carbon analysis was found to be low due to the formation of boron carbide in the elemental analysis equipment. The boron result is given as an average of several results as the compound would only decompose violently on careful treatment with slightly diluted nitric acid to obtain a solution.

Mass Spectrum

As with the other reactions with boron chlorides, the mass spectrum of the product was extremely complicated. The parent ion was expected at m/e 324 for $Ph_2B\Theta Me$ and a carboranyl species was seen at this mass. Logical breakdown products of this are $\overset{+}{PhB\Theta Me}$ (m/e 247) and Ph_2B^+ (m/e 165), both of these masses corresponded to peaks in the spectrum with related carboranyl pattern. However other higher mass species showing a carborane pattern were visible at m/e 358, 398 with weaker groups at m/e 436, 473 and 518. No logical interpretation of these higher masses could be found. It was thought that some of these species could have been formed in the mass spectrometer, as several of the species corresponded to peaks seen in the low temperature mass spectrum of $(Me\Theta)_2BCl$; these species also did not fit any logical explanation.

Raising the scan temperature failed to resolve the spectrum unlike the previous experiment as the product decomposed at similar temperatures, to give methyl carborane and diphenyl boron ions.

I.R.

A contact film infra red scan showed the following peaks:-

ν max. (cm^{-1}) 3055 , 2930 , 2573 (s) , 1594 ,
1477 (sh), 1435 (s) , 1388 , 1263 (s) , 1185 (w) ,
1135 (w) , 1098 (w) , 1070 (sh), 1030 (sh), 1019 (w) ,
998 (w) , 920 (sh), 892 (w) , 787 (w) , 770 ,
727 , 698 (s) , 677 , 638 , 616 (w)
602 (w) , 553 (w).

The following vibrations could be assigned, Aromatic C-H stretch (3055 cm^{-1}); aliphatic C-H stretch (2930 cm^{-1}); B-H stretch (2573 cm^{-1}); C=C stretch (1594); CH_3 δ as (1435 cm^{-1}); CH_3 δ s (1388 cm^{-1}); B-C stretch (1263 cm^{-1}).

The region 600-800 cm^{-1} showed a number of vibrations which appeared to be a mixture of cage vibrations and aromatic C-H o.o.p. deformations.

The spectrum of the product indicates that it contains a methyl carboranyl unit, phenyl units and at least one carbon-boron bond. It contains elements that closely resemble parts of the spectra of methyl carborane and diphenyl boron chloride whilst not containing every element of each. Notably no B-Cl stretch was seen in the product.

(iii) Discussion

The evidence from the elemental analysis and infra red indicate that the desired product $Ph_2B\Theta Me$ had been successfully prepared. Whilst the mass spectrum confused the results it did show peaks corresponding to the parent ion and expected breakdown species. It is interesting to note that the other mass spectral species to which a structure could not be allocated, also appeared in the mass spectrum from $(Me\theta)_2BCl$.

3.5.5 Reaction of Phenyl Boron Dichloride with Lithio Methyl-O-Carborane

(i) Experimental

$$PhBCl_2 + 2Me\theta Li \longrightarrow PhB(\theta Me)_2 + 2LiCl$$

Methyl o-carborane (2.07g; 13.1 m.moles) was added to a 100 ml, two necked round bottomed flask, and purged with dry nitrogen for 30 minutes. The solid was dissolved with stirring in 30 mls of dry benzene, and 7.94 mls (13.1 m.moles) of 1.65M n-butyl lithium in hexane added. The reaction mixture was stirred under dry nitrogen for 2 hours, cooled to 0°C and 0.87 mls (6.55 m.moles) of freshly vacuum distilled phenyl boron dichloride added by syringe. The reaction was stirred at 0°C for 6 hours, warmed to room temperature and stirred overnight under dry nitrogen.

The reactants were refluxed in a hot water bath for 2 hours and then filtered under nitrogen through a grade 4 sinter. The solid removed was washed with 10 mls of dry benzene and pumped dry.

The solvent was removed from the filtrate by pumping to yield an opaque brown viscous liquid which could not be crystallised at room temperature.

(ii) Results

Analysis

(Filtrate)

	C	H	B	Cl
% Found	37.23	8.70	53.2	0
$PhB(\theta Me)_2$ requires	35.82	7.72	56.46	0

(Solid)

	Li	Cl
% Found	8.64	44.2
LiCl requires	16.37	83.63

The analysis of the product indicates that it is probably the expected compound $PhB(\theta Me)_2$. The solid material however although containing lithium and chlorine in 1:1 ratio, consisted of some viscous material that seemed to be adsorbed onto the surface of the lithium chloride. Only repeated benzene washing removed it and on removal of the solvent it analysed as $PhB(\theta Me)_2$.

Mass Spectrum

The mass spectrum again was unhelpful. As with the boron trichloride and diphenyl boron chloride reactions carboranyl species were seen at about m/e 470, 430, 400 and 323. No evidence was found for the species $PhB(\theta Me)_2$ or its expected decomposition products except for methyl-o-carborane.

The fact that three different reactions have produced the same mass spectra at low temperature whilst analysis shows great differences in their compositions suggests that these species are created in the mass spectrometer.

At elevated scan temperature the product decomposed with only methyl o-carborane and phenyl peaks being observed.

I.R.

A contact film infra red scan showed the following peaks:-

ν max. (cm^{-1}) 3084 , 3067 , 3054 (w) , 3030 ,
2956 , 2925 , 2870 , 2580 (s) , 1958 (w) ,
1816 (w) , 1600 , 1478 , 1440 , 1422 ,
1411 (sh), 1386 , 1365 (sh), 1350 , 1332 (sh),
1253 (sh), 1224 , 1190 , 1150 , 1120 (w) ,

1034 , 996 (w) , 940 , 920 , 854 (w) ,
800 , 728 , 710 , 700 (sh), 687 (s) ,
590 (w) , 580 (w).

The following vibrations could be assigned:- Aromatic C-H stretch (3084 - 3030 cm^{-1}); aliphatic C-H stretch (2956 - 2970 cm^{-1}); B-H stretch (2580 cm^{-1}); ν C = C stretch (1600 & 1478 cm^{-1}); δ -CH_3 (1440 - 1386 cm^{-1}); B-C stretch (1253 - 1224 cm^{-1}).

The region 600 - 800 cm^{-1} showed peaks due to aromatic C-H o.o.p. deformations and more dominantly cage vibrations. There is no evidence of B-Cl stretching vibrations in the region 880 - 950 cm^{-1}.

The spectrum shows the presence of phenyl rings, methyl carborane and boron-carbon bonds (external of the cage).

(iii) Discussion

The evidence from elemental analysis and infra red indicate the successful preparation of the compound $PhB(\theta Me)_2$. Again the mass spectral data proved of little value, but showed the formation of other species in the spectrometer.

3.5.6 Conclusion

The preparation of the four new compounds described in this section [$(Me\theta)_2BCl$, $(Me\theta)_2BOH$, $Ph_2B\theta Me$ and $PhB(\theta Me)_2$] have revealed much about the steric factors involved in their formation.

Whilst the bonding of three carboranyl units around a central boron atom is sterically impossible, it is possible to bond two carboranes and a phenyl group. Although the phenyl group is approximately equal in width to the cross-section of a carborane cage, and has a similar cone angle for bonding, it can releave steric effects by tilting the ring plane out of the cage-boron-cage plane.

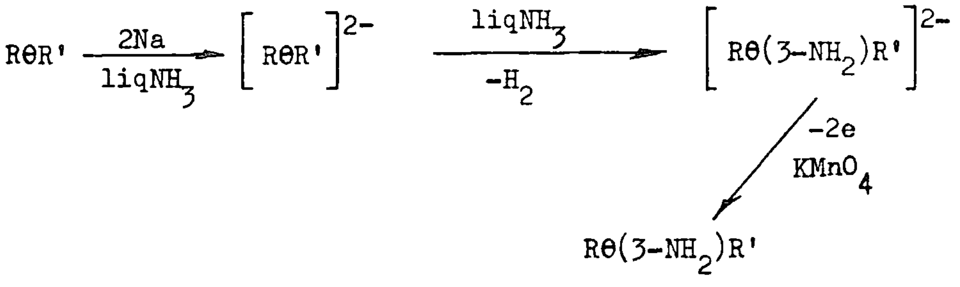
It is unfortunate that the mass spectral data werenot useful in the identification of some of the products although it is interesting that analytically different compounds produced similar yet unidentifiable species in the mass spectrum.

The use of these boron coupled compounds as possible polymer precursors is probably limited by their poor thermal stability. However the use of dilithio-m-carborane and phenyl boron dichloride may produce a higher molecular weight species which due to more restricted cages would most likely have better thermal stability.

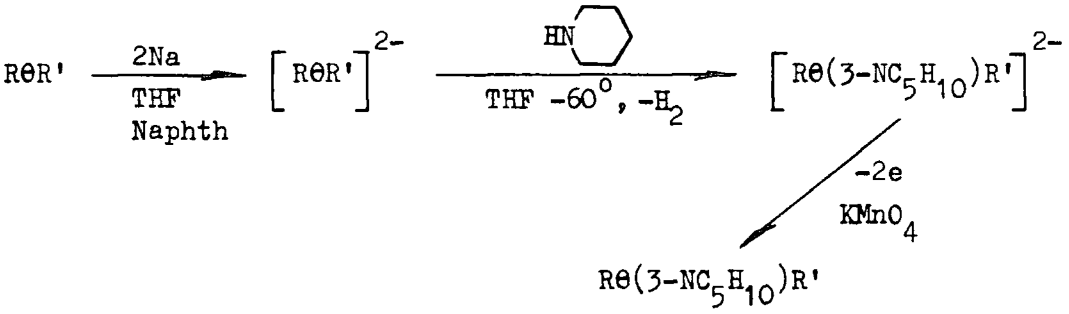
3.6 HETEROCYCLE COUPLED CARBORANES

3.6.1 Introduction

Carborane compounds containing B-N bonds have been prepared in high yields by the action of sodium in liquid ammonia. (176 - 178)



In some cases, sodium and naphthalene in THF are used to prepare the carborane dianion, such as the reaction with piperidine. (111)



In all these reactions, the substitution takes place at the 3-position boron atom, but repeating the reaction can in some cases force a second substitution at the 6-position.

Despite the large amount of work published on 3-position nitrogen substituents and their reactions, the possibility of using a secondary diamine to couple two carborane cages through the 3-position boron atom has been overlooked.

This section describes the investigation of the preparation of the 3-piperidino compound and the preparation of a coupled dicarboranyl piperazine compound.

3.6.2 Preparation of 3-Carboranyl Piperidine

(i) Experimental

To a solution of 1.74g of ortho-carborane (12.1 m.moles) and 0.12g of naphthalene in 25 mls of dry THF, was added 0.6g (26.1 m.moles) of sodium (freshly cut under dry hexane). The mixture was stirred for 2 hours under dry nitrogen during which time the solution turned dark green. Piperidine (1.21g, 14.2 m.moles) was then added and the mixture refluxed for 12 hours under dry nitrogen. The solution was allowed to cool to room temperature and then poured into 150 mls of liquid NH_3 held at -60°C and stirred for 10 minutes, after which 3.63g (22.9 m.moles) of finely powdered potassium permanganate was added. Stirring was continued for 30 minutes then the liquid NH_3 was allowed to warm up and evaporate in a controlled manner. 120 mls of water and 60 mls of toluene were added to the residue and the organic layer separated, washed with water and dried overnight over anhydrous magnesium sulphate. The magnesium sulphate was removed on a grade 3 sinter and washed with 10 mls of dry toluene. Removal of the solvent yielded 1.4g of product. (50.9%)

(ii) Results

Melting Point 63°C (Lit. 62°C)

Analysis

	C	H	B	N
% Found	38.97	11.32	46.7	6.27
$H_2\Theta(3\text{-}NC_5H_{10})$ requires	36.98	9.28	47.6	6.16

Mass Spectrum

The mass spectrum of the product showed a parent ion peak at m/e 229 with an associated characteristic carborane isotope pattern. This mass agrees with the expected product $^{12}C_7\ ^{11}B_{10}\ ^{1}H_{21}\ ^{14}N$.

Below the parent ion there were peaks attributable to the loss of piperidine fragments from the product, ortho-carborane peaks m/e 135 - 145 and piperidine peaks m/e 85.

I.R.

The infra-red spectrum showed the following peaks:-

ν max. KBr disc (cm^{-1}) 3150 (s) , 3023 , 2995 ,
2943 (s) , 2863 , 2530 (s,br), 1465 , 1453 (s) ,
1390 , 1367 , 1355 (s) , 1337 (s) , 1302 (s) ,
1246 , 1196 , 1128 (s) , 1082 , 1020 (s) ,
1003 (s) , 975 , 947 , 928 , 901 ,
870 , 860 , 810 (w) , 757 (w) , 705 ,
603 (w) , 438 (w).

The following vibrations could be assigned:- Carboranyl C-H stretch (3150 cm^{-1}); Aliphatic C-H stretch (2995 - 2863 cm^{-1}); B-H stretch (2530 cm^{-1}); δ s CH_2 scissoring (1465 - 1453 cm^{-1}); cage vibrations (705 cm^{-1}).

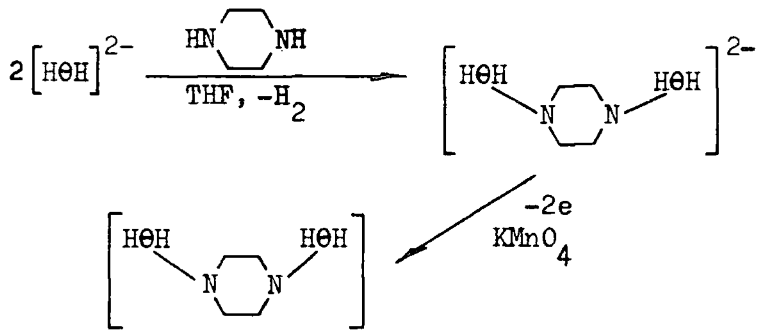
The most significant observations in the infra-red spectrum are the absence of N-H stretch and bending vibrations at ~ 3350 and 750 cm^{-1} respectively, and the reduction in cage vibrations (705 cm^{-1}) from a very strong absorption in ortho carborane to a relatively weak absorption in the piperidino-carborane. The fact that the B-H stretch does not vary in intensity between the two spectra whilst the cage vibrations do suggests that the incorporation of the piperidine at the 3-position restricts these vibrations.

(iii) Discussion

The above results confirm that 3-Carboranyl-piperidine can be prepared by the method outlined in the literature.

3.6.3 Reaction between $[C_2B_{10}H_{12}]^{2-}$ and Piperazine

(i) Experimental



To a solution of 0.98g of ortho-carborane (6.8 m.moles) and 0.07g of naphthalene in 25 mls of dry THF, was added 0.34g (14.8 m.moles) of sodium (freshly cut under hexane). The mixture was stirred for 2 hours during which it turned dark green. Piperazine (0.29g, 3.4 m.moles) was then added and the mixture refluxed for 12 hours under dry nitrogen. The mixture was then cooled and added to 100 mls of liquid NH_3 held at -60^oC and stirred for 30 minutes, after which 2.0g of finely powdered potassium permanganate was added slowly and the mixture stirred for 30 minutes. The addition of the potassium permanganate was made at a rate such that the purple permanganate colour remained visible. (If brown MnO_2 is visible, then the addition should be stopped for 5 minutes then continued slowly. The presence of MnO_2 in other reactions made product isolation difficult.)

After completion of the oxidation, the liquid NH_3 was allowed to warm up and evaporate in a controlled manner. 120 mls of water and 60 mls of toluene were added to the residue and the organic layer separated, washed with water and dried overnight over anhydrous magnesium sulphate. The magnesium sulphate was removed on a grade 3 sinter and washed with 10 mls of dry toluene. Removal of the solvent yielded 0.29g of product.

(ii) Results

Yield 23% w.r.t. piperazine

Analysis

	C	H	B	N
% Found	24.6	9.41	56.3	7.40
$3,3'(H\theta H)_2C_4H_8N_2$ requires	25.94	8.10	58.4	7.56

Mass Spectrum

The product gave a very clear mass spectrum with the parent ion visible at m/e 374 accompanied by a carboranyl isotope pattern. This matches the highest mass predicted from the formula $C_8B_{20}H_{30}N_2$ for dicarboranyl piperidine. (see Figure 3.6.1.)

Below the parent ion was a series of groups of peaks with carboranyl isotope patterns at m/e 265 - 272; 250 - 260, and 238 - 246. These were at too high a mass to represent a single carborane-piperazine fragment and too low a mass to represent two carboranes with a fragmenting piperazine bridge. They were therefore probably due to a fragmenting carborane cage.

At a m/e value of 221 - 230 was a group of peaks which could be assigned to $H_2\theta\text{-}NC_4H_8N^+$, and at m/e 179 - 188 a group attributable to $H_2\theta\text{-}NCH_2CH_2$. At lower masses were o-carborane peaks (m/e 135 - 145) and piperazine peaks (m/e 84). Other lower abundance peaks were visible which matched the piperazine breakdown pattern.

I.R.

The infra-red spectrum showed the following peaks:-

ν max. KBr disc (cm^{-1}) 3050 , 2956 (s) , 2917 (s) ,
2846 (s) , 2587 (s) , 2510 (sh), 1462 , 1452 ,
1411 , 1400 , 1375 (sh), 1258 , 1226 ,
1140 (sh) , 1102 , 1060 , 1019 (s) , 985 (sh) ,
860 (sh) , 799 , 728 (w) , 718 (w).

The following vibrations could be assigned:- Carboranyl C-H stretch (3050 cm^{-1}); Aliphatic C-H stretch (2956 - 2846 cm^{-1}); B-H stretch

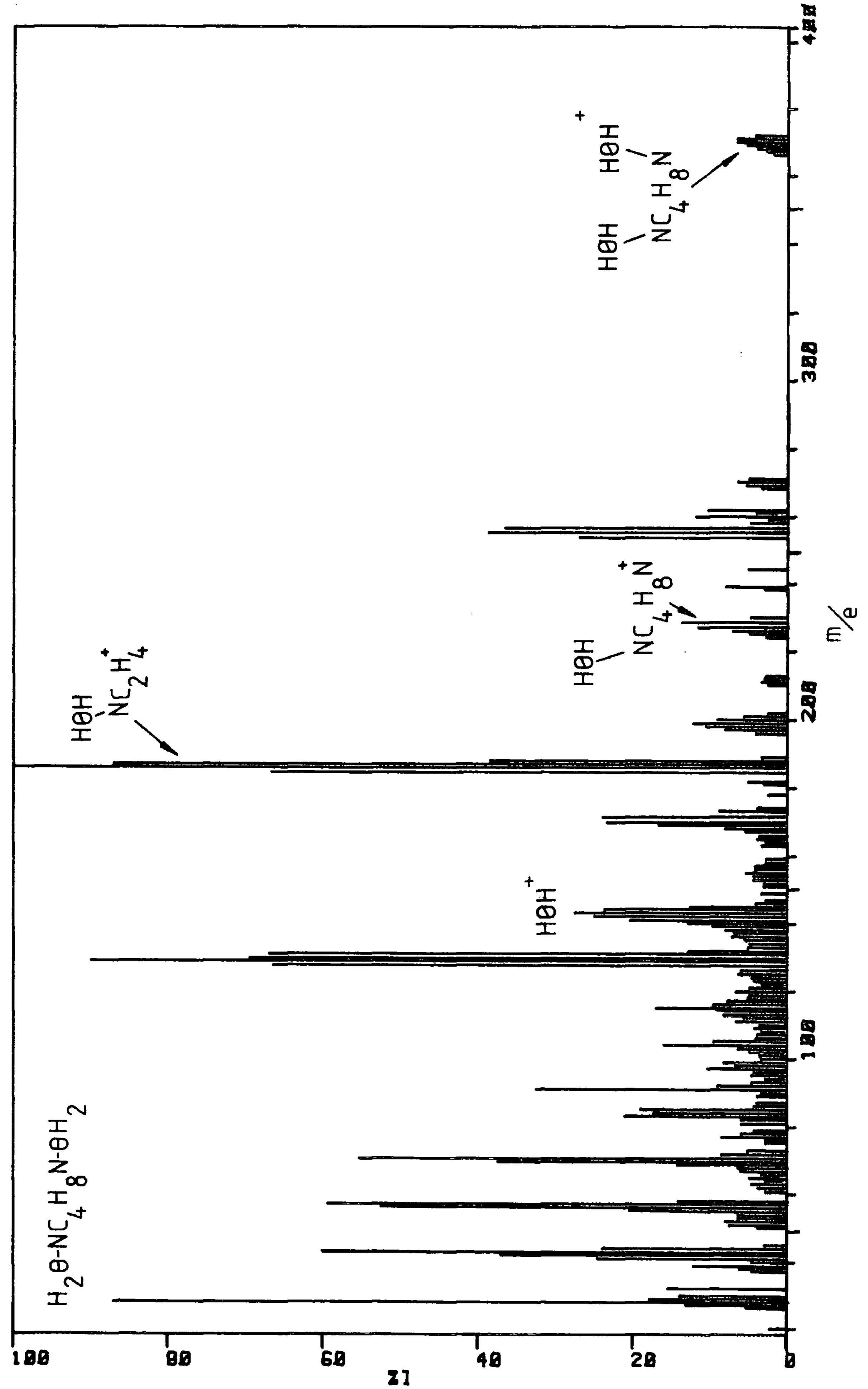

H_2O-NC_4H_8N-OH_2
HOH^+
HOH
$NC_2H_4^+$
HOH
$NC_4H_8N^+$
HOH HOH
NC_4H_8N $^+$
100
80
60
40
20
0
%I
100
200
300
400
m/e

Figure 3.6.1.

(2587 cm^{-1}); δ s CH_2 scissoring (1462 - 1411 cm^{-1}); C-N stretch (1258 cm^{-1}); cage vibrations (799 cm^{-1}).

The spectrum shows no evidence of N-H stretching or bending modes and generally broader absorptions than for piperazine or 3-carboranyl piperidine. This is probably due to many of the piperazine vibrations being damped or forbidden by the two carborane cages. The cage vibration is stronger than for 3-carboranyl piperidine but again broader due to presence of the piperazine, and it is also shifted to a slightly higher frequency. The B-H stretching mode shows a shoulder which is probably due to the effect of the piperazine on the adjacent B-H bonds.

(iii) Discussion

The results show that the unknown compound Di-(3,3'-o-carboranyl)-N,N-piperazine has been successfully prepared using sodium in THF and potassium permanganate in liquid NH_3.

The product could be useful as a polymer precursor as it has 4 available carboranyl C-H bonds for lithiation. It appears to have good thermal stability although the actual melting point was impossible to accurately determine. Like 3-carboranyl piperidine, the di-(3,3'-carboranyl)-N,N-piperazine compound is totally air stable which is an important criterion as a polymer precursor.

