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EXPLORATION OF NEW ROUTES TO BORANES AND CARBORANES

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ABSTRACT

The crystal chemistry of binary metal borides in the composition range M_4B to MB_{12} and the hydrolytic chemistry of reactive metal borides to give boranes are reviewed. The thermal interconversion reactions of the smaller volatile boranes from B_2H_6 to $B_{10}H_{14}$ is critically examined and a rationalisation of their reactions with the transient Lewis acid species $\{BH_3\}$, $\{B_3H_7\}$ and $\{B_4H_8\}$ is developed. This approach reveals a pattern of step-wise cage-growth for nido boranes which first seem to ligate a BH_3 unit and then eliminate H_2 giving the next higher homologue. Also, a structure-reactivity relationship for B_2H_6 and the arachno boranes is suggested where the terminal hydrogens of the BH_2 groups are thought to possess hydridic character which dominates their reactions with the Lewis acid intermediates. This work is partially extended to the cage-expansion and pyrolysis reactions of the anionic boron hydrides. A detailed review is presented of the pyrolysis of tetraalkylammonium borohydrides to give $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ in high yield. A study of the acidic hydrolysis of MgB_2 under a wide range of conditions is reported. The reactions of MgB_2 with 100% H_3PO_4 and with 7M H_3PO_4 under the influence of ultrasonics are found to be promising methods for increasing the borane yield. The anions $[B_{12}H_{12}]^{2-}$, $[B_{10}H_{10}]^{2-}$ and possibly $[B_9H_{14}]^-$ are shown to be important products from MgB_2 hydrolysis. A mechanism is proposed for this reaction incorporating initial production of $[B_6H_9]^-$ which is protonated to give B_6H_{10}; degradation of this borane in the acidic solution is thought to account for generation of B_5H_9 and B_4H_{10} which are the only other major volatile boron hydride products. Finally, some attempted "one-pot" carborane syntheses using MgB_2 as the boron source are discussed.

TABLE OF CONTENTS

. . . .

Chapter

1 Introduction

2 Borides: Structure and Hydrolysis

3 Neutral Borane Interconversions

TABLE OF CONTENTS (continued)

4 Borane Anion Interconversions

5 A Study of the Hydrolysis of Magnesium Diboride Under Acidic Conditions

TABLE OF CONTENTS (continued)

LIST OF FIGURES AND TABLES

LIST OF FIGURES AND TABLES (continued)

Table

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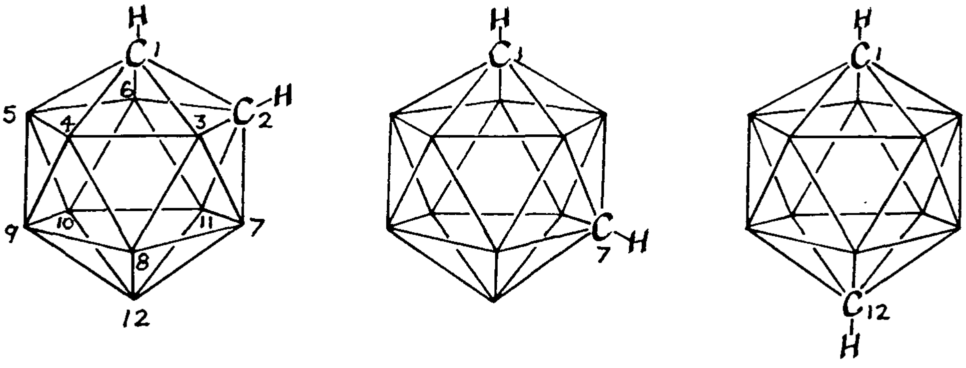
Chapter 1 Introduction

1.1 Background

Boranes[1,2,3] are molecular boron hydrides containing polyhedral networks of skeletal boron atoms; in carboranes[2,3,4] carbon atoms replace some of the boron atoms in the framework. The volatile and flammable smaller boranes were first studied in detail by Stock[3] in the early parts of this century. Experimental and theoretical academic study of the boranes proceeded at a steady pace until the 1950s when it was stimulated by efforts to manufacture high calorific value rocket fuels[2]. The preparation of carboranes emerged from this work, although neither they nor the boranes lived up to the purposes for which they were originally investigated.

The carboranes include some surprisingly thermally stable, base and oxidation-resistant compounds (particularly among the closo carboranes of formulae $C_2B_{n-2}H_n$) and the extensively studied, icosahedral carboranes, $C_2H_{10}H_{12}$ (see *fig. 1.1*), display a wide derivative chemistry. The C-H groups of these carboranes show typical aromatic behaviour and can be functionalised using techniques familiar from organic chemistry. Whilst these carboranes can be heated to ~600°C before cage degradation occurs, thermal isomerisation of ortho- to meta- and, at higher temperatures (with some decomposition), meta- to para-carborane takes place.



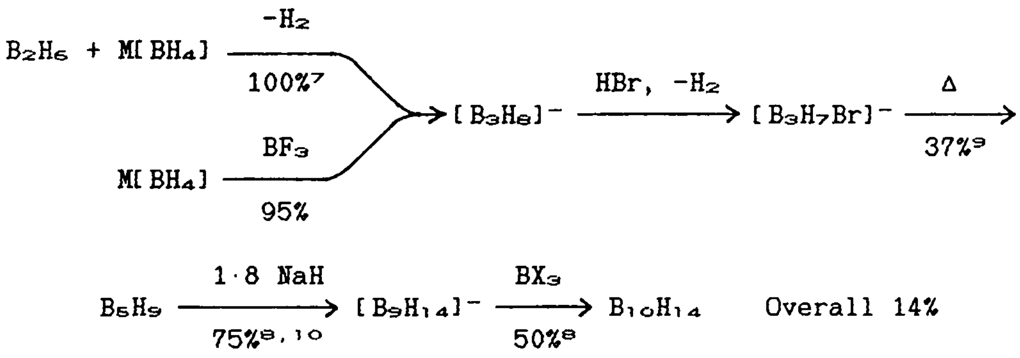
ortho **meta** **para**

Fig. 1.1 Structure of o-, m- and p- carborane, $C_2B_{10}H_{12}$

The above properties suggest the promising application of carboranes to thermally stable polymers[6]. Indeed, meta-carborane units have been incorporated into the backbone of the commercial elastomeric polysiloxane polymers "Dexsil" and "Ucarsil" which are used as high temperature sealants. Other potential uses for carboranes could be in materials with novel electrical/electronic properties or in ^{10}B neutron-capture cancer therapy in which a ^{10}B rich tumorphilic molecule could be made to behave as a "magic bullet". However, such uses have not been developed on a large scale because the boranes, which are the starting point for carborane preparation, are expensive and tedious to prepare.

1.2 The Synthesis of Boranes and Carboranes

The boranes B_5H_9 and $B_{10}H_{14}$ are stable at room temperature and are the commonest starting points for carborane formation. The currently most favoured bench scale preparations of these from B_2H_6 and $M[BH_4]$ are shown in *scheme 1.1* with the references for each step noted next to the yield. B_5H_9 and $B_{10}H_{14}$ can also be produced from pyrolysis of B_2H_6 on a pilot plant scale (ref. 2,



Scheme 1.1

p.91-101 for B_5H_9 and 102-15 for $B_{10}H_{14}$) but the toxicity of B_2H_6 and the potential for an explosion limits the industrial application of such methods.

Ortho-carboranes are accessible in ~85% yield by reaction of $B_{10}H_{14}$ with alkynes in the presence of alkyl sulphides or nitriles, reaction 1.1, and the closo carboranes $R'R''C_2B_nH_n$, n = 6 to 9, can be obtained by systematic degredation of $R'R''C_2B_{10}H_{10}$.[4]

$$B_{10}H_{14} \xrightarrow{2R_2S, -H_2} B_{10}H_{12}\cdot 2SR_2 \xrightarrow[-2R_2S, -H_2]{R'C\equiv CR''} R'R''C_2B_{10}H_{10} \tag{1.1}$$

However, a potentially useful preparation of the $R_2C_2B_8H_8$ system from 1:2'-$[B_5H_8]_2$ has recently been reported[11], 1.2, and the coupled-caged starting material can be synthesised efficiently from B_5H_9 [12]. The smaller closo carboranes, n= 3 to 5, are

$$2\ B_5H_9 \xrightarrow{PtBr_2} 1{:}2'\text{-}[B_5H_8]_2 \xrightarrow[2,6\text{-Lutidine}]{MeC\equiv CMe} \underset{33\%}{1,2\text{-}Me_2\text{-}C_2B_8H_8} \tag{1.2}$$

generated directly in low yields as the only volatile products from the gas phase flash reactions of B_4H_{10} and B_5H_{11} with actelyene[13]. However, they can be more efficiently prepared via the pyrolysis of nido-2,3-$C_2B_4H_8$ at 450-60°C[14]; this carborane is produced in 38% yield from the copyrolysis of B_5H_9 with acetylene at 215°C [15]. Several derivatives of nido-2,3-$RR'C_2B_4H_6$, can now also be prepared (except for the parent and R=R'=Ph) under mild conditions in good yields[16] by reaction of B_5H_9 with $RC\equiv CR'$ in the presence of a strong Lewis base, 1.3. Finally, the very direct

$$B_5H_9 + RC\equiv CR' + Et_3N \longrightarrow RR'C_2B_4H_6 + Et_3NBH_3 \tag{1.3}$$

carborane synthesis from the copyrolysis of BMe_3 and hydrogen at 450°C [17] should be mentioned. This gives a ~65% yield of mixed polymethyl derivatives of closo-$C_2B_5H_7$ but does not seem to have been further developed.

1.3 Aims of this Thesis

All but the last carborane synthesis in section 1.2 require the initial preparation of a polyhedral borane and a great deal of work has been directed toward developing and improving step-by-step cage-growth reactions like those shown in *scheme 1*. However, little if any attention has been paid to adaptation of Stock's original synthesis of boranes from the action of dilute acids upon magnesium boride, **1.4**. The conditions for this reaction are simple

$$MgB_2 + HA(aq) \longrightarrow B_4H_{10} + B_5H_9 + B_6H_{10} + H_2 \qquad \mathbf{1.4}$$

and it can yield up to 16% boranes, although this is more often in the range 2-5%. Thus only moderate improvements would be required to make it a competitive synthesis of B_5H_9 and $B_{10}H_{14}$; B_4H_{10} and B_6H_{10} can react to give $B_{10}H_{14}$ (see 3.3.6).

The experimental work presented in this thesis (chapter 5) examines the reaction of MgB_2 with protic acids under a wide range of conditions to see if any systematic methods can be found for increasing the borane yield. Results from this work are used to try and infer something of the mechanism of this reaction. Since acetylene itself can also be generated by the action of protic acids or water on metal acetylides, **1.5**, there is scope for a

$$CaC_2 + H_2O \longrightarrow Ca(OH)_2 + HC{\equiv}CH \qquad \mathbf{1.5}$$

reaction based on **1.6**. To test whether or not such a direct route

$$MgB_2 + CaC_2 \xrightarrow{HA(aq)} \text{Acetylene} + \text{Boranes} + \text{Carboranes} \qquad \mathbf{1.6}$$

to carboranes might be possible some attempted reactions of MgB_2 with acid in the presence of an acetylene are reported. To supplement this work chapter 2 contains a general introduction to the large range of known boride structures and stoichiometries as well as a review of the literature for the reaction of aqueous acids with metal borides, particularly MgB_2.

At present the most useful borane in the synthesis of carboranes is $B_{10}H_{14}$ and it is clearly desirable to determine how this might be prepared from the direct products of MgB_2 hydrolysis. Also, this project is concerned with a more general overview of borane interconversion reactions in the search for new routes to boranes and carboranes. Consequently, a critical review of thermal cage-expansion reactions for neutral boranes is presented in chapter 3. The purpose of this wider analysis of neutral borane chemistry is to see if any systematic methods for the production of the more stable, larger boranes, and ultimately carboranes, can be predicted. A pattern of cage-growth for the nido boranes is observed in this chapter and a mechanistic rationalisation is used to demonstrate a structure-reactivity relationship for the cage-growth reactions of B_2H_6 and the arachno boranes. In the long term it is hoped that such an approach may help to reveal commercially practical synthetic routes to polyhedral boron hydrides.

The pyrolysis of tetraalkylammonium borohydrides, which was first studied by Makhlouf, Hough and Hefferan[18], is a very simple method for the production of polyboron cages, 1.7. This reaction

$$[R_4N][BH_4] \xrightarrow{\Delta} [R_4N]_2[B_{10}H_{10}] + [R_4N]_2[B_{12}H_{12}] + H_2 + EtH + Et_3N \qquad 1.71$$

is currently being studied in other laboratories[19] because $[B_{10}H_{10}]^{2-}$ can be converted into $B_{10}H_{12}\cdot 2\ SR_2$ in good yields and this compound can be reacted with acetylenes, as in 1.1, to give carboranes. Whilst only preliminary studies of this reaction have been carried out in this laboratory a literature survey for $[R_4N][BH_4]$ pyrolysis is presented in section 4.2 of chapter 4.

This is followed, in section 4.3, by a critical review of the cage-growth and interconversion reactions of the anionic boron hydrides; this is intended to compliment chapter 3 although the information available for the individual anionic hydrides is not as detailed as for the neutral boranes. This chapter is also relevant to MgB_2 hydrolysis since $[B_{12}H_{12}]^{2-}$ (as well as other anions) is produced in this reaction.

It is hoped that the material presented in this thesis may be used as a basis for further research into the preparation of polyhedral boranes and carboranes.

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Chapter 2 Borides: Structure and Hydrolysis

2.1 Introduction

In this chapter, section 2.2 the crystal chemistry of the more reactive lower metal borides M_4B to M_3B is reviewed with some discussion of the higher borides MB_4 to MB_{12} which (unlike elemental boron and the even more boron rich boride phases) do not utilise B_{12} icosahedra in their structures. This is followed, in section 2.3 by a survey of what is known concerning the hydrolytic chemistry of the lower borides - principally magnesium diboride - to produce boron hydrides. The purpose here is to view magnesium diboride in a wider context showing its relationships to some of the other less well known borides. Also, it is argued in this thesis that the selection of boranes produced in the acid hydrolysis of MgB_2 is intimately related to the starting material's structure. Consequently it is hoped that this survey will provide the reader with an overview of this complicated field should it be desired to further pursue the hydrolytic chemistry of borides not necessarily isomorphous to MgB_2.

2.2 The Structures of Binary Metal Borides

Over the past two decades research into boride structures and their physical properties has grown into an extensive field. The industrial interest in borides, which are often simply made by calcining an appropriate mixture of the elements, has stemmed from the fact that many of them possess outstanding or extreme physical characteristics. Nearly all are refractory with high melting points, are very hard with good wear resistance and they often have much better thermal shock resistance than oxide ceramics. Also, whilst most possess good thermal and electrical conductivities, some can be good semiconductors or even superconductors. Lastly they are frequently chemically inert with good corrosion resistance and some can be used as catalysts. For wider coverage of boride synthesis and properties the reader is directed to refs 1 to 4 and 9 and it is from these texts that the more general information presented in this chapter is condensed.

Part 2.2.1 of this chapter is concerned with the lower borides with compositions from M_4B to MB in which the boron atoms seem to progress from being totally isolated from one another to forming chains through the lattice. Part 2.2.2 looks at the borides with formulations from $MB_{>1}$ to MB_3; many of these have close structural relationships to each other and contain mainly networks of hexagons of boron atoms of varying types - MgB_2 belongs to this group. Part 2.2.3 covers briefly the stoichiometry range MB_4 to MB_{12} in which fully cross-linked, three dimensional arrays of boron atoms have developed.

2.2.1 The Lower Borides, M_4B - MB

One of the more prevalent features in these borides is that the boron atoms frequently occupy sites where they have trigonal prismatic coordination to six metal atoms. However, this is only a rule of thumb since Archimedian square antiprismatic and distorted octahedral and tetrahedral coordination are also known. A good point of view to take with these borides is to regard the boron atoms as having a secondary role in modifying a lattice possessing the primary characteristics of a close-packed metallic array. In most cases the lower borides can be discussed in terms of layers of metal atoms, made up of triangles and squares, sandwiching boron atoms in between. However, there are a few borides in this group to which this type of description is not appropriate since they contain no clearly identifiable layers of metal atoms. With this picture of lower boride lattices in mind it is not surprising that transition metals with their high heats of vaporisation - and thus strong metallic bonding - dominate this stoichiometric range. As the boron content of these borides rises it appears that the metal atom arrays approach more closely the close-packed hexagonal networks seen in the layers of the simple diborides.

$Pt_{\approx 4}B$ [5] is currently held to be the most metal rich, distinct boride phase prepared to date (the compound until quite recently denoted Mn_4B is in fact Mn_2B [12]). This boride has a unique cubic structure of interlinked icosahedra, tetrahedra and trigonal prisms of platinum atoms in which it was thought that the boron atoms occupied only half the available trigonal prismatic sites. This was because full occupation would have given unreasonably short B-B bonds at 1·53Å, although the structure factors here were not accurate enough to permit definitive determination of the boron positions. This boride is not considered further here except to note that the shortest possible distance between boron atoms is 3·11Å so that they are all completely isolated from one another - the normal bonding distance lies roughly between 1·7 and 1·9Å.

The first important boride composition is M_3B for which two structural types are known. In both the boron atoms occupy trigonal prismatic sites in which their coordination has been extended from six to nine by contact with metal atoms placed over each of the rectangular faces of the prism, ie. a tricapped trigonal environment (*fig. 2.1a*). Tc_{3B} and Re_3B [6] display the simpler structure with columns of trigonal prisms stacked end to end running parallel to the a-axis where neighbouring columns are staggered by a/2 (*fig. 2.1b*). However, it is shown in *fig. 2.1c* that this structure can also be regarded in terms of stacked layers of triangles and rectangles of metal atoms when sliced through the {023} plane. The other structural type, observed in Co_3B, Ni_3B and Pd_3B [7], is isomorphous to Fe_3C (cementite) and both M_3B variants can be related geometrically in a fashion only slightly more complicated than, but similar to, that connecting the high temperature BeB- and CrB-type structures (*fig. 2.1d*). A simpler picture of this lattice of linked M_6B trigonal prisms appears when a section through the {103} plane is taken because

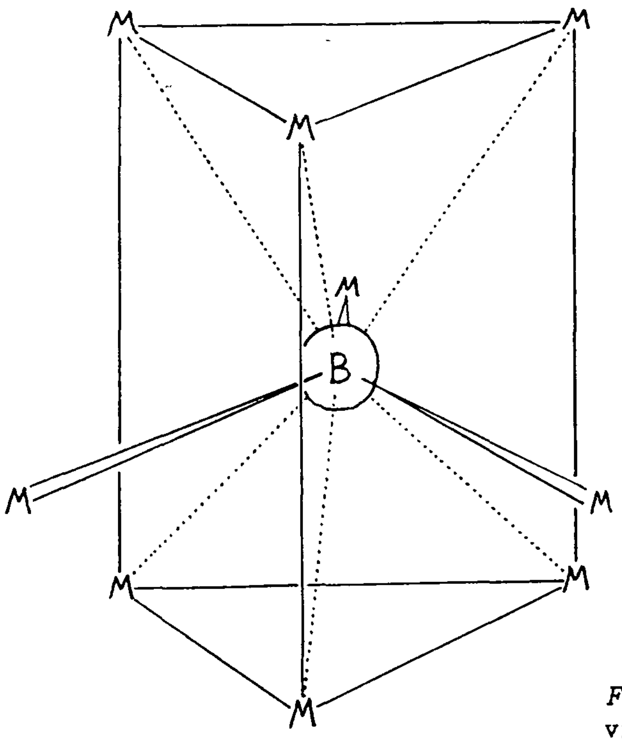


Fig. 2.1a Tricapped trigonal prismatic boron environment

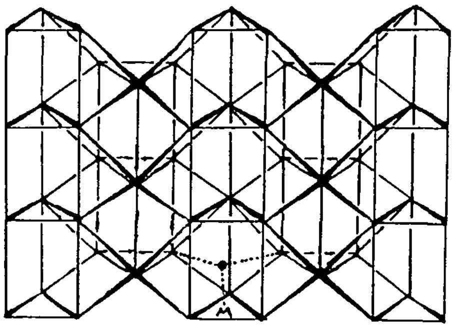


Fig. 2.1b Structure of $(Tc/Re)_3B$; view perpendicular to ac-plane

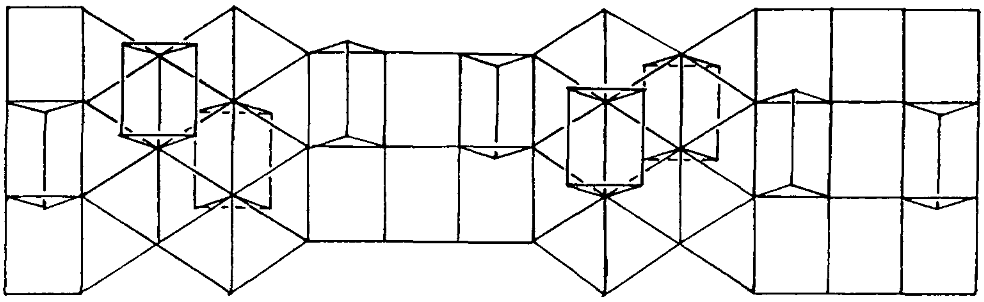


Fig. 2.1c Metal layers in $(Tc/Re)_3B$ parallel to {023}

this type of M_3B can also be represented as stacked layers of metal atoms (*fig. 2.1e*). Another unique but closely related structure containing isolated boron atoms adopting extended trigonal prismatic coordination is found in Pd_5B_2 [7a] which, once again, can be constructed from planes of metal atoms when viewed perpendicular to the ac-plane (*fig. 2.1f*).

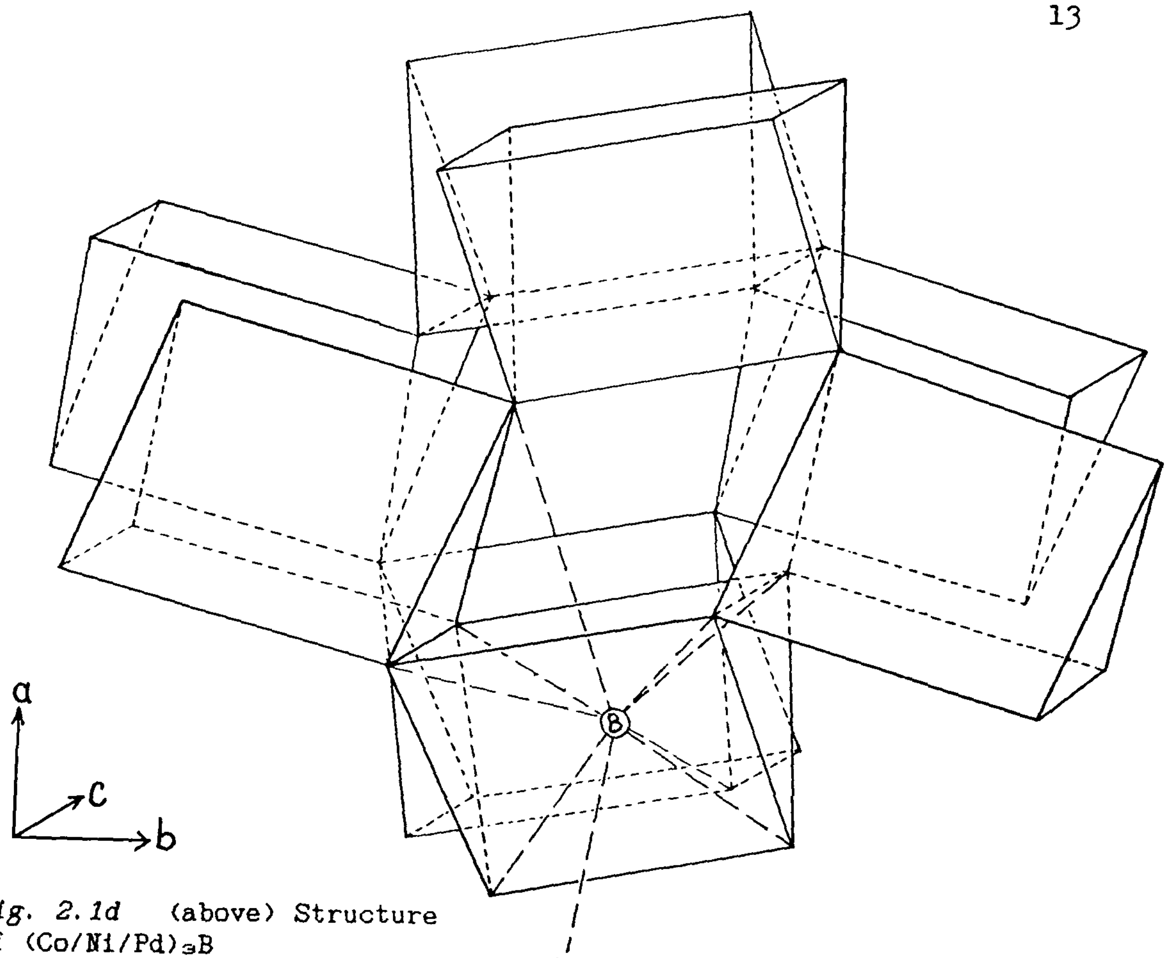


Fig. 2.1d (above) Structure of (Co/Ni/Pd)$_3$B

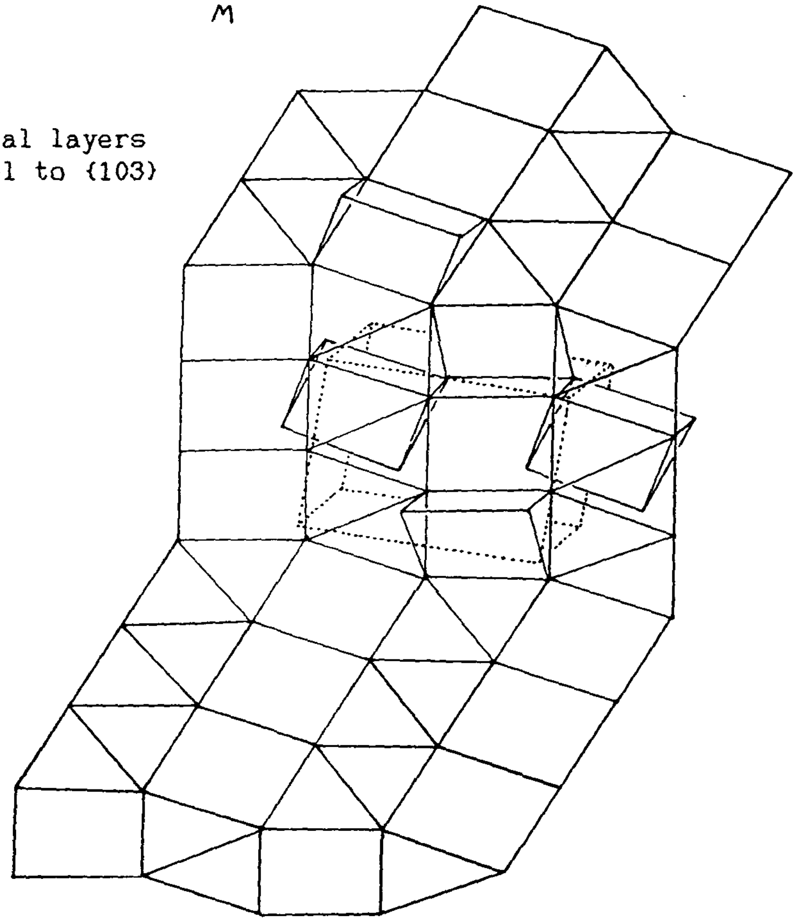


Fig. 2.1e (right) Metal layers in (Co/Ni/Pd)$_3$B parallel to (103)

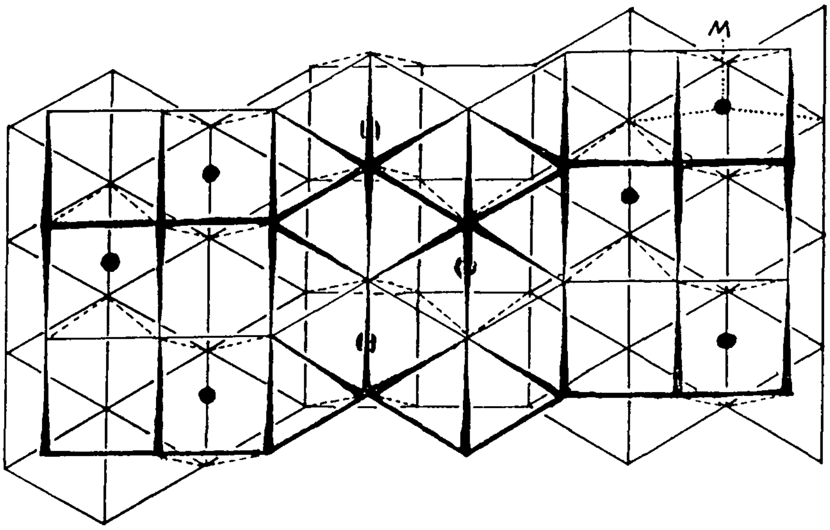


Fig. 2.1f Structure of Pd_6B_2; view perpendicular to ac-plane

The isomorphous hexagonal borides Rh_7B_3, Re_7B_3, Tc_7B_3 and Ru_7B_3 [8] (with a crystal structure very similar to that of Cr_7C_3) also possess isolated boron atoms in trigonal prismatic sites. These borides have previously been described in terms of columns of M_6 octahedra running parallel to the c-axic with M_4 tetrahedra packing the spaces between them. However an alternative representation, shown in *fig. 2.2*, again views the lattice as stacked, puckered layers of metal atoms. This perspective fits well with the recent report[9] of inversion boundaries in crystals of these borides where crystal domains are separated by their six-fold axes running in opposite directions.

