Synthesis and derivative chemistry of icosahedral carboranes

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SYNTHESIS AND DERIVATIVE CHEMISTRY OF ICOSAHEDRAL CARBORANES

by

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A thesis submitted for the degree of Doctor of
Philosophy in the University of Durham

Department of Chemistry
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To my parents.

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MEMORANDUM

The work described in this thesis was carried out in the University of Durham between September 1982 and September 1985. It has not been submitted for any other degree, and is the original work of the author except where acknowledged by reference.

One aspect of this work has formed the basis of the following publication:

> "Crystal Structure of the pentamethyldiethylenetriamine adduct of 1-lithio-2-methyl-1,2-dicarba-closo-dodecaborane, $Li(C_2B_{10}H_{10}Me)(MeN(CH_2CH_2NMe_2)_2)$, a compound containing a lithium atom terminally bonded to a six coordinate carbon atom",

by William Clegg, David A. Brown, Stephen J. Bryan and Kenneth Wade, Polyhedron, 1984, 3, No. 3, 307.

"Synthesis and Derivative Chemistry of Icosahedral Carboranes"

by

D. A. BROWN B.Sc.

ABSTRACT

A series of icosahedral carboranes including, ortho- 1-methyl-ortho- and 1-phenyl-ortho-carborane were prepared from decaborane and the appropriately substituted acetylenes. An investigation of the preparative route to ortho-carborane showed that improvements could be made to the literature method employed. Meta-carborane was obtained in high yields by the thermal isomerization of ortho-carborane.

The structurally-characterised compounds $Li(C_2B_{10}H_{10}Me)$ (PMDETA) and $Mg(C_2B_{10}H_{10}Me)_2(C_4H_8O_2)_2 \cdot C_7H_8$ contain unprecedented examples of group I and II metals covalently bonded to six-co-ordinate carbon atoms. Features of the structures are compared with those of other organolithium and organo-magnesium compounds and used to calculate the cone angles and steric requirements of icosahedral carboranyl and methyl-carboranyl ligands attached to metal atoms of various sizes.

Series of, carboranyl ketones of formulae RΘCOR' and $(R\Theta)_2CO$ (where R = H, Me, Ph and R' = Ph), carboranyl amides of formulae RNHCOΘCONHR and RNHCOΘ'CONHR (where R = Ph, Me, ^{t}Bu) and boranyl-carboranes of formulae $R\Theta BR'_2$ and $(R\Theta')_2BR'$ (where R = H, Me and R' = Ph), were synthesized and an investigation carried out to assess their relative stabilities to hydrolytic degradation. These studies revealed interesting trends within each series.

A series of C-hydroxy-derivatives including MeΘOH, PhΘOH, HΘOH, HΘ'OH and HOΘOH were successfully prepared by the reactions of the mono- or dilithio-carboranes with oxygen or with benzoyl peroxide. All of the hydroxy-carboranes with the exception of HOΘOH were crystalline solids. A number of tertiary ammonium salts of the ortho-carboranyl-C-hydroxy derivatives were prepared in high yields. No salts of the meta-derivative, HΘ'OH were obtained. All of the salts were white crystalline solids, their infra-red, ^{1}H, ^{11}B and COSY n.m.r. spectra showing interesting and significant differences to those of their corresponding hydroxy-derivatives, many of these differences, presumably attributable to increases in the C-O bond order and an increase in electron density within the cage.

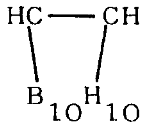
The previously unreported $Me\Theta OSiMe_3$ was prepared by the reaction of $Me\Theta OHNEt_3$ with Me_3SiCl and isolated as a stable, crystalline solid.

NOMENCLATURE

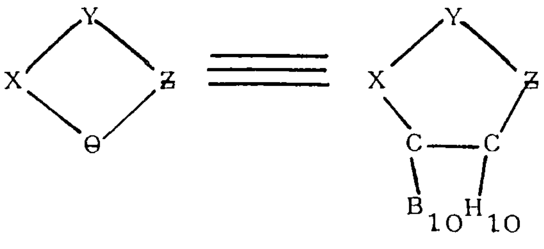
The nomenclature used throughout this thesis is based on that widely used in the current carborane literature with the exception of the Russian literature as indicated below.

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 - or meta-barene)
1,12 - $C_2B_{10}H_{12}$	Para-carborane; 1,12 - dicarbadodecaborane (12); (RUS: - para-barene)

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

NOMENCLATURE	SYMBOL	
Ortho carborane	HΘH;	
Meta carborane	HΘ'H	
Para carborane	H'Θ'H	

NOTE: Care should be taken with the interpretation of diagrams containing exocyclic rings. For example a ring which appears to be 4-membered and which contains the symbol Θ does in fact contain 5 atoms, and thus may be considered as a 5-membered ring, as shown below.



CHAPTER 1

STRUCTURE, BONDING AND DERIVATIVE CHEMISTRY OF THE ICOSAHEDRAL CARBORANES, $C_2B_{10}H_{12}$

CHAPTER 1

1.1 INTRODUCTION

Since the birth of icosahedral carborane chemistry in the early 50's many comprehensive reviews have been published, the most note worthy being Grimes's book "Carboranes" (1), which was published in 1970 and covered most aspects of carborane chemistry, and a more recent review published in 1981 in "Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry" (2) by R. W. Jotham.

It should therefore be noted that the following review has not been designed to update and cover all aspects of icosahedral carborane chemistry but rather to deal specifically with literature relevant to the work described within this thesis.

STRUCTURE AND BONDING OF CARBORANES

Carboranes can be broadly described as a group of polyhedral compounds containing both carbon and boron atoms in the skeletal framework. Dicarbaboranes, that is polyhedra containing two carbon atoms, are more numerous than the mono-, tri-, or tetracarbaboranes. These dicarbaboranes can be divided into three distinct classes based on their formulae. The closo- (closed) carboranes, these being the most synthetically important class, have the general molecular formula $C_2B_{n-2}H_n$ (n = 5 to 12), the nido- (nest like) carboranes have the general molecular formulae $C_2B_{n-x}H_{n+4-x}$ (where x = 1, 2, etc.; n = 5, 6 etc.) and the arachno- (web like) carboranes have the general formulae $C_2B_{n-x}H_{n+6-x}$ (where n = 5, 6 etc.; x = 0, 1, 2 etc.).

The highest members of the closo carborane series are the closo dicarbadodecaboranes (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 produces three possible isomers, 1,2 - dicarbadodecaborane (12) (or ortho-carborane) 1,7 - dicarbadodecaborane (12) (or meta-carborane) and 1,12 - dicarbadodecaborane (12)(or para-carborane).

The structures of the carboranes can be rationalised in terms of electron counting rules based on the total number of electron pairs available for skeletal bonding. (3,4)

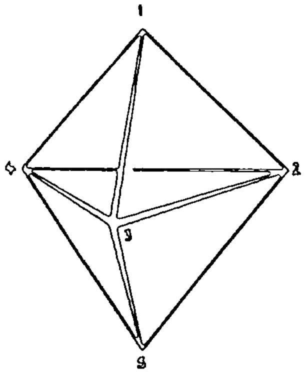
When assessing the number of electron pairs available the rules assume that each B-H unit is capable of donating 2e (1 pair of electrons) for skeletal bonding and each C-H unit is capable of donating 3e (or one and a half electron pairs).

For a borane or carborane based on a polyhedron of n vertices, the rules show that 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.

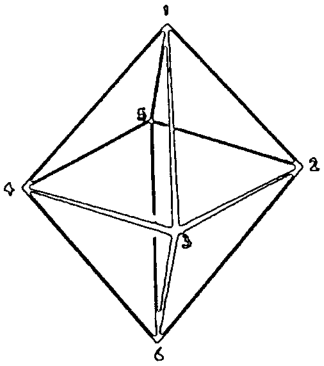
Carboranes have been described as pseudo aromatic species since the electrons donated by the C-H and B-H units for skeletal bonding are delocalised throughout the entire polyhedron.

PREPARATION AND PROPERTIES OF ICOSAHEDRAL CARBORANES

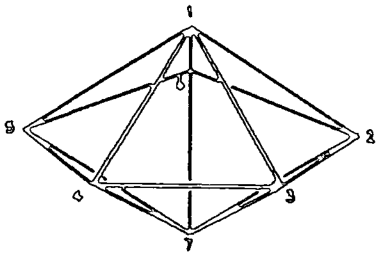
Lewis bases such as acetonitrile or diethyl sulphide can attack decaborane (14), $B_{10}H_{14}$ at the 6 and 9 positions with the loss of hydrogen and the formation



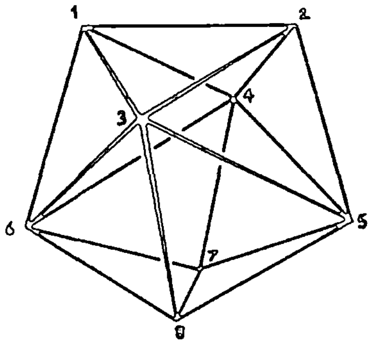
$C_2B_3H_5$



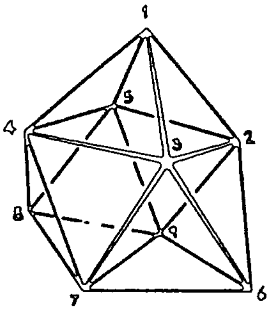
$C_2B_4H_6$



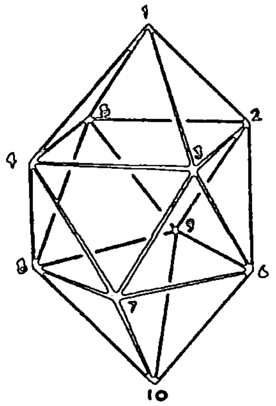
$C_2B_5H_7$



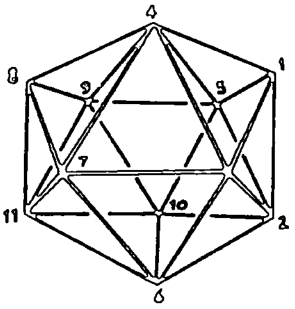
$C_2B_6H_8$



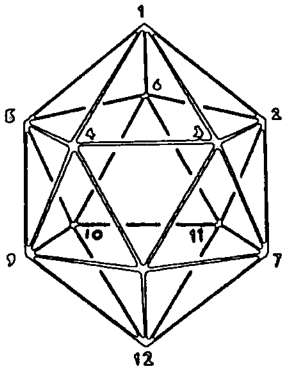
$C_2B_7H_9$



$C_2B_8H_{10}$



$C_2B_9H_{11}$



$C_2B_{10}H_{12}$

Figure 1.1.1. The Polyhedral Closo-Carborane Series

of a bis-ligand complex $B_{10}H_{12}L_2$. The reaction of this derivative with acetylene yields ortho-carborane (o-carborane). (5,6,7,8)

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

Substituted ortho-carboranes can be synthesised using the appropriately substituted acetylenes. However acetylenes containing alcohol or carboxylic acid groups cannot be used as these cause degradation of the decaborane cage.

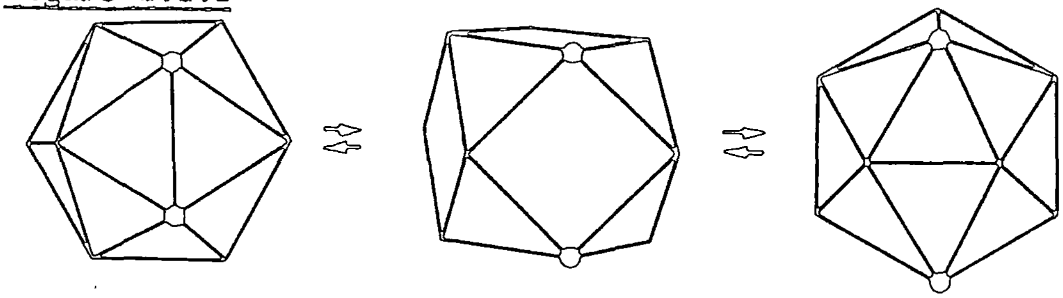
Unlike the boranes and small closo carboranes, ortho-carborane shows remarkable thermal stability. However, at 470°C in an inert atmosphere it rearranges smoothly to 1,7 - or meta-carborane (m-carborane) with near quantitative yields. (9,10,11,12,13,14) Meta-carborane isomerizes further at 620°C to give 1,12 - or para-carborane (p-carborane) although the yield is much smaller due to some cage degradation. (14,15) 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 1.1.2) appears to be the most likely. (1, 16-18) Other workers (9,19) have suggested a mutual rotation of the two pentagonal bipyramidal halves of the cage (see Figure 1.1.3).

The reverse isomerisation can be accomplished via a nido intermediate by treatment of para-carborane (20) or meta carborane (21,22) with alkali metals in liquid ammonia.

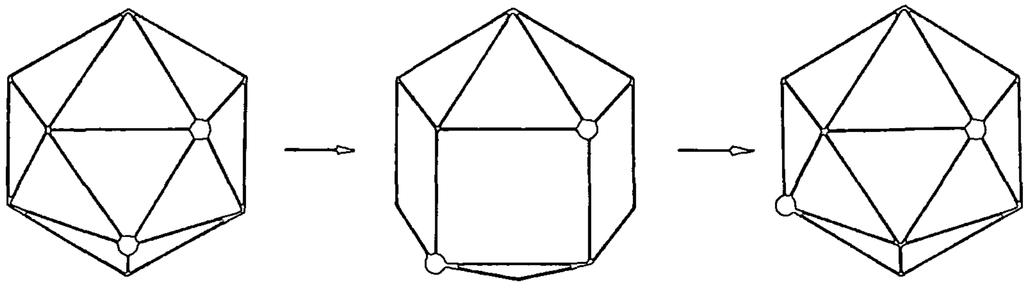
The chemical stability of the icosahedral carboranes allows a large amount of derivative chemistry to be performed at the carbon atoms or to a lesser extent at the boron atoms. Strong oxidizing agents such

Figure 1.1.2



"Diamond-Square-Diamond" Rearrangement

Figure 1.1.3



Mutual Rotation Rearrangement

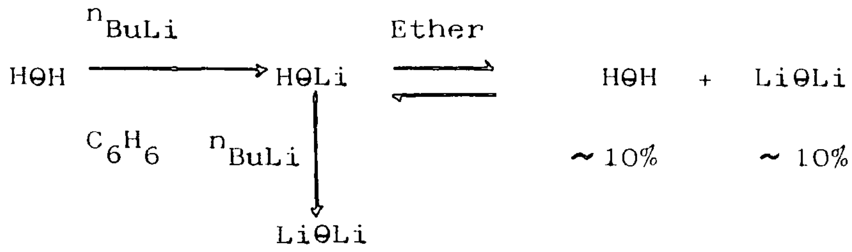
as nitric acid and bases such as methoxide ion or alkyl amines bring about degradation of the o-carborane cage.

The charge distribution in the icosahedral carboranes has been much studied (23-26) and these studies 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.

1.2 ALKALI METAL AND MAGNESIUM DERIVATIVES

ALKALI METAL DERIVATIVES

Due to the strong electron-withdrawing character of the ortho-carborane unit, the carboranyl C-H bond exhibits a greater degree of acidity than the C-H bonds in methane, butane or benzene and as a consequence is susceptible to attack by methyl-, n-butyl- or phenyllithium (27), to form the C-lithio derivative. In ether or in ether/benzene mixture an equilibrium exists between mono-lithiocarborane and both di-lithio carborane and unsubstituted carborane, but in benzene alone, only the mono-C-lithio derivative is formed.



If an excess of n-butyllithium is added to the mono-lithio derivative, the di-C-lithio derivative is formed.

Meta-carborane undergoes similar reactions with n-butyllithium although more forcing conditions are required. 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 has been explained by the weaker electron-withdrawing power of the m-carborane giving rise to less polar C-H bonds. However another possible explanation for the differences observed may be that when o-carborane is mono-lithiated the adjacent carboranyl C-H becomes further activated towards lithiation due to the combined electron-withdrawing effect of the cage and the lithium cation, an effect which would be less if at all significant in m-carborane since the cage carbon atoms in the meta derivative are non-adjacent. 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

The action of magnesium on C-halo-carboranes or the direct action of alkyl magnesium halides on the carborane cage results in the formation of carboranyl Grignard reagents.

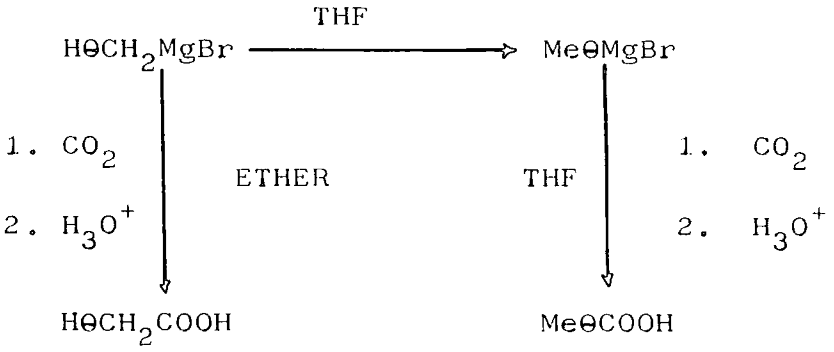
$$H\Theta X + Mg \longrightarrow H\Theta MgX$$

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

An equilibrium, analogous to that observed with the C-lithio-carboranes in ether, is found when the reactions are carried out in THF.

$$\underset{80\%}{2H\Theta MgBr} \rightleftharpoons \underset{\sim 10\%}{H\Theta Me} + \underset{\sim 10\%}{BrMg\Theta MgBr}$$

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. (28,29)



$$\begin{tikzcd}
H\Theta CH_2MgBr \arrow[r, "THF"] \arrow[d, "1.\ CO_2"', "2.\ H_3O^+"'] \arrow[d, phantom, "ETHER", shift left=8ex] & Me\Theta MgBr \arrow[d, "1.\ CO_2", "2.\ H_3O^+"] \arrow[d, phantom, "THF", shift right=8ex] \\
H\Theta CH_2COOH & Me\Theta COOH
\end{tikzcd}$$

The reaction in ether, in which very little rearrangement takes place, yields mostly carboranyl acetic acid. The 1-chloromethyl carborane behaves differently from the 1-bromomethyl derivative on reaction with magnesium in ether, affording mostly the rearranged Grignard compound, $Me\Theta MgCl$.

1.3 ALKYL AND HALOALKYL DERIVATIVES

SYNTHESIS OF ALKYL DERIVATIVES

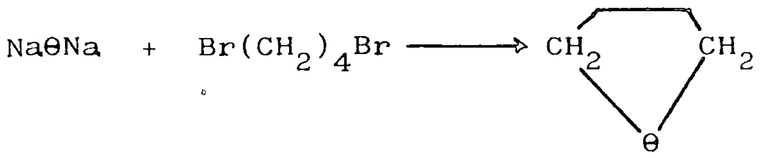
Carboranyl-C-alkyl derivatives can be prepared in several ways. One frequently used method for preparing C-aryl and C-alkyl carboranes is by the reaction of substituted acetylenes with bis-(acetonitrile) decarborane. (5,6)

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

However the most frequently used route is the reaction of C-lithio, C-sodio - or C-Grignard carboranyl derivatives with primary alkyl halides (usually the bromide or iodide) in ether, benzene or liquid ammonia.

$$Ph\theta Li \quad + \quad CH_3I \quad \xrightarrow[\text{Benzene}]{\text{Ether/}} \quad Ph\theta CH_3 \quad + LiI$$

Secondary or tertiary alkyl halides do not react. The method can be used for the preparation of exocyclic rings using di-C-metallo-o-carborane.



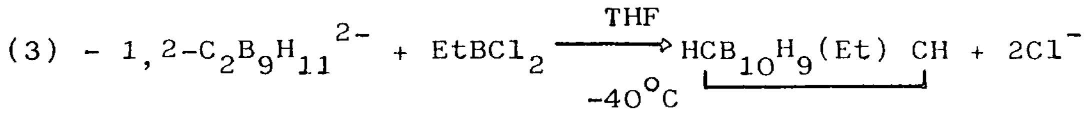
Carboranyl Grignards react readily with primary alkyl bromides and iodides, and di-alkylsulphates. (30)

$$R\theta MgBr \quad + \quad R^1CH_2Br \longrightarrow R\theta CH_2R^1 \quad + \quad MgBr_2$$

$$R \quad = \quad H, Me, Ph, \; CH = CH_2$$

Here again the secondary and tertiary alkyl halides and the primary alkyl chlorides are unreactive.

Alkylation at the boron atoms can be achieved by the reaction of the dicarbollide anion with alkyl boron dichloride. (31,32)



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

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

SYNTHESIS OF HALOALKYL DERIVATIVES

The reaction of haloalkyl acetylenes with bis (acetonitrile) decaborane, (33) or the reaction of halogens with Grignard reagents (34) results in the formation of haloalkyl carboranes.

$$R\theta CH_2MgBr \quad \xrightarrow{I_2} \quad R\theta CH_2I$$

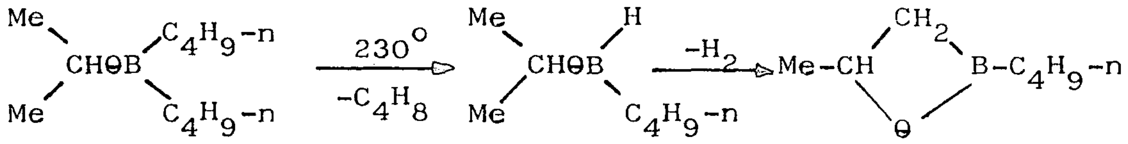
$$R \quad = \quad H, \; Me$$

1-Fluoromethyl-o-carborane can be prepared by the action of sulphur tetrafluoride on 1-hydroxymethyl-o-carborane. (35)

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

REACTIONS OF ALKYL AND HALOALKYL DERIVATIVES

Like ortho-, meta- and para-carborane the alkyl-o-carboranes are mostly stable, crystalline solids which are fairly inert to degradation and chemical attack. However, 1-isopropyl-2-di-n-butylboranyl-o-carborane when heated has been shown to yield a cyclic compound involving the alkyl substituents. (36,37)



The 1-haloalkyl carboranes show a much greater reactivity than the 1-alkyl derivatives, the β-halo-ethyl and γ-halopropyl carboranes being susceptible to nucleophilic attack at the halogenated carbon atom. (38)

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

and to Friedel Crafts attack on benzene with aluminium trichloride.

$$H\Theta CH_2CH_2X \quad + \quad C_6H_6 \xrightarrow{AlX_3} H\Theta CH_2CH_2C_6H_5$$

$$X = Cl,\ Br$$

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

1.4 CARBOXYLIC ACID AND ACID HALIDE DERIVATIVES

SYNTHESIS OF CARBORANYL CARBOXYLIC ACIDS

Decaborane (14) is readily degraded by carboxylic acid groups and therefore carboranyl carboxylic acids cannot be synthesised directly from an acetylenic carboxylic acid and bis (acetonitrile) decaborane. However carboxylic acid derivatives have been prepared by a number of alternative means.

Mono- and dicarboxylic acids can be prepared in good yields by the reaction of mono-lithio and dilithio-o-carborane with dry carbon dioxide. (27,28)

$$Li\theta Li \quad + \quad CO_2 \xrightarrow{H^+} HOOC\theta COOH$$

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.

Grignard reagents react in a similar manner but are particularly suited to forming long chain acids. (29)

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

$$n = 1\text{-}4$$

Carboranyl carboxylic acids have been synthesised by ester hydrolysis reactions. The esters, unlike the acids, can be synthesised directly from acetylenic esters and bis-(acetonitrile) decaborane. (5,27,28,39,40)

$$B_{10}H_{12}(MeCN)_2 + HC\equiv CCOOMe \xrightarrow[-H_2]{-2MeCN} H\theta COOMe \xrightarrow{H^+} H\theta COOH$$

Some carboranyl esters do not readily undergo hydrolysis. Di-methyl-1,2-o-carboranyl dicarboxylate was found to be stable to attack by refluxing concentrated hydrochloric acid, glacial acetic acid and trifluoroacetic acid. Cold 50% aqueous potassium-hydroxide causes saponification of the ester but the reaction gives poor yields. Ethyl-o-carborane-acetate has been shown to resist the action of 96% sulphuric acid at $100^{o}C$, but is hydrolysed under the action of 8N H_2SO_4 in dioxane. (41) In some cases, attempted alkaline ester hydrolysis leads to decarboxylation yielding the parent carborane.

$$R\Theta COOEt \xrightarrow[EtOH]{KOH} R\Theta H$$

These reactions are influenced by the strong electron-withdrawing power of the carborane cage and therefore the further the ester group is removed from the cage, the less prone it is to decarboxylation.

When a substituent is attached to the second cage carbon atom the carboranyl esters are more prone to decarboxylation. For example, 1-phenyl-carboran-2-yl carboxylate is converted quantitatively by 98% ethanol into 1-phenyl-o-carborane. (42)

$$Ph\Theta COOK \xrightarrow[20\%]{EtOH} Ph\Theta H \quad + \quad KHCO_3$$

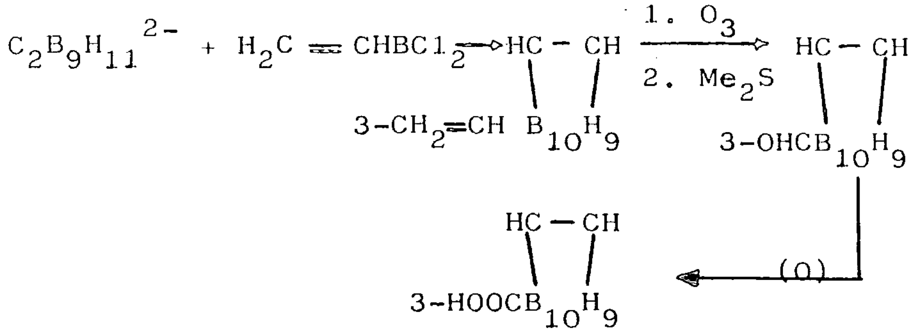
Organometallic reagents such as n-butyl lithium can also cause cleavage of the carboranyl esters. Organo lithium reagents cleave the ester at the carborane cage to give a lithio-carborane which can be converted back to a carboxylic acid with carbon dioxide and dilute acid. (43)

Carboranyl carboxylic acids may be synthesised from carboranyl alcohols by oxidation using chromium trioxide, potassium dichromate or alkaline potassium permanganate. (27,41,44)

$$H\Theta(CH_2)_n\ CH_2OH \xrightarrow[H_2SO_4]{CrO_3} H\Theta(CH_2)_n\ COOH$$

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

The preparation of boron substituted carboranyl carboxylic acids can be achieved by the following route,



3-Vinyl-m-carborane can be oxidised directly with chromium trioxide in sulphuric and acetic acid at room temperature. (45,46)

REACTIONS OF CARBORANE CARBOXYLIC ACIDS

The lower pKa values and higher acid strength of carborane carboxylic acids in comparison to the pKa values of the free acids is due to the strong electron withdrawing power of the cage. 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. Owing to the lesser positive charge at the 3-position in the cage, boron substituted - carborane acids are weaker than the C-substituted acids.

When substituents such as alkyl groups which give a + I effect are bonded to the cage at the 2– position carbon the acid strengths of the 1-o-carboranyl carboxylic acids decrease (47) and it has been noted that the greater the + I effect, the greater the increase in the pKa, or the lower the ionisation constant.

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. (1) (See Table 1.4.1) Carboxylic acids which are shielded from

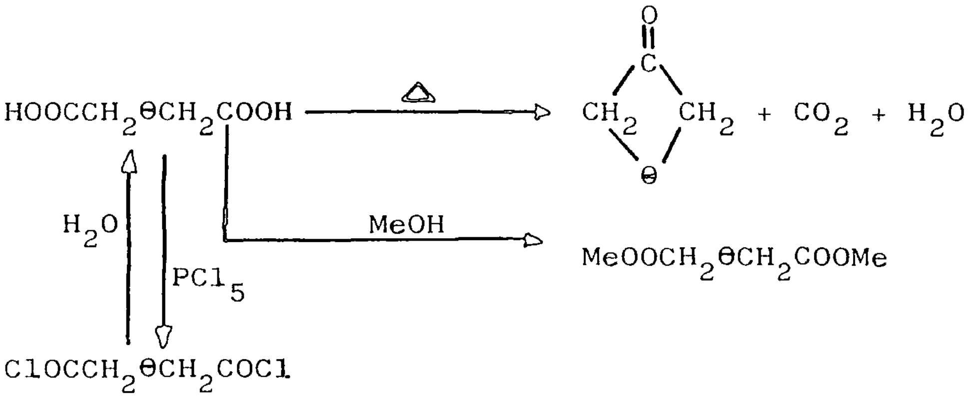
Table 1.4.1

pKa VALUES OF CARBORANE CARBOXYLIC ACIDS

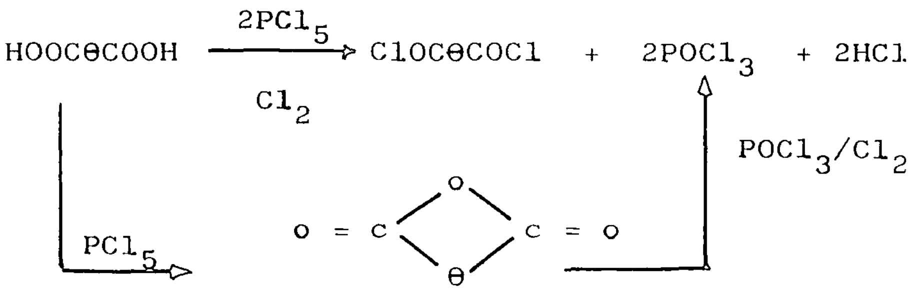
	R-Θ-R'		
R	R'	pKa	Solvent
H	COOH	2.48	A
H	COOH	2.61	B
CH_3	COOH	2.74	B
H	CH_2COOH	4.06	A
H	CH_2COOH	3.83	C
H	$(CH_2)_2COOH$	4.58	C
H	m-C_6H_4COOH	6.57	D
H	p-C_6H_4COOH	6.55	D
	R-Θ'-R'		
H	COOH	3.34	B
CH_3	COOH	3.14	B
H	m-C_6H_4COOH	6.96	D
H	p-C_6H_4COOH	6.79	D
	R-'Θ'-R'		
H	COOH	3.64	B
	H-Θ-H └(3)R		
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.

the cage by CH_2 groups tend to behave as normal acids, 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, (27) the former showing many reactions of a carboxylic acid.



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, the acid chloride can be obtained by reacting the acid with phosphorus pentachloride in the presence of a stream of chlorine gas. (28,48)



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. (49) Quantitative decarboxylation has been reported in the presence of beryllium and zirconium acetylacetonates. (50)

The chemistry of B-carboxylic acids is nearer that of the free organic acid owing to the reduced electron-withdrawal felt at the boron atoms. The formation of esters and acid chlorides proceeds normally. (46,51)

$$\begin{tikzcd} HCB_{10}H_{10-n}(COOH)_nCH \arrow[r, "MeOH"] \arrow[dr, "SOCl_2"'] & HCB_{10}H_{10-n}(COOMe)_nCH \\ & HCB_{10}H_{10-n}(COCl)_nCH \end{tikzcd}$$

1.5 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. (52,53,54)

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

Aldehydes can also be synthesised in almost quantitative yields by the ozonolysis of vinyl-o-carboranes. (45,55).

Other methods of synthesis include the Sonn-Müller reaction on the anilides of o- and m-carboranes, (52,53) although yields are not high.

$$\begin{tikzcd} o,m - H\Theta CONHC_6H_5 \arrow[r, "PCl_5"] & o,m - H\Theta CCl{=}NC_6H_5 \arrow[d, "SnCl_2/H_3O^+"] \\ & o,m - H\Theta CHO \end{tikzcd}$$

The hydrolysis of the methyl di-acetate derivative with water gives the C-aldehyde in a 40% yield. (53)

$$H\Theta CH(OCOCH_3)_2 \quad + \quad H_2O \longrightarrow H\Theta CHO$$

Di-aldehydes can be prepared by all of the above methods although an alternative route starting from dilithio-m-carborane has recently been published. (56)

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

B-substituted aldehydes have been prepared by the ozonolysis of 3-vinyl-o-carborane, (145) and 2-vinyl-m-carborane. (46)

SYTHESIS OF KETONES

There is a wide range of reactions for producing carboranyl ketones. The most widely used involves reacting lithio-carboranes with aliphatic, aromatic and even carboranyl acid chlorides. (57,58)

$$\mathrm{R\theta Li} + \mathrm{R'COCl} \xrightarrow{-\ \mathrm{LiCl}} \mathrm{R\theta COR'}$$

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

The action of oxalyl chloride on lithio carboranes results in the formation of di-ketones, but under the action of phosgene, a cyclic di-carboranyl- di-ketone is formed. (59) Cyclisation does not occur when lithio-m-carborane is reacted with phosgene since the carbons in m-carborane are non-adjacent unlike those in o-carborane.

$$2\ \mathrm{Ph\theta Li} + \mathrm{ClCOCOCl} \xrightarrow{-2\mathrm{LiCl}} \mathrm{Ph\theta COCO\theta Ph}$$

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 has been confirmed. (57)

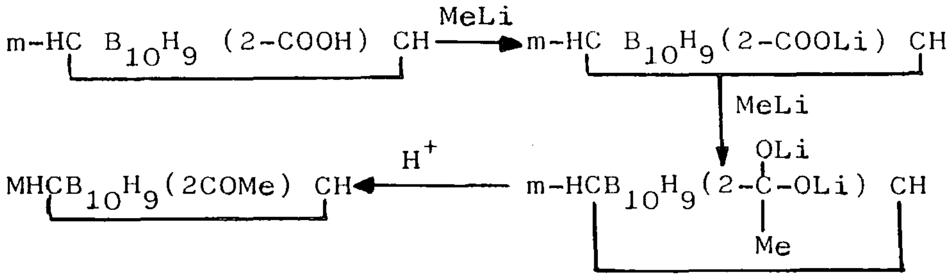
Carboranyl Grignard reagents react with acid chlorides in a similar manner to the lithio-carboranes. (60)

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. (57) The reaction of lithio-carborane with acid anhydrides and cyclic anhydrides gives ketones and keto acids respectively. (61)

Carboranyl ketones can also be prepared by the reaction of bis (acetonitrile) decaborane with the appropriately substituted acetylene.

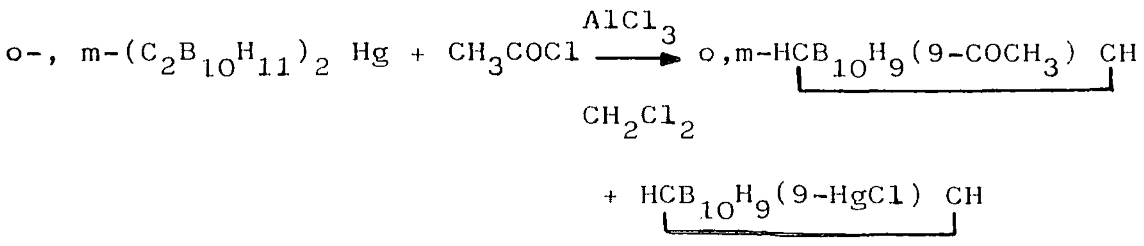
$$B_{10}H_{12}(MeCN)_2 \quad + \quad RC\equiv CCOR \xrightarrow[-H_2]{-2MeCN} R\Theta COR$$

B-substituted ketones can be synthesised from B-carboxylic acids by the action of methyl lithium and acid. (46)



$$m\text{-}HC\,B_{10}H_9\,(2\text{-}COOH)\,CH \xrightarrow{MeLi} m\text{-}HC\,B_{10}H_9(2\text{-}COOLi)\,CH \xrightarrow{MeLi} m\text{-}HCB_{10}H_9(2\text{-}\overset{OLi}{\underset{Me}{C}}\text{-}OLi)\,CH \xrightarrow{H^+} MHCB_{10}H_9(2COMe)\,CH$$

Methylation of the 3-substituted acid chloride by dimethylcadmium results in the formation of ortho-carboran-3-yl methyl ketone. (62) Until recently, only the meta-2- or ortho-3-substituted ketones were known, however a method for preparing ortho- and meta-9-substituted ketones has been devised using bis- (o-, m-carboran-9-yl) mercury (II). (63,64)



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

REACTIONS OF ALDEHYDES

Alkaline cleavage of carboranyl aldehydes results in the formation of the parent carborane. (52,53,65)

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. (66) Crampton found a similar reaction with meta and para, benzaldehyde derivatives on addition of methanol. (67)

Secondary alcohols are obtained when carboranyl aldehydes react with organo-lithium compounds. (53,55,65)

$$O - Me\Theta CHO \quad + \quad O\text{-}Me\Theta Li \longrightarrow (O\text{-}Me\Theta)_2\ CHOH$$

Grignard reagents in ether give two products on reaction with carboranyl aldehydes; one (I) via normal addition to the carboranyl group, the other (II) by reduction of the aldehyde to a primary alcohol. (53,65) The quantitative ratio of the formed alcohols (I) and (II) depends on the nature of the Grignard reagent. Thus in the case of ethylmagnesium bromide, normal addition to the carbonyl group proceeds in approximately 20%, and the reduction of the aldehyde to the hydroxymethyl-o-carborane predominates, evidently as a result of hydride transfer from the β atom of the ethyl group.

$$O\text{-}HCB_{10}H_{10}CCHO \quad + \quad RMgX \xrightarrow{Et_2O} O\text{-}HCB_{10}H_{10}CCH(OH)R$$

I

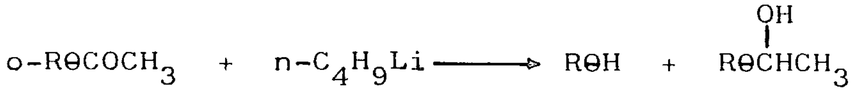
$$+\ O\text{-}HCB_{10}H_{10}CCH_2OH$$

II

Reduction of the carbonyl group of C-formyl-o-carborane also occurs in reactions with methyl magnesium iodide and phenylmagnesium bromide though to a lesser extent, the main product being the carbinol derivative rather than the hydroxymethyl-derivative.

REACTION OF KETONES

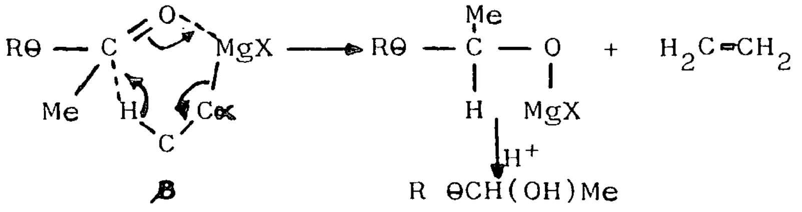
o-Carboranyl ketones are cleaved by both alkali and sodamide in liquid ammonia to give the parent carborane, (39,43,53,68,69) indeed presence of basic alumina used in thin layer chromatography is often enough to cause cleavage. (39,57,68) The action of organo lithium compounds on carboranyl ketones results in the formation of the parent carborane and can also produce secondary alcohols. (68)



$$\text{o-R}\Theta\text{COCH}_3 + \text{n-C}_4\text{H}_9\text{Li} \longrightarrow \text{R}\Theta\text{H} + \text{R}\Theta\overset{\text{OH}}{\overset{|}{\text{C}}}\text{HCH}_3$$

$R = CH_3$, Ph

Grignard reagents attack carboranyl ketones in a similar manner to organic ketones the products obtained depending on the reagent used. For example the carbonyl group of 1-methyl-2-acetyl-o-carborane is almost completely reduced to a secondary alcohol by ethyl magnesium bromide. (65,68) The equivalent reaction with methyl magnesium iodide in ether gives methyl-o-carborane, a tertiary alcohol and unreacted ketone. The decomposition of the unstable carboranyl tertiary alcohol in the above reaction produces the methyl-o-carborane. These standard observations can be explained by the fact that if the Grignard reagent has a hydrogen on the carbon adjacent to the point of attachment of -MgX (i.e. a β hydrogen as in the case of EtMgBr) then reduction can and does occur with the effect of adding H_2 to the carbonyl group.



The reaction of methyl lithium or methyl and ethyl magnesium halides on m-carboranyl ketones produces tertiary alcohols and this is thought to be due to the greater stability of the m-carboranyl tertiary alcoholates.

1.6 NITROGEN DERIVATIVES

SYNTHESIS OF AMINES

The reaction of amino acetylenes with bis- (acetonitrile) decaborane (5) results in the formation of C-amino-o-carboranes. These derivatives may also be prepared by the reduction of o-carboranyl cyanides and some amides with lithium aluminium hydride. (70,71,72)

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

Ortho- and meta-carboranyl amines can be synthesized from C-acyl chlorides by the action of sodium azide and sulphuric acid. (73,74)

$$o,m\text{-}R\Theta COCl \xrightarrow{NaN_3} R\Theta CON_3 \xrightarrow{H_2SO_4} R\Theta NCO \xrightarrow{H_2SO_4} R\Theta NH_2$$

The reduction of C-nitroso o- and m-carboranes with chloro aluminium hydride, n-butyl lithium or phenyl thiol in xylene also produces C-amines, although the latter two methods also produce some hydroxyaminocarborane. (75)

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, (34,76) and by this weakbase method even fluoromethyl o-carborane undergoes nucleophilic attack.

$$H\Theta CH_2X \quad + \quad Et_2NH \xrightarrow[20^{\circ}C]{C_6H_6} H\Theta CH_2NEt_2 \quad + \quad X^- \ {}^{+}NH_2Et_2$$

$X = Cl,\ Br,\ I$

Weaker bases than diethylamine are not strong enough nucleophiles to replace the halogen; stronger bases lead entirely to cage degradation.

The reactions between 1-halomethyl, 2-sodio-o-carborane and Schiffs bases in liquid ammonia have produced some interesting cyclic amines. (77)

B-amino carboranes have been much studied and more is known about these derivatives than the C-amino carboranes. They have been prepared in high yields by the action of sodium in liquid ammonia. (71,78,79)

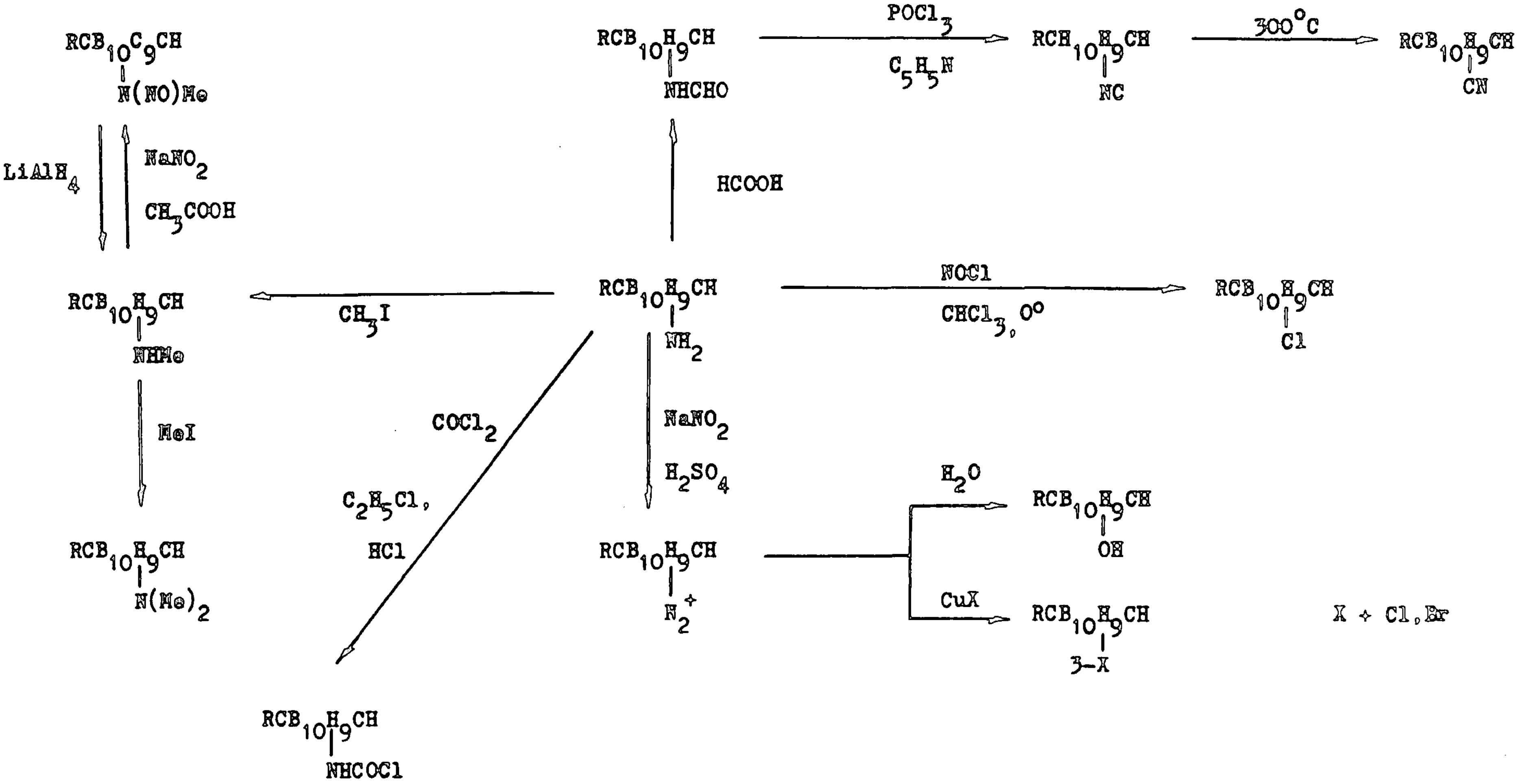
$$R\Theta R \xrightarrow[\text{liq } NH_3]{2Na} (R\Theta R^1)^{2-} \xrightarrow[\text{Liq } NH_3]{} [R\Theta(3\text{-}NH_2)R^1]^{2-} \xrightarrow[KMnO_4]{-2e} R\Theta(3\text{-}NH_2)R^1$$

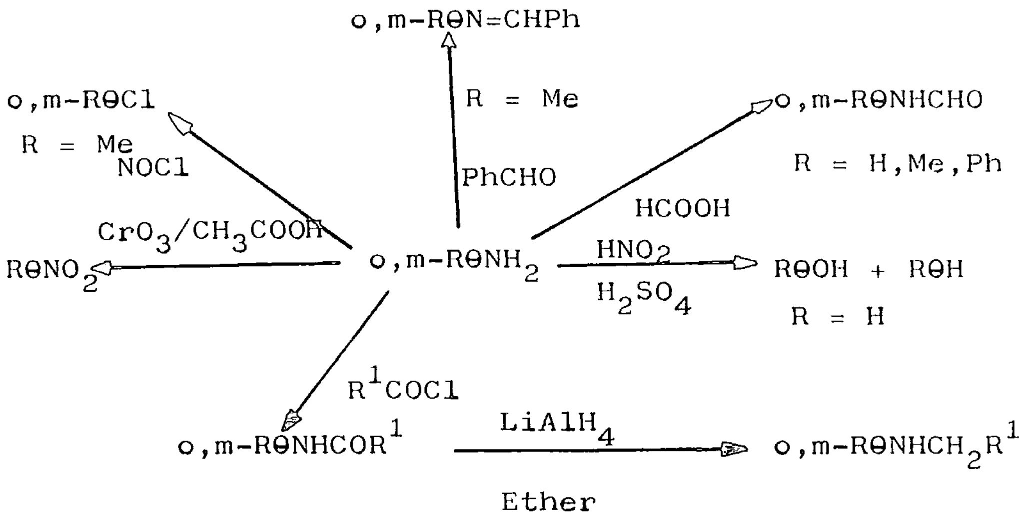
Only o-carborane derivatives can be prepared by this method, as the use of m-carborane gives o-carborane derivatives. (See Section 1)

REACTIONS OF AMINO DERIVATIVES

C-amino-o-carboranes are very weak bases, soluble in concentrated sulphuric acid but insoluble in dilute acid. (73,74,80,81) Oxidation of amines such as m-aminophenyl-o-carborane with 90% hydrogen peroxide and trifluoracetic acid gives the nitrophenyl derivative. (80)

The reactions of the C-amino and B-amino carboranes are summarised on the following pages. (75,78,79,82,83)


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



$R = H, Me, Ph;\ R^1 = H, Me$

SYNTHESIS OF AMIDES

C-carboranyl amides can be prepared by the reaction of bis- (acetonitrile) decaborane with acetylenic amides or by the direct combination of a carboranyl acid chloride with ammonia or an amine. (27,39,42)

Anilides can be formed by the reaction of phenyl isocyanate or isothiocyanate with lithio carboranes. (61) A sterically hindered di-amide can be made by the reaction of dilithio-o-carborane with N,N-dimethyl carbamoyl chloride. (84)

$$Li\Theta Li \quad + \quad 2Me_2NCOCl \xrightarrow[0^{o}C]{Ether} Me_2NCO\Theta CONMe_2$$

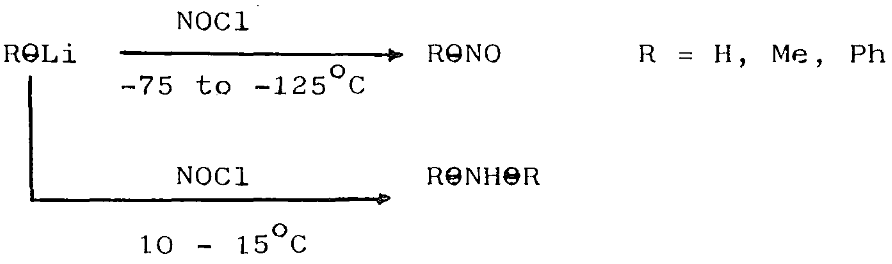
Ortho carboranyl amides are more stable towards C-C cleavage by sodium ethoxide in ethanol than the o-carboranyl esters and ketones. The action of boiling ethoxide in ethanol on o-carboran-1-yl amides does not result in the cleavage of the C-C bond but does cause cage degradation to the dicarbaundecaborate anion. (85) 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. Alkoxide cleavage can be prevented by separating the amide group from the cage by CH_2 groups.