CHAPTER 4

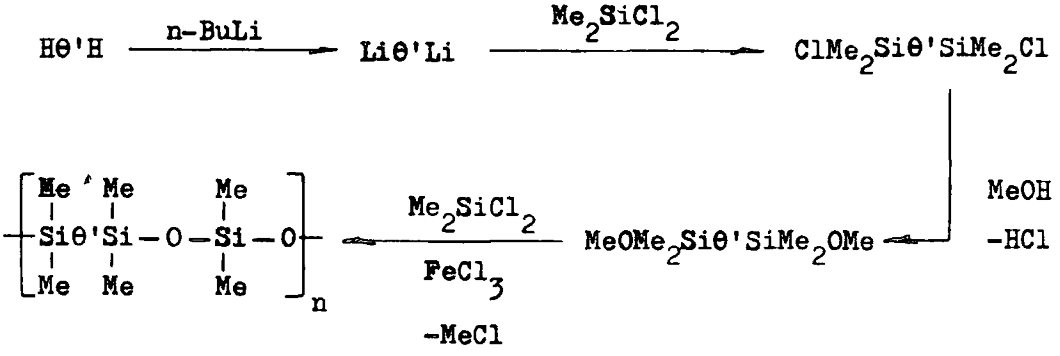
CARBORANE POLYMERS

4.1 INTRODUCTION

The field of carborane polymers is one of the few areas of carborane chemistry which has attracted commercial interest. This is attributable to the high thermal stabilities of carborane polymers in comparison to their purely organic analogs. A brief survey of carborane polymers was given in Chapter 1.15 and showed that they split into two distinct types; polymers in which the cage is pendant to the chain and polymers in which the cage forms part of the backbone of the chain. An investigation was therefore made into the preparative route to an example from each class, namely, polyvinyl carborane because of its small repeat unit and Dexsil 200 because of its high thermal stability.

4.2 PREPARATION OF DEXSIL 200

The preparation was based on the literature method. (432)



(i) Experimental

Freshly sublimed m-carborane (1.75g; 12.14 m.moles) was dissolved in 30 mls of diethyl ether under dry nitrogen and the solution cooled to $0^{\circ}C$. To this was added 20.36 mls (27.3 m.moles) of 1.34M n-butyl lithium in hexane with stirring and the mixture left to digest overnight. The mixture was then cooled down to liquid nitrogen temperature connected to a vacuum line and 3.58g (27.75 m.moles) of freshly distilled dimethyl-dichlorosilane vacuum transferred onto the mixture. The reaction vessel was then let down to dry nitrogen and allowed to slowly warm to 0°C at which it was stirred for 2 hours. The mixture was then filtered through a grade 3 sinter and the excess solvent removed from the filtrate under vacuum to yield a colourless liquid which was distilled at 102 - 104°C, 0.1 m.m. Hg to give pure bis(dimethylchlorosilyl)-m-carborane. This was then converted into bis-(methoxydimethyl(silyl)-m-carborane by stirring with an excess of dry methanol at room temperature until the initial two layers mixed. After an additional hour of stirring the excess methanol was removed under vacuum and the product distilled at 108 - 110°C, 0.1 m.m. Hg to yield 2.50g of monomer, (64.17%).

Approximately 1g of dimethyl-dichlorosilane was vacuum transferred into a preweighed rotaflo glass tube and the weight of the material accurately determined (0.9872g; 7.65 m.moles). An equimolar amount of bis-(methoxy-dimethyl-silyl)-m-carborane (2.2063g) was carefully weighed out into the reaction vessel and 1 mole% of anhydrous ferric chloride added. The reaction vessel was then cooled to liquid nitrogen temperature at which point it was evacuated and the dimethyl-dichlorosilane vacuum transferred into it. The mixture was then let down to dry nitrogen and a reflux condenser and magnetic stirrer added. The reactants were then heated to 100 - 200°C for 30 minutes after the initial reaction had ceased. A second portion of anhydrous ferric chloride was then added and the mixture heated to 180 - 185°C. Gas phase infra-red spectra were run on the exhaust gases until no methyl chloride could be detected, the mixture was then cooled and washed with acetone followed by 10% water in acetone and then acetone again until no iron was detectable in the product.

The polymer was then dried to yield a waxy solid.

(ii) Results

Melting Point > 300°C (sealed tube)

Analysis

	C	H	B	O	Si	Fe
% Found	26.75	8.2	30.5	-	24.6	0
Dexsil 200 requires	27.56	8.04	31.03	9.18	24.19	0

Mass Spectrum

The mass spectrum of the polymer yielded very little information due to high melting point and the involatile nature of the compound. Carborane peaks were barely detectable (m/e 132 - 146) and the only other peaks seen were at m/e 74 and m/e 58. These peaks were probably due to Me_2SiO^+ and Me_2Si^+.

I.R.

The infra-red spectrum showed the following peaks:-

max KBr disc (cm^{-1}) 2860 (s), 2655 (s), 1640 (w),
1450, 1400 (w), 1360, 1250 (s), 1124-1087 (s.br),
1000 (m), 952 (w), 893 (w), 858, 833 - 805 (s.br),
730.

The following vibrations could be assigned:- Aliphatic C-H stretch (2860 cm^{-1}); B-H stretch (2655 cm^{-1}); $\delta_{as}CH_3$ bend (1450 cm^{-1}); $\delta_s CH_3$ bend (1360 cm^{-1}); $Si-CH_3$ stretch (1250 cm^{-1}); Si-O-Si stretch (1124 - 1087 cm^{-1}); Si-O'-Si stretch (1000 cm^{-1}).

(iii) Discussion

Although this method is based on the literature method (432) a few adaptations have been made in order to achieve a high molecular weight product. Because the molecular weight of the polymer depends on the precise ratio of the monomers, a vacuum transfer technique was used to add the volatile dimethyl-dichlorosilane to the reaction mixture. In this way a high degree of accuracy was obtained in the monomer ratio allowing the successful preparation of high molecular weight polymer on a small scale.

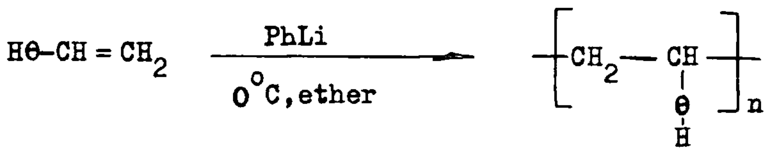
The average molecular weight of Dexil 200 produced by this method is unknown however, it is certainly $>10,000$ as lower molecular weights are soluble in acetone and other common organic solvents.

4.3 PREPARATION OF POLY VINYL-O-CARBORANE

Poly vinyl-o-carborane can be prepared by the following literature routes:-

$$ClCH_2CH(Cl)CH=CH_2 \xrightarrow[+KOH \sim 124^{\circ}C]{EtOCH_2CH_2OH} CH_2=CH-C\equiv CH$$

$$CH_2=CH-C\equiv CH + B_{10}H_{12}(MeCN)_2 \longrightarrow H\theta-CH=CH_2 \qquad (3)$$



$$H\theta-CH=CH_2 \xrightarrow[0^{\circ}C, ether]{PhLi} \left[CH_2-\underset{\underset{H}{\theta}}{CH}\right]_n \qquad (405)$$

These steps will be discussed in separate sections.

4.3.1 Preparation of Vinyl Acetylene

(i) Experimental

Two methods were used in order to prepare vinyl acetylene, firstly, a literature method(I) and secondly an improvement on that, method(II). Both methods will be described in full.

a) Method I

To a dry nitrogen purged, one litre, three necked flask was added 108g (1.93 moles) of potassium hydroxide and 160g of dry 2-ethoxy-ethanol and stirred with a mechanical stirrer until dissolved. 30g (0.24 moles) of 3,4-dichlorobut-1-ene was then added dropwise to the stirring solution. To the flask was fitted a reflux condenser attached to which was the drying and collection apparatus consisting of a water bubbler to remove any uncondensed ethanol, an anhydrous calcium chloride tower, a dry-ice /acetone cold trap followed by a liquid nitrogen cold trap and finally an oil bubbler. The nitrogen supply to the reaction vessel was adjusted to give a slow stream of nitrogen through the traps and the mixture was heated to 90°C for 3 hours. The temperature was slowly raised to 124 - 5°C at which a gas was evolved and the reaction continued for 10 - 12 hours under close temperature control.

b) <u>Method II</u>

This method used the same apparatus as Method I. 108g of potassium hydroxide (1.93 moles) was added to the reaction flask maintained at 0°C. 160g of dry 2-ethoxy ethanol was then added slowly over 5 - 10 minutes with stirring. With continued stirring the mixture was heated up to 90°C until all the potassium hydroxide had dissolved, then 26 mls of 3,4-dichlorobut-1-ene was added <u>dropwise</u> to the solution to give an instantaneous evolution of gas which was collected in the first cold trap. The reaction was stopped after the additon was complete. (30 - 45 minutes)

(ii) <u>Results</u>

<u>Yield</u>	Method I	11.75 g	94.2%
	Method II	11.31 g	90.5%

<u>Boiling Point</u> 5.1 °C literature

(iii) <u>Discussion</u>

Although Method II produces a slightly lower yield of vinyl acetylene than Method I, there is little doubt that it is the more convenient method for producing vinyl acetylene for normal laboratory use. I therefore regard Method II as being a significant improvement on the literature method.

4.3.2 Preparation of 1-Vinyl-o-carborane (11)

(i) Experimental

$$CH_2{=}CH{-}C{\equiv}CH \; + \; B_{10}H_{12}(MeCN)_2 \xrightarrow{\text{toluene}} H\theta - CH{=}CH_2 + H_2 + 2MeCN$$

To a two necked flask fitted with a reflux condenser connected to a dry ice/acetone condenser was added 45.7g (226 m.moles) of bis-(acetonitrile) decaborane and 150 mls of dry toluene with stirring under dry nitrogen. The mixture was then heated to 80 - 90°C for 1 hour, and the temperature adjusted to 85°C, where upon a cold solution of vinyl acetylene (225 m.moles) and xylene (1:1 by weight) was slowly added maintaining the reaction temperature between 90 - 100°C. On completion of the addition the reflux was continued for 1.5 - 2 hours, cooled and left to stand overnight. The majority of the solvent was then removed under vacuum and the residue distilled at 0.5 m.m Hg until the temperature reached 135 - 140°C. 1-Vinyl-o-carborane distils at 75 - 80° (0.5 m.m Hg).

Results

Yield 0.5g (1.3% based on bis(acetonitrile) decaborane.)

Analysis

	C	H	B
% Found	27.74	8.18	64.3
$H\theta CH{=}CH_2$ requires	28.22	8.23	63.55

Mass Spectrum

The mass spectrum of the product is shown in figure 4.3.1. This shows three distinct carboranyl groups of peaks at m/e 139 - 146, m/e 149 - 161 and m/e 164 - 172. These peaks were assigned as $H\theta^+$, $H\theta CH^+$ and $H\theta CH{=}CH_2$ respectively.

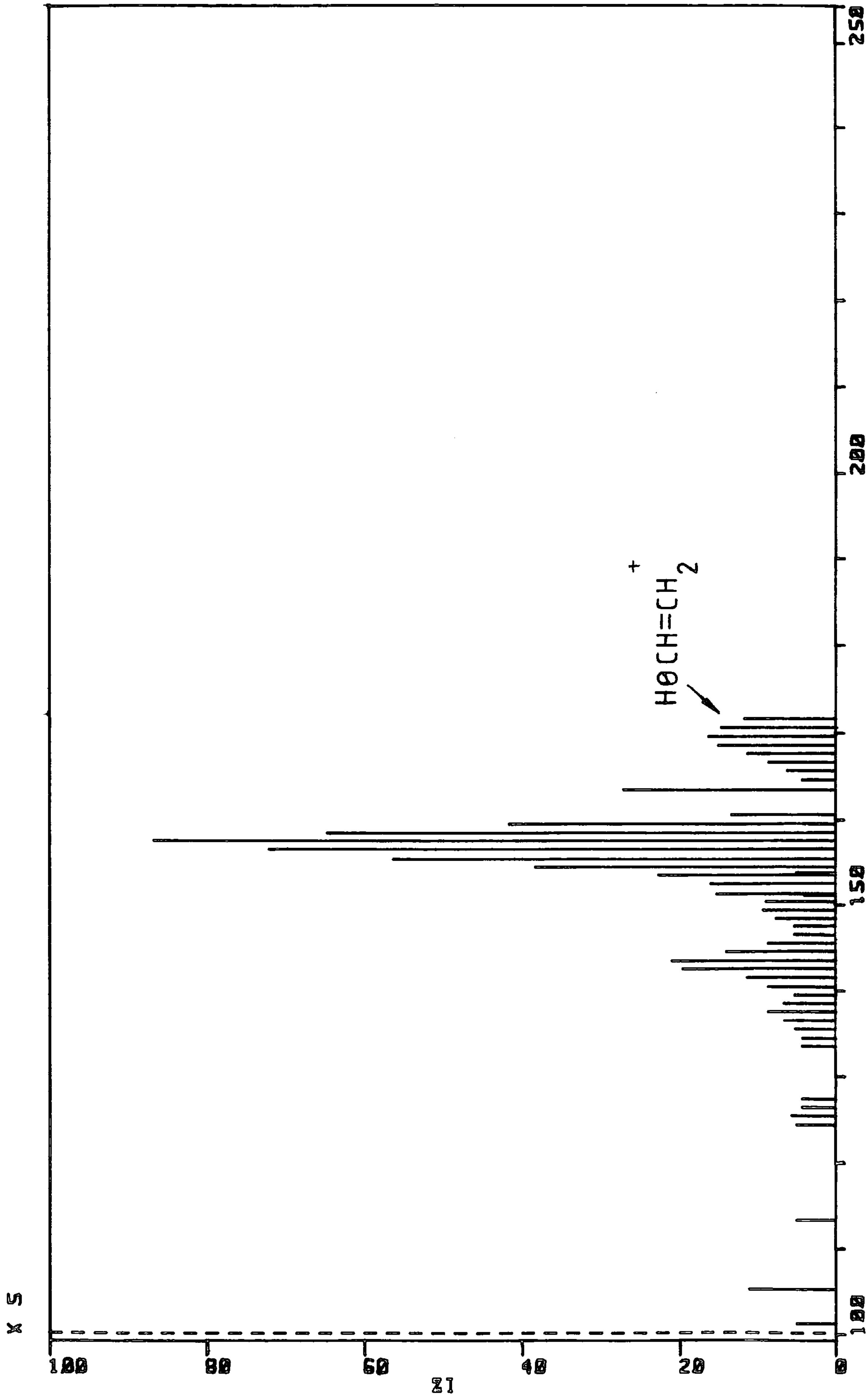


Figure 4.3.1.

Discussion

Whilst the results clearly show that 1-vinyl-o-carborane has been successfully prepared, it was not found possible to prepare it in sufficient quantity to undertake a polymer synthesis. The reasons for the poor yield are not apparent and further attempts at preparation by both myself and other workers failed to increase the yield above 1.5%. The use of solvents and starting materials of extremely high purity and dryness had no effect on the overall yield. It was felt that the method used lacked some experimental details causing the reduced yield.

CHAPTER 5

REACTIONS OF LITHIO-O-CARBORANES WITH CYANIDES

5.1 THE REACTIONS OF CYANOGEN COMPOUNDS WITH LITHIO-O-CARBORANES

5.1.1 Introduction

Lithio-o-carboranes are known to react with cyanogen chloride in ether/benzene mixture to give equimolar quantities of 1-cyano-o-carborane and 1-chloro-o-carborane. (167)

$$2\mathrm{Ph\theta Li} + 2\mathrm{ClCN} \longrightarrow \underset{\sim 50\%}{\mathrm{Ph\theta Cl}} + \underset{\sim 50\%}{\mathrm{Ph\theta CN}} + \mathrm{LiCl} + \mathrm{LiCN}$$

This mixture is difficult to separate if the cyano compound alone is required and so workers have devised an alternative method of preparation. (191)

$$\text{o,m}-\mathrm{R\theta Li} + \mathrm{PhOCN} \xrightarrow[\text{Ether/benzene}]{25^{\circ}} \text{o,m}-\mathrm{R\theta CN} + \mathrm{PhOLi}$$

$$\mathrm{R} = \mathrm{Me}, \mathrm{Ph}$$

This chapter describes the investigation of the reactions between 1-lithio,2-methyl-o-carborane and cyanogen iodide, and cyanogen itself. Based on the observed reaction of cyanogen chloride with lithio-o-carboranes in which equal amounts of the 1-chloro and 1-cyano derivatives are formed, one would expect with a cyanogen iodide reaction that chiefly a 1-iodo derivative would result because of the lower electronegativity of iodine compared to chlorine. The lower electronegativity might also give rise to electrophilic substitution by iodine at the 9-(12) position boron atom.

The reaction of cyanogen with lithio-o-carborane would be expected to give only a 1-cyano derivative. B-Cyano-o-carboranes have been prepared by a nucleophilic substitution reaction. (154)

$$\underline{HCB_{10}H_9ICH} \xrightarrow[300^{\circ}]{CuCN} \underline{HCB_{10}H_9CNCH}$$

The use of silver (I) cyanide in acetonitrile at reflux temperatures was investigated as a possible means of effecting this same substitution.

5.1.2 Preparation of Cyanogen Iodide

(i) Experimental

$$KCN + I_2 \xrightarrow{aq} ICN\downarrow + KI$$

To a stirred solution of potassium cyanide (10g, 0.154 moles) in 25 mls of water was slowly added 30g (0.123 moles) of finely powdered iodine under nitrogen over 1 hour. The iodine dissolved and white crystalline cyanogen iodide precipitated out of solution. When the addition was complete, the mixture was cooled to ~ 3°C for 2 hours and the cyanogen iodide removed on a grade 2 sinter washed with 10 mls of cold water and recrystallised from 30 mls of warm water.

NOTE: ICN decomposes above 50°C, on contact with filter paper and on contact with nickel spatulas.

(ii) Results

Yield 81.6% with respect to iodine (15.35g)

Analysis

	C	N	I
% Found	8.02	8.96	82.7
ICN requires	7.85	9.15	83.00

I.R.

The infra-red spectrum showed the following peaks:-

ν max KBr disc (cm^{-1}) 2168 , 2122 (w), 455 (s), 410 (sh), 331 (s).

The following vibrations could be assigned:- $-C\equiv N$ stretch (2168 cm^{-1}), I - C stretch (455 - 410 cm^{-1}).

5.1.3 Reaction Between ICN and 1-Lithio,2-Methyl-O-Carborane

(i) Experimental

1-Methyl-o-carborane (2.112g, 13.4 m.moles) was dissolved in 10 mls of dry diethyl ether under dry nitrogen. To this solution was added 8.54 mls (13.4 m.moles) of 1.57M n-butyl lithium with stirring. The mixture was left stirring for 3 hours then a solution of 2.04g of ICN (13.4 m.moles) in 20 mls of dry diethyl ether was added and stirred for 24 hours under dry nitrogen. 1 ml of water was then slowly added to the mixture and stirred for 30 minutes, dried over anhydrous magnesium sulphate and filtered through a grade 3 sinter. The solvent was removed from the filtrate to yield a white sublimable compound.

(ii) Results

Analysis

	C	H	N	B	I
% Found	10.34	3.83	0	-	51.3
$C_3B_{10}H_{13}CN$ requires	26.22	7.10	7.65	59.04	0
$C_3B_{10}H_{13}I$ requires	12.68	4.58	0	38.06	44.68

Mass Spectrum

The mass spectrum of the product showed three distinct groups of peaks with a carboranyl isotope pattern. These appeared at m/e 407 - 411, m/e 278 - 286 and m/e 150 - 159 and were respectively assigned to $MeC_2B_{10}H_9I_2$, $MeC_2B_{10}H_{10}I$ and $MeC_2B_{10}H_{11}$. Although only five peaks were detected by the computer for the highest mass species, these would be the five highest abundance peaks as predicted by computer programme. (See figure 5.1)

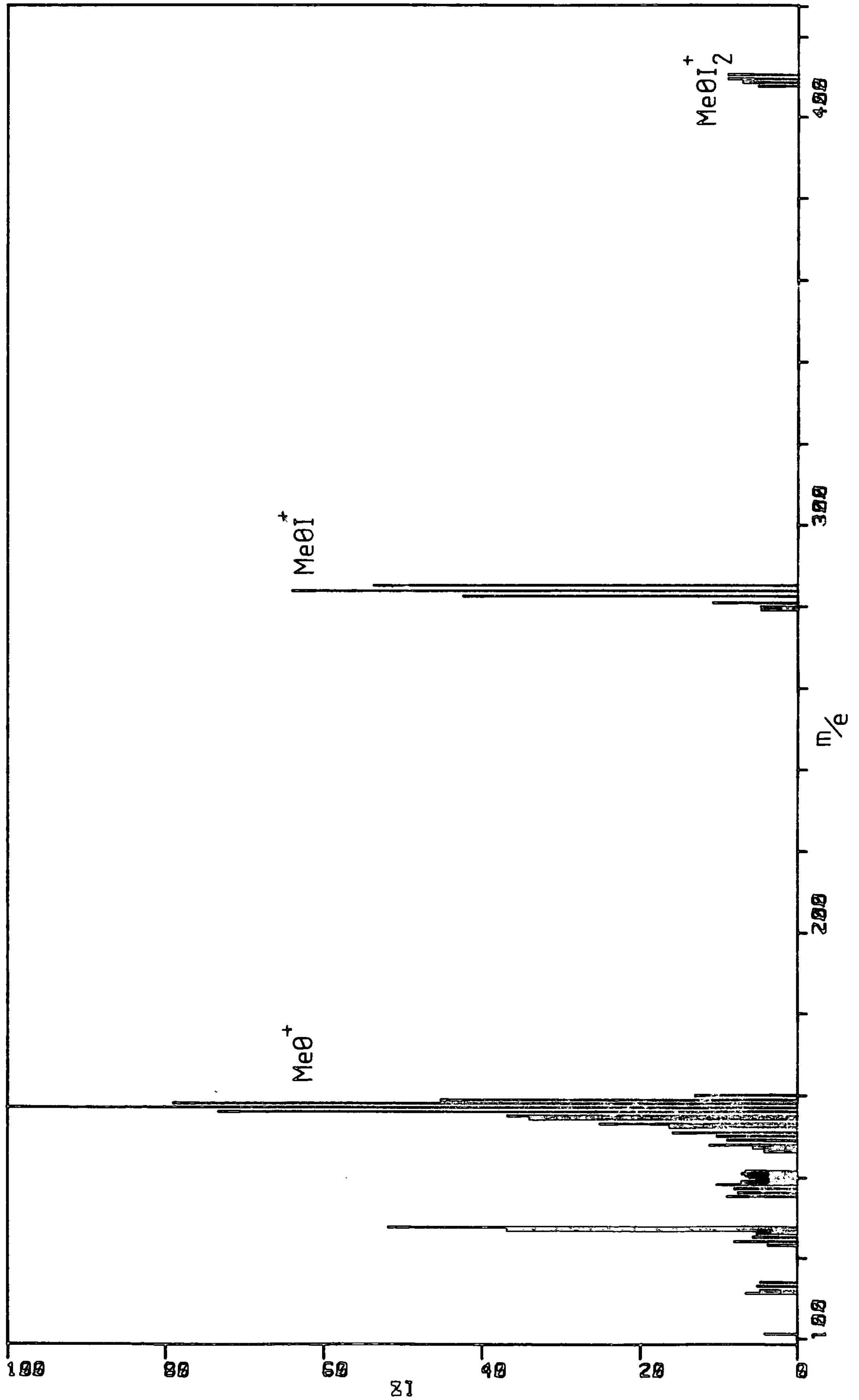


Figure 5.1.

I.R.