There are several structural types for the borides of stoichiometry M_2B of which the commonest (M=Cr, Mn, Fe, Co, Ni, Mo, W, Ta) contains the tetragonal stacking of metal layers shown in *fig. 2.3a*. In these the boron atoms now occupy square antiprismatic sites between the layers and the structure is isotypic with $CuAl_2$-θ [10]. Whilst these borides appear to have chains of boron atoms threaded through channels parallel to the c-axis the large B-B distance seems to preclude bonding, ranging

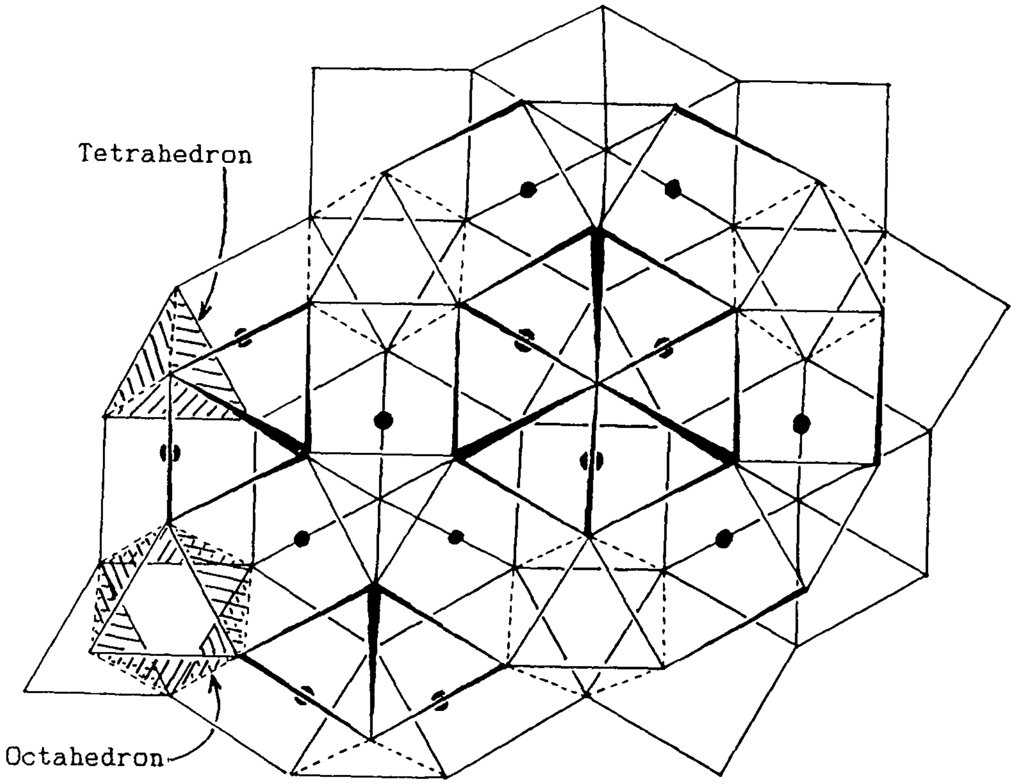


Fig. 2.2 Structure of (Rh/Re/Tc/Ru)$_7$B$_3$; view perpendicular to ab-plane

● = Boron

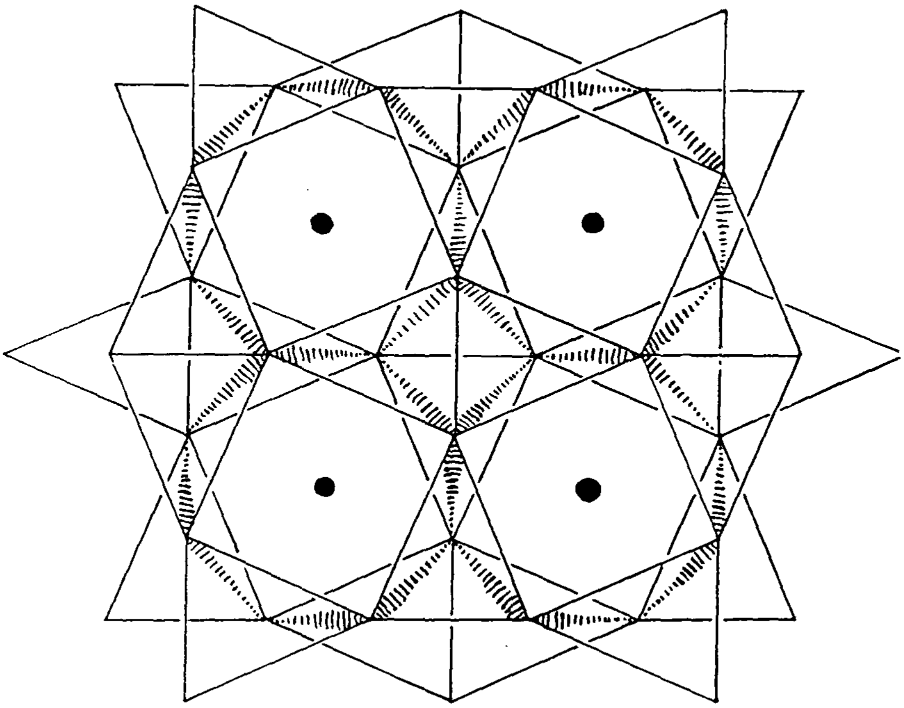


Fig. 2.3a Structure of CuAl$_2$-type M$_2$B; view perpendicular to ab-plane

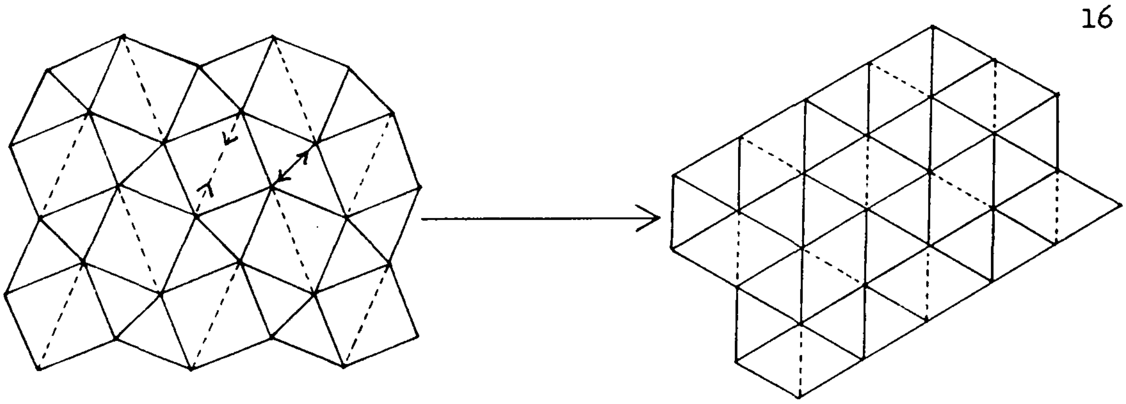


Fig. 2.3b Geometric relationship between $CuAl_2$-type M_2B and h.c.p. lattice

from 2·10Å in Mn_2B to 2·37Å in Mo_2B [11]. In *fig. 2.3b* it is demonstrated that the geometry of the layers of metal atoms can be regarded as distorted hexagonal and similar transformations can be found for every metal layer seen in this chapter. Chromium and manganese (the original Mn_4B) also have an orthorhombic M_2B boride[12] in which the boron atoms are again in square antiprismatic sites forming chains through the metal sublattice. However, even though the boron-boron distances are of about the same length as in tetragonal M_2B, the chains do not all run in the same direction but half are parallel to [011] and the remainder to $[01\overline{1}]$. The metal atom sublattice in orthorhombic M_2B has been described as being made up of layers of edge-fused hexagonal bipyramids but, because of the stacking sequence ABCDA...., orthorhombic symmetry, not hexagonal, is visible in the bulk crystal.

There are three other structural types belonging to borides of M_2B stoichiometry. The first is that of Rh_2B [13] which contains columns of trigonal prisms sharing triangular faces as in $(Tc/Re)_3B$ but here each column shares edges with two of its neighbours. Next is Pt_2B [5] which has a hexagonal MoS_2-type structure with hexagonal close-packed metal layers; it is a member of the family of borides related to AlB_2 and its stacking sequence can be written AH'ABH'BA.... where the H' type of boron layer is illustrated in *fig. 2.5c*. Lastly, Tergenius and Lundstrom[5,14] have described the boride Pd_2B which has an orthorhombically distorted,

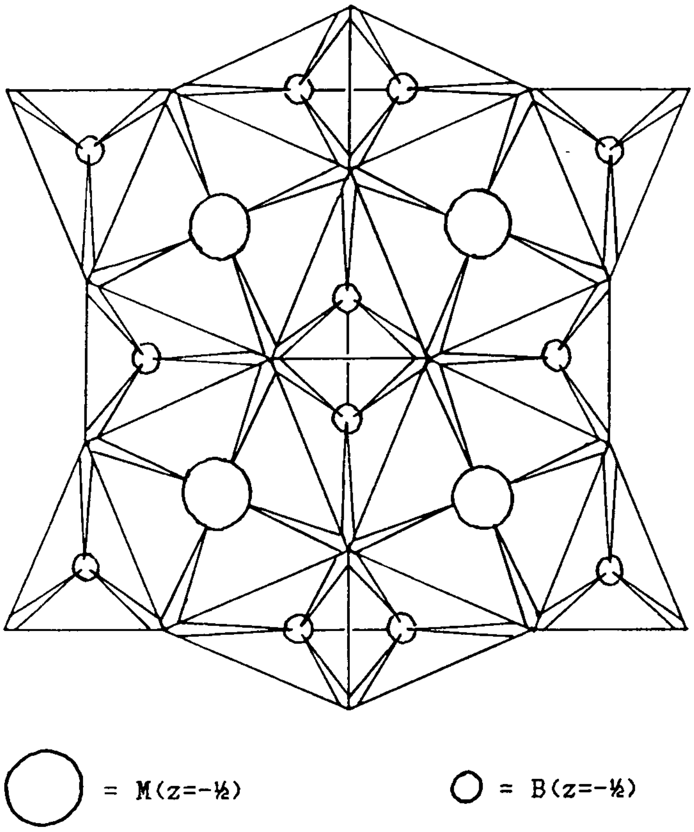


Fig. 2.3c Structure of (V/Nb/Ta)$_3$B$_2$; view perpendicular to ab-plane. Metal layers at z=0 identical to CuAl$_2$-type M$_2$B

hexagonal close-packed metal lattice. Although the boron atoms in their structure refinement were randomly distributed throughout the available octahedral sites a reinvestigation of the powder data suggested that they were in ordered positions similar to those of the calcium ions in anti-CaCl$_2$. If this structure is correct it places the boron atoms in lines parallel to the c-axis with a separation of 3.11Å. Thus Pd$_2$B seems to belong to the structural class containing PtB and Rh$_{\alpha 1.1}$ with every second boron atom removed.

Related to the common tetragonal M$_2$B are the borides V$_3$B$_2$, Nb$_3$B$_2$ and Ta$_3$B$_2$; these have a U$_3$Si$_2$-type structure with the same type of metal layer as in M$_2$B. However, each adjacent metal layer is now contiguous whilst the boron atoms are situated in trigonal prismatic sites forming pairs and extra metal atoms occupy the cubic sites between metal layers *(fig. 2.3c)*. Exactly intermediate between tetragonal M$_2$B and U$_3$Si$_2$-type M$_3$B$_2$ is

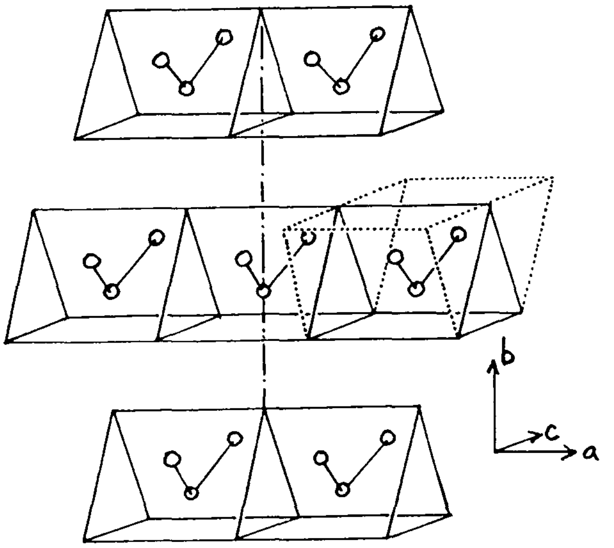


Fig. 2.4a (above) Structure of (V/Nb/Ta/Ni)B and β-(Cr/Mo/W)B

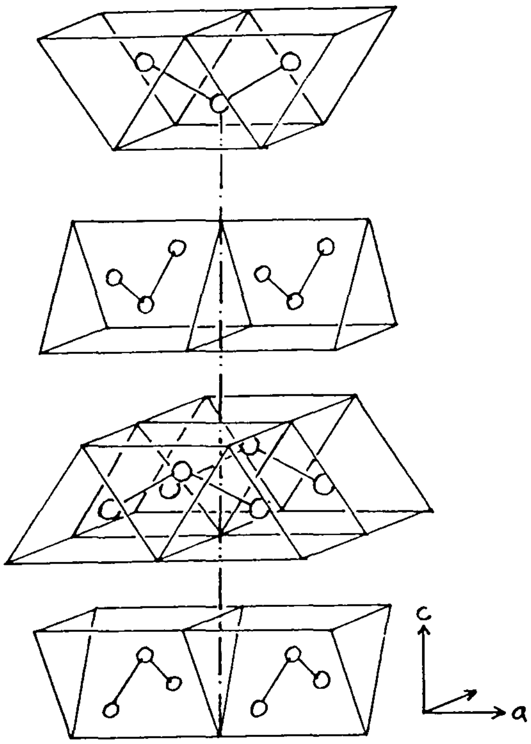


Fig. 2.4b (right) Structure of α-(Cr/Mo/W)B

Cr$_5$B$_3$ [15]. The stacking sequence of the metal layers in this boride can be written AABBA.... where between AB or BB chromium and boron are situated as for M$_3$B$_2$ and between AB as for M$_2$B. Another structure type in which the boron atoms are paired is observed in IrB$_{0.9}$ but here the axes of the adjacent trigonal prismatic sites are perpendicular.

The borides belonging to the stoichiometric range M$_{1.4}$B to M$_{1.0}$B have structures mostly based upon boron chains. Perhaps the simplest are the monoborides MB (M=V, Nb, Ta, Ni and the high temperature form for MB, M= Cr, Mo, W) in which neighbouring columns of trigonal prisms share two of their three faces to produce covalently bonded, zig-zag parallel chains of boron atoms through the structure having a bond length of ~1.76Å *(fig. 2.4a)*. A simple modification of this is seen in the low temperature forms of CrB, MoB and WB where consecutive layers of boron chains, parallel to the ac-plane are rotated relative to one another by π/2 *(fig. 2.4b)*. Also related are the monoborides M=Fe, Ti, Hf,

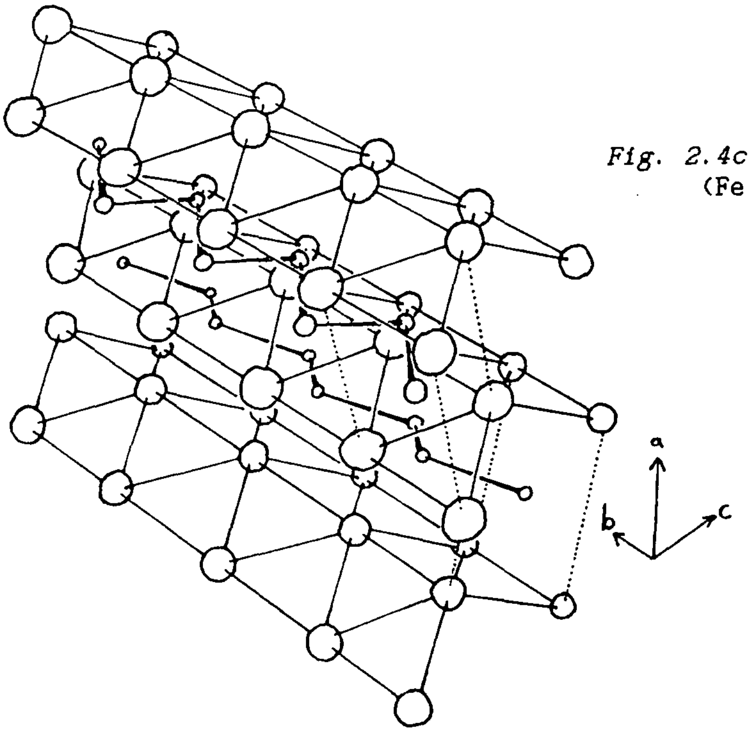


Fig. 2.4c Structure of (Fe/Ti/Hf/Mn/Co)B

Mn and Co in which the zig-zag of the boron chains is tipped out of the bc - plane and the chain tilt in consecutive layers is in opposite directions (*fig. 2.4c*). The FeB- and high temperature CrB-type structures can be geometrically interconverted [47] by sliding the unit cell of the former along a transposition vector relative to the neighbouring cell of, ideally, c/2.

Apart from the chain-containing borides listed above there are several other more irregular structures worthy of note in which the metal/boron ratio also approaches one. There are both orthorhombic and monoclinic (o- and m-) phases of the nickel boride ideally formulated Ni_4B_3 [16]. o-Ni_4B_3 actually contains slightly less boron and, unlike m-Ni_4B_3, seems to have a moderate homogeneity range as demonstrated by a variability of its lattice parameters. m-Ni_4B_3 is most easily described in terms of stacked metal layes parallel to {202} with boron chains perpendicular to this plane. The boron chains are unusual because, apart from the more common variety of trigonal prismatic environment, every third atom is situated in a distorted, square anti-prism of nickel atoms (*fig. 2.4d*). It is interesting to note that the planes of metal atoms in m-Ni_4B_3 not only bear similarities to the preceding types of metal layer (especially those identified in cementite-M_3B and

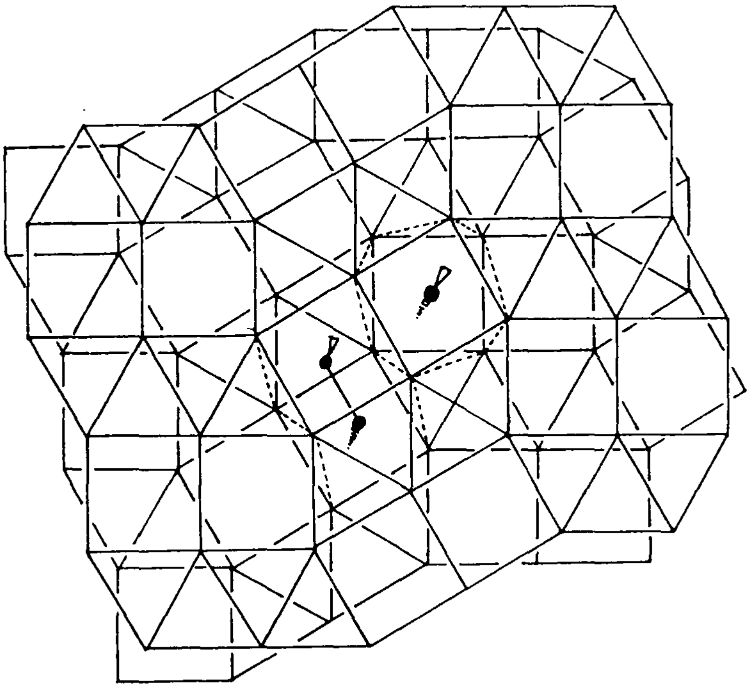


Fig. 2.4d Metal layers in m-Ni_4B_3 parallel to {202}

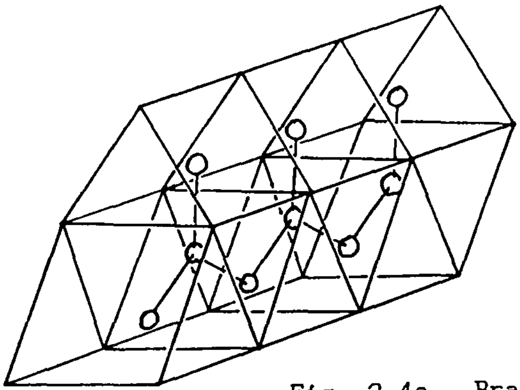


Fig. 2.4e Branched boron chains in $Ru_{11}B_8$

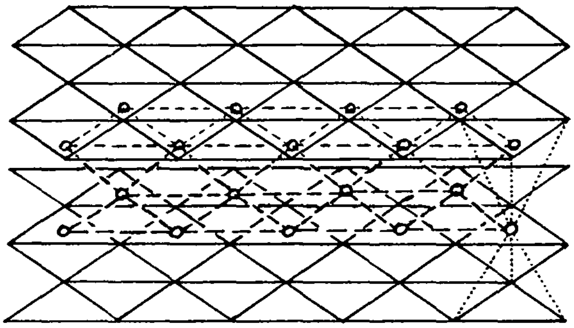


Fig. 2.4f Structure of PtB, $RhB_{\approx 1.1}$

$CaAl_2$-type M_2B) but are also closely related to the $\{10\bar{1}1\}$ plane of a close-packed hexagonal lattice (*fig. 2.5g*). o-Ni_4B_3 is a mixture of structure types containing both the boron chains observed in the simple monoborides and the columns of isolated, trigonal prismatically coordinated boron atoms seen in $(Tc/Re)_3B$ and Rh_2B. $Ru_{11}B_8$ [12] is another boride containing both columns and chains but here the chains (*fig. 2.4e*) are branched being intermediate between those of the simple monoborides and the double chains of M_3B_4 (*fig. 2.5d*).

There are two other structural types belonging to this stoichoimetric range which are closely related to each other but in these the tendency toward chain formation is very weak. First are the isomorphous borides PtB and $Rh_{\alpha 1.1}$. These have a close-packed hexagonal metal lattice, stacked ABA..., in which the boron atoms occupy the octahedral holes between the metal layers with an anti-NiAs-type ordering (*fig. 2.4f*). Chains of boron atoms parallel to the c-axis can be visualised here. However the boron-boron separation in these platinum and rhodium borides is 2·03 and 2·11Å respectively so that it is questionable whether or not direct bonding exists here. In the case of the platinum boride it has been reported as boron-deficient as $PtB_{0.67}$ and one suspects that linking of the boron atoms in this is even less likely. Rh_5B_4 [13] is very similar to the above two borides, again utilising the metal layer from a h.c.p. lattice, with boron atoms in the octahedral sites between (*fig. 2.4g*). However it possesses a more complicated stacking sequence, BABABCACACB..., and the boron seems to be in short chain lengths of four atoms (B-B=2.22Å).