Lithium aluminium hydride cleaves amides directly bonded to the cage, and the interposition of CH_2 groups results only in hydrogenation. (72) Sodium in liquid ammonia also causes cleavage of the C-C bond. (86)

NITRATES AND RELATED DERIVATIVES

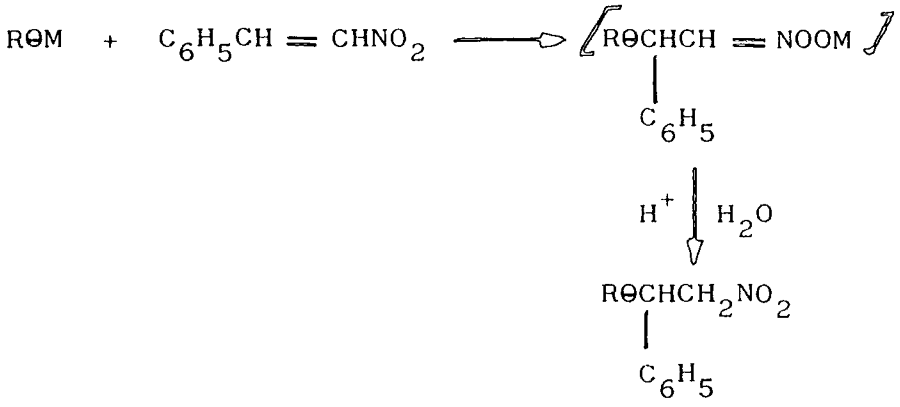
B-hydroxy and B-nitrate derivatives are obtained when o- or methyl-o-carborane are treated with 100% nitric acid in carbon tetrachloride at room temperature. Attack is thought to occur at the 9 (12) boron atom, this being the most negative atom in the cage. (87,88) Bis (hydroxymethyl)-o-carborane reacts with cold nitric acid giving the highly explosive C,C-dinitrate derivative. (33)

Nitroso derivatives of o-carborane can be made by the reaction of lithio carborane and nitrosyl chloride at about -100°C. However at temperatures above 10°C bis (o-carboranyl) amines are formed. (80,82)



m-Carboranyl nitroso derivatives have been prepared by the oxidation of C-amino-m-carboranes with chromium trioxide in acetic acid. Further oxidation in this medium gives 1-nitro-m-carborane. (82)

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. (89)



$$R\Theta M + C_6H_5CH = CHNO_2 \longrightarrow [R\Theta \underset{C_6H_5}{C}HCH = NOOM] \xrightarrow[H_2O]{H^+} R\Theta \underset{C_6H_5}{C}HCH_2NO_2$$

Where $R = CH_3, C_6H_5$

$M = Li, MgBr$

1.7 BORANYL-CARBORANE DERIVATIVES

SYNTHESIS OF CARBORANYL BORANES

Carboranyl-boranes have been synthesized by the reaction of lithio carboranes with trihalo-, alkyl-dihalo- and dialkyl-monohalo-boranes in benzene at 0°C. (36,90)

$$2Me\Theta Li + BCl_3 \xrightarrow[\text{TOLUENE} \\ -\ 2LiCl]{0^oC} (Me\Theta)_2\ BCl \xrightarrow[-HCl]{H_2O} (Me\Theta)_2\ BOH$$

Recent studies (90) have shown that only two carboranyl units may be attached to one boron atom, the reason for this being attributed to steric hindrance.

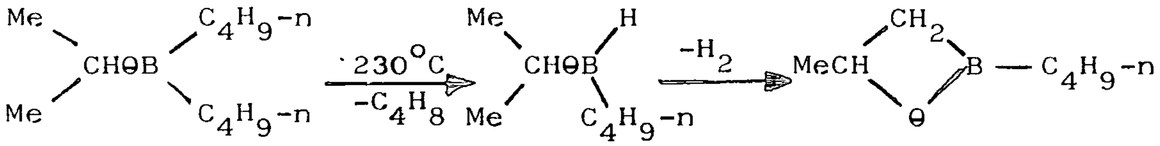
However two carboranylunits and a phenyl group, which is approximately equal in width to the cross-section of a carborane cage and which has a similar cone angle, can be attached to a single boron atom. The phenyl group, unlike the bulky icosahedral carboranyl unit, can relieve steric effects by tilting the ring plane out of the cage-boron-cage plane. (90)

$$3R\Theta Li + BCl_3 \not\longrightarrow (R\Theta)_3B$$

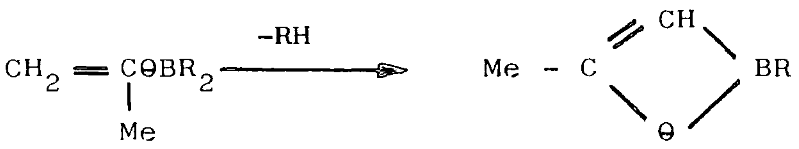
$$2R\theta Li + PhBCl_2 \xrightarrow[\text{TOLUENE}]{-2LiCl} (R\theta)_2\,BPh$$

REACTIONS OF BORANYL-CARBORANES

The action of heat on 1-isopropyl-2-di-n-butyl boranyl o-carborane has been shown to yield a cyclic compound involving the alkyl substituents. (36,37)



1-Vinyl and 1-isopropenyl-o-carborane derivatives also undergo cyclisation reactions when the 2-position substituent is a di-alkyl-boron. (37)



R = n-Bu, iso-Bu

3-Position organo derivatives of ortho and meta carborane can be made by the reaction of the dicarbollide ion with organo boron - and o-carboranyl boron - dichlorides. (31,32)

$$(3)-1,2\ C_2B_9H_{11}^{2-} + RBCl_2 \xrightarrow[-40^{\circ}C]{THF} \text{o-H}\underline{CB_{10}H_9RC}H + 2Cl^-$$

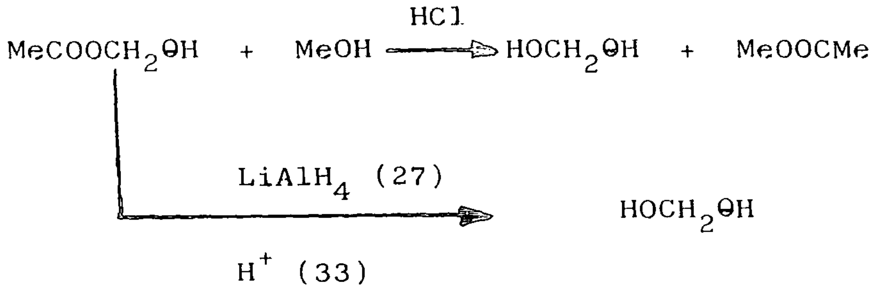
R = θH, Me, Et, Ph; CH = CH$_2$, OEt

1.8 ALCOHOL AND ETHER DERIVATIVES

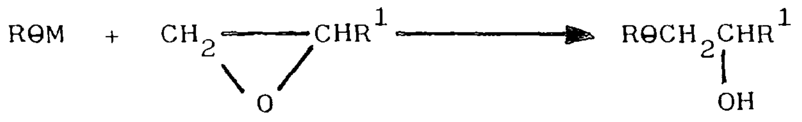
SYNTHESIS OF ALCOHOLS

O-Carboranyl alcohols cannot be synthesised directly from acetylenic alcohols and bis (acetonitrile) decaborane, since the decaborane cage is degraded by the alcohol groups.

One method of synthesis is to use an ester of the acetylenic alcohol and then convert the resulting carborane ester back to the alcohol by hydrolysis (27,28,33) or by transesterification. (40)

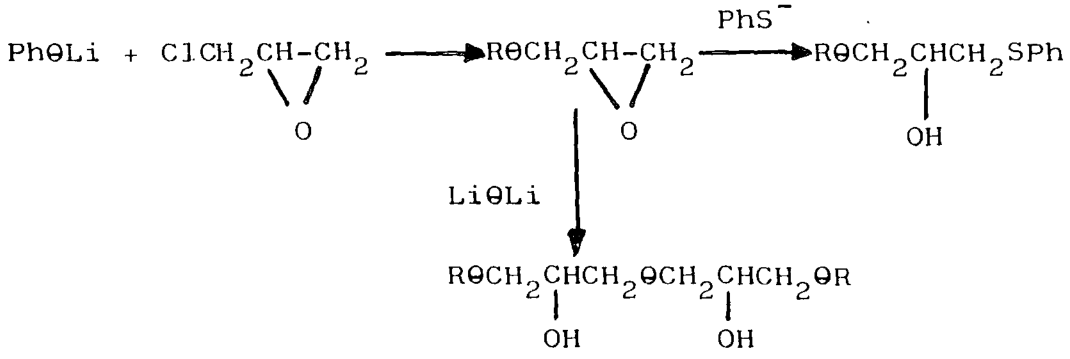


C-Alkali metal carborane derivatives react with esters, aldehydes, ketones and epoxides giving alcohols. Di-lithio-o-carborane reacts with ethylene oxide to give bis- (β-hydroxymethyl)-o-carborane. (27) Similar reaction with epoxides gives secondary alcohols. (91)

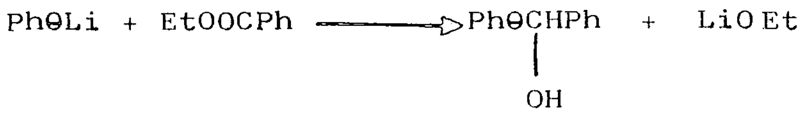


M = Li, Na ; R^1 = H, Me, Ph, CH_2Cl ; R = H, Me, CH_2= CH, Ph.

Secondary alcohols have been formed by the reaction of o-carboran-1-yl- 1,2-epoxypropanes with nucleophilic reagents such as alkoxides, thiophenolates, or lithio-carboranes. (92)



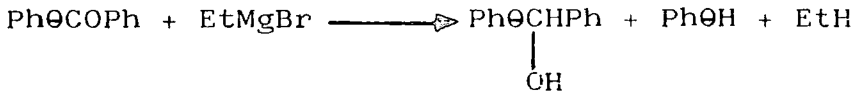
The reaction of ethyl benzoate with 1-phenyl-2-lithio-carborane gives a secondary alcohol, (61,93) whilst the reaction with methyl benzoate gives a ketone.



$$Ph\Theta Li + EtOOCPh \longrightarrow Ph\Theta CH(OH)Ph + LiOEt$$

$$Ph\Theta Li + MeOOCPh \longrightarrow Ph\Theta COPh$$

Organolithium compounds or Grignard reagents do not react with such carboranyl ketones, followed by hydrolysis to give the expected tertiary alcohols. Instead, secondary alcohols are formed, or cleavage of the ketone group from the cage occurs to give the parent carborane. (See Section 1.5)



$$Ph\Theta COPh + EtMgBr \longrightarrow Ph\Theta CH(OH)Ph + Ph\Theta H + EtH$$

Very little has been published on the synthesis and reactions of carboranyl-C-hydroxy derivatives. There are two routes for preparing these derivatives. One route (94) which one group of workers found ineffective (95) entails bubbling dry air through a suspension of a lithiocarborane in a hydrocarbon solvent.

$$Me\Theta Li \xrightarrow[\text{ii) } H_3O^+]{\text{i) Dry Air } (O_2)} Me\Theta OH + Me\Theta H$$

The other route employs benzoyl peroxide (96):-

$$2R\Theta Li + (PhCOO)_2 \xrightarrow[\text{ii) } H^+]{\text{i) } Et_2O} R\Theta OH + R\Theta COPh + PhCOOH$$

Several mono-hydroxy-ortho and meta-carboranes have been prepared by this latter method in yields of 35-40%.

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. (87) Potassium permanganate in acetic acid unselectively oxidises o- and m-carborane giving four isomeric B-hydroxy carboranes. Oxidation by chromium trioxide gives more selective substitution at the more negatively charged 9(12) boron atoms. Para-carborane only gives one product due to the equivalence of the boron atoms. (97) These B-hydroxy compounds are very susceptible to alkaline cleavage yielding dicarbaundecaborate (12) salts. (98)

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

SYNTHESIS OF ETHERS

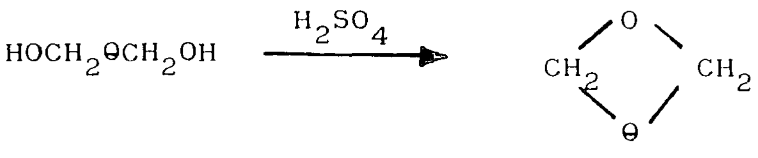
The reaction of acetylenic ethers with bis (acetonitrile) decaborane gives carboranyl ethers. (44)

$$2B_{10}H_{12}(MeCN)_2 + (HC\equiv CCH_2)_2\,O \xrightarrow[-2H_2]{-4MeCN} H\Theta CH_2OCH_2\Theta H$$

$$B_{10}H_{12}(MeCN)_2 + HC\equiv COEt \xrightarrow[-H_2]{-2MeCN} H\Theta OEt$$

There are no examples of bis (carboranyl) ethers, that is two icosahedral cages linked via a single oxygen atom, in the literature.

Several cyclic ethers have been formed by the dehydration or decarboxylation of other carboranyl ethers, alcohols or carboxylic acids. (27,44)



Some cage-oxygen-alkyl bonded ethers have been prepared by the reaction of 1-hydroxy carboranes with di-azo methane. (96)

$$R\Theta OH + CH_2N_2 \xrightarrow{-N_2} R\Theta OMe$$

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

REACTIONS OF ALCOHOLS

The electron withdrawal of the carborane cage is as apparent in the chemistry of alcohols as it is for the carboxylic acid derivatives. The further the alcohol group is separated from the cage by methylene groups, the more normal is its chemistry. This can be shown by comparing the reactions of hydroxymethyl-o-carborane with hydroxyethyl- and hydroxypropyl-o-carboranes. Both the hydroxyethyl- and hydroxypropyl derivatives can be oxidized to their acid salts by alkaline potassium permanganate whereas the hydroxymethyl derivative is converted directly to the parent carborane. (28) Hydroxymethyl-o-carborane also reacts with thionyl chloride in the presence of pyridine by replacement of the hydroxy group with chlorine.

The action of sodium forms the dimetallo-alcoholate which was found to be unreactive except towards hydrolysis. (27)

Most of the carboranyl alcohols react normally with aliphatic acids, acid anhydrides and acid chlorides to give esters.

$$R\Theta(CH_2)_2OH \quad + \quad RCOCl \xrightarrow{-HCl} R\Theta(CH_2)_2OOCR$$

The carboranyl-C-hydroxy derivatives are fairly acidic (pKa of 1-hydroxy-o-carborane = 5.25; pKa of 1-hydroxy-m-carborane = 8.24) due to the electron withdrawing character of the cage. (94) These derivatives react with diazo methane giving ethers and with acid chlorides producing esters. These C-hydroxy carboranes also react with bases such as triethylamine giving the corresponding salt. (96)

$$Me\Theta OH \quad + \quad Et_3N \xrightarrow{HEXANE} Me\Theta O^{-+}HNEt_3$$

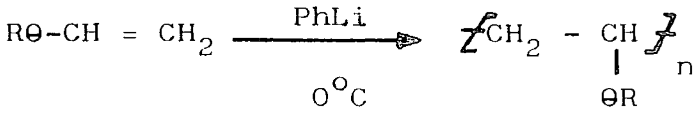
$$Me\Theta O^{-+}HNEt_3 \quad + \quad PhCOCl \xrightarrow{HEXANE} Me\Theta OOCPh + Et_3NHCl$$

1.9 POLYMER DERIVATIVES

Many specialized reviews have been published on carborane polymers since the discovery that the incorporation of icosahedral carboranes into polymers greatly improved the thermal stability of such polymers compared to their organic counterparts. (99-104) 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

One of the best examples of a pendant carborane polymer is polyvinyl-o-carborane, prepared by treating 1-vinyl-o-carborane with phenyl-lithium in ether at 0°C.

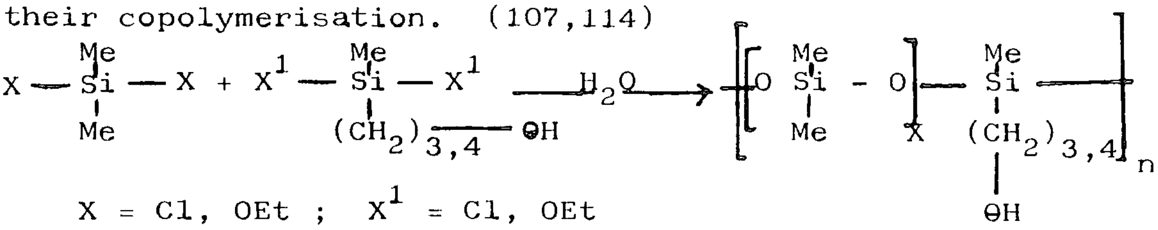


$$R\Theta\text{-}CH=CH_2 \xrightarrow[0^\circ C]{PhLi} \left[CH_2-\underset{\Theta R}{CH}\right]_n$$

R = H, (105) ; Et (106)

The resulting polymer has molecular weights between 50,000 - 140,000 and a softening point of about 250°C (105) whilst the ethyl derivative is air stable up to 360°C. (107) Direct polymerisation by exposure to γ radiation (108-110) or X-rays (110) has been achieved but molecular weights were no higher than 25,000. Copolymerisation of 1-vinyl-o-carborane with vinyl-benzene (112), ethylene (113) and 1,3-butadiene (111) have been reported.

Polysiloxane-o-carborane polymers have shown very high thermal stabilities and have been prepared by hydrolysis of o-carboranyl chloro- and ethoxy-silanes (114,115) or by their copolymerisation. (107,114)



$$X-\underset{Me}{\overset{Me}{Si}}-X + X^1-\underset{(CH_2)_{3,4}-\Theta H}{\overset{Me}{Si}}-X^1 \xrightarrow{H_2O} \left[\left[O\,\underset{Me}{\overset{Me}{Si}}-O\right]_x-\underset{\underset{\Theta H}{|}}{\overset{Me}{Si}}\text{(CH}_2)_{3,4}\right]_n$$

X = Cl, OEt ; X^1 = Cl, OEt

Polymers prepared from alkyl and aryl (o-carboranyl isopropyl) chlorosilanes have a liquid range from -108°C to 350°C at which they decompose. (1)

CARBORANYLIDENE POLYMERS

Chain linking carborane polymers, that is those in which the cage forms part of the polymer backbone, tend to exhibit greater thermal stability than the pendant carborane polymers or 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.

Carboranyl polyesters, of which there are many, have been synthesized by the reactions of carboranyl diacids or diacid chlorides, with organic diols. Similarly polyesters can be prepared by reacting carboranyl diols with either carboranyl - or organic diacid chlorides. (99, 116-121)

$$ClCO\theta'COCl + HO(CH_2)_2\theta(CH_2)_2\theta(CH_2)_2OH \xrightarrow[Et_3N]{-HCl} \left[\theta'COO(CH_2)_2\theta(CH_2)_2OCO\right]_n$$

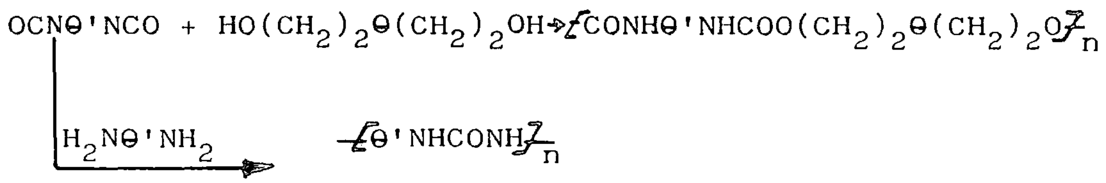
The reaction of boric acid with carborane diols or epoxides also leads to polyesters. (122)

$$HOCH_2\theta CH_2OH + H_3BO_3 \longrightarrow \left[OCH_2\theta CH_2OBOH\right]_n$$

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 phenyl diacid chlorides and 1,2 - diamino-o-carboranes yields carboranyl polyamides which in inert atmosphere can withstand temperatures of 900°C without weight loss. (123) Polyamides based on para-carborane dicarboxylic acid and various aryl- and alkyl-diamines have also been prepared by low temperature solution polycondensation the para-carboranyl polyamides were found to have better stability towards thermooxidative degradation than the ortho- or meta-carboranyl polyamides. (126)

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

Polycarbamates and polyureas have been prepared by the reaction of bis-isocyanato-m-carborane with carboranyl diols and diamines respectively. (124,125)

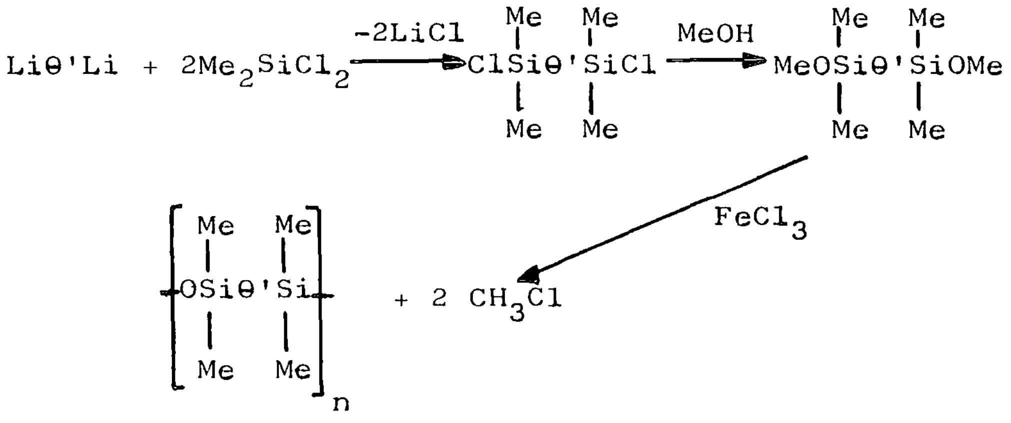


$$OCN\Theta'NCO + HO(CH_2)_2\Theta(CH_2)_2OH \rightarrow [CONH\Theta'NHCOO(CH_2)_2\Theta(CH_2)_2O]_n$$

$$OCN\Theta'NCO + H_2N\Theta'NH_2 \rightarrow [\Theta'NHCONH]_n$$

The largest group and by far the most studied of all the carborane polymers is the commercially available carboranyl polysiloxanes. These polymers, which are mainly based on meta-carborane are exceptionally heat resistant elastomers and are widely known as the Dexsil polymers.

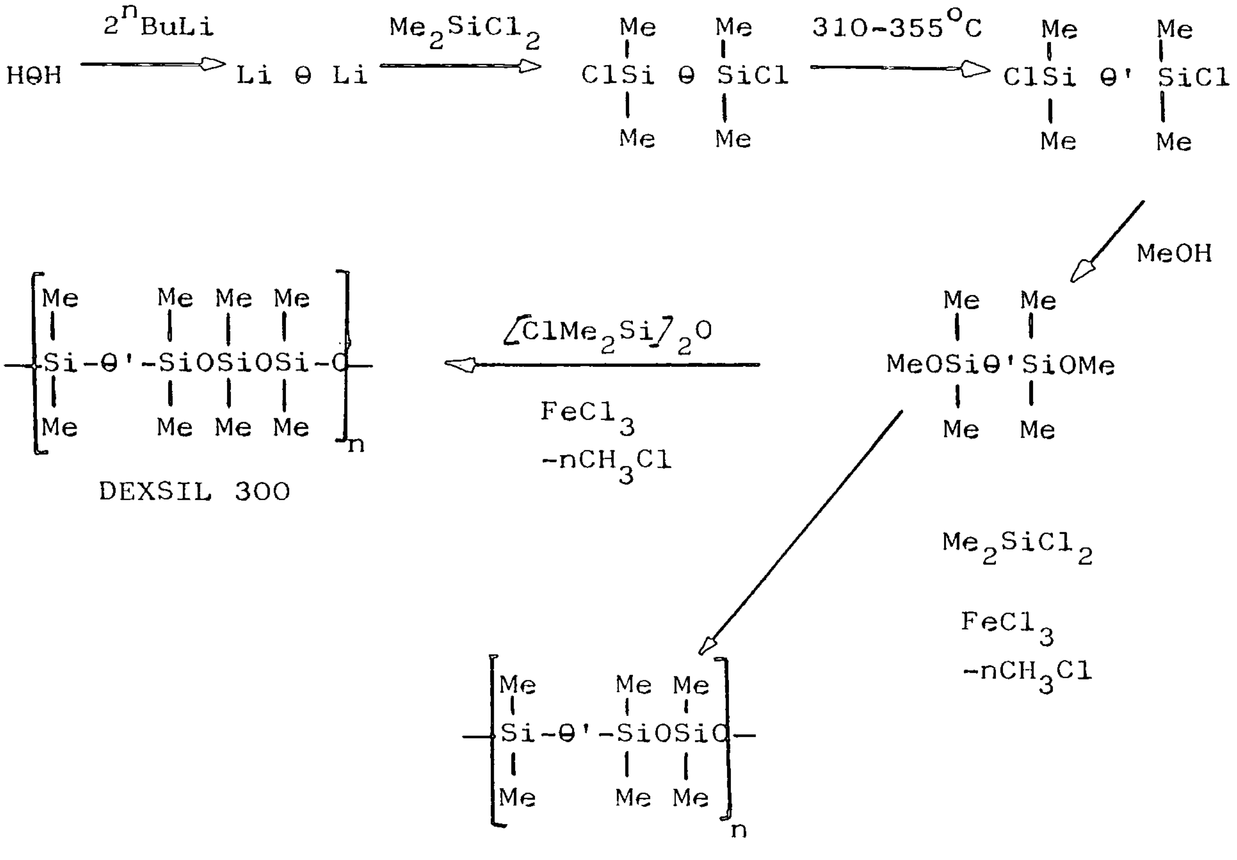
The first carboranyl polysiloxanes were prepared by the following route:- (127)



$$Li\Theta'Li + 2Me_2SiCl_2 \xrightarrow{-2LiCl} Cl\underset{Me}{\overset{Me}{Si}}\Theta'\underset{Me}{\overset{Me}{Si}}Cl \xrightarrow{MeOH} MeO\underset{Me}{\overset{Me}{Si}}\Theta'\underset{Me}{\overset{Me}{Si}}OMe \xrightarrow{FeCl_3} \left[O\underset{Me}{\overset{Me}{Si}}\Theta'\underset{Me}{\overset{Me}{Si}}\right]_n + 2\ CH_3Cl$$

DEXSIL 100

A series of other Dexsils up to Dexsil 400 have been prepared by similar means although many workers have started from o-carborane rather than m-carborane. (127-131)



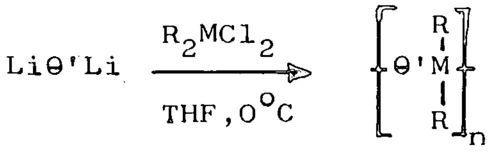
DEXSIL 300

DEXSIL 200

Cross-linking can be promoted by polymerising the Dexsils along with about 1% vinyl carborane. Dexsil 300 and 500 have also been prepared by hydrolytic polycondensation in water/ether/THF solutions at 0°C. (132)

The electron-withdrawing effect of the meta-carborane cage is thought to be the reason for the high thermal stability exhibited by the Dexsils. This is evident in the observed reduction in thermal stability as the number of siloxy groups increases. The thermo-oxidation of the polymers in air, which is thought to start at the silicon bonded methyl groups, follows the trend:- Dexsil 100 > 450°C; Dexsil 200 and 300, ≈ 355°C and Dexsil 400, ≈ 325°C.

Chain polymers in which carborane icosahedra are joined by single atoms in place of the more flexible siloxane or ester linkage are hard materials with thermoplastic properties. Polymers of this type with linking atoms from groups IV, V and VI of the periodic table have been prepared. Group IV polymers are synthesised by the reaction of a dialkyl metal dichloride with dilithio-m-carborane in THF. (133,134,135)



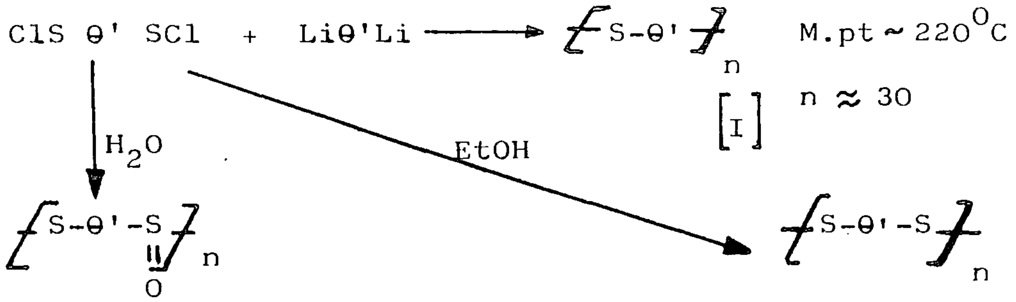
$$\mathrm{Li}\theta'\mathrm{Li} \xrightarrow[\mathrm{THF},\,0^{o}\mathrm{C}]{R_2MCl_2} \left[\theta'\overset{R}{\underset{R}{M}}\right]_n$$

M = Ge, Sn, Pb

R = Me, Et, n-Bu, Ph

A few p-carborane polymers of this type have been reported, and these remain hard up to relatively high temperatures (300-400^{o}C). Reaction of diphenyl-tin dichloride with 1,12-dilithio-p-carborane yields products averaging 11 repeating units, but the use of dimethyltin dichloride results in a polymer which is insoluble in ordinary organic solvents and is air-stable to 425^{o}C. (128) Related germanium species have melting points up to 480^{o}C. (133)

Group VI element polymers have been prepared from carboranyl sulphur derivatives. (136)



The equivalent para-carborane product to (I) is reported to be insoluble in common organic solvents and exhibited a softening point above 420^{o}C. (136) No examples of oxygen-linked chains have been reported however there are some examples of selenium and telurium linked materials.

A polymer consisting simply of m-carborane icosahedra connected by mercury atoms has been reported. (137)

$$\mathrm{Li}\theta'\mathrm{Li} + \mathrm{HgCl_2} \xrightarrow{-n\mathrm{LiCl}} [\theta' - \mathrm{Hg}]_n$$

M.pt > 300^{o}C

M.Wt ≈ 10,000

CHAPTER 2

THE PREPARATION OF ORTHO-, 1-METHYL-ORTHO-, 1-PHENYL-ORTHO- AND META-CARBORANE

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THE PREPARATION OF ORTHO-, 1-METHYL-ORTHO-, 1-PHENYL-ORTHO- AND META-CARBORANE

2.1 INTRODUCTION

Unsubstituted icosahedral carboranes of the formula $C_2B_{10}H_{12}$ have been synthesized from non-icosahedral starting materials by three distinct routes, these being:-

1. The reaction of ultra-pure acetylene gas with bis-(acetonitrile) - or bis (diethylsulphide) - decaborane, $B_{10}H_{12}L_2$ for 40 hours giving unsubstituted ortho-carborane in 70% yield. (8)

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. (138)

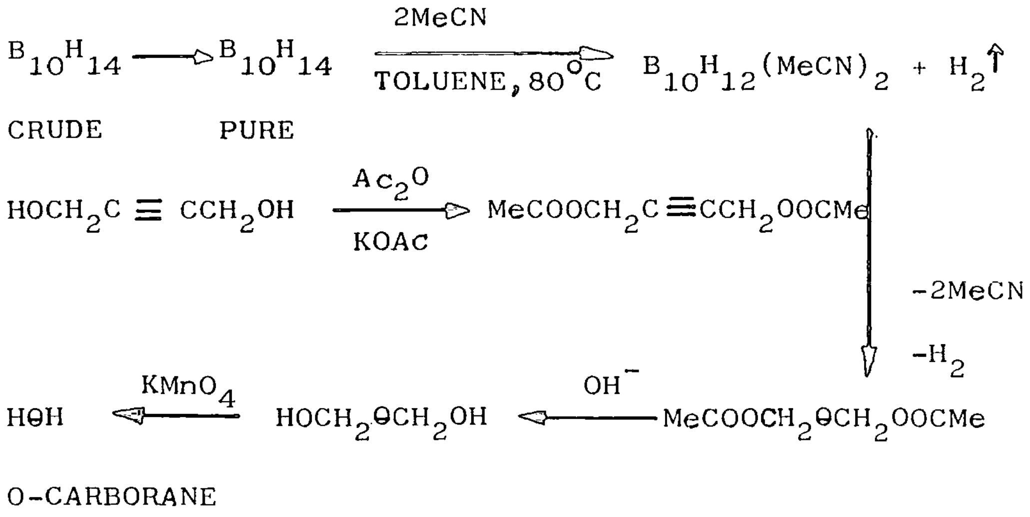
3. The pyrolysis of nido-2-CB_5H_9 to give meta-carborane in only 16% yield. (139)

For the purposes of routine laboratory preparation of ortho-carborane method (2) above was adopted. This method, although producing lower yields of ortho-carborane, does not require the use of a complicated purification train for the substituted acetylene nor does it produce explosive intermediates or require overnight supervision, and is consequently a safer and simpler method being based on the oxidative degradation of 1,2 - bis (hydroxymethyl)-o-carborane.

The following section describes investigations made into this second method of preparing ortho-carborane and shows improvements made to and problems associated with the method described in the literature. (138)

2.1(a) REACTION SCHEME

The steps described in this section have been outlined in the following reaction scheme.



2.1(b) PURIFICATION OF DECABORANE (14)

Commercially available decaborane usually contains a certain proportion of yellow polymeric material, the concentration of which depends on the length of time and the conditions under which the material has been stored. Purified decaborane when left in air for several weeks starts to show signs of polymer build up, the main indication being a slight colour change from white to pale yellow. The use of very pure decaborane in the syntheses of substituted and unsubstituted ortho-carboranes is essential, since a small concentration of the polymeric material is sufficient to cause noteable decreases in the yields obtained, and may also lead to unstable side products.

Three techniques are normally used for purifying crude decaborane. These include Soxhlet extraction, or recrystallization from benzene or heptane, and sublimation.

I have found through thorough investigation that the latter method, a technique also favoured in the literature (8), produces very pure decaborane. I have also found from quantitative sublimation experiments (see Results) that about 90-95% of pure decaborane can be safely obtained from crude commercially available decaborane, the remaining 5-10% being non-volatile yellow/orange polymeric material. It has been suggested in the literature that the violent decomposition of decaborane at temperatures approaching 100°C may be due to this non-volatile polymeric material and that the likelihood of such an occurrence increases as the concentration of polymer increases. I found that this danger could be minimised by using an inert atmosphere, low temperature/high vacuum sublimation technique.

The purification of decaborane by recrystallization from benzene or heptane, whilst giving fairly pure decaborane, was found to be an unwieldy technique, especially when carried out on a small scale.

Purification by Soxhlet extraction with benzene does not produce pure decaborane in large quantities as reported. (140) The main reason for this is that a small proportion of the yellow polymeric material is actually soluble in the benzene and, therefore the decaborane obtained was not of a high standard of purity. A combination of Soxhlet extraction and recrystallization did result in pure decaborane being obtained, however this was a very time consuming process.

i) EXPERIMENTAL

Purification by Quantitative Sublimation

A weighed amount of crude decaborane (14) was placed in the sublimation apparatus, which had been flushed with dry nitrogen prior to use. The system was heated to 40°C and evacuated to 0.001 mm Hg. The pure white sublimate was collected on a liquid nitrogen cooled cold finger.

ii) RESULTS

Weight of crude $B_{10}H_{14}$ used = 12.47g

Weight of pure $B_{10}H_{14}$ obtained after 3 hr = 11.56g

Therefore % pure white decaborane obtained = 92.7

Therefore % yellow polymeric material remaining = 7.3

Analysis

	B	H
% FOUND	88.3	11.5
$B_{10}H_{14}$ requires	88.5	11.4

Mass Spectrum

The mass spectrum showed a highest mass peak at $\frac{m}{e}$ 124, $^{11}B_{10}\,^{1}H_{14}$. Below this peak was an isotope pattern due to the various combinations of ten atoms of ^{10}B and ^{11}B. The pattern is characteristic of species containing a large number of boron atoms. Boranes and carboranes often show half mass peaks due to doubly charged parent ions and for decaborane these are seen at $\frac{m}{e}$ 57-62 (i.e. $\frac{m}{2e}$ 114-124).

I.R.

The infra-red spectrum showed the following peaks:-

ν max, KBr disc (cm^{-1}) 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 (1008cm^{-1}), (725 cm^{-1}).

Melting Point

Melting point of white solid = 99°C /Lit 99.7°C (23) /

2.1(c) PREPARATION OF BIS (ACETONITRILE)-DECABORANE

i) EXPERIMENTAL

$$B_{10}H_{14} + 2\ MeCN \xrightarrow[80^{o}C]{TOLUENE} B_{10}H_{12}\ (MeCN)_2 + H_2\uparrow$$

26.4g (0.216 mole) of purified decaborane was dissolved in 50 mls (large excess) of freshly dried acetonitrile and 20 mls of dry toluene. 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 toluene and dried under vacuum. The unreacted decaborane was recovered by removal of the solvent from the filtrate.

ii) RESULTS

Weight of $(MeCN)_2\ B_{10}H_{12}$ obtained = 38 g

Therefore % yield = 86

Analysis

	C	H	B	N
% FOUND	22.8	8.4	52.9	13.7
$B_{10}H_{12}(MeCN)_2$ requires	23.7	8.9	53.4	13.8

Mass Spectrum

The mass spectrum showed a highest mass peak at $\frac{m}{e}$ 206 with an associated borane isotope pattern. This was attributed to bis (acetonitrile) decaborane. Below this was a group of peaks at $\frac{m}{e}$ 164 due to loss of an MeCN unit. Both of these groups of peaks had equivalent $\frac{m}{2e}$ peaks.

I.R.

The infra-red spectrum showed the following peaks:-
ν max 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 skeletal vibration (1020-998 cm^{-1}).

The spectrum does not show any $C\equiv N$ stretch from acetonitrile showing that the acetonitrile is bonded through the CN group.

3.1(d) PREPARATION OF 2-BUTYNE-1, 4-DIACETATE

i) EXPERIMENTAL

2-Butyne-1, 4-diacetate is not commercially available but it can be easily synthesised from 2-butyne-1, d-diol by the following route:-

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

ii) RESULTS

Melting point of white crystalline product = 30-31^{o}C
(Lit 30-31^{o}C (138))

Analysis

	C	H	O
% FOUND	56.4	5.9	-
$MeCOOCH_2C\equiv C\ CH_2OOCMe$ requires	56.5	5.9	37.6

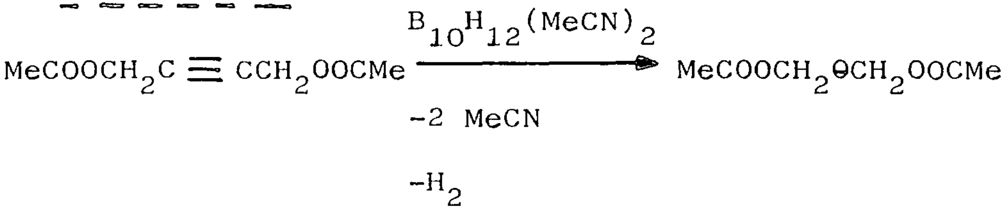
I.R.

The infra-red spectrum showed the following peaks:-
ν max, contact film (cm^{-1}) 3472(vw), 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(e) PREPARATION OF 1,2-BIS (ACETOXYMETHYL)-O-CARBORANE

I) EXPERIMENTAL



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

19.36 g (0.096 mole) of bis (acetonitrile)-decaborane was added to a solution of 16.26g (0.096 mole) of 2-butyne-1,4-diacetate in 100 mls of dry benzene and 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 100 mls of dry methanol to destroy any remaining bis (acetonitrile) decaborane. The volume was then reduced to 40 mls under vacuum and the solution cooled to -35°C to induce crystallization. The crystals were removed on a grade 4 sinter and the volume of the filtrate was reduced in order to induce further crystallization. The addition of 2-3 drops of distilled water to the viscous orange liquid resulted in further product crystallizing out of solution. Excessive addition of water resulted in the formation of a yellow/orange oil and further extraction of product from this oil proved to be difficult. The pale yellow crystalline solid was dried under vacuum for 2-3 hours.

ii) RESULTS

Yield = 65.6% (18.4g)

Melting point = 44-45°C [Lit 47-48°C (138)]

Analysis

	C	H	B	O
% FOUND	33.1	7.3	37.2	-
$(MeCOOCH_2)_2\Theta$ requires	33.3	6.9	37.5	22.2

Mass Spectrum

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

I.R.

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(f) PREPARATION OF ORTHO CARBORANE FROM 1,2-BIS (ACETOXY METHYL) 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 mmoles) was stirred with 300 mls of 20% aqueous potassium hydroxide until the immiscible layer had disappeared leaving a clear pale yellow solution (5-10 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. Keeping the temperature at 0°-5°C, about 35g of potassium metabisulphite was added, immediately followed by ice-cold 35% aqueous sulphuric acid. Addition of the sulphuric acid caused a large amount of effervescence on top of which the crude off-white 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 hexane for several days, the solvent removed under vacuum and the ortho-carborane residue further purified by sublimation at 45°C and 0.01 mm Hg.

ii) RESULTS

Yield = 42.7% (with respect to $B_{10}H_{14}$)
Melting point of pure o-carborane = 297°C (sealed tube)
/Lit. 287-288°C (28); 320°C (138)/

Analysis

	C	H	B
% FOUND	16.5	8.6	74.7
$C_2B_{10}H_{12}$ requires	16.6	8.3	75.0

Mass Spectrum

The mass spectrum of the product showed a high mass group of peaks with a carboranyl isotope pattern with the highest mass peak at $\frac{m}{e}$ 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 $\frac{m}{e}$ 66-73 due to $\frac{m}{2e}$ (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}).

2.1(g) DISCUSSION

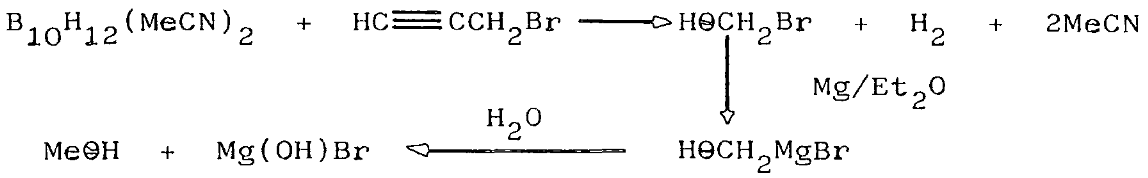
Although the method described above for the preparation of o-carborane is essentially that used by Kutal et al (138) attempts have been made to modify and in some ways simplify this method.

The use of a large excess of acetonitrile, rather than the stoichiometric amounts used by Kutal, in the preparation of bis-(acetonitrile) decaborane was found to increase the yields by 5-10%. 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 thereby saving valuable starting material.

In order to obtain yields similar to those in the literature (138), a large excess of 20% KOH (i.e. above that already used in the literature method) was required to ensure that conversion of the bis-(acetoxymethyl)- to the bis (hydroxymethyl)-o-carborane was complete. Yields were found to be greatly reduced (10-15% below the literature value) if this conversion was incomplete. It was also found that the $KMnO_4$ oxidation of the bis-(hydroxymethyl) derivative to the carborane itself was complicated by the presence of small amounts of bis (acetoxymethyl)-o-carborane.