The infra-red spectrum showed the following peaks:-

ν max KBr disc (cm^{-1}) 3061 (s), 2990, 2940,
2870, 2580 (s,br), 2350 (sh), 1930, 1845,
1440, 1385, 1270, 1227, 1210,
1190, 1132, 1095, 1080 (sh), 1033,
1017, 997, 975, 935, 916,
900, 880 (w), 863, 840, 787,
722 (s), 670, 653, 496.

The following vibrations could be assigned:- Carboranyl C-H stretch (3061 cm^{-1}); Aliphatic C-H stretch (2990 - 2870 cm^{-1}); C-H bend (1440 - 1385 cm^{-1}); Cage vibrations (722 cm^{-1}).

(iii) Discussion

The results indicate that ICN has reacted with 1-lithio,2-methyl o-carborane as expected to yield a mixture of two compounds, $MeC_2B_{10}H_{10}I$ and $MeC_2B_{10}H_9I_2$. The presence of a strong carboranyl C-H stretch in the infra-red spectrum suggests that in the case of the mono-iodo compound the substitution occurred at the 9-position boron atom. It is not clear from the data whether the site of substitution of the second iodine is at a second boron atom or at the free carbon atom. From the mass spectrum, the di-iodo compound appears in much lower concentration than the mono-iodo compound thus any C-I stretch may be obscured in the infra-red spectrum.

There is no evidence from the analytical data for any cyano-carborane species and this agrees with the expected reaction based on electronegativity arguments.

5.1.4 Reaction Between Cyanogen and 1-Lithio-2-Methyl-O-Carborane

(i) Experimental

Cyanogen was prepared by standard literature methods according to the formula.

$$4KCN + 2CuSO_4 \longrightarrow (CN)_2\uparrow + 2K_2SO_4 + 2CuCN$$

1-Methyl-o-carborane (0.791g, 5 m.moles) was dissolved in 30 mls of dry diethyl ether under dry nitrogen. To this was added 3.18 mls of 1.57M n-butyl lithium with stirring and the mixture left to digest for 2 hours. The mixture was then cooled to liquid nitrogen temperature and the reaction vessel attached to a vacuum line. 5 m.moles of cyanogen was then condensed onto the reaction mixture under vacuum. The flask was isolated from the line, let down to dry nitrogen and allowed to warm up to room temperature during which time the solution changed from colourless to deep cherry red with a deeper red oil below it. These two layers were separately syringed off and each added to 1 ml of water. The solutions were dried over anhydrous magnesium sulphate, filtered through a grade 3 sinter and the solvent removed from the filtrates. The top layer yielded a pale yellow powder whilst the lower darker red solution yielded a bright orange solid.

(ii) Results

Analysis

(Yellow Powder)

	C	H	N	B
% Found	23.24	8.76	0.6	67.8
$MeC_2B_{10}H_{11}$	22.77	8.85	0	68.37
$MeC_2B_{10}H_{10}CN$ requires	26.21	7.1	7.65	59.04

(Orange Solid)

	C	H	N	B
% Found	52.41	-	45.3	0

Mass Spectrum

The mass spectrum of the yellow powder showed only the presence of 1-methyl-o-carborane with peaks at m/e 150 - 161. No cyano-o-carborane was evident in the spectrum.

The bright orange solid proved to be very involatile and only 1-methyl-o-carborane was detected as a trace impurity on the first few scans. The remainder of orange material remained intact on the probe.

I.R.

The infra-red spectrum of the yellow powder was identical to that of 1-methyl-ortho-carborane.

The infra-red spectrum of the orange solid was poorly resolved and contained only very broad bands in the 2000 cm^{-1} and 1600 cm^{-1} regions. No clear assignments could be made from these bands.

(iii) Discussion

The analytical data indicates that the cyanogen has not reacted with 1-lithio,2-methyl-o-carborane to give a cyano-carborane. It seems likely that the orange solid was poly-cyanide as it did not incorporate any methyl-carborane residues, and that the lithio-methyl-carborane merely acted as a catalyst for the polymerisation.

5.1.5 Reaction Between Silver (I) Cyanide and Iodo-1-Methyl-o-Carborane

In phosphorus chemistry, silver (I) cyanide is known to react with phosphorus iodides in acetonitrile to give phosphorus cyanides. Silver cyanide was therefore reacted with the product from reaction 5.13 between ICN and MeΘLi to try and affect a substitution of one or both of the iodine atoms.

(i) Silver cyanide was prepared by the addition of excess aqueous potassium cyanide to an aqueous solution of silver nitrate in the dark.

$$AgNO_3 + KCN \longrightarrow AgCN\downarrow + KNO_3$$

The precipitate of silver cyanide was removed on a grade 2 sinter and thoroughly washed with distilled water followed by a portion of ethanol to yield a white, light sensitive powder. The silver (I) cyanide was dried over anhydrous calcium chloride in a vacuum dessicator overnight. The dry product was then stored in a dark bottle under dry nitrogen until required.

0.34g of the iodo,1-methyl-o-carborane was dissolved in 20 mls of dry acetonitrile under dry nitrogen. Silver (I) cyanide (~ 1.5g) was added to the solution and the mixture refluxed in the dark for 6 hours and then in the light for a further 6 hours. The mixture was filtered through a grade 2 sinter and the solvent removed from the filtrate to yield a white powder.

(ii) Results

Analysis

(Precipitate)

	Ag	C	N
% Found	78.6	8.73	11.10
AgCN requires	80.58	8.96	10.46

(White Powder)

	C	H	N	B	I
% Found	10.29	3.69	0	-	51.8
MeθCN requires	26.22	7.10	7.65	59.04	0

Mass Spectrum

The mass spectrum showed only peaks attributable to $Me\theta^+$, $Me\theta I^+$ and $Me\theta I_2^+$. No evidence was found for a cyano-carborane species.

I.R.

The infra-red spectrum of the product was found to be identical to that of the product from the reaction between ICN and MeΘLi.

(iii) Discussion

The analytical data does not show the presence of any cyano-carboranes indicating that silver (I) cyanide in acetonitrile is not a strong enough nucleophile to effect a substitution and that the cage-Iodine bond is stronger than a P-I bond in PI_3.

5.1.6 Conclusion

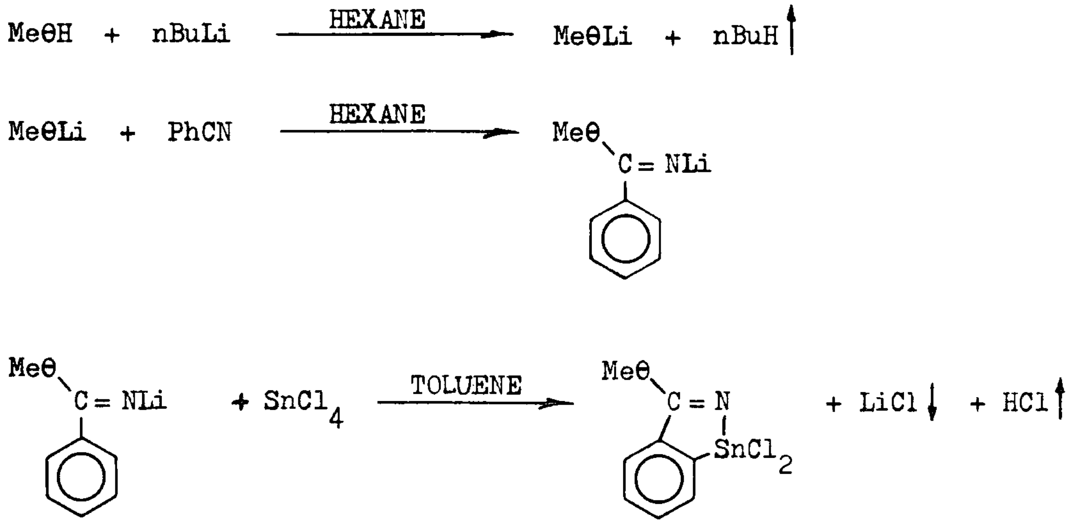
This chapter has shown that the reaction between ICN and MeΘLi agrees with predicted reaction on purely electronegativity arguments. In contrast to ICN, $(CN)_2$ proved unreactive towards MeΘLi and instead appeared to polymerise.

Silver (I) cyanide in acetonitrile was shown to be incapable of causing nucleophilic substitution at a B-I bond.

5.2 REACTION OF 1-LITHIO,2-METHYL-O-CARBORANE WITH BENZONITRILE AND TIN (IV) CHLORIDE

5.2.1 Introduction

This reaction was conceived in order to determine if 1-methyl-o-carborane could be incorporated into a system which was capable of undergoing an ortho-metallation reaction in the presence of tin (IV) chloride. The proposed reaction scheme was as follows:-



Such a compound would be of interest from the structural point of view and also to see if the electron withdrawal of cage had any influence on the other atoms as detectable in the Cl NQR signal compared to more conventional ortho metallated compounds.

(i) Experimental

1-Methyl-o-carborane (1.25g, 7.91 m.moles) was dissolved in 30 mls of dry hexane under dry nitrogen. The solution was then stirred whilst 4.8 mls (7.91 m.moles) of 1.65M n-butyl lithium in hexane was added. The mixture was stirred at room temperature for 2 hours, when 0.81 mls (7.91 m.moles) of dry benzonitrile was added and refluxed gently for 3 - 4 hours. The hexane was removed under vacuum, replaced by 20 mls of dry toluene and 0.925 mls (7.87 m.moles) of freshly distilled tin (IV) chloride added and stirred for 3 hours. The solution was then warmed to 60 - 70°C and filtered through a grade 3 sinter in a second flask. The filtrate was placed in a freezer at -25°C for 2 days producing fine needle like crystals which were removed on a grade 2 sinter, washed with 10 mls of cold (-36°C) toluene and pumped dry.

(ii) Results

Analysis

	C	H	N	B	Cl	Sn
% Found	55.40	3.55	9.63	0	17.25	13.8

Assuming a single tin atom, this implies an empirical formula of $SnCl_{4.2}N_{5.9}C_{39.7}H_{30.5}$. Clearly this is not a carborane species.

Mass Spectrum

The mass spectrum of the product showed several groups of peaks with the distinctive tin isotope pattern and were assigned as follows m/e 256-264 $SnCl_4$; m/e 221-229 $SnCl_3^+$; m/e 186 - 190 $SnCl_2$; m/e 152 - 157 $SnCl^+$ and m/e 116 - 122 Sn. At a lower mass of m/e 103 occurred the most intense peak in the spectrum and this was assigned to C_6H_5CN (mass 103) and the M + 1 peak had a relative abundance of 8.87 whilst mass spectral tables predict M + 1 abundance of 8.07 for $C_7H_5N_1$ so clearly there is good agreement.

I.R.

The infra-red spectrum of the product showed the following peaks:-

ν max, Nujol Mull (cm^{-1}) 3070 , 3060 , 2950 (sh),
2920 (s) , 2850 (s), 1622 , 1603 (sh), 1590 ,
1570 (w) , 1522 (s), 1463 (s) , 1448 (s) , 1370 (s) ,
1300 , 1175 , 1146 (w) , 1070 , 1030 ,
1003 (w) 976 (w), 943 (w) , 930 (w) , 843 ,
765 , 760 , 745 (s) , 685 (s) , 647 ,
558 , 488.

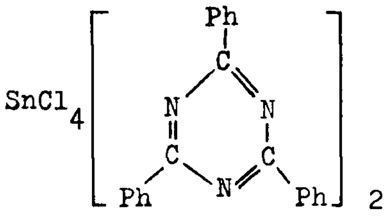
The following vibrations could be assigned:- Aromatic C - H stretch (3070 - 3060 cm^{-1}); Nujol (2950 - 2850 cm^{-1}); -C=N- or $C\underset{\cdots}{-}C$ ring stretch (1522 cm^{-1}); Nujol (1463 - 1370 cm^{-1}); In plane C - H bend (1070 - 976 cm^{-1}); Out of plane C - H bend (745 cm^{-1}).

(iii) Discussion

The data shows that the crystalline product is not a carborane species and that it is probably a $SnCl_4$ adduct of some type. The infra-red suggests that aromatic rings are a component and the mass spectrum shows the presence of benzonitrile as either a consistuent or a breakdown product. Assuming from the analytical data that we have a $SnCl_4$ adduct then this implies that the adduct itself could be a number of benzonitriles. Taking the number of benzonitriles as six we have good agreement with the analytical data.

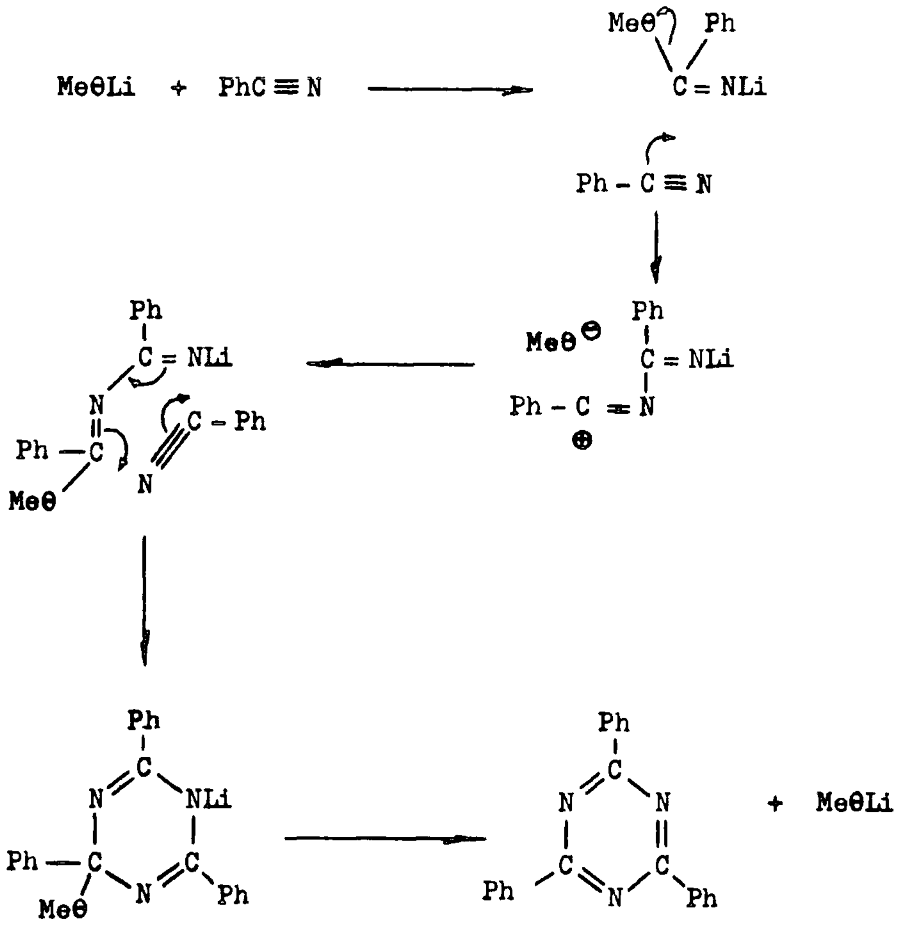
	C	H	N	Sn	Cl
% Found	55.40	3.55	9.63	13.8	17.25
$SnCl_4(PhCN)_6$ requires	57.37	3.42	9.56	13.51	16.14

It is unlikely that these are free benzonitriles as there is no -C=N frequency observed in the infra-red but instead there is a strong peak at 1522 cm^{-1} which could be -C=N- stretch. Taking this into account and the fact that $SnCl_4$ usually forms adducts of the type $SnCl_4.L_2$ then it is probable that the product is:-



These are well known ring systems, the formation of which was probably caused by MeΘLi.

Working up the remainder of the filtrate from the experiment yielded more product and 1-lithio,2-methyl o-carborane.



CHAPTER 6

METALLOCARBORANES

6.1 Introduction

In comparison to the transition metal icosahedral and "sandwich" metallocarboranes, the number of main group element derivatives is small, and the number of compounds containing two carbon atoms and a main group element in an icosahedral framework is even smaller. To date the only such known derivatives are those of beryllium, aluminium, gallium, thallium, germanium, tin and lead.

The beryllium compound is formed by the reaction of dimethyl or diethyl beryllium in ether with nido-1,2-$C_2B_9H_{13}$. (320,321) The product is a solid etherate of an icosahedral $BeC_2B_9H_{11}$.

$$1,2\text{-}C_2B_9H_{13} + BeR_2.2\ O(Et)_2 \xrightarrow[\text{Benzene}]{\text{ether}} 2RH + 3\text{-}\ (Et)_2O\ \text{-}3,1,2\text{-}BeC_2B_9H_{11} + (Et)_2O$$

R = Me, Et

Aluminium and gallium icosahedra have been synthesised by the action of heat on the nido-μ-$(Et)_2AlC_2B_9H_{12}$, μ-$(Me)_2AlC_2B_9H_{12}$ and μ-$(Et)_2$-$GaC_2B_9H_{12}$ metallocarboranes in dry benzene. The nido species are produced by the reactions of aluminium and gallium trialkyls with nido-1,2-$C_2B_9H_{13}$. The icosahedral 1,2-derivatives readily isomerise to the 1,7 analogues on heating, however at high temperature the gallium species decompose to yield mostly closo-$C_2B_9H_{11}$. (324) Aluminium species may also be prepared by the reaction of ethyl aluminium dichloride with a THF solution of the dicarbollide ion.

A thallium metallocarborane can be conveniently prepared by the addition of aqueous thallous acetate to an aqueous solution of $K^+C_2B_9H_{12}^-$

precipitating a yellow thallium salt. (322)

$$2TlOAc + C_2B_9H_{12}^- \longrightarrow Tl^+[TlC_2B_9H_{11}]^- + AcOH + AcO^-$$

The thallium (I) salt is completely air and moisture stable and has been used as a convenient starting material for the formation of other metallocarboranes for example reaction in THF with the dichlorides of iron, cobalt, platinum and palladium. (322)

Germanium, tin and lead metallocarboranes can all be prepared by the reaction of the metal dichloride with a THF solution of the dicarbollide ion. (323 - 327)

$$1,2\text{-}C_2B_9H_{11}^{2-} + MX_2 \longrightarrow 3,1,2\text{-}MC_2B_9H_{11} + 2X^-$$

M = Sn, Pb, X = Cl; M = Ge X = I

The Group IV metallocarboranes contain a bare metal atom (Figure 6.1) over the open face of the carborane residue although the precise position of metal atoms has not been determined due to the formation of distorted lattices on crystallisation. As a result, the structures have been deduced by analytical, ^1H and ^{11}B nmr, ir and mass spectral data. All three compounds are sublimable solids, the temperature of sublimation increasing from 80 - 140 - 250° down the group. They are degraded to $1,2\text{-}C_2B_9H_{12}^-$ by methanolic potassium hydroxide, and treatment of $SnC_2B_9H_{11}$ with hydrogen chloride generates nido-$C_2B_9H_{13}$ and tin dichloride. (327) The germanium derivative isomerises at 600°C to give the $2,1,7\text{-}GeC_2B_9H_{11}$. This product can also be produced by the reaction of $(3)\text{-}1,7\text{-}C_2B_9H_{11}^{2-}$ with germanium di-iodide, (328) whilst the reaction of tin dichloride with the same ion in benzene leads to the reduction of the tin dichloride to tin metal, pyrolysis of $1,2\text{-}SnC_2B_9H_{11}$ yields similar products.

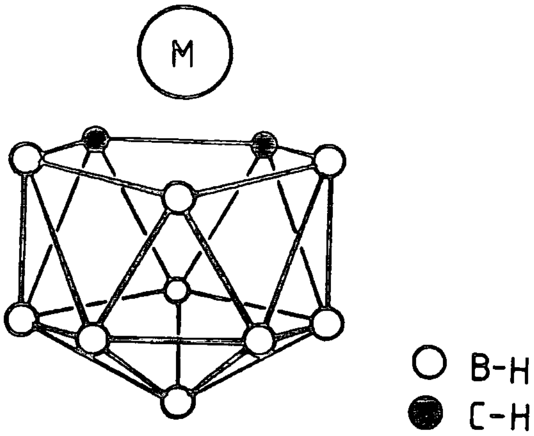


Figure 6.1.

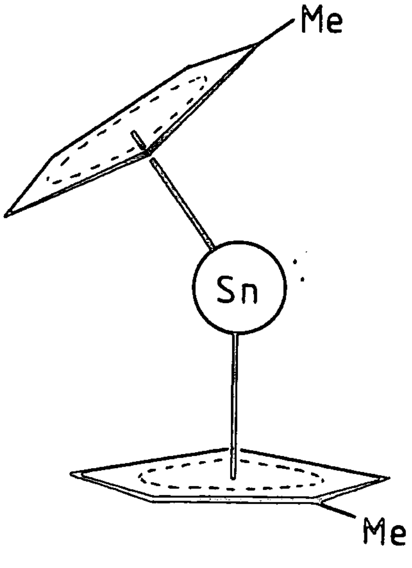
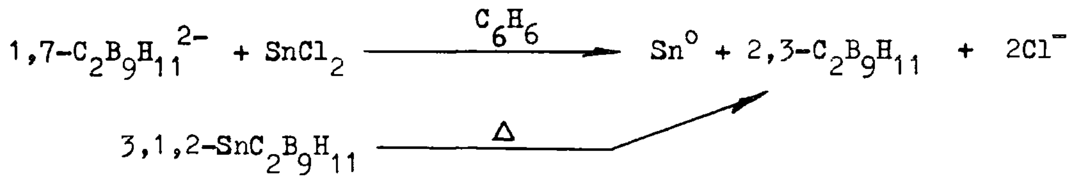


Figure 6.2.



$$1,7\text{-}C_2B_9H_{11}^{2-} + SnCl_2 \xrightarrow{C_6H_6} Sn^0 + 2,3\text{-}C_2B_9H_{11} + 2Cl^-$$

$$3,1,2\text{-}SnC_2B_9H_{11} \xrightarrow{\Delta} Sn^0 + 2,3\text{-}C_2B_9H_{11}$$

A study of $3,1,2\text{-}SnC_2B_9H_{11}$ using tin-119 Mössbauer techniques showed that the tin atom has a formal oxidation state of 2. (329)

The transition metal metallocarborane derivatives discussed in chapter 1.16 differ from the known main group metallocarborane in respect to the preparation of sandwich compounds. There are no reports in the literature of any synthesis of main group element sandwich compounds or attempts to prepare such. The reason for this is not clear especially as tin and lead both form co-ordination compounds with two cyclopentadiene rings. (330,331) (Figure 6.2)

Tin can form upto tetra-(penta-hapto) compounds with cyclopentadienides, by the reaction of tin dichloride with sodium cyclopentadienide.

Considering that the open face of the dicarbollide ion has been regarded as equivalent to the cyclopentadienide ion in terms of orbital availability then clearly in theory it must be considered possible to synthesise tin sandwich compounds using the dicarbollide ion in place of a cyclopentadienide. (See section 1.16)

A series of reactions was undertaken in order to ascertain whether or not tin and germanium could form such sandwich compounds. If the dichlorides of the metals react with the dicarbollide ion in THF to give icosahedral metallocarboranes in which the metals have a formal oxidation state of 2+ then it was reasoned that the equivalent reaction using a stoichiometric amount of the dicarbollide ion with a tetrachloride of the metal could give a Group IV sandwich compound.