2.2.2 The Intermediate Borides, $MB_{>1}$ - MB_3

As the boron content rises to approach the composition MB_2 the chains observed in the simple monoborides tend to become more and more cross-linked so that at MB_2 they form fully interconnected, two-dimensional networks of tesselated hexagons. The commonest structural type in this category is that first observed in AlB_2 in which close packed layers of metal atoms, stacked AAA..., are separated by planar nets of boron hexagons with the boron atoms occupying all the available trigonal prismatic sites (*fig. 2.5a*). Of all the structural types it is the most ubiquitous having representatives in the early transition metals (Sc-Mn, Y-M, Hf-W), later lanthanides (Sm - Lu except Eu) as well as Al, U, Pu and Mg. These diborides are usually classified amongst the lower borides because of their massive use of trigonal prismatic boron coordination and lack of a three-dimensional boron sublattice. However there are two good reasons for giving them an intermediate status:-

a) A comparison of these borides' unit cell dimensions[2] showed that the hexagonal

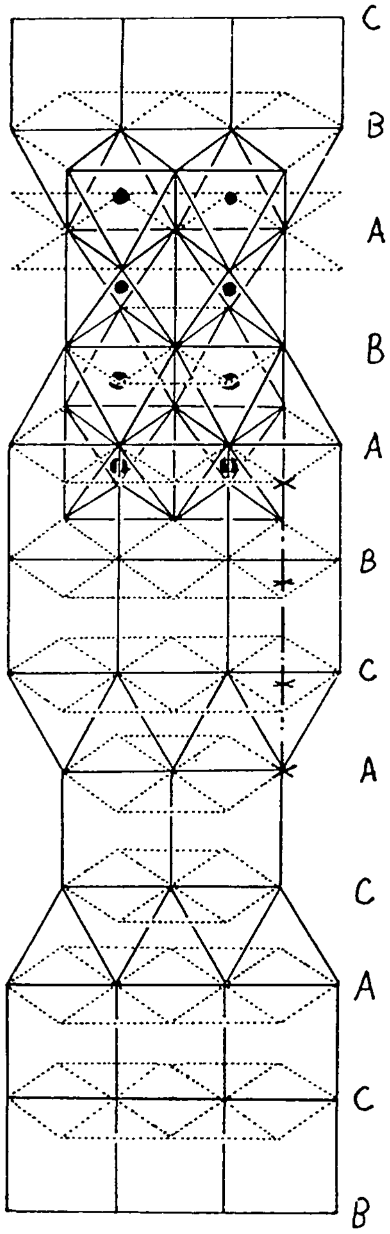
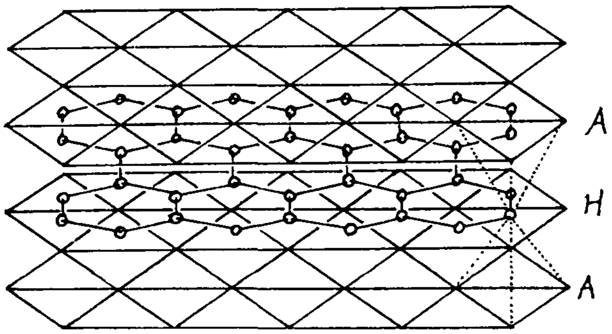


Fig. 2.4g (above) Structure of Rh_6B_4

Fig. 2.5a (below) Structure of AlB_2-type MB_2



a-dimension (in the plane of the boron netowrk) varied relatively little, from 2·97 to 3·31Å, whilst the c-dimension (perpendicular to the boron network) ranged from 3·04 - 3·99Å. Also, the latter was mainly dependent upon, and increased with the radius of the metal ion. Thus the metal atoms now seem to be modifying the boron sublattice.

b) There is evidence to suggest that, in borides more metal rich than MB_2, electrons are donated from boron to the metal sublattice. However, for diborides and other higher borides the situation is thought to be reversed giving cationic metal and anionic boron atoms so that in the extreme case, $M^{2+}(B^-)_2$, this would make the boron network comparable to isoelectronic graphite.

The magnesium diboride used in this project belongs to the above class of diborides and is peculiar amongst its isostructural group for two reasons:-

a) It is the only such diboride known of a solely divalent metal. This seems to be because the radius of magnesium is in the middle of the range which this hexagonal lattice has so far been seen to accommodate. Calcium is too large and only forms a typical hexaboride (and perhaps a tetraboride?) whilst small amphoteric beryllium forms a complex boride, BeB_3; this contains 82 boron atoms in the unit cell which are incorporated into icosahedra and other polyhedra[20].

b) Magnesium diboride is well known for its atypically high chemical reactivity and it has the lowest thermal stability of all the diborides. Whilst there appear to have been no detailed theoretical studies of MgB_2 the nature of its electronic structure has been infered from an electronic band-structure calculation for AlB_2 (see ref. 1, p. 46-50). In AlB_2-type borides there is no direct inter-layer bonding between consecutive boron networks and it seems that there should not only be weaker intermetallic bonding within the close-packed layers of magnesium but also a weaker metal-boron linkage than in AlB_2. Thus it is not surprising that MgB_2 is the more thermally labile of the pair. Furthermore, whilst AlB_2 is more stable than MgB_2 and melts incongruently at ~1350°C, this is still at least 700°C below the fusion temperatures of the other common diborides. All these, excepting ScB_2 and YB_2 have four or more available valence electrons and this would seem to be the ideal number for a highly stable diboride.

Possibly related to the chemical reactivity of MgB_2 is its ionicity which might be expected to be similar to if not greater than, that of AlB_2 which was calculated at $Al^{+1.884} (B^{-0.942})_2$ from an analysis of the density of states. This question of polarity has not yet really been satisfactorily resolved and a more recent calculation for ZrB_2 [48] placed much of the electron density in interstitial space as opposed to "on" either type of atom. However, this may not be relevant to MgB_2 because the band structure of ZrB_2 could be usefully compared to the graphite intercalation compound LiC_6 in which the metal has almost completely donated its electrons. Parity broke down because zirconium's s,p states, strongly hybridised with its d bands, entered the energy range of E_F and the σ-bands, but for magnesium the s,p states are substantially higher in energy so that it should be much more clearly ionised.

Two other structural types of diboride exist and similarly contain networks of boron hexagons sandwiched between close-packed metal layers. In the first, the hexagons are no longer planar but adopt the chair conformation so that the boron atoms in these puckered networks are now roughly tetrahedrally coordinated (*fig. 2.5b*). TcB_2 and ReB_2 [21] are the only binary borides to display just this type of boron network. Using the now standard notation for this kind of boron network, the stacking sequence may be written AK'BK'A... and it will be noted how the K'-type network makes it impossible to superimpose consecutive metal layers. The remaining diboride type, so far only exemplified by RuB_2 and OsB_2

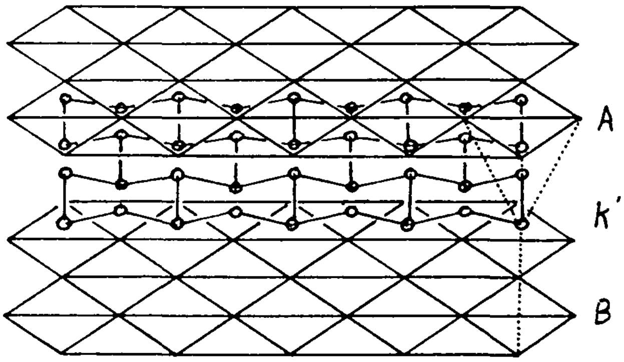


Fig. 2.5b Structure of (Tc/Re)B_2

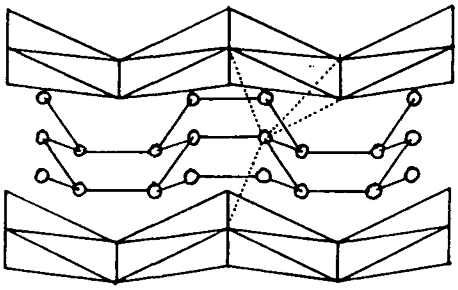


Fig. 2.5c Structure of (Ru/Os)B_2

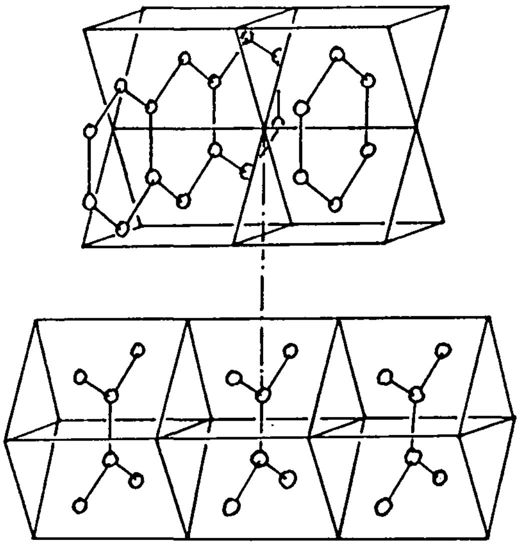


Fig. 2.5d Structure of (Mn/Ta/Nb/V/Ti)$_3B_4$

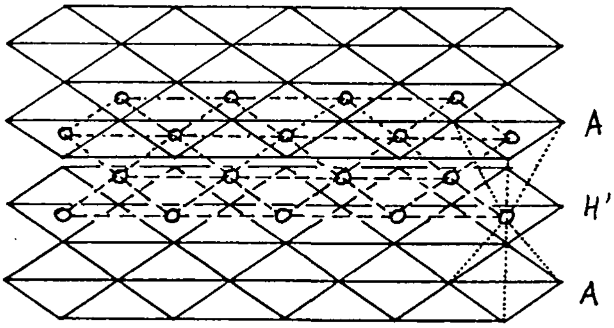
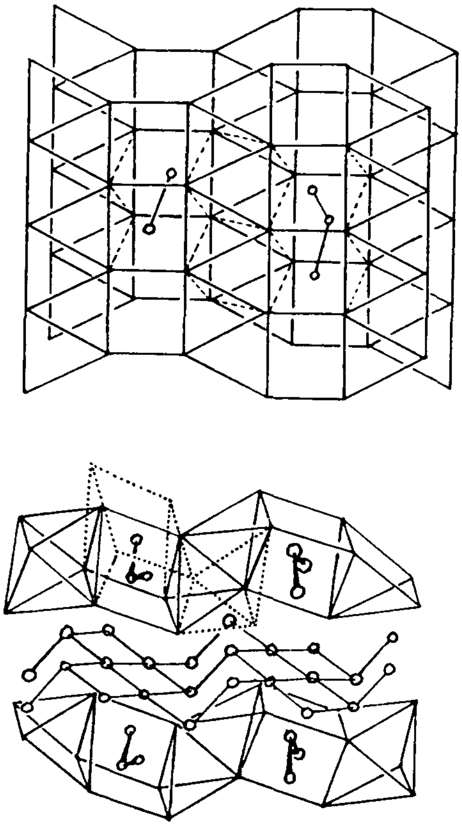


Fig. *2.5e* H' Boron network

[22], again has tetrahedrally coordinated boron atoms in puckered networks of hexagons sandwiched between close-packed metal layers. However, the boron hexagons in these borides adopt the boat conformation and this causes the metal layers to become corrugated (*Fig. 2.5c*). Extending the stacking notation, this structure could be written ALALA... although this type of network has not so far been identified in any other binary diboride.

There are several boride structures which combine features of those containing two-dimensional networks with those of the more



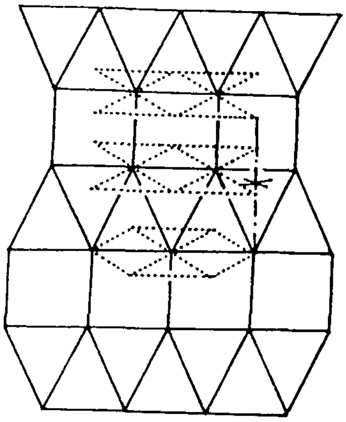


Fig. 2.5f (left) Structure of Ir$_2$B$_{3-x}$; top, view perpendicular to ab-plane; bottom, view perpendicular to ac-plane

Fig. 2.5g (above) The (10$\bar{1}$1) plane of a h.c.p. lattice

metal rich compounds. First are those intermediate between planes and chains of boron atoms. In M$_3$B$_4$ (M=Cr, Mn, Ta, Nb, V, Ti) pairs of chains are linked together as in *fig. 2.5d* and the borides V$_5$B$_6$ and V$_2$B$_3$ fit neatly on either side of M$_3$B$_4$ - the former containing single and double chains, the latter containing triple chains. Second, there is a pair of isomorphous borides, Ru$_2$B$_3$ and Os$_2$B$_3$, which have both isolated boron atoms (as already encountered in Pt$_2$B) and boron networks of the (Re/TcB)B$_2$- type so that the stacking sequence may be written AH'AK'BH'BK'A.... The H'-type of boron arrangement is illustrated in *fig. 2.5e* where the letter H signifies a relationship to the AlB$_2$-type network and the dash indicates that this is a regular defect where every second boron atom is removed from an H layer. The dash is included in the K' notation for the same reason but in fact the corresponding K-type network, where another boron atom is placed at the centre of each chair conformation hexagon, does not seem to exist.

Lastly, there is the peculiar boride Ir_2B_{3-x} [22,23] (often formulated $IrB_{1.35}$) which takes the structure shown in *fig. 2.5f*. In this boride the trigonal prismatic sites in the double metal layers are only about 50% occupied but whether or not this is in an ordered fashion is unknown. With its unique variety of undulating boron network Ir_2B_{3-x} has not been previously classified, however it can be related to the many other borides with elements of hexagonal symmetry by noting that each plane of iridium atoms is like a corrugated version of the $(10\bar{1}1)$ plane for a h.c.p. lattice (*fig. 2.5g*).

Another class of borides related to the simple diborides illustrated in *figs. 2.5a and b*, combines both types of layer in one structure so that MoB_2 and WB_2 [24a] are found to have the stacking sequence AHAK'BHBK'CHCK'A...(Kempter and Fries[24b] suggest that there are also isomorphous Ru and Os phases). These diborides, originally formulated M_2B_{5-x} because of their variable composition e.g. $MoB_{1.92}$, are distinct from their known AlB_2-type counterparts and were at first thought to possess K-type boron networks because the boron locations had earlier been assigned on space-filling criteria. It is interesting to note that these two hybrid borides lie between the elements of group Va, with only H-type networks in their diborides, and technetium and rhenium of group VIIa with their characteristic K' layers.

The final structural type linked to those of the simple diborides is seen in a molybdenum boride now formulated $Mo_{1-x}B_3$ [25a] for which there is perhaps a tungsten analogue[25b]. It again utilises the H-type boron network but here the close packed metal layers are defective, missing every third atom in an ordered fashion, so that the stacking sequence is written A'HB'HA'.... In fact the metal layers are not fully occupied ($x \simeq 0{\cdot}2$) so this is the most metal rich boride yet known not to have a cross linked three dimensional boron sublattice.

2.2.3 The Higher Borides, MB_4 - MB_{12}

These borides contain a covalently bonded, fully cross-linked, three-dimensional boron sublattice. Throughout the borides no example of a boron-boron connectivity higher than six has yet been observed with the consequence that the sublattice has a quite open structure containing large cavities. Thus, the metal ions which occupy these sites interstitially must be correspondingly quite large. As a result the rare earth metals predominate as the metal cation in this group of structures and it seems that they are not so much present as stoichiometrically critical units but instead act to just stabilise the boron framework. A quite good example of this seems to be that of ThB_6 for which unit cell dimensions, X-ray and neutron diffraction intensities and density measurements all support the view that the boron sublattice can withstand as little as 78% occupancy of the thorium sites without disrupting its structure although it also seems that LaB_6 has a very limited homogeneity range[5]. An exceptional example is found amongst the borides based upon the B_{12} icosahedron as a structural unit where heating NaB_{15} above 950°C drives off all the sodium. Whilst α- and β- rhombohedral elemental boron are found in the residue a metastable monotrope isostructural with NaB_{15}, but totally devoid of sodium, is also present; this is to some degree possible with KB_6.

Tetraborides with the structure illustrated in *fig. 2.6a* are quite common and have been reported for Y, all the lanthanides (except Eu and of course Pm), Th, U ad Pu and powder patterns suggest that there might be a CaB_4 phase [26]. These borides were first regarded as intermediate between the AlB_2-type diborides and hexaborides because they have both trigonal prismatically coordinated boron atoms, reminiscent of the former, and B_6 octahedra similar to those in the latter. However it is questionable whether or not this is a chemically valid perspective: firstly, YB_4 showed that nearly one in four of the

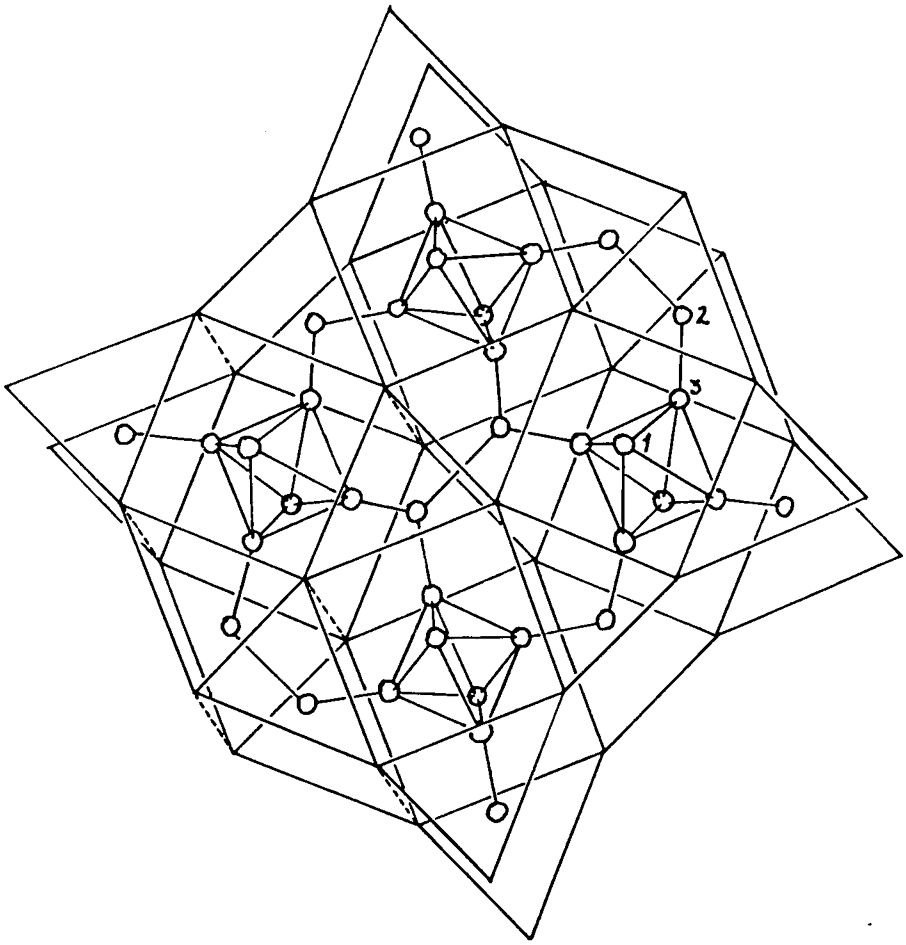


Fig. 2.6a Structure of the common tetraborides

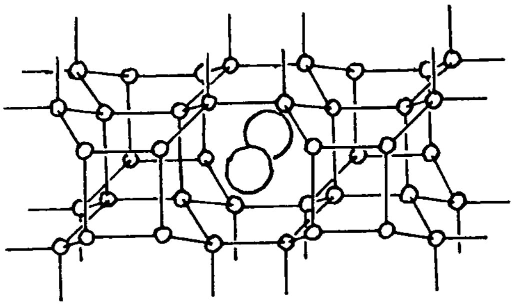


Fig. 2.6b Structure of MnB_4

B(3) sites was vacant whilst the B(2) site was fully occupied; secondly, this lattice clearly possesses the same planes of metal atoms already noted in the $CuAl_2$-type M_2B and M_3B_2. Instead one can regard all three structures as a tetragonal packing of tetrahedra with other species filling the interstitial sites: MB_4 is thus made up of M_2B_2 tetrahedra with B_6 octahedra in the interstitial sites, i.e. $(M_2B_2)(B_6)$; M_3B_2 also contains M_2B_2 tetrahedra but with only metal atoms in the interstitial sites, i.e. $(M_2B_2)M$; M_2B is made up of M_4 tetrahedra and retains just the apical, B(1), boron atoms of MB_4 in the interstices.

There are two other structural types known with tetraboride stoichiometry. Orthorhombic CrB_4 has the structure shown in *fig. 2.6b* and MnB_4 is a very similar monoclinic distortion of this[27]. In these the metal atoms are coordinated to twelve boron atoms and reside in octagonal prismatic channels running through the boron sublattice parallel to the c-axis although there is probably only weak metal-metal bonding. One interesting way to regard the boron sublattice in these two borides is as derived from that in $(Ru/Os)B_2$. Every atom in the original planes of fused boat conformation boron hexagons now has an extra bond perpendicular to the plane (giving it distorted tetrahedral geometry) which links it to a boron atom in an adjacent plane; each plane is contiguous but inverted relative to its neighbours.

The last known tetraboride structure is unique to magnesium[28] and is shown in *fig. 2.6c*. In this, chains of pentagonal pyramids, sharing edges, run parallel to the c-axis with the apices of each consecutive pyramid on opposite sides of the cross-linked chains. The magnesium atoms form zig-zag chains in the large channels in the boron sublattice also parallel to the c-axis. One would guess that the peculiar structure of this boride is the product of magnesium's purely divalent nature (c.f. diboride stability) since the metal species in all the other well characterised tetraborides have oxidation states higher than two available.

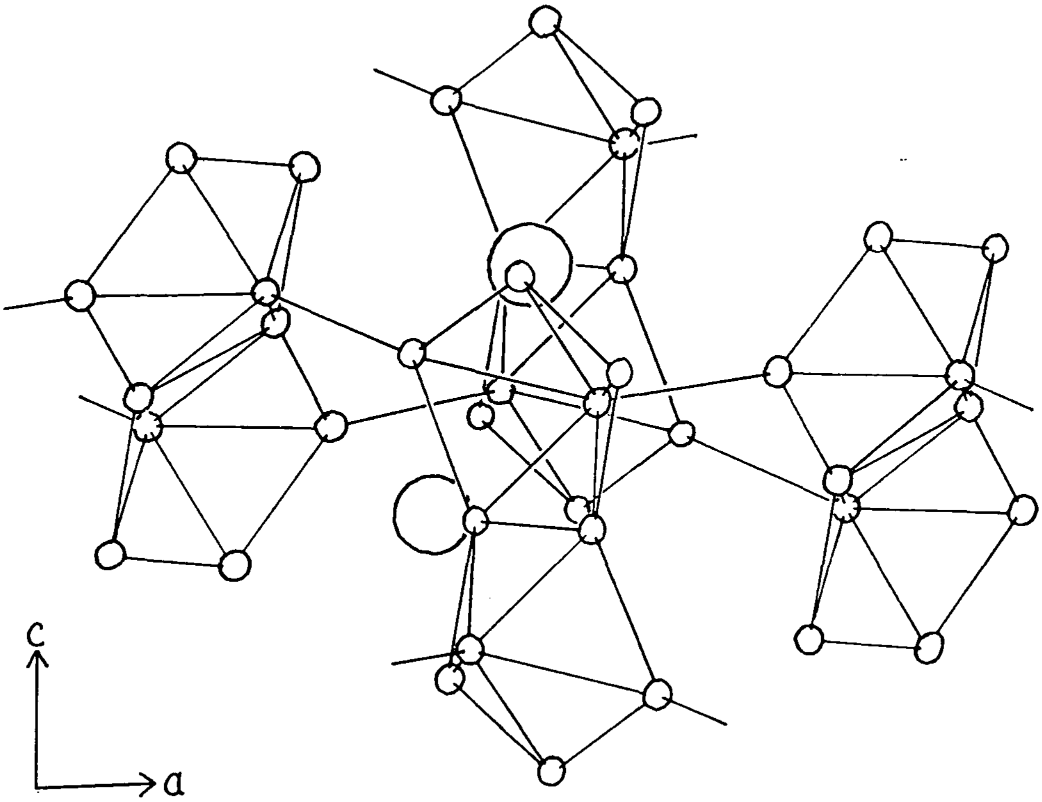


Fig. 2.6c Structure of MgB_4

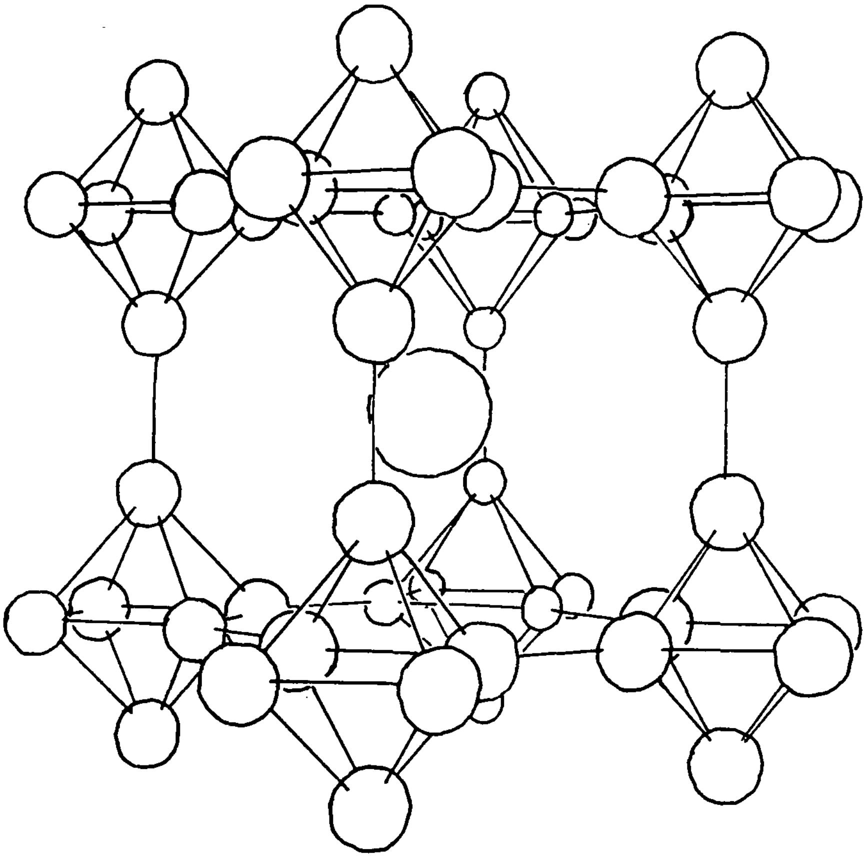


Fig. 2.7 Structure of the hexaborides

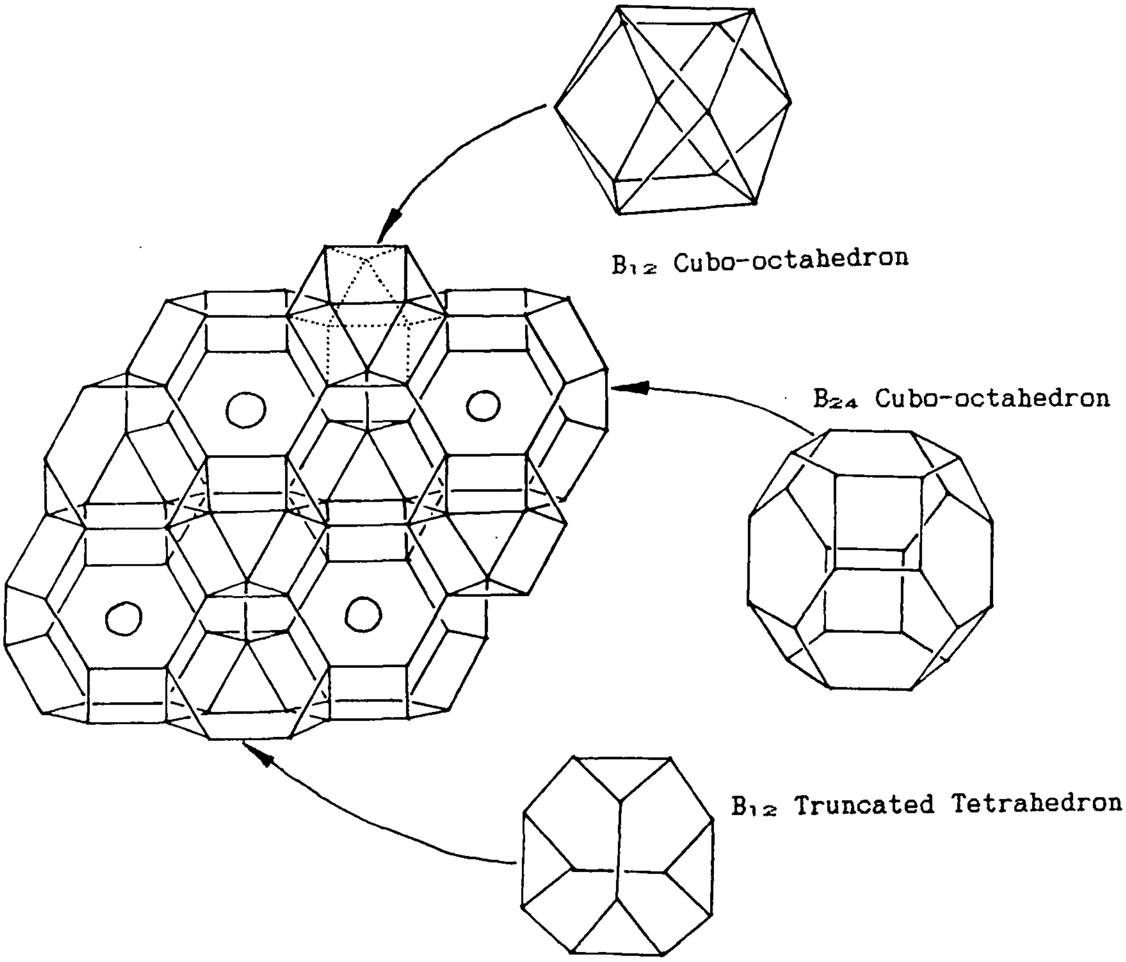


Fig. 2.8 Structure of the dodecaborides

Proceeding to borides of higher boron content, the next group is that of the hexaborides MB_6, M=K, possibly Na, Ca, Sr, Ba, the lanthanides (except Pm, Tm and Lu), Np, Pu and Am; all of them have the structure shown in *fig. 2.7*. The boron sublattice in these borides consists of a simple cubic array of fully interlinked B_6 octahedra. From PSEPT one would expect every metal atom to have to donate two electrons to the boron framework but the electronic situation is certainly more complicated than this as is clearly illustrated by the existence of KB_6.