2.2 PREPARATION OF 1-METHYL-O-CARBORANE

1-Methyl-o-carborane was prepared by the method used by Hawthorne et al. (8)



$$\begin{tikzcd} B_{10}H_{12}(MeCN)_2 + HC\equiv CCH_2Br \arrow[r] & H\Theta CH_2Br + H_2 + 2MeCN \arrow[d, "Mg/Et_2O"] \\ MeΘH + Mg(OH)Br & H\Theta CH_2MgBr \arrow[l, "H_2O"'] \end{tikzcd}$$

i) RESULTS

Yield = 92% (Lit. 93%)
Melting point = 212°C (Lit. 211-213°C)

Analysis

	C	H	B
% FOUND	22.6	8.8	67.9
1-Methyl-o-carborane requires	22.7	8.8	68.3

Mass Spectrum

The mass spectrum showed an M+1 peak at $\frac{m}{e}$ 161 where M = $^{12}C_3\,^{11}B_{10}\,^{1}H_{14}$ with a corresponding carborane isotope pattern from $\frac{m}{e}$ 147-160. A group of half-mass peaks at $\frac{m}{e}$ 73.5-80 ($\frac{m}{2e}$ 147-160) could also be observed.

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}); δas CH_3 (1445 cm^{-1}); δs CH_3 (1391 cm^{-1}); Cage vibration (720 cm^{-1}).

ii) DISCUSSION

Very high yields of pure 1-methyl-o-carborane were obtained by Hawthorne's method and consequently no improvements were found to be necessary.

2.3 PREPARATION OF 1-PHENYL-O-CARBORANE

1-Phenyl-o-carborane was prepared by the method used by Stanko et al. (141)

$$B_{10}H_{12}(MeCN)_2 \quad + \quad PhC \equiv CH \xrightarrow[80^{o}C]{TOLUENE} Ph\Theta H \quad + \quad H_2 \quad + \quad 2MeCN$$

i) RESULTS

Yield = 50% (lit. 65%)

Melting point = 68-70°C (Lit. 69-70°C)

Analysis

	C	H	B
% FOUND	43.7	8.0	48.9
PhΘH requires	43.6	7.3	49.1

Mass Spectrum

The mass spectrum showed a highest mass peak at $\frac{m}{e}$ 222 corresponding to $^{12}C_8\ ^{11}B_{10}\ ^{1}H_{16}$, accompanied by the characteristic carborane isotope pattern from $\frac{m}{e}$ 212-222. A group of half-mass peaks at $\frac{m}{e}$ 106-111 ($\frac{m}{2e}$ 212-222) were also observed.

I.R.

The infra-red spectrum showed the following peaks:-
νmax, Nujol mull (cm^{-1}) 3060(s), 2920(s), 2850(s),
2620-2540(s), 1581(w), 1490(m), 1458(sh), 1447(s),
1374, 1337, 1314, 1276, 1260,
1193, 1160, 1120, 1104, 1070(s),
1037, 1020, 1004(s), 933, 918,
873(m), 860(sh), 799(m), 753(s), 732(s),
725, 688(s), 663, 598, 560,
484.

The following vibrations could be assigned:- Carboranyl C-H stretch (3060 cm^{-1}); B-H stretch (2620-2540 cm^{-1}); Cage vibrations (753-725 cm^{-1}).

2.4 ISOMERIZATION OF O-CARBORANE (1,2-$C_2B_{10}H_{12}$) TO M-CARBORANE (1,7-$C_2B_{10}H_{12}$) (9)

The conversion of ortho to meta-carborane (9) in 2-3g batches was achieved in a 165 ml stainless steel autoclave by heating to 470 ± 3°C, under 1 atmosphere of argon, for 24-48 hours. Sublimation of the crude product resulted in white chromatographically and spectrally pure meta-carborane.

i) RESULTS

Yield = 75% (Lit. 80%)

Melting point = 262-265°C (Lit. 263-265°C)

Analysis

	C	H	B
% FOUND	16.6	8.3	75.0
m-Carborane requires	16.6	8.3	75.0

Mass Spectrum

The mass spectrum showed high mass group of peaks with associated carboranyl isotope pattern, with the highest mass peak at $\frac{m}{e}$ 146 attributable to $^{12}C_2{}^{11}B_{10}{}^{1}H_{12}$. A group of half-mass peaks at $\frac{m}{e}$ 66-74 ($\frac{m}{2e}$ 132-148) were also observed.

I.R.

The infra-red spectrum showed the following peaks:-
ν max, Nujol mull (cm^{-1}) 3060(s), 2920(s), 2855(s), 2598(s), 1452, 1373, 1158(s), 1070(s), 1022, 990, 719(s).

The following vibrations could be assigned:- Carboranyl C-H stretch (3060 cm^{-1}); B-H stretch (2598 (cm^{-1})); Cage vibrations (719 cm^{-1}).

CHAPTER 3

SOME METAL DERIVATIVES OF ICOSAHEDRAL CARBORANES CONTAINING METAL-CARBON σ BONDS

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SOME METAL DERIVATIVES OF ICOSAHEDRAL CARBORANES CONTAINING METAL-CARBON σ BONDS

3.1 INTRODUCTION

Although there is a wealth of structural information available on polyhedral boranes, carboranes and their metalla derivatives (2, 142-144), no carborane with a main group I or II metal atom covalently bonded in an exo position appears to have been structurally characterised, despite the extensive use of such substances as intermediates in the synthesis of other carboranyl derivatives (145). During the course of the present study two compounds, the pentamethyldiethylenetriamine (PMDETA) adduct of 1-lithio-2-methyl-1, 2-dicarba-closo-dodecaborane, $Li(C_2B_{10}H_{10}Me)$ (PMDETA), and the bis (1,4 dioxan) adduct of magnesium bis (2-methyl-1, 2-dicarba-closo-dodecaborane), $Mg(C_2B_{10}H_{10}Me)_2(C_4H_8O_2)_2 \cdot C_7H_8$, have been prepared and structurally characterised. The crystallographic studies were performed by Dr. W. Clegg (Göttingen University); at the time of writing preliminary results only are available on the magnesium derivative. In describing the two characterised compounds features of their structures are compared with related features of other organolithium and organomagnesium compounds, while the structural data are used to calculate the cone angles and steric requirements of icosahedral carboranyl, and methyl-carboranyl, ligands attached to metal atoms of various sizes.

3.2(a) PREPARATION OF 1-LITHIO-2-METHYL-1, 2-DICARBA-CLOSO-DODECABORANE, $LiC_2B_{10}H_{10}Me$

i) EXPERIMENTAL

A solution of n-butyl lithium (10 mmole) in hexane was added to a solution of 1-methyl-o-carborane, (1.58 g, 10 mmole) in 15 ml of dry toluene. The mixture was stirred at room temperature for three hours during which time the lithio-carborane precipitated from solution. The solvent volume was reduced by pumping, the remaining solution filtered, and the solid material washed with 5 ml of cold dry pentane. The resultant white solid was identified as 1-lithio-2-methyl-1,2-dicarba-closo-dodecaborane.

ii) RESULTS

Analysis

	C	H	B	Li
% FOUND	20.5	9.2	-	4.5
$LiC_2B_{10}H_{10}Me$ requires	21.9	8.0	65.9	4.2

I.R.

The infra-red spectrum showed the following peaks:-
νmax, (Nujol mull) (cm^{-1}) 2580(s), 1253(w), 1225(w),
1130(w), 1093(m), 1080(w,sh), 1032(m), 1016(m),
994(m), 872(w), 834(w), 815(w), 786(m),
767(w), 723(s), 652(w), 492(w).

The following vibrations can be assigned:- B-H stretch (2580 cm^{-1}); Cage vibrations (723 cm^{-1}). No carboranyl C-H was observed as expected. However on exposure to air peaks at 3600 cm^{-1} and 3070 cm^{-1} appeared due to LiOH and the carboranyl C-H stretch respectively.

Attempts to recrystallize the compound failed, decomposition usually resulting.

3.2(b) PREPARATION OF 1-(PMDETA) LITHIO-2-METHYL-1,2-DICARBA-CLOSO-DODECABORANE

i) EXPERIMENTAL

A solution of n-butyl lithium (10 mmole) in hexane was added to a solution of 1-methyl-o-carborane (1.58 g, 10 mmole) in 30 ml of dry toluene. The mixture was stirred at room temperature for three hours during which time the lithiated carborane, 1-Li-2-Me$C_2B_{10}H_{10}$, precipitated from solution. Pentamethyldiethylenetriamine, PMDETA, (1.73 g, 10 mmole), was added, the solution warmed to dissolve the remaining precipitate, filtered and the filtrate placed in a freezer maintained at -30°C. Crystals were deposited which were filtered, washed with a small amount of cold pentane, and pumped dry. Recrystallization from dry toluene afforded colourless crystals identified as 1-(PMDETA) lithio-2-methyl-1,2-dicarba-closo-dodecaborane.

ii) RESULTS

Melting point = 195-197°C

Analysis

	C	H	N	B	Li
% FOUND	42.5	10.2	12.1	-	2.0
$Li(C_2B_{10}H_{10}Me)$ (PMDETA) requires	42.7	10.8	12.5	31.9	2.1

I.R.

The infra-red spectrum showed the following peaks:- ν max, Nujol mull, (cm^{-1}) 2595(m,sh), 2580(s), 2550(m,sh), 2512(m,sh), 1358(m), 1318(w), 1297(m,sh), 1289(m), 1252(w), 1172(w), 1158(w), 1119(w), 1102(w), 1060(m), 1041(s), 1024(m), 992(w), 947(m,sh), 943(s), 937(m,sh), 905(w), 799(m), 783(m), 770(w), 758(w), 737(m), 730(m,sh), 695(w), 671(w), 660(w), 603(m), 577(w), 548(w), 508(w).

The compound was very air and moisture-sensitive, decomposing immediately upon exposure to air.

Mass Spectrum

Attempts to record its mass spectrum afforded evidence of the ligand PMDETA ($\frac{m}{e}$ 173) and fragments thereof, and of the carboranyl residue $C_2B_{10}H_{10}Me$ at $\frac{m}{e}$ 161 with a corresponding carborane isotope pattern from $\frac{m}{e}$ 147-160 and fragments thereof.

3.2(c) ADDITION OF PENTAMETHYLDIETHYLENETRIAMINE TO 1-LITHIO-2-PHENYL-1,2-DICARBA-CLOSO-DODECABORANE

i) EXPERIMENTAL

Phenyl-o-carborane (1.91 g, 8.57 mmole) was dissolved in 40 ml of dry toluene and to this was added, 4.44 ml (8.57 mmole) of a 1.63M n-butyl lithium solution in hexane. The resultant solution was refluxed for one hour during which time a precipitate formed. The slurry was cooled and the PMDETA (1.6 g, 8.57 mmole) was added, the solution was refluxed for three to four hours during which time the precipitate dissolved leaving a red/brown clear solution. The solution was filtered and the volume reduced under vacuum. The solution was placed in a freezer maintained at -30°C. Crystals were deposited, which were filtered, washed with a small amount of cold pentane and pumped dry. Recrystallization from toluene afforded off-white crystals identified as 1-(PMDETA)-lithio-2-phenyl-1,2-dicarba-closo-dodecaborane.

ii) RESULTS

Melting Point = The crystals appeared to decompose between 150°-160°C and had totally melted at 175°C.

Analysis

	C	H	N	B	Li
% FOUND	49.8	9.2	10.6	-	1.8
$Li(C_2B_{10}H_{10}Ph)$ (PMDETA) requires	51.1	9.5	10.5	27.0	1.9

I.R.

The infra-red spectrum showed the following peaks:-

ν max, Nujol mull, (cm^{-1}) 2598(sh), 2550(s), 2350(sh),

1580(m), 1440(s), 1373(m), 1360(m), 1350(m), 1300(s),
1282(s), 1245(m), 1210(w), 1180(sh), 1173(sh), 1169(s),
1158(w), 1151(s), 1127(w), 1105(s), 1075(sh), 1070(s),
1059(s), 1031(s), 1015(s), 1005(m), 989(s), 970(sh),
940(sh), 933(s), 899(s), 880(w), 875(sh), 840(m),
805(s), 789(s), 763(s), 757(s), 730(m), 694(s),
660(m), 620(w), 597(s), 565(m), 495(s), 465(sh),
448(sh), 430(m), 418(m).

The compound was air and moisture-sensitive, decomposing immediately upon exposure to air.

Mass Spectrum

Attempts to record its mass spectrum afforded evidence of the ligand PMDETA ($\frac{m}{e}$ 173) and fragments thereof, and of the carboranyl residue $C_2B_{10}H_{10}Ph$ at $\frac{m}{e}$ 220 with a corresponding carborane isotope pattern, and fragments thereof.

3.3(a) PREPARATION OF 1-BROMO-2-METHYL-1,2-DICARBA-CLOSO-DODECABORANE (146)

$$Me\Theta Li \quad + \quad Br_2 \xrightarrow{Et_2O} Me\Theta Br \quad + \quad LiBr$$

i) EXPERIMENTAL

A diethyl ether/hexane solution of 1-lithio-2-methyl-o-carborane was slowly added to a stirred solution of bromine in ether at 0°C. The resulting solution was heated for one hour after which time the solution was shaken with dilute aqueous sodium thiosulphate, to remove any excess bromine, the ether layer separated and dried over anhydrous magnesium sulphate. Filtration and removal of the ether by pumping yielded a white solid which was purified by sublimation (80°C, 0.004 mm Hg) and identified as 1-Bromo-2-methyl-o-carborane.

ii) RESULTS

Yield = 85%

Melting Point = 220-222°C (Lit 220-221°C)

Analysis

	C	H	B	Br
% FOUND	15.3	5.7	45.5	34.1
MeΘBr requires	15.2	5.5	45.6	33.7

I.R.

The infra-red spectrum showed the following peaks:-

ν max, Nujol mull (cm^{-1}) 2568(s,br), 1263(s), 1190(w), 1155(w), 1100(m,br), 1040(m), 1020(m,br), 990(m), 940-930(m,br), 921(w), 905(w), 875(s), 855(m), 795(s), 775(w), 730(s), 673(w), 658(w).

The following variations could be assigned:- B-H stretch (2568 cm^{-1}); C-B-C vibrations (1263 cm^{-1}); Cage C-Br stretch (795 cm^{-1}); Cage vibrations (730 cm^{-1}). No carboranyl C-H stretch was observed as expected.

Mass Spectrum

The mass spectrum showed a number of carboranyl isotope patterns and these were identified as:-

$\frac{m}{e}$ 230-237 ($Me\Theta^{+}Br$); $\frac{m}{e}$ 151-157 ($Me\Theta^{+}$);

$\frac{m}{e}$ 135-146 (Θ^{+}); $\frac{m}{e}$ 116-120 ($\frac{m}{2e}$ 232-240, $Me\Theta^{2+}Br$)

3.3(b) PREPARATION OF BIS (DIOXAN) MAGNESIUM - BIS (2-METHYL-1,2-DICARBA-CLOSO-DODECABORANE)

$$2Me\Theta Br \xrightarrow{Mg/Et_2O} 2Me\Theta MgBr \xrightarrow[\text{TOLUENE}]{\text{Dioxan}} (Me\Theta)_2\ Mg\ (DIOXAN)_2$$

$$+\ MgBr_2(DIOXAN)_2$$

i) EXPERIMENTAL

A solution of 1-bromo-2-methyl-o-carborane (1.81 g, 7.63 mmol.) in 20 ml of dry diethyl ether was slowly added to magnesium turnings (0.35 g, 10.29 mmol.) in 10 ml of refluxing diethyl ether. A small crystal of iodine was added to initiate the Grignard reaction. At the end of the addition the reaction was refluxed for a further period of three hours and then filtered to remove unreacted magnesium. 1,4-Dioxan (5 ml) was then added to the clear solution which resulted in the precipitation of a white solid. After stirring overnight the solvent was removed by pumping, the resulting solid, extracted with 15 ml of hot dry toluene, and filtered to yield a colourless solution which deposited colourless crystals upon cooling. The crystals were identified as bis (1,4 dioxan) magnesium bis (2-methyl-1,2 dicarba-closo-dodecaborane), $Mg(C_2B_{10}H_{10}Me)_2(C_4H_8O_2)_2 \cdot C_7H_8$.

ii) RESULTS

Melting point = 180-185°C (Decomposed)

Analysis

	C	H	B	Mg
% FOUND	40.0	10.3	33.2	3.8
$C_{21}H_{50}B_{20}MgO_4$ requires	41.5	8.3	35.6	4.0

I.R.

The infra-red spectrum showed the following peaks:- ν max (Nujol mull), cm^{-1} 2565(s,br), 1299(m), 1264(m), 1223(w), 1131(s), 1096(w), 1047(s), 1017(w,sh), 972(w), 937(w,br), 895(m), 878(s), 846(w), 823(m), 793(w), 773(w), 763(s), 697(w), 670(w), 654(w), 621(m), 573(w), 503(w), 467(w), 458(w).

The compound was extremely air and moisture-sensitive.

Mass Spectrum

The mass spectrum showed evidence of peaks due to the fragmentation of dioxan as well as the characteristic isotope peak pattern of $MeC_2B_{10}H_{10}$ (high mass $\frac{m}{e}$ 159).

3.4(a) THE CRYSTAL STRUCTURE OF THE PENTAMETHYLDIETHYLENETRIAMINE ADDUCT OF 1-LITHIO-2-METHYL-1,2-DICARBA-CLOSO-DODECABORANE: $Li(C_2B_{10}H_{10}Me)(MeN(CH_2CH_2NMe_2)_2)$

A characteristic of organolithium chemistry is the multicentre bonding normally found between the ligand carbon and metal atoms. (142,147,148) Lithium alkyls, such as the tetrahedral tetrameric $(LiMe)_4$ or the chair-shaped hexameric $(Li\text{-cyclohexyl})_6$ have strongly associated structures which persist even in solution in donor solvents, being held together by four centre two electron bonds. (149,150) The presence of a chelating mono-, di-or tridentate base can reduce the number of ligand carbon atoms to which each lithium atom bonds. Thus, phenyl lithium, for example, crystallizes in the presence of tetramethyl-ethylenediamine (TMDEDA) as the dimer $(LiPhTMEDA)_2$, held together by three-centre Li...C...Li bonds. (151) The degree of association can be reduced or indeed prevented by use of sterically bulky organic ligands and it is significant that one of the only two organolithium compounds known prior to the present study to have unassociated structures, $(PMDETA)LiCH(SiMe_3)_2$ (152), contains the very bulky ligand $CH(SiMe_3)_2$ (see Figure 3.4.1(a)). The Li-C bond in this compound was described in terms of a two-centre two-electron covalent interaction due to the similarity in its length (2.13(5)Å) to that of the associated organolithium compound 2-lithio-2-methyldithiane (153) (see Figure 3.4.1(b)) where the Li-C bond, of length 2.186(5)Å was shown to be essentially covalent by electron density plots.

The only other organolithium compound known to be unassociated, 2-lithio-2-phenyldithiane (see Figure 3.4.1 (c)) (153), which has a longer Li-C bond (2.280(5)Å was shown to have considerably more ionic character, again on the basis of an electron density plot.

The compound described in the present study, Li($C_2B_{10}H_{10}$Me) (PMDETA) (see Figure 3.4.1(d)), was synthesized in the expectation (now realised) that for a combination of electronic and steric reasons it would have a monomeric structure, so providing an unprecedented example of lithium terminally attached to a six-coordinate carbon atom. The compound is, additionally, the first structurally characterised example of a carboranyl unit bonded exo-skeletally to a Group I metal.

The results of the crystallographic study are illustrated in Figure 3.4.2 while selected bond lengths and angles are given in Table 3.4.1. Crystals of Li($C_2B_{10}H_{10}$Me) (PMDETA) are monoclinic, space group P21/M, with a = 8.242(1), b = 13.522(1), c = 10.799(1)Å, B = 108.75(1)°, Z = 2. A plane of symmetry passes through the atoms C(1), N(1), Li, C(6), C(7) and C(8) of the molecule, (see Figure 3.4.2). The four coordinate lithium atom is terminally attached to the six-coordinate carbon atom of the carborane cage by a bond of length 2.176(8)Å which is similar to those of 2.186(5)Å, in 2-lithio-2-methyldithiane (153) (see Figure 3.4.1(b)) and 2.13(5)Å, in (PMDETA) Li-CH($SiMe_3)_2$, (152) (see Figure 3.4.1(a)), though somewhat shorter than that of 2.280(5)Å, in 2-lithio-2-phenyldithiane (153) (see Figure 3.4.1(c)).

In view of the higher coordination number of the carbon atom in Li($C_2B_{10}H_{10}$Me) (PMDETA), the Li-C bond length might have been expected to be somewhat longer, although the sp hybridisation commonly assumed for the skeletal atoms of icosahedral carboranes would require a relatively short exo bond. In unsolvated $(MeLi)_4$ the fractional order Li-C bond (2.36Å) (149) is longer as might be expected, than the

Figure 3.4.1

Compounds containing two-centre carbon-lithium bonds.

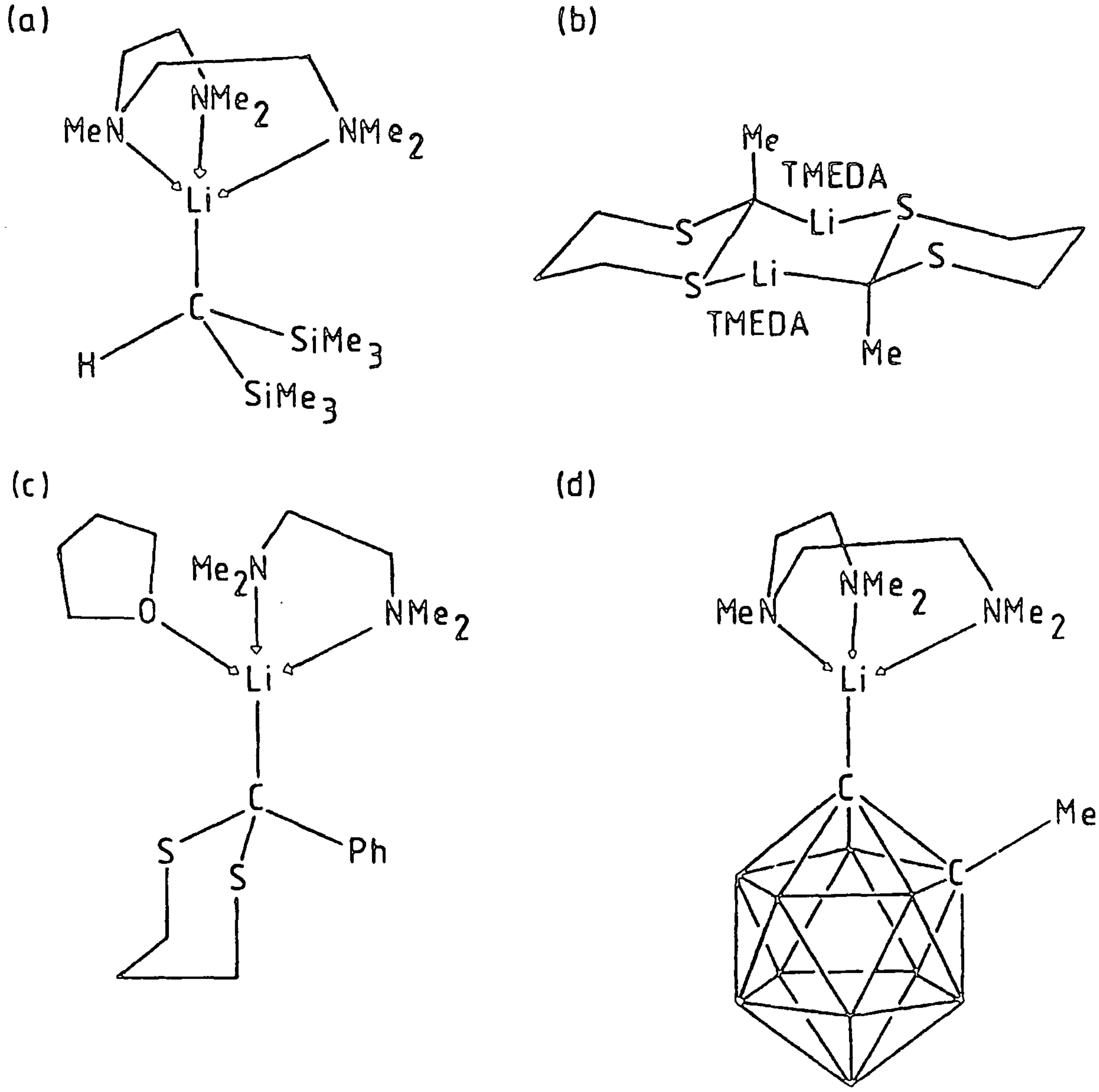


Table 3.4.1

Selected bond lengths (Å) and angles (°) for $Li(C_2B_{10}H_{10}Me)(PMDETA)$

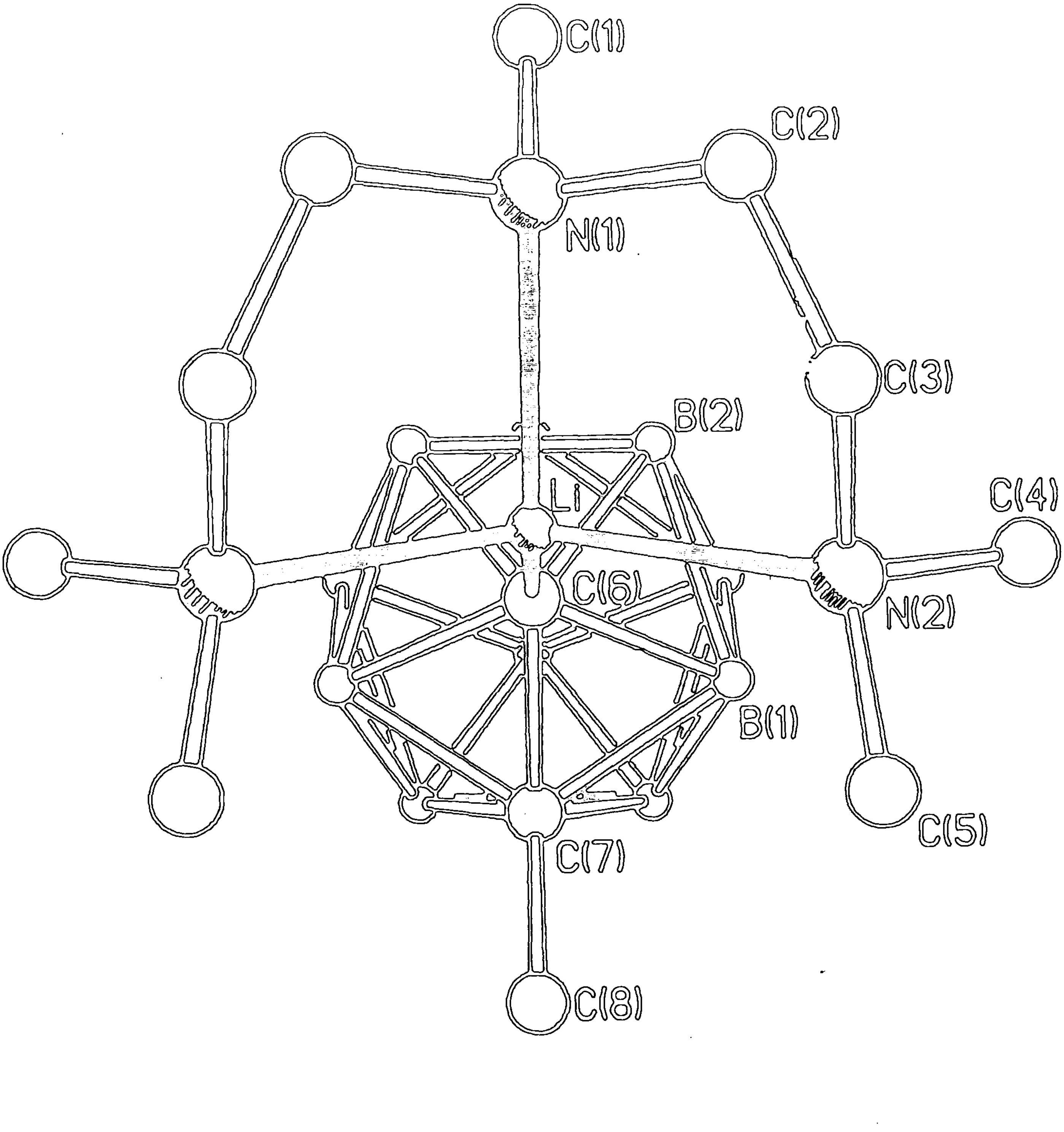
Li - N(1)	2.134(9)	Li - N(2)	2.169(5)
Li - C(6)	2.176(8)	N(1) - C(1)	1.454(10)
N(1) - C(2)	1.435(7)	C(2) - C(3)	1.434(11)
C(3) - N(2)	1.452(7)	N(2) - C(4)	1.412(6)
N(2) - C(5)	1.436(10)	C(6) - C(7)	1.681(7)
C(6) - B(1)	1.707(6)	C(6) - B(2)	1.709(8)
C(7) - C(8)	1.516(11)	C(7) - B(1)	1.653(7)

N(1)-Li-N(2)	85.6(2)	N(1)-Li-C(6)	124.1(5)
N(2)-Li-C(6)	119.1(2)	N(2)-Li-N(2)	114.4(4)
Li-N(1)-C(1)	115.2(4)	Li-N(1)-C(2)	104.9(3)
C(1)-N(1)-C(2)	109.9(4)	C(2)-N(1)-C(2)	111.9(5)
N(1)-C(2)-C(3)	117.0(5)	C(2)-C(3)-N(2)	117.2(5)
Li-N(2)-C(3)	100.9(4)	Li-N(2)-C(4)	111.5(3)
C(3)-N(2)-C(4)	111.8(5)	Li-N(2)-C(5)	118.0(4)
C(3)-N(2)-C(5)	105.2(5)	C(4)-N(2)-C(5)	109.1(5)
Li-C(6)-C(7)	129.3(5)	Li-C(6)-B(1)	122.2(4)
Li-C(6)-B(2)	118.0(3)	C(6)-C(7)-C(8)	115.7(4)

Figure 3.4.2

Molecular structure of Li($C_2B_{10}H_{10}$Me)(PMDETA)

(hydrogen atoms omitted)



terminal Li-C bonds. However the terminal Li-C bonds are actually longer than some of the bonds formally of order $\leqslant 1$ in other associated lithium alkyls or aryls, where bond lengths in the range 2.11 to 2.47Å have been reported (148). The correlation between bond length and bond order in the organo-lithium derivatives is thus less clear cut and indeed these bonds must be regarded as being at, or beyond, the limit of what can be looked upon as a covalent interaction. (147,154-156)

The features of the coordination of the tridentate PMDETA ligand to the lithium atom are unexceptional; the $N\hat{Li}N$ bond angles reflect the characteristic "bite" of the tridentate ligand and the Li-N bonds are of normal length (ca. 2.15Å). The orientation of the ligand is such that its plane of symmetry coincides with that of the carboranyl residue, minimising steric interactions with the carboranyl-carbon-bonded methyl group. The <u>exo</u> bonds, between C(6) and Li, and between C(7) and C(8), both show slight deviations from their expected orientations as if both <u>exo</u>-bonded substituents were shifted parallel to the C(6)-C(7) axis in the same direction. Rather than the two mutually-repellent groups moving in opposite directions as might have been expected, this has the effect of bringing the methyl group attached to C(7) slightly nearer C(6).

From the structural data obtained on (PMDETA) $Li(C_2B_{10}H_{10}Me)$ it is possible to calculate the effective cone angle subtended by the 2-methyl-o-carboranyl group at a metal atom such as lithium. The concept of cone angles, first introduced by Tolman (157) to facilitate the discussion of steric effects in crowded transition - metal coordination complexes, is particularly helpful in assessing how many bulky, pseudo-spherical, ligands such as icosahedral carboranyl groups can be attached to a particular metal atom.

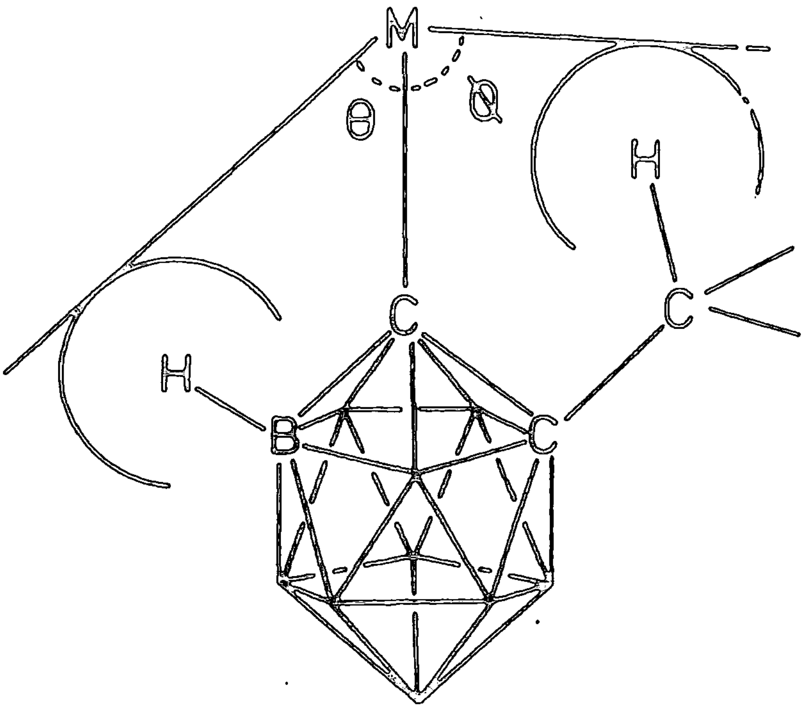
The approximate cone angles were determined, as outlined in Figure 3.4.3, by summing the calculated angles,

Table 3.4.2 Cone angles for the ligands (a) $C_2B_{10}H_{11}$, (b) C_6H_5, (c) 2-Me-1,2-$C_2B_{10}H_{10}$ (d) 2-Me-C_6H_4 as a function of the metal-carbon distance

M-C distance (Å)		1.60	1.95	2.18	2.45
Cone angle (°)	(a)	154	140	132	120
	(b)	153	138	130	120
	(c)	169	158	149	138
	(d)	183	169	159	148

FIGURE 3.4.3

Cone angle for the carboranyl ligand 2-Me-1,2-$C_2B_{10}H_{10}$



θ and ϕ, between the *exo* C-M bond and the surface of the nearest hydrogen atoms. These were either of a C-H or B-H group or of a C-Me group in the *ortho* position relative to the metallated carbon atom. A hydrogen Van der Waals radius of 1.2Å was assumed. Table 3.4.2 lists the cone angles for (a) unsubstituted carboranyl units $C_2B_{10}H_{11}$, (C) 2-methyl-o-carboranyl ligands $MeC_2B_{10}H_{10}$ and for comparison the cone angles for (b) phenyl and (d) ortho-tolyl groups, for a representative range of metal-carbon bond lengths. The cone angles for *ortho*-tolyl, when calculated in the plane of the aromatic ring are seen to be slightly greater than those of 2-methyl-o-carboranyl ligand.

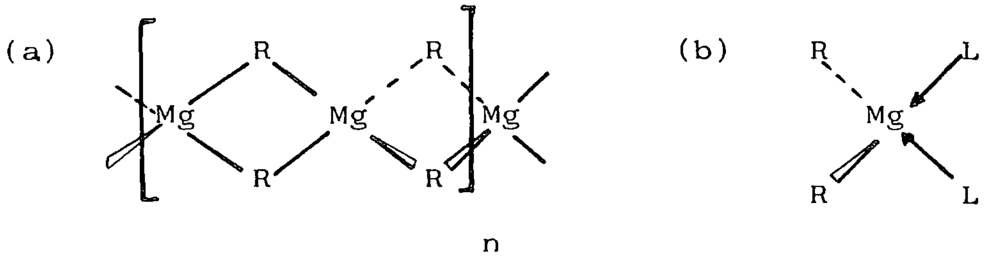
The results from the cone angle calculations showed that it would be sterically possible for uncoordinated 1-lithio-2-methyl-o-carborane to adopt a dimeric structure $(LiC_2B_{10}H_{10}Me)_2$, in which the carboranyl groups, like the phenyl groups of $(LiPh\ TMEDA)_2$ (151) perform a bridging role between the metal atoms. Such a conformation would seem unlikely on electronic grounds since the capacity of the carbon atoms to participate in multicentre bonding outside the cage would probably be reduced by the electron-withdrawing character of the carborane group. A further implication of the data in Table 3.4.2 is that it is not realistic to expect more than two $C_2B_{10}H_{11}$ units, let alone ortho-methylated carboranyl units, to be linked to a single boron, carbon or nitrogen atom, where an *exo* bond length of ca.1.52 to 1.62Å would be expected. Three $C_2B_{10}H_{11}$ icosahedra might just be accommodated on a larger second-row element such as aluminium, silicon or phosphorus but it would be unrealistic to expect three ortho-methylated carboranyl units to do likewise.

3.4(b) THE X-RAY CRYSTAL STRUCTURE OF THE BIS (1,4 DIOXAN) ADDUCT OF MAGNESIUM BIS (2-METHYL-1, 2-DICARBA-CLOSO-DODECABORANE): $Mg(C_2B_{10}H_{10}Me)_2(O_2C_4H_8)_2.C_7H_8$

Dialkyl magnesium compounds, MgR_2 (R = Me, Et) (158, 159) have been shown by X-ray determination to be linear polymeric molecules with symmetrically bridging alkyl groups (see Figure 3.4.4). The bonding may be formalised in terms of electron-deficient three-centre two-electron covalent (but polar) links, each metal having an approximately tetrahedral coordination of four ligands.

Figure 3.4.4

STRUCTURES OF THE POLYMERIC DIALKYLMAGNESIUM COMPOUNDS $(MgR_2)_n$ AND MONOMERIC ADDUCT DERIVATIVES MgR_2L_2



It has also been shown by X-ray determination that the adducts $MgR_2(L_2)$ (R = Me, L = quinuclidine (160) or L_2 = TMEDA (161); R = Ph, L_2 = TMEDA (162)) have monomeric structures (see Figure 3.4.4(b)) with distorted tetrahedral geometry around magnesium while the metal-carbon bonding may be described in terms of two-centre two-electron covalent interactions. The Mg-C bond lengths in these compounds (ca. 2.16Å), while being somewhat shorter than the formally half-order Mg-C bonds in the polymeric dialkyl magnesiums $(MgMe_2)_n$ and $(MgEt_2)_n$, which have lengths of 2.24Å and 2.26Å respectively (158, 159), are similar to those of some ether-coordinated alkyl- and aryl-, magnesium halides, $RMgX(L_2)$ (163), which possess similar two-centre linkages.

The compound described in the present study, Mg $(C_2B_{10}H_{10}Me)_2$. $(O_2C_4H_8)_2$. C_7H_8, is a further example of a monomeric ether-adduct species. The compound contains a unique example of magnesium bonded to a six-coordinate carbon atom by means of a two-centre two-electron bond, and is the first structurally characterised example of an <u>exo</u>-bonded group II carboranyl derivative. The compound was synthesised by the addition of 1,4 dioxan to a diethyl ether solution of the corresponding carboranylmagnesium bromide, this being a well established route to ether-coordinated diorganylmagnesium compounds. (163)

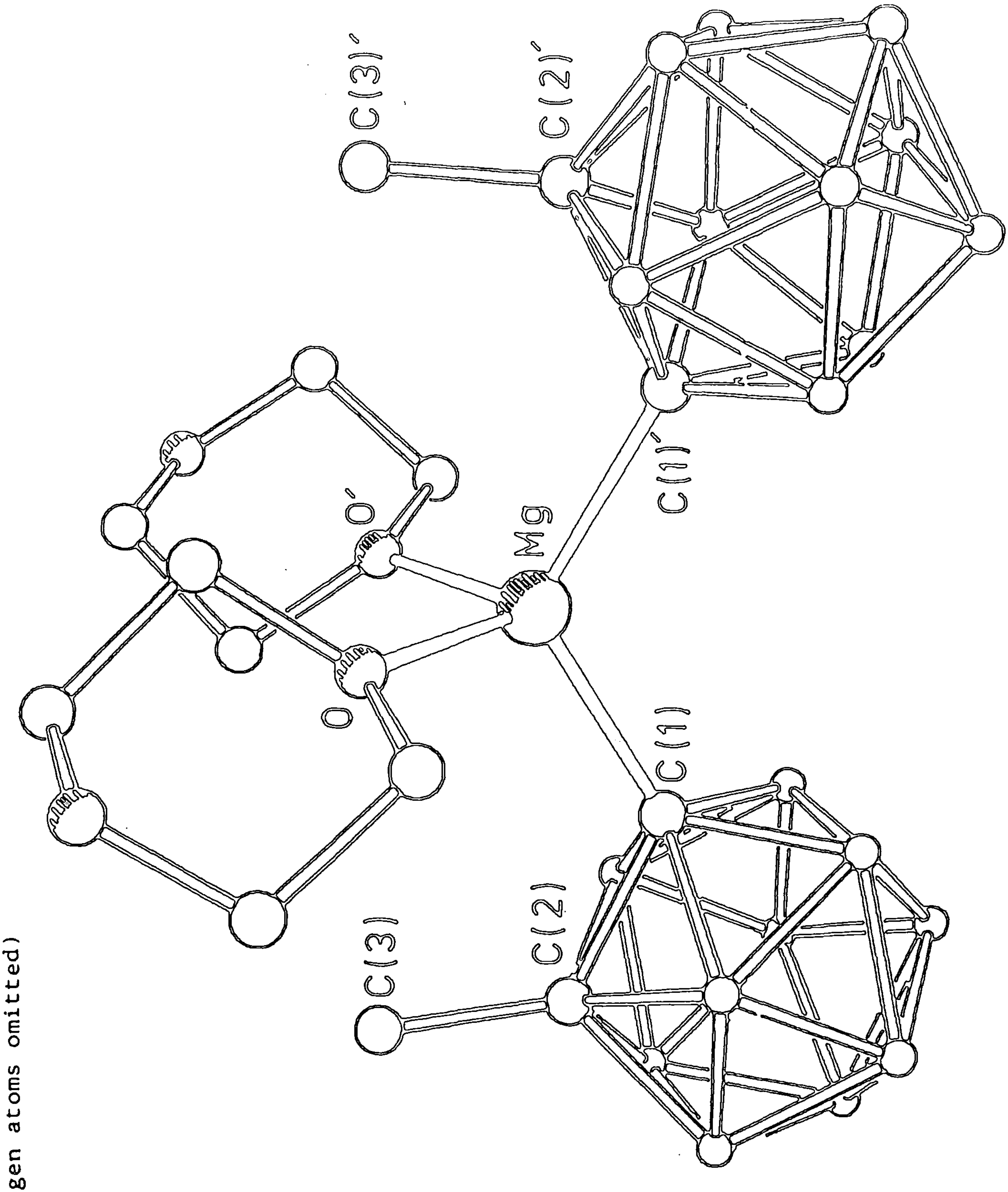
$$2MeC_2B_{10}H_{10}MgBr \quad + \quad 4\ C_4H_8O_2 \longrightarrow (MeC_2B_{10}H_{10})_2Mg(C_4H_8O_2)_2$$

$$+ \quad MgBr_2\ (C_4H_8O_2)_2$$

The $MgBr_2$ $(C_4H_8O_2)_2$ can be separated from the carboranylmagnesium compound by removing the ether solvent, in which both are soluble, and extracting with hot toluene, in which the $MgBr_2$ $(C_4H_8O_2)_2$ is totally insoluble.

The preliminary results of an X-ray crystallographic study on $Mg(C_2B_{10}H_{10}Me)_2(C_4H_8O_2)_2$. C_7H_8 are presented in Figures 3.4.5 and 3.4.6 and in Table 3.4.3. The crystal lattice contains one molecule of toluene per magnesium unit as can be seen on Figure 3.4.6. The unit $Mg(C_2B_{10}H_{10}Me)_2$ $(C_4H_8O_2)_2$ contains a two-fold axis of symmetry passing through the magnesium atom (see Figure 3.4.5), while the geometry around magnesium is very similar to that in the bis- (carboranyl) dimethyl germanium compound $(C_2B_{10}H_{11})_2$ ~~Ge-Me~~$_2$ (164). The four /(coordinate magnesium atom is terminally attached to the six-coordinate carbon atom of the carborane cage by a bond of length 2.16(2)Å which is essentially identical to those of 2.167Å, in $Ph_2Mg(TMEDA)$, and 2.166Å, in $Me_2Mg(TMEDA)$ and is also similar to that of ca. 2.2Å, in $PhMgBr(OEt_2)_2$, (163) confirming the bonding to be of a similar covalent nature.