6.2 PREPARATION OF STARTING MATERIALS

6.2.1 Preparation of Dicarbollide Ion

The preparation of the dicarbollide ion was carried out in two stages.

(a) Preparation of trimethylammonium-1,2-dicarbaundecaborate(12), (305)

(b) Conversion of trimethyl ammonium -1,2-dicarbaundecaborate to dicarbollide ion with sodium in THF. (312)

(a) Preparation of Trimethylammonium-1,2-dicarbaundecaborate(12)

(i) Experimental

A solution of 0.4g of potassium hydroxide (7.13 m.moles) in 6 mls of dry ethanol was added to 0.560g of freshly sublimed ortho-carborane (3.88 m.moles) with stirring and kept at room temperature for 1 hour. The reaction mixture was then refluxed for 2 hours with stirring after which a further 5 mls of dry ethanol was added and the solution allowed to cool to room temperature. A slow stream of carbon dioxide (produced from warm solid carbon dioxide) was bubbled through the vigorously stirred solution for 1 hour. The resulting precipitate of potassium carbonate was removed on a grade 3 sinter and washed with 10 mls of dry ethanol. A solution of 0.4g of trimethyl ammonium chloride (4.26 m.moles) in 20 mls of water was added to the stirred filtrate and a white precipitate removed on a grade 4 sinter washed with 50 mls of water and dried over anhydrous calcium chloride in a vacuum desiccator.

(iii) Results

Yield 96.4%

Analysis

	C	H	N	B
% Found	31.8	11.0	6.8	48.1
$Me_3NH^+C_2B_9H_{12}^-$ requires	31.0	11.4	7.2	50.3

^{11}B n.m.r.

The ^{11}B n.m.r. spectrum at 19 M.Hz in 90/10, benzene/THF. is shown in Figure 6.3 and it clearly shows the two groups of peaks that are characteristic of nido-carboranes of this type.

I.R.

The infra-red spectrum showed the following peaks:-

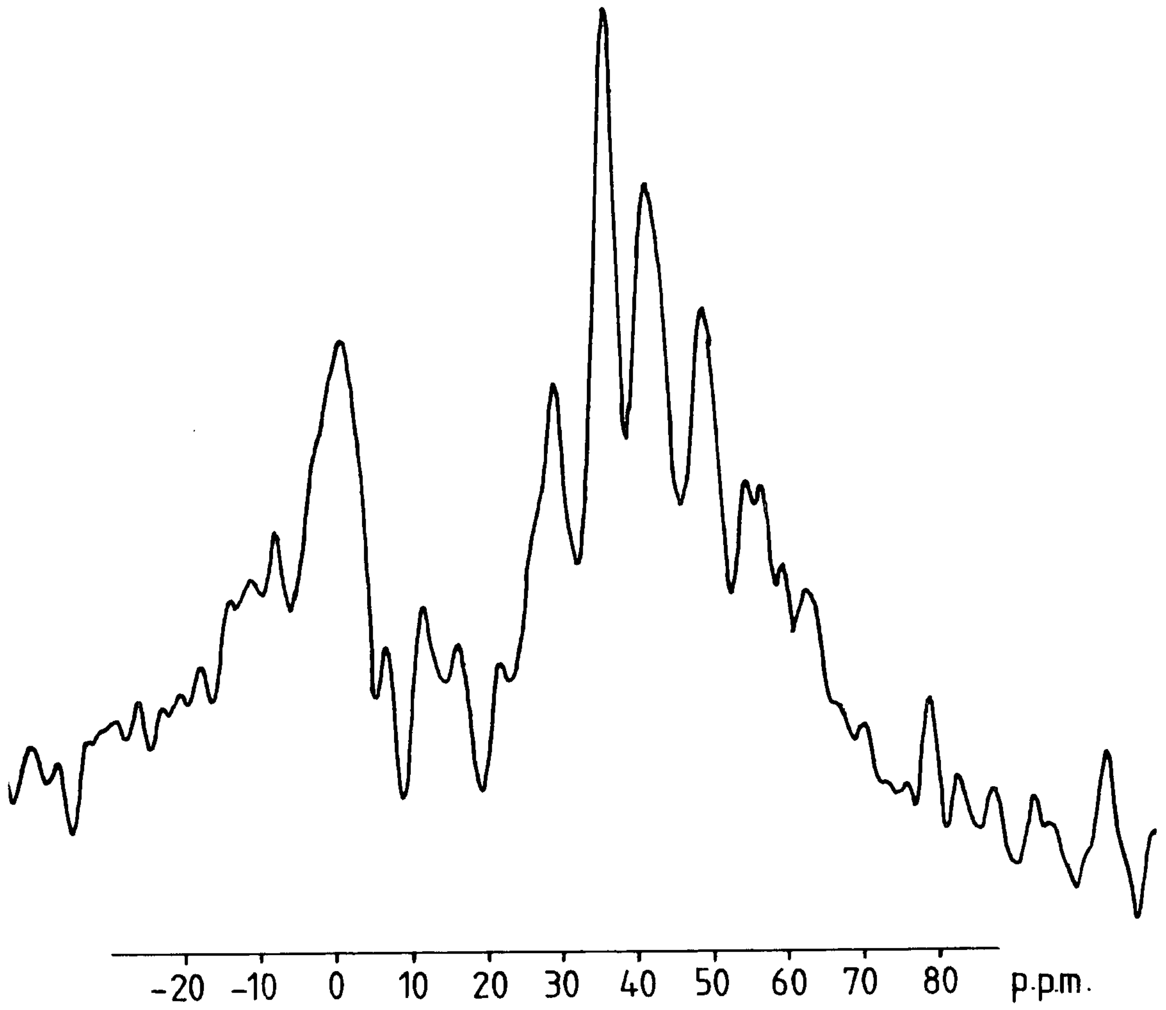
ν max. (cm^{-1}) 3040 (vs), 3028 (s) , 2964 (w) , 2840 (w) ,
2750 (s) , 2485 (vs), 2380 (sh), 1476 (sh), 1467 (vs),
1452 (s) , 1413 (s) , 1387 (s) , 1252 , 1232 ,
1178 , 1089 , 1024 (s) , 973 (vs), 913 (w) ,
876 , 834 (w) , 813 , 754 , 740 (sh)
727 (sh), 700 (sh), 630 (w) , 608 (w) , 540 (w) ,
500 (w).

(b) Preparation of Dicarbollide ion, $C_2B_9H_{11}^{2-}$. (312)

(i) Experimental

$$Me_3NHC_2B_9H_{12} + 2Na \longrightarrow Na_2C_2B_9H_{11} + Me_3N + H_2$$

1.119g of trimethyl ammonium dicarbaundecaborate(12) (5.79 m.moles) was dissolved in 30 mls of dry THF with stirring and about ten small pieces of freshly cut sodium (8 m.moles) were added. The reaction mixture was stirred for 2 hours at room temperature then refluxed for 3 hours. During the last half hour of the reflux a slow stream of nitrogen was bubbled through the solution to flush out most of the trimethylamine evolved in the reaction although this was found not to be sufficient to remove all the trimethylamine from solution contrary to literature reports. The solution was filtered through a grade 2 sinter to remove excess sodium and the sinter washed with 10 mls of dry THF. The filtrate was a THF solution of



$Me_3NH^+C_2B_9H_{12}^-$ 19 MHz ^{11}B nmr

Figure 6.3.

$Na_2C_2B_9H_{11}$. Removal of the THF under vacuum yielded solid $Na_2C_2B_9H_{11}$ and efficiently removed the last traces of dissolved trimethylamine. The $Na_2C_2B_9H_{11}$ was then redissolved in 40 mls of dry THF and stored under dry nitrogen.

6.3 REACTIONS OF $C_2B_9H_{11}^{2-}$ WITH TIN CHLORIDES

6.3.1 Reaction of Tin (IV) Chloride with Dicarbollide Ion in THF.

(i) Experimental

0.754g of tin IV chloride (0.34 mls, 2.89 m.moles) was dissolved in 50 mls of dry THF with stirring. On first addition of the tin (IV) chloride to the THF a white precipitate of $SnCl_4.(THF)_2$ adduct was formed which slowly dissolved on stirring. The tin IV chloride solution was transferred to a dropping funnel and added to the previously prepared solution of dicarbollide ion in THF over a period of 10 minutes with stirring under nitrogen. The reaction mixture was stirred at room temperature for 2 hours and then refluxed for 2 hours, cooled and the solvent slowly removed producing a white precipitate which was removed on a grade 4 sinter. Elemental analysis of the precipitate showed it to be $SnCl_4.(THF)_2$. Mass spectral analysis of the solution showed only the presence of the $SnCl_4.(THF)_2$ adduct and dicarbollide ion.

As a result of these observations, acetonitrile was used in further reactions.

6.3.2 Reaction of Tin (IV) Chloride with Dicarbollide Ion in Acetonitrile

(i) Experimental

A fresh solution of $Na_2C_2B_9H_{11}$ in THF was prepared as in 6.3.1 and the THF removed under vacuum, replaced by 20 mls of freshly dried acetonitrile and refluxed for half an hour with stirring. To the resulting suspension, was added 10 mls of acetonitrile containing 0.240g of previously prepared bis(acetonitrile) tin (IV) chloride, $SnCl_4.(MeCN)_2$. The reaction mixture was refluxed at 100°C for 5 hours with stirring, and then the solvent was removed leaving a white solid.

A mass spectral analysis of the crude product showed two main groups of high mass peaks at m/e 303 - 309 and 246 - 253. Sublimation of the crude product at about 200 - 230°C and 0.001 mm Hg separated a white material. The mass spectrum of the sublimed material showed the same two high mass groups of peaks, whereas the residue did not.

(ii) Results

Melting Point $>350°C$ (sealed tube)

Analysis

(Sublimate)	C	H	N	Sn	B	Cl
% Found	12.77	5.19	0	32.1	45	0
$Sn(C_2B_9H_{11})_2$ requires	12.52	5.74	0	31.0	50.8	0

I.R.

The infra-red spectrum showed the following peaks:-

ν max. KBr disc (cm^{-1}) 2960 (sh), 2920 (s), 2855 (s), 2530(s/br), 2350 (sh), 1660 (sh), 1640 (w), 1615 (sh), 1550 (w), 1530 (w), 1460, 1410, 1380, 1263 (s), 1090 (s/br), 1020 (s/br), 967 (w), 900 (w), 880 (sh), 863, 803 (s) 395.

^{11}B n.m.r.

The ^{11}B n.m.r. will be discussed on page 221.

Mass Spectrum

The mass spectrum will be discussed on page 218.

6.3.3 Reaction of Tin (IV) Chloride with $Tl^+[TlC_2B_9H_{11}]^-$

$Tl^+[TlC_2B_9H_{11}]^-$ was prepared by the addition of aqueous thallium (I) acetate to an aqueous alkaline solution of $K^+C_2B_9H_{12}^-$. (322) The insoluble $Tl^+[TlC_2B_9H_{11}]^-$ was washed with water and dried in vacuo.

0.11g of tin (IV) chloride (0.434 m.moles, 0.051 mls) in 20 mls of dry acetonitrile was added to a stirred suspension of 0.469g of thallio carborane $Tl^+[TlC_2B_9H_{11}]^-$ (0.867 m.moles) in 30 mls of dry acetonitrile. The reaction mixture left stirring for 12 hours during which time the colour of the suspension turned slowly from pale yellow to white. The mixture was refluxed for 4 hours and cooled to room temperature. The white precipitate was removed on a grade 4 sinter and washed with 10 mls of dry acetonitrile and dried in vacuo. The solvent was removed from the filtrate yielding a white solid.

(ii) Results

Analysis

(Filtrate)	C	H	N	Sn	B	Cl
% Found	12.46	5.51	0	31.8	46	0
$Sn(C_2B_9H_{11})_2$ requires	12.52	5.74	0	30.96	50.76	0

(Precipitate)	Tl	Cl
% Found	84.6	14.9
TlCl requires	85.22	14.78

I.R.

The infra-red spectrum of the filtrate was identical to that of the sublimate from experiment (iii).

Mass Spectrum

The mass spectrum will be discussed on page 218.

^{11}B nmr.

The ^{11}B nmr. will be discussed on page 221.

The elemental analysis data from experiments 6.3.2 and 6.3.3 indicated that the unknown dicarboranyl tin sandwich compound appeared to have been successfully prepared by the use of dicarbollide ion or thallio-carborane $Tl^+[TlC_2B_9H_{11}]^-$. In order to confirm the analysis results, experiment

6.3.4. was carried out to prepare the known $SnC_2B_9H_{11}$ species so that a direct comparison of the compounds could be made using, infra red, Raman, MS and ^{11}B nmr.

6.3.4 Reaction of Tin (II) Chloride with Dicarbollide Ion. (326,327)

(i) Experimental

$$Na_2C_2B_9H_{11} + SnCl_2 \longrightarrow SnC_2B_9H_{11} + 2NaCl$$

0.2395g of trimethylammonium dicarbaundecaborate(12), (1.2 4 m.moles) was dissolved in 50 mls of benzene and 20 mls of THF, (Benzene alone was not used (327) as the salt was insoluble in it) and about ten small pieces of sodium (2.5 m.moles) added with stirring. The mixture was stirred at room temperature for 2 hours during which time the solution turned from colourless to red. The solution was refluxed for 3 hours and allowed to cool to room temperature. The excess sodium was removed on a grade 2 sinter and the sinter washed with 10 mls of dry THF. A solution of 1.2g of anhydrous tin (II) chloride (6.33 m.moles) in 20 mls of dry THF was prepared and 5.1 mls of this solution was added to the filtrate. (This represents a 30% excess over the stoichiometric amount). The solution gradually turned cloudy, the cloudiness slowly increasing during 2 hours of reflux at 105°C. The reaction mixture was then cooled and the solvent slowly removed under vacuum to give a white residue. The product was soxhlet extracted from the residue with benzene, and recovered on removal of the solvent. The product was further purified by vacuum sublimation at 140°C under vacuo onto a liquid nitrogen cooled cold finger.

(ii) Results

Analysis

	C	H	N	Sn	B	Cl
% Found	9.72	4.0	0	46.8	38.65	0
$SnC_2B_9H_{11}$ requires	9.56	4.38	0	47.29	38.76	0

Mass Spectrum

The mass spectrum of the product will be discussed below.

^{11}B nmr.

The ^{11}B nmr will be discussed below.

I.R.

The infra-red spectrum showed the following peaks:

ν max. KBr disc (cm^{-1}) 3030 , 2760 , 2570 (sh),
2500 (sbr), 1242 , 1230 , 1165 (w) , 1088 ,
1039 (sh) , 1023 , 1004 , 973 (s) , 964 (sh),
948 (sh) , 916 (w) , 892 , 880 , 857 ,
840 , 811 (w) , 775 (sh), 765 (sh), 754 (sh),
740 (sh) , 731 (sh), 724 (s) , 706 (sh), 613 (w) ,
570 (w) , 237 (s).

6.3.5 Results Comparison

For the purposes of the comparison of results from $SnC_2B_9H_{11}$ and the suspected $Sn(C_2B_9H_{11})_2$ compounds, the latter will be referred to as compound A.

(i) Analytical Data

The analytical data for compound A shows very good agreement with the molecular formula $Sn(C_2B_9H_{11})_2$ shows that the method of analysis is accurate for all the elements.

(ii) Mass Spectra

The mass spectra of the mono carboranyl tin (Figure 6.4) and compound A (Figure 6.5) are shown on the following pages. Figure 6.4 shows the expected breakdown pattern of $SnC_2B_9H_{11}$ with a parent ion peak at m/e 258, corresponding to $^{12}C_2{}^{11}B_9{}^{1}H_{11}{}^{124}Sn$ (326,327), a characteristic tin isotope pattern at m/e 116 - 120 and a $C_2B_9H_{11}$ isotope pattern at m/e 126-137.

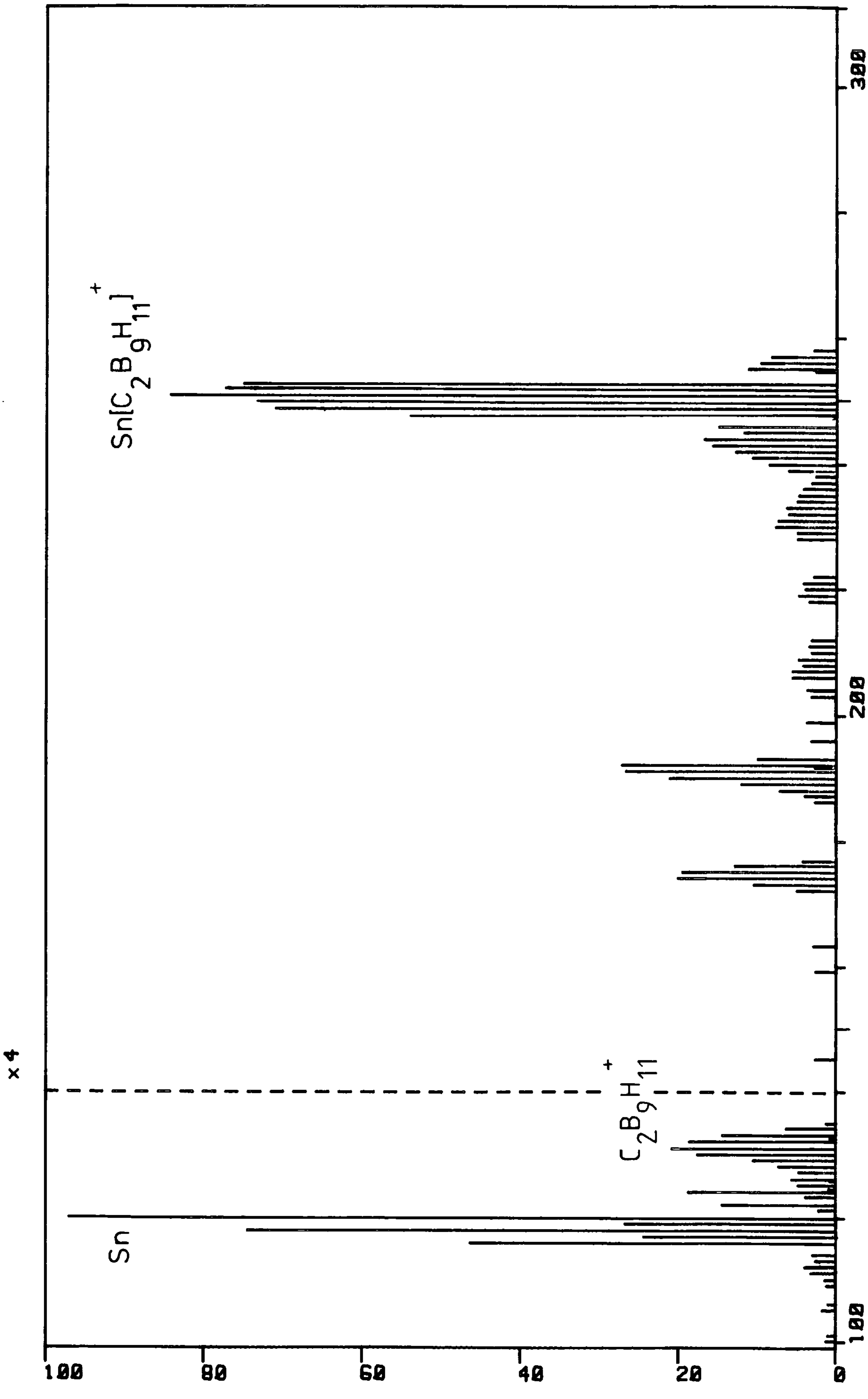


Figure 6.4.

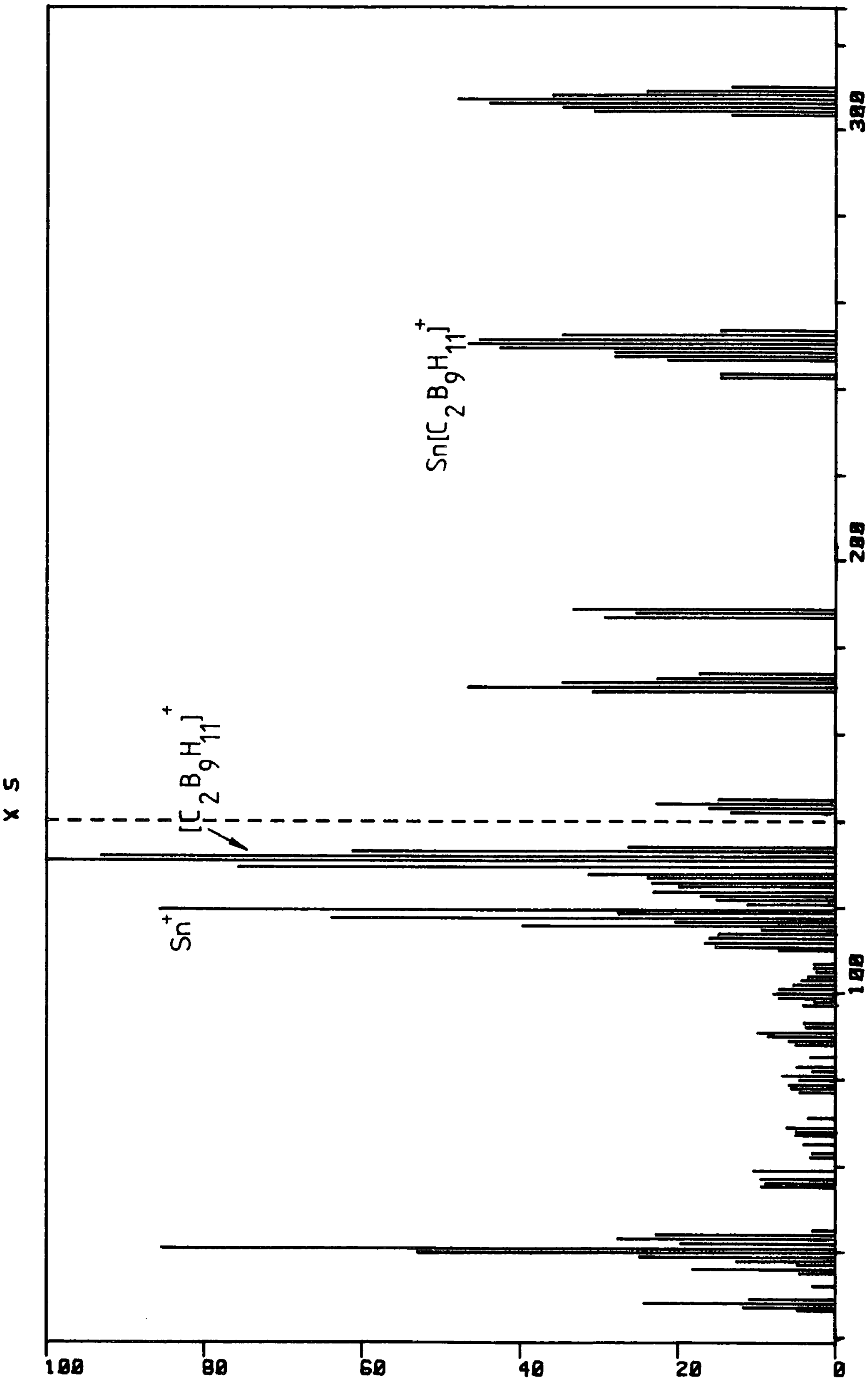


Figure 6.5.