The last series of borides covered here is the cubic dodecaborides (*fig. 2.8*) MB_{12}, M=Y, Zr, Tb, Ky, Ho, Er,Tm, Yb La, U and Pu. ScB_{12} should be added to this list because it is a tetragonal distortion of the structure caused by the relatively small size of scandium. Dodecaborides are included here because they are the last group of borides not to adopt the B_{12} icosahedron present in elemental boron as the principal structural motif. Even so, the boron sublattice can be regarded as a close-packed array of B_{12} cubo-octahedra and these are only slightly deformed icosahedra. The boron sublattice can also be generated by a close-packed array of B_{12} truncated tetrahedra or of edge fused B_{24} cubo-octahedra and it is within the latter cavities that the metal atoms reside. These materials are thermally highly stable but there are relatively few of them compared to the hexaborides. This seems to be due to the great inflexibility of the multiply buttressed boron skeleton toward containing anything less than ideal metal atoms. This is reflected in the observed range of linear variation in the unit cell dimensions of the known borides, where MB_6 flexes by over 4·2% but all MB_{12} only vary by 1·3% at most.

Once the boron to metal ratio exceeds twelve, structural units derived from the icosahedron come to dominate the crystal chemistry of borides. There are also some such borides with a lower B/M ratio, particularly amongst the borides of metals ocuring early on in the periodic table. MgB_7 (originally thought to be MgB_6) is in fact isotypic to $MgAlB_{14}$ and closely related to NaB_{15}. These all have structures based around B_{12} icosahedra and MgB_7 is the highest magnesium boride phase characterised to date; Markovskii, Kondrashev ad Kaputovskaya[40] suggest the existence of another still higher magnesium boride phase. Finally there are several examples of borides where very small concentrations of metal atoms stabilise highly complex, distinct phases relative to elemental boron; one of the best known of these is YB_{66} in which the main structural fragment is $B_{12}(B_{12})_{12}$ where a central B_{12} icosahedron is sheathed by twelve pendant icosahedra, one bound to each vertex.

2.3 The Hydrolytic Chemistry of Borides

The reaction of a boride with aqueous acid was first closely examined by Stock[30] in his seminal work of the early parts of this century. He prepared a boron/magnesium alloy formulated Mg_3B_2 (from the reaction of boric oxide and magnesium metal) which reacted vigorously with dilute hydrochloric acid to produce a small yield of highly reactive boron hydrides. These boranes consisted mainly of tetraborane-(10), B_4H_{10}, pentaborane-(9), B_5H_9, and hexaborane-(10), B_6H_{10} with traces of decaborane-(14), $B_{10}H_{14}$, and pentaborane-(11), B_5H_{11}, the last of which could possibly derive from tetraborane decomposition (see chap. 3). The total percentage conversion of boron in the starting material to boranes never exceeded 1.2% in this original work. Later Steele and Mills[31] obtained yields of up to 5% boranes from reacting borides of aluminium and of cerium (presumably AlB_2 and CeB_4) with 8M H_3PO_4; hearing of this Stock claimed an 11% yield of boranes from Mg_3B_2 when reacted with phosphoric acid. The highest claimed yield to date from a magnesium boride was observed by Mikheeva and Markina[32]. They prepared Mg_3B_2 by sintering the appropriate proportion of amorphous boron with elemental magnesium and reported that this reacted with 8M H_3PO_4 to give 14-16% boranes. Also they prepared a range of stoichiometries of magnesium borides by Stock's method and found that the yield for the reaction with dilute hydrochloric acid reached a maximum at Mg_3B_2; a smaller maximum was also seen around the formulation MgB_2. The result is surprising since, despite earlier claims, Stock's boride is not a single phase[33] and an X-ray powder photograph for this material shows only the lines for Mg_2 and MgO [33].

Stock noted that the yellow solutions remaining after Mg_3B_2 acid hydrolysis often had reducing properties and in several papers Ray[34] tried to ascertain what substances might be causing this. He reported that salts $[MgOH]_3B_2H_3$ and $K_2[B_2O_2H_4]$ were prepared from the reactions of Mg_3B_2 with HCl in 90% alcoholic solution at -10°C, and with KOH respectively. Whilst the reducing products from acid hydrolysis do not seem to have been isolated, Davies and Gottbrath[35] refuted Ray's proposal that his compounds contained B-B bonds and suggested that they were in fact partially hydrolysed tetrahydroborate salts instead. This opinion was confirmed firstly by Mikheeva and Surs[36] who, after dissolution of Mg_3B_2 in water and this solution's treatment with KOH, isolated a salt $K[HB(OH)_3]$. Solutions of this compound released hydrogen upon acidification, were decolourised and oxidised by I_2 and precipitated a nickel boride when added to nickel sulphate solution - all well known properties of $[BH_4]^-$. Secondly, King et al[37] were able to use the reaction of MgB_2 with 3M KOH as a preparation of $K[BH_4]$ in 13% yield and performed a similar reaction with $[Me_4N]OH$.

In Duhart's[38] detailed study of magnesium diboride's acidic and neutral hydrolysis it was found that only about three quarters of the boron present in the resultant solutions was in the form of fully oxidised boron. Oxidation with $K[MnO_4]$ was required to convert the outstanding boron to borate before the analysis could account quantitatively for the boron in the initial MgB_2. Titrating the solution for boron[46] before and after oxidation showed that when MgB_2 reacted with 1M HCl at 15°C, 21·5% of the boron in solution was not fully oxidised whilst in its reaction with water this figure rose to 26%. There is presumably a connection between this and the quantities of hydrogen evolved in each case where 2·6 moles of hydrogen per mole of MgB_2 were produced with the acid but this fell to just 2 moles when water was used. This should be compared with ref. 40 where reaction with hot HCl gave only 2·11-2·12 moles of H_2 per mole of MgB_2. Furthermore, Duhart noted that the reaction of MgB_2 containing an admixture of magnesium metal with hydrochloric acid reduced the proportion of dissolved unidentified boron species to only 12% but raised the borane yield from about 1·5 to 3-4% so that the high yield from the Mg_3B_2 alloy was thought to be a manifestation of this same effect.

The most recent study of the reaction of magnesium diboride with phosphoric acid was conducted by Timms and Phillips[41], who agreed with Stock concerning the major borane products. They found that Mg_3B_2 prepared from magnesium and technical amorphous boron reacted with 8M H_3PO_4 giving a 10·6% yield of volatile boranes but this fell remarkably to only 4·2% when 99·5% pure, crystaline boron was used in Mg_3B_2 manufacture under identical conditions. Furthermore, when MgB_2 (prepared from technical amorphous boron) was used instead of Mg_3B_2 the yield was also low at 4·2% although using this material hexaborane-(10) constituted a larger proportion of the volatiles than with Mg_3B_2. Timms and Phillips also reported that the yield of boranes and their distribution varied noticably with the temperature of formation and with the time of processing of the boride. It should be noted that only the studies of Stock and of Timms and Phillips give reliable accounts of the volatile products since all the other authors cited herein used a crude analytical system that would give only the overall borane yield. This system was based on the assumption that diborane and tetraborane were the only boranes present. The volatile products were first passed through water and then through alkali so that titration of the resultant solutions should give the B_2H_6:B_4H_{10} ratio. In fact if any other boranes were present this would give misleading results because, although B_2H_6 [42] is rapidly hydrolysed by water, both B_5H_{11} [43] and B_6H_{12} [44] react to give B_4H_{10} and boric acid; B_4H_{10}, B_5H_9 and B_6H_{10} are insoluble in pure water and thus hydrolyse very slowly but are quantitatively taken up by alkali.

Only Markovskii and Bezruk[45] seem to have made a systematic study of the acid hydrolysis of a range of stoichiometries of borides for several other elements apart from magnesium. They studied Mn_2B (orthorhombic or tetragonal?) with and without an excess of manganese, MnB, Mn_3B_4, MnB_2, FeB, Ni_2B, m-Ni_4B_3, NiB, Co_3B, Co_2B, CB, Cr_2B, Cr_5B_3, CrB and CrB_2. Although they used the same flawed analytical technique as that discussed above they did discern two trends: firstly, as the degree of boron-boron connectivity rose the rate of each metal's borides' reaction with hydrochloric acid fell; secondly, the borane yield also dropped in this order. The manganese and chromium borides reacted fastest and Cr_2B was found to give the highest borane yield at 2·2%. Two other interesting effects were noted: an alloy of Mn_2B with excess manganese gave a higher borane yield than that of the pure boride phase and this was paralleled to the higher productivity of Mg_3B_2; also, with the exception of Cr_2B, the amount of hydrogen evolved was found to be consistant with an equation where the metal was thought to enter solution in its lowest oxidation state and the boron was imagined to be present as the dissolved suboxide, BO.

In chapter 5 of this thesis it is argued that the anionic species $[B_6H_9]^-$ is an intermediate in the hydrolysis of MgB_2 and one can easily imagine this species' formation from the boron networks of hexagonal AlB_2-type diborides. However in the above article[45] borides with boron atoms in double and single chains, as well as in pairs and in isolation, are also examined. Clearly reactions of these other borides could be valuably reexamined to obtain a more accurate picture of the boranes produced. It is possible that patterns may emerge relating the starting borides' structure to the product distribution and perhaps a higher borane yield might be obtained if phosphoric acid were used.

Finally, in the review of Greenwood, Parish and Thornton[4] the data for a large number of borides (of most of the structural types covered in Section 2.2 of this chapter) are tabulated according to whether or not they will dissolve in hydrochloric and/or sulphuric acids, although no mention is made of borane evolution. From this the only clear rule appears to be that hexaborides and higher boron content compounds do not dissolve whilst the more metal rich a boride the more likely it is that it will.

2.4 Summary

In this chapter a brief discussion of the expansive field of boride structural chemistry is presented along with a review of the limited information available concerning boride hydrolysis, with an emphasis upon magnesium diboride. It is suggested that in future studies one might be able to find a link between the two areas and that if the yield from hydrolysis reactions could be raised this might be exploited. This could be particularly profitable in the case of tetraborides; these have not in the past been noted to give boranes upon hydrolysis but this could well be because of their slow reaction times and the requirement for harsher reaction conditions. However, tetraborides already contain cages reminiscent of free boranes and techniques are discussed in chapter 5 for MgB_2, particularly ultrasonics, which increase the borane yield and the rate of the reaction under conditions where it is normally very slow. These techniques might be applicable to the tetraborides.

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Chapter 3 Neutral Borane Interconversions

3.1 Introduction

In this project the experimental work has been dedicated mostly to the preparation of the boranes B_4H_{10}, B_5H_9 and B_6H_{10}. However, it is not easy to synthesise carboranes from these small boranes and it seemed that it would be useful to undertake a study of the conversion of these and, more generally, the other well known smaller boranes to more stable and versatile higher boranes, especially $B_{10}H_{14}$. Consequently, a detailed and critical review of the decomposition and interconversion reactions of the neutral boranes up to B_{10} is presented in this chapter. A secondary aim here is to see if any underlying patterns to cage-growth can be found. These might be used to predict more systematic and efficient routes to the higher boranes rather than the somewhat uncontrollable pyrolyses used previously. Thus, Section 3.2 discusses the premises used in this chapter to outline possible reaction mechanisms and the trends that the approach adopted reveals. Section 3.3 examines closely the evidence for the reaction pathways of each borane and the implications raised in this chapter for each case.

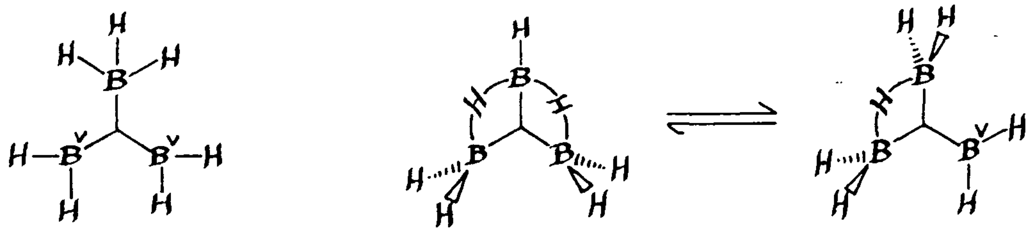
The ideas presented in this chapter, especially concerning the smaller boranes up to B_6, are largely based upon the experimental work of Greenwood and his collaborators (refs 1c, 2, 18, 19, 22 and 37) which contains the most definitive study to date of the pyrolysis of a series of boranes. One of the more far reaching of these authors' conclusions was that the high reactivity of B_4H_{10} towards other boranes derived almost entirely from its equilibrium with $\{B_4H_8\}$ and H_2 (in this chapter the notation $\{B_pH_q\}$ indicates a transient intermediate). This finding negates many of Long's key inferences in his earlier reviews of borane interconversions[1a,b] which were based upon the supposition that

B_4H_{10} reacted principally by "symmetrical" fission to $\{B_3H_7\}$ and $\{BH_3\}$. However, the overview of borane interconversions presented in this chapter differs significantly from that of Greenwood and Greatrex[1c] in one important aspect; the bimolecular "self-reactions" of $\{BH_3\}$, $\{B_3H_7\}$ and $\{B_4H_8\}$, or the combinations of any dissimilar pair of these three molecules, are ruled out even though they may be energetically feasible. For, although all three of these highly reactive, unsaturated Lewis acids are strongly implicated in borane reaction mechanisms, they will be generated in a bulk medium containing far higher concentrations of comparatively stable boranes with which they ought to be able to react; thus the self-reactions are ignored.

3.2 Reactive Intermediates and Mechanisms

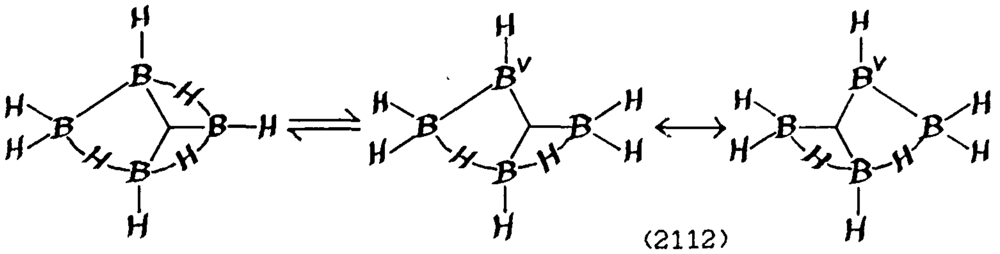
Whilst there seems to be little argument concerning the predicted structure of $\{BH_3\}$ - a trigonal planar molecule with a vacant orbital perpendicular to the atomic plane acting as a strong Lewis acid - the nature of the intermediates $\{B_3H_7\}$ and $\{B_4H_8\}$ is not entirely clear from the theoretical studies to date[30].

The consensus for $\{B_3H_7\}$ seems to be that there are two accessible low energy isomers of which the one containing the orbital vacancy is less stable by ~4 kcal mol^{-1} and these are illustrated, probably in equilibrium, in *fig. 3.1a* (B^v indicates the site of the vacant orbital and the numbers in parenthesis below each structure are their styx topological designations[53]). The (0104) structure of $\{B_3H_7\}$ is included because the bridging hydrogens in the (2102) isomer are thought to adopt an asymmetric disposition closer to the doubly bridged boron atom, reminiscent of (0104). For $\{B_4H_8\}$ the situation appears to be similar, *fig. 3.1b*, where the vacancy (2112) is again the less stable structure by ~4 kcal mol^{-1}. It is notable that this molecule is thought to retain the butterfly-shaped arrangement of the boron



(0104) (2102) (1103)

Fig. 3.1a $\{B_3H_7\}$

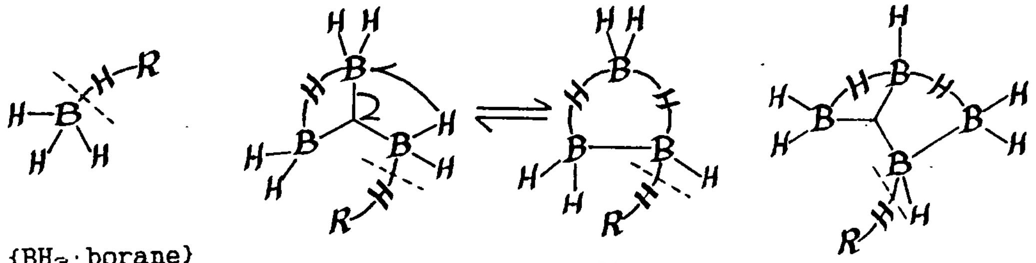


(3111) (2112)

Fig. 3.1b $\{B_4H_8\}$

atoms observed in the neutral borane B_4H_{10}. The geometrical relationship between the two isomers of both intermediates is simple where a terminal hydrogen of a BH_2 group in the vacancy configuration of *fig. 3.1* is bent around to donate electron density into its vacant orbital giving the lower energy isomer; the energetic advantages of bond formation are almost offset by strain.

The adducts $B_3H_7 \cdot CO$ [12] and $B_4H_8 \cdot PF_2(NMe_2)$ [31] have both been characterised by X-ray crystallography and are related to the predicted structures of their respective free, transient boron hydrides simply by removal of the ligand. Whilst this will of course entail some adjustments of bond lengths and angles, it gives the atomic arrangement of the slightly less stable vacancy isomers. Consequently one would expect $\{B_3H_7\}$ and $\{B_4H_8\}$ to react as their (1103) and (2112) forms respectively via initial electron donation into the vacant orbitals. When these species react with other boranes it is expected that the two fragments in the starting activated complex will be linked by a hydrogen bridge bond, $R{-}H\mu{\to}\{B_pH_q\}$, where a terminal hydrogen of the stable borane is the electron donor. This can be rationalised: whilst the inter-boron bonds of the cage surface can be considered as a series of canonical forms containing some three-center-two-electron bonds and the bridging hydrogens also participate in three-center-two-electron bonding, the terminal hydrogens are necessarily involved in two-center-two-electron bonding. Thus these bonds will possess relatively high electron density and several authors have referred to the terminal hydrogen atoms as having hydridic character; B_6H_{10} is an exception to this, since a basic basal B-B bond dominates its reactivity. However, such a mechanism implies at least partial donation of a hydride ligand, so it is suggested here that the pendant Lewis acid moieties will resemble their respective well known anions (i.e. hydride adducts - $[BH_4]^-$, $[B_3H_8]^-$ and $[B_4H_9]^-$). As a result of this nearly all the activated complexes proposed in this chapter take the structures shown in *fig. 3.2*. The low



$\{BH_3\cdot$borane$\}$

(1104) (2013)

$\{B_3H_7\cdot$borane$\}$

$\{B_4H_8\cdot$borane$\}$

Fig. 3.2 Presumed structures of activated complexes in the reactions of $\{BH_3\}$, $\{B_3H_7\}$ and $\{B_4H_8\}$ with stable boranes.

temperature ^{11}B NMR of $[B_4H_9]^-$ [32] is consistent with its being isostructural to $B_4H_8\cdot PF_2(NMe_2)$, i.e. $[B_4H_8\cdot H]^-$, so that the structure of $\{B_4H_8\cdot$Borane$\}$ is easily derived here. However, the crystal structure of $[B_3H_8]^-$ [33] is consistent with a (2103) topology, but because this anion's fluxionality has been attributed to its rapid equilibrium with the (1104) topology the structure of $\{B_3H_7\cdot$Borane$\}$ is probably more closely related than it at first appears.

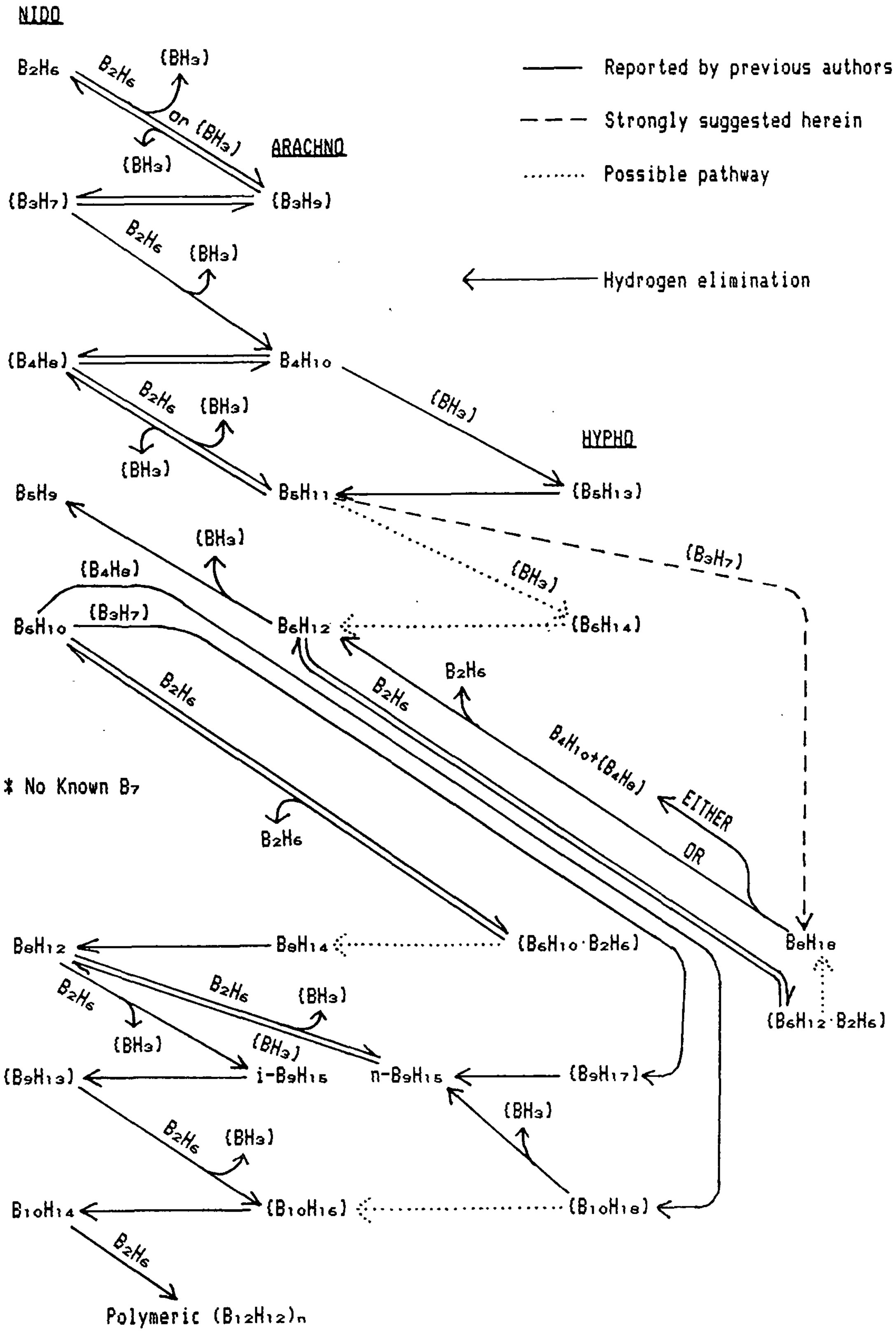
With these ideas in mind possible mechanisms for several known reactions are drawn out in this chapter, the choice of the next step being made to give the product's geometry as simply as possible. Whilst this will give a very crude picture of borane reaction mechanisms it does lead to the structure activity relationship that B_2H_6, $\{B_3H_9\}$, B_4H_{10}, B_5H_{11} and B_6H_{12} may all react with the Lewis acid intermediates by use of the terminal hydrogens belonging to their BH_2 groups. Although this may be just coincidental or an artifact of this crude approach, other authors have often noted that these boranes have several types of parallel reaction (particularly with respect to their reactions with Lewis bases) and so it is likely that there is a more fundamental electronic relationship between them.

Taking a larger scale view of inter-borane reaction mechanisms *scheme 3.1* summarises the established reaction pathways examined more closely in section 3.3. The clearest trend visible here is the ability of nido boranes to add a borane-(3) unit giving an arachno borane containing one more boron atom (or the reverse) which then loses hydrogen to a nido borane again. Although the second hydrogen elimination step is not as universal as the first cage-growth step this can be summarised by equation 3.1 and in

$$B_nH_{n+4} + BH_3 \longrightarrow B_{n+1}H_{n+7} \xrightarrow{H_2} B_{n+1}H_{(n+1)+4} \qquad 3.1$$

this analysis of the literature similar features seem to be appearing weakly between the arachno and transient hypho boranes. The other feature easily seen in *scheme 3.1* is the absence of any B_7 hydrides which disrupts the patterns seen up to B_6 and from B_8 onward. Whilst there is in fact one B_7 hydride known this is a fused cage system, 2:1',2'-$[B_5H_8][B_2H_5]$ [49], which one would not expect to prepare by BH_3 addition to one of the B_6 species. Even so $\{B_7H_{11}\}$ has been evoked by some authors to explain certain mechanisms and there are reasonable grounds for postulating $\{B_6H_{10}\cdot BH_3\}$. Clarification of whether or not B_7 hydrides exist

Scheme 3.1 Patterns of Cage-growth Amongst the Neutral Boranes



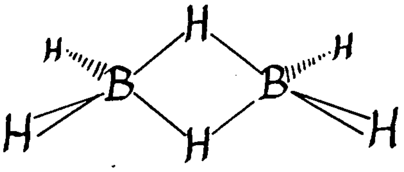
would certainly help in the interpretation of patterns in neutral borane inter-reactions; the existence of (B_7H_{11}) has been tentatively claimed from mass spectrometetric experiments[38].