Figure 3.4.5



(hydrogen atoms omitted)

Figure 3.4.6 Crystal lattice structure of $Mg(C_2B_{10}H_{10}Me)_2(C_4H_8O_2)_2 \cdot C_7H_8$

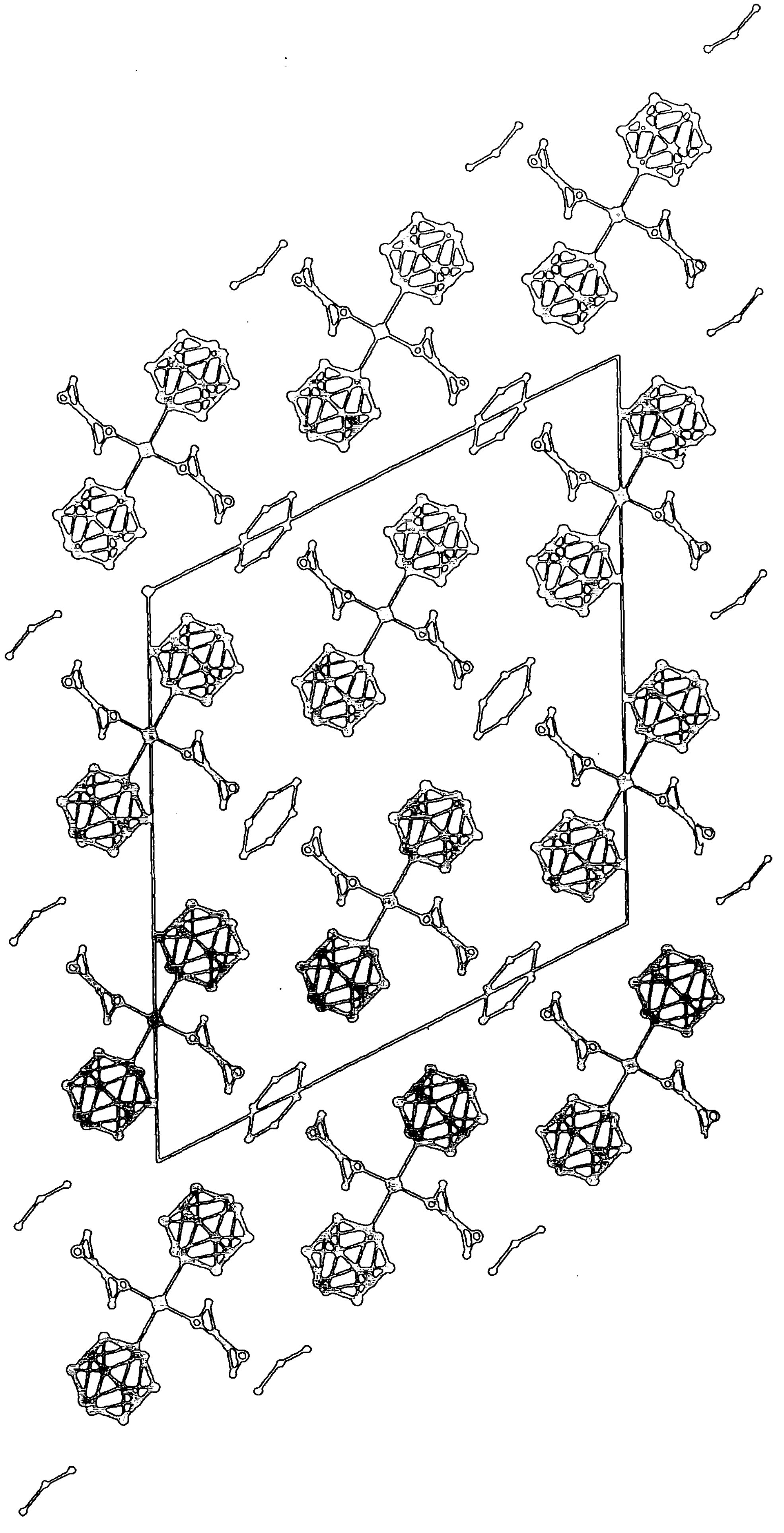


Table 3.4.3

Preliminary structural data for the compound $Mg(C_2B_{10}H_{10}Me)_2(C_4H_8O_2)_2C_7H_8$

Bond lengths (Å)

Mg - C(1)	2.16(2)	Mg - O	2.03(1)

Bond angles (°)

C(1) - Mg - C(1)'	121.2(9)	C(1) - Mg - O	107.2(5)
C(1) - Mg - O'	109.4(5)	O - Mg - O'	100.5(6)
Mg - C(1) - C(2)	126(1)	C(1) - C(2) - C(3)	116(1)

No firm conclusions can be drawn as to the effect on the Mg-C linkage of an increase in the coordination number of carbon from four in $R_2Mg(L_2)$ to six, due to the large e.s.d. value associated with the bond length. However it has already been noted that minimal, if any, such effect is seen in $Li(C_2B_{10}H_{10}Me)$ (PMDETA), while the Ge-C bond lengths of 2.01(1)Å and 2.04(1)Å in $(C_2B_{10}H_{11})_2$ $GeMe_2$ (164) are only slightly longer than those of ca. 1.95Å associated with a bond from germanium to four-coordinate carbon.

The $O\hat{Mg}O^1$ angle of $100.5(6)^o$ reflects the distortion of the magnesium environment, this distortion being due to the steric interaction of the two bulky carboranyl ligands. The Mg-O bond lengths of 2.03(1)Å are very similar to those observed in a series of ether-coordinated alkyl-and aryl-magnesium bromides, $RMgBr(OR^1{}_2)_2$. (163)

In connection with the distortion of the tetrahedral environment around magnesium, it is interesting to compare the observed $C(1)\ \hat{Mg}\ C(1)^1$ angle of $121.2(9)^o$ with that which might have been predicted on the basis of the carboranyl cone angles discussed earlier. For a metal-carbon bond length of 2.16Å, the angle θ (see Figure 3.4.3) between the M-C axis and the surface of the boron-bonded hydrogen <u>ortho</u> to the metallated carbon, is calculated to be 66^o. Thus, if one set of <u>ortho</u> B-H units, on each of the two carboranyl ligands in a compound such as $Mg(C_2B_{10}H_{10}Me)_2\ (C_4H_8O_2)_2$ were aligned co-planar with the atoms (C(1), Mg and $C(1)^1$, the minimum possible angle $C(1)\ \hat{Mg}C(1)^1$ would be expected to be 132^o (i.e. 2 x 66^o), somewhat greater than the observed value. However the carboranyl ligands of $Mg(C_2B_{10}H_{10}Me)_2\ (C_4H_8O_2)_2$ adopt a conformation such that the methyl-carbon atoms C(3) and $C(3)^1$ are twisted out of the plane $C(1)MgC(1)^1$ (see Figure 3.4.5) allowing the <u>ortho</u> B-H units of the two carboranyl ligands to "mesh" together to a certain extent. This allows the carboranyl units to approach each other more closely (reducing the distortion around Mg) and accounts for the observed $C(1)\hat{Mg}C(1)^1$ angle of $121.2(9)^o$.

CHAPTER 4

THE PREPARATION AND ATTEMPTED HYDROLYTIC DEGRADATION OF A SERIES OF CARBORANYL-KETONES

CHAPTER 4

4.1 INTRODUCTION

This section describes investigations carried out to characterise and determine the relative stability, to hydrolytic degradation, of a series of carboranyl ketones. In order to quantify the results obtained similar degradation reactions were performed on the organic ketone, benzophenone (or diphenyl ketone). It is known that the icosahedral carboranes can be regarded as pseudo-aromatic and therefore one might expect bis- (carboranyl) ketones to exhibit similar properties to diaryl ketones, such as benzophenone.

The carboranyl ketones described herein were prepared by the following routes:- (57)

i) $R\Theta Li + R'COCl \xrightarrow{-LiCl} R\Theta COR'$

Where $R = H, Me, Ph$

$R' = Ph$

ii) $2R\Theta Li + ClOCR''COCl \xrightarrow{-2LiCl} R\Theta COR''CO\Theta R$

Where $R = H, Me$

$R'' = \Theta', C_6H_4$

4.2(a) PREPARATION OF 1-METHYL-2-BENZOYL-O-CARBORANE, MeΘCOPh

$$Me\Theta Li + PhCOCl \xrightarrow[TOLUENE]{-LiCl} Me\Theta COPh$$

i) EXPERIMENTAL

Methyl-o-carborane (1.479g, 9.36 mmol.) was dissolved in dry toluene (40 ml) and to this was added 6.1 ml (9.36 mmol.) of a 1.54M n-butyl lithium solution in pentane. The solution was heated until a pale yellow precipitate appeared. The slurry was allowed to stir at 80°C for 30 min. before being cooled and the benzoyl chloride was added the solution became clear and pale orange in colour. The solution was heated for 30 min. during which time a precipitate appeared. The slurry was allowed to stir for a further 2 hours before being filtered. The filtrand was washed several times with dry toluene until a white solid remained on the filter stick. The pale orange filtrate was pumped on under vacuum leaving a pale orange crystalline solid. Recrystallization from hexane gave pale yellow crystals identified as 1-methyl-2-benzoyl-o-carborane.

ii) RESULTS

Yield = 81.6%

Melting point = 65-66°C (Lit 66°C)

Analysis

	C	H	B	O	Cl
% FOUND	46.1	8.4	43.2	-	ABSENT
MeΘCOPh requires	45.8	6.8	41.2	6.1	-

I.R.

The infra-red spectrum showed the following peaks:-
ν max, Nujol mull, (cm^{-1}) 2910(s), 2849(s), 2589(s), 1780(w), 1723(s), 1675(s), 1590(s), 1452(sh), 1448, 1440(s), 1375(s), 1310(w), 1245(s), 1180(s), 1125(m), 1100(w), 1085(m), 1065(w), 1015(m,br), 990(sh), 948(s), 917(w), 870(s), 850(w), 835(w), 825(w), 800(sh), 780(sh), 761(s), 740(s), 725(s), 708(s), 690(s), 681(s), 610(s), 570(w).

The following bands in the infra-red could be assigned:- B-H stretch (2589 cm^{-1}); C = O stretch (1723 cm^{-1}), phenyl ring $\mathrm{C}\overset{\text{- - -}}{\text{——}}\mathrm{C}$ (1675 cm^{-1}, 1590 cm^{-1}), C-B-C cage vibrations (1245 cm^{-1}); Cage vibrations (761 cm^{-1}).

Mass Spectrum

The mass spectrum showed a number of carboranyl isotope patterns and these were identified as:-

$\frac{m}{e}$ 255-266 $\text{Me}\theta^{+}\text{COPh}$; $\frac{m}{e}$ 240-250 $^{+}\theta\text{COPh}$;

$\frac{m}{e}$ 184-194 $\text{Me}\theta^{+}\text{CO}$; $\frac{m}{e}$ 169-176 $^{+}\theta\text{CO}$; $\frac{m}{e}$ 150-160

$\text{Me}\theta^{+}$; $\frac{m}{e}$ 132-146 θ^{+}; $\frac{m}{e}$ 73-80 ($\frac{m}{2e}$ 147-160)

$\text{Me}\theta^{2+}$; $\frac{m}{e}$ 66-73 ($\frac{m}{2e}$ 132-146 θ^{2+})

4.2(b) PREPARATION OF 1-PHENYL-2-BENZOYL-O-CARBORANE, PhθCOPh

$$\text{Ph}\theta\text{Li} + \text{PhCOCl} \xrightarrow[\text{TOLUENE}]{-\text{LiCl}} \text{Ph}\theta\text{COPh}$$

i) EXPERIMENTAL

1-Phenyl-2-benzoyl-o-carborane was prepared in a similar manner to 1-methyl-2-benzoyl-o-carborane (see 4.2(a)).

ii) RESULTS

Yield = 65%

Melting Point of pale yellow crystals = 87-88°C (Lit 88°C)

Analysis

	C	H	B	O
% FOUND	55.9	5.9	31.7	-
PhθCOPh requires	55.6	6.2	33.3	4.9

I.R.

The infra-red spectrum showed the following peaks:-

ν max, Nujol mull, (cm^{-1}) 3040(w), 2660(w), 2580(s), 1690(s), 1595(w), 1255(s), 1240(sh), 1185(m), 1120(m), 1065(m), 955(m), 940(sh), 880(w), 850(w), 790(w), 760(m), 740(m), 725(m), 690(s), 665(w), 610(w), 600(w), 555(w).

The following vibrations could be assigned:- Aromatic C-H stretch (3040 cm^{-1}), B-H stretch (2580 cm^{-1}), C=O stretch (1690 cm^{-1}), C-B-C cage vibrations (1255 cm^{-1}), Cage vibrations (760-725 cm^{-1}).

Mass Spectrum

The mass spectrum showed a number of carboranyl isotope patterns and these were identified as:-

$\frac{m}{e}$ 316-326 $Ph\theta^{+}COPh$; $\frac{m}{e}$ 241-248 $PhCO\theta^{+}$ or $Ph\theta CO^{+}$; $\frac{m}{e}$ 212-222 $Ph\theta^{+}$; $\frac{m}{e}$ 132-146 θ^{+};

$\frac{m}{e}$ 158-163 ($\frac{m}{2e}$ 316-326); $\frac{m}{e}$ 106-111 ($\frac{m}{2e}$ 212-222);

$\frac{m}{e}$ 66-73 ($\frac{m}{2e}$ 132-146 θ^{2+})

4.2(c) THE PREPARATION OF $Me\theta CO\,C_6H_4CO\theta Me$

$$2Me\theta Li \;+\; ClCOC_6H_4COCl \xrightarrow[Et_2O]{-2LiCl} Me\theta COC_6H_4CO\theta Me$$

i) EXPERIMENTAL

Methyl-o-carborane (1.1755 g, 7.44 mmol.) was dissolved in dry diethyl ether (50 ml) and to this was added 4.83 ml (7.44 mmol.) of a 1.54M ^{n}BuLi solution in pentane. A pale yellow solution was obtained and stirred at 20°C for 30 min. before terephthalyl chloride (o.7562 g 3.72 mmol.) dissolved in 20 ml of diethyl ether was added. On addition the solution became very dark red almost black. The solution was allowed to stir overnight at room temperature. After this time the solution remained dark red but a precipitate had now appeared. The solution was filtered, the filtrand was washed several times with dry toluene until a white solid remained on the filter stick. The dark red filtrate was pumped on under vacuum leaving a dark red/brown solid.

ii) RESULTS

Yield = 52%

Melting Point of red/brown solid = 125-130°C

Analysis

	C	H	B	O	Cl
% FOUND	35.4	7.5	46.7	-	ABSENT
$Me\Theta COC_6H_4CO\Theta Me$ requires	37.8	6.8	48.6	7.2	-

I.R.

The following peaks in the infra-red could be assigned:- B-H stretch (2580 cm^{-1}); C=O stretch (1690 cm^{-1}); Aromatic $C \overset{---}{=} C$ (1600 cm^{-1}); C-B-C cage vibrations (1250 cm^{-1}); para-disubstituted aromatic ring (810 cm^{-1}); Cage vibrations (720 cm^{-1}).

Mass Spectrum

The mass spectrum showed a number of carboranyl isotope patterns and these were identified as:-

$\frac{m}{e}$ 439-451 $Me\Theta^{+}COC_6H_4CO\Theta Me$;

$\frac{m}{e}$ 288-295 $Me\Theta^{+}COC_6H_4CO$; $\frac{m}{e}$ 258-265 $Me\Theta^{+}COC_6H_4$;

$\frac{m}{e}$ 220-225 ($\frac{m}{2e}$ 439-451); $\frac{m}{e}$ 147-160 $Me\Theta^{+}$;

$\frac{m}{e}$ 132-146 Θ^{+}; $\frac{m}{e}$ 73-80 ($\frac{m}{2e}$ 147-160, $Me\Theta^{2+}$).

4.2(d) THE CONVERSION OF META-CARBORANE-1,7-DICARBOXYLIC ACID TO ITS DIACID DICHLORIDE (59)

$$\mathrm{HOOC\Theta'COOH} \xrightarrow[\text{TOLUENE}]{\mathrm{PCl_5}} \mathrm{ClOC\Theta'COCl}$$

i) EXPERIMENTAL

A mixture of m-carborane-1,7-dicarboxylic acid (6.3796 g, 0.027 mol.) and phosphorus pentachloride (11.4546 g, 0.055 mol.) in toluene was heated for one hour. After this time the toluene and phosphorus oxychloride were removed by distillation. The remaining crude m-carborane-1,7-diacid dichloride was purified by vacuum distillation, (67°C at 0.1 mm Hg).

ii) RESULTS

Weight of low melting solid = 5.34 g

Yield = 73.5%

Boiling Point = 67°C at 0.1 mm Hg (Lit. 67°C at 0.1 mm Hg)

Analysis

	C	H	B	O	Cl
% FOUND	18.2	4.1	39.5	-	25.5
$\mathrm{ClCO\Theta'COCl}$ requires	17.8	3.7	40.1	11.8	26.2
$\mathrm{HOOC\Theta'COOH}$ requires	20.5	5.1	46.5	27.6	-

I.R.

The infra-red spectrum showed the following peaks:-

ν max, Nujol Mull ($\mathrm{cm^{-1}}$), 2970(sh), 2940(s), 2869(s), 2639(s), 1780(s), 1460(s), 1380(s), 1260(w), 1165(s), 1050(s), 945(s), 915(s), 885(s), 855(sh), 840(s), 770(sh), 760(s), 740(sh), 685(m), 660(w), 630(m).

The following vibrations could be assigned:- B-H stretch (2639 cm^{-1}), CO stretch in COCl (1780 cm^{-1}), C-B-C stretch (1165 cm^{-1}), Cage vibrations (760 cm^{-1}), C-Cl stretch in COCl (685 cm^{-1}).

As expected, no OH stretch at 3540 cm^{-1} was observed.

The m-carborane-1,7-diacid dichloride was fairly readily hydrolysed back to the dicarboxylic acid, and consequently was freshly distilled prior to use.

4.2(e) THE REACTION OF DILITHIO-O-CARBORANE WITH M-CARBORANE-1,7-DICARBOXYLIC ACID DICHLORIDE

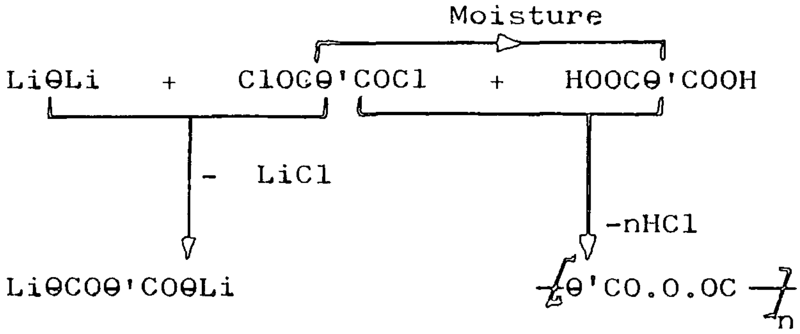
$$\mathrm{Li\Theta Li} + \mathrm{ClOC\Theta'COCl} \xrightarrow[-\mathrm{nLiCl}]{\mathrm{Ether}} \left[\Theta\text{-CO-}\Theta'\text{-CO}\right]_n$$

i) EXPERIMENTAL

o-Carborane (0.4158 g, 2.887 mmol.) was dissolved in dry diethyl ether (40 ml) and the solution cooled to 0°C before 3.66 ml (5.775 mmole) of a 1.58M n-butyllithium solution in pentane was added. On addition of the n-butyllithium a white precipitate formed. The slurry was stirred at room temperature for 1 hr.

In a second flask, 0.777g (2.887 mmol.) of freshly distilled m-carborane-1,7-dicarboxylic acid dichloride was dissolved in dry diethyl ether (20 ml). This clear solution was transferred by syringe to the first flask containing the dilithio-o-carborane. As the diacid dichloride was added the white precipitate disappeared leaving a clear yellow solution. After several hours stirring at room temperature a white precipitate had formed. The solution was filtered and the filtrand was washed several times with dry toluene until a white solid remained on the filter stick. The yellow filtrate was pumped on under vacuum leaving a yellow solid.

Preliminary studies carried out on the crude yellow solid seemed to indicate the presence of possibly two or more species, one being a carboranyl ketone derivative and the other species being anhydride type derivatives. The presence of such compounds may be explained by considering the following reaction pathway:-



Due to the sensitivity of the m-carborane-1,7-dicarboxylic acid dichloride to moisture it seems likely that some m-carborane-1,7-dicarboxylic acid may also have been present and consequently a condensation reaction may have occurred, eliminating hydrogen chloride and producing the observed anhydride species.

In order to remove the anhydride material from the desired carboranyl ketone derivative, the crude yellow solid was redissolved in ether and extracted several times with a sodium bicarbonate solution. The ethereal layer containing the ketone derivative was dried over anhydrous $MgSO_4$, filtered and the ether removed under vacuum leaving a pale yellow solid. The sodium bicarbonate washings were acidified and extracted with ether. The ether was separated, dried over anhydrous $MgSO_4$ filtered and the ether removed under vacuum leaving an off-white solid.

ii) RESULTS

Analysis

	C	H	B	O	Cl
% FOUND FOR PALE YELLOW SOLID	19.1	7.1	66.8	-	ABSENT

	C	H	B	O	Cl
HθCOθ'COθH requires	19.8	6.6	67.1	6.6	-
% FOUND FOR OFF-WHITE SOLID	21.1	6.0	45.9	-	ABSENT
HOOCθ'COOH requires	20.5	5.1	46.5	27.6	-

I.R.

The infra-red spectrum for the off-white solid was found to be identical to that of m-carborane-1,7-dicarboxylic acid.

The infra-red spectrum for the pale yellow solid, showed the following peaks:- ν max, Nujol mull (cm^{-1})

3080(m), 2960(sh), 2940(s), 2870(s), 2600(s), 1710(s),
1610(m), 1455(s), 1380(s), 1325(w), 1265(s), 1185(m),
1090(m,br),1030(m), 849(sh), 810(s), 739(m), 675(sh).

The following bands could be assigned:- Carboranyl C-H stretch (3080 cm^{-1}), B-H stretch (2600 cm^{-1}), C = O stretch (1710 cm^{-1}), C-B-C cage vibrations (1265 cm^{-1}), Cage vibrations (739 cm^{-1}).

Mass Spectrum

The mass spectrum of the off-white solid was identical to that for m-carborane-1,7-dicarboxylic acid. The mass spectrum of the pale yellow solid showed a number of carboranyl isotope patterns and these were identified as:-

$\frac{m}{e}$ 480-489 $^{+}$θCOθ'COθH; $\frac{m}{e}$ 340-347 $^{+}$COθ'COθH;

$\frac{m}{e}$ 310-318 $^{+}$θ'COθH; $\frac{m}{e}$ 240-245 ($\frac{m}{2e}$ 480-489);

$\frac{m}{e}$ 132-146 θ^{+}; $\frac{m}{e}$ 66-73 ($\frac{m}{2e}$ 132-146 θ^{2+})

4.2(f) THE PREPARATION OF MeΘCOΘ'COΘMe

$$2Me\Theta Li \quad + \quad ClCO\Theta'COCl \xrightarrow[-2LiCl]{Ether} Me\Theta CO\Theta'CO\Theta Me$$

i) EXPERIMENTAL

Methyl-o-carborane (1.0716 g, 6.7 mmol.) was dissolved in dry diethyl ether (30 ml) and the solution cooled to $0^{o}C$ before 4.24 ml (6.7 mmol.) of a 1.58M n-butyl-lithium solution was slowly added by syringe. The pale yellow solution was allowed to stir at $30-40^{o}C$ for 1 hr. After this time a solution of freshly distilled meta-carborane-1,7-dicarboxylic acid dichloride (0.9016 g, 3.335 mmol.) in diethyl ether (20 ml) was added by syringe to the MeΘLi/ether solution. On addition the pale yellow solution became dark orange/red and a white precipitate appeared. After several hours stirring at $30-40^{o}C$ the slurry was filtered and the filtrand was washed several times with dry toluene until a white solid remained on the filter stick. This white solid was positively identified by analysis as lithium chloride. The orange/red filtrate was pumped on under vacuum leaving an orange/red solid. Preliminary studies carried out on the crude orange/red solid seemed to indicate the presence of possibly two or more compounds, one being the expected carboranyl ketone MeΘCOΘ'COΘMe and the other species being anhydride type derivatives.

In order to remove the anhydride material from the desired carboranyl ketone derivative, the crude orange/red solid was redissolved in ether and extracted several times with a sodium bicarbonate solution. The ethereal layer containing the ketone derivative was dried over anhydrous $MgSO_4$, filtered and the ether removed under vacuum leaving a pale orange/yellow solid. The sodium bicarbonate washings were acidified and extracted with ether. The ether was separated, dried over anhydrous $MgSO_4$, filtered and the ether removed under vacuum leaving an off-white solid. This off-white solid was positively identified by infra-red, mass spectral and microanalytical data to be meta-carborane-1,7-dicarboxylic acid, $HOOC\theta'COOH$.

ii) RESULTS

Analysis

	C	H	B	O	Cl
% FOUND FOR PALE/ ORANGE/YELLOW SOLID	22.8	6.8	61.8	-	ABSENT
$Me\theta CO\theta'CO\theta Me$ requires	23.4	7.0	63.3	6.3	-

I.R.

The infra-red spectrum showed the following peaks:-

ν max, Nujol mull, (cm^{-1}) 2950(sh), 2920(s), 2850(s), 2570(s),
1650(s), 1500(w), 1450(s), 1370(s), 1300(s), 1255(s),
1225(s), 1180(sh), 1145(w), 1085(m), 1055(m), 1015(m),
935(w), 910(w), 870(m), 830(sh), 799(s), 724(s).

The following vibrations could be assigned:- B-H stretch (2570(cm^{-1}), C = O stretch (1650 cm^{-1}), C-O stretch (1145 - 1085 cm^{-1}), C-B-C cage vibrations (1255 cm^{-1}), Cage vibrations (724 cm^{-1}).

Mass Spectrum

The mass spectrum showed a number of carboranyl isotope patterns and the following could be assigned:-

$\frac{m}{e}$ 504-516 $Me\theta^{+}CO\theta'CO\theta Me$;

$\frac{m}{e}$ 347-358 $Me\theta CO\theta'CO^{+}$; $\frac{m}{e}$ 319-329 $Me\theta CO\theta^{+}$;

$\frac{m}{e}$ 179-187 $Me\theta CO^{+}$; $\frac{m}{e}$ 147-160 $Me\theta^{+}$;

$\frac{m}{e}$ 132-146 θ^{+}; $\frac{m}{e}$ 252-258 ($\frac{m}{2e}$ 504-516);

$\frac{m}{e}$ 73-80 ($\frac{m}{2e}$ 147-160 $\mathrm{Me}\theta^{2+}$)

4.2(g) DISCUSSION

It is apparent from the results that in the reactions of 1-lithio-2-methyl-and dilithio-o-carborane with m-carborane-1,7-dicarboxylic acid dichloride an anhydride derivative, which appears to contain m-carboranyl units only was formed, along with the expected carboranyl ketone derivatives. It seems likely that this anhydride derivative was formed in a condensation type reaction between the m-carborane-1,7-dicarboxylic acid and its diacid dichloride. It is as yet unknown whether the anhydride derivative is present in the m-carborane-1,7-diacid dichloride/ether solutions used in these reactions or whether it is formed during the course of the reaction with the lithio-carboranyl derivatives.

4.3 THE ATTEMPTED HYDROLYTIC DEGRADATION OF A SERIES OF CARBORANYL-KETONES

Although the preparation and characterisation of a large number of carboranyl ketones has been described in the literature (57,58), very little is known of the stability of the carbonyl linkage in these derivatives to hydrolytic degradation. It was with this thought in mind, that we prepared (see Section 4.2(a) - (g)) and attempted to hydrolytically degrade a series of carboranyl ketone derivatives. In order to quantify the results obtained we also subjected the organic ketone benzophenone (diphenylketone) to similar degradation reactions. Benzophenone was specifically chosen because it is known that the icosahedral carboranes can be regarded as pseudo-aromatic species and therefore one might expect the carboranyl ketones to exhibit similar properties to diaryl ketones.

i) EXPERIMENTAL

(a) The Attempted Degradation of the - CO - linkage in 1-methyl-2-benzoyl-o-carborane, MeΘCOPh, by Cold/Warm/Boiling Water

1-Methyl-2-benzoyl-o-carborane, MeΘCOPh (1.28 g) was placed in a round bottom flask and distilled water (50 ml) was added. The water/MeΘCOPh mixture was stirred at room temperature for 1 hour. No change was observed during this period and so the temperature was raised slowly from 20°C to 95°C. At approximately 65°C the orange solid began to melt. The mixture was heated at temperatures above 90°C for 24 hours before being cooled and extracted with diethyl ether. The ether layer was separated, dried over anhydrous $MgSO_4$, filtered and the ether removed under vacuum leaving an orange crystalline solid. This solid was positively identified as the starting material 1-methyl-2-benzoyl-o-carborane.

Results

Weight of orange solid = 1.24 g
Therefore Weight Loss = 0.04 g
Therefore % Loss = 3%
Melting Point of orange solid = 65-66°C (Lit. 66°C)

Analysis

	C	H	B	O
% FOUND	45.9	7.4	42.1	-
MeΘCOPh requires	45.8	6.8	41.2	6.1

The infra-red and mass spectral data was found to be identical to that for 1-methyl-2-benzoyl-o-carborane.

From the relatively small weight loss incurred one may conclude that the - CO - linkage in 1-methyl-2-benzoyl-o-carborane is moderately stable to boiling water over long periods.

The above degradation experiment was repeated for PhΘCOPh, $\mathrm{Me\Theta COC_6H_4CO\Theta Me}$, HΘCOΘ'COΘH, MeΘCOΘ'COΘMe and $\mathrm{C_6H_5COC_6H_5}$ (benzophenone). The results from these degradation reactions are summarized on Table 4.3.1.

(b) The Attempted Degradation of the - CO - linkage in 1-Methyl-2-Benzoyl-o-carborane, MeΘCOPh by warm 20% aqueous Hydrochloric and 10% aqueous Sulphuric Acid

1-Methyl-2-benzoyl-o-carborane (1.05 g) was placed in a round bottom flask and to this was added 50 ml of a 20% aqueous HCl solution. The MeΘCOPh/20% HCl mixture was stirred vigorously and heated to 70-80°C for several hours. After this time the HCl solution was extracted with ether, the ether was dried over anhydrous $\mathrm{MgSO_4}$, filtered and the ether removed leaving an orange crystalline solid. The aqueous layer was made basic and extracted with ether. The ether was dried over anhydrous $\mathrm{MgSO_4}$, filtered and the ether removed under vacuum, no material was obtained from this extract. The orange crystalline solid was positively identified as 1-methyl-2-benzoyl-o-carborane, MeΘCOPh. Similar results were obtained when 10% aqueous sulphuric acid was used rather than the 20% aqueous HCl.

RESULTS

i) The Attempted Degradation of MeΘCOPh by 20% Aqueous HCl

Weight of MeΘCOPh used = 1.05 g
Weight of MeΘCOPh recovered = 1.02 g

Therefore Weight of MeΘCOPh lost = 0.03 g

Therefore % Lost = 2.8%

ii) The Attempted Degradation of MeΘCOPh by 10% aqueous H_2SO_4.

Weight of MeΘCOPh used = 0.98 g
Weight of MeΘCOPh recovered = 0.93 g

Therefore Weight of MeΘCOPh lost = 0.05 g

Therefore % Lost = 5.1%

From the relatively small weight losses incurred in the acid degradation processes, one may conclude that the - CO - linkage in 1-methyl-2-benzoyl-o-carborane is moderately stable to attack by both 20% aqueous HCl and 10% aqueous H_2SO_4 at room and elevated temperatures (70-80°C).

The above degradation experiment was repeated for PhΘCOPh, $Me\Theta COC_6H_4CO\Theta Me$, HΘCOΘ'COΘH, MeΘCOΘ'COΘMe and $C_6H_5COC_6H_5$ (benzophenone). The results from these degradation reactions are summarized on Table 4.3.1.

(c) The Attempted Degradation of the - CO - linkage in 1-Methyl-2-benzoyl-o-carborane, MeΘCOPh by 5% aqueous NaOH solution

1-Methyl-2-benzoyl-o-carborane, MeΘCOPh (1.2 g) was placed in a round bottom flask and 50 ml of a 5% aqueous NaOH solution was added. The MeΘCOPh/5% aqueous NaOH mixture was stirred vigorously for several hours. Initially no change was observed, however after 1-2 hours the orange colouration of MeΘCOPh had disappeared and the solution had become cloudy. The NaOH solution was extracted with ether, the ether layer was separated, dried over anhydrous $MgSO_4$, filtered and the ether removed under vacuum leaving a pale yellow solid. This pale yellow solid was positively identified as 1-methyl-o-carborane, MeΘH. The aqueous layer was acidified and extracted with ether. The ether layer was separated, dried over anhydrous $MgSO_4$, filtered and the ether removed under vacuum leaving a white solid. This white solid was positively identified as benzoic acid, PhCOOH.

RESULTS

Melting Point of pale yellow solid = 210-211°C (Lit. 211-213)

Analysis

	C	H	B	O
% FOUND FOR PALE YELLOW SOLID	22.7	8.7	67.4	-
MeΘCOPh requires	45.8	6.8	41.2	6.1
MeΘH (Methyl-o-carborane) requires	22.8	8.8	68.4	-
% FOUND FOR WHITE SOLID	68.3	5.1	ABSENT	-
Benzoic Acid requires	68.8	4.9	-	26.2

I.R.

The following vibrations in the infra-red spectrum of the pale yellow solid could be assigned:- Carboranyl C-H stretch (3058 cm^{-1}), B-H stretch (2610-2530 cm^{-1}); Cage vibrations (720 cm^{-1}). The infra-red spectrum of the pale yellow solid was found to be identical to that of methyl-o-carborane.

The infra-red spectrum of the white solid was found to be identical to that for benzoic acid.

Mass Spectrum

The mass spectrum for the pale yellow solid showed an M + 1 peak at $\frac{m}{e}$ 161 where M = $^{12}C_3\ ^{11}B_{10}\ ^{1}H_{14}$ with a corresponding isotope pattern from $\frac{m}{e}$ 147-160.

It would appear from the results obtained that 1-methyl-2-benzoyl-o-carborane, MeΘCOPh is hydrolytically cleaved at room temperature by a 5% aqueous NaOH solution, giving as degradation products methyl-o-carborane, MeΘH and benzoic acid.

The above degradation experiment was repeated for PhΘCOPh, $\mathrm{Me\Theta COC_6H_4CO\Theta Me}$, HΘCOΘ' COΘH, MeΘCOΘ' COΘMe and $\mathrm{C_6H_5COC_6H_5}$ (benzophenone). The results from these degradation reactions are summarized on Table 4.3.1.

4.4 DISCUSSION

The carboranyl ketones employed in these hydrolytic degradation experiments were all found to be stable to both boiling water and hot aqueous hydrochloric and sulphuric acids over long periods ranging from 8 to 48 hours (see Table 4.3.1). This stability towards hydrolytic degradation by water and acid was found to be comparable to that of the diaryl ketone, benzophenone, this possibly being a further indication of the pseudo aromatic nature of the icosahedral carboranes.

The relatively small weight losses incurred, these ranging from 0.02-0.05 g, (2-5%), when the carboranyl ketones were subjected to boiling water and acid degradation, were also observed when benzophenone was subjected to similar hydrolytic degradation conditions and subsequently it is believed that these weight losses were not due to hydrolytic degradation but rather to inadequate work up procedures.

Although the carboranyl ketones were found to exhibit a high degree of resistance to hydrolytic degradation by water and acid, comparable to that of benzophenone, significant differences were observed when the same ketones were hydrolytically degraded by cold aqueous NaOH. All of the carboranyl ketones studied were found to be totally degraded by cold aqueous NaOH, giving as degradation products the free carborane and a carboxylic acid, the nature of which was dependent on the ketone used (see Table 4.3.1).

$$\mathrm{Me\Theta COC_6H_4CO\Theta Me} \xrightarrow{\text{aq 5\% NaOH}} \mathrm{2Me\Theta H} + \mathrm{HOOCC_6H_4COOH}$$

Methyl-o Carborane   Terephthalic Acid

At no time was the icosahedral cage degraded by the base, only its link to the carboranyl group was actually attacked.

It is interesting to note that the diaryl ketone, benzophenone (or diphenyl ketone), was not degraded even when very strong aqueous NaOH was employed and the solution heated to 60-70°C for long periods. One possible explanation for the observed differences in the hydrolytic stability of the carboranyl ketones and that of benzophenone to aqueous NaOH is that the electron-withdrawing character of the icosahedral cage is such that it activates the - CO - link towards attack by nucleophiles such as OH^- and subsequently the carboranyl ketones are much more readily degraded by base than benzophenone. This would also help to explain the differences observed in the rates of degradation between different carboranyl ketones (see Table 4.31). For example when 1-methyl-2-benzoyl-o-carborane, MeΘCOPh was degraded by 5% aqueous NaOH the process took 1-2 hours to complete whereas when similar conditions were used to degrade both HΘCOΘ'COΘH and MeΘCOΘ'COΘMe the reactions were found to be slightly exothermic and were completed in a fraction of the time. These differences may again be explained by the electron-withdrawing effects of the icosahedral carborane cage. In the carboranyl ketones HΘCOΘ'COΘH and MeΘCOΘ'COΘMe there are essentially two cages pulling electron density away from the - CO - link, whereas in MeΘCOPh there is only one, and therefore the carbonyl linkages in HΘCOΘ'COΘH and MeΘCOΘ'COΘMe are even more susceptible to attack by nucleophiles such as OH^-.

It is interesting to note that on hydrolytic degradation of the carboranyl ketones by base, the carboxylic acids obtained were always those which had the highest pKa values. This trend is clearly shown in Table 4.3.2.

Table 4.3.2.

COMPOUND	POSSIBLE CARBOXYLIC ACIDS FROM BASE DEGRADATION	ACTUAL CARBOXYLIC ACID OBTAINED
$\mathrm{Me\theta COPh}$	$\mathrm{Me\theta COOH}$ pKa = 2.74 PhCOOH pKa = 4.2	PhCOOH
$\mathrm{Ph\theta COPh}$	$\mathrm{Ph\theta COOH}$ pKa = 3.12 PhCOOH pKa = 4.2	PhCOOH
$\mathrm{Me\theta COC_6H_4CO\theta Me}$	$\mathrm{Me\theta COOH}$ pKa = 2.74 $\mathrm{HOOCC_6H_4COOH}$ pKa = 3.5 pKa_2 = 4.8	$\mathrm{HOOCC_6H_4COOH}$
$\mathrm{H\theta CO\theta'CO\theta H}$	$\mathrm{H\theta COOH}$ pKa = 2.49 $\mathrm{HOOC\theta'COOH}$ pKa = 3.20	$\mathrm{HOOC\theta'COOH}$
$\mathrm{Me\theta CO\theta'CO\theta Me}$	$\mathrm{Me\theta COOH}$ pKa = 2.74 $\mathrm{HOOC\theta'COOH}$ pKa = 3.20	$\mathrm{HOOC\theta'COOH}$

Table 4.3.1

COMPOUND	DEGRADATION CONDITIONS		PRODUCTS OF DEGRADATION
	INEFFECTIVE	EFFECTIVE	
MeθCOPh	a) Boiling water for 24 hours b) 20% aqu. HCl, 8 hours at 70-80°C	c) 5% aqu. NaOH, 1-2 hours at 20°C	MeθCOPh MeθCOPh MeθH + PhCOOH
PhθCOPh	a) Boiling water for 48 hours b) 20% aqu. H_2SO_4, 8-10 hours at 50-60°C	c) 10% aqu. NaOH, 1 hour at 20°C	PhθCOPh PhθCOPh PhθH + PhCOOH
MeθCOC$_6$H$_4$COθMe	a) Boiling water for 48 hours b) 10% aqu. H_2SO_4, 8 hours at 70-80°C	c) 5% aqu. NaOH, 30 minutes at 20°C	MeθCOC$_6$H$_4$COθMe 2MeθH + HOOC-C$_6$H$_4$COOH
HθCOθ'COθH	a) Boiling water for 48 hours b) 20% aqu. HCl, 20 hours at 60-70°C c) 10% aqu. H_2SO_4, 20 hours at 50°C	d) 5% aqu. NaOH, 10 minutes at 20°C	HθCOθ'COθH " " 2HθH + HOOCθ'COOH

Table 4.3.1

COMPOUNDS	DEGRADATION CONDITIONS		PRODUCTS OF DEGRADATION
	INEFFECTIVE	EFFECTIVE	
MeΘCOΘ'COΘMe	a) Boiling water for 48 hours		MeΘCOΘ'COΘMe
	b) 20% aqu. HCl, 20 hours at 70°C		"
	c) 20% aqu. H_2SO_4, 20 hours at 50°C		"
		d) 5% aqu. NaOH, 15 minutes at 20°C	2MeΘH + HOOCΘ'COOH
$C_6H_5COC_6H_5$ (BENZOPHENONE)	a) Boiling water for 48 hours		$C_6H_5COC_6H_5$
	b) 20% aqu. HCl, 24 hours at 80°C		"
	c) 20% aqu. H_2SO_4, 20 hours at 70°C		"
	d) 5% aqu. NaOH, 10 hours at 20°C		"
	e) 20% aqu. NaOH, 8 hours at 70°C		"
	f) 40% aqu. NaOH, 20 hours at 70°C		"

CHAPTER 5

THE PREPARATION AND ATTEMPTED HYDROLYTIC DEGRADATION OF A SERIES OF CARBORANYL-AMIDES

CHAPTER 5

5.1 INTRODUCTION

This section describes investigations carried out to characterise and determine the relative stability, to hydrolytic degradation, of, a series of carboranyl amide derivatives of general formulae $\mathrm{RNHCO\Theta CONHR}$ and $\mathrm{RNHCO\Theta' CONHR}$ (where R = Ph, ^{t}Bu, Me).

The carboranyl amide derivatives described herein were prepared by the reaction of dilithio-o- and m-carboranes with alkyl- and aryl isocynanates. (61)

$$\mathrm{Li\Theta Li} \quad + \quad \mathrm{2RNCO} \xrightarrow[\text{ii) } \mathrm{H^{+}}]{\text{i) } \mathrm{Et_2O/TOLUENE}} \mathrm{RNHCO\Theta CONHR}$$

where R = Ph, Me, ^{t}Bu

5.2(a) PREPARATION OF PhNHCOΘ'CONHPh

$$\mathrm{Li\Theta' Li} \quad + \quad \mathrm{2PhNCO} \xrightarrow[\text{ii) } \mathrm{HCl/H_2O}]{\text{i) } \mathrm{Et_2O/TOLUENE}} \mathrm{PhNHCO\Theta' CONHPh}$$

i) EXPERIMENTAL

m-Carborane (1.7193 g, 11.94 mmol.) was dissolved in dry toluene (40 ml) and to this was added 15.5 ml (23.88 mmol.) of a 1.54M ^{n}BuLi solution in pentane. The resulting clear solution was refluxed for one hour during which time an off-white precipitate appeared. The toluene was removed under vacuum and replaced by anhydrous diethyl ether giving an opaque pale yellow/green solution. The solution was stirred at room temperature for 30 minutes before freshly distilled phenyl isocyanate, PhNCO (2.59 ml, 23.88 mmol.) was added. As the PhNCO was added an off-white precipitate immediately formed, the exothermic reaction causing the solvent to boil. The suspension was heated for several hours before being cooled and 20% aqueous HCl added. The ether layer was separated and dried over anhydrous $MgSO_4$ for 24 hours. Filtration and removal of the solvent under vacuum resulted in a pale yellow solid which was recrystallized from hot methanol.

ii) RESULTS

Weight of PhNHCOθ'CONHPh obtained = 4.46 g
Theoretical Weight of PhNHCOθ'CONHPh = $\overset{4}{\cancel{5}}$.56 g

Yield = ~~80~~.2%

Melting point = 135-140°C

Analysis

	C	H	N	B	O
% FOUND	50.2	6.4	7.1	27.9	-
PhNHCOθ'CONHPh requires	50.3	5.8	7.3	28.3	8.4

I.R.

The following vibrations in the infra-red could be assigned:- secondary amide N-H stretch (3295 cm^{-1}(s,br)); B-H stretch (2590 cm^{-1}); CO stretch (1670 cm^{-1}); Aromatic C$\overset{\dots}{=}$C stretch (1599 cm^{-1}); Cage vibrations (740 cm^{-1}); Mono-substituted benzene ring (690 cm^{-1}).

Mass Spectrum

The mass spectrum showed a number of carboranyl-isotope patterns; the following could be assigned:-

$\frac{m}{e}$ 379-384 PhNHCO$^+$θ'CONHPh; $\frac{m}{e}$ 301-308 PhNHCOθ'CONH$^+$;

$\frac{m}{e}$ 286-293 PhNHCOθ'CO$^+$; $\frac{m}{e}$ 258-265 PhNHCOθ'$^+$;

$\frac{m}{e}$ 167-174 θ'CO$^+$; $\frac{m}{e}$ 132-146 θ'$^+$; $\frac{m}{e}$ 66-73 ($\frac{m}{2e}$ 132-146) θ'$^{2+}$.

5.2(b) PREPARATION OF PhNHCOθCONHPh

$$\text{Li}\theta\text{Li} \quad + \quad 2\text{PhNCO} \xrightarrow[\text{ii) HCl/H}_2\text{O}]{\text{i) Ether}} \text{PhNHCO}\theta\text{CONHPh}$$

i) EXPERIMENTAL

PhNHCOθCONHPh was prepared in a similar manner to its m-carborane analogue, PhNHCOθ'CONHPh (see 5.2(a)).

ii) RESULTS

Yield of PhNHCOθCONHPh = 77%

Melting Point = 108-110°C

Analysis

	C	H	N	B	O
% FOUND	50.1	6.0	7.1	28.1	-
PhNHCOθCONHPh requires	50.3	5.8	7.3	28.3	8.4

I.R.

The following vibrations in the infra-red spectrum could be assigned:- Secondary amide NH stretch (3395 cm^{-1} (s,br)); B-H stretch (2570 cm^{-1}(s)); CO stretch (1685 cm^{-1} (s)); Aromatic C$\overset{\cdots}{=}$C stretch (1599 cm^{-1}); Cage vibrations (725 cm^{-1}(s)); Mono-substituted benzene ring (690 cm^{-1}(s)).

Mass Spectrum

The mass spectrum showed a number of carboranyl isotope patterns; the following could be assigned:-

$\frac{m}{e}$ 379-384 $\text{PhNHCO}\theta^{+}\text{CONHPh}$; $\frac{m}{e}$ 301-308 $\text{PhNHCO}\theta^{+}\text{CONH}$;

$\frac{m}{e}$ 286-294 $\text{PhNHCO}\theta^{+}\text{CO}$; $\frac{m}{e}$ 257-264 $\text{PhNHCO}\theta^{+}$;

$\frac{m}{e}$ 167-174 ΘCO^+; $\frac{m}{e}$ 132-146 Θ^+; $\frac{m}{e}$ 66-73 ($\frac{m}{2e}$ 132-146) Θ^{2+}

5.2(c) PREPARATION OF $MeNHCO\Theta CONHMe$

$$Li\Theta Li \quad + \quad 2MeNCO \xrightarrow[\text{ii)}\ H^+]{\text{i)}\ \text{Ether}} MeNHCO\Theta CONHMe$$

i) EXPERIMENTAL

$MeNHCO\Theta CONHMe$ was prepared in a similar manner to $PhNHCO\Theta' CONHPh$ (see 5.2.(a))

ii) RESULTS

Yield = 65%

Analysis

	C	H	N	B	O
% FOUND	28.6	7.4	10.1	41.0	-
$MeNHCO\Theta CONHMe$ requires	27.9	7.0	10.8	41.8	12.4

I.R.

The following vibrations in the infra-red spectrum could be assigned:- secondary amide N-H stretch (3345 cm^{-1} (s)); B-H stretch (2590 cm^{-1}(s)); CO stretch (1660 cm^{-1} (s)); Cage vibrations (725 cm^{-1}(s)).

Mass Spectrum

The mass spectrum showed a number of carboranyl isotope patterns; the following could be assigned:-

$\frac{m}{e}$ 252-262 $MeNHCO\Theta^+ CONHMe$; $\frac{m}{e}$ 238-247 $MeNHCO\Theta CONH^+$;

$\frac{m}{e}$ 223-232 $MeNHCO\Theta CO^+$; $\frac{m}{e}$ 195-204 $MeNHCO\Theta^+$;

$\frac{m}{e}$ 167-174 θCO^+; $\frac{m}{e}$ 132-146 θ^+; $\frac{m}{e}$ 126-131 ($\frac{m}{2e}$ 252-262)

$MeNHCO\theta^{2+}CONHMe$; $\frac{m}{e}$ 66-73 ($\frac{m}{2e}$ 132-146) θ^{2+}.