Figure 6.5 shows all of these features which would be common to both mono and dicarboranyl tin but does not show a parent ion peak at m/2 392 which would correspond to $^{12}C_4{}^{11}B_{18}{}^{1}H_{22}{}^{122}Sn_1$. The parent ion appears at m/e 314 and is thought to be due to the breakdown of a higher mass species, most probably $Sn(C_2B_9H_{11})_2$. This would represent a loss of a fragment of m/e 78.

The loss of a cage fragment rather than Sn - Cage splitting would imply that the tin atom is strongly bonded into the carborane cage.

(iii) ^{11}B nmr.

^{11}B nmr spectra were run on both compounds using a catting Fourier Transform 19 MHz machine. The samples were dissolved in 90% dry benzene 10% dry THF. The addition of the THF was necessary because compound A unlike $SnC_2B_9H_{11}$ is insoluble in neat benzene. Figure 6.6. shows the ^{11}B spectrum for mono-carboranyl tin, Figure 6.7 that of compound A, Figure 6.8 shows the spectrum of compound A at narrower sweep width and Figure 6.9 at 28.87 MHz.

A comparison of Figures 6.6 and 6.7 shows that the two compounds are clearly different although the spectra possess very similar characteristics. Voorhees (326) and Rudolph (327) reported the 32.1 MHz ^{11}B spectrum of $SnC_2B_9H_{11}$ as consisting of two doublets ($J_{BH} = 141$ Hz) at +24.8 and +31.8 p.p.m. (relative to $B(OMe)_3$) superimposed on a broad unresolved signal which peaked at 30 p.p.m. Figure 6.9 shows that the 28.87 MHz ^{11}B nmr spectrum of compound A consists of 4 doublets superimposed on top of a broad unresolved signal. The presence of 4 doublets could be due to the dicarboranyl tin adopting a slipped structure in which the two carboranyl residues are angled relative to each other in a carboranyl analogue of dicyclopentadienyl tin (Figure 6.10). This would give rise to non-equivalent boron atoms in the two cages and hence four doublets instead of two for a symmetric sandwich

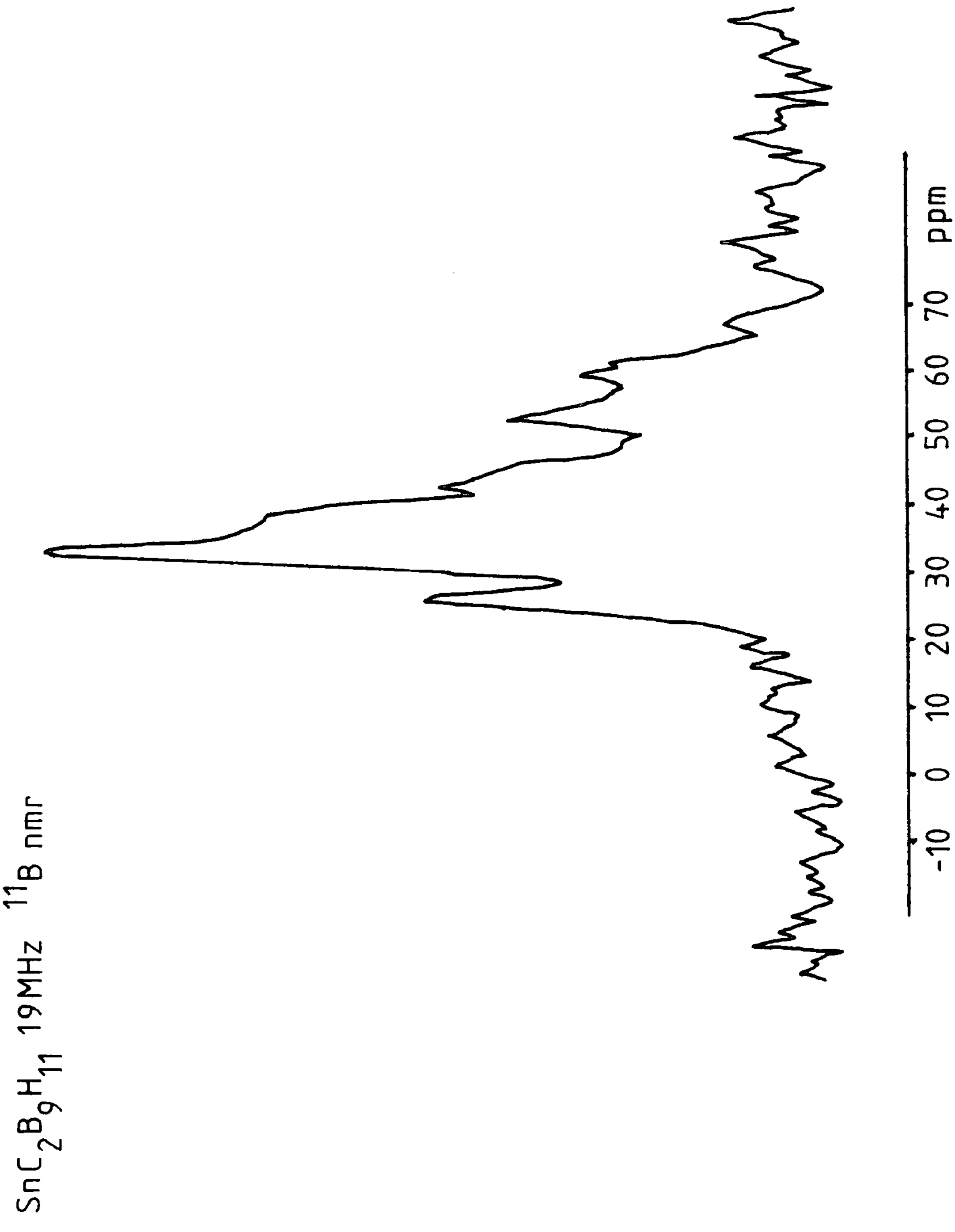


Figure 6.6.

Compound A 19MHz ^{11}B nmr

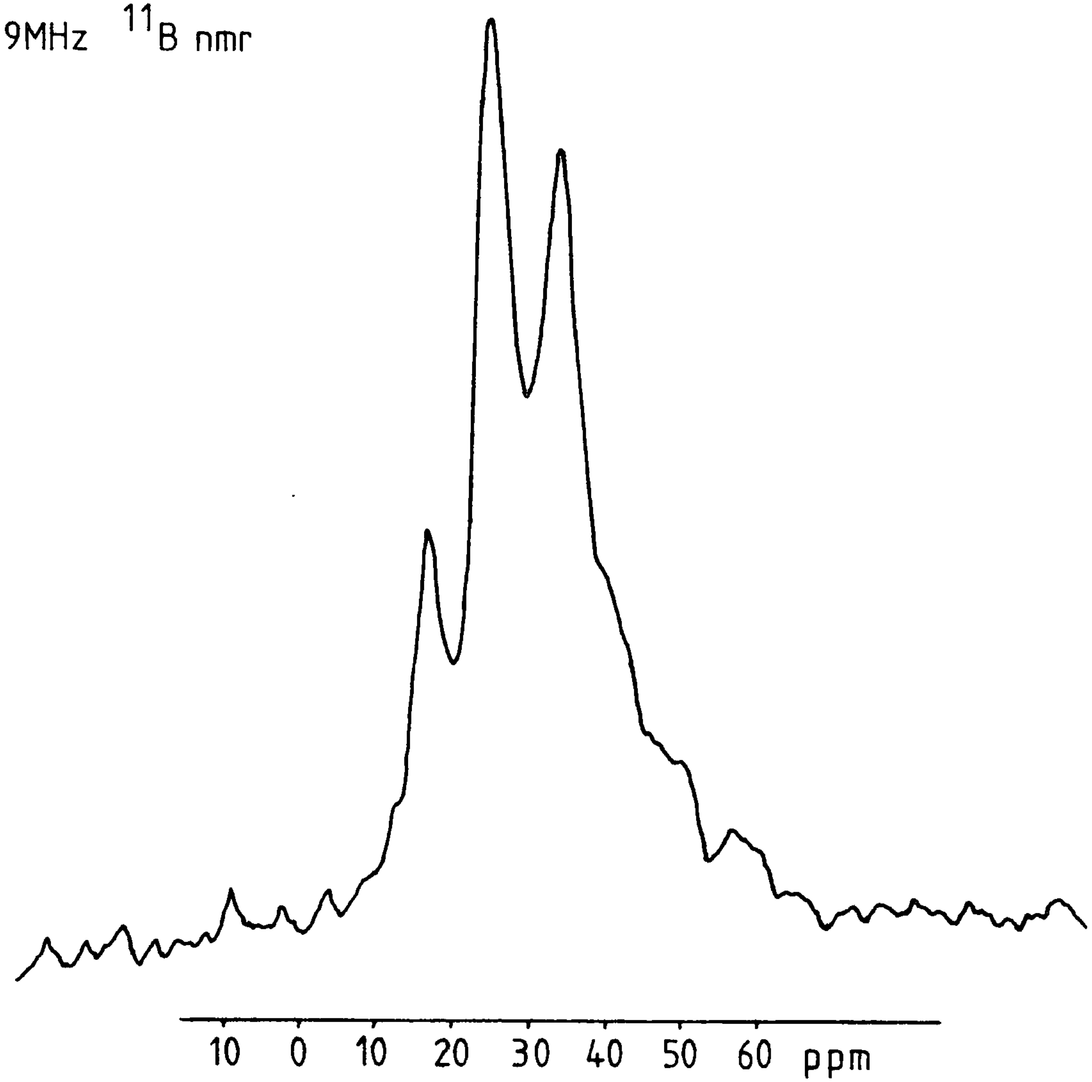


Figure 6.7

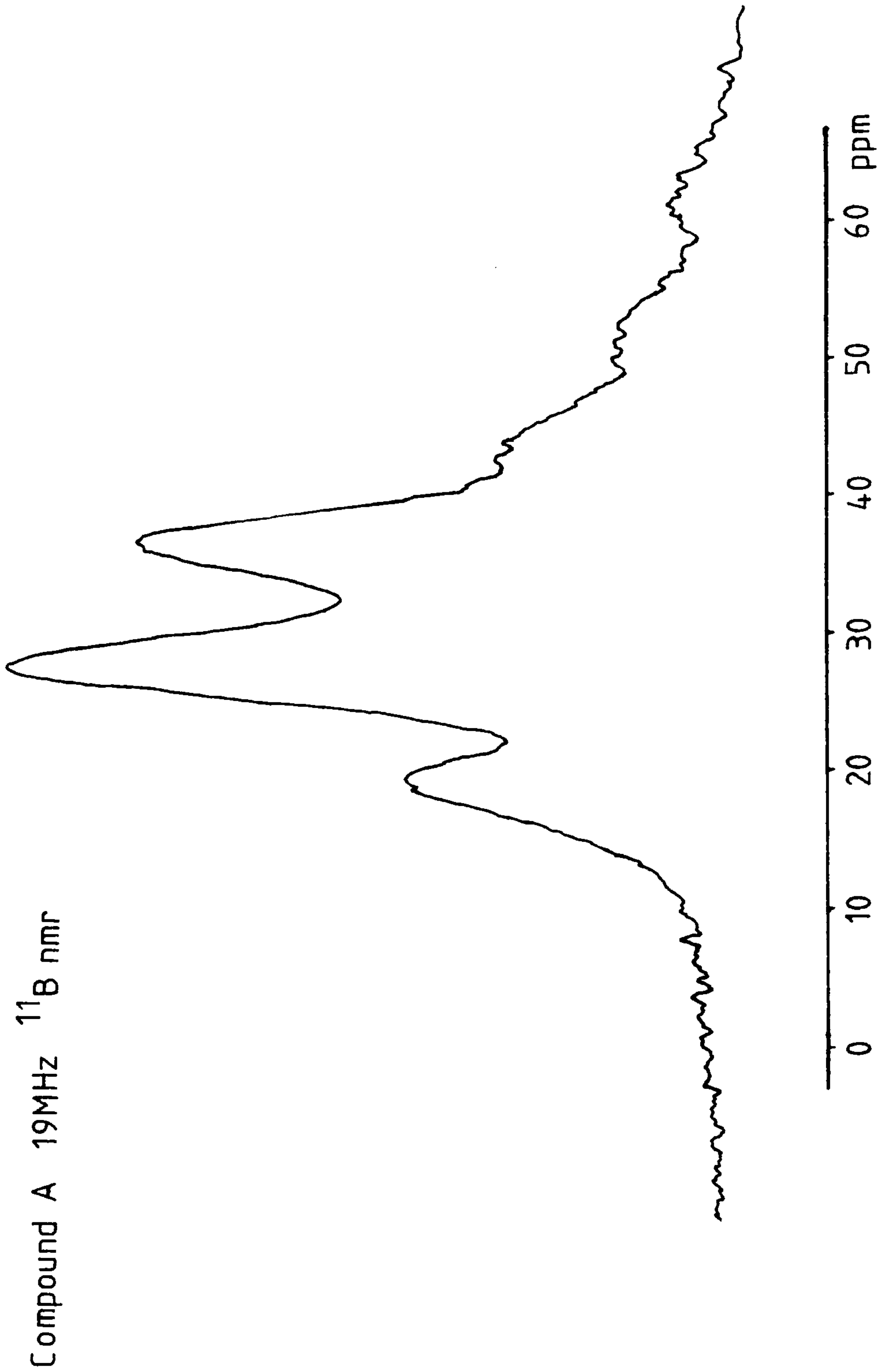


Figure 6.8.

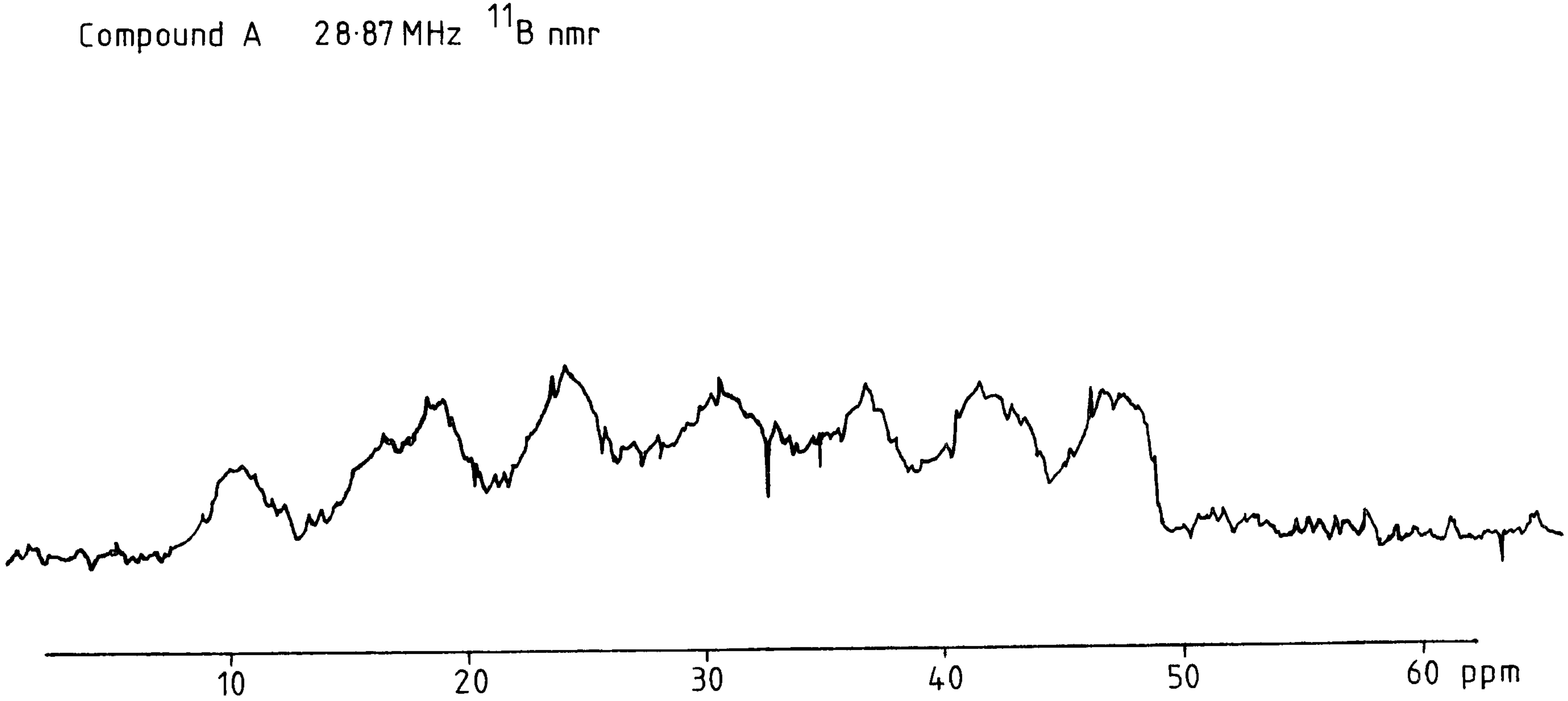


Figure 6.9.

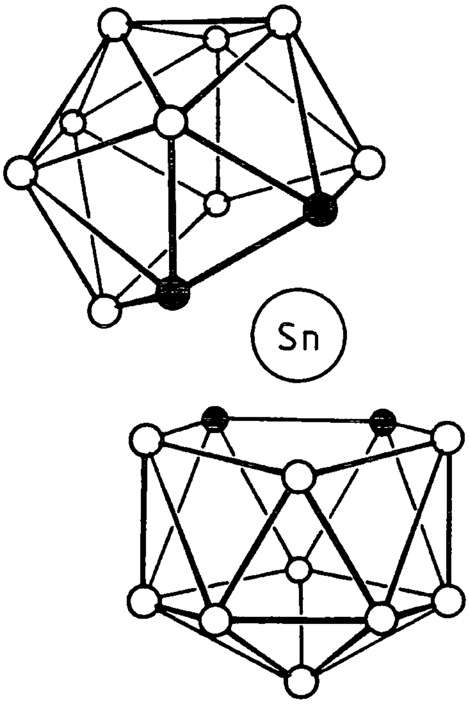
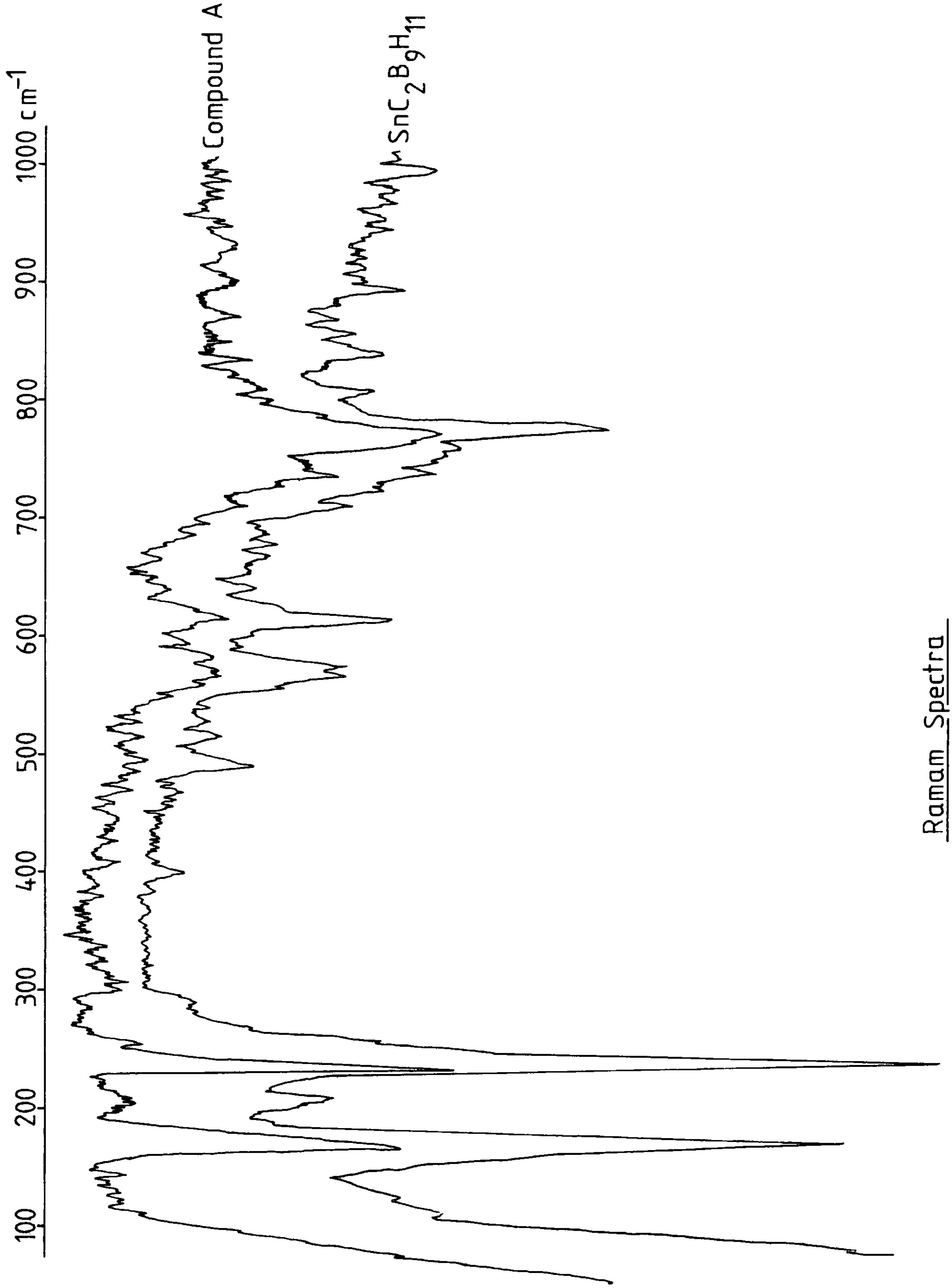


Figure 6.10.



Ramam Spectra

Figure 6.11.

compound at about 30 MHz.

This novel structure is proposed for the dicarboranyl tin compound against the more normal transition metal d^8, d^9 or d^{10} assymmetric carborane slipped sandwich purely on the basis of ^{11}B nmr results. ^{11}B nmr studies of the slipped transition metal compounds have shown the presence of a distinctive low field doublet. (441) Observance of similar low field doublets have also been observed in some icosahedral metallocarboranes. (327)

Work by Wallbridge et al has shown that in icosahedral metallocarboranes the amount of slip distortion increases as the electron density of the metal atom increases. With d^{10} metals such as Hg the metal is co-ordinated via a single Hg - B pseudo σ-bond. With the $d^{10}s^2$ thallous ion no strong Tl - C_2B_3 face bond exists and the species is formally regarded as an ion - pair (450) although the thallium atom has been shown to be more symmetrically positioned. (442) Generally as the distortion increases the low-field doublet shifts to lower fields, however d^{10} $(HgPPh_3)C_2B_9H_{11}$ and $d^{10}s^2$ $[TlC_2B_9H_{11}]^-$ show no low-field doublet despite their slipped configuration.

The lack of a low field doublet in compound A does not therefore imply a symmetric positioning of the tin atom above the two C_2B_3 faces.