Set out below in section 3.3 is the evidence for the pathways shown in *scheme 3.1*, discussing the stable boranes in order of the increasing number of boron atoms in the cage. The sub-sections examine the decomposition or pyrolysis of each borane as well as its reactions with hydrides smaller than itself.

3.3. Pyrolysis and Interconversion reactions of the Neutral Boranes

3.3.1 Diborane

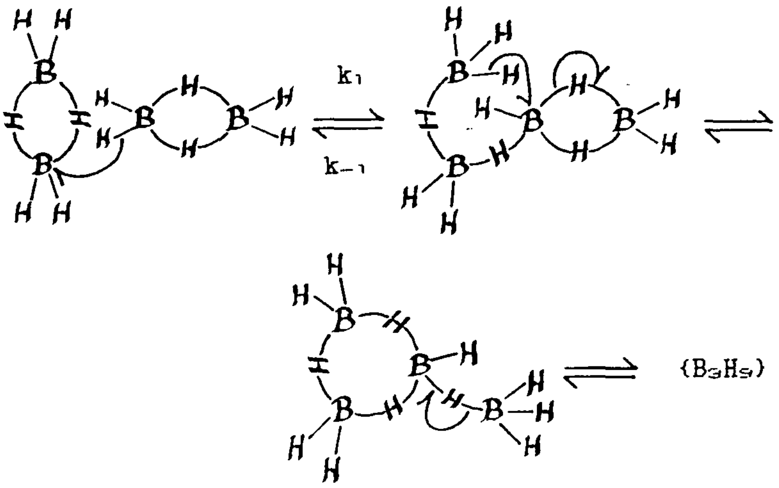
Fig. 3.3 B_2H_6



The most recent study of B_2H_6 pyrolysis was conducted by Gibb et al[2] whose general observations agreed with those of previous authors[3,4]. The decomposition was found to be slow at 100°C, becoming much faster toward 120°C, and gave principally B_5H_9, B_5H_{11} and $B_{10}H_{14}$ with smaller amounts of B_4H_{10}. Also observed at lower temperatures were traces of B_6 species, B_6H_{12} and B_9H_{15}. The careful kinetic study of Fernandez, Grotewold and Previtali,[4] who used a recirculating device to trap products less volatile than B_2H_6, showed in common with other authors that this was a 3/2 order reaction. However, they observed a relatively low activation energy of 10·16 kcal mol^{-1} whereas, if the decomposition was carried out in a static system, the activation energy rose to 23 kcal mol^{-1} (c.f. ref. 3a, 29 kcal mol^{-1} and ref. 3b, 27·4 and 25·5 kcal mol^{-1} from different methods - both reports sampled sealed bulbs). Other disagreements between their's and previous results were larger rate constants and a small Arrhenius preexponential factor. These effects were shown to be due to hydrogen inhibition and the decomposition of products (particularly B_5H_{11}) in the static system.

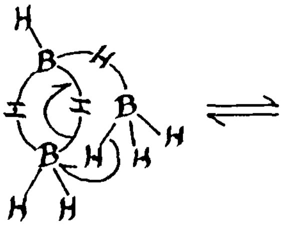
B_4H_{10} seems to be the initial stable product from this pyrolysis, despite B_5H_{11} being the major product, because, as Schaeffer[16] has pointed out, B_4H_{10} is produced in high yields without polymeric hydride residue in "hot-cold" reactors. In such reactors[17] a hot surface is narrowly separated from one cool enough to condense all the higher boranes except B_2H_6 so that the more reactive B_4H_{10} is trapped before it can react further; in a sealed bulb B_4H_{10} will undergo rapid copyrolysis with B_2H_6 to give B_5H_{11}.

The mechanism proposed by Fernandez, Grotewold and Previtali for the steps to B_4H_{10} are given in equations 3.2 to 3.5. The steps involving attack of a Lewis acid intermediate are drawn out according to the principles in section 3.2; if the forward reaction of 3.2 is regarded as the reverse of that between $\{BH_3\}$ and $\{B_3H_9\}$ the mode of interaction of the two molecules of B_2H_6 in this bimolecular step is dictated by the principle of microreversibility. Reaction 3.2 is favoured over the previously assumed homolytic fission of B_2H_6 into two $\{BH_3\}$ fragments on the basis of Long's[1a,1b] reexamination of the mass spectrometric evidence of Baylis et al[6]; notably Greenwood and Greatrex[11] still cite homolytic fission as the first step but without amplification of their reasons. Baylis et al noted that under conditions of very low pressure B_2H_6 did not start to decompose until 750K (probably to mainly H_2 and elemental boron with a little $\{BH_3\}$[7]). However, when the pressure of B_2H_6 was increased to $>5\text{x}10^{-6}$atm (and they remarked that the diameter of the reaction vessel now exceeded the mean free path) the decomposition temperature dropped to 525K where a B_3 species constituted 50% of the products but there was no B_4 or B_5. From this Long concluded that 3.2 had a much lower activation energy than the simpler unimolecular pathway. However, Long's analysis of the other steps was flawed; he thought that the reverse of 3.2 and 3.3 was negligible and,



{B_3H_9} + {BH_3} 3.2

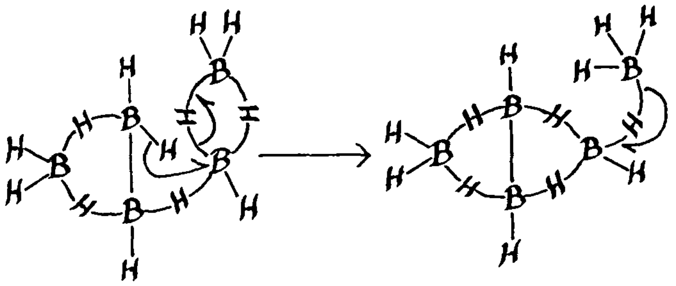
B$_2$H$_6$ + {BH_3} $\underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}$



{B_3H_9} 3.3

{B_3H_9} $\xrightarrow{k_3}$ {B_3H_7} + H_2 RDS 3.4

B_2H_6 + {B_3H_7} $\xrightarrow{k_4}$



$\longrightarrow$ B_4H_{10} + {BH_3} 3.5

instead, proposed the reaction 2{B_3H_9}$\rightarrow$3B_2H_6. This was necessary to account for the hydrogen exchange between B_2H_6 and B_2D_6 which was also 3/2 order in diborane but zero order in hydrogen[8] (At 75°C this became first order at low pressures but, with hindsight, this could have been due to a low level of 3.4). In fact it is apparent that Long's mechanism does not give the observed order of B_2H_6 pyrolysis whilst a stationary state analysis of the suite of reactions 3.2 to 3.5 does, but only if both 3.2 and 3.3 are equilibria. (See Appendix 1, parts i, ii and iii for a stationary state analysis of the three suggested mechanisms - only 3.2 to 3.5

seem to fit the experimental rate expression). Enrione and Schaeffer[5] proposed that hydrogen elimination from $\{B_3H_9\}$, 3.5, was the rate determining step (RDS) in B_2H_6 pyrolysis to account for the decomposition of B_2D_6 being five times slower and this step was the one thought to be inhibited by hydrogen.

3.3.2 Triborane-(7) and Triborane-(9)

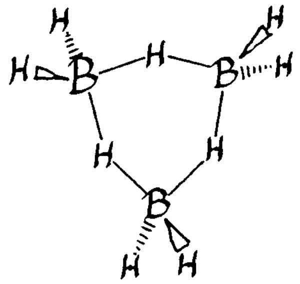
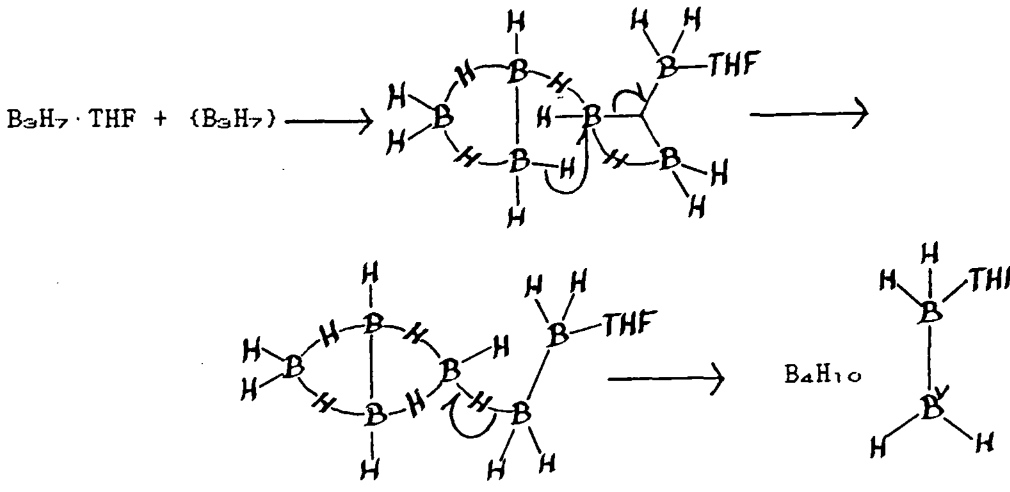


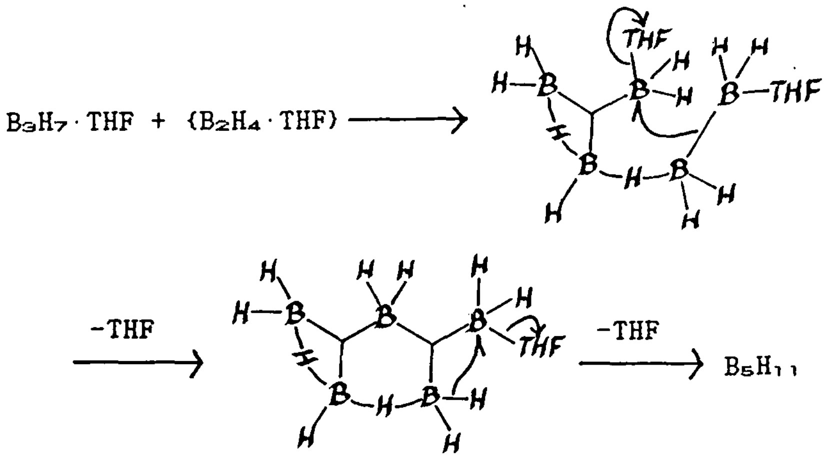
Fig. 3.4 $\{B_3H_9\}$

Although neither of these reactive triborane species have been isolated several reactions have been performed in which they are thought to be the principal reactive species present. One would expect $\{B_3H_9\}$ to be the first species formed in the reaction of triborohydride anion with protic acids. Assuming this, Schaeffer and Tebbe[10] proposed that reactions 3.4 and 3.5 accounted for the generation of wing tip boron labeled $^{11}B^{10}B_3H_{10}$ when Na[$^{10}B_3H_8$] was protonated with HCl in the presence of isotopically normal $^nB_2H_6$. Also the observation that [Me_4N][B_3H_8] reacts with phosphoric acids to give mainly B_4H_{10} [9] is consonant with this picture although other types of reaction should be suspected (see below); the other products are 14% pentaborane (B_5H_9· B_5H_{11} or both?), 4% B_6H_{12}, 0·8% B_8H_{18}, (2:2'-[B_4H_9]$_2$) and a trace of B_2H_6.

The reaction of B_3H_7·THF with BF_3 at -45°C, which has been regarded as the self-reaction of $\{B_3H_7\}$ [12], gives 45% B_8H_{18} as the major product. B_4H_{10}, B_5H_{11}, B_6H_{12}, and, of course, BF_3·THF are also produced along with traces of B_2H_6, B_5H_9 and H_2; the yield of B_8H_{18} at 0°C is only 31% probably due to its decomposition. Using the rationalisation of mechanisms set out in section 3.2 reaction 3.6 is proposed to occur first. However, since the product B_2H_4·THF will also be a strong Lewis acid, it too would be



3.6



3.7

expected to react with the starting material and reaction 3.7 is suggested. Whilst these two reactions may appear to be taking inference too far a reaction of B_5H_{11} and $\{B_3H_7\}$ to give B_8H_{18} (See p. 64, 3.3.5, reaction 3.16) is an appealing next step. This is not only because of its stoichiometry but also because of its geometry when the hydridic nature of BH_2, developed in this chapter, is assumed.

Another reaction that has been presumed to entail a $\{B_3H_7\}$ self-reaction is that between $[n\text{-}Bu_4N][B_3H_8]$ and equimolar quantities of BBr_3 at 0°C without a solvent[18]. This yields 67% B_4H_{10}, $[n\text{-}Bu_4N][HBBr_3]$ and traces of B_2H_6 and B_5H_9. However, this hydride abstraction reaction could equally well be interpreted as the reaction of $\{B_3H_7\}$ and $[B_3H_8]^-$. The reaction of $\{B_3H_7\}$ and $[B_3H_8]^-$ may be similar to 3.6 giving B_4H_{10} and $\{[B_2H_5]^-\}$, since $[B_3H_8]^-$ is isoelectronic to $B_3H_7\cdot THF$, but no speculation is offered here as to the fate of $\{[B_2H_5]^-\}$. It is suggested that since {$[B_2H_5]^-$} is anionic a reaction with $[B_3H_8]^-$ is unlikely so that it is not surprising that the yield of tetraborane approaches the theoretical limit for $2[B_3H_8]^- + BBr_3 \rightarrow [HBBr_3]^- + [B_3H_8]^- + \{B_3H_7\} \rightarrow [HBBr_3]^- + B_4H_{10} + \{[B_2H_5]^-\}$. Both the above mechanisms have necessitated cleavage of an arachno triborane into mono- and diboron species; such a reaction is, in fact, known for $B_3H_7 \cdot L$ ($L = (Me_2)NPF_2$, HPF_2) which reacts with further ligand to give $B_2H_4 \cdot 2L$ and $BH_3 \cdot L$ [13]. Also a kinetic study of $Na[B_3H_8]$ pyrolysis between 80 and 100°C[14] gave a first order rate law for which the RDS was thought to be fragmentation of the anion into $[BH_4]^-$ and $\{B_2H_4\}$.

3.3.3 Tetraborane

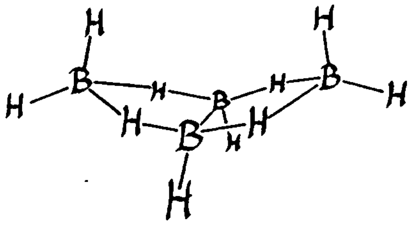


Fig. 3.5 B_4H_{10}

Greatrex, Greenwood and Potter[18] have recently reported a very detailed examination of the pyrolysis of this borane using sensitive mass spectroscopic techniques refined over several years study in this field. All their kinetic information was derived by extrapolation of the results of individual experiments to zero time so as to take into consideration the known inhibition of this reaction by hydrogen. They found that, between 40·2 and 77·8°C, B_5H_{11} was the only volatile hydride produced right from the start of the reaction where 0.44 moles were consistently formed per mole of B_4H_{10}. The other major product was an involatile polymeric hydride, deposited mainly on the lower surfaces of the reaction flask, the decomposition of which by loss of hydrogen was thought to account for the greater hydrogen yield at higher temperatures. The other boranes which were observed during the pyrolysis only appeared after quite lengthy induction periods which increased when the pressure was reduced; at 40·2°C with an initial pressure of B_4H_{10} of 3·89 mmHg, B_6H_{12} was first seen after ~45 mins whilst B_2H_6 and $B_{10}H_{14}$ only appeared after ~80 mins. B_5H_9 and B_6H_{10} were not seen except after very long decomposition times when some breakdown of B_5H_{11} might be expected. The pyrolysis was found to be first order in B_4H_{10} consumption and approximately so in B_5H_{11} production (actually between 1·11 and 1·21) whilst the activation energy was 23·7 kcal mol^{-1} with respect to B_4H_{10}.

Over the years there has been much disagreement as to whether equilibrium **3.8a** or **3.8b** is responsible for the high reactivity of

$$B_4H_{10} \rightleftharpoons (B_4H_8) + H_2 \qquad \textbf{3.8a}$$

$$B_4H_{10} \rightleftharpoons (B_3H_7) + (BH_3) \qquad \textbf{3.8b}$$

B_4H_{10}. (B_4H_8) has been identified as a "stable" boron hydride in molecular beam mass spectral experiments[28] and **3.8a** best explains the formation of $B_4H_8 \cdot C_2D_4$ (i.e. not $B_4H_7D \cdot C_2D_3H$) from B_4H_{10} and C_2D_4 [54]. Also, the reverse of **3.8a** is known to occur since $B_4H_8 \cdot CO$ reacts with D_2 to give $\mu,1\text{-}D_2B_4H_8$ [21] but Koski's report that D_2 did not exchange with B_4H_{10} [19a] seems to leave only the possibility of **3.8b**. However, Greatrex, Greenwood and Potter[19b] have also studied the B_4H_{10}/D_2 system using their superior techniques. They demonstrated conclusively that firstly, even at 42°C, B_4H_{10} does exchange hydrogen with D_2 and secondly, of the two mechanistic choices, only **3.8a** could account for their data. This led them to propose a simple three step mechanism for B_4H_{10} pyrolysis incorporating **3.8a** and **3.9** as the first two steps with

$$B_4H_{10} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (B_4H_8) + H_2 \qquad \textbf{3.8a}$$

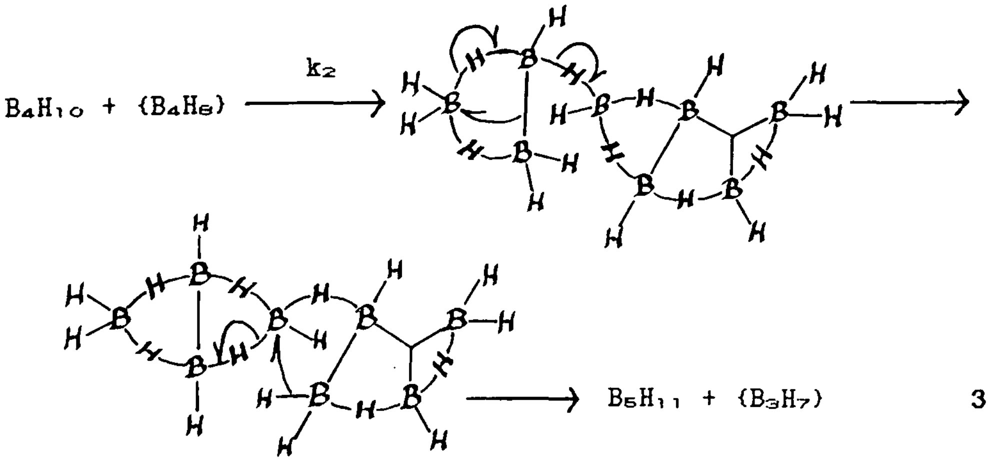
$$B_4H_{10} + (B_4H_8) \xrightarrow{k_2} B_5H_{11} + (B_3H_7) \qquad \textbf{3.9}$$

$$2(B_3H_7) \xrightarrow{k_3} \underset{\text{(polymeric hydride)}}{B_6H_{14-2m}} + mH_2 \qquad \textbf{3.10a}$$

the self-reaction of {B_3H_7} as the third, **3.10a** to give the polymer and hydrogen . Steady state analysis of this mechanism (see Appendix 1, part iv) gave a rate constant for B_4H_{10} destruction of $2k_1$, and for B_5H_{11} generation of k_1. This was fine tuned by allowing for approximately 12% self-reaction of {B_4H_8} to give polymer and hydrogen too so that the experimentally determined ratio of these rate constants (0·44) could be reproduced along with the known polymer stoichiometry. Although this mechanism did reproduce the experimental results rather well one must express reservations, especially concerning the required self-reactions of the two Lewis acid transient hydrides. In this respect it is noted that a major argument for the self-reaction polymerisation of {B_3H_7} was the absence of involatile hydride in B_4H_{10}/B_2H_6 copyrolysis ({B_3H_7} is not involved in this mechanism - see below) but B_2H_6 pyrolysis in a hot-cold reactor (which does involve {B_3H_7}) gave no polymer either. Furthermore, the suggestion of some {B_4H_8} polymerisation by self-reaction implies that some polymer should still form in the B_4H_{10}/B_2H_6 copyrolysis. However, as pointed out in section 3.1, it seems unreasonable for a transient hydride, present in undetectable concentrations (on this occasion <0.5%), to undergo in a bimolecular self- reaction when one can easily imagine it copolymerising with the large quantities of B_4H_{10} already present, equation **3.10b**. This mechanism is preferred here, even though it has the disadvantage that it now gives a rate constant ratio for B_5H_{11} formation versus B_4H_{10} consumption of only 0.33.

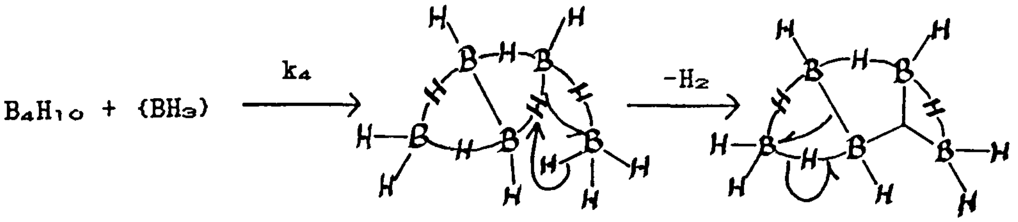
It is here that another of the assumptions of Greenwood, Greatrex and Potter can be brought into question, namely that they rejected any potential step containing {BH_3} on the grounds that B_2H_6 should then appear early on in the pyrolysis. This, however, contains the hidden assumptions a) that even if two {BH_3} moieties should meet, a collision activated {$BH_3 \cdot BH_3$}* can be converted to stable B_2H_6 and, more importantly, b) that {BH_3} cannot react rapidly with B_4H_{10}. In fact these same authors suspected that {BH_3} reacted very rapidly with B_4H_{10} in B_2H_6/B_4H_{10} copyrolysis to

$$B_4H_{10} \xrightarrow{k_1} \{B_4H_8\} + H_2$$ 3.8a



$$B_4H_{10} + \{B_4H_8\} \xrightarrow{k_2} \longrightarrow \longrightarrow B_5H_{11} + \{B_3H_7\}$$ 3.9

$$B_4H_{10} + \{B_3H_7\} \xrightarrow{k_3} \underset{\text{(polymeric hydride)}}{B_{7-n}H_{17-3n-2m}} + mH_2 + n\{BH_3\}$$ 3.10b



$$B_4H_{10} + \{BH_3\} \xrightarrow{k_4} \xrightarrow{-H_2} \longrightarrow B_5H_{11}$$ 3.11

give B_5H_{11} and H_2 so that their previously noted assumptions are surprising. As a result the above suite of reactions, **3.8a** to **3.11**, is suggested here to account for B_4H_{10} pyrolysis. If n=1, as might be expected for the implied transient B_7 species, the rate constant ratio for the appearance and disappearance of B_5H_{11} and B_4H_{10} respectively is 0·5; the parameters m and n can be adjusted to give the experimental results under any given conditions (see Appendix 1, part v). Whilst this mechanism may well be nearer the truth than those previously published, the negative criteria above would probably allow other types of polymerisation than **3.10b** so that no further speculation is offered here. However a relevant, useful insight might be obtained by reacting B_4H_{10} with $\{B_3H_7\}$ directly (generated from $B_3H_7 \cdot THF$ + BF_3).

The thermolysis of B_4H_{10} in the presence of excess H_2 has also been studied by Greenwood and Greatrex[1c]. Apart from inhibition of the thermolysis by the reverse of **3.8a**, two major differences to B_4H_{10} pyrolysis alone were observed; polymer formation was negligible and large amounts of B_2H_6 were formed along with the expected B_5H_{11}. This is entirely explained by the reaction of $\{B_3H_7\}$ (from **3.9**) with H_2 to give B_2H_6 via the reverse of 3.2 to **3.4**. Another major difference in this pyrolysis to that without added H_2 was that B_6H_{12} and $B_{10}H_{14}$ failed to appear. Greenwood and Greatrex ascribed this change to inhibition of a reaction between $\{B_3H_7\}$ and B_5H_{11} producing B_6H_{12} and B_2H_6 (this is discussed further on p.64, 3.3.6). Their other alternative suggestion of a reaction between $\{B_4H_8\}$ and B_5H_{11} is rejected here because they also noted that the major sink for $\{B_4H_8\}$ in B_5H_{11} pyrolysis would have to be in its reaction with B_5H_{11} to give an involatile hydride, possibly via n-B_9H_{15}.