5.2(d) PREPARATION OF MeNHCOθ'CONHMe

$$Li\theta'Li \quad + \quad 2MeNCO \xrightarrow[\text{ii) } H^+]{\text{i) Ether/Toluene}} MeNHCO\theta'CONHMe$$

i) EXPERIMENTAL

MeNHCOθ'CONHMe was prepared in a similar manner to PhNHCOθ'CONHPh (see 5.2(a)).

ii) RESULTS

Yield = 72%

Analysis

	C	H	N	B	O
% FOUND	28.2	7.4	9.9	40.7	-
MeNHCOθ'CONHMe requires	27.9	7.0	10.8	41.8	12.4

I.R.

The following vibrations in the infra-red spectrum could be assigned:- secondary amide NH stretch (3395 cm^{-1} (s,br)); B-H stretch (2590 cm^{-1}(s)); CO stretch (1668 cm^{-1} (s)); Cage vibrations (735 cm^{-1}(s)).

Mass Spectrum

The mass spectrum showed a number of carboranyl isotope patterns; the following could be assigned:-

$\frac{m}{e}$ 252-262 $MeNHCO^{+}\theta'CONHMe$; $\frac{m}{e}$ 238-247 $MeNHCO\theta'CONH^+$;

$\frac{m}{e}$ 223-232 $MeNHCO\theta'CO^+$; $\frac{m}{e}$ 195-204 $MeNHCO\theta'^{+}$;

$\frac{m}{e}$ 167-174 $\Theta'CO^+$; $\frac{m}{e}$ 132-146 Θ'^+; $\frac{m}{e}$ 126-131 ($\frac{m}{2e}$ 252-262)

$MeNHCO^{2+}\Theta'CONHMe$; $\frac{m}{e}$ 66-73 ($\frac{m}{2e}$ 132-146) Θ'^{2+}.

5.2(e) PREPARATION OF ${}^tBuNHCO\Theta'CONH^tBu$

$$Li\Theta'Li + 2\,{}^tNuNCO \xrightarrow[\text{ii) } H^+]{\text{i) Ether/Toluene}} {}^tBuNHCO\Theta'CONH^tBu$$

i) EXPERIMENTAL

${}^tBuNHCO\Theta'CONH^tBu$ was prepared in a similar manner to $PhNHCO\Theta'CONHPh$.

ii) RESULTS

Yield = 81%

Melting point of ${}^tBuNHCO\Theta'CONH^tBu$ = 118-120°C

Analysis

	C	H	N	B	O
% FOUND	42.4	8.7	8.3	30.4	-
${}^tBuNHCO\Theta'CONH^tBu$ requires	42.1	8.8	8.2	31.6	9.4

I.R.

The following vibrations in the infra-red could be assigned:- secondary amide N-H stretch (3390 cm^{-1}(s,br)), B-H stretch (2540 cm^{-1}(s)); CO stretch (1615 cm^{-1}(s)), Cage vibrations (729 cm^{-1}(s)).

Mass Spectrum

The mass spectrum showed a number of carboranyl isotope patterns; the following could be assigned:-

$\frac{m}{e}$ 336-344 $^{t}BuNHCO^{+}\Theta'CONH^{t}Bu$; $\frac{m}{e}$ 321-329 $Me_2C^{+}NHCO\Theta'CONH^{t}Bu$;

$\frac{m}{e}$ 306-314 $Me^{+}CNHCO\Theta'CONH^{t}Bu$; $\frac{m}{e}$ 279-287 $^{t}BuNHCO\Theta'CONH^{+}$;

$\frac{m}{e}$ 264-272 $^{t}BuNHCO\Theta'CO^{+}$; $\frac{m}{e}$ 236-244 $^{t}BuNHCO\Theta'^{+}$;

$\frac{m}{e}$ 192-200 $CO\Theta'CO^{+}$; $\frac{m}{e}$ 168-172 ($\frac{m}{2e}$ 336-344);

$\frac{m}{e}$ 164-172 $\Theta'CO^{+}$; $\frac{m}{e}$ 132-146 Θ'^{+}; $\frac{m}{e}$ 66-73

($\frac{m}{2e}$ 132-146) Θ'^{2+}.

5.3 THE ATTEMPTED HYDROLYTIC DEGRADATION OF A SERIES OF CARBORANYL-AMIDE DERIVATIVES

It is known that organic amides, RCONHR$'$ are the least susceptible of the various acid derivatives of general formula RCOX (where X = Cl, OH, RNH, OR) to nucleophilic attack at the carbonyl carbon. They are hydrolytically degraded to their acids by moderately concentrated alkali or acid and are only slowly hydrolysed by boiling water. In base the carboxylate anion and ammonia gas are formed, whereas in acid, the products are the carboxylic acid and ammonium ion.

$$RCONH_2 + OH^- \xrightarrow{\text{Heat}} RCOO^- + NH_3$$

$$RCONH_2 + H_3O^+ \xrightarrow{\text{Heat}} RCOOH + NH_4^+$$

The reason the organic amides are less susceptible to nucleophilic attack at the carbonyl carbon stems from the fact that the unshared electron pair on nitrogen can supply electron density to the carbonyl group.

In this section we attempted to hydrolytically degrade a series of carboranyl-amide derivatives of general formulae RNHCOΘCONHR and $\underset{\smile}{\overset{\frown}{R}}$NHCO$\Theta'$CONHR (where R = Me, Ph, ^{t}Bu), to assess whether these derivatives exhibit similar stability to hydrolytic degradation as exhibited by the organic amides, and also to determine whether the bulk and inductive effect of the R groups attached to the nitrogen affects the stability of the carboranyl-amides towards hydrolytic degradation.

i) EXPERIMENTAL

(a) The Attempted Degradation of PhNHCOΘCONHPh by Boiling Water

PhNHCOΘCONHPh (1.0 g) was placed in a round bottom flask and to this was added distilled water (50 ml). The PhNHCOΘCONHPh/water mixture was stirred at room temperature for 10 minutes before the slurry was heated to 90-95°C. The slurry was stirred vigorously and the temperature maintained at 90-95°C for 24 hours. After this time the slurry was cooled and extracted with diethyl ether. The ether layer was separated, dried over anhydrous $MgSO_4$, filtered and the ether removed under vacuum leaving an off-white solid. This solid was positively identified as PhNHCOΘCONHPh.

ii) RESULTS

Weight of PhNHCOΘCONHPh used = 1.0 g
Weight of PhNHCOΘCONHPh recovered = 0.96 g

Weight loss = 0.04 g
Therefore % loss = 4%

Melting point of off-white solid = 107-109°C

Analysis

	C	H	N	B	O
% FOUND	51.0	6.1	7.2	27.9	-
PhNHCOΘCONHPh requires	50.3	5.8	7.3	28.3	8.4

I.R.

The following vibrations in the infra-red spectrum could be assigned:- secondary amide N-H stretch (3395 cm^{-1}(s,br)); B-H stretch (2570 cm^{-1}(s)); CO stretch 1685 cm^{-1}(s)); Aromatic C=C stretch (1599 cm^{-1}); Cage vibrations (725 cm^{-1}(s)); Mono-substituted benzene ring (690 cm^{-1}(s)).

The mass spectrum was found to be identical to that for PhNHCOΘCONHPh.

From the relatively small weight loss incurred one may conclude that the - NHCO - linkages in the carboranylamide, PhNHCOΘCONHPh, are moderately stable to boiling water over long periods.

The above degradation experiment was repeated for PhNHCOΘ'CONHPh, MeNHCOΘCONHMe, MeNHCOΘ'CONHMe and ^{t}BuNHCOΘ'CONH^{t}Bu. The results from these degradation experiments are summarized on Table 5.3.1.

(b) The Attempted Degradation of PhNHCOΘCONHPh by 20% aqueous HCl

PhNHCOΘCONHPh (1.2 g) was placed in a round bottom flask and to this was added 50 ml of a 20% aqueous HCl solution. The PhNHCOΘCONHPh/20% aqueous HCl mixture was stirred vigorously and heated to 60-70^{o}C for several hours. After this time the solution was extracted with ether, the ether was dried over anhydrous $MgSO_4$, filtered and the ether removed under vacuum leaving an off-white solid. The aqueous layer was made basic and extracted with ether. The ether was dried over anhydrous $MgSO_4$, filtered and the ether removed under vacuum, no material was recovered from this extract. The off-white solid was positively identified as PhNHCOΘCONHPh.

RESULTS

Weight of PhNHCOΘCONHPh used = 1.2 g
Weight of PhNHCOΘCONHPh recovered = 1.18 g
Weight of PhNHCOΘCONHPh lost = 0.02 g

Therefore % lost = 1.7%

Melting point of off-white solid = 108-110°C

Analysis

	C	H	N	B	O
% FOUND	50.8	6.1	7.2	28.0	-
PhNHCOΘCONHPh requires	50.3	5.8	7.3	28.3	8.4

The infra-red and mass spectral data were found to be identical to those for PhNHCOΘCONHPh (see 5.2(b)). From the relatively small weight loss incurred one may conclude that the - NHCO - linkages in PhNHCOΘCONHPh are moderately stable to attack by 20% aqueous HCl at elevated temperatures (60-70°C).

The above degradation experiment was repeated for PhNHCOΘ'CONHPh, MeNHCOΘCONHMe, MeNHCOΘ'CONHMe and ^{t}BuNHCOΘ'CONH^{t}Bu. The results from these degradation experiments are summarised on Table 5.3.1.

(c) The Attempted Degradation of PhNHCOΘCONHPh by 20% aqueous NaOH solution

PhNHCOΘCONHPh (1.0 g) was placed in a round bottom flask and to this was added 50 ml of a 20% aqueous NaOH solution. The mixture was stirred vigorously at room temperature for several hours. No change was observed during this period and so the temperature was raised slowly from 20 to 70°C. The mixture was stirred vigorously for 48 hours at 70°C during which time the solution had become pale yellow. The NaOH solution was extracted with ether, the ether layer was separated, dried over anhydrous $MgSO_4$, filtered and the ether removed under vacuum leaving an off-white solid. This off-white solid was identified as ortho-carborane, HΘH. The aqueous layer was acidified and extracted with ether. The ether layer was separated, dried over anhydrous $MgSO_4$, filtered and the ether removed under vacuum leaving a pale yellow liquid. This liquid was identified as aniline, $PhNH_2$.

RESULTS

Weight of off-white solid obtained = 0.29 g.
Theoretical amount of HΘH which could be obtained on complete degradation of PhNHCOΘCONHPh = 0.38 g.

Melting Point of off-white solid = 289-290°C
(Lit. M.Pt of HΘH = 287-288°C)

Analysis

	C	H	N	B	O
% FOUND FOR OFF-WHITE SOLID	17.2	8.8	ABSENT	74.3	-
PhNHCOΘCONHPh requires	50.3	5.8	7.3	28.3	8.4
HΘH requires	16.6	8.3	-	75.0	-
% FOUND FOR YELLOW LIQUID	76.4	14.9	7.8	ABSENT	-
$PhNH_2$ (aniline) requires	76.6	14.8	7.4	-	-

I.R.

The following vibrations in the infra-red spectrum of the off-white solid could be assigned:- Carboranyl C-H stretch (3069 cm^{-1}(s)); B-H stretch (2590 cm^{-1}(s)); Cage vibrations (716 cm^{-1}(s)).

The infra-red spectrum of the off-white solid was found to be identical to that of o-carborane. The infra-red spectrum of the pale yellow liquid was found to be identical to that for aniline, $PhNH_2$.

Mass Spectrum

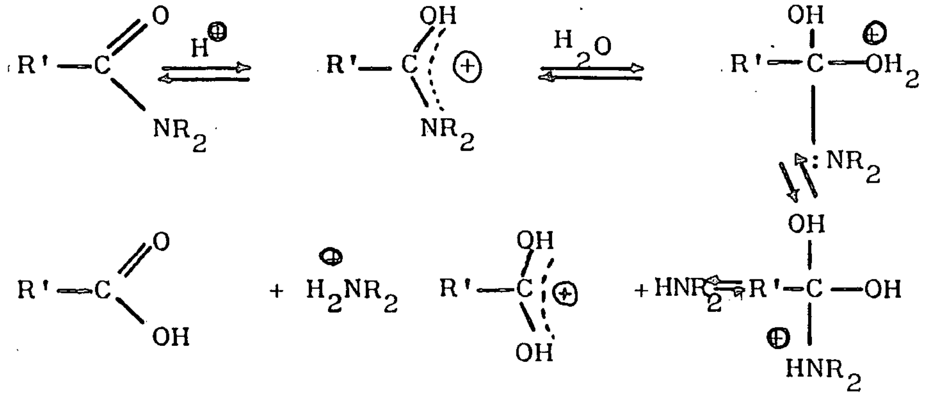
The mass spectrum for the off-white solid showed an M+1 peak at $\frac{m}{e}$ 146 where M = $^{12}C_2\ ^{11}B_{10}\ ^{1}H_{12}$ with a corresponding isotope pattern from $\frac{m}{e}$ 132-146.

It would appear from the results obtained that PhNHCOΘCONHPh is hydrolytically cleaved by 20% aqueous NaOH at elevated temperatures over a 48 hour period giving as degradation products o-carborane, HΘH and aniline, $PhNH_2$.

The above degradation experiment was repeated for PhNHCOΘ'CONHPh, MeNHCOΘCONHMe, MeNHCOΘ'CONHMe and ^{t}BuNHCOΘ'CONH^{t}Bu. The results from these degradation reactions are summarised on Table 5.3.1.

5.4. DISCUSSION

The carboranyl amide derivatives studied were found to be hydrolytically stable to boiling water and hot aqueous hydrochloric and sulphuric acids over long periods (see Table 5.3.1). It is interesting to note that organic amides such as PhNHCOPh, unlike the carboranyl amides, are totally and fairly readily hydrolytically degraded by hot acid, the mechanism shown by kinetic studies to be as follows:- (165,166,167)



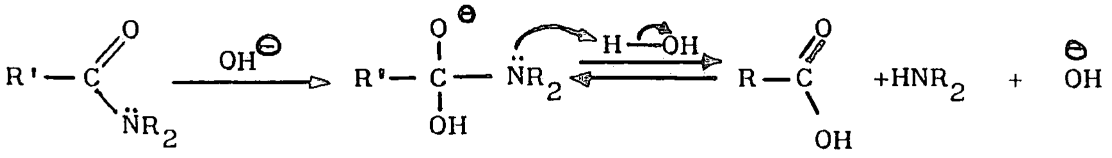
The significant difference in stability exhibited by the carboranyl amides to that exhibited by organic amides may be explained by considering both the above mechanism and the electron-withdrawing nature of the cage. If R' in the above mechanism was an electron-withdrawing group, such as a carboranyl cage, then the oxygen of the carbonyl group would be more positive due to the electron pull of the cage and this would subsequently make attack by H^+ less likely. The overall consequence of this being that the carboranyl-amides are less susceptible to acid degradation.

Although the carboranyl amides were found to exhibit a high degree of resistance to hydrolytic degradation by boiling water and hot acid significant differences were observed when the same carboranyl-amides were hydrolytically degraded by hot 20-30% aqueous NaOH. All of the carboranyl amides studied were found to be totally degraded by hot 20-30% aqueous NaOH over a 48 hour period, giving as degradation products the free carborane and a primary amine, the nature of which was dependent on the carboranyl-amide being degraded (see Table 5.3.1).

$$\mathrm{PhNHCO\Theta'CONHPh} \xrightarrow[48\mathrm{hr},\ 60-70^{\circ}\mathrm{C}]{20\%\ \mathrm{aq.\ NaOH}} 2\mathrm{PhNH_2} + \mathrm{H\Theta'H} + 2\mathrm{CO_2}$$

ANILINE m-CARBORANE

In the alkaline hydrolysis of organic amides the nucleophilic hydroxide ion adds to the carbonyl carbon to form a tetrahedral intermediate which, with the help of the aqueous solvent expels the nitrogen as the free amine.



Tetrahedral Intermediate

We believe that in the alkaline hydrolysis of the carboranyl amides, the nucleophilic hydroxide ion adds to the carbonyl

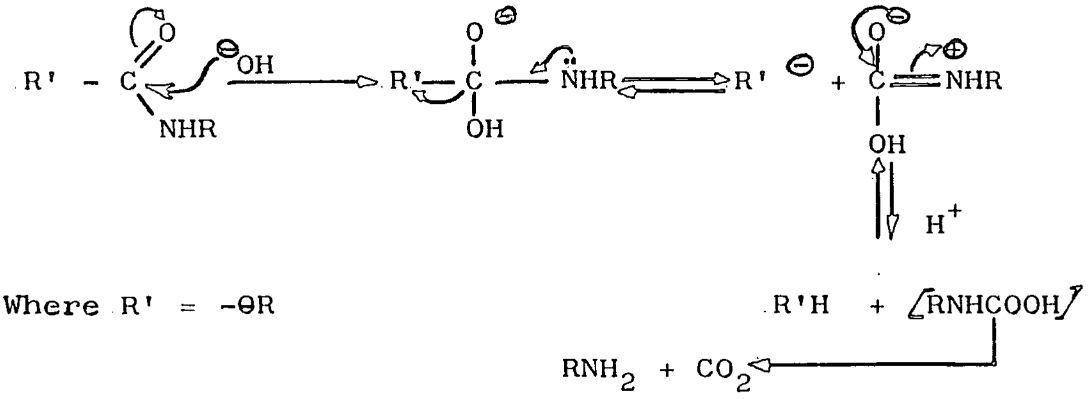
Table 5.3.1

COMPOUND	DEGRADATION CONDITIONS		PRODUCTS OF DEGRADATION
	INEFFECTIVE	EFFECTIVE	
PhNHCOΘCONHPh	a) Boiling water for 24 hours		PhNHCOΘCONHPh
	b) 20% aqu. HCl, for 10 hours at 70°C		"
		c) 20% aqu. NaOH for 48 hours, at 70°C	2PhNH$_2$ + HΘH
PhNHCOΘ'CONHPh	a) Boiling water for 48 hours		PhNHCOΘ'CONHPh
	b) 20% aqu. HCl, for 10 hours at 60°C		"
		c) 20% aqu. NaOH for 48 hours, at 70°C	2PhNH$_2$ + HΘ'H
MeNHCOΘCONHMe	a) Boiling water for 48 hours		MeNHCOΘCONHMe
	b) 20% aqu. H_2SO_4, for 10 hours at 60°C		"
		c) 20% aqu. NaOH for 48 hours, at 70°C	2MeNH$_2$ + HΘH
MeNHCOΘ'CONHMe	a) Boiling water for 48 hours		MeNHCOΘ'CONHMe
	b) 20% aqu. HCl, for 10 hours at 70°C		"
	c) 30% aqu. HCl, for 48 hours at 70°C		"
		d) 20% aqu. NaOH for 48 hours at 70°C	2MeNH$_2$ + HΘ'H

Table 5.3.1

COMPOUND	DEGRADATION CONDITIONS		PRODUCTS OF DEGRADATION
	INEFFECTIVE	EFFECTIVE	
$^{+}$BuNHCOΘ'CONH^{+}Bu	a) Boiling water for 48 hours		$^{+}$BuNHCOΘ'CONH^{+}Bu
	b) 20% aqu. HCl, for 48 hours at 70°C		"
	c) 20% aqu. H_2SO_4, for 20 hours at 70°C		"
		d) 20% aqu. NaOH for 48 hours, at 70°C	2 $^{+}BuNH_2$ + HΘ'H

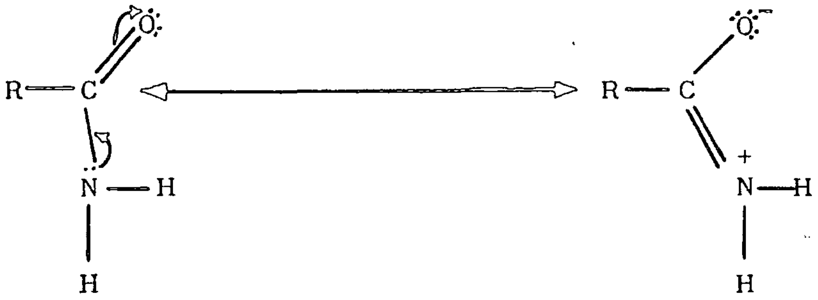
carbon producing a similar tetrahedral intermediate to that shown above. However when this intermediate comes in contact with water the free carborane and an unstable carbamic acid intermediate are produced rather than the expected carboranyl-dicarboxylic acid and free amine. It seems likely that if R' in the tetrahedral intermediate shown above was an electron-withdrawing carboranyl cage then the pull of electron density away from both the oxygen and nitrogen of the amide group would make the next stage of the mechanism unfavourable. We believe that when R' is an electron withdrawing group the following alternative mechanism may occur.



Where R' = -ΘR

One piece of evidence which favours this mechanism is that the experimentally observed products of base degradation of the carboranyl amides were the free carboranes and free amines rather than the carboranyl dicarboxylic acids and free amines.

It is interesting to compare the stability of the carboranyl amides and carboranyl ketones to base degradation (see Tables 4.3.1 and 5.3.1). The carboranyl amides tend to exhibit greater stability towards attack by strong bases than the carboranyl ketones. This difference may be due to the fact that in the carboranyl amides the unshared pair of electrons on nitrogen can supply electron density to the carbonyl group and consequently the amides are less susceptible to nucleophilic attack than are the carboranyl ketones. Note this phenomenon applies to all organic amides as well as the carboranyl amides and can be represented by the two resonance contributors:-



CHAPTER 6

THE PREPARATION AND HYDROLYTIC DEGRADATION OF A SERIES OF BORANYL-CARBORANE DERIVATIVES

CHAPTER 6

6.1 INTRODUCTION

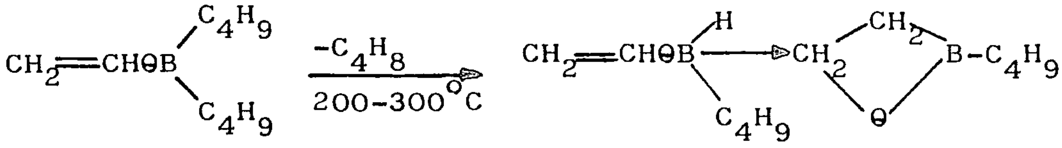
In contrast to certain other areas of carborane derivative chemistry very little has been published on the synthesis and properties of the boranyl carborane derivatives. These derivatives have been synthesized by the reaction of trihalo-, alkyldihalo- and dialkyl monohalo boranes with lithio carboranes. (36,37,168)

$$\mathrm{R\theta Li} + \mathrm{R_2'BCl} \xrightarrow{\mathrm{LiCl}} \mathrm{R\theta BR'_2}$$

Where R = $i\text{-}C_3H_7$, Et, $CH_2{=}CH$, $CH_2{=}\underset{\substack{|\\ \mathrm{Me}}}{C}$

R' = Bu, i-Bu

Although the thermal degradation of a number of boranyl-carborane derivatives has been investigated,



very little is known of the hydrolytic stability of these derivatives. It was with this thought in mind that we set out to prepare and study the hydrolytic stability of a series of boranyl o- and m-carboranyl derivatives.

6.2(a) PREPARATION OF MeθBPh$_2$

$$\mathrm{Me\theta Li} + \mathrm{Ph_2BCl} \xrightarrow[\mathrm{TOLUENE}]{\mathrm{-LiCl}} \mathrm{Me\theta BPh_2}$$

i) EXPERIMENTAL

Methyl-o-carborane (1.58 g, 10 mmol.) was dissolved in dry toluene (40 ml) and the solution cooled before 6.54 ml (10 mmol.) of a 1.53M n-butyl lithium solution in pentane was added. The reaction mixture was heated for 1 hour before being cooled to 0°C and 1.3 ml (10 mmol.) of freshly vacuum distilled diphenyl boron chloride added by syringe. The reaction mixture was heated for 2 hours during which time a white precipitate appeared. The slurry was cooled and filtered. The filtrand was washed several times with toluene and dried under vacuum. The solvent was removed from the filtrate leaving a clear pale yellow viscous liquid.

ii) RESULTS

Yield of pale yellow oil = 72%

Analysis

	C	H	B	Li	Cl
% FOUND FOR WHITE SOLID	ABSENT	ABSENT	ABSENT	15.8	80.7
LiCl requires	-	-	-	16.4	83.6
% FOUND FOR PALE YELLOW OIL	53.9	6.9	36.1	ABSENT	ABSENT
$\mathrm{Me}\ominus\mathrm{BPh}_2$ requires	55.9	7.1	36.9	ABSENT	ABSENT

I.R.

The infra-red spectrum showed the following peaks:-
ν max, CONTACT FILM (cm^{-1}), 3056, 2932, 2572(s), 1594, 1477(sh), 1435(s), 1388, 1264(s), 1185(w), 1135(w), 1098(w), 1071(sh), 1031(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 (3056 cm^{-1}); aliphatic C-H stretch (2932 cm^{-1}); B-H stretch (2572 cm^{-1}); $\mathrm{C}\overset{\text{- - -}}{\text{——}}\mathrm{C}$ stretch (1594 cm^{-1}); B-C stretch (1264 cm^{-1}); C-B-C Cage vibrations (727 (cm^{-1})).

Mass spectrum

The mass spectrum showed a number of peaks with carboranyl isotope patterns. These were identified as,

$\frac{m}{e}$ 314-324 $Me\Theta^{+}BPh_2$; $\frac{m}{e}$ 237-247 $Me\Theta\overset{+}{B}Ph$

$\frac{m}{e}$ 165 (Ph_2B^{+}); $\frac{m}{e}$ 147-160 $Me\Theta^{+}$; $\frac{m}{e}$ 132-146

Θ^{+}; $\frac{m}{e}$ 73.5-80 ($\frac{m}{2e}$ 147-160 $Me\Theta^{2+}$).

6.2(b) PREPARATION OF $(Me\Theta)_2BPh$

$$2Me\Theta Li \quad + \quad PhBCl_2 \xrightarrow{\text{TOLUENE}} (Me\Theta)_2BPh \quad + \quad 2LiCl$$

i) EXPERIMENTAL

$(Me\Theta)_2BPh$ was prepared in a similar manner to $Me\Theta BPh_2$. (see 6.2(a))

ii) RESULTS

Yield of $(Me\Theta)_2BPh$ = 64%

Analysis

	C	H	B	Cl
% FOUND FOR PALE BROWN OIL	36.1	8.0	54.8	ABSENT
$(Me\Theta)_2BPh$ requires	35.8	7.7	56.4	-

I.R.

The infra-red spectrum showed the following peaks:-

ν max, CONTACT FILM (cm^{-1}), 3080, 3066, 3054(w), 3029, 2956, 2925, 2870, 2580(s), 1958(w), 1816(w), 1600, 1478, 1440, 1422, 1414(sh), 1386, 1365(sh), 1350, 1334(sh), 1253(sh), 1224, 1190, 1150, 1120(w), 1034, 996(w), 940, 920, 854, 800, 728(s), 710, 700(sh), 687(s), 590(w), 580(w).

The following vibrations could be assigned:- Aromatic C-H stretch (3080-3029 cm^{-1}); aliphatic C-H stretch (2956-2870 cm^{-1}); B-H stretch (2580 cm^{-1}); C$\equiv$C stretch (1600 cm^{-1}); B-Ph, (B-C stretch) (1253-1224 cm^{-1}); Cage vibrations (728 cm^{-1}); Out of plane C-H bend, Ph ring (687 cm^{-1}).

Mass Spectrum

The mass spectrum showed a number of peaks with a carboranyl isotope pattern. These were identified as:-

$\frac{m}{e}$ 393-404 $(\mathrm{Me}\theta)_2\overset{+}{\mathrm{B}}\mathrm{Ph}$; $\frac{m}{e}$ 236-247 $\mathrm{Me}\theta\overset{+}{\mathrm{B}}\mathrm{Ph}$;

$\frac{m}{e}$ 147-160 $\mathrm{Me}\theta^+$; $\frac{m}{e}$ 132-146 θ^+; $\frac{m}{e}$ 88 PhB^+;

$\frac{m}{e}$ 73.5-80 ($\frac{m}{2e}$ 147-160 $\mathrm{Me}\theta^{2+}$).

6.2(c) PREPARATION OF $(\mathrm{H}\theta')_2$ BPh

$$2\mathrm{H}\theta'\mathrm{Li} + \mathrm{PhBCl}_2 \xrightarrow{\text{TOLUENE}} (\mathrm{H}\theta')_2\mathrm{BPh} + \mathrm{LiCl}$$

i) EXPERIMENTAL

$(\mathrm{H}\theta')_2\mathrm{BPh}$ was prepared in a similar manner to $\mathrm{Me}\theta\mathrm{BPh}_2$ and $(\mathrm{Me}\theta)_2\mathrm{BPh}$. (See 6.2(a))

ii) RESULTS

Yield of pale yellow oil, $(\mathrm{H}\theta')_2\mathrm{BPh}$ = 61%

Analysis

	C	H	B	Cl
% FOUND	31.8	8.4	59.8	ABSENT
$(\mathrm{H}\theta')_2\mathrm{BPh}$ requires	32.1	7.2	60.7	-

I.R.

The infra-red spectrum showed the following peaks:-

ν max, CONTACT FILM (cm^{-1}), 3081(m), 3061(s), 3053(w), 3030, 2954, 2924, 2869, 2592(s), 1958(w), 1816(w), 1600(s), 1478, 1441, 1422, 1386, 1352, 1332(sh), 1250, 1225, 1158, 1140(sh), 1069, 1022, 990, 940, 920, 805, 720(s), 695(s), 645(w), 595(s).

The following vibrations could be assigned:- Aromatic C-H stretch (3081-3030 cm^{-1}); Carboranyl C-H stretch (3061 cm^{-1}); B-H stretch (2592 cm^{-1}); $C \equiv C$ stretch (1600 cm^{-1}); B-C stretch (1250-1225 cm^{-1}); C-B-C cage vibrations (1158-1022 cm^{-1}); Cage vibrations (720 cm^{-1}); aromatic out of plane C-H bend (695 cm^{-1}).

Mass Spectrum

The mass spectrum showed a number of peaks with carboranyl isotope patterns. These were identified as:-

$\frac{m}{e}$ 365-376 $(H\Theta')_2B^+Ph$; $\frac{m}{e}$ 222-233 $H\Theta'\overset{+}{B}Ph$

$\frac{m}{e}$ 131-145 $H\Theta'^+$; $\frac{m}{e}$ 88 PhB^+; $\frac{m}{e}$ 65-73 ($\frac{m}{2e}$ 131-145, $H\Theta'^{2+}$).

6.2(d) PREPARATION OF $Ph_2B\Theta'BPh_2$

$$Li\Theta'Li + 2Ph_2BCl \xrightarrow{TOLUENE} Ph_2B\Theta'BPh_2 + 2LiCl$$

i) EXPERIMENTAL

$Ph_2B\Theta'BPh_2$ was prepared in a similar manner to $Me\Theta BPh_2$. (See 6.2(a))

ii) RESULTS

Yield of opaque viscous oil = 82%

Analysis

	C	H	B	Cl
% FOUND FOR OPAQUE OIL	60.3	4.5	26.9	ABSENT
$Ph_2B\Theta'BPh_2$ requires	61.1	4.2	27.5	-

I.R.

The infra-red spectrum showed the following peaks:-
ν max, CONTACT FILM (cm^{-1}), 3060(sh), 3045(s), 3020(sh)
2950(s), 2920(s), 2860(m), 2582(s), 1590(s),
1440(s,br), 1360(br), 1345(s), 1290(w), 1230(s,br),
1205(m), 1112(m), 1080(s), 998(s), 939, 910
890, 840, 780(sh), 730(s), 695(s), 649(w), 592(s),
461(w), 440(s).

The following vibration could be assigned:- Aromatic C-H stretch (3060-3020 cm^{-1}); B-H stretch (2582 cm^{-1}); $C\underline{---}C$ stretch (1590 cm^{-1}); B-C stretch (1440-1230 cm^{-1}); C-B-C cage vibrations (1205-1080 cm^{-1}); Cage vibrations (730 cm^{-1}); aromatic C-H o.o.p. (695 cm^{-1}).

Mass Spectrum

The mass spectrum showed a number of peaks with a carboranyl isotope pattern. These were identified as:-

$\frac{m}{e}$ 464-475 $Ph_2B\Theta'^{+}BPh_2$; $\frac{m}{e}$ 387-398 $Ph_2B\Theta'B^{+}Ph$;

$\frac{m}{e}$ 299-310 $Ph_2B\Theta'^{+}$; $\frac{m}{e}$ 222-233 $PhB\overset{+}{\Theta}'$;

$\frac{m}{e}$ 165 Ph_2B^{+}; $\frac{m}{e}$ 132-146 Θ'^{+}; $\frac{m}{e}$ 66-73($\frac{m}{2e}$ 132-146 Θ'^{2+}).

6.3 THE ATTEMPTED HYDROLYTIC DEGRADATION OF A SERIES OF BORANYL CARBORANE DERIVATIVES

(a) The Attempted Hydrolytic Degradation of MeΘBPh$_2$ by Boiling Water

(i) EXPERIMENTAL

MeΘBPh$_2$ (1 g.) was placed in a round bottom flask and 50 ml of distilled water was added. The mixture was stirred at 70-80°C for 8 hours before being cooled to room temperature and 30 ml of a 5% aqueous NaOH solution added. The basic solution was extracted with diethyl ether and the ether layer separated and dried over anhydrous $MgSO_4$. The ether was filtered and the solvent removed under vacuum leaving an off-white solid. The aqueous layer was acidified and extracted with ether. The ether layer was dried over anhydrous $MgSO_4$, filtered and the ether removed under vacuum leaving a white solid.

(ii) RESULTS (see Table 6.3.1)

Melting point of off-white solid = 209-210°C
(Lit. Melting point of MeΘH = 210-211°C)

Melting point of white solid = 263-266°C
(Lit. Melting point of Ph$_2$BOH = 264-267°C)

Analysis

	C	H	B	O
% FOUND (OFF-WHITE SOLID)	23.1	9.2	67.8	-
MeΘH requires	22.8	8.8	68.4	-
MeΘBPh$_2$ requires	55.9	7.1	36.9	-
% FOUND (WHITE SOLID)	77.9	6.5	6.1	-
Ph$_2$BOH requires	79.0	6.0	5.9	8.8

I.R.

FOR OFF-WHITE SOLID:- The following vibrations in the infra-red spectrum could be assigned:- Carboranyl C-H stretch (3058 cm^{-1}); B-H stretch (2610-2530 cm^{-1}); Cage vibrations (720 cm^{-1}).

The infra-red spectrum of the off-white solid was found to be identical to the infra-red spectrum of methyl-o-carborane.

FOR WHITE SOLID:- The following vibrations in the infra-red spectrum could be assigned:- B-OH stretch (3605-3490 cm^{-1}); aromatic C-H stretch (3080-3020 cm^{-1}); $C\overset{\cdots}{=}C$ stretch (1598 cm^{-1}); B-Ph (1439 cm^{-1}); B-C symmetric stretch (690 cm^{-1}).

Mass Spectrum

The mass spectrum for the off-white solid showed an M+1 peak at $\frac{m}{e}$ 161 where M = $^{12}C_3\ ^{11}B_{10}\ ^{1}H_{14}$ with a corresponding isotope pattern from $\frac{m}{e}$ 147-160.

(b) The Attempted Hydrolytic Degradation of $(MeO)_2BPh$ by Warm Water

(i) EXPERIMENTAL

$(MeO)_2BPh$ (1.3 g) was placed in a round bottom flask and 60 ml. of distilled water was added. The mixture was stirred at 40-50°C for 1-2 hours before being cooled to room temperature and 30 ml of a 5% aqueous NaOH solution added. The basic solution was extracted with diethyl ether and the ether layer was separated and dried over anhydrous $MgSO_4$. The ether was filtered and the solvent removed under vacuum leaving an off-white solid, which was positively identified as methyl-o-carborane. The aqueous layer was acidified and extracted with ether. The ether layer was dried over anhydrous $MgSO_4$, filtered and the ether removed under vacuum leaving a white solid which was identified as benzeneboronic acid, $PhB(OH)_2$.

(ii) RESULTS (see Table 6.3.1)

Melting point of off-white solid = 210-211°C
(Lit. M.pt of $Me\Theta H$ = 210-211°C)

Melting point of white solid = 213-215°C
(Lit. Mp.pt of $PhB(OH)_2$ = 215-216°C)

Analysis

	C	H	B	O
% FOUND (OFF-WHITE SOLID)	21.8	9.0	67.1	-
$Me\Theta H$ requires	22.8	8.8	68.4	-
$(Me\Theta)_2BPh$ requires	35.8	7.7	56.4	-
% FOUND (WHITE SOLID)	60.3	5.1	8.4	-
$PhB(OH)_2$ requires	59.1	5.7	8.8	26.2

I.R.

FOR OFF-WHITE SOLID:- The infra-red spectrum of the off-white solid was found to be identical to that of methyl-o-carborane.

FOR WHITE SOLID:- The following vibrations in the infra-red spectrum could be assigned:- B-OH stretch (3610-3480 cm^{-1}); aromatic C-H stretch (3070-3025 cm^{-1}); $C\underline{\overset{- - -}{\quad}}C$ stretch (1599 cm^{-1}); B-Ph (1438 cm^{-1}); B-O stretch (1350-1330 cm^{-1}); B-C asymmetric stretch (1298 cm^{-1}); B-C sym. stretch (688 cm^{-1}).

Mass Spectrum

The mass spectrum for the off-white solid was identical to that for methyl-o-carborane.

(c) The Attempted Hydrolytic Degradation of $(H\Theta')_2BPh$ by Boiling Water

(i) EXPERIMENTAL (see 6.3(a) and Table 6.3.1)

(ii) RESULTS

Melting point of white crystalline solid = 261-264°C
(Lit. M.pt of HΘ'H = 263-265°C)

Melting point of white solid ($PhB(OH)_2$) = 214-216°C
(Lit. M.pt of Benzeneboronic acid = 215-216°C)

Analysis

	C	H	B	O
% FOUND WHITE CRYSTALLINE SOLID	16.1	9.2	73.8	-
HΘ'H requires	16.7	8.3	75	-
$(H\Theta')_2BPh$ requires	32.1	7.2	60.7	-
% FOUND WHITE SOLID	58.7	5.2	9.3	-
$PhB(OH)_2$ requires	59.1	5.7	8.8	26.2

I.R.

FOR WHITE CRYSTALLINE SOLID:- The following vibrations in the infra-red spectrum could be assigned:- Carboranyl C-H stretch (3055 cm^{-1}); B-H stretch (2592 cm^{-1}); C-B-C vibrations (1159-990 cm^{-1}); Cage vibrations (719 cm^{-1}).

The infra-red spectrum of the white crystalline solid was found to be identical to that of meta-carborane, HΘ'H.

FOR WHITE SOLID:- The following vibrations in the infra-red spectrum could be assigned:- B-OH stretch (3610-3480 cm^{-1}); aromatic C-H stretch (3070-3025 cm^{-1}); $C\equiv C$

stretch (1599 cm^{-1}); B-Ph (1438 cm^{-1}); B-O stretch (1350-1330 cm^{-1}); B-C asym. stretch (1298 cm^{-1}); B-C sym stretch (688 cm^{-1}).

Mass Spectrum

The mass spectrum of the white crystalline solid showed an M+1 peak at $\frac{m}{e}$ 147 where M = $^{12}C_2\ ^{11}B_{10}\ ^{1}H_{12}$ with a corresponding isotope pattern from $\frac{m}{e}$ 136-146.

(d) The Attempted Hydrolytic Degradation of $Ph_2B\Theta'BPh_2$ by Boiling 20% aqueous NaOH

i) EXPERIMENTAL

$Ph_2B\Theta'BPh_2$ (2 g) was placed in a round bottom flask and 60 ml of a 20% aqueous NaOH solution was added. The mixture was stirred vigorously and maintained at 80-90°C for 10 hours before being cooled to room temperature and extracted with diethyl ether. The ether layer was dried over anhydrous $MgSO_4$, filtered and the ether removed under vacuum leaving a white solid. The aqueous layer was acidified and extracted with ether. The ether layer was dried over anhydrous $MgSO_4$, filtered and the ether removed under vacuum leaving an off-white solid.

ii) RESULTS (See Table 6.3.1)

Melting point of white solid = 260-264°C
(Lit. M.pt. of $H\Theta'H$ = 263-265°C)

Melting point of white solid from acidified aqueous layer = 213-215°C
(Lit. M.pt. of $PhB(OH)_2$ = 215-216°C)
(Lit. M.pt. of $Ph_2B(OH)$ = 264-267°C)

Table 6.3.1

COMPOUND	DEGRADATION REACTION CONDITIONS		PRODUCTS OBTAINED
	INEFFECTIVE	EFFECTIVE	
$Me\Theta BPh_2$	(a) Cold water for 3 hours	(b) Boiling water, 8 hours	$Me\Theta BPh_2$ $Me\Theta H + Ph_2BOH$
$(Me\Theta)_2BPh$	(a) Cold water for 1-2 hours	(b) Water 40-50°C for 2 hours	$(Me\Theta)_2BPh$ $2Me\Theta H + PhB(OH)_2$
$(H\Theta')_2BPh$	(a) Cold water for 8 hours	(b) Boiling water, 8 hours	$(H\Theta')_2BPh$ $2\ H\Theta'H + PhB(OH)_2$
$Ph_2B\Theta'BPh_2$	(a) Cold water for 48 hours (b) Boiling water for 10 hours	(c) 20% aqueous NaOH, 80-90°C for 8-10 hours	$Ph_2B\Theta'BPh_2$ $Ph_2B\Theta'BPh_2$ $H\Theta'H + 2PhB(OH)_2 + C_6H_6$

Analysis

	C	H	B	O
% FOUND FOR WHITE SOLID (EXTRACTED FROM BASIC LAYER)	16.4	8.4	74.1	-
$H\Theta'H$ requires	16.7	8.3	75	-
$Ph_2B\Theta'BPh_2$ requires	61.1	4.2	27.5	-
% FOUND FOR WHITE SOLID (EXTRACTED FROM ACID LAYER)	59.8	5.5	9.1	-
$PhB(OH)_2$ requires	59.1	5.7	8.8	26.2
Ph_2BOH requires	79.0	6.0	5.9	8.8

I.R.

FOR WHITE SOLID EXTRACTED FROM BASIC LAYER:- The infra-red spectrum of the white solid was found to be identical to that for meta-carborane, $H\Theta'H$.

FOR WHITE SOLID EXTRACTED FROM ACID LAYER:- The following vibrations in the infra-red spectrum could be assigned:- B-OH stretch (3610-3480 cm^{-1}); aromatic C-H stretch (3070-3025 cm^{-1}); $C\overset{---}{\text{—}}C$ stretch (1599 cm^{-1}); B-Ph (1438 cm^{-1}); B-O stretch (1350-1330 cm^{-1}); B-C asym stretch (1298 cm^{-1}); B-C sym. stretch (688 cm^{-1}).

Mass Spectrum

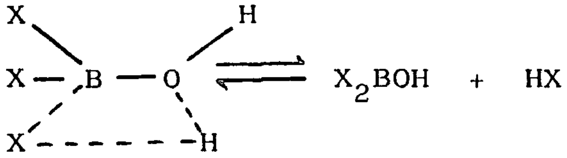
The mass spectrum of the white solid showed an M+1 peak at $\frac{m}{e}$ 147 where M = $^{12}C_{12}$ $^{11}B_{10}$ $^{1}H_{12}$ with a corresponding isotope pattern from $\frac{m}{e}$ 136-146.

6.4 DISCUSSION

It is apparent from the results obtained (see Table 6.3.1) that the hydrolytic degradation of the boranyl-o- and m-carboranes proceeds via cleavage of the exo-skeletal cage carbon to boron bond giving as degradation products the free carborane and either diphenyl-boric or benzeneboronic acid. It also seems apparent that the degree of hydrolytic stability of the exo-skeletal B-C bond can be related to the degree of polarization of this bond. This is clearly shown by the fact that the boranyl-o-carborane derivatives are more readily hydrolytically degraded than the corresponding boranyl-m-carborane derivatives. Further evidence for this comes from the fact that when two cages are attached to one boron atom as in $(Me\Theta)_2BPh$ and $(H\Theta')_2BPh$ the combined pull of electron density is such that the polarization of the exo-skeletal B-C bond is increased and consequently these derivatives are more readily hydrolytically degraded. (See Table 6.3.1)

It is interesting to compare the hydrolytic stability of the boranyl-carborane derivatives to that of other tri-coordinate boranes such as the trihalo-, trialkyl- and triarylboranes. Reactivity among the tricoordinate boranes is primarily a reflection of the Lewis acidity or acceptor strength of the borane and the ease with which a ligand may be displaced, since many reactions of tricoordinate boranes are either nucleophilic additions or nucleophilic additions followed by an elimination. (170)

(i) $BX_3 + OH_2 \rightleftharpoons X_3\ B\ OH_2$

(ii) 

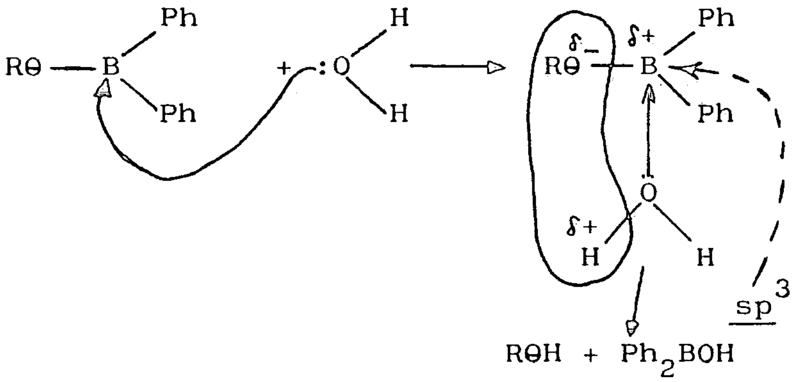
For all strongly electrophilic boranes (i.e. strong Lewis acids such as BCl_3, BBr_3 and Ph_3B) step (i) above is very fast provided that steric factors do not impose a severely restricted orientational angle for effective collision of reactants. With trialkylboranes, which are relatively weak acceptor molecules neither hydrolysis nor complex formation with water occurs at moderate temperatures. For these compounds it is believed that due to the weak Lewis acidity, the concentration may be too small or the lifetime too short lived for the $R_3B\ OH_2$ species shown in the mechanism above, to provide a facile path to R_2BOH, $R\ B(OH)_2$ or $B(OH)_3$ products. (170)

It is worth note that from a purely thermodynamic point of view all of the tricoordinate boranes with the exception of BF_3, should, from bond enthalpy considerations, be readily hydrolytically degraded by water (see Table 6.4.1) It is however clear that the relative stabilities and reactivities of the tricoordinate boranes cannot simply be based on thermodynamic considerations alone. For example Me_3B should from thermodynamic considerations be less stable towards hydrolytic degradation than Ph_3B. However in practice Me_3B is not hydrolytically very sensitive whereas Ph_3B is fairly readily degraded by water. This example clearly shows that other factors such as Lewis acidity, reaction kinetics and steric hindrance must also be considered when looking at the reactivities of the tricoordinate boranes. (170)

Table 6.4.1 (169)

COMPOUND	BOND ENTHALPY TERMS		
	E (B - X) kJmol^{-1}	E (B - C) kJmol^{-1}	E (B - O) kJmol^{-1}
BF_3	644.3		
BCl_3	442.3		
BBr_3	367.1		
$B(OH)_3$			521.7
B_2O_3			523.0
BMe_3		350.9	
BEt_3		344.3	
BPh_3		434.2	

We believe that three factors must be considered when trying to assess the relative stability or reactivity of the boranyl-carborane derivatives. Firstly we must consider the inductive effect of the icosahedral cage which would increase the polarization of the B-C bond, thus making it more susceptible to attack by boiling water or base. Secondly we must consider the fact that the polarization of the B-C bond would increase as the boron atom passed from the sp^2 to sp^3 valence state as shown below, this factor would also make the boranyl-carboranes less stable towards hydrolytic degradation.