(iv) Vibrational Spectra

ν max Raman $SnC_2B_9H_{11}$

3043 (s) , 3026 (sh), 2970 (w) , 2955 , 2890 (w) ,
2590 (s) , 2565 (s) , 2558 (s) , 2528 (s) , 2437 (w) ,
2163 (w) , 1910 , 1893 (w) , 1745 (w) , 1330 (w) ,
1112 (w) , 907 (w) , 854 (w) , 821 (w) , 786 ,
772 (w) , 751 , 724 (w) , 644 (sh), 623 ,
591 (sh), 584 (w) , 574 , 566 (sh), 498 (w) ,

403 (w), 237 (vs), 210 (w), 169 (vs), 53 (vs),
38 (vs) cm^{-1}.

ν max Raman $Sn(C_2B_9H_{11})_2$

3054 (s), 3028, 2928 (w), 2832 (w), 2626 (s),
2592 (s), 2563 (s), 843 (w), 779, 769 (sh),
746, 620 (w), 588 (w), 570 (w), 253 (w),
237, 171 (s), 56 (s), 42 (vs) cm^{-1}.

A comparison of the Raman spectra shows that the two compounds are clearly related. Figure 6.11 shows the 0-1000 cm^{-1} region in which the cage vibrations and cage-metal stretch occur. The cage vibrations (450 - 1000 cm^{-1}) show a change between $SnC_2B_9H_{11}$ and compound A with the weaker peaks being broadened weakened or absent in the latter case. The stronger peaks in the 700 - 800 cm^{-1} region again show slight broadening and the resolution of the shoulder in the $SnC_2B_9H_{11}$ into two well defined peaks in compound A.

The region 0-350 cm^{-1} shows a great reduction in the size of the peaks compared to the cage vibration bands in compound A relative to $SnC_2B_9H_{11}$. This could be due to a restriction in the movement of the tin atom in $Sn(C_2B_9H_{11})_2$.

Infra red data on the two compounds was given in the experimental section. Both spectra show vibrations identifiable as cage motions 400 - 810 cm^{-1}, δB-H 810 - 1050 cm^{-1}, δC-H 1050 - 1300 cm^{-1}, νB-H ~ 2500 cm^{-1} νC-H ~ 3050 cm^{-1}. Neither spectrum reveals much structural information.

(v) Conclusions

The results show conclusively that compound A is $Sn(C_2B_9H_{11})_2$ and is therefore the first recorded main group element carborane "sandwich" compound.

It is unfortunate that as with the reported failures in the literature to crystallize $SnC_2B_9H_{11}$ for X-ray crystallographic study, I was unable to produce crystals of either $SnC_2B_9H_{11}$ or $Sn(C_2B_9H_{11})_2$.

6.4 REACTIONS OF $C_2B_9H_{11}^{2-}$ COMPOUNDS WITH GERMANIUM (IV) CHLORIDE

6.4.1 Introduction

In section 6.3 it was shown that Sn(IV) compounds reaction with $C_2B_9H_{11}^{2-}$ based compounds to yield a $Sn(C_2B_9H_{11})_2$ sandwich species. In this section the equivalent reactions with Ge(IV) compounds are investigated.

6.4.2 Reaction of Germanium (IV) Chloride with Dicarbollide Ion in Acetonitrile

(i) Experimental

A solution of dicarbollide in 50 mls of dry THF was prepared from 0.385g of trimethylammonium dicarbaundecaborate (2.0 m.moles) and the THF removed under vacuum and replaced by 75 mls of dry acetonitrile. 0.117 mls of freshly vacuum distilled germanium (IV) chloride. (1.0 m.moles) in 10 mls of dry hexane was added to the stirred suspension of dicarbollide ion.

The mixture was refluxed for 6 hours, cooled to room temperature and filtered using a grade 4 sinter. The material removed by the sinter consisted of a liquid immiscible with acetonitrile/hexane mixture and a solid. Removal of the solvent from the filtrate gave a white solid which was purified by fractional sublimation. The crude product was heated in a sublimation apparatus to 85°C under vacuo and held at that temperature for 15 minutes to separate any $GeC_2B_9H_{11}$ formed by sublimation onto a cold finger. (Sublimation point of $GeC_2B_9H_{11}$ is 80°C under vacuo). The apparatus was then cooled to room temperature and transferred to a glove box. The sublimate was removed from the cold finger and stored under dry nitrogen. The cold finger was carefully cleaned and reconnected to the sublimation apparatus. A second sublimation was then performed on the residue with the temperature being raised to ~ 190°C to sublime any remaining volatile materials. A thin coating was formed on the cold finger which was removed under the same conditions as the first sublimate.

(ii) Results

Analysis

% Found	C	H	Cl	Ge	B
1st sublimate	12.36	5.71	0	28.1	-
2nd sublimate	14.8	6.22	0	22.4	56.7
$GeC_2B_9H_{11}$ requires	11.72	5.37	0	35.43	47.48
$Ge(C_2B_9H_{11})_2$ requires	14.23	6.52	0	21.53	57.70

On the basis of the chemical analysis the 2nd sublimate appears to match the desired product and will be referred to as such.

6.4.3 Reaction of Germanium IV Chloride with $Tl^+[\underline{Tl}C_2B_9H_{11}]^-$ in Acetonitrile

11.4076g of $Tl^+[TlC_2B_9H_{11}]^-$ (2.6 m.moles) was added to 50 mls of dry acetonitrile containing 1.3 m.moles of freshly vacuum distilled germanium(IV) chloride. The mixture was stirred for 24 hours during which time the colour of the suspension turned from pale yellow to white. The reaction mixture was then refluxed for 3 hours, cooled to room temperature and the precipitate removed on a grade 4 sinter, and washed with 10 mls of dry acetonitrile. Analysis showed the precipitate to be a mixture of thallium (I) chloride and unreacted thallio carborane. No germanium was found in the precipitate.

The excess solvent was removed from the filtrate under vacuum leaving a white solide which was further purified by fractional vacuum sublimation, as detailed in section 6.4.2.

(ii) Results

Analysis

% Found		C	H	Cl	Ge	B
1st sublimate		12.31	5.68	0	33.26	50.1
2nd sublimate		13.9	6.31	0	22.73	56.3
$GeC_2B_9H_{11}$	requires	11.72	5.37	0	35.43	47.48
$Ge(C_2B_9H_{11})_2$	requires	14.23	6.52	0	21.53	57.70

On the basis of the chemical analysis the 2nd sublimate appears to match the desired product and will be referred to as such.

6.4.4 Results Comparison

(i) Analaytical Data

The analytical data indicated that $Ge(C_2B_9H_{11})_2$ had been prepared.

(ii) Mass Spectra

The mass spectra from the products of experiments 6.4.2 and 6.4.3 are shown in Figures 6.12 and 6.13 respectively.

The main feature of Figure 6.13 is a group of peaks from m/e 120 - 136 attributable to $C_2B_9H_{11}$, above this is a succession of small groups of peaks leading up to a group of peaks showing a characteristic carborane pattern at m/e 200 - 210. This mass range is consistent with the known $GeC_2B_9H_{11}$ compound. The filtrates from experiments 6.4.2 and 6.4.3 also showed higher groups of peaks. The highest mass of these were a group of fairly low intensity ranging from m/e ~ 332 - 342. (Figure 6.12(a)) In the case of experiment 6.4.3, these could be explained by the species $TlC_2B_9H_{11}$. However from the product of experiment 6.4.2 exactly the same peaks were observed. These peaks are therefore probably due to $Ge(C_2B_9H_{11})_2$ which would give a range of peaks from m/e 320 - 344. The

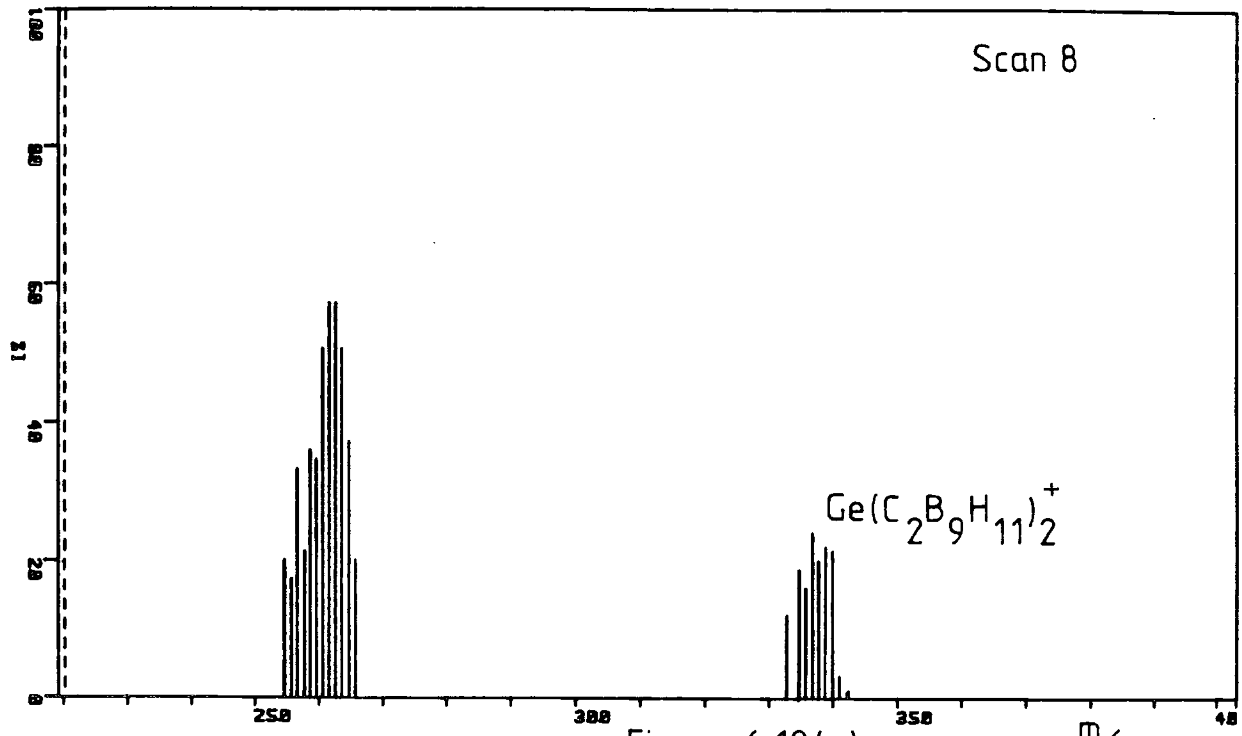


Figure 6.12(a).

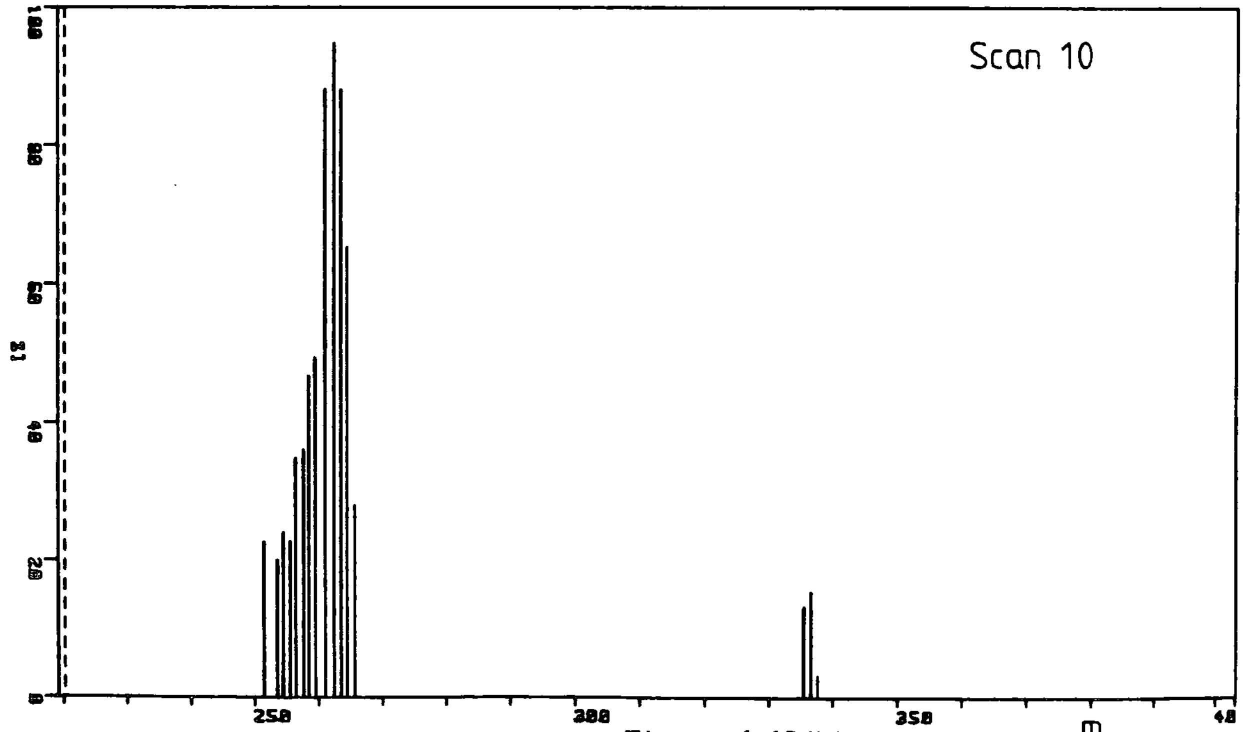


Figure 6.12(b).

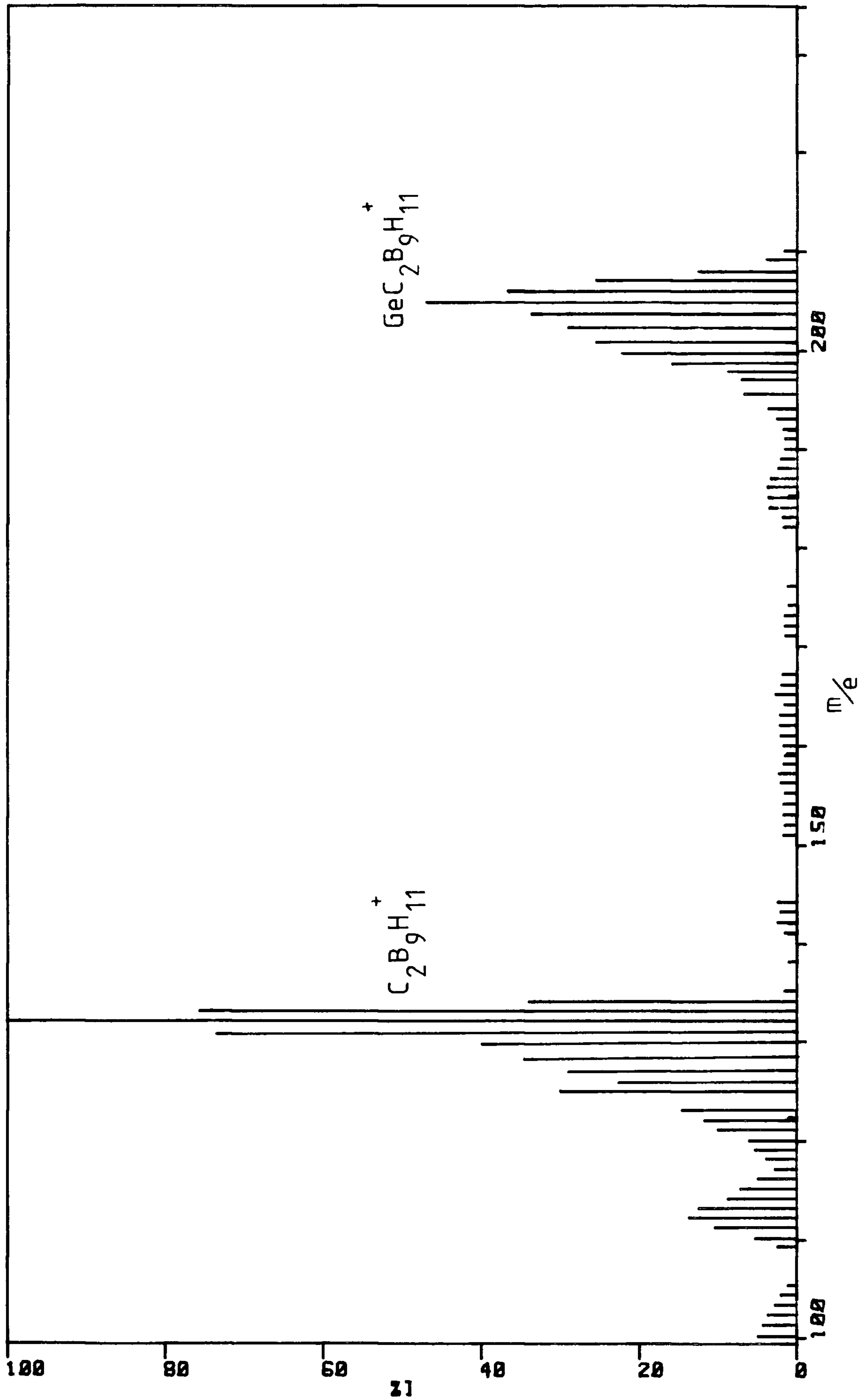


Figure 6.13.

low ion current of this compound appears to have rendered the lower peaks and the highest two peaks undistinguishable from the background noise. Despite this the carborane isotope pattern is still clearly visible.

At lower m/e values of about 254 - 265 there is another group of peaks showing a carborane type isotope pattern. These are due to the loss of a fragment of about m/e 78 (c.f. $Sn(C_2B_9H_{11})_2$) from the parent ion as signified by the temporary increase in the m/e 254 - 265 species ion current as the parent ion current decreased. This was followed by a slow reduction (Figures 12(a-b)) in the lower species ion current after the parent ion had disappeared with a subsequent increase in the $GeC_2B_9H_{11}$ ion current.

The mass spectra of the products from experiments 6.4.2 and 6.4.3 fit the results that would be expected for the species $Ge(C_2B_9H_{11})_2$. There is also good correlation between the mass spectra from the germanium compounds and those from the tin compounds described in the previous section. It is interesting to note that both parent species appear to lose a similar fragment of about 78 mass units.

In studying the mass spectra of $GeC_2B_9H_{11}$, $SnC_2B_9H_{11}$, and $PbC_2B_9H_{11}$, Rudolph et all (327) noted that relative intensity of the parent ion to the rest of the spectrum decreased in the order $GeC_2B_9H_{11} > SnC_2B_9H_{11} > PbC_2B_9H_{11}$. This, he deduced, reflected the relative stability of the icosahedra which decreased in the same order. Based on this and the weak peaks observed for the $Ge(C_2B_9H_{11})_2$ parent ion it is not unreasonable that under the same conditions, no parent ion was detected by the computer for $Sn(C_2B_9H_{11})_2$.

(iii) ^{11}B nmr.

19 MHz ^{11}B nmr. was run on the products from experiments 6.4.2 and 6.4.3 using the same conditions, equipment, and solvents as for $SnC_2B_9H_{11}$

and $Sn(C_2B_9H_{11})_2$. Figure 6.14 shows the ^{11}B nmr spectrum of product of experiment 6.4.2 and Figure 6.15 the spectrum of the material recovered from the 1st sublimation.

A comparison of Figure 6.14 with Figures 6.7 and 6.8 reveals a striking similarity towards the dicarboranyl tin spectra, whilst Figure 6.15 compares favourably with Figure 6.6 of mono-carboranyl tin. Unfortunately 28.87 MHz ^{11}B nmr. facilities were no longer available to give a better spectrum of the product but the 19 MHz spectra show enough detail to predict a similar structure for the product $Ge(C_2B_9H_{11})_2$.

(iv) Raman

No Raman spectrum is available for the product as severe charring was encountered and the resultant spectrum could not be relied upon as an accurate record of the original compound. Even at low laser power there were significant differences between successive runs indicating some decomposition.

(v) Conclusions

Based upon the analytical evidence from A.A., elemental analysis, ^{11}B nmr. and M.S., and comparing these results with those obtained from analogous tin reactions, I conclude that the previously unknown $Ge(C_2B_9H_{11})_2$ dicarboranyl germanium compound has been successfully prepared. Unfortunately, as with the $Sn(C_2B_9H_{11})_2$ species, no X-ray information could be obtained as $Ge(C_2B_9H_{11})_2$ did not form regular crystals despite the employment of many techniques.

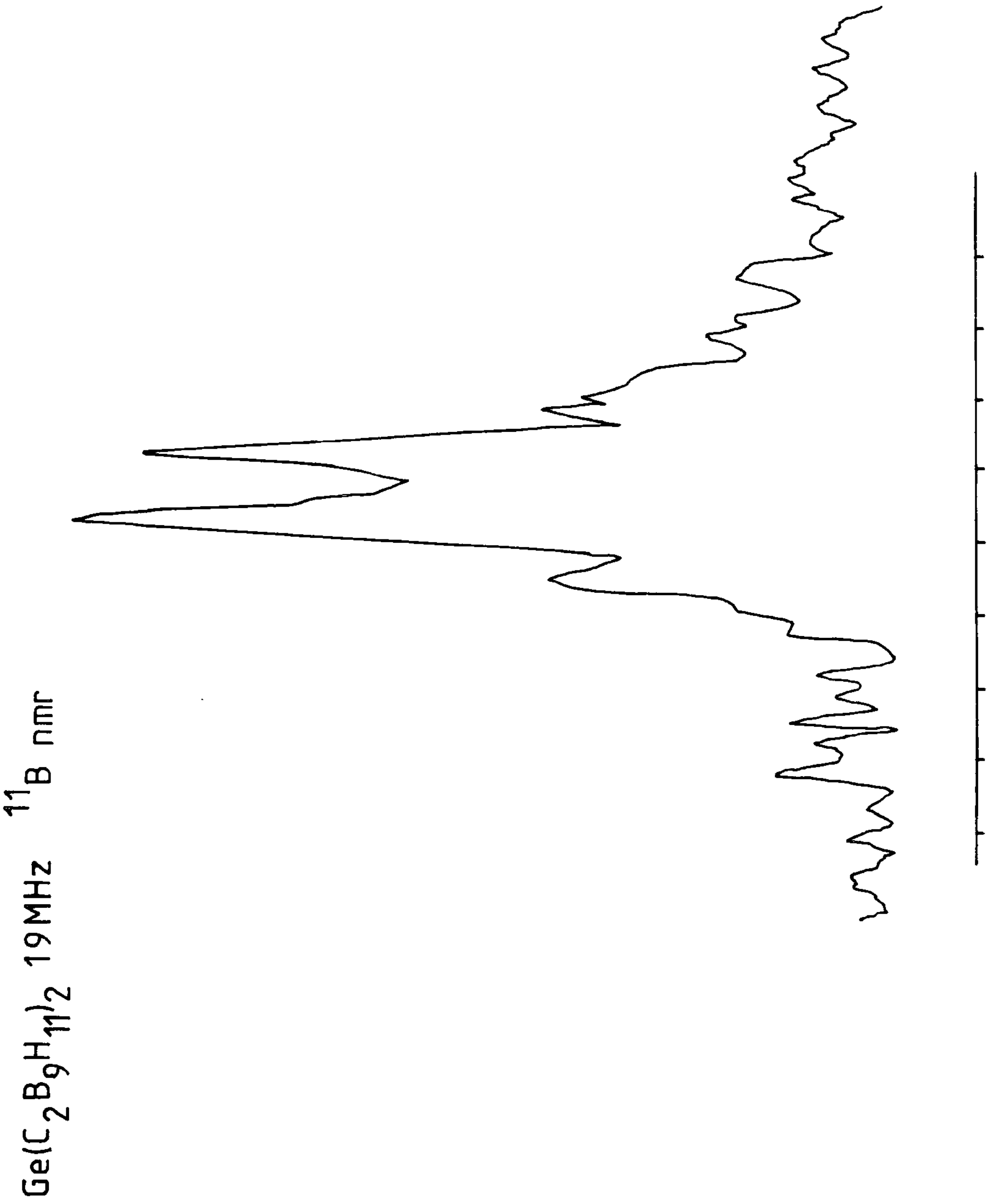


Figure 6.14.