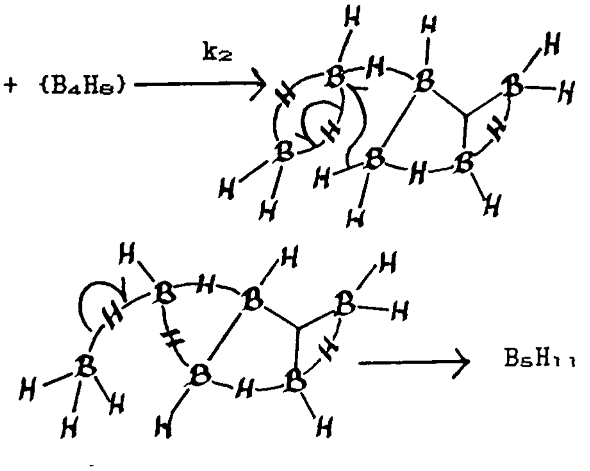
Since B_4H_{10} is significantly less stable than B_2H_6 the copyrolysis of these compounds would be expected to be initiated by the same unimolecular activation step as in the pyrolysis of B_4H_{10} alone. In their kinetic study of this reaction, which has often been represented by the pseudo-equilibrium 3.12, Dupont and

$$2B_4H_{10} + 2B_2H_6 \rightleftharpoons 2B_5H_{11} + H_2 \qquad 3.12$$

Schaeffer[20] favoured the activation step **3.8a** because it was already accepted that $\{B_3H_7\}$ probably reacted rapidly with B_2H_6 to give B_4H_{10}. Thus, if **3.8b** had been correct, the reaction should have been inhibited by B_2H_6. They found that between 72·5 and 92·9°C the reaction was first order in B_4H_{10} with an activation energy of 24·3 kcal mol^{-1}, but independent of B_2H_6, so that initial generation of $\{B_4H_8\}$ seemed the best model. To account for the equilibrium they proposed reactions **3.8a** and 3.13 but did not comment on how the {BH_3}, which accumulates on the right hand side of these equations, might be consumed to give the observed stoichiometry of **3.12**. There are three clear options; a) the self-reaction of {BH_3}, b) a reaction between {B_4H_8} and {BH_3} and c) the reaction of B_4H_{10} and {BH_3}. One can again dismiss the first two possibilities on the grounds of the low concentrations of transient hydrides. However, in their study of tetraborane pyrolysis, which was predicted to have an experimental rate constant for B_4H_{10} consumption of $2k_1$, Greatrex, Greenwood and Potter[18] noted that a stationary state kinetic analysis gave c) a rate constant of $2k_1$, (See Appendix 1, part vi) whilst a) and b) only gave k_1 for the copyrolysis. Arrhenius plots for B_4H_{10} pyrolysis and its copyrolysis with B_2H_6 gave the same straight line so c) was thought to be the final step in the suite of reactions below. Whilst some doubt has been raised in this chapter

$B_4H_{10} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \{B_4H_8\} + H_2$ RDS **3.8a**

$B_2H_6 + \{B_4H_8\} \xrightarrow{k_2}$



$\longrightarrow B_5H_{11} + \{BH_3\}$ **3.13**

$B_4H_{10} + \{BH_3\} \xrightarrow{k_3} B_5H_{11} + H_2$ **3.11**

as to Greatrex, Greenwood and Potter's mechanism the basic argument for **3.11** still stands. This is because the first two steps for B_4H_{10} pyrolysis are very probably correct so that it is hard to imagine a scheme that would predict an experimental rate constant of <2k_1. Here it is appropriate to mention the reaction between B_4H_{10} and CO to give $B_4H_8 \cdot CO$ [52] which is first order in B_4H_{10} with an activation energy of 24·6 kcal mol^{-1} - very nearly identical to those for B_4H_{10} pyrolysis and B_4H_{10}/B_2H_6 copyrolysis. It is also independent of CO so that the initial formation of {B_4H_8} in **3.8a** is thought to be the RDS here too.

The last reaction considered here is the hydrogen exchange between B_4H_{10} and B_2D_6 at 45°C [47]. This reaction occurs only in the gas phase to give tetraborane deuteration of the wing tip, 2,4-, and bridge positions, the majority in the former, but no deuteration of the 1,3- positions. The exchange is thought to occur with different rates and different activation energies to both sites (with at least one of the processes incurring boron exchange as well). Also, whilst both processes are first order in B_4H_{10}, they seem to have orders subunity in B_2H_6. Since {B_4H_8} reacts with D_2 to give μ,1-$D_2B_4H_8$ [21] it is clear that the two boranes are not exchanging molecular hydrogen via **3.4** (p. 50 , 3.3.1) and **3.8a**. Although no firm conclusions are drawn here, and this reaction would certainly deserve further study, the hydridic nature of the BH_2 moieties suggested in this chapter could perhaps account for these exchanges. They might proceed via the {$B_4H_{10} \cdot B_2H_6$} complexes shown in *fig. 3.6* where exchange via **a** is analogous to the known 1,4-hydrogen exchange of B_6H_{12} with B_2D_6 (p. 69 , 3,3,7) and exchange via **b** is very similar to the mechanism of {B_3H_9} formation (p.50 , 3.2).

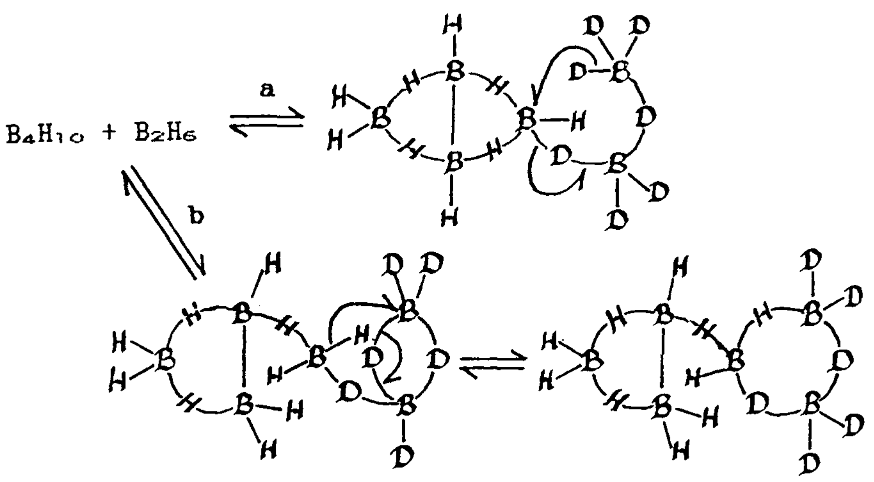


Fig. 3.6 Possible structures for {$B_4H_{10} \cdot B_2D_6$}

3.3.4 Pentaborane-(9)

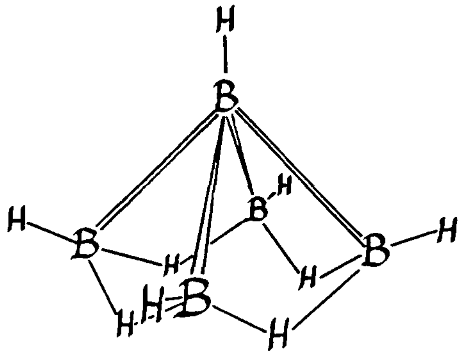


Fig. 3.7 B_5H_9

B_5H_9 is one of the most thermally stable boranes and does not start to decompose until about 190-200°C, possibly via a radical mechanism[23b] - c.f. B_6H_{10} which almost certainly does. The pyrolysis is first order producing only polymeric hydride and three moles of H_2 per mole of B_5H_9 with no isolable intermediates[23a]. Even at 250°C, when substantial decomposition occurs, there is no boron exchange between ${}^{n}B_5H_9$ and ${}^{10}B_5H_9$ although at 200°C there is hydrogen exchange.

The copyrolysis of B_5H_9 and B_2H_6 was studied by Hillman, Mangold and Norman[25] in a sealed tube at 77·5°C for 24 hours where large amounts of polymeric hydride were produced along with some $B_{10}H_{14}$. The latter was shown to derive half its boron from each reactant by mass spectrometric techniques using boron labelled starting materials. Whilst this conclusion was questioned by a referee[25b] it was partly supported by the observation that neither B_5H_9 [26] nor $B_{10}H_{14}$ [51] exchanged boron with B_2H_6 even during reaction. Since the temperature of this study was well below the decomposition temperature of B_5H_9 it is tempting to suggest that the $B_{10}H_{14}$ derived from an interaction of B_5H_9 with (B_3H_7). This copyrolysis was also studied in a continuous flow system at 140°C by Dobson, Maruca and Schaeffer[26] and they isolated several other hydrides, including all three[27] isomers of $[B_5H_8]_2$ as well as the products of B_2H_6 pyrolysis alone. The n-B_9H_{15} recovered from the reaction of ${}^{n}B_5H_9$ and ${}^{10}B_2H_6$ was at least partially specifically labelled (although the product $B_{10}H_{14}$ was almost completely scrambled) showing that it was probably an intermediate in B_5H_9/B_2H_6 copyrolysis and did not just derive from B_2H_6.

The copyrolysis of B_5H_9 and B_4H_{10} at 75°C has also been examined to some extent[22]. Whilst most of the products probably came from B_4H_{10} pyrolysis alone, a slight fall in the final B_5H_9 concentration and a slight increase in the yields of B_2H_6 and $B_{10}H_{14}$ relative to B_4H_{10} pyrolysis indicated that there had been a small degree of copyrolysis.

3.3.5 Pentaborane (11)

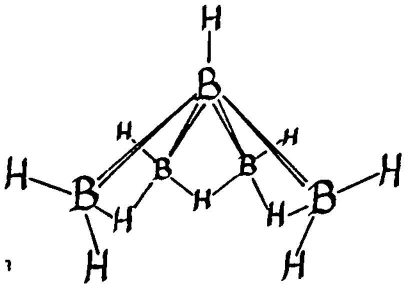
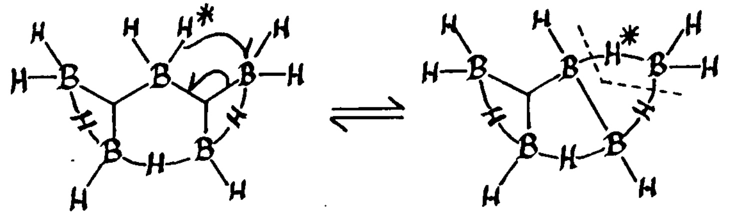


Fig. 3.8 B_5H_{11}

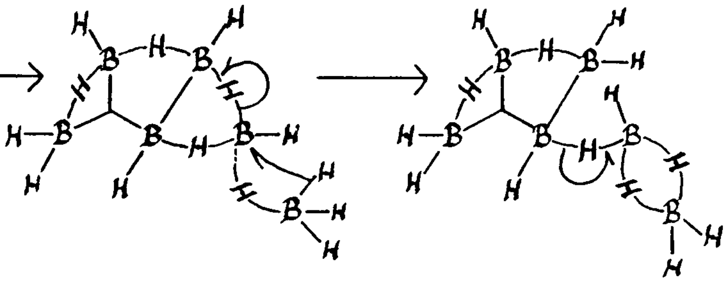
Greenwood and Greatrex[1c] have recently conducted a kinetic study of the pyrolysis of B_5H_{11} over the ranges of pressure and temperature 1·8 to 10·4 mmHg and 60-150°C. They found that the main volatile products were H_2 and B_2H_6 which had approximate initial rates of appearance of 1 and 0·5 mole per mole of B_5H_{11} consumed. B_4H_{10} was observed but did not accumulate during the reaction, whilst B_5H_9, the other major volatile hydride product[2], was not detected in the initial stages of the reaction. A low concentration of $B_{10}H_{14}$ was also produced but as much as 50% of the B_5H_{11} ended up as a solid involatile hydride. Under the conditions of a molecular beam study[28] B_5H_{11} was seen to fragment into $\{B_4H_8\}$ and $\{BH_3\}$, **3.14**. This is now thought to be the most likely first step under normal pyrolytic conditions especially since theoretical considerations have recently indicated that hydrogen elimination, previously used to explain B_5H_9 formation, is orbitally forbidden.[29] Greenwood and Greatrex observed that B_5H_{11} pyrolysis followed first order kinetics, with an activation energy of 17·5 kcal mol^{-1}, in line with this point of view. Thus reaction **3.14** represents the RDS of B_5H_{11} pyrolysis where H* in *fig. 3.8*, often referred to as the "anomalous" bridge hydrogen, is presumed here to adopt the less symmetrical position shown so that fragmentation will give the accepted structure of $\{B_4H_8\}$ directly.

Greenwood and Greatrex suggested that the next step was direct combination of two $\{BH_3\}$ moieties. However, it is once again noted here that it seems far more reasonable for the reactive intermediate to react rapidly with the starting material and so **3.15a** is proposed as the next step. It is also noted that the reaction of B_5H_{11} with $\{BH_3\}$ might be expected to bear some qualitative similarities to that between B_4H_{10} and $\{BH_3\}$ so that **3.15b** would appear feasable at this crude level of analysis. Although the presence of B_6H_{12} was not noted during B_5H_{11} pyrolysis, if it were destroyed rapidly by $\{BH_3\}$ abstraction, for instance by $\{BH_3\}$ or $\{B_4H_8\}$, the occurence of **3.15b** as a minor pathway could perhaps account for the appearance of B_5H_9 in the products.

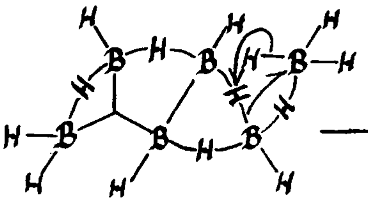


$\longrightarrow$ $\{B_4H_8\}$ + $\{BH_3\}$ **3.14**

B_5H_{11} + $\{BH_3\}$ $\longrightarrow$



$\longrightarrow$ B_2H_6 + $\{B_4H_8\}$ **3.15a**



$\longrightarrow$ B_6H_{12} + H_2 **3.15b**

The picture of B_5H_{11} pyrolysis presented in **3.14** and **3.15a** is probably fairly accurate as far as it goes, however it does not predict the fate of $\{B_4H_8\}$ which is by no means clear on this occasion. Greenwood and Greatrex conjectured that it might react with B_5H_{11} giving n-B_9H_{15} and two molecules of H_2 - under their conditions n-B_9H_{15} would decompose by loss of $\{BH_3\}$ to B_8H_{12}. This would adequately explain the experimental initial rates of B_2H_6 and H_2 production, assuming that nearly all the B_8H_{12} was incorporated into the polymer. It would also explain the production of $B_{10}H_{14}$. Whilst such a reaction may in fact be the case an alternative, suggested by analogy to the reaction suspected to occur between B_5H_{11} and $\{B_3H_7\}$ (**3.16**), is that B_5H_{11} and $\{B_4H_8\}$ first combine to give 2:2'-$[B_5H_{10}][B_4H_9]$. Such a molecule is clearly set up to lose H_2 (c.f. B_4H_{10}) or $\{BH_3\}$ (c.f. B_5H_{11}), although it is not yet possible to predict the outcome of the intra-molecular rearrangements which would be expected to follow such steps. Whatever the mechanism of the reaction of B_5H_{11} and $\{B_4H_8\}$ two of the products are likely to be B_2H_6 and $B_{10}H_{14}$ (or a direct precursor) because these two boranes appear in B_4H_{10} pyrolysis only after B_5H_{11} has accumulated.

Examination of the proposed mechanisms of the reactions between the transient Lewis acid hydrides and the arachno boranes, plus B_2H_6, ($B_2H_6+\{BH_3\}$ **3.3**, $B_2H_6+\{B_3H_7\}$ **3.5**, $B_2H_6+\{B_4H_8\}$ **3.13**, $B_3H_9+\{BH_3\}$ **3.2**, $B_4H_{10}+\{BH_3\}$ **3.11**, $B_4H_{10}+\{B_4H_8\}$ **3.9** and $B_5H_{11}+\{BH_3\}$ **3.15**) reveals a trend. In these reactions the choice of which terminal hydrogen should donate to the vacant orbital of the Lewis acid has been made on the rather simplistic grounds that it gave the transition state most easily related to the product's geometry. However, it will be noted that in all the above reactions it is the terminal hydrogen of a BH_2 group that is initially donating to the vacant orbital of the Lewis acid. Also, even though it is clear from the precepts of section 3.2 that B_2H_6 and $\{B_3H_9\}$ can react with the Lewis acids in no other way, examination of the alternative activated complexes for B_4H_{10} and B_5H_{11}, *fig. 3.9*, reveals no easy path to the known products

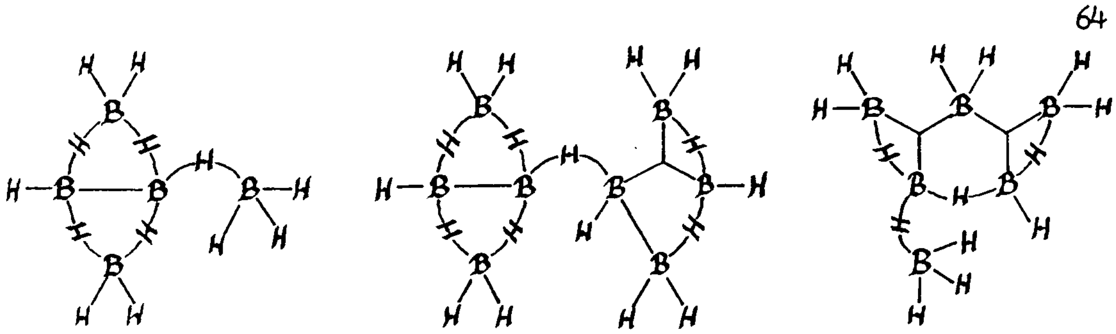
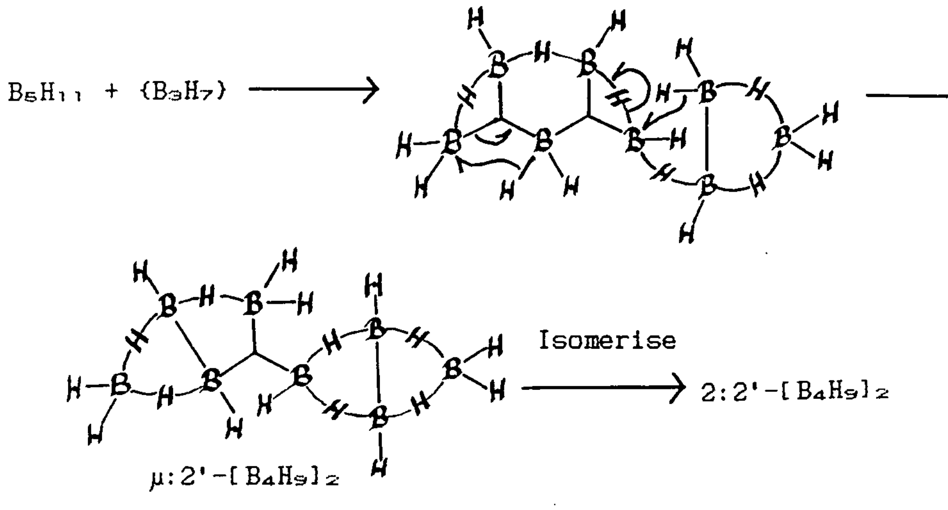


Fig. 3.9 Alternative isomers of $R\text{-}H_{\mu}\rightarrow\{B_pH_q\}$

without highly complex rearrangements. Another reaction which adds weight to the implied hydridic nature of the BH_2 groups is the exchange between B_6H_{12} and B_2D_6 (p. 69 ,3.3.7). This gave 1,1,4,4-$D_4B_6H_8$ and proved extremely difficult to interpret mechanistically without such assumed reactivity. Whilst this structure-reactivity relationship may just be coincidental or an artifact of the crude analysis of the mechanisms used here, it seems more likely that it is in fact due to a more fundamental electronic parallel between the boranes B_2H_6, B_4H_{10}, B_5H_{11} and B_6H_{12}. In this respect it has been observed by many authors that these boranes have similar aspects to their chemistry, e.g. they all suffer a cleavage reaction with two equivalents of ammonia giving the cation $[H_2B(NH_3)_2]^+$ and the anions $[BH_4]^-$ [55a], $[B_3H_8]^-$ [55b], $[B_4H_9]^-$ [55c] and $[B_5H_{10}]^-$ [55d] respectively.

With this picture in mind it is here proposed that B_5H_{11} and $\{B_3H_7\}$ react according to the mechanism in **3.16**; the second step,



3.16

after formation of a H_{μ} bridge from the BH_2 group of B_5H_{11} to $\{B_3H_7\}$, has features similar to the reaction of B_2H_6 and $\{B_3H_7\}$

(p.50 , 3.5). It is this reaction which is suggested here to give the high yield of B_8H_{18} when B_3H_7·THF reacts with BF_3. It can also account for the appearance of B_6H_{12} in B_4H_{10} pyrolysis, but only after B_5H_{11} has been produced, since B_8H_{18} decomposes to give 8% B_6H_{12} at room temperature[9b]. The mechanism of B_8H_{18} decomposition is not known and whilst a unimolecular fission to B_6H_{12} and B_2H_6 seems plausible (since B_2H_6 is also produced along with over 50% B_4H_{10}) its reaction with {B_4H_8} seems more likely. This is because B_8H_{18} has been used as an effective source of {B_4H_8} [36] and, since {B_4H_8} can abstract a BH_3 fragment from B_4H_{10}, the initial production of {B_4H_9-B_3H_6} seems reasonable. This could then possibly undergo an intramolecular attack of the B_3 Lewis acid unit upon the B_4 unit bringing about ejection of another molecule of {BH_3} leaving B_6H_{12}.

3.3.6 Hexaborane-(10)

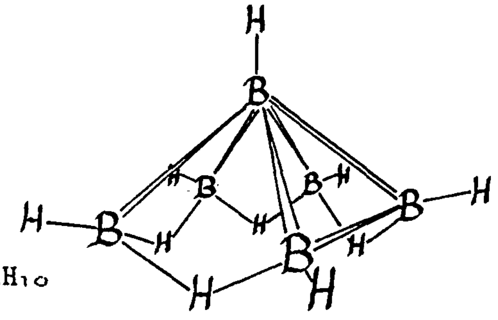
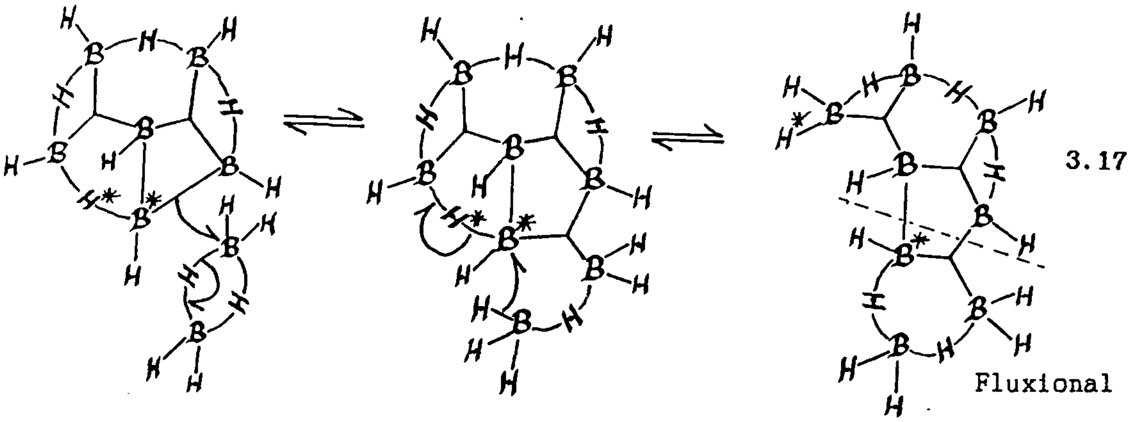


Fig. 3.10 B_6H_{10}

Greatrex, Greenwood and Jump[37] performed a detailed study of the pyrolysis of this borane and found that, when pure, it was more stable than had earlier been thought[2] decomposing only slowly at 120°C. The reaction was second order giving initially one mole H_2 per mole of B_6H_{10} consumed and as much as 90% of the starting boron was deposited as an involatile hydride. The only volatile borane products to accummulate were B_5H_9 and $B_{10}H_{14}$, produced in a ratio of about 5:1 respectively, although B_2H_6, B_8H_{12}, B_9H_{15} and B_{13-15} hydrides could also be detected in trace amounts during the reaction. Originally it was thought that the RDS could be the decomposition of an activated complex {$B_{12}H_{20}$}, but later work showed that this reaction almost certainly proceeded via a radical chain mechanism[1c].

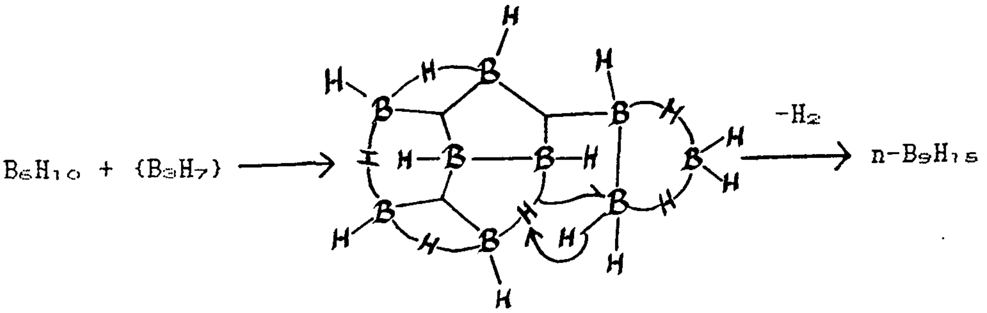
At -20°C B_6H_{10} undergoes a peculiar hydrogen exchange with B_2D_6 [39] where only the basal terminal hydrogens exchange but without boron exchange[40]. B_2D_6 does not exchange with B_5H_9 until 200°C and the unbridged basal B-B bond of B_6H_{10} is well known to have Lewis base properties[41]. Thus it seems most likely that B_6H_{10} attacks diborane, as would any other ligand[55*], by cleaving one of the bridge bonds. In the second step suggested for equilibrium **3.17** the B_3 fragment would have to be fluxional (perhaps like $[B_3H_8]^-$) to account for exchange of only terminal



3.17

hydrogens. Furthermore, in the reverse of **3.17**, H* would have to reattach to B* or there would also be exchange of H_μ.

The copyrolysis of B_6H_{10} and B_2H_6, in the temperature range 100-198°C, is 3/2 order in B_2H_6 and independant of B_6H_{10} with the main product, apart from H_2, being up to 40% $B_{10}H_{14}$ [1c]. Thus it seems that neither the radical mechanism of B_6H_{10} decomposition in isolation nor **3.17** is important to the cothermolysis where the formation of $\{B_3H_7\}$, as in B_2H_6 pyrolysis, is probably the RDS. The outcome of the reaction between $\{B_3H_7\}$ and B_6H_{10} is probably that observed by Rathke and Schaeffer[42] under far milder conditions. They reacted BF_3 with a mixture of B_6H_{10} and $B_3H_7 \cdot THF$ at 0°C and found that B_9H_{15} and H_2 were the major products. When $^{10}B_3H_7 \cdot THF$ was used in this reaction the product n-B_9H_{15} was labeled in the 3,4,9- positions so that the mechanism in **3.18**

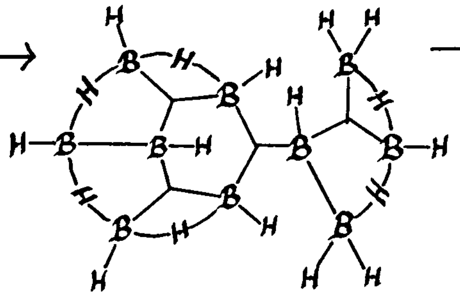


3.18

was proposed. However, under the conditions of B_6H_{10}/B_2H_6 copyrolysis the moderately unstable n-B_9H_{15} will be converted first, by initial decomposition to B_8H_{12} and then, via {B_9H_{13}}, to $B_{10}H_{14}$.

In the copyrolysis of B_6H_{10} with B_4H_{10} [1a,2] a similar situation pertained as did with B_2H_6. The reaction was found to be first order in B_4H_{10} but independant of B_6H_{10} and this was consistent with generation of {B_4H_8} by 3.8a being the RDS. Since this cothermolysis occured at lower temperatures than that between B_6H_{10} and B_2H_6 it was possible to identify B_9H_{15} as the major product early on in the reaction. The reaction between excess B_6H_{10} and {B_4H_8} (as either B_4H_8·CO or B_8H_{16}) was also tested by Rathke and Schaeffer[42] under mild conditions. They found that it gave almost quantitative n-B_9H_{15}, as well as a little $B_{10}H_{14}$, and the expected B_2H_6 or BH_3·CO, 3.19. Whilst this is expected to be the major reaction during B_6H_{10}/B_4H_{10} copyrolysis there is no obvious mechanism for how the presumed {B_6H_{10}·B_4H_8} activated complex could eject {BH_3}. No speculation is offered here since a prerequisite in such a mechanism would be transfer of one bridge hydrogen from the B_6 to the B_4 unit for which there is no model system. Rathke and Schaeffer did however suggest a mechanism for a minor pathway directly to $B_{10}H_{14}$ by two consecutive hydrogen eliminations from {B_6H_{10}·B_4H_8}.