Note if we only consider the degree of polarization of the B-C bond then we would expect the boranyl-carborane derivatives to be less stable towards hydrolytic degradation than the triarylboranes. However it is apparent from our studies that the boranyl-carborane derivatives are actually less sensitive to hydrolysis than the triarylboranes. In order to explain this observation we must consider steric factors. It seems likely that the cage, would impose a severely restricted orientational angle for effective collision of reactants, much more so than a phenyl ring and this would subsequently reduce the reactivity of the boranyl-carborane derivatives.

CHAPTER 7

THE PREPARATION AND SOME DERIVATIVE CHEMISTRY OF THE CARBORANYL-C-HYDROXY DERIVATIVES

CHAPTER 7

7.1 INTRODUCTION

Carboranyl-C-hydroxy derivatives

In contrast to certain other areas of carborane derivative chemistry, very little has been published on the synthesis and properties of carboranyl-C-hydroxy derivatives. There are two routes thereto in the literature. One route, (1) which one group of workers found ineffective (2), entails bubbling dry air through a suspension of a lithio-carborane in a hydrocarbon solvent.

$$\mathrm{Me\Theta Li} \xrightarrow[\text{(ii) } H^+]{\text{(i) Dry air}} \mathrm{Me\Theta OH}$$

The other route employes benzoyl peroxide (3);-

$$2\mathrm{R\Theta Li} + (\mathrm{PhCOO})_2 \xrightarrow[\text{(ii) } H^+]{\text{(i) Ether/benzene}} \mathrm{R\Theta OH} + \mathrm{R\Theta COPh} + \mathrm{PhCOOH}$$

Several mono-hydroxy-ortho- and meta-carboranes have been prepared by this latter method in yields of 30-40%. The carboranyl-C-hydroxy derivatives are fairly acidic (pK_a of 1-hydroxy-o-carborane = 5.25; pKa of 1-hydroxy-m-carborane = 8.24; pK_a of phenol = 10) due to the electron withdrawing character of the cage. (1) These derivatives readily react with diazo methane giving the methoxy derivatives. (3)

$$\mathrm{Me\Theta OH} + \mathrm{CH_2N_2} \xrightarrow{\text{HEXANE}} \mathrm{Me\Theta OMe} + \mathrm{N_2}$$

The o-carboranyl-C-hydroxy derivatives react with bases such as triethylamine giving the corresponding salt. These salts will react with acid chlorides producing esters. (3).

$$\mathrm{Me\Theta OH} + \mathrm{Et_3N} \xrightarrow{\text{HEXANE}} \mathrm{Me\Theta OHNEt_3}$$

$$\mathrm{H\Theta OHNEt_3} + \mathrm{RCOCl} \xrightarrow{\text{HEXANE}} \mathrm{H\Theta OOCR} + \mathrm{Et_3NHCl}$$

Where R = Ph, Me

7.2(a1) THE ATTEMPTED PREPARATION OF 1-HYDROXY-2-METHYL-O-CARBORANE

$$\mathrm{Me\Theta H} \xrightarrow{\text{nBuLi}} \mathrm{Me\Theta Li} \xrightarrow[\text{ii) } H_2O/OH^-]{\text{i) Dry Oxygen}} \mathrm{Me\Theta OH} + \mathrm{Me\Theta H}$$

i) EXPERIMENTAL

Methyl-o-carborane (1.20 g, 7.61 mmol) was dissolved in anhydrous diethylether (50 ml) and the solution cooled to $0^{o}C$. To this was added 5 ml (7.63 mmol.) of a 1.58M ^{n}BuLi solution in hexane, the resultant pale yellow solution was stirred at room temperature for 30 minutes. After this time dry oxygen was passed through the solution for 10 hours. The mixture was hydrolysed with distilled water, and the organic layer was washed twice with a weak alkali solution. The ether layer was separated, dried over anhydrous $MgSO_4$, and filtered. The ether was removed under vacuum leaving an off-white solid, this solid being positively identified as methyl-o-carborane. The aqueous layer was acidified and extracted with ether. The ether layer was separated, dried over anhydrous $MgSO_4$ and then filtered. The solvent was removed from the pale yellow filtrate leaving a crude off-white solid. This solid was recrystallized from dry hexane and positively identified as 1-hydroxy-2-methyl-o-carborane, MeΘOH.

ii) RESULTS

Weight of unreacted MeΘH = 0.903 g

Weight of MeΘOH obtained = 0.31 g

Therefore Yield = 23%

Analysis

FOR WHITE CRYSTALLINE SOLID

	C	H	B	O
% FOUND	20.4	8.9	61.1	-
MeΘOH requires	20.7	8.0	62.1	9.2

FOR OFF-WHITE SOLID

	C	H	B
% FOUND	22.1	8.4	68.0
MeΘH requires	22.8	8.8	68.4

I.R.

FOR OFF-WHITE SOLID:- The following vibrations in the infra-red spectrum could be assigned:- Carboranyl C-H stretch (3059 cm^{-1}); B-H stretch (2610-2540 cm^{-1}); Cage vibrations (720 cm^{-1}).

The infra-red spectrum of the off-white solid was found to be identical to that of methyl-o-carborane.

FOR WHITE CRYSTALLINE SOLID:- The following vibrations could be assigned:- Carboranyl C-OH stretching frequencies (3650-3320 cm^{-1}); B-H stretch (2579 cm^{-1}); O-H bend (1595 cm^{-1}); Carboranyl C-O stretch (1222 cm^{-1}); Cage vibrations (720 cm^{-1}).

Mass Spectrum

FOR OFF-WHITE SOLID:- The mass spectrum for the off-white solid showed an M+1 peak at $\frac{m}{e}$ 161 where M = $^{12}C_3\,^{11}B_{10}\,^{1}H_{14}$ with a corresponding isotope pattern from $\frac{m}{e}$ 147-161.

FOR WHITE CRYSTALLINE SOLID:- The mass spectrum for the white crystalline solid showed an M+1 peak at $\frac{m}{e}$ 176 where M = $^{12}C_3\ ^{11}B_{10}\ ^{1}H_{14}\ ^{16}O$ with a corresponding isotope pattern from $\frac{m}{e}$ 164-176. Half mass peaks were also observed between $\frac{m}{e}$ 82-88 ($\frac{m}{2e}$ 164-176).

7.2(a2) THE PREPARATION OF 1-HYDROXY-2-METHYL-O-CARBORANE, MeΘOH (3)

$$2Me\Theta Li \quad + \quad (PhCOO)_2 \xrightarrow[30-40^{\circ}C]{Ether} Me\Theta OH \; + \; Me\Theta COPh \quad + \quad PhCOOH$$

i) EXPERIMENTAL

Methyl-o-carborane (2.35 g, 15.00 mmol.) was dissolved in dry diethyl ether (30 ml) and to this solution was added 9.2 ml (15.00 mmol.) of a 1.63 M n-butyl lithium solution in pentane. The pale yellow solution was allowed to stir at 30°C for 1 hr. After this time a solution of benzoyl peroxide (1.82 g, 7.5 mmol.) in dry toluene (30 ml) was added slowly by syringe. The orange solution was heated at 30-40°C for 3-4 hr. during which time a precipitate formed. After this time the solution was hydrolysed with distilled water and the organic layer washed twice with a 2% aqueous NaOH solution. The combined aqueous extracts were acidified and extracted with diethyl ether. The ether layer was separated and washed with a sodium bicarbonate solution to remove the benzoic acid. The ether layer was then dried over anhydrous $MgSO_4$, filtered and the ether removed leaving a pale yellow semi-solid. The semi-solid was dissolved in dry pentane and the resultant pale yellow solution was cooled to -35°C. Crystals were deposited, which were filtered and recrystallized from hexane. The white crystals were identified as 1-hydroxy-2-methyl-o-carborane. The original ether layer was found to contain the 1-methyl-2-benzoly-o-carborane, MeΘCOPh and this was readily converted back to the unsubstituted methyl-o-carborane by hydrolytic degradation in 10% aqueous sodium hydroxide.

ii) RESULTS

Yield of MeθOH = 68%

The white crystals of MeθOH sublimed between 250-265°C.

Analysis

	C	H	B	O
% FOUND	20.9	8.7	59.9	-
MeθOH requires	20.7	8.0	62.1	9.2

I.R.

The infra-red spectrum showed the following peaks:-
ν max, Nujol mull (cm^{-1}), 3650(m); 3510(s); 3320(s,br);
2920(s); 2855(s); 2750(w); 2579(s); 1595(m); 1460(sh);
1448(s); 1377(s); 1320(m); 1275(sh); 1222(s); 1159(w);
1088(s); 1032(s); 1020(s); 951(s); 935(sh); 920(m);
905(w); 833(w); 802(s); 760(s); 735(sh); 728(s);
700(w); 680(m); 640(m); 568(w); 555(w); 510(w);
480(w).

The following vibrations could be assigned:- Carboranyl C-OH stretching frequencies (3650-3320 cm^{-1}); B-H stretch (2579 cm^{-1}); O-H bend (1595 cm^{-1}); Carboranyl C-O stretch (1222 cm^{-1}).

Mass Spectrum

The mass spectrum showed a highest mass peak at $\frac{m}{e}$ 176 corresponding to the species $^{12}C_3\,^{1}H_{14}\,^{11}B_{10}\,^{16}O$ accompanied by the usual isotopic distribution between $\frac{m}{e}$ 164-176. Half mass peaks were also observed between $\frac{m}{e}$ 82-88 ($\frac{m}{2e}$ 164-176). The usual fragmentation pattern for the carborane cage was also observed.

7.2(b1) THE ATTEMPTED PREPARATION OF 1,2-DIHYDROXY-O-CARBORANE, HOΘOH

$$\text{Li}\Theta\text{Li} \xrightarrow[\text{ii) } H_2O/OH^-]{\text{i) Dry Oxygen}} \text{HO}\Theta\text{OH} + \text{H}\Theta\text{H}$$

i) EXPERIMENTAL

Ortho-carborane (0.893 g, 6.20 mmol.) was dissolved in anhydrous diethyl ether (100 ml) and the solution cooled to 0^{o}C. To this was added 8 ml (12.4 mmol.) of a 1.58M ^{n}BuLi solution in hexane. The solution was allowed to stir at room temperature for 30 minutes during which time a white precipitate formed. Dry oxygen was passed through the LiΘLi/ether slurry and the white precipitate immediately disappeared leaving a clear pale yellow solution. After approximately 10 hours the solution had become opaque and a viscous yellow material had coated the walls of the flask. On hydrolysis with 5% aqueous NaOH this viscous yellow oil dissolved in the alkaline solution. The ether layer was washed several times with weak alkali, separated, dried over anhydrous $MgSO_4$, filtered and the ether removed under vacuum leaving an off-white solid which was positively identified as ortho-carborane. The aqueous extract was acidified and extracted with ether. The ether layer was separated, dried over anhydrous $MgSO_4$, filtered and the ether removed leaving a crude pale yellow semi-solid. The semi-solid was dissolved in dry hexane and the resultant pale yellow solution was cooled to -35^{o}C. No crystalline material was deposited and so the hexane was removed. Purification of this crude material resulted in a clear pale yellow oil.

ii) RESULTS

Weight of unreacted HΘH = 0.65 g

Weight of HOΘOH = 0.24g

Yield = 21.9%

Analysis

	C	H	B	O
% FOUND FOR OIL	12.4	9.6	58.4	-
$HO\theta OH$ requires	13.6	6.8	61.4	18.2
$H\theta OH$ requires	15.0	7.5	67.5	10

I.R.

The infra-red spectrum of the clear pale yellow oil showed the following bands:- max (cm^{-1}) CONTACT FILM:- (3650-3020(v,br)); 2950(s); 2920(s); 2845(sh); 2580(vs); 1700(v,br); 1600(v,br); 1440(br); 1375(s); 1250(vs); 1090(m); 1065(m); 1030(vs); 940(v,br); 855(s); 810(s); 770(w); 720(vs); 680(w).

The following vibrations could be assigned:- Carboranyl C-OH stretching frequencies (3650-3020 cm^{-1}); B-H stretch (2580 cm^{-1}); O-H bend (1700-1600 cm^{-1}); Carboranyl C-O stretch (1250 cm^{-1}); Cage vibrations (720 cm^{-1}).

Mass Spectrum

The mass spectrum showed a number of carboranyl isotope patterns. These were identified as:-

$\frac{m}{e}$ 166-176 $^{+}\theta(OH)_2$; $\frac{m}{e}$ 153-164 $^{+}\theta OH$;

$\frac{m}{e}$ 136-146 θ^{+}; $\frac{m}{e}$ 83-88 ($\frac{m}{2e}$ 166-176 $^{2+}\theta(OH)_2$).

Other higher mass species showing a carborane pattern were visible at $\frac{m}{e}$ 248, 234, 220 and 205. These species can be explained by considering the degree of hydration of 1,2 - dihydroxy-o-carborane, as shown below:-

$\frac{m}{e}$ 240-251 $^{+}\theta(OH)_2 . 4H_2O$; $\frac{m}{e}$ 223-234 $^{+}\theta(OH)_2 . 3H_2O$;

$\frac{m}{e}$ 205-214 $^{+}\theta(OH)_2 . 2H_2O$; $\frac{m}{e}$ 186-196 $^{+}\theta(OH)_2 . H_2O$.

7.2(b2) THE PREPARATION OF 1-HYDROXY-O-CARBORANE, HΘOH

$$2H\Theta Li + (PhCOO)_2 \xrightarrow[30-40^{\circ}C]{Ether/Toluene} H\Theta OH + H\Theta COPh + PhCOOH$$

i) EXPERIMENTAL

Procedure as for the preparation of 1-hydroxy-2-methyl- and 1-hydroxy-2-phenyl-o-carborane.

ii) RESULTS

Yield of white crystalline HΘOH = 31%

Melting point of crystals = 307-309 (Lit. 308-310°C)

Analysis

	C	H	B	O
% FOUND	15.9	8.1	66.1	-
HΘOH requires	15.0	7.5	67.5	10.0

I.R.

The following vibrations could be assigned:-

Carboranyl C-OH frequencies (3630 cm^{-1}(s), 3500 cm^{-1}(s,br), (3450-3200 cm^{-1}(vbr)); Carboranyl C-H stretch (3059 cm^{-1}); B-H stretch (2590 cm^{-1}); O-H band (1600 cm^{-1}); Carboranyl C-O stretch (1250 cm^{-1}(s)); Cage vibrations (720 cm^{-1}).

Mass Spectrum

The mass spectrum showed a highest mass peak at $\frac{m}{e}$ 162 corresponding to the species $^{12}C_2\,^{1}H_{12}\,^{16}O$ accompanied by the usual isotopic distribution between $\frac{m}{e}$ 152-162. Half mass peaks were also observed between $\frac{m}{e}$ 76-81 ($\frac{m}{2e}$ 152-162).

7.2(c) THE PREPARATION OF 1-HYDROXY-2-PHENYL-O-CARBORANE, PhΘOH

$$2Ph\Theta Li + (PhCOO)_2 \xrightarrow[30-40^{o}C]{Ether/Toluene} Ph\Theta OH + Ph\Theta COPh + PhCOOH$$

i) EXPERIMENTAL

1-Hydroxy-2-phenyl-o-carborane was prepared in an identical manner to the 1-hydroxy-2-methyl-o-carborane.

ii) RESULTS

Melting point of white crystalline PhΘOH = 84-86°C.

Analysis

	C	H	B	O
% FOUND	40.1	6.6	44.3	-
PhΘOH requires	40.7	6.8	45.7	6.8

I.R.

The following vibrations could be assigned:- Carboranyl C-OH (3620-3235 cm^{-1}); B-H stretch (2615-2550 cm^{-1}); O-H band and $C\equiv C$ ring stretch (1610 cm^{-1}); Carboranyl C-O stretch (1228 cm^{-1}).

Mass Spectrum

The mass spectrum showed a highest mass peak at $\frac{m}{e}$ 239 corresponding to the species $^{12}C_8\ ^{1}H_{16}\ ^{11}B_{10}\ ^{16}O$ accompanied by the usual isotopic distribution between $\frac{m}{e}$ 229 and 239. Half mass peaks were also observed between $\frac{m}{e}$ 114.5 and 119.5 ($\frac{m}{2e}$ 229-239). The usual fragmentation pattern for the carborane cage was also observed.

7.2(d1) THE ATTEMPTED PREPARATION OF 1,7-DIHYDROXY-M-CARBORANE, HOΘ'OH

$$\mathrm{Li\Theta'Li} \xrightarrow[\text{ii)}\ H_2O/OH^-]{\text{i)}\ \text{Dry Oxygen}} \mathrm{HO\Theta'OH} + \mathrm{H\Theta'H}$$

i) EXPERIMENTAL

1,7-Dihydroxy-m-carborane was prepared in a similar manner to 1,2-dihydroxy-o-carborane. (See 7.2(b)).

ii) RESULTS

Weight of unreacted HΘ'H = 0.35 g
Weight of product obtained = 0.34 g

Yield = 46.9%

Analysis

	C	H	B	O
% FOUND FOR CRYSTALLINE PRODUCT	14.8	7.2	65.3	-
HΘ'OH requires	15	7.5	67.5	10
HOΘ'OH requires	13.6	6.8	61.4	18.2

I.R.

The following vibrations could be assigned:- Carboranyl C-OH stretching frequencies (3530-3150 cm^{-1}); Carboranyl C-H stretch (3058 cm^{-1}); B-H stretch (2590 cm^{-1}); OH bands (1670, 1600 cm^{-1}); Carboranyl C-O stretch (1200 cm^{-1}); C-B - - - C cage vibrations (1130 - 1069 cm^{-1}); Cage vibrations (728 cm^{-1}).

Mass Spectrum

The mass spectrum showed a highest mass peak at $\frac{m}{e}$ 162 corresponding to the species $^{12}C_2\,^{1}H_{12}\,^{11}B_{10}\,^{16}O$ accompanied by the usual isotopic distribution, between $\frac{m}{e}$ 152-162. Half mass peaks were also observed between $\frac{m}{e}$ 76-81 ($\frac{m}{2e}$ 152-162).

7.2(d2) THE PREPARATION OF 1-HYDROXY-M-CARBORANE, $H\Theta'OH$

$$2H\Theta'Li + (PhCOO)_2 \xrightarrow[30-40^{\circ}C]{Ether/Toluene} H\Theta'OH + H\Theta'COPh + PhCOOH$$

i) EXPERIMENTAL

(For procedure see method used to prepare 1-hydroxy-2-methyl-o-carborane.)

ii) RESULTS

Yield of pale yellow crystals = 54%

The pale yellow crystals sublimed between 257-259°C.

Analysis

	C	H	B	O
% FOUND	16.7	8.1	65.1	-
$H\Theta'OH$ requires	15.0	7.5	67.5	10.0

I.R.

The following vibrations could be assigned:- Carboranyl C-OH stretching frequencies (3530 cm^{-1}(s), 3450-3150 cm^{-1}(s,v.br)); Carboranyl C-H stretch (3058 cm^{-1}); B-H stretch (2590 cm^{-1}); OH bands (1670 cm^{-1}), 1600 cm^{-1}(br)); Carboranyl C-O stretch (1200 cm^{-1} (vs)); C-B---C cage vibrations (1130 cm^{-1}, 1069 cm^{-1}); Cage vibrations (728 cm^{-1}(s)).

Mass Spectrum

The mass spectrum showed a highest mass peak at $\frac{m}{e}$ 162 corresponding to the species $^{12}C_2\ ^{1}H_{12}\ ^{11}B_{10}\ ^{16}O$ accompanied by the usual isotopic distribution, between $\frac{m}{e}$ 152-162. Half mass peaks were also observed between $\frac{m}{e}$ 76-81 ($\frac{m}{2e}$ 152-162).

7.3(a) THE PREPARATION OF THE TRIETHYLAMMONIUM SALT OF 1-HYDROXY-2-METHYL-O-CARBORANE, MeΘOHNEt$_3$

$$\text{MeΘOH} + \text{Et}_3\text{N} \xrightarrow[\text{ROOM TEMPERATURE}]{\text{HEXANE}} \text{MeΘOHNEt}_3$$

i) EXPERIMENTAL

1-Hydroxy-2-methyl-o-carborane (1.5 g, 9.3 mmol.) was dissolved in dry hexane (40 ml) and to this was added dry triethylamine (0.93 g, 9.3 mmol.). On addition of the triethylamine a white precipitate formed and the solution became hot. The white precipitate was filtered and washed several times with cold hexane (5 ml). The crude MeΘOHNEt$_3$ was recrystallized from a hot hexane (20 ml)/toluene (5 ml) solution. The white crystalline material obtained was identified as MeΘOHNEt$_3$.

ii) RESULTS

Yield of white crystalline MeΘOHNEt$_3$ = 72%

Melting point of crystals = 136-138°C (Lit. 120-122°C).

Analysis

	C	H	N	B	O
% FOUND	37.6	12.2	4.6	42.2	-
MeΘOHNEt$_3$ requires	39.2	10.5	5.1	39.3	5.8

I.R.

The following vibrations could be assigned:-

B-H stretch (2565 cm^{-1}(s) and 2540 cm^{-1}(s)); N-H$^+$ stretch (2490-2100 cm^{-1}(v.br)); Carboranyl C-O stretch (1290 cm^{-1} (vs)); Cage vibrations (728 cm^{-1}(vs)).

Significant differences were observed between the spectra of 1-hydroxy-2-methyl-o-carborane and its triethylammonium salt. In the spectrum of MeΘOHNEt$_3$ no OH stretching bands were seen, as expected, but a broad peak at 2490-2100 cm^{-1} was observed, this being assigned to the H-bonded NH stretch of the Et$_3$NH$^+$ group. The carboranyl C-O stretch, which appears at 1222 cm^{-1} in the infra-red spectrum of MeΘOH, is significantly shifted to higher wavenumbers in the spectrum of MeΘOHNEt$_3$, appearing as a strong peak at 1290 cm^{-1}. One possible explanation for this dramatic shift may be that on salt formation the C-O bond length is reduced and this is why it starts to shift towards C=O stretching frequencies.

Mass Spectrum

Attempts to record its mass spectrum afforded evidence of the triethylamine ($\frac{m}{e}$ 101) and fragments thereof, and of the 1-hydroxy-2-methyl-o-carborane at $\frac{m}{e}$ 176 accompanied by the usual isotopic distribution between $\frac{m}{e}$ 164-176. Half mass peaks were also observed between $\frac{m}{e}$ 82-88 ($\frac{m}{2e}$ 164-176). The usual fragmentation pattern for the carborane cage was also observed.

7.3(b) THE PREPARATION OF THE TRIETHYLAMMONIUM SALT OF 1-HYDROXY-O-CARBORANE, HΘOHNEt$_3$

$$H\Theta OH \quad + \quad Et_3N \xrightarrow{\text{HEXANE}} H\Theta OHNEt_3$$

i) EXPERIMENTAL

The triethylammonium salt of 1-hydroxy-o-carborane was prepared in an identical manner to the salt of 1-hydroxy-2-methyl-o-carborane.

ii) RESULTS

Yield of white crystalline $H\Theta OHNEt_3$ = 69%

Melting point of crystals = 124-127°C

Analysis

	C	H	N	B	O
% FOUND	38.1	11.1	5.0	40.1	-
$H\Theta OHNEt_3$ requires	36.8	10.3	5.4	41.4	6.1

I.R.

The following vibrations could be assigned:-

Carboranyl C-H stretch (3058 cm^{-1}(s)); B-H stretch (2558 cm^{-1}(vs)); $N-H^+$ stretch (2490-2200 cm^{-1}very broad peak); Carboranyl C-O stretch (1299 cm^{-1}(vs)); Cage vibrations (722 cm^{-1}).

Again significant differences were observed between the infra-red spectra of the hydroxy derivative and its triethylammonium salt. Most noticeable was the absence of OH stretching bands, the appearance of an NH stretching band (2490-2200 cm^{-1}) and the dramatic shift of the carboranyl C-O stretch to higher wavenumbers.

Mass Spectrum

The mass spectrum afforded evidence of the triethylamine (at $\frac{m}{e}$ 101) and fragments thereof, and of the 1-hydroxy-o-carborane at $\frac{m}{e}$ 162 accompanied by the usual isotopic distribution between $\frac{m}{e}$ 152-162. Half mass peaks were also observed between $\frac{m}{e}$ 76-81 ($\frac{m}{2e}$ 152-162).

7.3(c) THE PREPARATION OF THE PYRIDINIUM SALT OF 1-HYDROXY-2-METHYL-O-CARBORANE

$$\text{Me}\Theta\text{OH} + :\text{NC}_5\text{H}_5 \xrightarrow{\text{HEXANE}} \text{Me}\Theta\text{OHNC}_5\text{H}_5$$

i) EXPERIMENTAL

The pyridinium salt of 1-hydroxy-2-methyl-o-carborane was prepared in a similar manner to the triethylamine salt of the same derivative. It should however be noted that unlike the triethylamine salt, which is insoluble in hexane, the pyridinium salt was found to be very soluble in hexane and subsequently crystals were obtained by concentrating a hexane solution of the salt until small crystals just appeared and then heating the saturated solution and allowing it to cool slowly.

ii) RESULTS

Yield of the pale yellow crystals = 80%

Melting point of crystals = 88-90°C

Analysis

	C	H	N	B	O
% FOUND	37.8	9.1	5.2	41.3	-
$\text{Me}\Theta\text{OHC}_5\text{H}_5$ requires	37.8	7.5	5.5	42.5	6.3

I.R.

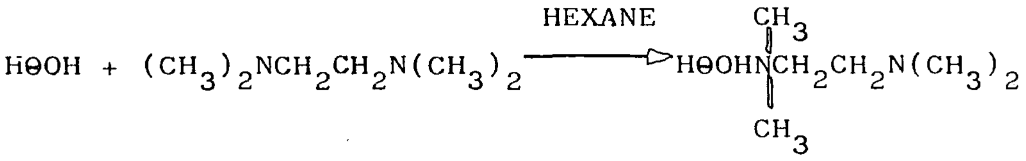
The following vibrations could be assigned:-

Aromatic C-H stretch (3050 cm^{-1}(m)); B-H stretch (2560 cm^{-1}); Pyridinium N-H^+ stretch (2440-2280 cm^{-1}(br)); Pyridinium $C{=}C$ and $C{=}N$ ring stretch (1599 cm^{-1}(s), 1485 cm^{-1}(w)); Carboranyl C-O stretch (1230 cm^{-1}(m,br)); Cage vibrations (721 cm^{-1}(m)). Again significant differences were observed between the spectra of the hydroxy derivative and its pyridinium salt. No OH stretching bands were observed as expected, and the characteristic N-H$^+$ stretch at (2440-2280 cm^{-1}) was apparent. The carboranyl C-O stretch had shifted to higher wavenumbers as expected on salt formation, however the shift was only 8 cm^{-1} compared to a shift of 77 cm^{-1} in the case of the triethylammonium salt.

Mass Spectrum

The mass spectrum afforded evidence of pyridine ($\frac{m}{e}$ 79) and fragments thereof and of the 1-hydroxy-2-methylcarborane at $\frac{m}{e}$ 176 accompanied by the usual isotopic distribution between $\frac{m}{e}$ 164-176. Half mass peaks were also observed between $\frac{m}{e}$ 82-88 ($\frac{m}{2e}$ 164-176). The usual fragmentation pattern for the carborane cage was also observed.

7.3(d) THE PREPARATION OF THE 2-DIMETHYLAMINOETHYLDIMETHYLAMMONIUM SALT OF 1-HYDROXY-O-CARBORANE



$$H\Theta OH + (CH_3)_2NCH_2CH_2N(CH_3)_2 \xrightarrow{\text{HEXANE}} H\Theta OH\overset{CH_3}{\underset{CH_3}{N}}CH_2CH_2N(CH_3)_2$$

i) EXPERIMENTAL

The TMEDA salt of 1-hydroxy-o-carborane was prepared in a similar manner to the triethylammonium salt of 1-hydroxy-2-methyl-o-carborane.

ii) RESULTS

Yield of white crystalline solid = 63%

Melting point of crystals = 94-96°C

Analysis

	C	H	N	B	O
% FOUND	34.9	11.6	9.7	37.8	-
$H\theta O^{+}HTMEDA$ requires	34.8	10.1	10.1	39.1	5.8
$H\theta O^{+}HTMEDAH^{+}O\theta H$ requires	27.5	9.2	6.4	49.5	7.3

I.R.

The following vibrations in the infra-red spectrum could be assigned:- Carboranyl C-H stretch (3050 cm^{-1}(w)); B-H stretch (2550 cm^{-1}(s)); TMEDA NH^{+} stretch (2480-2200 cm^{-1}). Carboranyl C-O stretch (1295 cm^{-1}(s)); Cage vibrations (720 cm^{-1}).

Mass Spectrum

The mass spectrum afforded evidence of TMEDA and of the 1-hydroxy-o-carborane at $\frac{m}{e}$ 162 accompanied by the usual isotopic distribution between $\frac{m}{e}$ 152-162. Half mass peaks were also observed between $\frac{m}{e}$ 76-86 ($\frac{m}{2e}$ 152-162). The usual fragmentation pattern for the carborane cage was also observed.

7.3(e) THE PREPARATION OF THE TRIMETHYLAMMONIUM SALT OF 1-HYDROXY-O-CARBORANE, $H\theta OHNMe_3$

i) EXPERIMENTAL

The trimethylammonium salt of 1-hydroxy-o-carborane was prepared in an identical manner to the triethylammonium salt of 1-hydroxy-2-methyl-o-carborane.

ii) RESULTS

Yield of white crystalline $H\Theta OHNMe_3$ = 81%

Melting point of crystals = 176-178°C

Analysis

	C	H	N	B	O
% FOUND	26.9	9.8	6.0	51.0	-
$H\Theta OHNMe_3$ requires	27.4	9.6	6.4	49.3	7.3

I.R.

The following vibrations could be assigned:-

Carboranyl C-H stretch (3060 cm^{-1}(s)); B-H stretch (2560 cm^{-1}(vs)); N-H^{+} stretch (2700-2000 very broad peak); Carboranyl C-O stretch (1290 cm^{-1}(s)); C-B-C cage vibrations (1220 cm^{-1}(s)); Cage vibrations (722 cm^{-1}(s)). Again significant differences were observed between the infra-red spectra of the trimethylammonium salt and the hydroxy derivative. Most noticeable was the absence of OH stretching bands, the appearance of an NH stretching band (2700-2000 cm^{-1}) and the dramatic shift of the carboranyl C-O stretch to higher wavenumbers.

Mass Spectrum

The mass spectrum afforded evidence of the trimethylamine and fragments thereof, and of the 1-hydroxy-o-carborane at $\frac{m}{e}$ 162 accompanied by the usual isotopic distribution between $\frac{m}{e}$ 152-162. Half mass peaks were also observed between $\frac{m}{e}$ 76-81 ($\frac{m}{2e}$ 152-162).

7.4(a) THE PREPARATION OF 1-TRIMETHYLSILOXY-2-METHYL-O-CARBORANE, $Me\theta OSiMe_3$

a) $$Me\theta OH + Et_3N \xrightarrow{\text{HEXANE}} Me\theta OHNEt_3$$

b) $$Me\theta OHNEt_3 + Me_3SiCl \xrightarrow[60^{\circ}C]{\text{Toluene/Hexane}} Me\theta OSiMe_3 + Et_3NHCl$$

i) EXPERIMENTAL

The triethylammonium salt of 1-hydroxy-2-methyl-o-carborane, $Me\theta OHNEt_3$ (1.710 g, 6.218 mmol.) was dissolved in dry toluene (20 ml) and hexane (10 ml). The clear solution obtained was stirred at room temperature for 10 minutes before the trimethylchloro-silane, Me_3SiCl (0.8 ml, 6.218 mmol.) was added slowly by syringe. The solution was heated to 60° and maintained at this temperature for 2 hours. During this time a white precipitate had formed. The slurry was cooled to room temperature and filtered. The filtrand was washed several times with cold hexane, and dried under vacuum. The solvent was removed from the clear filtrate leaving a white crystalline solid which was identified as 1-trimethylsiloxy-2-methyl-o-carborane, $Me\theta OSiMe_3$.

ii) RESULTS

The white precipitate formed in the reaction was positively identified by infra-red and micro analysis to be triethylamine hydrochloride.

Yield of white crystalline $Me\theta OSiMe_3$ = 69%

Melting point of white crystalline material = 77-79°C

Analysis

	C	H	N	B	O	Si
% FOUND	28.9	9.2	-	39.9	-	10.9
$Me\theta OSiMe_3$ requires	29.2	8.9	-	40.6	9.9	11.4

I.R.

The following vibrations could be assigned:-

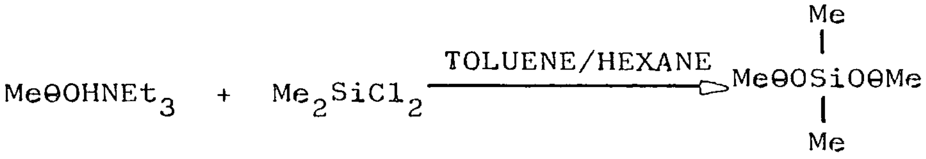
B-H stretch (2560 cm^{-1}(s,br)); Si-CH$_3$ stretch and carboranyl C-O stretch (1290-1248 cm^{-1}(s,br)); Si-O stretch (870-835 cm^{-1}(vs)); Si-CH$_3$ bend (760 cm^{-1}(s,br)); Cage vibrations (725 cm^{-1}(s)).

Significant differences were observed between the spectra of 1-hydroxy-2-methyl-o-carborane and 1-trimethylsiloxy-2-methyl-o-carborane. In the spectrum of MeΘOSiMe$_3$ no OH bands were observed, as expected however the carboranyl C-O stretch was significantly shifted by 28 cm^{-1} to higher wavenumbers and the Si-O stretch was located approximately 100 cm^{-1} towards lower wavenumbers than expected. One possible explanation for this may be that on formation of the trimethylsiloxy derivative the C-O bond length shortens and the Si-O bond length increases. Note similar observations were made for the salts of the C-hydroxy-carboranes, that is on salt formation it is believed that the C-O bond length decreases.

Mass Spectrum

The mass spectrum afforded evidence of MeΘOSiMe$_3$ as well as what appears to be a dimeric species (MeΘOSiMe$_3$)$_2$ having exactly double the $\frac{m}{e}$ value for the monomeric species MeΘOSiMe$_3$. A characteristic isotopic distribution was observed for both the monomeric and dimeric species, along with characteristic fragmentation patterns. Half mass peaks at $\frac{m}{e}$ 112-117 ($\frac{m}{2e}$ 222-234 corresponding to MeΘ^{2+}OSiMe$_2$ were also observed. At the present time of writing it is not yet known whether the dimeric species observed in the mass spectrometer actually exists or whether it was formed in the mass spectrometer.

7.4(b) THE PREPARATION OF $\mathrm{Me\Theta O}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{Si}}}\mathrm{O\Theta Me}$



$$\mathrm{Me\Theta OHNEt_3} + \mathrm{Me_2SiCl_2} \xrightarrow{\text{TOLUENE/HEXANE}} \mathrm{Me\Theta O}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{Si}}}\mathrm{O\Theta Me}$$

i) EXPERIMENTAL

The triethylammonium salt of 1-hydroxy-2-methyl-o-carborane $\mathrm{Me\Theta OHNEt_3}$ (2.1 g, 7.64 mmol.) was dissolved in dry toluene (30 ml) and hexane (10 ml). The resultant clear solution was stirred for 10 minutes at room temperature before dimethyldichlorosilane, $\mathrm{Me_2SiCl_2}$ (0.46 ml, 3.82 mmol) was added by syringe. The solution was heated to 60°C for 1 hour during which time a white precipitate formed. The slurry was filtered and the filtrand washed several times with cold hexane and then pumped dry under vacuum. The solvent was removed from the clear filtrate leaving an opaque viscous oil which was identified as $\mathrm{Me\Theta OSi(Me)_2O\Theta Me}$.

ii) RESULTS

The white precipitate formed in the reaction was positively identified by infra-red and micro analysis to be triethylamine hydrochloride, $\mathrm{Et_3NHCl}$.

Yield of opaque viscous oil = 70%

Analysis

	C	H	B	O	Si	N	Cl
% FOUND	23.1	8.0	53.1	-	6.8	ABSENT	ABSENT
$\mathrm{Me\Theta O}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{Si}}}\mathrm{O\Theta Me}$ requires	23.8	7.4	54.2	7.4	7.1	-	-

I.R.

The following vibrations could be assigned:-

B-H stretch (2585 cm^{-1}(s)); Si-CH$_3$ stretch and carboranyl C-O stretch (1270-1248 cm^{-1}(s,br)); Si-O stretch (870-850 cm^{-1}(s,br)); Cage vibrations (726 cm^{-1}(s)).

The infra-red spectrum of MeΘOSi(Me)$_2$OΘMe was found to be very similar to that of MeΘOSiMe$_3$ as one might expect. However unlike the MeΘOSiMe$_3$, the MeΘOSi(Me)$_2$OΘMe was found to be very moisture sensitive hydrolytically decomposing to give two equivalents of 1-hydroxy-2-methyl-o-carborane and what may be a siloxy type polymer containing no boron. The infra-red spectrum of a hydrolytically decomposed sample of MeΘOSi(Me)$_2$OΘMe clearly showed the presence of a carboranyl C-OH stretch positioned at 3520 cm^{-1} and a Si-OH stretch at 3200 cm^{-1}.

The infra-red also showed a significant shift in the carboranyl C-O stretching frequency towards that observed in 1-hydroxy-2-methyl-o-carborane. In an attempt to identify the degradation products a sample of MeΘOSi(Me)$_2$OΘMe was allowed to decompose in air. After approximately one hour the degraded sample was dissolved in dry hexane and to this solution was added triethylamine. On addition of the Et$_3$N a white precipitate formed. The precipitate was filtered, washed several times with dry hexane and positively identified as the triethylammonium salt of 1-hydroxy-2-methyl-o-carborane. On removal of the hexane from the filtrate a viscous clear oil was obtained, analysis of which clearly showed it to contain no boron or nitrogen but a fairly high percentage of silicon and carbon. The infra-red spectrum of the viscous oil showed mainly Si-OH, Si-O-Si and Si-CH$_3$ stretching frequencies. It seems likely that the viscous oil may be a siloxy type polymer or oligomer although as yet the exact nature of the oil is unknown.

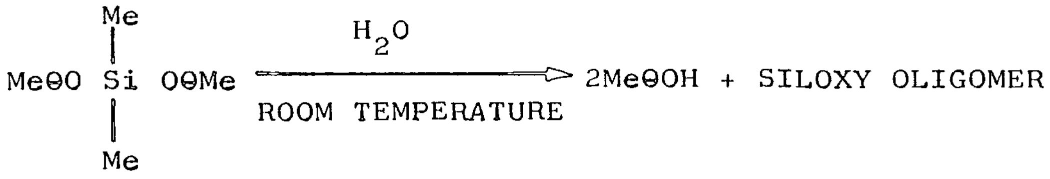
One possible explanation for the apparent sensitivity of $Me\Theta OSi(Me)_2O\Theta Me$ to moisture, is that the combined electron withdrawing effects of the cages weakens the Si-O bond and makes the silicon more susceptible to attack. The reason $Me\Theta OSiMe_3$ is less sensitive to hydrolytic degradation may be due to the electron-donating effect of the methyl groups attached to the silicon atom that is they may counteract the electron withdrawing effect of the carborane cage and consequently the Si-O bond in $Me\Theta OSiMe_3$ is slightly stronger.

7.5 DISCUSSION

Our studies have clearly shown that carboranyl-C-hydroxy derivatives may be prepared in moderate yields (20-50%) by either bubbling dry oxygen through suspensions of lithiocarboranes or by reaction of the lithiocarboranes with dry benzoylperoxide, as described in the literature. (94,95,96) All of the hydroxy-derivatives isolated were white or pale yellow crystalline solids with the exception of the previously unknown compound, 1,2-dihydroxy-o-carborane, which was isolated as clear viscous oil. The mass spectrum of this viscous oil clearly showed the presence of the dihydroxy-carboranyl species at $\frac{m}{e}$ 176 as expected, however higher mass peaks, also showing a carboranyl pattern, were seen at $\frac{m}{e}$ 251, 234, 214 and 196 and we believe these may be attributed to hydrated carboranyl-C-hydroxy species of general formula $\Theta(OH)_2.nH_2O$ (where n = 0 to 4). Attempts to prepare 1,7-dihydroxy-m-carborane, HOΘ'OH by a similar method failed, producing instead the monohydroxy-m-carboranyl derivative, HΘ'OH.

On formation of the triethylammonium, trimethylammonium, 2-dimethylamino ethyldimethylammonium and to a lesser extent pyridinium salts of the mono-C-hydroxy-o-carboranes, HΘOH and MeΘOH, significant differences were observed between the infra-red spectra of the hydroxy-derivatives and their salts. For example in the spectrum of the triethylammonium salt of 1-hydroxy-2-methyl-o-carborane no OH stretching bands were observed, however a broad peak at 2490-2100 cm^{-1} was now present and this was thought to be due to the H-bonded NH^+ stretch of the Et_3NH^+ group. The carboranyl C-O stretch on salt formation was significantly shifted towards C=O stretching frequencies. This is thought to be due to a shortening of the C-O bond on salt formation, the degree of shortening being dependent on the strength of the base used. It is worth note that when a strong base such as triethylamine was used the shift in the C-O stretching frequency was more dramatic than that observed when a weaker base, such as pyridine, was employed. ^1H, ^{11}B and COSY n.m.r studies on the hydroxy-C-carboranes and their salts have also revealed some interesting differences. The results of these studies and discussion thereof have been presented separately in section 7.6.

In the reaction between trimethylsilylchloride, Me_3SiCl and the triethylammonium salt of 1-hydroxy-2-methyl-o-carborane the previously unknown compound 1-trimethylsiloxy-2-methyl-o-carborane was obtained. This white, low melting crystalline solid was found to be air and moisture stable. Mass spectral data for 1-trimethylsiloxy-2-methyl-o-carborane afforded evidence of $Me\theta OSiMe_3$ as well as what appeared to be a dimeric species $(Me\theta OSiMe_3)_2$. In contrast to $Me\theta OSiMe_3$, which was found to be air and moisture stable, $Me\theta OSi(Me)_2O\theta Me$ was found to be very moisture sensitive giving as degradation products two equivalents of 1-hydroxy-2-methyl-o-carborane, $Me\theta OH$ and a siloxy type oligomer containing no boron. One possible explanation for the difference observed may be that in $Me\theta OSi(Me)_2O\theta Me$ the combined electron withdrawing effects of the icosahedral cages weakens the Si-O bond and makes the silicon more susceptible to attack by moisture, whereas in $Me\theta OSiMe_3$ the methyl groups attached to the silicon atom donate electron density and this may counteract the electron withdrawing effect of the cage and consequently the Si-O bond in $Me\theta OSiMe_3$ is stronger and the silicon atom is less susceptible to attack by moisture.



$$\mathrm{Me\Theta O}\ \overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{Si}}}\ \mathrm{O\Theta Me} \xrightarrow[\text{ROOM TEMPERATURE}]{H_2O} \mathrm{2Me\Theta OH} + \text{SILOXY OLIGOMER}$$

7.6 ^{1}H, ^{11}B and ^{11}B COSY N.M.R. Studies of C-Hydroxy-Carboranes and their Salts

The following section describes the ^{1}H, ^{11}B and ^{11}B COSY n.m.r. spectra of some carboranyl-C-hydroxy compounds and their salts.

A. ^{1}H n.m.r.

Very few ^{1}H n.m.r. spectra of the icosahedral carboranes have been reported due to the complexity of such spectra and consequent limitations for structural elucidation. The reasons why ^{1}H n.m.r. has been little used to study carboranes become apparent on consideration of the simple interaction of a ^{11}B nucleus with a single ^{1}H nucleus, in a magnetic field:-

$$\begin{array}{ccc} ^{11}\mathrm{B} & \text{——} & ^{1}\mathrm{H} \\ I = \frac{3}{2} & & I = \frac{1}{2} \end{array} \qquad \Uparrow H$$

From the standpoint of the ^{1}H nucleus: since the ^{11}B nucleus has a spin of $\frac{3}{2}$, the ^{1}H nucleus essentially "sees" four different fields, $(2nI+1)$, and consequently its n.m.r. absorption spectrum will be a quartet. If all the ^{11}B-^{1}H interactions in a carborane are taken into account, it becomes clear that in the ^{1}H n.m.r. spectrum a very complex multiplet would result. Furthermore the line widths are much larger than are normally found in the spectra of hydrogen attached to carbon, due to the large quadrupole moment of ^{11}B, and consequently the ^{1}H n.m.r. spectra of the carboranes are very poorly resolved and of little use. It is however, possible to obtain resolved cage proton spectra by using a technique known as broad band decoupling. This technique involves decoupling the boron atoms of the cage from the protons.

We have used this method to study the C-hydroxy-carboranes and their salts. While no assignment of the individual signals has been possible the spectra obtained do clearly illustrate the advantages of this technique. Although we have been unable to assign the B-H protons, the ^1H (^{11}B b.b. decoupled) n.m.r. spectra have been extremely useful for confirming the structure of the substituents attached to the cage carbon atoms and also attached to the oxygen atom in the C-hydroxy-carboranes and their salts.