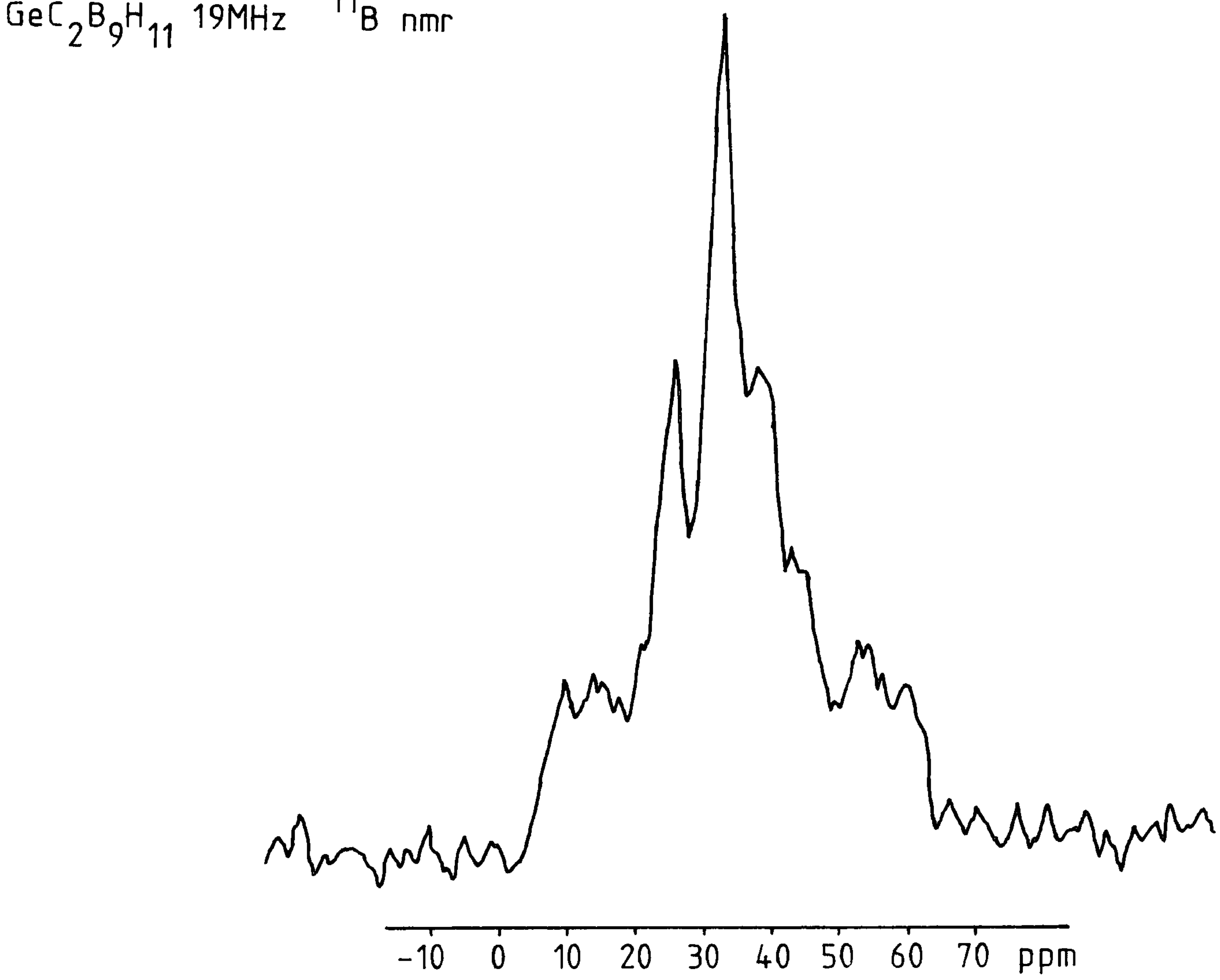


Figure 6.15.

6.5 REACTIONS OF $C_2B_9H_{11}{}^{2-}$ COMPOUNDS WITH SILICON (IV) CHLORIDE

6.5.1 Reaction of Silicon (IV) Chloride with $Tl^+[TlC_2B_9H_{11}]^-$

(i) Experimental

1 ml of freshly vacuum distilled silicon (IV) chloride was made up to 100 mls with dry acetonitrile under dry nitrogen. 6.8 mls of this solution (.594 m.moles $SiCl_4$) was added to a stirred suspension of 0.642g $Tl^+[TlC_2B_9H_{11}]^-$ (1.19 m.moles) in 40 mls of dry acetonitrile under dry nitrogen. The mixture was refluxed for 3 hours and allowed to cool to room temperature. During the reflux, the original pale yellow suspension changed in colour to grey. The suspension was removed on a grade 4 sinter and washed with 10 mls of dry acetonitrile. The volume of the filtrate was reduced under vacuum yielding a white powder.

(ii) Results

Analysis

% Found		C	H	Si	B	Tl	Cl
Precipitate		0.94	0.5	0.70	3.8	78.8	13.8
Filtrate		7.3	3.1	-	30.7	58.1	-
$SiC_2B_9H_{11}$	requires	14.98	6.86	17.51	60.66	-	-
$Si(C_2B_9H_{11})_2$	requires	16.41	7.52	9.59	66.48	-	-
TlCl		-	-	-	-	85.22	14.78

Mass Spectrum

Mass spectrum analysis of the precipitate and filtrate gave very similar results. (Figure 6.16) Some features of the mass spectrum that are not shown in Figure 6.16 were peaks at m/e 338 attributable to $TlC_2B_9H_{11}$ and m/e 203 and 205 due to Tl^+. The spectrum in Figure 6.16 shows two groups of carboranyl peaks at m/e 125 - 134 ($C_2B_9H_{11}$) and at m/e 151-160. It is not

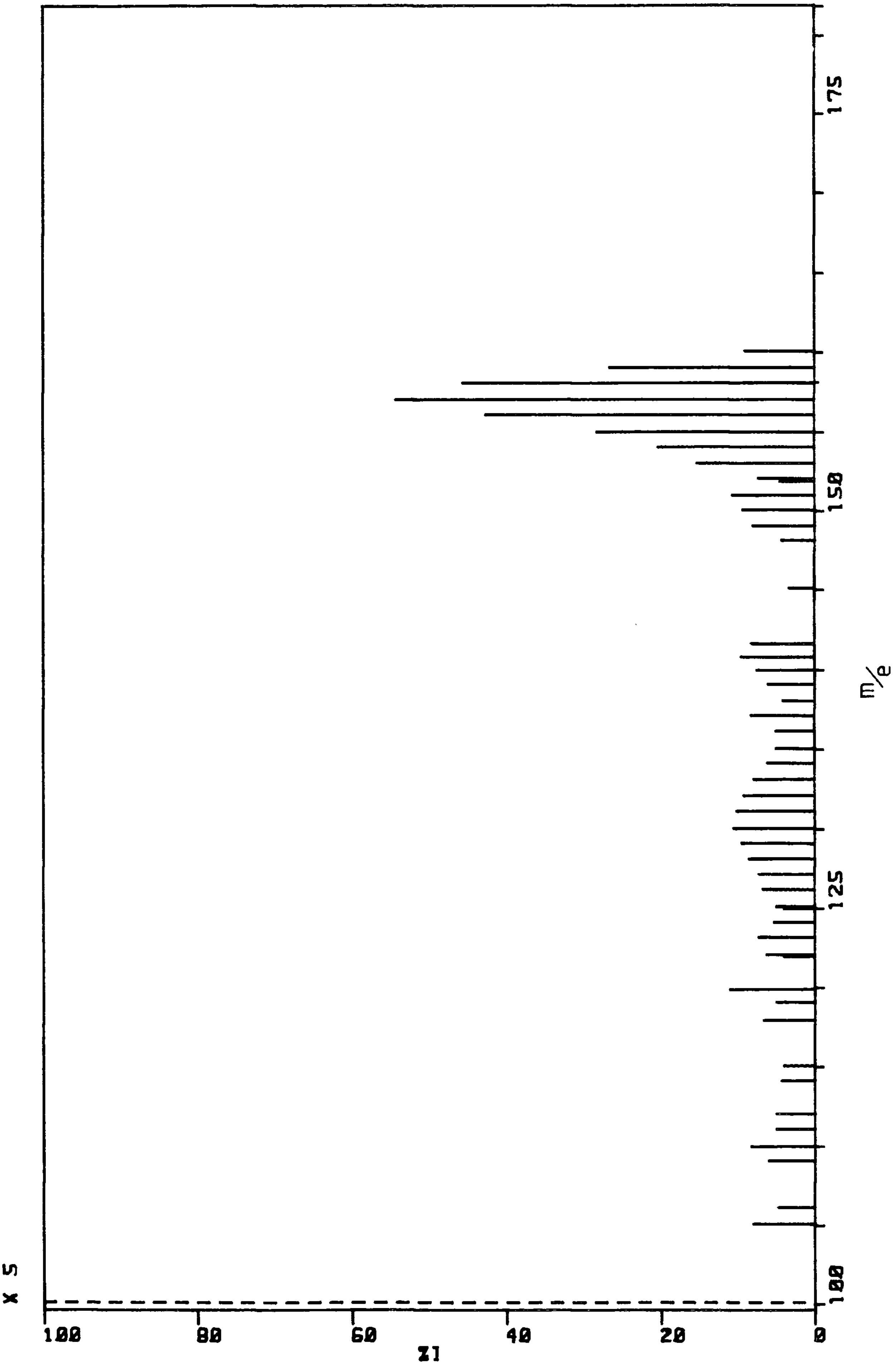


Figure 6.16.

clear what species the latter group represents as $SiC_2B_9H_{11}$ would have m/e values of 153 - 164. Measurement error can be ruled out as the ^{203}Tl and ^{205}Tl peaks were correctly assigned. The logical combination of atoms which could give rise to the observed spectrum is $(CN)C_2B_9H_{11}$ but whilst this is unlikely, it cannot be proved or disproved by the data available.

Unfortunately the work reported above was carried out at the end of the 3 year study and insufficient time was available to gather further data.

6.6 REACTIONS OF $C_2B_9H_{11}^{2-}$ COMPOUNDS WITH ZINC (II) CHLORIDE

6.6.1 Introduction

Whilst transition metal carboranyl derivatives have been prepared for most of the transition metals, icosahedral and sandwich compounds have not been prepared for zinc or cadmium. Mercury derivatives have been prepared but these have been shown to contain an Hg - B bond to the unique boron on the open face of the carborane cage. Although this is still a twelve atom unit the mercury atom is considerably distorted from the centre of the 5 membered carboranyl face with only weak bonding to the other boron atoms of the face. (442)

Zinc and cadmium d^{10} derivatives would also be expected to possess this same distortion. Attempts were made to prepare the unknown zinc derivative.

6.6.2 Preparation of Zinc (II) Chloride

(i) Experimental

About 8g of zinc dust was added to 150 mls of dry diethyl ether in a 150 mls round bottomed three necked flask fitted with a dry nitrogen inlet and a reflux condenser. A separate nitrogen supply was connected through a glass T piece to a delivery tube under the surface of the ether and a cylinder of dry hydrogen chloride gas connected to the third arm of the T piece. The reaction flask was cooled in an ice bath and a nitrogen diluted stream of dry hydrogen chloride bubbled through the stirred zinc suspension for about 3 hours or until most of the zinc had disolved. The solution was then filtered through a grade 3 sinter to remove any unreacted zinc dust and the solvent removed under vacuum leaving a sticky residue. Heating the residue to 150°C under vacuum for 4 hours removed the last traces of ether. The anhydrous zinc (II) chloride was stored under dry nitrogen until required.

6.6.3 Reaction of Zinc (II) Chloride with Dicarbollide Ion in THF

(i) Experimental

0.225g of anhydrous zinc (II) chloride (1.65 m.moles) in 10 mls of dry THF was added to a solution of dicarbollide ion (1.65 m.moles) in 50 mls of dry THF and the mixture refluxed for 4 hours. The mixture was cooled to room temperature filtered through a grade 3 sinter and the solvent removed from the filtrate under vacuum leaving a white solid.

(ii) Results

Analaysis

	C	H	B	Zn	Cl
% Found	25.4	4.54	22.4	13.4	14.5
$ZnC_2B_9H_{11}$ requires	12.14	5.56	4 92	33.1	0

Mass Spectrum

Mass spectral analysis showed only peaks attributable to the following species: m/e 69, 70, THF; m/e 127 - 133 $C_2B_9H_{11}$, m/e 208, $ZnCl_2$.THF, m/e 28 5 $ZnCl_2.(THF)_2$. No indication was given of any zinc carborane species, the mass spectral data agreeing with the analytical data which also shows the presence of only unreacted dicarbollide ion and zinc (II) chloride THF adduct.

6.6.4 Reaction of Zinc (II) Chloride with Dicarbollide Ion in Acetonitrile

(i) Experimental

0.789g of anhydrous zinc (II) chloride (5.79 m.moles) in 10 mls of dry acetonitrile was added to a stirred solution of dicarbollide ion (5.79 m.moles) in 50 mls of dry acetonitrile and the mixture refluxed for 4 hours. The reaction mixture was then allowed to cool to room temperature. The solution was filtered through a grade 3 sinter and the solvent removed under vacuum from the filtrate to yield a white solid.

(ii) Results

Analaysis and mass spectral studies of the solid revealed only the presence of starting material.

6.6.5 Reaction of Zinc (II) Chloride with $Tl^+[TlC_2B_9H_{11}]^-$ in THF

(i) Experimental

0.3336g of $Tl^+[TlC_2B_9H_{11}]^-$ (0.62 m.moles) was stirred in THF with an excess of anhydrous zinc (II) chloride for 24 hours. During this time the yellow colour of the thallio carborane changed to white. The mixture was then refluxed for 3 hours and allowed to cool to room temperature. The precipitate was removed on a grade 3 sinter and washed with 10 mls of dry THF. The THF was removed from the filtrate under vacuum and the white solid produced analysed.

(ii) Results

Elemental analysis and mass spectral analysis of the product showed no evidence for the formation of a zinc carborane. Only starting material was detected.

6.6.6 Discussion

It is apparent from the results that the reactions of zinc (II) chloride with dicarbollide ion and $Tl^+[TlC_2B_9H_{11}]^-$ failed to produce a $ZnC_2B_9H_{11}$ metallocarborane. This is particularly surprising as in the latter reaction the initial yellow colour of the thallio carborane gave way to a white colour which in the tin and germanium reactions was indicative of thallium (I) chloride and thus metallocarborane formation. No explanation can be given for this observation except that it could indicate the preparation of a zinc salt of $[TlC_2B_9H_{11}]^-$.

$$ZnCl_2 + 2\overset{+}{Tl}[TlC_2B_9H_{11}]^- \longrightarrow Zn^{2+}[TlC_2B_9H_{11}]^-_2 + 2TlCl$$

Attempts to recover a crystalline product failed and so this reaction is open to speculation.

6.7 THIRTEEN VERTEX CAGE STRUCTURES

6.7.1 Introduction

In the previous sections polyhedral expansion has been attempted using eleven vertex nido cages and inserting a lone heteroatom to complete the icosahedron. Theoretically there is no reason why the analogous expansion from a twelve vertex nido cage $C_2B_{10}H_{12}^{2-}$ to a thirteen vertex closo structure. Such a reaction has been reported for cobalt by Hawthorne.(443)

$$NaC_5H_5 + CoCl_2 + Na_2C_2B_{10}H_{12} \longrightarrow \overset{1\%}{(\pi\text{-}C_5H_5)CoC_2B_9H_{11}}$$

$$+ \underset{\text{red}\quad 50\%}{(\pi\text{-}C_5H_5)CoC_2B_{10}H_{12}} + \underset{12\%}{(C_2H_{10}H_{12})_2Co^-}$$

The structure of the basic metal cage unit has been shown by X-ray studies to be based on an icosahedron with one carbon atom distorted out of the plane of the open face. (444) (Figure 6.17)

The dicarbadodecaborate dianion is prepared by the action of sodium on a solution of ortho carborane in THF usually in the presence of a trace of naphthalene. (See chapter 1.16)

No main group elements have been successfully incorporated into a thirteen vertex polyhedron indeed there are no literature reports of attempts to prepare such compounds. This section reports the work carried out in investigations of possible routes to such compounds.

6.7.2 Reaction between Tin (II) Chloride and $Na_2C_2B_{10}H_{12}$ in THF

(i) Experimental

0.489g of freshly sublimed ortho carborane (3.4 m.moles) was dissolved in 50 mls of dry THF and about 0.2g of freshly cut sodium (<6.8 m.moles) added with a trace of naphthalene to the stirred solution. After half to

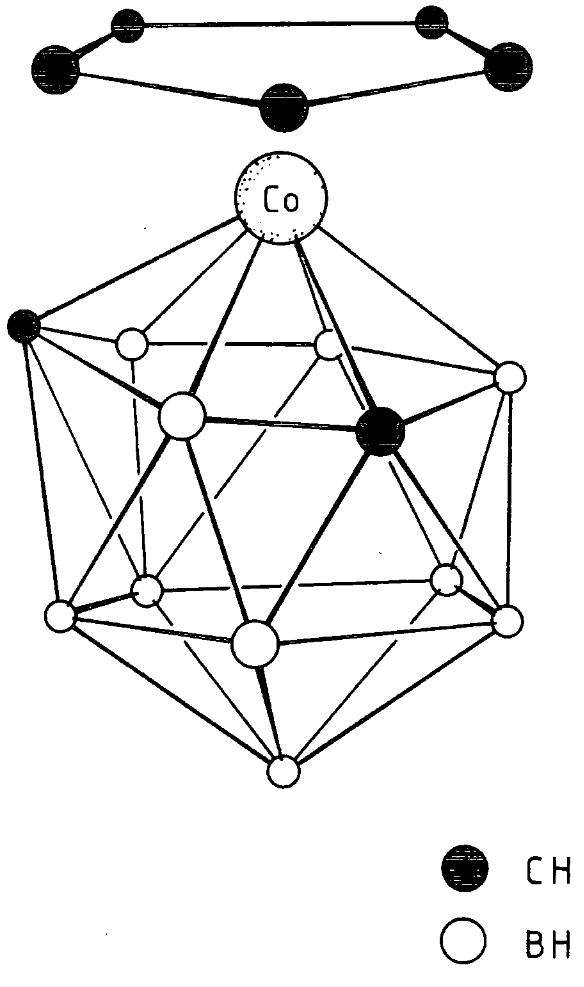


Figure 6.17.

one hour the solution turned dark green due to the formation of free radicals. The stirring at room temperature was continued for a further 3 hours and the solution was then refluxed for 2 hours, allowed to cool to room temperature and filtered through a grade 3 sinter. An extra 50 mls of dry THF was added to the solution together with 0.645g of anhydrous, tin (II) chloride (3.4 m.moles) in 10 mls of dry THF. A dark brown precipitate was immediately formed. The mixture was stirred overnight and the precipitate removed on a grade 4 sinter. Removal of the THF from the filtrate gave a white solid.

(ii) Results

Analysis

Elemental analysis of the white solid showed it to consist of ortho-carborane, sodium chloride and naphthalene with no detection of tin. However analysis of the precipitate showed it to be entirely tin.

Mass Spectrum

The above results were confirmed by mass spectral analysis.

The reaction was repeated with an additional purification of the $Na_2C_2B_{10}H_{12}$ before addition of the tin (II) chloride solution. The solution of $Na_2C_2B_{10}H_{12}$ in THF with naphthalene was evaporated to dryness under vacuum and the residue subjected to high vacuum at 60°C for 4 hours. Analysis of the $Na_2C_2B_{10}H_{12}$ by mass spectrum revealed no evidence of naphthalene. However on addition of the solution of tin (II) chloride a similar brown precipitate was formed which also analysed as tin metal. No evidence of tin was found in the residue.

(iii) Discussion

$Na_2C_2B_{10}H_{12}$ appears to be capable of reducing tin (II) compounds to metal whilst it is oxidized back to ortho carborane. Under these conditions it seems unlikely that a thirteen vertex cage can be synthesised with tin although it may prove to work with metal ions that are less easily reduced to the metal.

6.7.3 'Hot Atom' Reaction of Tin with Ortho-Carborane

(i) Introduction

The technique of 'hot atom' synthesis has been known for some years and has its roots in transition metal cyclopentadienyl derivative chemistry. The method in its simplest form involves heating a metal to very high temperatures under vacuum by passing a high current through a conductive crucible containing the metal and co-condensing the metal vapour together with a suitable ligand on the walls of the vessel cooled with liquid nitrogen. In this manner, transition metal sandwich compounds can be prepared such as ferrocene, cobaltocene, dibenzene chromium.

In the field of metallo carboranes, polyhedra have been prepared containing two cobalt atoms starting from small nido carboranes and using the hot atom method.

There have also been reports in the literature of the preparation of rare earth metallo carboranes by similar techniques.

The technique cannot be used with compounds such as dicarbollide ion because the ionic species cannot be sublimed onto the walls of the reactor. Instead ortho carborane and closo dicarbaundecaborane(11) were used, the latter being more capable of undergoing polyhedral expansion to a stable icosahedral structure.

Two different types of apparatus were used for the reactions (Figure 6.18), the metal used in each case being tin because of its low melting point.

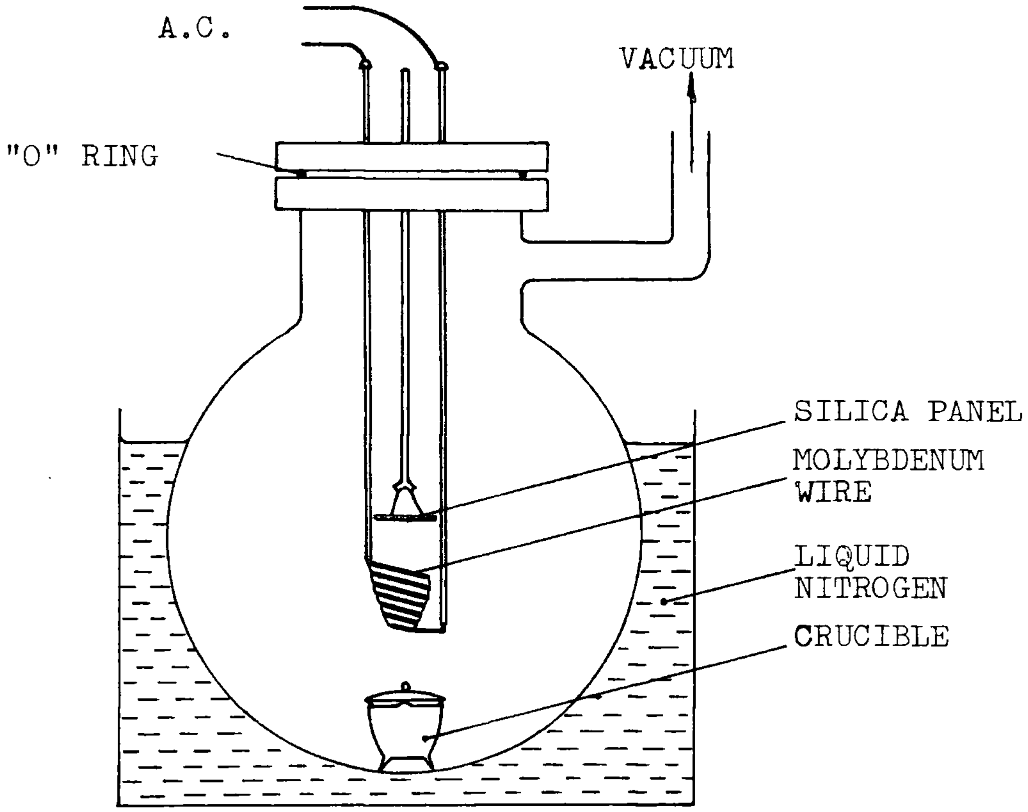


Figure 6.18a.