B_6H_{10} + {B_4H_8} $\longrightarrow$



$\longrightarrow$ n-B_9H_{15} + ½ B_2H_6 3.19

Finally Rathke and Schaeffer have also examined the reactions between B_6H_{10} and the two higher homologous nido Lewis acids B_8H_{12} and $\{B_9H_{13}\}$ (from freshly prepared i-B_9H_{15}). They found that although the 1:1 adduct with B_8H_{12} decomposed to the starting materials above -45°C, the product from the reaction with $\{B_9H_{13}\}$, $B_{16}H_{23}$, was probably closely related to the more familiar $B_9H_{13}\cdot L$ adducts.

3.3.7 Hexaborane-(12)

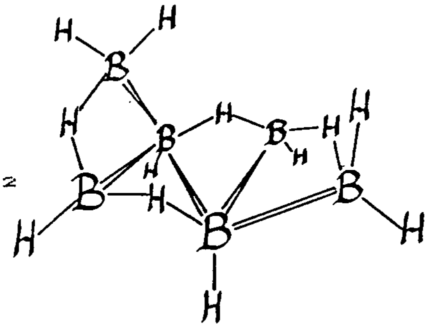
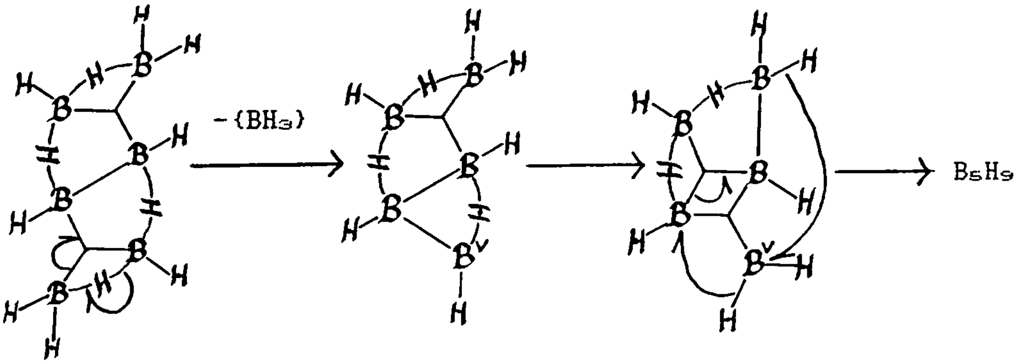
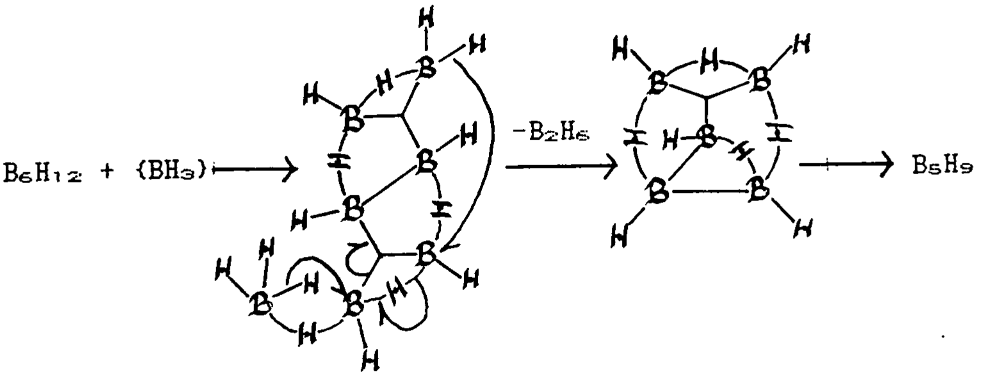


Fig. 3.11 B_6H_{12}

A recent study of the pyrolysis of this borane[43] showed that it is one of the "cleanest" for any individual borane with >70% of the starting boron remaining in the gas phase as mainly B_5H_9 and B_2H_6. The reaction is first order in B_6H_{12} consumption and H_2 production with both its activation energy (17·5 kcal mol^{-1}) and preexponential factor similar to those for B_5H_{11} thermolysis. Hence 3·20 is thought to be the RDS and $\{BH_3\}$ attack on B_6H_{12}, 3.21, is once again prefered here over direct combination of



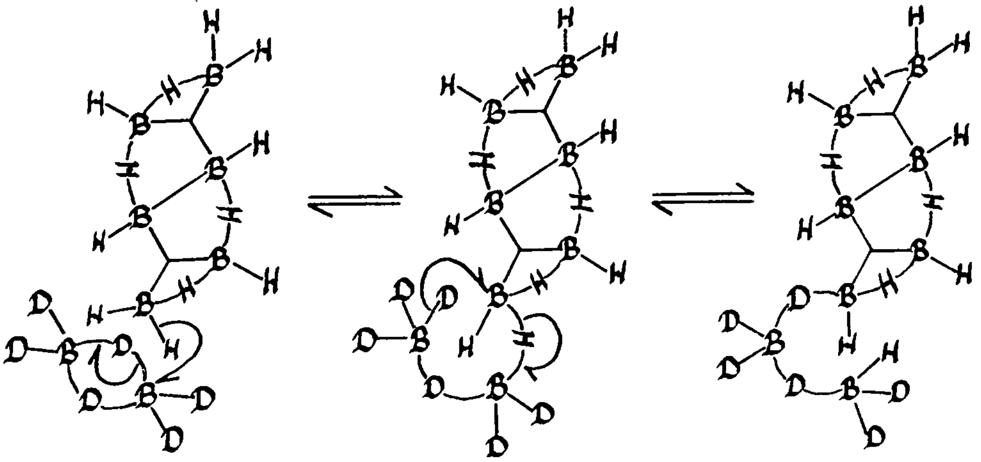
3.20



3.21

two $\{BH_3\}$ moieties to explain B_2H_6 production. However, it is clear from examination of the structure of B_6H_{12} that exscission of BH_3 from either the 1- or 4- position does not naturally lead to the known structure of B_5H_9 and moreover, that migration of a bridge hydrogen is required at its simplest level. Three structures of a possible $\{B_5H_9\}$ prior to rearrangement are shown here: the first tentative suggestion in 3.20 is a vacancy structure allowing for minimal atomic motion during fission, reminscent of $\{B_3H_7\}$ and $\{B_4H_8\}$; the second structure includes the breaking of a bridge bond which might explain the necessary migration. Alternatively, as shown in 3.21, $\{BH_3\}$ loss might be concerted with bridge bond formation to the remaining BH_2 group so that the resulting $\{B_5H_9\}$ would have a peculiar base-apex hydrogen bridge which might perhaps rearrange without a transient vacancy structure.

At room temperature B_6H_{12} and B_2D_6 undergo complete hydrogen exchange but at -31°C this exchange gives only 1,1,4,4-$D_4B_6H_8$ ^{45} and during the same reaction using $^{10}B_2H_6$ no boron exchange occurs. It is very hard to interpret this except by accepting the hydridic character of BH_2 groups, as postulated in this chapter, when equilibrium 3.22 is easily suggested. B_6H_{12} does not appear


3.22

to have been copyrolysed with B_2H_6. However, its reaction with a large excess of B_2H_6, left at room temperature and high pressure for two days^{45}, has been examined and it appears to be qualitatively similar to the reaction of B_5H_{11} and B_2H_6 ^{34} under comparable conditions. The main products are B_4H_{10}, B_5H_9, n-B_9H_{15} and a little $B_{10}H_{14}$ and this might be a reflection of $(B_6H_{12}\cdot B_2H_6)$ being able to fragment by a different mechanism to that in 3.22 - this being another isomer of B_8H_{18}. There may, however, be a different type of reactivity as was seen in the hydrogen exchange and copyrolysis of B_6H_{10} with B_2H_6. Finally, B_6H_{12} and B_4H_{10} have been copyrolysed at 75° [22]. Whilst the final B_2H_6 and $B_{10}H_{14}$ concentrations were higher than those that would be expected from the reaction simply being the sum of the two separate pyrolyses, it is not possible to arrive at any firm conclusions at present.

3.3.8 Octaborane-(12) and Octaborane-(14)

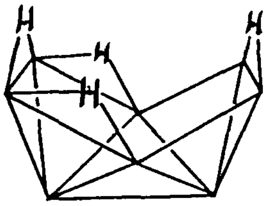


Fig. 3.12 B_8H_{12}

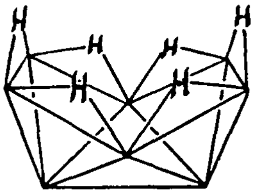


Fig. 3.13 B_8H_{14}

B_8H_{12} is probably a very important intermediate during the production of $B_{10}H_{14}$ by the thermal degradation of the lower boranes and yet it is one of the least well characterised of the established boranes. After three hours at room temperature it is completely decomposed giving polymeric hydride and 52% $B_{16}H_{20}$ [42] (a fused cage borane notable for its total lack of molecular symmetry), although mass spectroscopic studies have suggested a first order decomposition to B_6H_{10} [46]. B_8H_{12} is, however, greatly stabilised in etherial solution where a labile adduct, $B_8H_{12}\cdot OEt_2$, is suspected[46]. Although its stationary structure is usually taken to be that in *fig. 3.12* "B-NMR shows only two doublets of equal area so that is is thought to be fluxional - this is similar to its isoelectronic, and probably isostructural, analogue $C_2B_6H_{10}$ where the carbon positions are known to be fluxional.[48]

Dobson and Schaeffer[46] have studied the reaction of B_8H_{12} with excess B_2H_6 at -30°C and found that it gave about equal proportions of n-B_9H_{15} and $B_{10}H_{14}$. Maruca, Odom and Schaeffer[34] have also studied this reaction with the same conditions but using a sixfold excess $^{10}B_2H_6$. They obtained an 80% conversion of $B_8H_{12}$to n-B_9H_{15} and $B_{10}H_{14}$, this time in a ratio of approximately 2:1, which they remarked was probably dependant upon the initial diborane concentration. From this two competing reaction pathways, 3.23a and 3.23b, were proposed where the i-B_9H_{15} in the

$$\begin{tikzcd} & n\text{-}B_9H_{15} & \\ B_8H_{12} + \tfrac{1}{2}\, B_2H_6 \arrow[ur] \arrow[dr] & & \\ & i\text{-}B_9H_{15} \arrow[r, "Q"] & B_{10}H_{14} \end{tikzcd}$$

3.23a

3.23b

latter did not accumulate (since it reacts rapidly with B_2H_6 via (B_9H_{13}). This opinion was somewhat substantiated by the observation of traces of $B_{18}H_{22}$ - a major decomposition product of i-B_9H_{15}. During the reaction B_8H_{12} did not exchange boron with $^{10}B_2H_6$ but did quite rapidly exchange hydrogen with B_2D_6.

Only Dobson and Schaeffer[46] appear to have studied B_8H_{14} experimentally but it was not possible to perform a thorough characterisation because they reported that it decomposed very readily to B_8H_{12} during manipulation. Recent evidence corroborating the decomposition of B_8H_{14} by hydrogen elimination comes from the isoelectronic $C_2B_6H_{12}$ [49] which, although stable to 65°C, also decomposes by hydrogen elimination and produces $C_2B_6H_{10}$ in high yield. The reason that this rare hydride is mentioned here is that, because of its instability, it is unlikely that it could have been detected even in the most sensitive experiments to date and yet it could be an important intermediate in some reactions, e.g. perhaps in B_5H_9/B_2H_6 copyrolysis, $(B_5H_9 \cdot B_3H_7) \rightarrow B_8H_{14} + H_2$?

3.3.9 n- and i- Nonaborane-(15)

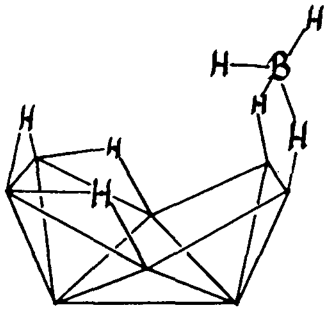


Fig. 3.14 n-B_9H_{15}

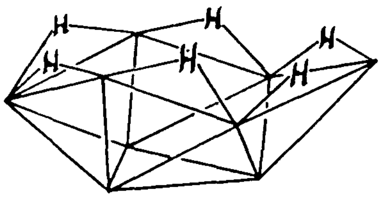


Fig. 3.15 i-B_9H_{15}

Normal, n-, B_9H_{15} is by far the most stable of these two isomeric hydrides and it seems that the RDS for its decomposition is that shown in **3.24**. Amongst other evidence, this was the

$$n\text{-}B_9H_{15} \rightleftharpoons B_8H_{12} + (BH_3) \qquad \mathbf{3.24}$$

conclusion drawn from the results of its reaction with excess $^{10}B_2H_6$ at room temperature for one day[34], in which the ^{10}B distribution in the products was identical to that expected from the reaction of $^{10}B_2H_6$ and B_8H_{12}. Also the exchange of ^{10}B with the starting n-B_9H_{15} was faster than the rate of the reaction so that **3.24** is represented as an equilibrium.

Iso, i-, B_9H_{15} decomposes above -30°C [50] and, from its quantitative reaction with excess MeCN to give $B_9H_{13}\cdot$MeCN, hydrogen elimination 3.25 is thought to be the RDS. The major

$$i\text{-}B_9H_{15} \longrightarrow (B_9H_{13}) + H_2 \qquad 3.25$$

products from this decomposition are B_8H_{12} and $B_{10}H_{14}$ in roughly equal proportions, plus the fused cage species $B_{16}H_{22}$. The yield of the latter rises at the expense of the former pair when the rate of the reaction is low and thus Dobson, Keller, and Schaeffer[50] proposed 3.26 and 3.27 to account for this

$$i\text{-}B_9H_{15} + (B_9H_{13}) \longrightarrow n\text{-}B_{18}H_{22} + 3\ H_2 \qquad 3.26$$

$$2(B_9H_{13}) \longrightarrow B_8H_{12} + B_{10}H_{14} \qquad 3.27$$

observation. Under the conditions of most of the reactions discussed in this chapter the concentration of i-B_9H_{15} will be so low that 3.26 and 3.27 are negligible. In the reaction of i-B_9H_{15} with excess B_2H_6 at -30°C a 36% conversion of B_9H_{15} to $B_{10}H_{14}$ was achieved[34] (far higher than in i-B_9H_{15} decomposition) and this indicated that reaction 3.28 had occurred.

$$(B_9H_{13}) + \tfrac{1}{2}\ B_2H_6 \longrightarrow (B_{10}H_{16}) \longrightarrow B_{10}H_{14} + H_2 \qquad 3.28$$

3.3.10 Decaborane-(14)

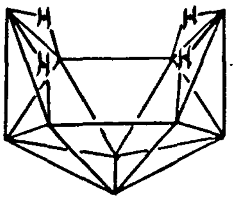


Fig. 3.16 $B_{10}H_{14}$

Whilst this compound is often regarded as a stable end product it should be noted that it does in fact react with diborane to yield a polymeric hydride[51] made up of a 1:1 molar ratio of the starting materials, 3.29. Since this polymer decomposes by further

$$n\ B_{10}H_{14} + n\ B_2H_6 \longrightarrow (B_{12}H_{12})_n + 4n\ H_2 \qquad 3.29$$

hydrogen evolution the above equation's stoichiometry was assigned by an extrapolation of hydrogen evolved to zero time, but the rather crude procedure used also allowed room for loss of 3 or 5 molecules of hydrogen per B_{12} formula weight. It was also proposed that this involatile hydride might consist of icosahedral B_{12} units since no bridging hydrogen bands could be identified in its infra red spectrum - taken from a film deposited on NaCl plates from B_5H_9 solution.

3.4 Conclusion

In this chapter a systematic analysis of borane interconversion reactions and their mechanisms has been conducted which has provided the overall patterns evident in *scheme 1*. Also, it has been observed that B_2H_6 and the arachno boranes probably react with Lewis acid species by initial formation of a bridge hydrogen bond from a BH_2 group. This has led to the prediction that B_6H_{12} is generated by the reaction of B_5H_{11} and $\{B_3H_7\}$ in borane pyrolysis and such a reaction could be tested by the addition of BF_3 to a mixture of B_5H_{11} and $B_3H_7\cdot THF$. Furthermore, it is suggested that the reactions of B_2H_6 and the arachno boranes with the intermediate $\{BH_3\}$, $\{B_3H_7\}$ and $\{B_4H_8\}$ could and should all be similarly tested. This would have the purpose of showing, firstly, that the combinations known in the gas phase behave similarly under mild conditions and, secondly, seeing if any new coupled cage species might be generated, particularly with B_5H_{11} and B_6H_{12}. Such reactions could provide the presently unknown intermediates in the path to $B_{10}H_{14}$ and a similar approach has already proved valid with B_6H_{10}.

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53. s= number of $B-H_\mu-B$ links
    t= number of central BBB three center bonds (the open BBB is no longer considered important in the topological formalism of transient boronhydrides[30a])
    y= number of B-B two center bonds
    x= number of BH_2 fragments (for BH_3 x = 2)

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Chapter 4. Borane Anion Interconversions

4.1 Introduction

It has been shown in chapter 3 that there are several possible systematic routes to the higher polyboron cages that could be developed from the inter-reactions of the neutral boron hydrides. However, because of the lower boranes' volatility, toxicity and dangerous flamability on contact with the air these may not be practically useful, especially on a large scale. For this reason this chapter is concerned with the interconversion and cage-growth reactions of the anionic boron hydrides which are necessarily solids and thus easier to handle if stable at room temperature.

In section 4.2 of this chapter the pyrolysis of tetraalkylammonium borohydrides, $[R_4N][BH_4]$, is examined in a chronological review of the literature to date. This is a highly efficient and very simple reacton for obtaining the anions $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ in almost quantitative yields from a monoboron starting material. It is already used as a convenient preparation of $B_{10}H_{12}\cdot 2SMe_2$ which reacts with acetylenes to give ortho-carboranes directly. It would be extremely valuable if this, or a related pyrolysis, could be manipulated under more controlled conditions to relinquish the smaller nido and arachno anions; these probably occur as transient intermediates at the temperature of this reaction but are stable at room temperature.

In section 4.3 the pyrolyses and interconversions, especially by reaction with B_2H_6, of most of the anionic single cage boron hydrides are critically reviewed. The aim here is the same as in chapter 3, section 3.3 for the neutral boranes, where patterns of reactivity and predictions of reaction pathways are sought to help in the construction of directed synthetic strategies. An added significance here is that during this project $[B_{10}H_{10}]^{2-}$,

$[B_{12}H_{12}]^{2-}$, possibly $[B_9H_{14}]^-$ and several other probably anionic species were observed for the first time as products from the acidic hydrolysis of MgB_2. If this reaction can be controlled to give predominantly boron hydrides it might become an important source of these salts in the future.

4.2 Discussion of the Pyrolysis of Tetraalkylammonium Borohydrides

Nowadays cation exchange[3,5,6] is the method of choice for $[R_4N][BH_4]$ preparation from alkali metal borohydrides, although metathesis can also be used effectively[10]. The pyrolysis of $[R_4N][BH_4]$ (R=Me, Et) was first studied in detail by Makhlouf, Hough and Hefferan[1] where the salts were heated in a steel autoclave at 185°C for 16 hours. They claimed an almost quantitative conversion of $[Et_4N][BH_4]$ to the closo polyhedral anions $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ (in yields of $\leq 94\%$ and 6% respectively) and accounted for the formation of $[B_{10}H_{10}]^{2-}$ by equation **4.1**. However, when $[Me_4N][BH_4]$ was treated identically,

$$10[Et_4N][BH_4] \longrightarrow [Et_4N]_2[B_{10}H_{10}] + 8\ Et_3N + 11\ H_2 + 8\ EtH \tag{4.1}$$

gas evolution had ceased after only one hour and Me_3NBH_3 was the major product with just traces of B_{10}, B_{11} and B_{12} cages present. Since $Li[BH_4]$ and $K[BH_4]$ are completely stable at 185°C [2] a reaction of the cation with $[BH_4]^-$ seemed the most reasonable first step in $[Et_4N][BH_4]$ pyrolysis. Consequently, Makhlouf, Hough and Hefferan proposed **4.2**, even though they did not report

$$[R_4N][BH_4] \longrightarrow R_3NBH_3 + RH \tag{4.2}$$

isolating the adduct. Furthermore, they concluded that since no $[Et_3NH]^+$ salts could be detected amongst the products (only $[Et_4N]^+$ salts) then the higher cages resulted from the reaction of Et_3NBH_3 and $[BH_4]^-$ and not just pyrolysis of the adduct alone.

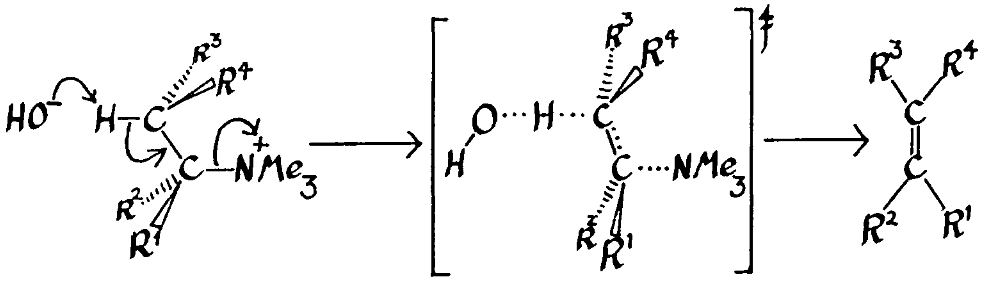
This is almost certainly the case because, apart from a polymeric material, Agafonov, Solnstev and Kuznetsov[3] could identify only 2% $[Et_3NH]_2[B_{12}H_{12}]$ in the residue from Et_3NBH_3 pyrolysis in a similar temperature regime. In other experiments Makhlouf, Hough and Hefferan pyrolysed several $M[B_3H_8]$ ($M= K^+$, Cs^+, $[Me_4N]^+$) and obtained $[BH_4]^-$ as well as those anions expected from $[Et_4N][BH_4]$ pyrolysis (but in differing proportions). From this they inferred that $[B_3H_8]^-$ was an important intermediate and whilst this is in fact so, pyrolysis of $[B_3H_8]^-$ in isolation probably does not completely account for that of $[Et_4N][BH_4]$.

Guillevic et al[4] were the next group to examine the pyrolysis of $[R_4N][BH_4]$ (R=Me,Et) as part of a study to devise an efficient synthesis of $B_{10}H_{12}\cdot 2SEt_2$ from $[BH_4]^-$. They found that pyrolysis of $[Et_4N][BH_4]$ ceased when the autogenous pressure inside an autoclave exceeded 12 atm and that for $[Me_4N][BH_4]$ the reaction halted below 10atm. As a result, open systems instead of autoclaves were recommended. Also, they confirmed earlier reports[13b] that $[B_{10}H_{10}]^{2-}$ and Et_3NBH_3 react giving $[B_{12}H_{12}]^{2-}$ and they used this fact to explain the falling proportion of $[B_{10}H_{10}]^{2-}$ in the products from pyrolyses of longer duration. Furthermore, pyrolysis of $[Me_4N][BH_4]$ in Et_3NBH_3 gave the $[Me_4N]^+$ salts (ie. not $[Et_4N]^+$) of $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$. Me_3N and MeH were the major volatiles isolated, with only traces of Et_3N, so that it seems that there is no thermodynamic reason why $[Me_4N][BH_4]$ should not behave similarly to $[Et_4N][BH_4]$. Makhlouf, Hough and Hefferan thought that this difference might be because **4.2** was much faster for R=Me than for Et so that there was not sufficient time for a reaction of Me_3NBH_3 and $[Me_4N][BH]_4$.

Hill, Johnson and Hosmane[5] studied $[R_4N][BH_4]$ pyrolysis (R_4=Me_4, Et_4, n-$BuMe_3$, s-$BuMe_3$, t-$BuMe_3$) with the same aims as Guillevic et al. Notably they concluded that Et_3NBH_3 did not enter into the cage-growth process. This was because pyrolysis of $[Et_4N][BH_4]$ under dynamic vacuum (10^{-4}mmHg) still gave 20·4% $[B_{10}H_{10}]^{2-}$ -c.f. 59·8% at 760 mmHg - even though large quantities of Et_3NBH_3 distilled from the reaction flask and this compound was thought to volatilise too quickly to react. Despite this evidence it is probably an erroneous conclusion, see below.

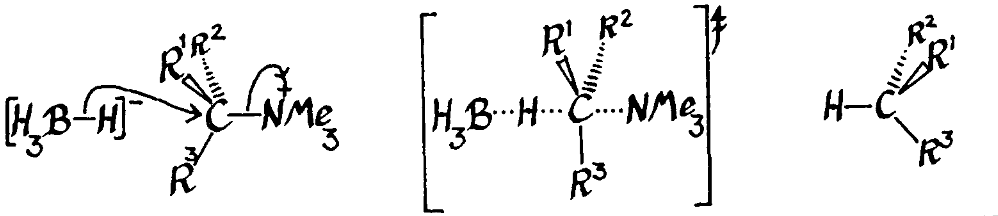
Hill, Johnson and Hosmane consistently obtained lower $[B_{10}H_{10}]^{2-}$ yields than those of Guillevic et al. Also their yields were erratic (the more so the larger the charge of borohydride) but they were always significantly higher in steel rather than glass reactors. An elevated yield could also be achieved by placing metal fragments in a glass reactor. A catalytic effect was ruled out here because the results were independent of the metal's composition. Instead it was thought that the metal conducted heat away from local hot spots in the solid, since the start of the reaction is known to be exothermic, and prevented run away $[B_{12}H_{12}]^{2-}$ production at the expense of $[B_{10}H_{10}]^{2-}$. From the ^{11}B NMR spectrum of the pyrolysate it was tentatively suggested that $[B_9H_9]^{2-}$ and $[B_6H_6]^{2-}$ were present in addition to the $[B_{10}H_{10}]^{2-}$, $[B_{12}H_{12}]^{2-}$ and traces of $[B_{11}H_{14}]^-$ observed by previous authors.

Initial decomposition temperatures were found to rise according to the substituent on the cation in the order $[t\text{-BuNMe}_3]^+ < [s\text{-BuNMe}_3]^+ < [n\text{-BuNMe}_3]^+$. Hill, Johnson and Hosmane related this to the identical order of stability of the quaternary ammonium hydroxides which decompose by the E2 mechanism shown in 4.3a. The



4.3a

$+Me_3N + H_2O$



4.3b

$+Me_3N + \{BH_3\}$

products of **4.3a** are alkene, amine and water but $[R_4N][BH_4]$ gives only the saturated alkane, so that the mechanisms are clearly not the same. Instead an S_N mechanism, something like that in **4.3b**, is proposed here on the grounds that $[BH_4]^-$ reacts primarily as a hydride donor. This mechanism could be simply tested by looking for inversion in the alkane derived from a chiral cation, e.g. $[(MeEtPrC^*)NMe_3]^+$; it is however noted that the above order of $[R_4N][BH_4]$ stability rises as the stability of R^+ falls.