RESULTS

(i) 1-Hydroxy-2-methyl-o-carborane, MeΘOH

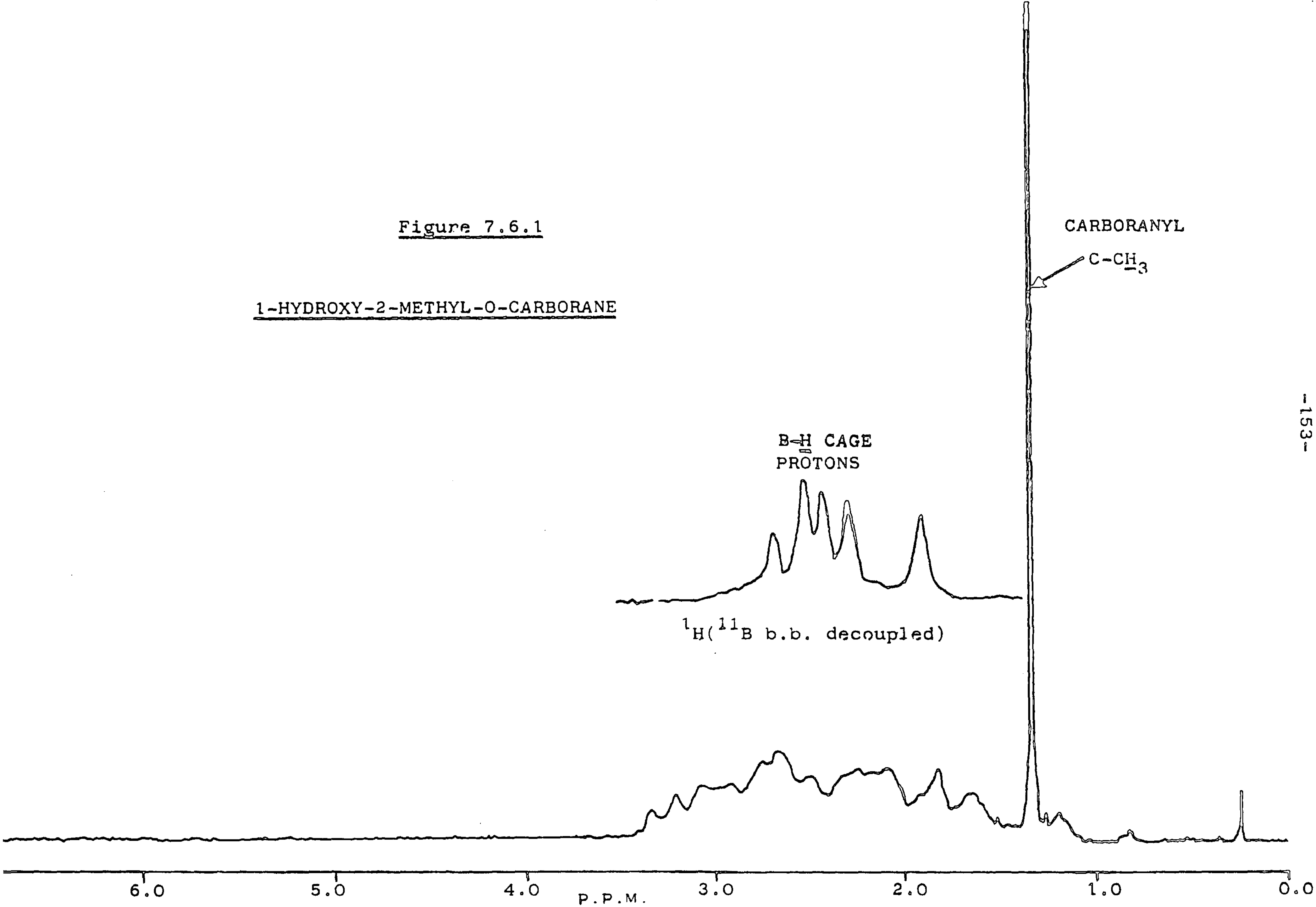
(360.134 MHz. Solvent C_6D_6 relative to C_6D_5H at 7.1612 p.p.m.) (See Fig. 7.6.1)

RESONANCE PATTERN	δ p.p.m.	INTEGRAL	ASSIGNMENT
$^1H\{^{11}B$ bb decoupled$\}$			
m/s	2.74	13 H	SKELETAL B-$\underline{H}$ AND C-O$\underline{H}$ PROTONS
m/s	2.57		
m/s	2.48		
m/s	2.35		
m/s	1.96		
s/s	1.38	3 H	$\underline{CH_3}$ GROUP

The ^1H (^{11}B broad band decoupled) n.m.r. spectrum of 1-hydroxy-2-methyl-o-carborane clearly shows the protons

Figure 7.6.1

1-HYDROXY-2-METHYL-O-CARBORANE



of the methyl group at 1.38 p.p.m.. It seems likely that the singlet at 1.38 p.p.m. of integral 3 H is indeed due to the methyl protons since this is the only signal which remains unchanged in both the ^{11}B coupled and ^{11}B broad band decoupled spectra this being indicative of the fact that these protons are not connected to or coupled to a boron atom, as is the case for the methyl protons in MeΘOH.

The multiplets, between 2.74 - 1.96 p.p.m., in the ^{1}H (^{11}B coupled) spectrum which collapse to broad singlets in the ^{1}H (^{11}B broad band decoupled) spectrum arise due to the B-H protons of the cage. However the proton integration (i.e. 13 H) suggests that the hydroxyl proton (OH) as well as the 10 B-H protons are included in these signals and that there may be some water associated with the sample. Unfortunately the expected singlet in, both the ^{1}H (^{11}B coupled) and ^{1}H (^{11}B broad band decoupled) spectra, for the OH proton was not observed. The reason for this may be due to the fact that the singlet for the OH proton may be much broader than expected due to hydrogen bonding with the associated water molecules and subsequently this broadened singlet would be masked by the broad singlets of the B-H cage protons.

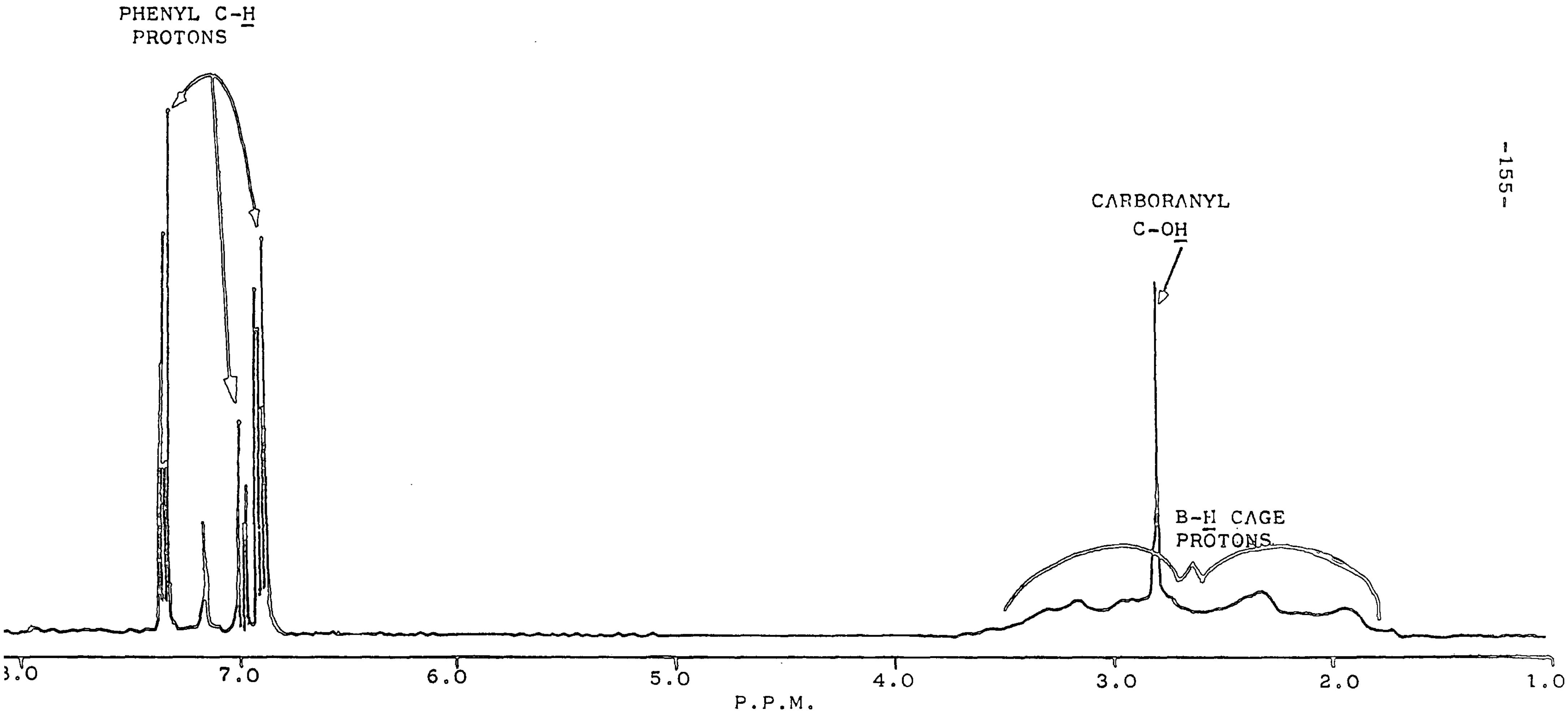
(ii) 1-Hydroxy-2-phenyl-o-carborane, PhΘOH

(360.134 MHz. Solvent C_6D_6 relative to C_6D_5H at 7.1619 p.p.m.) (See Fig. 7.6.2)

RESONANCE PATTERN	δp.p.m.	INTEGRAL	ASSIGNMENT
^{1}H (^{11}B coupled)			
m	7.36-7.33	2 H	AROMATIC C-H (ORTHO)
m	6.99-6.92	1 H	AROMATIC C-H (PARA)
m	6.91-6.88	2 H	AROMATIC C-H (META)
s	2.83	1 H	CARBORANYL C-OH
m	3.5-1.5	13 H	10 B-H AND H_2O

Figure 7.6.2

1-HYDROXY-2-PHENYL-O-CARBORANE



The ^{1}H (^{11}B coupled) n.m.r. spectrum of 1-hydroxy-2-phenyl-o-carborane clearly shows the ortho, meta and para protons of the phenyl ring.

The multiplets between 3.5 and 1.5 p.p.m. arise due to the 10 B-H cage protons although the integration of ~ 13 H would seem to suggest the presence of associated water. It is interesting to note that unlike the ^{1}H (^{11}B coupled) n.m.r. spectrum of MeΘOH, where no singlet for the O$\underline{H}$ proton was observed, the ^{1}H n.m.r. spectrum of PhΘOH clearly shows the expected singlet at 2.83 p.p.m..

(iii) <u>1-Hydroxy-m-carborane, HΘ'OH</u>

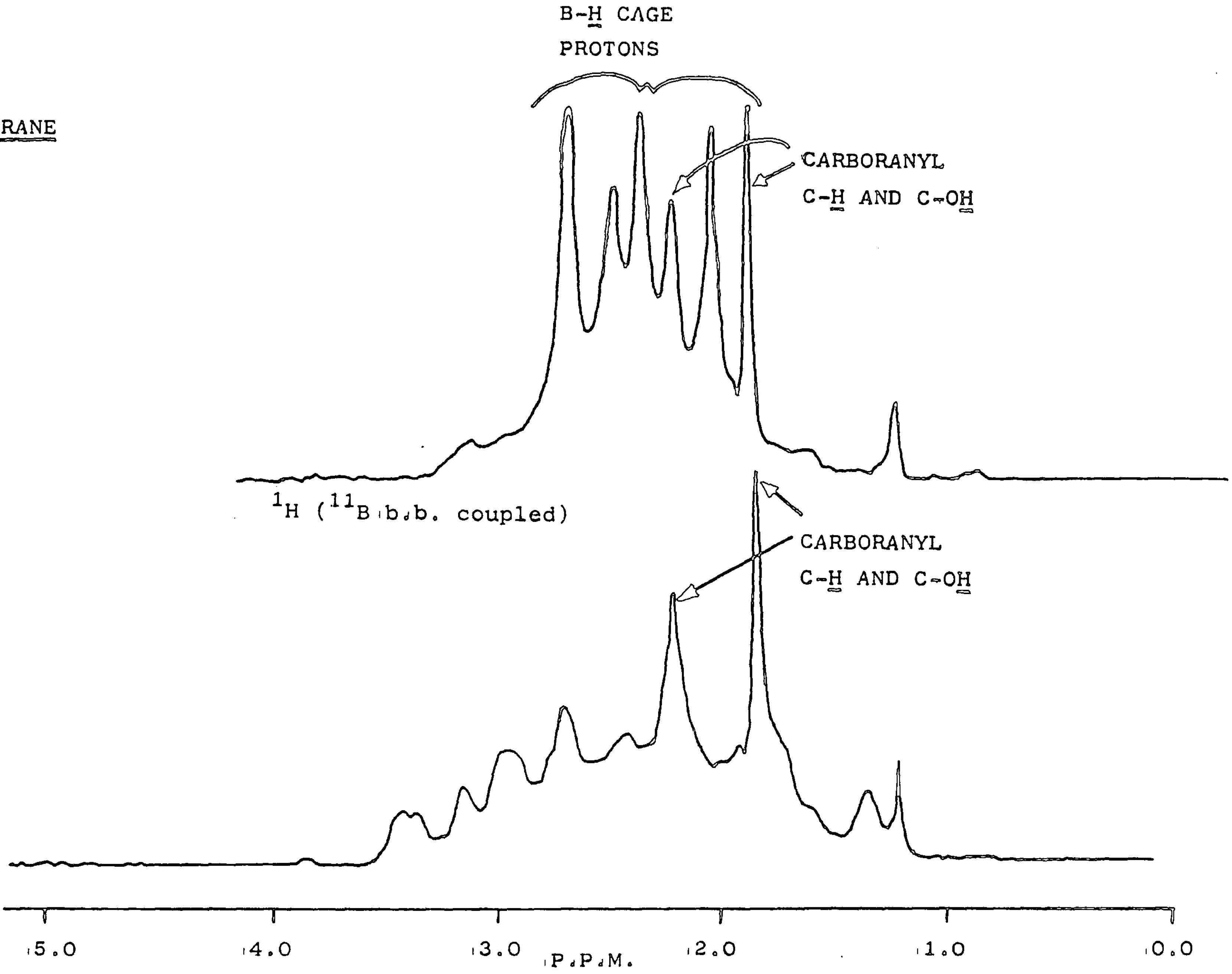
(360.134 MHz. Solvent C_6D_6 relative to C_6D_5H at 7.1608 p.p.m.) (See Fig. 7.6.3)

RESONANCE PATTERN	δ p.p.m.	INTEGRAL	ASSIGNMENT
^{1}H (^{11}B b.b. decoupled)			
br. m/s	2.96	10 H	SKELETAL B-$\underline{H}$
br. m/s	2.50		
br. m/s	2.37		
br. m/s	2.06		
s/s	2.24	1 H	CARBORANYL C-$\underline{H}$ AND C-O$\underline{H}$
s/s	1.89	1 H	

The broad multiplets between 2.96 - 2.06 p.p.m. in the ^{1}H (^{11}B coupled) spectrum, which collapse to singlets in the ^{1}H (^{11}B broad band decoupled) spectrum arise due to the 10 B-$\underline{H}$ protons of the cage.

Figure 7.6.3.

1-HYDROXY-M-CARBORANE



In the ^{11}B coupled spectrum, only two sharp signals are observed, at 2.24 and 1.89 p.p.m., these are unaffected by decoupling the protons from the boron atoms as shown on the ^{1}H (^{11}B broad band decoupled) spectrum and can therefore be assigned as the carboranyl C-H and C-OH protons.

It seems likely from the integration that, unlike MeΘOH and PhΘOH, no water is associated with HΘ'OH.

(iv) Triethylammonium salt of 1-Hydroxy-2-methyl-o-carborane, $\text{Me}\Theta\text{O}^{-}\ {}^{+}\text{HNEt}_3$

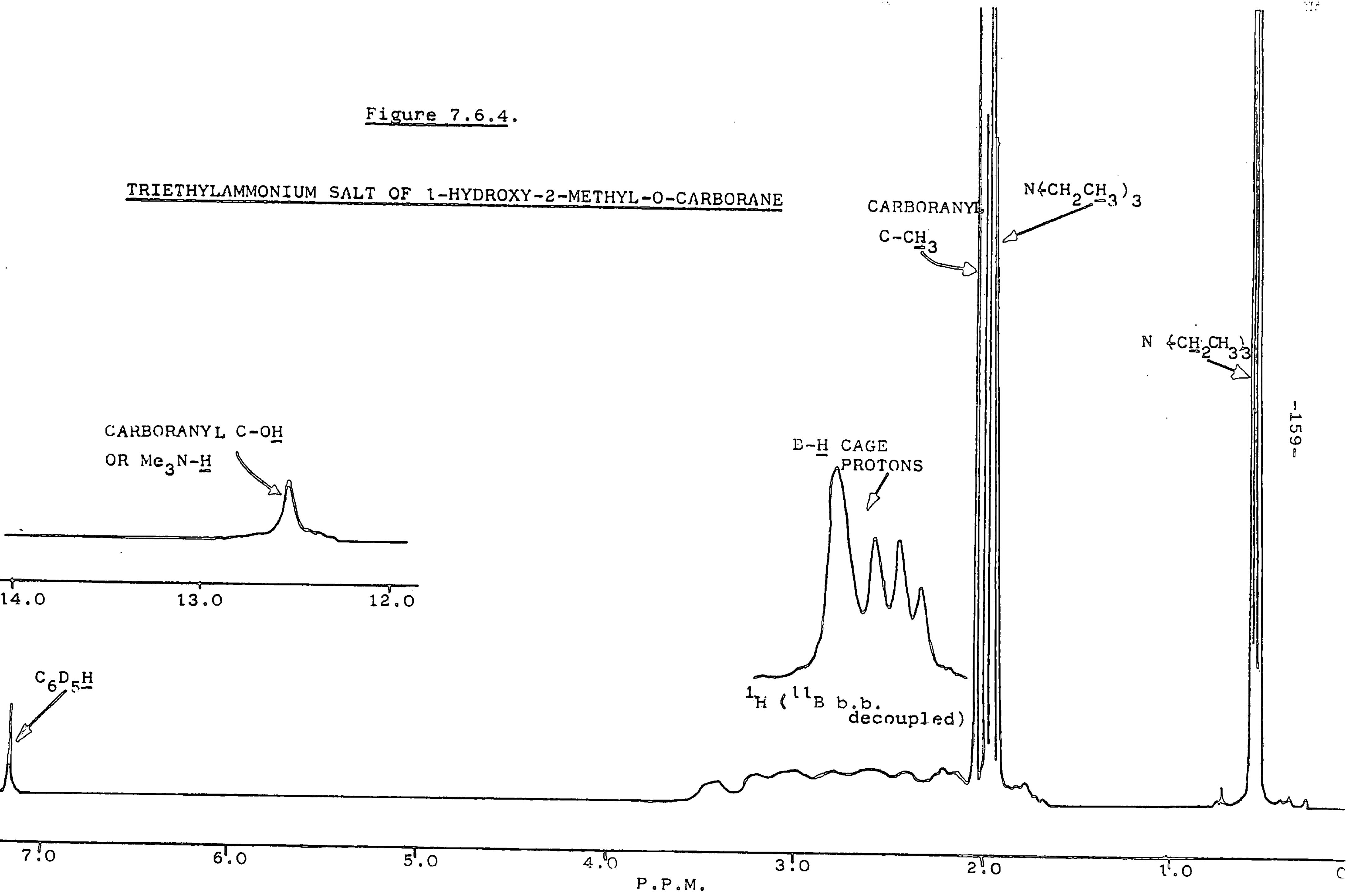
(360.134 MHz. Solvent C_6D_6, relative to C_6D_5H at 7.1597 p.p.m.) (See Fig. 7.6.4)

RESONANCE PATTERN	δ p.p.m.	INTEGRAL	ASSIGNMENT
^{1}H (^{11}B coupled)			
s	12.54	1 H	CARBORANYL C-OH OR $Et_3\overset{+}{N}$-H
m (centred at)	2.56	10 H	B-H
s	2.03	3 H	CARBORANYL C-CH_3
q	1.98	6 H	ETHYL -CH_2-
	1.96		
	1.94		
	1.92		
t	0.57	9 H	ETHYL -CH_3-
	0.55		
	0.53		

} Same.

Figure 7.6.4.

TRIETHYLAMMONIUM SALT OF 1-HYDROXY-2-METHYL-O-CARBORANE



The ^1H (^{11}B coupled) and ^1H (^{11}B broad band decoupled) n.m.r. spectra are clearly indicative of the compound MeΘOHNEt$_3$.

It is apparent from a comparison of the ^1H (^{11}B broad band decoupled) n.m.r. spectra of MeΘOH and MeΘOHNEt$_3$ that, on salt formation, the hydroxyl proton ($O-\underline{H}$) becomes significantly deshielded and consequently the signal for the $O-\underline{H}$ proton is substantially shifted downfield by approximately 6 p.p.m.

It seems apparent from infra-red and ^1H (^{11}B b.b. decoupled) spectral data, that the hydroxyl proton, on salt formation, becomes more strongly associated with the nitrogen atom of the base rather than the oxygen atom connected to the cage carbon atom and subsequently we believe that the salts of the carboranyl-C-hydroxy derivatives may be viewed as consisting of the discrete ions Et_3NH^+ and MeΘO$^-$.

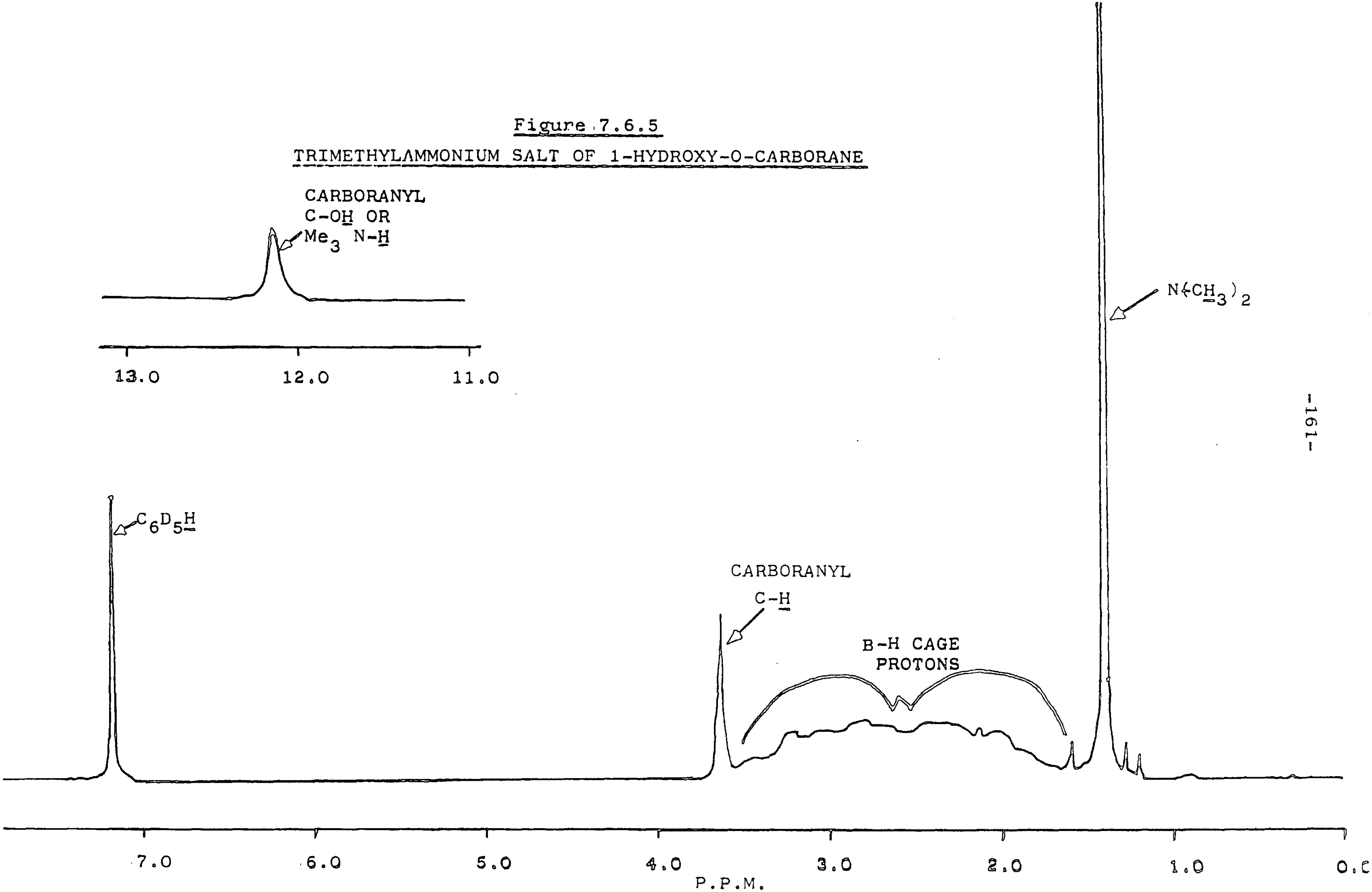
(v) Trimethylammonium salt of 1-Hydroxy-o-carborane, HΘOH

(360.134 MHz. Solvent C_6D_6, relative to C_6D_5H at 7.1602 p.p.m.) (See Fig. 7.6.5)

RESONANCE PATTERN	δ p.p.m.	INTEGRAL	ASSIGNMENT
^1H (^{11}B coupled)			
s	12.14	1 H	CARBORANYL-O$\underline{H}$ OR $Me_3N-\underline{H}$
s	3.63	1 H	CARBORANYL C-$\underline{H}$
m (centred at)	2.39	10 H	B-$\underline{H}$
s	1.39	9 H	$N(C\underline{H}_3)_3$

Figure 7.6.5

TRIMETHYLAMMONIUM SALT OF 1-HYDROXY-O-CARBORANE



The ^1H (^{11}B coupled) n.m.r. spectrum is clearly indicative of the compound HΘOHNMe$_3$.

Again the signal for the hydroxyl (or N-H) proton appears quite substantially downfield at 12.14 p.p.m..

(vi) <u>Pyridinium salt of 1-Hydroxy-2-methyl-o-carborane</u>

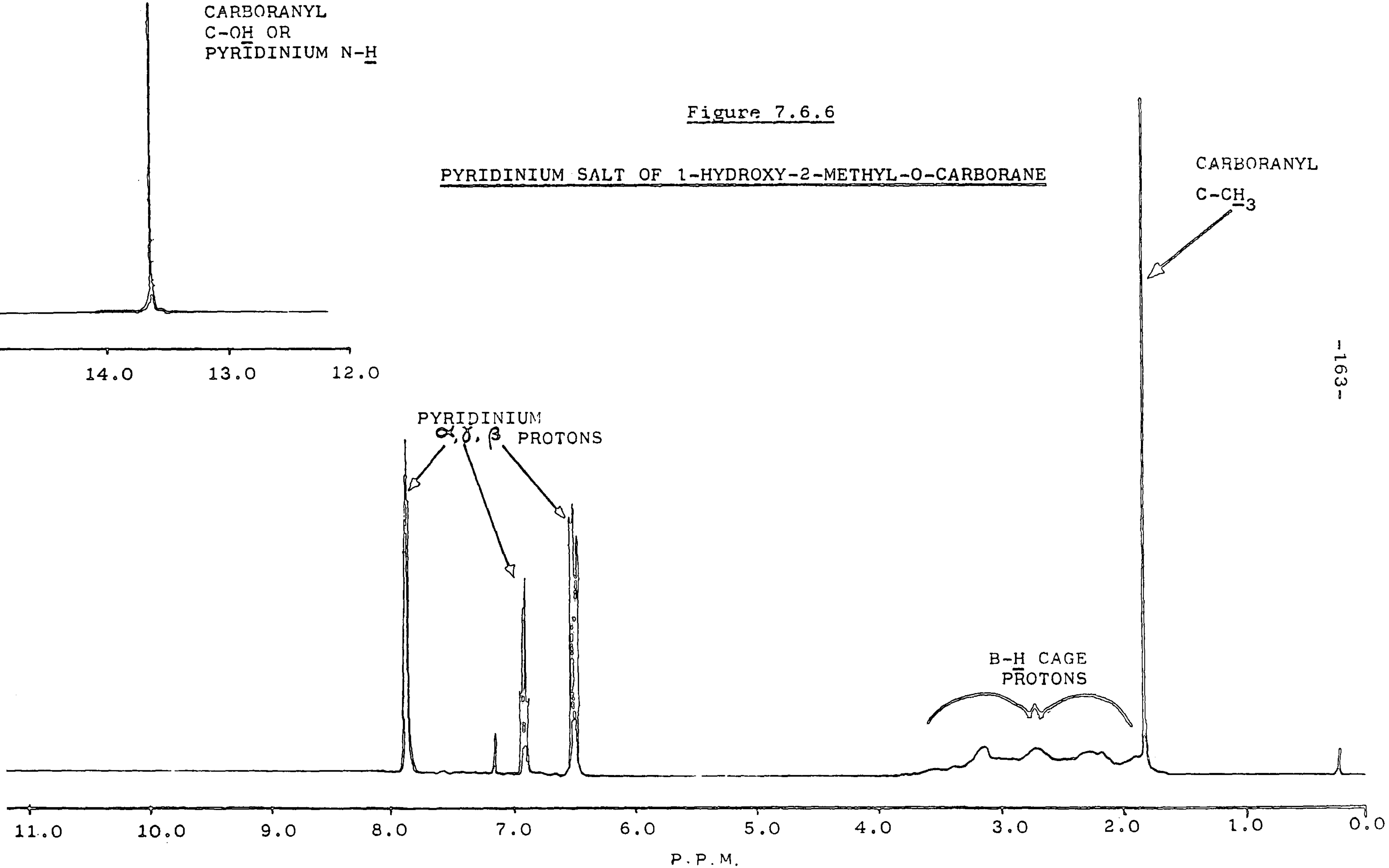
(360.134 MHz. Solvent C_6D_6, relative to C_6D_5H at 7.1600 p.p.m.) (See Fig. 7.6.6.)

RESONANCE PATTERN	δ p.p.m.	INTEGRAL	ASSIGNMENT
^1H (^{11}B coupled)			
s	13.64	1 H	CARBORANYL C-O$\underline{H}$ OR PYRIDINIUM N-$\underline{H}$
m	7.87→7.85	2 H	PYRIDINIUM α OR β C-$\underline{H}$
m	6.92→6.87	1 H	PYRIDINIUM γ C-$\underline{H}$
m	6.53→6.49	2 H	PYRIDINIUM α OR β C-$\underline{H}$
s	1.85	3 H	CARBORANYL C-C$\underline{H}_3$

The ^1H (^{11}B coupled) n.m.r. spectrum is clearly indicative of the pyridinium salt of 1-hydroxy-2-methyl-o-carborane. Again the signal for the hydroxy (or N-H) proton appears substantially downfield at 13.64 p.p.m. It is worth note, that this is the largest downfield shift of the hydroxyl (or N-H) proton observed, and that pyridine was the least basic of the bases employed for salt formation. It also seems significant that in the infra-red spectrum of the pyridinium salt of 1-hydroxy-2-methyl-o-carborane only a very

Figure 7.6.6

PYRIDINIUM SALT OF 1-HYDROXY-2-METHYL-O-CARBORANE



minor shift in the C-O stretching frequency (towards that of the C=O stretching frequencies) was observed, whereas much greater shifts were observed for the triethyl- and trimethylammonium salts.

(vii) 2-Dimethylaminoethyldimethylammonium salt of 1-Hydroxy-o-carborane

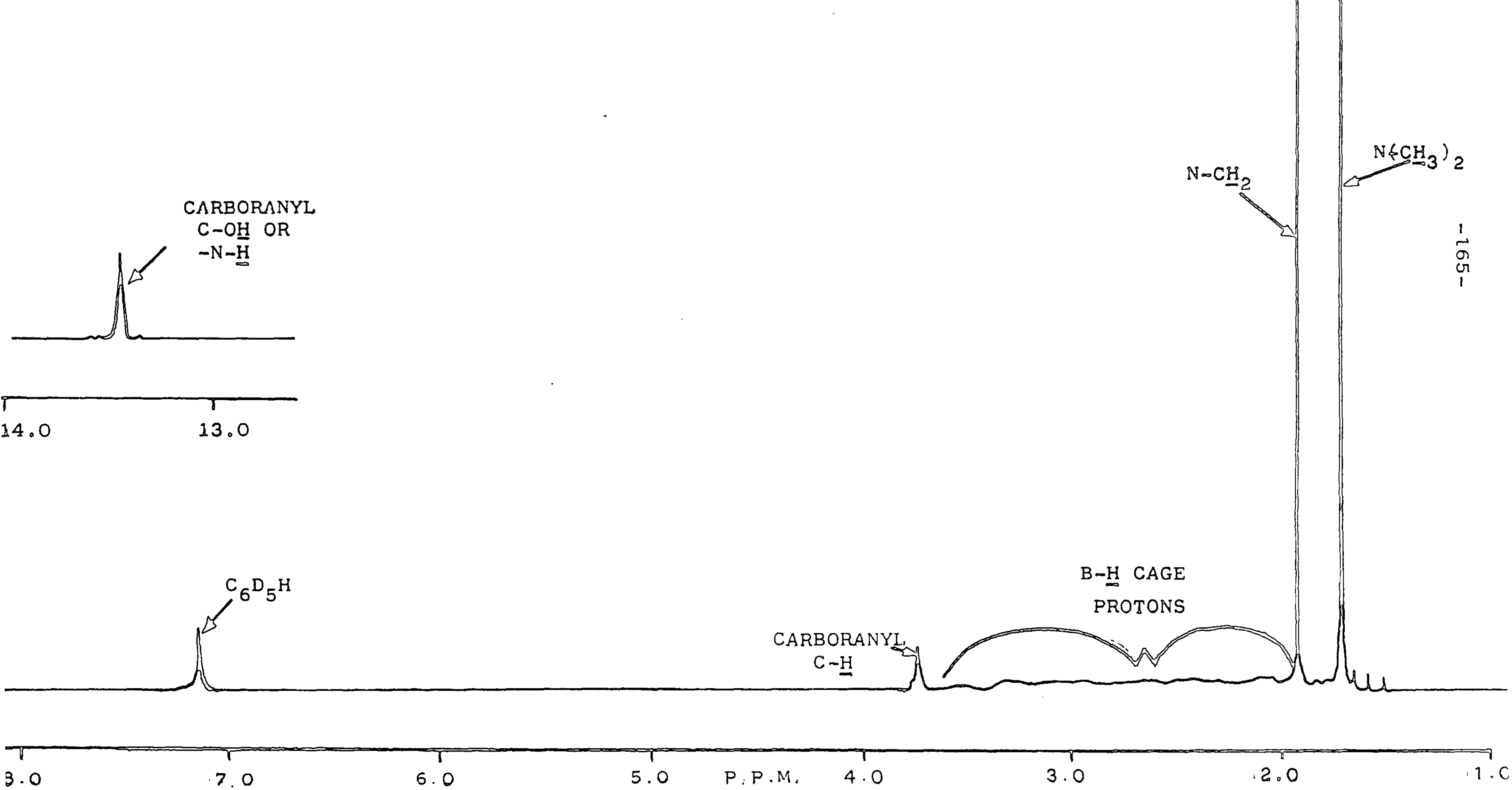
(360.134 MHz. Solvent C_6D_6, relative to C_6D_5H at 7.1611 p.p.m.) (See Fig. 7.6.7)

RESONANCE PATTERN	δ p.p.m.	INTEGRAL	ASSIGNMENT
^1H (^{11}B b.b. decoupled)			
s/s	13.44	1 H	CARBORANYL O-$\underline{H}$ OR R-N-$\underline{H}$
s/s	3.74	1 H	CARBORANYL C-$\underline{H}$
m/s	2.95	10 H	B-$\underline{H}$
m/s	2.81		
m/s	2.70		
m/s	2.54		
m/s	2.42		
d/d	1.944	4 H	TMEDA $C\underline{H}_2$
	1.940		
s/s	1.73	12 H	TMEDA $C\underline{H}_3$

The singlet for the hydroxyl (or N-H) proton appears substantially downfield at 13.44 p.p.m., a shift which is similar to that observed in the pyridinium salt of 1-hydroxy-

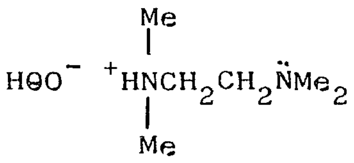
Figure 7.6.7

2-DIMETHYLAMINO ETHYL DIMETHYLAMMONIUM SALT OF 1-HYDROXY-O-CARBORANE



2-methyl-o-carborane.

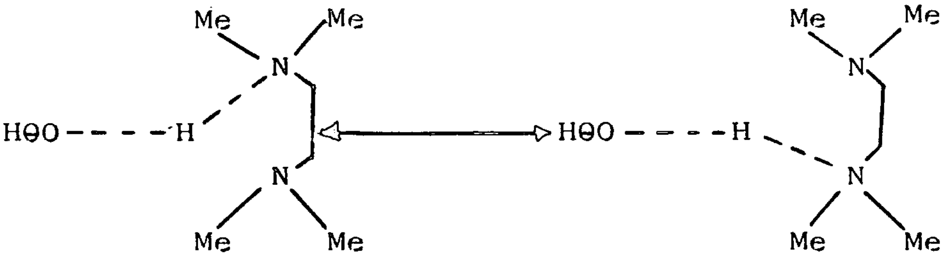
From the structural formula of the 2-dimethylaminoethyldimethylammonium salt of 1-hydroxy-o-carborane;



$$H\theta O^{-}\ {}^{+}H\overset{Me}{\underset{Me}{N}}CH_2CH_2\ddot{N}Me_2$$

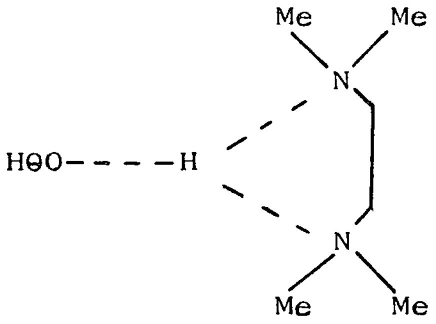
you would expect to see two different types of methyl groups and two different types of $C\underline{H}_2$ protons in the ^1H n.m.r. spectrum. However it is apparent from the actual ^1H (^{11}B broad band decoupled) spectrum that all of the methyl groups are identical and appear as a singlet at 1.73 p.p.m. (integral 12 H), as are all of the methylene protons which appear as a doublet at 1.94 p.p.m. (integral 4 H).

A probable explanation may be that in solution, the 2-dimethylaminoethyldimethylammonium salt of 1-hydroxy-o-carborane may exist as fluxional species as shown:-



If the fluxional process occurred very rapidly, then it would be very difficult to observe the discrete species on the n.m.r. time scale and consequently the actual observed ^1H n.m.r. spectrum would result.

An alternative explanation for the observed ^1H n.m.r. results may be that the hydroxyl proton is strongly associated with both the nitrogen atoms of the base rather than just one, and this results in the formation of a proton bridged species as shown:-



(viii) 1-Trimethylsiloxy-2-methyl-o-carborane, MeΘOSiMe$_3$

(360.134 MHz. Solvent C_6D_6, relative to C_6D_5H at 7.1610 p.p.m.)

RESONANCE PATTERN	δ p.p.m.	INTEGRAL	ASSIGNMENT
$^1H(^{11}B$ coupled)			
m (centred at)	2.50	10 H	B-$\underline{H}$
s	1.57	3 H	CARBORANYL C-$C\underline{H}_3$
s	0.01	9 H	Si $(C\underline{H}_3)_3$

The ^1H (^{11}B coupled) n.m.r. spectrum clearly shows the carboranyl-methyl protons and the methyl groups attached to the silicon.

B. ^{11}B and ^{11}B COSY (2-D) n.m.r.

^{11}B n.m.r., although widely used for structural elucidation of polyhedral borane and heteroborane cluster compounds, has serious limitations as a structural probe. There are two primary problems associated with ^{11}B n.m.r.

These are

1) broad signals (50-150 Hz) arising in part from unresolved ^{11}B—^{11}B coupling (172) and

2) the absence of a broadly applicable theory of ^{11}B shifts.

Consequently, it is frequently the case that the ^{11}B n.m.r. spectrum of a boron cluster of unknown geometry conveys little more than symmetry information. Unlike the chemical shifts exhibited by ^{1}H and ^{13}C nuclei, ^{11}B ($I = \frac{3}{2}$, 80% abundance) exhibits few general, reliable correlations with molecular structure this being highlighted by the fact that, even in molecules of established geometry, the complete unambiguous assignment of ^{11}B n.m.r. spectra may not be possible or may require laborious studies involving isotopic labelling or single-frequency decoupling. (173)

Over the last few years n.m.r. spectroscopy has undergone a rapid growth, not least in the field of two dimensional techniques. (174) One of the potentially most useful of these methods is the technique of homonuclear chemical shift correlation spectroscopy (COSY). (175) The COSY technique has proved to be a great asset in the determination of polyhedral borane structures since it provides a means of showing how boron nuclei are interlinked.

We have used ^{11}B (^{1}H broad band decoupled) and COSY n.m.r. spectroscopy, to study the C-hydroxy-carboranes and their salts. The ^{11}B (^{1}H b.b. decoupled) n.m.r. results for ortho- and meta-carborane are also presented for reference purposes.

RESULTS

(i) Ortho-Carborane, HΘH (176)

(115.548 MHz. Solvent C_6D_6, relative to $BF_3.OEt_2$ at 0 p.p.m.) (See Figure 7.6.12)

RESONANCE PATTERN	δ p.p.m.	INTEGRAL	ASSIGNMENT
^{11}B(^{1}H b.b. decoupled)			
d/s	-1.50	2 B	B(9,12)
d/s	-8.32	2 B	B(10,8)
distorted triplet (d/s	-12.84	4 B	B(4,5,7,11)
(d/s	-14.12	2 B	B(3,6)

(ii) Meta-Carborane, HΘ'H (176)

(115.548 MHz. Solvent C_6D_6, relative to $BF_3.OEt_2$ at 0 p. p.m.) (See Figure 7.6.12)

RESONANCE PATTERN	δ p.p.m.	INTEGRAL	ASSIGNMENT
^{11}B(^{1}H b.b. decoupled)			
d/s	-5.85	2 B	B(5,12)
d/s	-9.50	2 B	B(9,10)
d/s	-12.51	4 B	B(4,6,8,11)
d/s	-16.43	2 B	B(2,3)

The unambiguous assignment of all of the resonances in the ^{11}B (^{1}H b.b. decoupled) spectra of ortho- and meta-carborane was recently achieved by Grimes, using COSY two-dimensional n.m.r.. (176) Prior to these two-dimensional n.m.r. experiments, only the resonances due to boron atoms B(3,6) and B(4,5,7,11) in ortho-carborane and boron-atoms B(2,3) and B(4,6,8,11) in meta-carborane could be unambiguously assigned.

(iii) <u>1-Hydroxy-m-carborane, HΘ'OH</u>

(115.548 MHz. Solvent C_6D_6 relative to $BF_3.OEt_2$ at 0 p.p.m.)
(See Figure 7.6.12)

RESONANCE PATTERN	p.p.m.	INTEGRAL	ASSIGNMENT
$^{11}B(^{1}H$ b.b. decoupled)			
d/s	-3.80	1 B	B(5 or 12)
d/s	-10.44	2 B	
d/s	-12.12	2 B	
d/s	-12.96	1 B	B(5 or 12)
d/s	-15.08	4 B	

In the compound HΘ'OH there are essentially six different types of boron atoms, these include B(5), B(12), B(2,3), B(9,10), B(8,11) and B(4,6). Therefore the $^{11}B(^{1}H$ b.b. decoupled) n.m.r. spectrum should consist of six resonances corresponding to these distinct groups of boron atoms. However the actual spectrum consisted of only five resonances and as a result we have been unable to unambiguously assign any of the resonances. It seems likely that the resonances at -3.80 p.p.m. (integral 1B) and -12.96 p.p.m. (integral 1B) are due to boron atoms B(5) and B(12) since these atoms are essentially unique. However, which boron atom produces which resonance cannot be determined from the available data.

(iv) (a) <u>1-Hydroxy-2-methyl-o-carborane, MeΘOH</u>

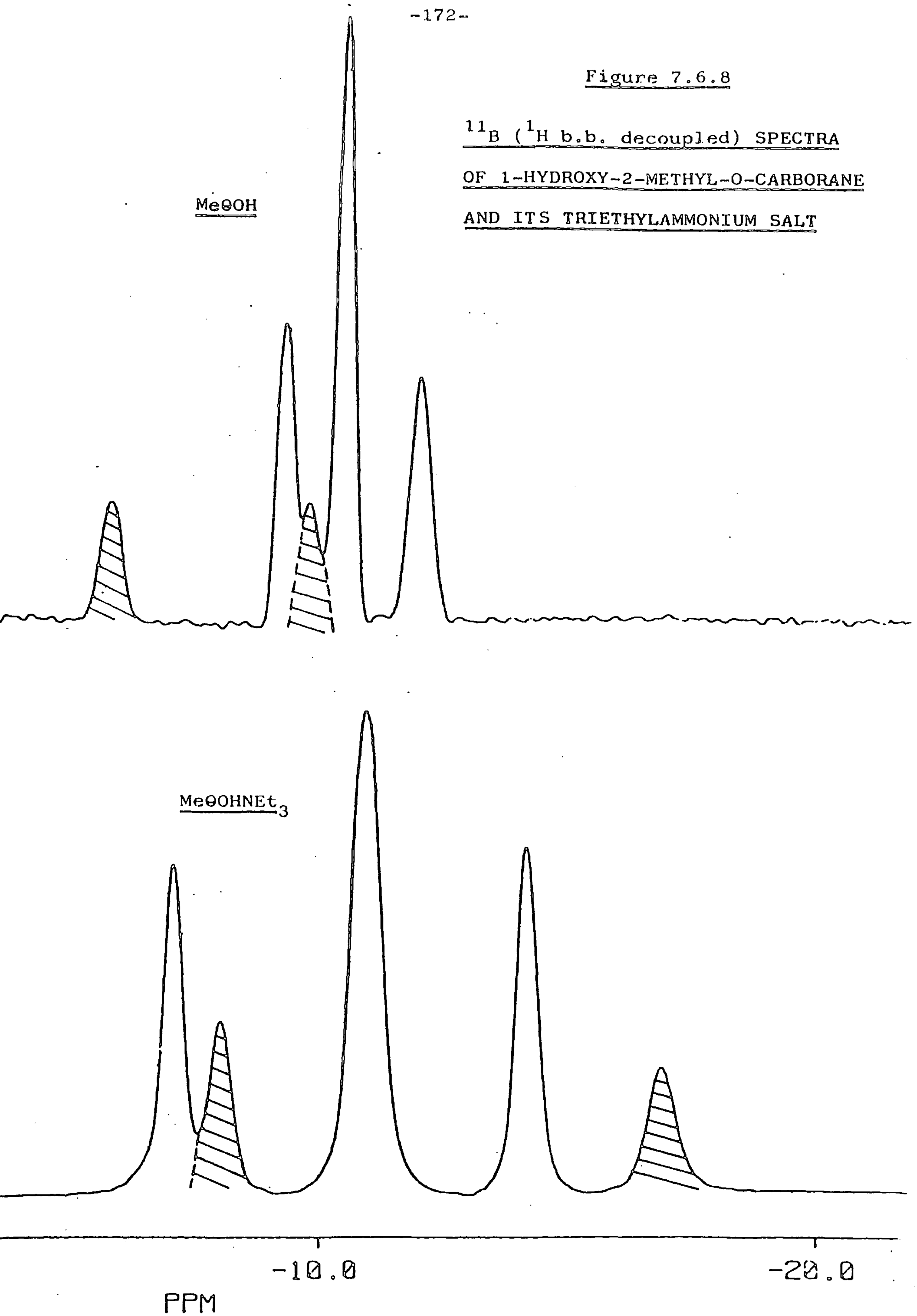
(115.548 MHz. Solvent C_6D_6, relative to $BF_3.OEt_2$ at 0 p.p.m.) (See Figure 7.6.8 and 7.6.12)

RESONANCE PATTERN	δ p.p.m.	INTEGRAL	ASSIGNMENT
$^{11}B(^{1}H$ b.b. decoupled)			
d/s	-5.66	1 B	B(9 or 12)
distorted quartet (d/s	-9.18	2 B	
d/s	-9.68	1 B	B(9 or 12)
d/s	-10.39	4 B	
d/s	-11.91	2 B	

As was the case for the species HΘ'OH the only signals that may be partially assigned with any certainty are the two signals at -5.66 p.p.m. (integral 1B) and -9.68 p.p.m. (integral 1B) which correspond to the 2 unique boron atoms i.e. B(9) and B(12).