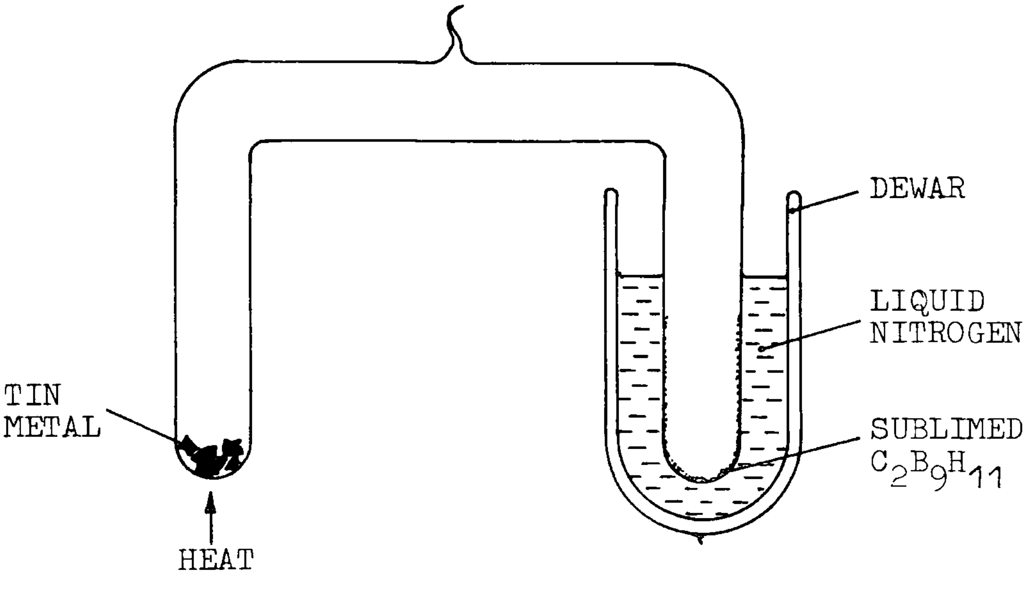


Figure 6.18b.

Figure 6.18(a) shows the more conventional type of hot atom apparatus with the central inlet nozzle for ligand introduction and the crucible containing the metal to be electrically heated constructed out of thick molybdenum wire with ceramic filler between the coils of the crucible. The entire central unit of the apparatus is sealed into a stainless steel cylindrical cap which has a machined groove on the underside to accept an "O" ring. The top of the reaction flask has a glass to metal joint onto a similarly machined stainless steel ring. Under vacuum the compression of the "O" ring produces an efficient seal. The central unit can be replaced by a cold finger assembly for recovery of product.

This apparatus was adapted for use with volatile solids such as carboranes by the inclusion of a silica crucible in the base of the apparatus. The crucible was raised from the bottom of the reaction vessel on thin silica legs to minimise thermal contact with the cold reaction vessel wall. The crucible lid was also raised slightly to allow the volatile carborane to escape and most importantly to prevent any molten metal falling into the carborane if the crucible broke. Such a break would otherwise cause a violent explosion.

A thin silica panel was suspended from the unused ligand entry nozzle to prevent metal atoms from coating the upper part of the vessel thus obscuring the view of the interior of the vessel during an experimental run.

(ii) Experimental

2g of resublimed ortho carborane (13.9 m.moles) was placed inside the silica crucible at the bottom of the reaction vessel and about 6g of tin beads placed in the molybdenum wire crucible. The apparatus was assembled and evacuated to about 0.001 mm Hg by a mercury diffusion pump backed by an oil pump. The reaction vessel was surrounded by liquid nitrogen and the current across the molybdenum crucible was increased until the tin melted and then further increased until it glowed white hot and deposition of tin on the wall of the reaction vessel could plainly be seen. The increases in current were carried out fairly rapidly in order to start the deposition of tin on the vessel walls as soon as possible, before the more volatile carborane had sublimed on to the walls. Deposition of the tin was continued for 1 hour or until all the metal had evaporated. The current was then slowly reduced over 10 minutes to zero thus preventing the fracture of the ceramic filler by rapid cooling. The liquid nitrogen bath was removed and the reaction vessel isolated from the vacuum line and let down to dry nitrogen. With dry nitrogen purging into the vessel, the central unit was removed and replaced by the cold finger assembly and nitrogen allowed to purge out of the tap in the cold finger for five minutes. The tap was then closed, the flask evacuated and liquid nitrogen introduced to the cold finger whilst the exterior of the flask was warmed with hot water $\sim 65^{o}C$ causing unreacted ortho carborane to sublime onto the cold finger. The entire reaction flask and cold finger apparatus was isolated from the vacuum line and transfered to a dry nitrogen atmosphere glove box. The sublimed material was removed for analysis and the reaction vessel washed with 50 mls of dry THF. The THF solution was transfered to a flask by syringe and the solvent removed under vacuum.

(iii) Results

Elemental analysis of the sublimate and the THF washings residue showed only the presence of ortho carborane. Mass spectral analysis of both product showed a parent ion peak at m/e 146 and a characteristic carborane isotope pattern. There was no evidence of any tin isotope pattern.

(iii) Discussion

The failure of this reaction could be due to the reluctance of the stable icosahedron to expand to a thirteen atom polyhedron without the prior formation of a nido carborane by chemical means, the tin atoms being unable to provide enough energy to cause cage opening.

Alternatively the low melting point of tin could cause the evaporation of the metal in small clusters and not single atoms. This is one of the limitations of this type of apparatus when applied to relatively low melting point metals unless the current can be controlled very finely.

For further experiments, closo-dicarbaundecaborane(11) was used in place of ortho carborane the former being more likely of undergoing polyhedral expansion to the more stable icosahedron. The reactions were carried out in sealed tubes to facilitate a finer control of temperature.

6.7.4 Hot Atom Reaction of Tin with Dicarbaundecaborane(11)

(a) Preparation of Dicarbaundecaborane (11)

(i) Experimental

Potassium dicarbaundecaborate ($K^+C_2B_9H_{12}^-$) was prepared by the method previously described and dried in a vacuum dessicator over anhydrous calcium chloride. 0.0187 moles of the potassium salt was heated at 125° for 2 hours with 15g of polyphosphoric acid and 35 mls of toluene under dry nitrogen. An addition 35 mls of toluene was added and the mixture heated again to 125° for 30 mins. The excess toluene was removed under vacuum and the dicarbaundecaborane(11) sublimed from the residue at 80°C under high vacuum. The product was further purified by resublimation.

(ii) Results

Analysis

	C	H	B
% Found	17.75	8.81	72.4
$C_2B_9H_{11}$ requires	18.14	8.32	73.54

I.R.

The infra-red spectrum showed the following peaks:-

ν max. (cm^{-1}) 3070 (m) , 2880 (sbr), 2585 (s) ,
1460 (s) , 1377 (s) , 1345 (m) , 1305 (w) ,
1265 (w) , 1213 (m) , 1150 (m) , 1090 (w) ,
1045 (sh), 1035 (mw) , 1015 (m) , 985 (w) ,
919 (w) , 877 (w) , 787 (w) , 720 (w) ,
745 (m) , 720 (s) , 443 (w).

Mass Spectrum

The mass spectrum of the product showed a parent ion peak at m/e 134. This corresponds to $C_2^{12}\,B_9^{11}\,H_{11}^{1}$. Below this were a number of lower intensity peaks of carboranyl pattern due to the breakdown of $C_2B_9H_{11}$.

(b) Hot Atom Reaction

(i) Experimental

3g powdered tin was introduced to the apparatus shown in Figure 6.18(b) with 0.3g of dicarbaundecaborane(11) under a dry nitrogen atmosphere. The apparatus was evacuated to ~ 0.001 mm Hg and heat sealed at the constriction. The reaction mixture was carefully tapped into one of the side arms which was then heated in a boiling water bath whilst the other arm of the silica tube was cooled in liquid nitrogen producing a fine deposit of carborane in the second arm. The remaining tin powder was then slowly heated to white heat and the tin vapour condensed in the arm cooled by the liquid nitrogen. After 10 minutes the tin was cooled to room temperature and the cold arm allowed to warm up. The unreacted $C_2B_9H_{11}$ was then driven out of the condensing arm by immersion in boiling water. The condensing arm was then recooled depositing a second thin layer of $C_2B_9H_{11}$, and the whole process repeated twice more until most of the tin had been condensed in the second arm. The whole apparatus was then transferred to a glove box and the soluble material extracted with dry n-pentane. Evaporation of the solvent yielded a white solid which was purified by sublimation at 100°C under high vacuum leaving no residue.

(ii) Results

Analysis

	C	H	B	Sn
% Found	17.88	8.46	-	0
$SnC_2B_9H_{11}$ requires	9.56	4.38	38.76	47.29
$C_2B_9H_{11}$ requires	18.14	8.32	73.54	0

Mass Spectrum

There was no visible evidence for the formation of $SnC_2B_9H_{11}$, the parent ion being at m/e 134 $\equiv C_2B_9H_{11}$. No tin isotope pattern was visible in the region m/e 116 - 122.

(iii) Discussion

Clearly there has been no reaction of tin vapour with $C_2B_9H_{11}$. There are several reasons why these hot atom experiments failed to produce polyhedral expansion. The closo structures may be too energetically stable to allow the expansion without the prior and independant formation of a nido starting material. Secondly, tin may not be the ideal metal to use as its low melting point may well give rise to the evaporation of small cluster of atoms rather than single atoms.

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APPENDIX A

EXPERIMENTAL TECHNIQUES

1. Handling Techniques

All compounds in this thesis were treated as being air and moisture sensitive. Reactions were therefore carried out in dry apparatus under a positive pressure of dry nitrogen. Moisture sensitive solutions such as n-butyl lithium in n-pentane were stored under dry nitrogen and transferred by glass syringe fitted with a Louer lock stainless steel needle. Volatile moisture sensitive compounds were stored under their own vapour pressure in Rotaflo ampoules and transferred under vacuum into reaction vessels.

(a) Nitrogen Supply

The nitrogen supply was obtained as boil-off from the liquid nitrogen generation plant, passed through a de-oxygenation plant and dried at the bench by passage through two 60 cm high phosphorus pentoxide towers.

(b) Glove-Box

The glove-box used during the study was fed with a positive pressure of dry nitrogen supplied as detailed above, and continuously recycled through a separate phosphorus pentoxide column. A dish of phosphorus pentoxide was also kept inside the glove-box with a hair hygrometer to monitor the dryness of the glove-box.

Chemicals and apparatus were taken into the glove-box through an entry port which was purged for 45 minutes with dry nitrogen supplied from the recirculation system. Whenever necessary samples for infra-red, raman, mass spectra and elemental analyses were prepared inside the glove-box.

(c) Vacuum Line

The handling of volatiles was performed in a glass vacuum line fitted with hand ground high vacuum glass taps lubricated by Apeazon or Silcone high vacuum grease. The vacuum line was fitted with liquid nitrogen cooled muck traps to prevent volatiles entering the high vacuum mercury diffusion pump and the backing rotary oil pump. The line pressures were monitored by a mercury column and a gauge allowing pressure measurements to be made over the range 760 m.m. Hg to 0.001 m.m. Hg. The vacuum line also incorporated a detachable fractionation train consisting of three isolatable cold traps connected in series and also attached to a common manifold. Dry nitrogen could be introduced into the line via a preset needle valve.

2. Spectroscopic Data

(a) Infra-red Spectra

Infra-red spectra were run either by a dry nujol mulls between KBr plates or as individually pressed KBr or CsI discs. The spectra were recorded by Perkin-Elmer 457, 577 and 467 grating spectrometers.

(b) Raman Spectra

Raman spectra were obtained using a Cary 82 spectrometer and a 632.8 n.m. Spectra Physics 125 laser.

(c) Mass Spectra

Mass spectra were obtained using an A.E.I. MS9 mass spectrometer interfaced with a p.d.p.8 computer. Output was as either a computer drawn spectrum or directly onto Kodak recording paper.

(d) ^{11}B-n.m.r. Spectra

^{11}B n.m.r. spectra were obtained using a purpose built 19MHz ^{11}B n.m.r. spectra were run on a Varian H.A. 100. $B(OMe)_3$ was used as a reference.

3. Analyses

Carbon, hydrogen and nitrogen were determined using a Perkin-Elmer 240 Elemental Analyser. Halogens were determined by oxygen flask combustion followed by potentiometric titration.

Boron analyses on carboranes were made on boric acid prepared by careful hydrolysis of the carborane with 90% nitric acid solutions. Boric acid was then determined by titration.

Metals were determined using a Perkin-Elmer 403 Atomic Absorption Spectrometer.

APPENDIX B

1. Preparation and Purification of Starting Materials

(i) Acetonitrile (CH_3CN)

A 2 litre round bottomed flask was half filled with acetonitrile under dry nitrogen. Crushed calcium hydride was slowly added to the stirred bulk until approximately 5 cms of solid remained in the bottom of the flask. Stirring overnight was followed by 6 hours of reflux. The acetonitrile was then distilled onto phosphorus pentoxide and refluxed (with further additions of phosphorus pentoxide if an orange colouration appeared) for 3 - 4 hours. The dry acetonitrile was finally distilled onto activated 4A molecular sieve and stored under dry nitrogen.

(ii) Thionyl Chloride ($SOCl_2$)

Crude thionyl chloride was thoroughly mixed with triphenyl phosphite (10% by weight) and fractionated through a 12" column, the middle fraction being collected and redistilled to give a clear liquid. The purified liquid was stored in the dark in a rotaflo ampoule.

(iii) Tetrahydrofuran (THF)

Tetrahydrofuran was refluxed for 8 hours with sodium wire and then fractionally distilled onto washed activated 4A molecular sieve and stored under dry nitrogen.

(iv) Benzonitrile (PhCN)

Benzonitrile was refluxed with anhydrous magnesium sulphate for 12 hours and then distilled onto washed activated 4A molecular sieve.

(v) The following materials were purified by distillation *in vacuo*

(a) Tin IV chloride ($SnCl_4$);

(b) Silicon IV chloride ($SiCl_4$)

(c) Germanium IV chloride ($GeCl_4$)

(d) Diphenyl boron chloride (Ph_2BCl)

(e) Phenyl boron dichloride ($PhBCl_2$)

(f) Boron trichloride (BCl_3)

(g) Dimethyl-dichlorosilane (Me_2SiCl_2)

(vi) The following solvents were dried using sodium wire

(a) Diethyl ether

(b) Hexane

(c) Benzene

(d) Toluene

(e) n-Pentane.

(vii) The following materials were purified by resublimation

(a) Ortho-carborane

(b) Meta-carborane.

APPENDIX C

The Board of Studies in Chemistry requires that each postgraduate research thesis should contain an appendix listing all research colloquia, seminars and lectures (by external speakers) arranged by the Department of Chemistry during the period when research for the thesis was carried out.

Research Colloquia, Seminars and Lectures Arranged by the Department of Chemistry between October 1977 and September 1980

19 October 1977

Dr. B. Heyn (University of Jena, D.D.R.), "σ- Organo-Molybdenum Complexes as Alkene Polymerisation Catalysts"

27 October 1977

Professor R.A. Filler (Illinois Institute of Technology), Reactions of Organic Compounds with Xenon Fluorides"

2 November 1977

Dr. N. Boden (University of Leeds), "N.M.R. Spin-Echo Experiments for Studying Structure and Dynamical Properties of Materials Containing Interacting Spin-$\frac{1}{2}$ Pairs"

9 November 1977

Dr. P.A. Madden (University of Cambridge), "Raman Studies of Molecular Motions in Liquids"

14 December 1977

Dr. R.O. Gould (University of Edinburgh), "Crystallography to the Rescue in Ruthenium Chemistry"

25 January 1978

Dr. G. Richards (University of Oxford), "Quantum Pharmacology"

1 February 1978

Professor K.J. Ivin (Queens University, Belfast), "The Olefin Metathesis Reaction: Mechanism of Ring-Opening Polymerisation of Cycloalkenes"

3 February 1978

Dr. A. Hartog (Free University, Amersterdam), "Some Surprising Recent Developments in Organo-Magnesium Chemistry"

22 February 1978

Professor J.D. Birchall (Mond Division, I.C.I. Ltd.), "Silicon in the Biosphere"

1 March 1978

Dr. A. Williams (University of Kent), "Acyl Group Transfer Reactions"

3 March 1978

Dr. G. van Koten (University of Amsterdam), "Structure and Reactivity of Arylcopper Cluster Compounds"

15 March 1978

Professor G. Scott (University of Aston), "Fashioning Plastics to Match the Environment"

22 March 1978

Professor H. Vahrenkamp (University of Freiburg), "Metal-Metal Bondsin Organometallic Complexes"

19 April 1978

Dr. M. Barber (U.M.I.S.T.), "Secondary Ion Mass Spectra of Surfaces Adsorbed Species"

15 May 1978

Dr. M.I. Bruce (University of Adelaide), "New Reactions of Ruthenium Compounds with Alkynes"

16 May 1978

Dr. P. Ferguson (C.N.R.S., Grenoble), "Surface Plasma Waves and Adsorbed Species on Metals"

18 May 1978

Professor M. Gordon (University of Essex), "Three Critical Points in Polymer Science"

22 May 1978

Professor D. Tuck (University of Windsor, Ontario), "Electrochemical Synthesis of Inorganic and Organometallic Compounds"

24/25 May 1978

Professor P. von R. Schleyer (University of Erlangen, Nurnberg),

(i) "Plannar Tetra-Coordinate Methanes, Perpendicular Ethylenes and Planar Allenes"

(ii) "Aromaticity in Three Dimensions"

(iii) "Non-Classical Carbocations"

21 June 1978

Dr. S.K. Tyrlik (Academy of Sciences, Warsaw), "Dimethylglyoxime-Cobalt Complexes - Catalytic Black Boxes"

23 June 1978

Professor W.B. Person (University of Florida), "Diode Laser Spectroscopy at 16μm"

27 June 1978

Professor R.B. King (University of Georgia, Athens, Georgia, U.S.A.), "The Use of Carbonyl Anions in the Synthesis of Organometallic Compounds"

30 June 1978

Professor G. Mateescu (Cape Western Reserve University), "A Concerted Spectroscopy Approach to the Characterisation of Ions and Ion Pairs: Facts, Plans and Dreams"

15 September 1978

Professor W. Siebert (University of Marburg, West Germany), "Boron Heterocycles as Ligands in Transition Metal Chemistry"

22 September 1978

Professor T. Fehlner (University of Notre Dame, U.S.A.), "Ferraboranes: Syntheses and Photochemistry"

12 December 1978

Professor C.J.M. Stirling (University of Bangor), "Parting is Such Sweet Sorrow - the Leaving Group in Organic Reactions"

14 February 1979

Professor B. Dunnell (University of British Columbia), "The Application of N.M.R. to the Study of Motions in Molecules"

16 February 1979

Dr. J. Tomkinson (Institute Laue-Langevin, Grenoble), "Studies of Adsorbed Species"

14 March 1979

Dr. J.C. Walton (University of St. Andrews), Pentadienyl Radicals"

28 March 1979

Dr. A. Reiser (Kodak Ltd.), "Polymer Photography and the Mechanism of Cross-link Formation in Solid Polymer Matrices"

5 April 1979

Dr. S. Larsson (University of Uppsala), "Some Aspects of Photoionisation Phenomena in Inorganic Systems"

25 April 1979

Dr. C.R. Patrick (University of Birmingham), "Chlorofluorocarbons and Stratospheric Ozone: An Appraisal of the Environmental Problem"

1 May 1979

Dr. G. Wyman (European Research Office, U.S. Army), "Excited State Chemistry in Indigoid Dyes"

2nd May 1979

Dr. J.D. Hobson (University of Birmingham), "Nitrogencentred Reactive Intermediates"

8 May 1979

Professor A. Schmidpeter (Institute of Inorganic Chemistry, University of Munich), "Five-membered Phosphorus Heterocycles Containing Dicoordinate Phosphorus"

9 May 1979

Dr. A.J. Kirby (University of Cambridge), "Structure and Reactivity in Intramolecular and Enzymic Catalysis"

9 May 1979

Professor G. Maier (Lahn-Giessen), "Tetra-tert-butyltetrahedrane"

10 May 1979

Professor G. Allen, F.R.S. (Science Research Council), "Neutron Scattering Studies of Polymers"

16 May 1979

Dr. J.F. Nixon (University of Sussex), "Spectroscopic Studies on Phosphines and their Coordination Complexes"

23 May 1979

Dr. B. Wakefield (University of Salford), "Electron Transfer in Reactions of Metals and Organometallic Compounds with Polychloropyridine Derivatives"

13 June 1979

Dr. G. Heath (University of Edinburgh), "Putting electrochemistry into mothballs (redox processes of metal porphyrins and phthalocyanines)"

14 June 1979

Professor I. Ugi (University of Munich), "Synthetic uses of super nucleophiles"

20 June 1979

Professor J.D. Corbett (Iowa State University, U.S.A.), "Zintl ions: synthesis and structure of homopolyatomic anions of the post-transition elements"

27 June 1979

Dr. H. Fuess (University of Frankfurt), "Study of electron distribution in crystalline solids by X-ray and neutron diffraction"

21 November 1979

Dr. J. Muller (University of Bergen), "Photochemical reactions of NH_3"

28 November 1979

Professor B. Cox (University of Stirling), "Macrobicyclic cryptate complexes: dynamics and selectivity"

5 December 1979

Dr. G.C. Eastmand (University of Liverpool), "Synthesis and properties of some multi-component polymers"

12 December 1979

Dr. C.I. Ratcliffe, "Rotor motions in solids"

18 December 1979

Dr. K.E. Newman (University of Lausanne), "High pressure multinuclear n.m.r. in the elucidation of the mechanisms of fast, simple inorganic reactions"

30 January 1980

Dr. M.J. Barrow (University of Edinburgh), "The structures of some simple inorganic compounds of silicon and germanium - pointers to structural trends in Group IV"

14 May 1980

Dr. R. Hutton (Waters Associates), "Recent developments in multi-milligram and multi-gram scale preparative high performance liquid chromatography"

21 May 1980

Dr. T.W. Bently (University College of Wales, Swansea), "Medium and structural effects on solvolytic reactions"

10 July 1980

Professor P. des Marteau (University of Heidelburg), "New developments in organonitrogen fluorine chemistry".