Figure 7.6.8

^{11}B (^{1}H b.b. decoupled) SPECTRA OF 1-HYDROXY-2-METHYL-O-CARBORANE AND ITS TRIETHYLAMMONIUM SALT



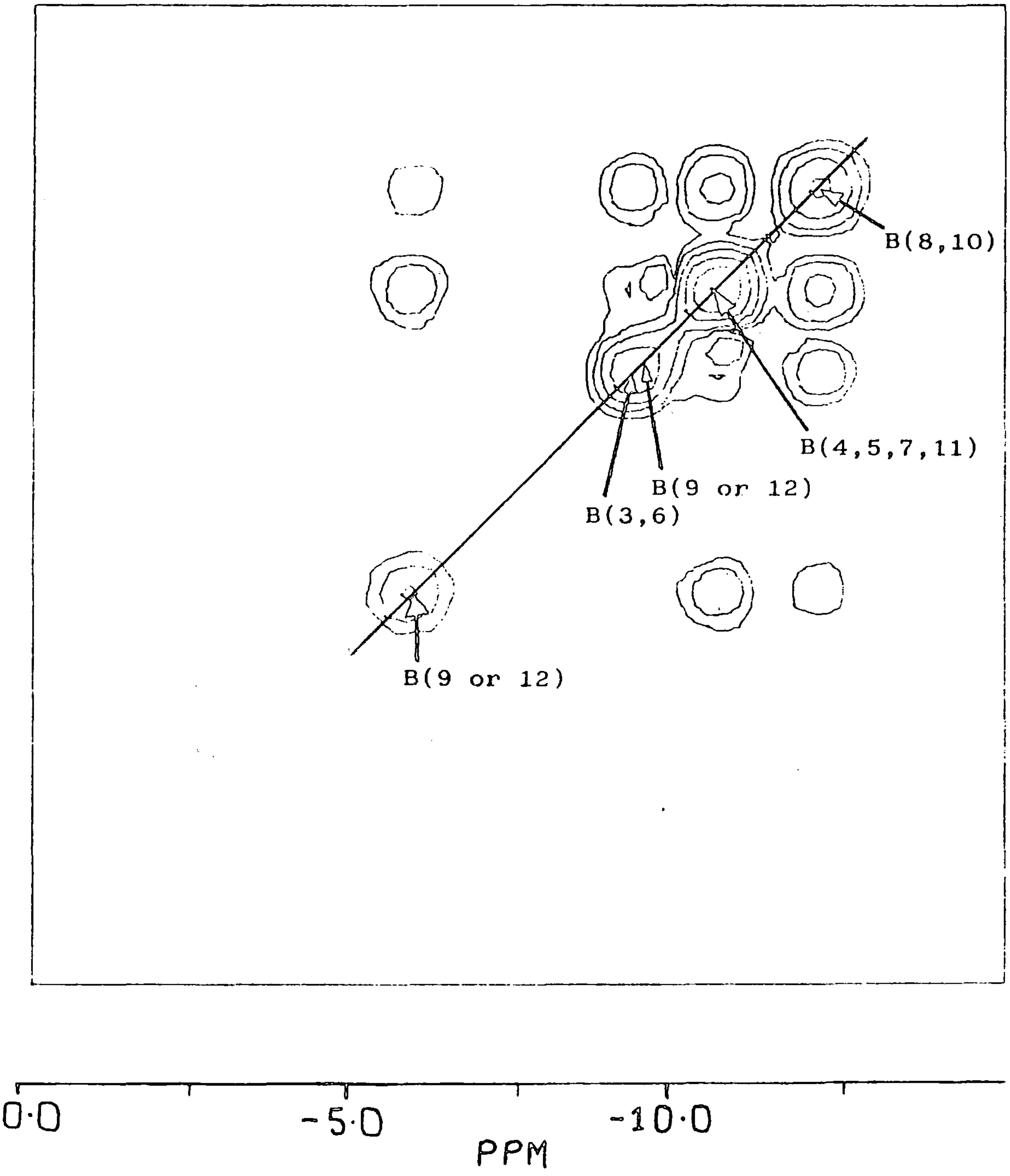
(b) ^{11}B-^{11}B Couplings detected in the COSY spectrum of 1-Hydroxy-2-methyl-o-carborane. (See Figure 7.6.9.)

^{11}B Nucleus	δ p.p.m.	^{11}B Couplings Detected
B(9 or 12)	-5.66	B(4,5,7,8,10,11)
B(3,6)	-9.18	B(4,5,7,8,10,11)
B(9 or 12)	-9.68	B(4,5,7,8,10,11)
B(4,5,7,11)	-10.39	B(3,6,8,9,10,12)
B(8,10)	-11.91	B(3,4,5,6,7,9, 11,12)

The COSY two-dimensional spectrum in conjunction with the assumptions that, the resonances at -5.66 and -9.68 p.p.m. are due to boron atoms B(9) and B(12), and the resonance at -10.39 p.p.m. (which may actually be a coincidental combination of two resonances) is due to boron atoms B(4,5,7,11), has allowed us to assign almost every resonance in the spectrum of 1-hydroxy-2-methyl-o-carborane. It must however be noted that these assignments, being partially based on the above assumptions, cannot be regarded as being totally unambiguous.

Figure 7.6.9

COSY 2-D N.m.r. SPECTRUM OF 1-HYDROXY-2-METHYL-O-CARBORANE, MeOOH



(v) Triethylammonium salt of 1-hydroxy-2-methyl-o-carborane

(115.548 MHz. Solvent C_6D_6 relative to $BF_3.OEt_2$ at 0 p.p.m.)
(See Figure 7.6.8 and 7.6.12)

RESONANCE PATTERN	δ p.p.m.	INTEGRAL	ASSIGNMENT
$^{11}B(^1H$ b.b. decoupled)			
distorted triplet (d/s	-7.06	2 B	
(d/s	-8.01	1 B	B(9 or 12)
d/s	-10.96	4 B	
d/s	-14.16	2 B	
d/s	-16.91	1 B	B(9 or 12)

As was found for both MeΘOH and HΘ'OH the only signals in the $^{11}B(^1H$ b.b. decoupled) spectrum of $MeΘOHNEt_3$ which may be assigned with any certainty are the two signals at -8.01 and -16.91 p.p.m. which correspond to the two unique boron atoms i.e. B(9) and B(12). (See Figure 7.6.12)

A comparison of the ^{11}B (^1H b.b. decoupled) spectrum obtained for the triethylammonium salt of 1-hydroxy-2-methyl-o-carborane with that obtained for 1-hydroxy-2-methyl-o-carborane clearly shows that on salt formation, there is a marked effect on the chemical shifts of the boron atoms of the cage. (See Figure 7.6.8). It is also apparent that the effects felt by each boron atom varies greatly throughout the cage. This is clearly illustrated by the fact that one of the two resonances thought to be due to boron atoms B(9) and B(12), (shown as shaded peaks in Figure 7.6.8) is significantly shifted upfield by approximately 8 p.p.m. whereas the other resonance is only slightly shifted upfield by approximately 2.5 p.p.m. Overall there is an upfield shift of approximately 2 p.p.m., suggesting that, on salt formation, there may be an increase in electron density within the cage.

(vi) (a) Trimethylammonium salt of 1-hydroxy-o-carborane

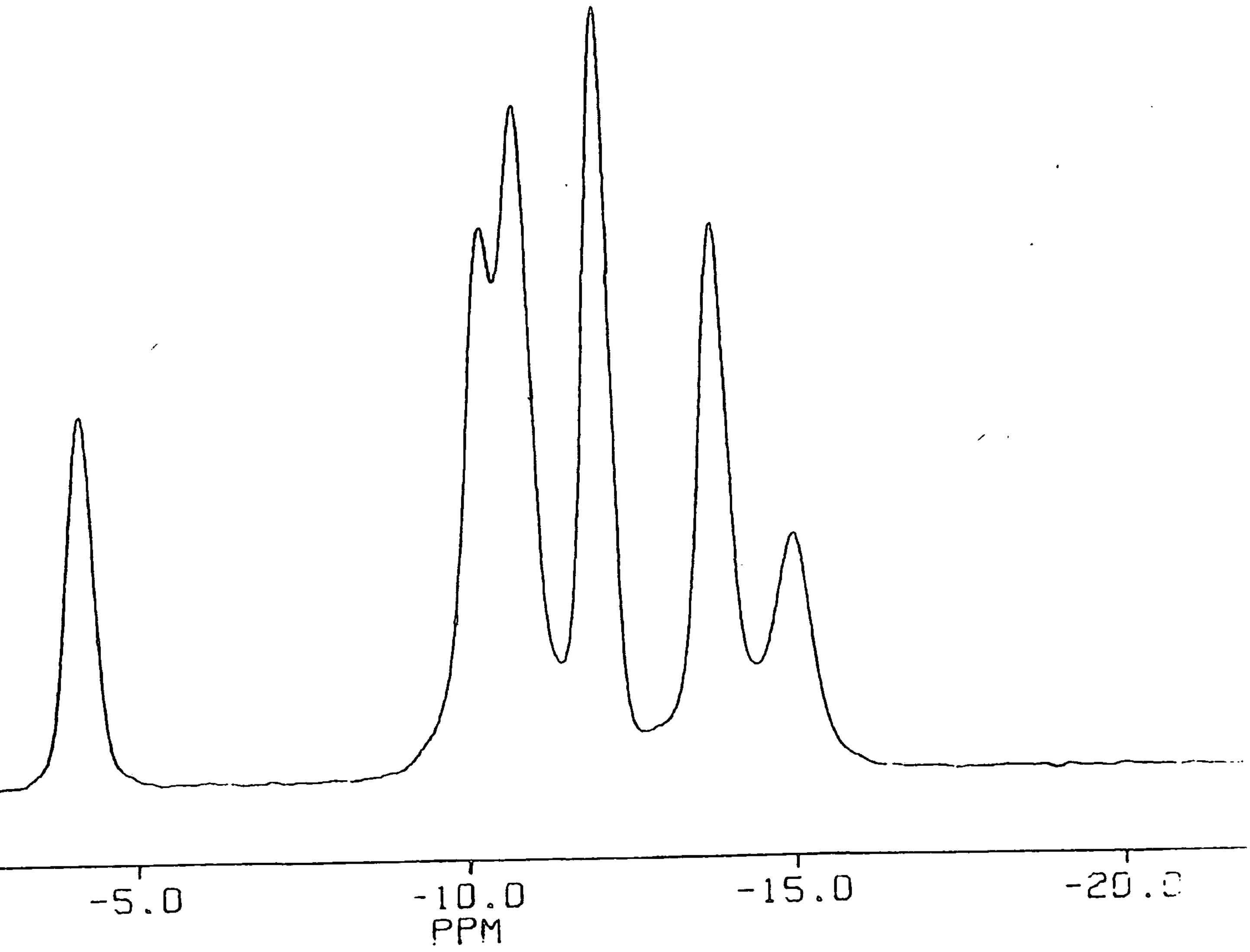
(115.548 MHz. Solvent C_6D_6, relative to $BF_3.OEt_2$ at 0 p.p.m.)
(See Figure 7.6.10. and 7.6.12)

RESONANCE PATTERN	δ p.p.m.	INTEGRAL	ASSIGNMENT
$^{11}B(^{1}H$ b.b. decoupled)			
d/s	-4.13	1 B	B(9 or 12)
d/s	-10.26	2 B	
d/s	-10.78	2 B	
d/s	-12.01	2 B	
d/s	-13.76	2 B	
d/s	-14.98	1 B	B(9 or 12)

The only signals in the $^{11}B(^{1}H$ b.b. decoupled) spectrum of $H\Theta OHNMe_3$ which may be assigned with any certainty are the two signals at -4.13 and -14.98 p.p.m., which correspond to the two unique boron atoms, i.e. B(9) and B(12).

Figure 7.6.10

^{11}B (^{1}H b.b. decoupled) SPECTRUM OF THE TRIMETHYLAMMONIUM SALT OF 1-HYDROXY-O-CARBORANE, $H\Theta OHNMe_3$



Unlike the spectrum obtained for the triethylammonium salt of 1-hydroxy-2-methyl-o-carborane, which consists of only five resonances in the ratios 2:1:4:2:1, the observed ^{11}B(^{1}H b.b. decoupled) spectrum of the trimethylammonium salt of 1-hydroxy-o-carborane, consists of six resonances in the ratios 1:2:2:2:2:1 (see Figures 7.6.8 and 7.6.10). It is worth note that there are essentially six different types of boron atoms in both $\mathrm{Me\Theta OHNEt_3}$ and $\mathrm{H\Theta OHNMe_3}$, these include B(3,6), B(4,5), B(7,11), B(8,10), B(9) and B(12), and therefore the expected ^{11}B(^{1}H b.b. decoupled) spectrum should consist of six resonances. It seems likely that in the spectrum of $\mathrm{Me\Theta OHNEt_3}$ (see Figure 7.6.8) the intense resonance at -10.96 p.p.m. (integral 4B), may be due to the coincidental combination of two resonances and this may be the reason why only five resonances were observed rather than the expected six resonances.

(b) ^{11}B-^{11}B Couplings detected in the COSY spectrum of the Trimethylammonium salt of 1-Hydroxy-o-carborane

(See Figure 7.6.11)

^{11}B Nucleus	δ p.p.m.	^{11}B Couplings Detected
B(9 or 12)	-4.13	B(8,10,(4,5 or 7,11))
B(3,6)	-10.26	B(4,5,7,8,10,11)
B(4,5 or 7, 11)	-10.78	B(3,6,8,10, 9 or 12)
B(8,10)	-12.01	B(3,4,5,6,7,9,11, 12)
B(4,5 or 7, 11)	-13.76	B(3,6,8,10, 9 or 12)
B(9 or 12)	-14.98	B(8,10 (4,5 or 7,11))

Figure 7.6.11

COSY 2-D N.m.r. SPECTRUM OF HΘOHNMe$_3$

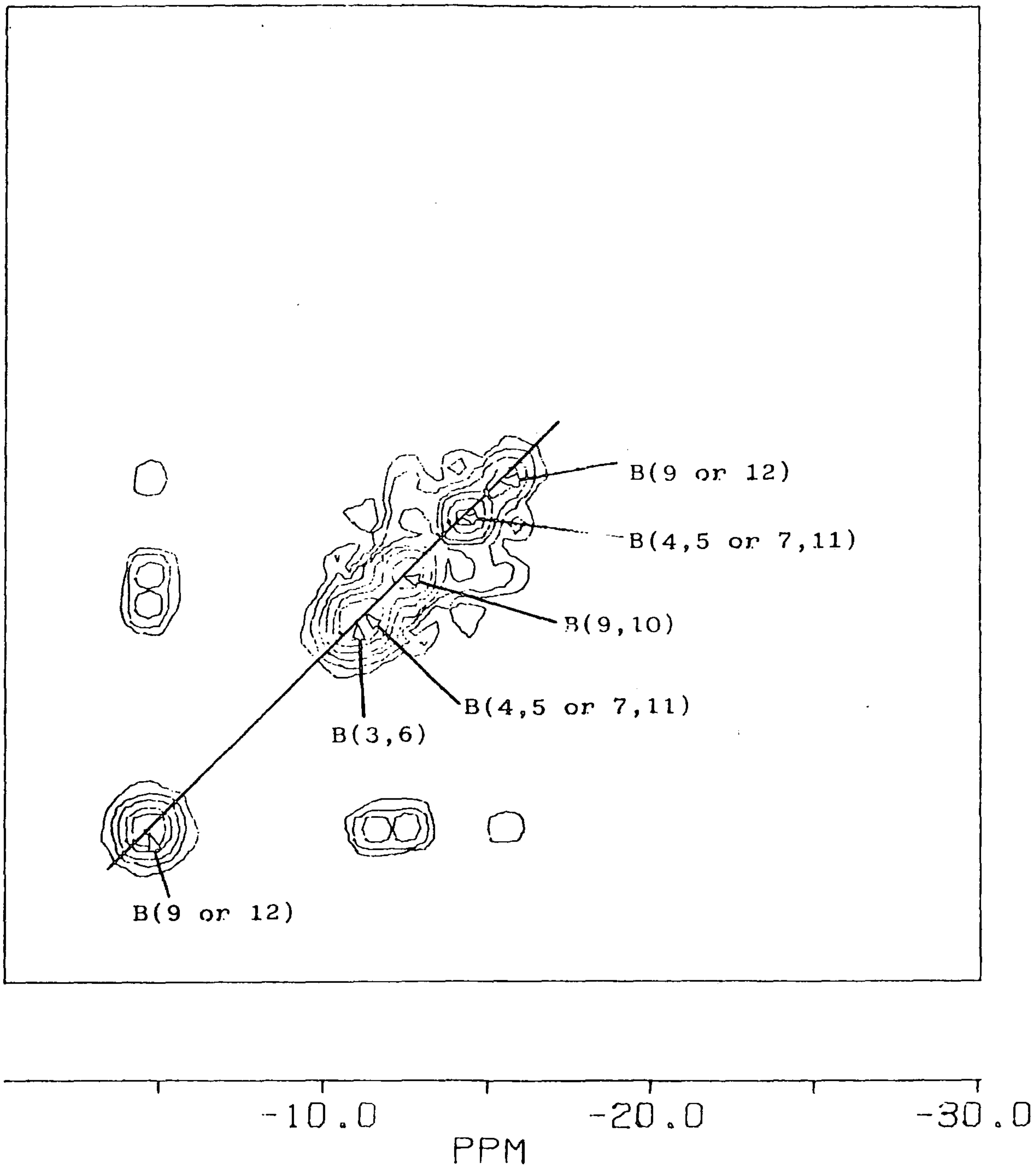
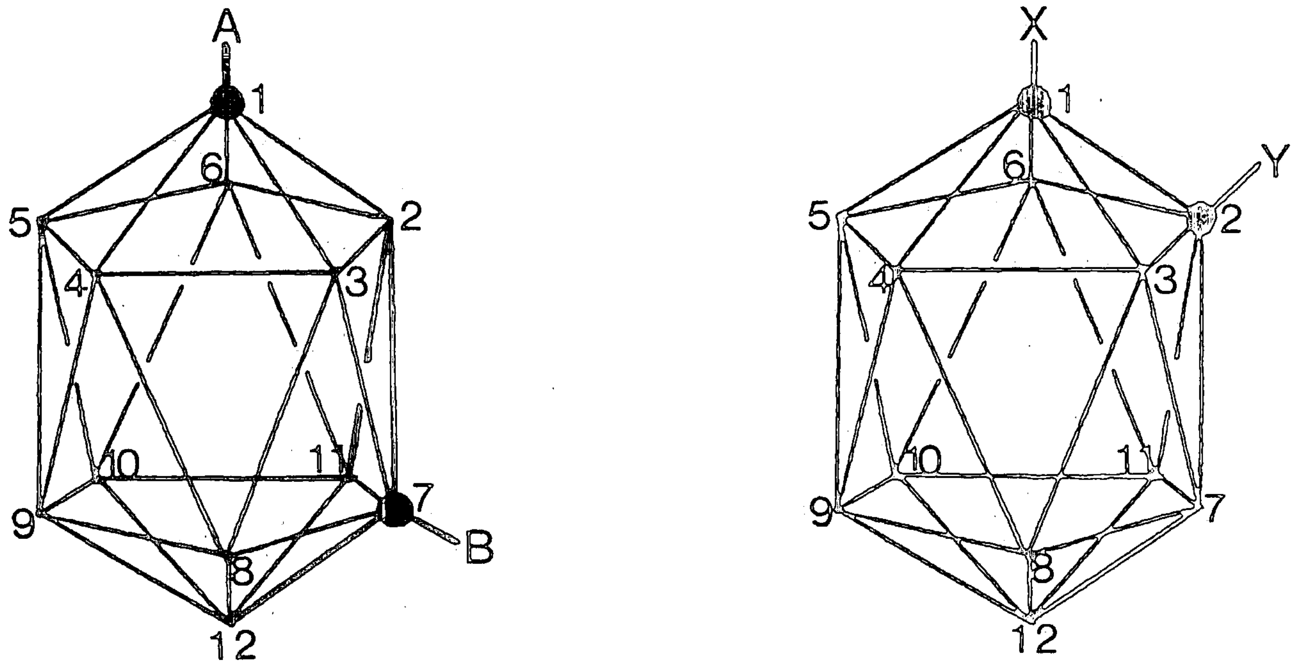


Figure 7.6.12



A = H and B = H for HΘ'H

A = H and B = OH for HΘ'OH

X = H and Y = H for HΘH

X = Me and Y = OH for MeΘOH

X = Me and Y = $OHNEt_3$ for $MeΘOHNEt_3$

X = H and Y = $OHNMe_3$ for $HΘOHNMe_3$

The COSY two-dimensional spectrum has allowed the unambiguous assignment of the resonances at -10.26 and -12.01 p.p.m., these being assigned to boron atoms B(3,6) and B(8,10) respectively. However it has not allowed the unambiguous assignment of the resonances due to boron atoms B(4,5), B(7,11), B(9) and B(12).

It is worth note that the resonance assigned to boron atoms B(8,10) in the spectrum of HΘOHNMe$_3$ appears between the resonances thought to be due to boron atoms B(4,5) and B(7,11), whereas in the spectrum of MeΘOHNEt$_3$ the resonance thought to be due to boron atoms B(8,10) appears upfield of the large resonance at -10.96 p.p.m. believed to be due to boron atoms B(4,5,7,11). (See Figures 7.6.8 and 7.6.10) No realistic predictions can be made, from the available data, as to why this may be occurring.

Unfortunately the work reported above was carried out at the end of the three year study and insufficient time was available to gather further data. It seems likely, from our preliminary studies, that further one and two-dimensional n.m.r. experiments, in conjunction with a series of theoretical calculations on the hydroxy-carboranes and their salts, may allow the unambiguous assignment of all the resonances in their ^{11}B(^{1}H b.b. decoupled) spectra and this in turn may lead to an understanding of the electronic changes occurring within the cage.

X-ray crystallographic studies may provide valuable information about the structural changes occurring when the carboranyl-C-hydroxy derivatives are converted to their salts. These studies have been undertaken, although, as yet no data is available.

APPENDIX A

GENERAL EXPERIMENTAL TECHNIQUES

APPENDIX A

1. GENERAL HANDLING TECHNIQUES

Most compounds in this thesis were treated as being air and moisture sensitive. All operations were therefore performed under vacuum, or in an atmosphere of dry nitrogen, as appropriate. Moisture sensitive solutions such as n-butyl lithium in n-pentane were stored under dry nitrogen and transferred by syringe against a counter-current of dry nitrogen. Volatile moisture sensitive compounds were stored under their own vapour pressure in rotaflo ampoules and transferred under vacuum into reaction vessels.

2. NITROGEN SUPPLY

Nitrogen gas was supplied to the laboratory as the boil-off from a tank containing liquid nitrogen, the gas was passed through a de-oxygenation plant and dried at the bench by passage through columns packed with phosphorus pentoxide.

3. GLOVE-BOX

Compounds of limited air sensitivity were handled in a glove box of simple design, the dry nitrogen atmosphere of which was maintained by continuous recycling through columns packed with phosphorus pentoxide. The box was periodically purged with fresh dry nitrogen to avoid the build-up of oxygen and volatiles. A hair hygrometer was kept inside the box to monitor the moisture level. Compounds of more extreme air-sensitivity were handled in a glove box designed to maintain levels of oxygen and moisture below one part per million. Oxygen was removed from the box by recycling through columns of catalytically activated copper, moisture was removed by passage through a column of activated molecular sieve.

4. SOLVENTS

Hydrocarbon solvents and diethyl ether were dried and stored over freshly extruded sodium wire. Other ether solvents were dried by refluxing with potassium metal until the addition of a single crystal of benzophenone yielded a permanent blue colouration. The liquids were then distilled onto extruded sodium wire and stored under dry nitrogen. Deuterated n.m.r solvents were obtained commercially and used as supplied.

5. STARTING MATERIALS

Solids were generally either freshly sublimed or recrystallized from an appropriate solvent prior to use. Liquid reagents were generally distilled, either under an atmosphere of dry nitrogen or under vacuum, as appropriate. Nitriles were dried by successive distillation from calcium hydride and phosphorus pentoxide. PMDETA and TMEDA were distilled from calcium hydride and stored over molecular sieve. Solutions of alkyl-lithium reagents were standardized by titration against a 0.1 M solution of sec-butanol in xylene, (171) 1,10-phenanthroline being used as an indicator.

6. INSTRUMENTATION

(a) Infra-red spectra

Infra-red spectra in the range 4000 cm^{-1} to 250 cm^{-1} were recorded on a Perkin-Elmer 457 or 577 grating spectrometer. Samples were mounted as either nujol mulls or liquid films between KBr plates, or as pressed KBr discs.

(b) ^{1}H n.m.r. spectra

Spectra were recorded on a Bruker 360 MHz spectrometer operating at 360.134 MHz.

(c) ^{11}B n.m.r and ^{11}B COSY spectra

Spectra were recorded on a Bruker 360 MHz spectrometer operating at 115.548 MHz. The deuterated solvent employed (normally C_6D_5H, d_6-benzene) was used as the internal reference standard, while boron was referenced externally to the ^{11}B signal of $BF_3.Et_2O$ in C_6D_6 at 0.00 p.p.m.

(d) Mass spectra

Mass spectra were recorded on an A.E.I. MS9 spectrometer at 70eV and an accelerating potential of 8kV, with a source temperature of 150-250°C, or on a V.G. 7070E spectrometer. The spectrum was scanned electromagnetically. Samples were introduced into the source by direct insertion.

7. ANALYTICAL METHODS

Carbon, hydrogen and nitrogen were determined using a Perkin-Elmer 240 Elemental Analyser. Air sensitive samples were sealed in pre-weighed aluminium capsules in a glove box. Halogens were determined by oxygen flask combustion followed by potentiometric titration. Metals were determined using a Perkin-Elmer 403 Atomic Absorption Spectrometer. Boron analyses on carboranes were made on boric acid, obtained by careful hydrolysis of the carborane with 90% nitric acid solutions. Boric acid was then determined by titration.

APPENDIX B

RESEARCH COLLOQUIA, SEMINARS, LECTURES AND CONFERENCES, 1982-85

APPENDIX B

COLLOQUIA AND CONFERENCES

The Board of Studies in Chemistry requires that each postgraduate research thesis contains an appendix listing :

(a) details of the first-year postgraduate induction course,

(b) all research colloquia, research seminars and lectures arranged by the Department of Chemistry and the Durham University Chemical Society during the period of the writer's residence as a postgraduate student,

(c) all research conferences attended and papers read out by the writer of the thesis during the period when the research for the thesis was carried out.

A. POSTGRADUATE INDUCTION COURSE

A series of lectures was given to explain the services available in the department.

Departmental organisation - Dr. E.J.F. Ross

Safety matters - Dr. M.R. Crampton

Electrical appliances and infra-red - Mr. R.N. Brown

Spectroscopy

Chromatography and microanalysis - Mr. T.F. Holmes

Atomic absorption spectrometry and inorganic analysis - Mr. R. Coult

Mass spectrometry - Dr. M. Jones

N.M.R. spectrometry - Dr. R.S. Matthews

Glassblowing techniques - Mr. R. Hart and Mr. G. Haswell

B. DEPARTMENTAL COLLOQUIA AND DURHAM UNIVERSITY CHEMICAL SOCIETY (D.U.C.S.) LECTURES

13.10.82 Dr. W.J. Feast (University of Durham), "Approaches to the synthesis of conjugated polymers".

14.10.82 Prof. H. Suhr (University of Tubingen, FRG), "Preparative Chemistry in Non-equilibrium plasmas".

14.10.82 Mr. F. Shenton (County Analyst, Durham), "There is death in the pot". (D.U.C.S.)

27.10.82 Dr. C.E. Housecroft (Oxford High School/Notre Dame University, USA), "Bonding capabilities of butterfly-shaped Fe_4 units; implications for C-H bond activation in hydrocarbon complexes".

28.10.82 Prof. M.F. Lappert, F.R.S., (University of Sussex), "Approaches to asymmetric synthesis and catalyses using electron-rich olefins and some of their metal complexes".

"The Chemistry of some Unusual Subvalent Compounds of the Main Group IV and V Elements". (D.U.C.S.)

4.11.82 Dr. D.H. Williams (University of Cambridge), "Studies on the Structures and Modes of action of antibiotics". (D.U.C.S.)

11.11.82 Dr. J. Cramp (I.C.I. Ltd.), "Lasers in Industry". (D.U.C.S.)

15.11.82 Dr. G. Bertrand (University of Toulouse, France), "Curtius rearrangement in organo-metallic series. A route for hybridised species".

24.11.82 Prof. G.G. Roberts (Applied Physics, University of Durham), "Langmuir-Blodgett films: solid state polymerisation of diacetylenes".

25.11.82	Dr. D.H. Richards (P.E.R.M.E., Ministry of Defence), "Terminally functional polymers; their synthesis and uses". (D.U.C.S.)
2.12.82	Dr. G.M. Brook (University of Durham), "The fate of the ortho-fluorine in 3,3-sigmatropic reactions involving polyfluoroaryl and -heteroaryl systems".
8.12.82	Dr. G. Wooley (Trent Polytechnic), "Bonds in transition metal cluster compounds".
12.1.83	Dr. D.C. Sherrington (University of Strathclyde), "Polymer-supported phase transfer catalysts".
27.1.83	Prof. D.W.A. Sharp (University of Glasgow), "Some redox reactions in fluorine chemistry". (D.U.C.S.)
3.2.83	Dr. R. Manning (Department of Zoology, University of Durham), "Molecular mechanisms of hormone action". (D.U.C.S.)
9.2.83	Dr. P. Moore (University of Warwick), "Mechanistic studies in solution by stopped flow F.T.-N.M.R. and high pressure N.M.R. line broadening".
10.2.83	Sir Geoffrey Allen, F.R.S. (Unilever Ltd.), "U.K. Research Ltd.". (D.U.C.S.)
17.2.83	Prof. A.G. MacDiarmid (University of Pennsylvania, USA), "Metallic Covalent Polymers: $(SN)_x$ and $(CH)_x$ and their derivatives". (D.U.C.S., R.S.C. Centenary Lecture)
21.2.83	Dr. R. Lynder-Bell (University of Cambridge), "Molecular motion in the cubic phase of NaCN".
2.3.83	Dr. D. Bloor (Queen Mary College, University of London), "The solid state chemistry of diacetylene monomers and polymers".
3.3.83	Prof. A.C.T. North (University of Leeds), "The

	use of a computer display system in studying molecular structures and interactions". (D.U.C.S.)
8.3.83	Prof. D.C. Bradley, F.R.S. (Queen Mary College, University of London), "Recent developments in organo-imido-transition metal chemistry".
9.3.83	Dr. D.M.J. Lilley (University of Dundee), "DNA, sequence, symmetry, structure and supercooling".
11.3.83	Prof. H.G. Viehe (University of Louvain, Belgium), "Oxidations on sulphur", "Fluorine substitutions in radicals". (Musgrave lecture).
16.3.83	Dr. I. Gosney (University of Edinburgh), "New extrusion reactions: organic synthesis in a hot tube".
25.3.83	Prof. F.G. Baglin (University of Nevada, USA), "Interaction induced Raman spectroscopy in supra-critical ethane".
21.4.83	Prof. J. Passmore (University of New Brunswick, Canada), "Novel selenium-iodine cations".
4.5.83	Prof. P.H. Plesh (University of Keele), "Binary ionisation equilibria between two ions and two molecules. What Ostwald never thought of".
10.5.83	Prof. K. Burger (Technical University of Munich, FRG), "New reaction pathways from trifluoromethyl substituted heterodienes to partially fluorinated heterocyclic compounds".
11.5.83	Dr. N. Isaacs (University of Reading), "The application of high pressures to the theory and practice of organic chemistry".
13.5.83	Dr. R. de Koch (Caloin College, Michigan, USA/ Free University, Amsterdam, Netherlands),

"Electronic structural calculations in organometallic cobalt cluster molecules. Implications for metal surfaces".

16.5.83 Prof. R.J. Lagow (University of Texas, USA), "The chemistry of polylithium organic compounds. An unusual class of matter".

18.5.83 Dr. D.M. Adams (University of Leicester), "Spectroscopy at very high pressures".

25.5.83 Dr. J.M. Vernon (University of York), "New heterocyclic chemistry involving lead tetraacetate".

15.6.83 Dr. A. Pietrzykowski (Technical University of Warsaw, Poland/University of Strathclyde), "Synthesis, structure and properties of aluminoxanes".

22.6.83 Dr. D.W.H. Rankin (University of Edinburgh), "Floppy molecules - the influence of phase on structure".

5.7.83 Prof. J. Miller (University of Camfinas, Brazil), "Reactivity in nucleophilic substitution reactions".

5.10.83 Prof. J.P. Maier (University of Basel, Switzerland), "Recent approaches to spectroscopic characterisation of cations".

12.10.83 Dr. C.W. McLeland (University of Port Elizabeth, Australia), "Cyclisation of aryl alcohols through the intermediacy of alkoxy and aryl radical cations".

19.10.83 Dr. N.W. Alcock (University of Warwick), "Aryl tellurium (IV) compounds, patterns of primary and secondary bonding".

20.10.83	Prof. R.B. Cundall (University of Salford), "Explosives". (D.U.C.S.)
26.10.83	Dr. R.H. Friend (Cavendish Laboratory, University of Cambridge), "Electronic properties of conjugated polymers".
3.11.83	Dr. G. Richards (University of Oxford), "Quantum pharmacology". (D.U.C.S.)
10.11.83	Dr. J. Harrison (Stirling Organic Ltd.), "Applied chemistry and the pharmaceutical industry". (D.U.C.S.)
24.11.83	Prof. D.A. King (University of Liverpool), "Chemistry in two dimensions". (D.U.C.S.)
30.11.83	Prof. I. Cowie (University of Stirling), "Molecular interpretation of non-relaxation processes in polymer glasses".
1.12.83	Dr. J.D. Coyle (The Open University), "The problem with sunshine". (D.U.C.S.)
14.12.83	Prof. R.J. Donovan (University of Edinburgh), "Chemical and physical processes involving the ion-pair states of the halogen molecules".
10.1.84	Prof. R. Hester (University of York), "Nanosecond laser spectroscopy of reaction intermediates".
18.1.84	Prof. R.K. Harris (University of East Anglia), "Multi-nuclear solid state magnetic resonance".
26.1.84	Prof. T.L. Blundell (Birkbeck College, University of London), "Biological recognition: Interactions of macromolecular surfaces". (D.U.C.S.)
2.2.84	Prof. N.B.H. Jonathan (University of Southampton), "Photoelectron spectroscopy- a radical approach". (D.U.C.S.)

8.2.84	Dr. B.T. Heaton (University of Kent), "Multinuclear n.m.r. studies".
15.2.84	Dr. R.M. Paton (University of Edinburgh), "Heterocyclic syntheses using nitrile sulphides".
16.2.84	Prof. D. Phillips (The Royal Institution), "Luminescence and photochemistry- a light entertainment". (D.U.C.S.)
23.2.84	Prof. F.G.A. Stone, F.R.S. (University of Bristol), "The use of carbene and carbyne groups to synthesise metal clusters" (D.U.C.S. The Waddington Memorial Lecture)
1.3.84	Prof. A.J. Leadbetter (Rutherford Appleton Laboratory), "Liquid crystals". (D.U.C.S.)
7.3.84	Dr. R.T. Walker (University of Birmingham), "Synthesis and biological properties of some 5-substituted uracil derivatives; yet another example of serendipity in antiviral chemotherapy".
8.3.84	Prof. D. Chapman (Royal Free Hospital School of Medicine, University of London), "Phospholipids and biomembranes: basic structure and future techniques". (D.U.C.S.)
21.3.84	Dr. P. Sherwood (University of Newcastle), "X-ray photoelectron spectroscopic studies of electrode and other surfaces".
23.3.84	Dr. A. Ceulemans (Catholic University of Leuvan, Belgium), "The development of field-type models of the bonding in molecular clusters".
28.3.84	Prof. H. Schmidbaur (Technical University of Munich, FRG), "Ylides in coordination sphere of metals: synthetic, structural and theoretical aspects". (D.U.C.S., R.S.C. Centenary Lecture)

2.4.84	Prof. K. O'Driscoll (University of Waterloo, Canada), "Chain ending reactions in free radical polymerisation".
3.4.84	Prof. C.H. Rochester (University of Dundee), "Infra-red studies of absorption at the solid-liquid interface".
25.4.84	Dr. R.M. Acheson (Department of Biochemistry, University of Oxford), "Some heterocyclic detective stories".
27.4.84	Dr. T. Albright (University of Houston, USA), "Sigmatropic rearrangements in organometallic chemistry".
14.5.84	Prof. W.R. Dolbier, Jr. (University of Florida, USA), "Cycloaddition reactions of fluorinated allenes".
16.5.84	Dr. P.J. Garratt (University College, London), "Syntheses with dilithiated vicinal diesters and carboximides".
22.5.84	Prof. F.C. De Schryver (Catholic University of Leuven, Netherlands), "Configurational and conformational control in excited state complex formation". "The use of luminescence in the study of micellar aggregates".
23.5.84	Prof. M. Tada (Waseda University, Japan), "Photochemistry of dicyanopyrazine derivatives".
29.5.84	Dr. A. Haaland (University of Oslo, Norway), "Electron diffraction studies of some organometallic compounds".
11.6.84	Dr. G.B. Street (I.B.M. San Jose, USA). "Conducting polymers derived from pyrroles".

19.9.84	Dr. C. Brown (IBM San Jose), "New Superbase Reactions - Organic Compounds".
21.9.84	Dr. H.W. Gibson (Signal UOP Research Centre, Des Plaines, Illinois), "Isomerization of Polyacetylene".
18.10.84	Dr. N. Logan (University of Nottingham), "N_2O_4 and Rocket Fuels". (D.U.C.S.)
19.10.84	Dr. A. Germain (Universite du Languedoc, Montpellier), "Anodic Oxidation of Perfluoro Organic Compounds in Perfluoralkane Sulphonic Acids".
24.10.84	Prof. R.K. Harris (University of Durham), "NMR of Solid Polymers".
25.10.84	Dr. W.J. Feast (University of Durham), "Syntheses of Conjugated Polymers. Why and How?". (D.U.C.S.)
1.11.84	Prof. B.J. Aylett (Queen Mary College, University of London), "Silicon - Dead Common or Refined". (D.U.C.S.)
7.11.84	Prof. W.W. Porterfield (Hampden-Sydney College, USA), "There is No Borane Chemistry (Only Geometry)".
7.11.84	Dr. H.S. Munro (University of Durham), "New Information from ESCA Data".
15.11.84	Prof. B.T. Golding (University of Newcastle-upon-Tyne), "The Vitamin B_{12} Mystery". (D.U.C.S.)
21.11.84	Mr. N. Everall (University of Durham), "Picosecond Pulsed Laser Raman Spectroscopy".
22.11.84	Prof. D.T. Clark (ICI New Science Group), "Structure, Bonding, Reactivity and Synthesis as

	Revealed by ESCA". (D.U.C.S.)
27.11.84	Dr. W.J. Feast (University of Durham), "A Plain Man's Guide to Polymeric Organic Metals".
28.11.84	Dr. T.A. Stephenson (University of Edinburgh), "Some Recent Studies in Platinum Metals Chemistry".
29.11.84	Prof. C.J.M. Stirling (University College of North Wales), "Molecules Taking the Strain". (D.U.C.S.)
5.12.84	Mr. P.J. Lux (University of Durham), "IR and GC Studies of the Interaction of CH_3OH with High Silica Zeolites".
6.12.84	Prof. R.D. Chambers (University of Durham), "The Unusual World of Fluorine". (D.U.C.S.)
12.12.84	Dr. K.B. Dillon (University of Durham, "31P NMR Studies of Some Anionic Phosphorus Complexes".
11.1.85	Prof. Emeritus H. Suschitzky (University of Salford), "Fruitful Fissions of Benzofuroxanes and Isobenzimadazoles (umpolung of o-phenylenediamine)".
24.1.85	Dr. A.K. Covington, (University of Newcastle-upon-Tyne), "Chemistry with Chips". (D.U.C.S.)
31.1.85	Dr. M.L.H. Green (University of Oxford), "Naked Atoms and Negligée Ligands". (D.U.C.S.)
7.2.85	Prof. A. Ledwith (Pilkington Bros.), "Glass as a High Technology Material". (D.U.C.S.)
13.2.85	Dr. G.W.J. Fleet (University of Oxford), "Syntheses of some Alkaloids from Carbohydrates".
14.2.85	Dr. J.A. Salthouse (University of Manchester), "Son et Lumiere" (A Chemical Energy Show) (D.U.C.S.)

19.2.85	Dr. D.J. Mincher (University of Durham), "Stereoselective Syntheses of Some Novel Anthracyclinones Related to the Anti-Cancer Drug Adriamycin and to the Steffimycin Antibiotics".
21.1.85	Prof. P.M. Maitlis, FRS (University of Sheffield), "What Use is Rhodium?". (D.U.C.S.)
27.2.85	Dr. R.E. Mulvey (University of Durham), "Some Unusual Lithium Complexes".
7.3.85	Dr. P.W. Atkins (University of Oxford), "Magnetic Reactions". (D.U.C.S.)
7.3.85	Dr. P.J. Rodgers (ICI plc, Agricultural Division, Billingham), "Industrial Polymers from Bacteria".
12.3.85	Prof. K. J. Packer (B.P. Research Centre), "NMR Investigations of the Structure of Solid Polymers".
14.3.85	Prof. A.R. Katritzky, FRS (University of Florida), "Some Adventures in Heterocyclic Chemistry".
21.3.85	Dr. M. Poliakoff (University of Nottingham), "New Methods for Detecting Organometallic Intermediates in Solution".
28.3.85	Prof. H. Ringsdorf (Organic Chemistry Institute, University of Mainz), "Polymeric Liposomes as Models for Biomembranes and Cells?".
24.4.85	Dr. M.C. Grossel (Bedford College, University of London), "Hydroxypyridone Dyes - Bleachable One-Dimensional Metals?".
1.5.85	Dr. D. Parker (ICI plc, Petrochemical & Plastics Division, Wilton), "Applications of Radioisotopes in Industrial Research".
7.5.85	Prof. G.E. Coates (formerly of University of Wyoming, USA), "Chemical Education in Britain and

America: Successes and Deficiencies".

8.5.85 Prof. D. Tuck (University of Windsor, Ontario), "Lower Oxidation State Chemistry of Indium".

9.5.85 Prof. R.K. Harris (University of Durham), "Chemistry in a Spin: Nuclear Magnetic Resonance".

14.5.85 Prof. J. Passmore (University of New Brunswick), "The Synthesis and Characterisation of some Novel Selenium-Iodine Cations, Aided by ^{77}Se NMR Spectroscopy".

15.5.85 Dr. J.E. Packer (University of Auckland, New Zealand), "Studies of Free Radical Reactions in Aqueous Solution Using Ionising Radiation".

17.5.85 Prof. I.D. Brown (Institute of Materials Research, McMaster University, Canada), "Bond Valence as a Model for Inorganic Chemistry".

21.5.85 Dr. D.L.H. Williams (University of Durham), "Chemistry in Colour".

22.5.85 Dr. R. Grimmett (University of Otago, Dunedin, New Zealand), "Some Aspects of Nucleophilic Substitution in Imidazoles".

22.5.85 Dr. M. Hudlicky (Virginia State University, Blacksburg), "Preferential Elimination of Hydrogen Fluoride from Vicinal Bromofluorocompounds".

4.6.85 Dr. P.S. Belton (Food Research Institute, Norwich), "Analytical Photoacoustic Spectroscopy".

13.6.85 Dr. D. Woollins (Imperial College, University of London), "Metal-Sulphur-Nitrogen Complexes".

14.6.85 Prof. Z. Rappoport (The Hebrew University, Jerusalem), "The Rich Mechanistic World of Nucleophilic Vinylic Substitution".

19.6.85	Dr. T.N. Mitchell (University of Dortmund), "Some Synthetic and NMR-Spectroscopic Studies of Organotin Compounds".
26.6.85	Prof. G. Shaw (University of Bradford), "Synthetic Studies on Imidazole Nucleosides and the Antibiotic Coformycin".
12.7.85	Dr. K. Laali (Hydrocarbon Research Institute, University of Southern California), "Recent Developments in Superacid Chemistry and Mechanistic Considerations in Electrophilic Aromatic Substitutions; A Progress Report".

C. RESEARCH CONFERENCES

13-15th September, 1982	"Intraboron III". University of Leeds
11-15th July, 1983	"IMEBORON V: Fifth International Symposium on Boron Chemistry". University of Swansea
April, 1984	Graduate Symposium, Durham
September, 1984	"Intraboron IV", University of Durham
April, 1985	Graduate Symposium, Durham

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REFERENCES

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