Ouassas and Frange[6] employed a different approach to $[Et_4N][BH_4]$ pyrolysis; a mixture of $M[BH_4]$ and excess $[Et_4N]X$ (M=Na, K, X=Cl, Br) were first moistened with a small amount of water and then dried before being heated in suspension in refluxing trans-decalin. The proportions of $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ in the pyrolysate were found to vary with both M and X and it was thought that a different reaction to that in pure $[Et_4N]BH_4]$ pyrolysis might be occuring, perhaps involving $[H_3BOH]^-$ since ^{11}B NMR clearly showed its presence during the hydrolysis of $[BH_4]^-$. However, a new mechanism is not necessarily implied by their results: firstly, the reaction did not start until 180-185°C, as with pure $[Et_4N][BH_4]$; secondly, the varying product ratios were probably just a reflection of the degree of completion of the metathesis reaction. An elevated $[B_{12}H_{12}]^{2-}$ yield might be expected here because $Na[BH_4]$ is known to react quantitatively with a fivefold excess of Et_3NBH_3 to give $[B_{12}H_{12}]^{2-}$ [3,13b] and an excess of $M[BH_4]$ was used in the $[Et_4N]X/M[BH_4]$ reaction. In this respect one notes that, no matter which M or X, the B_{10}/B_{12} ratio obtained was always lower than that from pure $[Et_4][BH_4]$ pyrolysed under the same conditions. Ouassas and Frange further reported that no reaction occurred without prior moistening of the starting material; also no reaction occurred if the metathesis was conducted in alkali or in the presence of Et_3N.

Power and Spalding[7] were the next to study $[Et_4N][BH_4]$ pyrolysis and attempted to test the mechanism for potential B_9 intermediates. They also confirmed that $[Et_4N]_2[[B_{10}H_{10}]$ gave

$[B_{12}H_{12}]^{2-}$ when reacted with an excess of Et_3NBH_3 and expected $[B_9H_9]^{2-}$ to behave similarly. They were surprised to find that $Cs_2[B_9H_9]$ and Et_3NBH_3 did not react and thus it was dismissed as an intermediate. However, this need not be so and the negative result could be interpreted as an effect of the salt's low solubility in Et_3NBH_3; CsCl(aq) has frequently been used to precipitate the B_9 to B_{12} anions from solutions. The possible fates of $[Et_4N][B_9H_{12}]$ and $[Et_4N][B_9H_{14}]$ were tested in their copyrolyses with equimolar quantities of $[Et_4N][BH_4]$. Both these anions were also dismissed as intermediates because the products of the copyrolyses seemed to be the sum of those expected from pyrolysing the two components of the mixtures separately. However, it is felt that this conclusion is not completely convincing and that the arachno and nido B_9 species should also have been copyrolysed with Et_3N and with Et_3NBH_3. This is because both the adduct and free base can be produced in quite high concentrations during $[Et_4N][BH_4]$ pyrolysis whilst, if either B_9 species really is an intermediate, it is present in very low concentrations, ie. it forms in a large excess of Et_3N and Et_3NBH_3 with which it might react. However, in the copyrolyses of Power and Spalding the concentration of either B_9 species was necessarily far higher than those of both nitrogenous compounds and so an important reaction may have gone unnoticed.

The study of Colombier, Atchekzai and Mongeot[6] was the first to note how the concentrations of the different products, determined by ^{11}B NMR, varied with time when pyrolysing a suspension of $[Et_4N][BH_4]$ in a mixture of refluxing decane and dodecane at 185°C. Their results were highly reproducible, due to the even heating of the entire borohydride charge, and, unlike previous studies where some $[Et_4N][BH_4]$ remained at the end of the experiment, they achieved quantitative conversion of the $[BH_4]^-$ into higher cages. This was ascribed to continuous removal of Et_3N by distillation from their apparatus. This opinion was confirmed by a preliminary experiment in this laboratory in which $[Et_4N][BH_4]$ was pyrolysed at 185·5°C for 16 hrs in a steel autoclave with a fivefold excess of Et_3N; Et_3NBH_3 was the only major species recovered with a trace of $[B_{12}H_{12}]^{2-}$.

The most important finding of Colombier, Atchekzai and Mongeot was that after two hours as much as 25% of the starting boron could be present as $[B_3H_8]^-$ but that after 12 hrs it was completely consumed. This confirmed the earlier supposition of Makhlouf, Hough and Hefferan that $[B_3H_8]^-$ was indeed an intermediate. Copyrolysing a 1:1 mixture of $[Et_4N][BH_4]$ and Et_3NBH_3 gave an almost identical product distribution to that from $[Et_4N][BH_4]$ alone and, moreover, the reaction was completed in about half the time. After 15 mins >36% of the starting boron was present as $[B_3H_8]^-$ and at the end of the reaction 97% of the boron from both the salt and adduct was incorporated into higher polyhedral anions. This, combined with evidence from other experiments, demonstrated that high Et_3NBH_3 concentrations produced high $[B_3H_8]^-$ concentrations. Thus, including the earlier deduction of Makhlouf, Hough and Hefferan that Et_3NBH_3 and $[Et_4N][BH_4]$ should react, they proposed that **4.4a** was the second

$$[BH_4]^- + Et_3NBH_3 \rightleftharpoons [B_2H_7]^- + Et_3N \qquad \textbf{4.4a}$$

step of the reaction. It was thought that continuous removal of Et_3N encouraged this step and that $[B_2H_7]^-$ then reacted further to give $[B_3H_8]^-$ (See section 4.3.2, **4.5** for a perhaps more tenable explanation of this next step than that proposed in ref. 8).

Having established $[B_3H_8]^-$ as an intermediate, Columbier, Atchekzai and Mongeot next conducted some experiments on its pyrolysis. Pyrolysis of $[B_3H_8]^-$ salts with simple main group metal cations (see section 4.3.3) produces significant quantities of $M[BH_4]$. Thus it should be expected that pyrolysis of $[Et_4N][B_3H_8]$ at ≥185°C should be substantially different if Et_3N or Et_3NBH_3 can react with $[B_3H_8]^-$ or its direct decomposition products. Indeed, ^{11}B NMR of the pyrolysate from a reaction at 185°C under atmospheric pressure showed a yield of 47% $[B_9H_9]^{2-}$

(far higher than that from $M[B_3H_8]$) as well as 3·2% Et_3NBH_3; at 10^{-2} mmHg this still gave 41% $[B_9H_9]^{2-}$ with 19% Et_3NBH_3 although the salt was not isolated on either occasion. This fits well with their observation that when $[B_3H_8]^-$ attains its highest concentration in $[Et_4N][BH_4]$ pyrolysis, $[B_9H_9]^{2-}$ is also at a maximum after which time it tails off again. However, copyrolysing $[Et_4N][B_3H_8]$ and Et_3NBH_3 reduced the $[B_9H_9]^{2-}$ yield to only 13% whilst those of $[B_{11}H_{14}]^-$ and $[B_{12}H_{12}]^{2-}$ almost doubled. Although they did not consider it, this could be interpreted as an enhancement of $[B_9H_9]^{2-}$ yield by Et_3N and so copyrolysis of $[Et_4N][B_3H_8]$ and Et_3N should be examined. Et_3NBH_3 may be involved in some steps of $[B_9H_9]^{2-}$ formation but it seems that its role in $[B_9H_9]^{2-}$ destruction is more important.

Finally, Colombier, Atchekzai and Mongeot discussed how the proportions of the other anions, $[B_{10}H_{10}]^{2-}$, $[B_{11}H_{14}]^-$ and $[B_{12}H_{12}]^{2-}$, changed with the degree of completion of $[Et_4N][BH_4]$ pyrolysis. The fraction of $[B_{10}H_{10}]^{2-}$ is at a maximum compared to the other species after about 2 hrs before falling to an intermediate minimum. This coincides with the $[B_9H_9]^{2-}$ maximum and is followed by a second rise in its proportion of the products - perhaps this is due to a reaction of $[B_9H_9]^{2-}$ producing $[B_{10}H_{10}]^{2-}$. The fraction of $[B_{11}H_{14}]^-$ in the pyrolysate does not pass through a maximum but instead rises slowly through the first 5 hrs of the reaction and thereafter remains constant. It was found that $[B_{12}H_{12}]^{2-}$ was the predominant anion early in the reaction and this was associated with high $[BH_4]^-$ and Et_3NBH_3 concentrations. The final yield of $[B_{12}H_{12}]^{2-}$ from a pyrolysis of the dry salt run at 185°C and atmospheric pressure for 24 hrs was 46·6%, but when this was repeated at 30 mmHg (when Et_3N is expelled but Et_3NBH_3 is retained) the yield fell to only 15·2%. Thus it seems that the amine could encourage $[B_{12}H_{12}]^{2-}$ formation and consequently could be responsible for the high initial $[B_{12}H_{12}]^{2-}$ fraction. This is because at the start of the reaction in refluxing hydrocarbon the concentration of $[Et_4N][BH_4]$ (and therefore of Et_3N) will be high although the Et_3N will distil away fairly rapidly thereafter.

Most recently Mongeot et al[9] have studied $[Et_4N][BH_4]$ pyrolysis but were mainly concerned with obtaining $[Et_4N]_2[B_{10}H_{10}]$, free of B_9 and B_{11} species, so that it could be used directly to form $B_{10}H_{12}\cdot 2SEt_2$ [5] and then carboranes. They stated (unfortunately without experimental notes) that $[B_9H_9]^{2-}$ reacted quite rapidly with Et_3NBH_3 to give $[B_{10}H_{10}]^{2-}$ and, contrary to previous authors' [5,13b] opinions, that $[B_{11}H_{14}]^-$ did not react with Et_3NBH_3 - this last point is discussed further in section 4.3.13, p.114 .

4.3 Pyrolysis and Interconversion Reactions of the Anionic Boranes

4.3.1 Introduction

An attempt is made here to construct an overview of the literature on anionic boron hydrides similar to that for the neutral boranes presented in chapter 3. However, because of the far larger number of known single cage anions and the fact that they have not been studied in as much detail as the individual boranes, it is not possible to obtain such a refined picture of their types of reactivity. In particular, no attempt is made to tie down any structure-reactivity relationships except that two qualitative rules are followed on occasions when mechanisms are considered:-

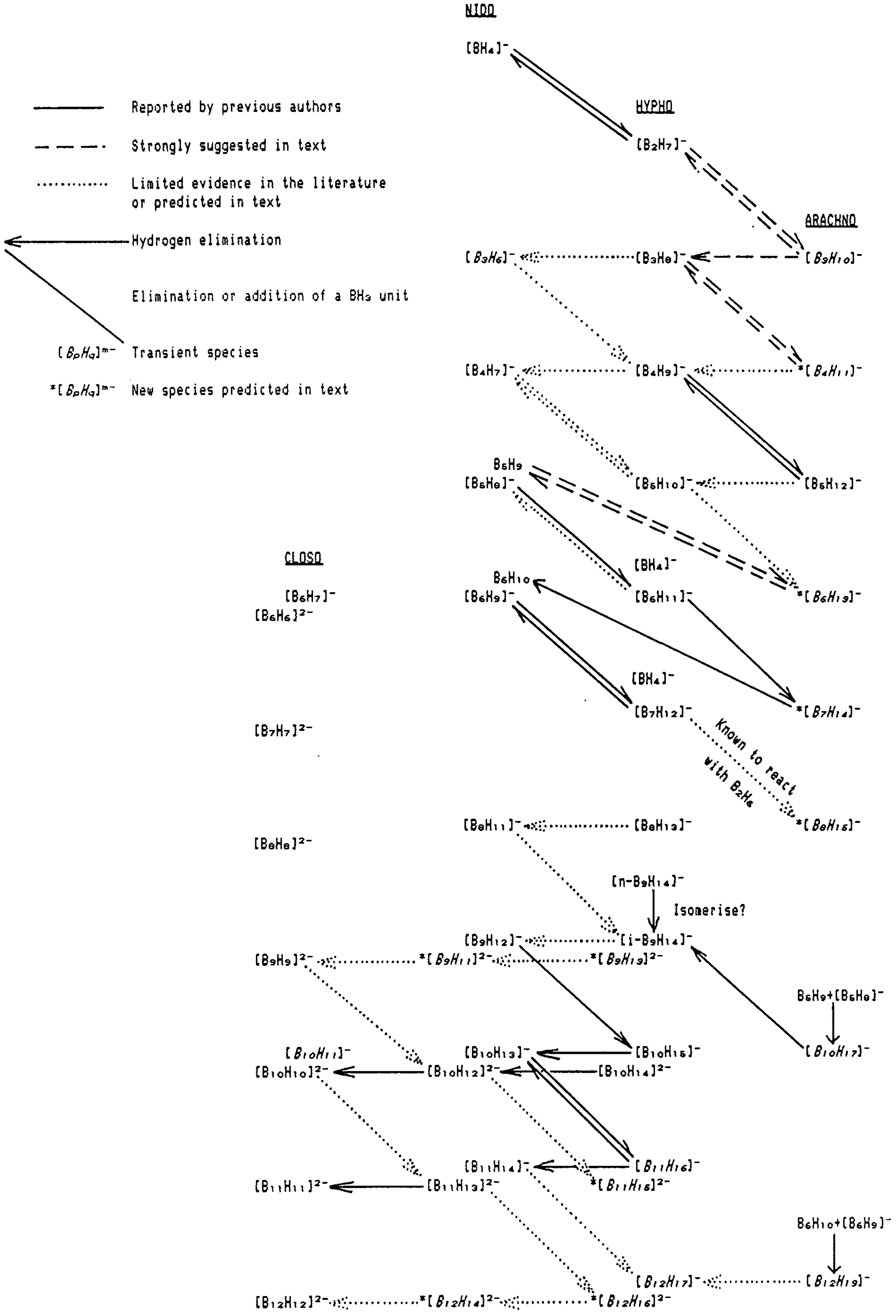
a) The three very well characterised nido anions, $[B_5H_8]^-$, $[B_6H_9]^-$ and $[B_{10}H_{13}]^-$ are all isostructural to their neutral counterparts except that they lack one bridging proton. This creates a direct B-B bond in the open face of the skeleton which in all three cases is known to act as a Lewis base (c.f. B_6H_{10}). This site is here thought to cleave B_2H_6 and ligate a BH_3 unit, like other Lewis bases, as the first step in cage-growth reactions. Because of this it is suspected that the nido B_8, B_9 and B_{11} systems might be able to engage in cage-growth by a similar mechanism.

b) The B_2 to B_6 arachno anions are isoelectronic and isostructural to known adducts of the nido boranes and so could be regarded as hydride adducts. Consequently the most hydridic, and therefore basic, hydrogen is considered to be that which would be replaced by another ligand in an adduct. Thus, extending this to the whole series, the cage-growth reactions of the arachno anions with B_2H_6 are believed to begin by formation of an adduct with $\{BH_3\}$ where this fragment is linked to the anion by a hydrogen bridge bond to the hydridic hydrogen.

Scheme 4.1 shows most of the known anions and the pathways thought to link them. The dotted arrows, which are all discussed under the heading of the appropriate anion, are the weak links in the scheme and of three major types: first, for some there is limited evidence in the literature; second, (especially in the case of hydrogen elimination from the arachno anions) the neutral counterparts of these species are already known to undergo a suggested reaction so that if the anion is isostructural (and thus electronically related) the same reaction should be possible; third, a neighbouring homologue of one more or one less boron atom is known to undergo a specific type of reaction so that the species in question may be expected to react similarly. The last point is usually applied to $\{BH_3\}$ addition but it is the least reliable argument since it presupposes that each series of anions possesses a structure-reactivity relationship - perhaps like those outlined in a) and b) above. There is, as yet, no pronounced pattern of reactivity in the anions, however it is expected that a stepwise cage-growth pattern will emerge here, as with the neutral boranes, involving alternating $\{BH_3\}$ addition and hydrogen loss.

The anions are discussed below in order of rising number of boron atoms in the cage. The references above each heading direct

Scheme 4.1 Patterns of Cage-growth Amongst the Anionic Boranes



the reader to each species' preparation, ^{11}B and ^{1}H NMR spectra and structure when available.

4.3.2 Heptahydrodiborate (1-)[11]

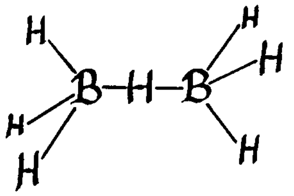


Fig. 4.1 $[B_2H_7]^-$

The formation and decomposition of this anion can be regarded as being dependant upon equilibrium **4.4** where conditions force

$$[B_2H_7]^- \rightleftharpoons [BH_4]^- + \{BH_3\} \qquad \mathbf{4.4}$$

it in either direction. For instance, in the presence of Lewis bases equilibrium **4.4b** is observed: Et_3N cleaves $[B_2H_7]^-$

$$[BH_4]^- + L\cdot BH_3 \rightleftharpoons [B_2H_7]^- + L \qquad \mathbf{4.4b}$$

completely[11a,b]; the equilibrum constant for the reaction of Me_2S with $[Ph_3PMe][B_2H_7]$ in dichloromethane (DCM) at 21°C is 7·84[11b]. Also it is noted that whilst the $[PH_3PMe]^+$ salts of $[B_2H_7]^-$ + $[^{10}BH_4]^-$ do not exchange boron in DCM[11b] they do in diglyme[11d]. Thus, although a THF solution of $[PH_3PMe][B_2H_7]$ shows no evidences of boron exchange on the ^{11}B NMR time scale, equilibrium **4.4b** most probably also applies to ethers.

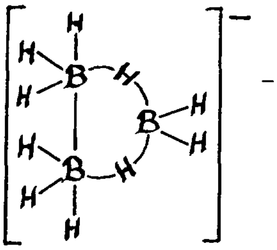
At 100°C in vacuo $[PH_3PMe][B_2H_7]$ decomposes according to **4.4c** but in a sealed tube the stoichiometry of the reaction is that in **4.4d**. Also, $[BH_4]^-$ and B_2H_6 will react at ~0°C to form $[B_2H_7]^-$

$$[B_2H_7]^- \xrightarrow{\text{100°C, in vacuo}} [BH_4]^- + \tfrac{1}{2}\,B_2H_6 \qquad \mathbf{4.4c}$$

$$2\,[B_2H_7]^- \xrightarrow{\text{100°C, sealed tube}} [B_3H_8]^- + [BH_4]^- + H_2 \qquad \mathbf{4.4d}$$

but at temperatures, usually above ambient, the same reactants give $[B_3H_8]^-$. The above reactions suggest that $[B_3H_8]^-$ formation is the result of (BH_3) attack upon $[B_2H_7]^-$. Indeed Levichev and Titov[15a] report observing $[B_2H_7]^-$ as a transient species during the slow formation of the magnesium and strontium triborohydrides from their respective borohydrides and B_2H_6. As a result, $[B_3H_8]^-$ formation is here suggested to occur via the mechanism in **4.5**;

$[B_2H_7]^- + \frac{1}{2} B_2H_6$



$-H_2$

$[B_3H_8]^-$ **4.5**

this mechanism was also proposed by Dunbar[12] to account for the appearance of $[B_3H_8]^-$ under the more rarefied conditions of negative ion cyclotron spectroscopy of B_2H_6. The alternative, where $[B_2H_7]^-$ initially eliminates hydrogen to the almost unknown $[B_2H_5]^-$ [12], is dismissed because $[B_2H_5]^-$ or its decomposition products (probably $[B_3H_8]^-$ by BH_3 abstraction from the remaining $[B_2H_7]^-$) should then have been observed in **4.4c**. If **4.5** is correct, the transient $[B_3H_{10}]^-$ intermediate will be first in the homologous series of hypho anions.

4.3.3 Octahydrotriborate(1-) (Triborohydride)[13]

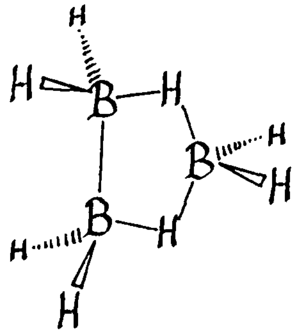


Fig. 4.2 $[B_3H_8]^-$

Rozenberg et al[14] recently studied the slow thermolysis of unsolvated $Na[B_3H_8]$ and found that the reaction stoichiometry closely fitted **4.6** with the production of both B_5H_9 and H_2

$$5\ Na[B_3H_8] \xrightarrow{80\text{-}100^\circ C} 5\ Na[BH_4] + 2\ B_5H_9 + H_2 \qquad \textbf{4.6}$$

following first order rate laws. They noted that the observed activation energy was close to an estimate of the dissociation energy of B_2H_6 into two $\{BH_3\}$ units (they associated this mainly with the cleavage of two B-H_μ bonds) and suggested that the RDS might be the fragmentation of $[B_3H_8]^-$ into $[BH_4]^-$ and $\{B_2H_4\}$. The latter species was thought to undergo a self-reaction to form B_5H_9 but it is here felt more likely that $\{B_2H_4\}$ would react with $[B_3H_8]^-$ rather than with itself. If, as suggested by the stoichiometry, $[B_5H_{12}]^-$ was the second intermediate the fact that it too decomposes giving B_5H_9 as the only volatile borane product would be consistent with $Na[B_3H_8]$ pyrolysis, **4.7a**. However,

$$2[B_3H_8]^- \longrightarrow [B_3H_8]^- + \{B_2H_4\} + [BH_4]^- \longrightarrow [B_5H_{12}]^- + [BH_4]^- \quad \textbf{4.7a}$$

$$2[B_3H_8]^- \longrightarrow [B_3H_8]^- + [B_3H_6]^- + H_2 \longrightarrow [B_5H_{10}]^- + [BH_4]^- + H_2 \quad \textbf{4.7b}$$

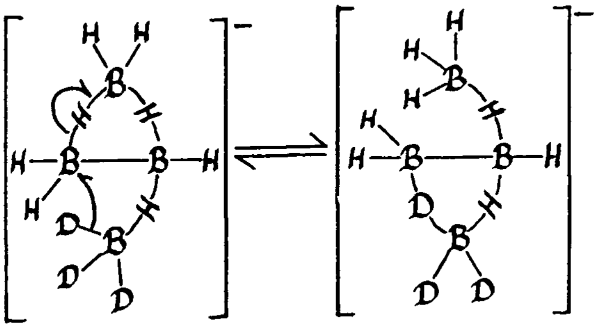
hydrogen elimination to produce the, as yet hypothetical, nido $[B_3H_6]^-$ might also be considered as another potential reaction for the RDS of this decomposition. The neutral counterpart of $[B_3H_8]^-$, $\{B_3H_9\}$, is known to behave in this manner (see 3.3.2). Thus the second step in **4.7b** seems as likely as that in **4.7a** because B_5H_9 is also the only volatile borane produced in $[B_5H_{10}]^-$ decomposition.

The decompositions of $K[B_3H_8]$ [15a] at 130°C and that of $Na[B_3H_8]\cdot$dioxan[15b] were each found to be very similar to that of $Na[B_3H_8]$, except that the B_5H_9 and $[BH_4]^-$ yields were both slightly reduced from the ideal stoichiometry in **4.6** in favour of a small amount of $[B_{12}H_{12}]^{2-}$ and a trace of B_2H_6. This was thought to be the result of a secondary reaction between B_5H_9 and $[BH_4]^-$ (see 4.3.6, p.99) although the primary reaction was still thought to be represented by **4.6**. The pyrolyses[15a] of $Mg[B_3H_8]_2\cdot 2$ diglyme, $Sr[B_5H_8]_2\cdot 2$ diglyme and $Ca[BH_4][B_3H_8]\cdot 2$ diglyme all gave results related to those above except that even more $[B_{12}H_{12}]^{2-}$ and less B_5H_9 were produced in each case.

The alkali metal triborohydrides have also been pyrolysed under a variety of other conditions where, despite a very different selection of products to those above, the initial reaction steps and intermediates must surely have been similar. In high boiling point, polyether solvents $[B_{12}H_{12}]^{2-}$ has often been recorded to be the main product[13b,15a,16] whilst Klanberg and Muetterties[17] have isolated up to 27% $[B_9H_9]^{2-}$ from quite rapid pyrolysis of these salts at high temperatures. $[B_{11}H_{14}]^-$ and $[B_{10}H_{10}]^{2-}$ are also claimed to have been major products from the pyrolyses of $Cs[B_3H_8]$ and $K[B_3H_8]$ at 185°C[1] respectively. Agafonov et al[18a] have pyrolysed $Na[B_3H_8]\cdot 3$ dioxan in a hydrocarbon suspension at 195°C to yield 14% $[B_6H_6]^{2-}$. This indicates that the production of 5-10% $[B_6H_6]^{2-}$ from the reaction of B_2H_6 and excess $Na[BH_4]$ in refluxing diglyme[18b] probably also proceeds via $[B_3H_8]^-$.

In this chapter it has been noted that $[B_2H_7]^-$ probably reacts with B_2H_6 to form $[B_3H_8]^-$ via $\{BH_3\}$ abstraction to give an intermediate $[B_3H_{10}]^-$. Also it is established that $[B_4H_9]^-$ reacts with B_2H_6 to give $[B_6H_{12}]^-$ so that one would expect $[B_3H_8]^-$ to perform a similar reaction with B_2H_6 giving $[B_4H_{11}]^-$. Whilst no such hydride has been isolated one can postulate its transient existence from the hydrogen exchange of $[B_3H_8]^-$ and $[BD_4]$ at -45°C which will only occur when B_2H_6 is added to the system (ref. 13g. footnote 7). Under these conditions B_2H_6 and $[BD_4]^-$ will be in equilibrium with $[B_2H_7]^-$ (4.4) so that partially deuterated $B_2H_{6-n}D_n$ will be generated and this seems to be acting as a deuterium transfer agent between the two anions. Equilibrium 4.8a is proposed to account for this hydrogen exchange where the

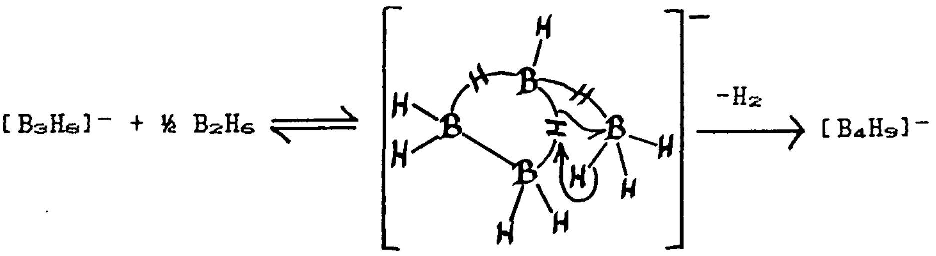
$$[B_3H_8]^- + B_2H_5D \xrightleftharpoons{-\{BH_3\}}$$



$$\xrightleftharpoons{\{BH_3\}} [B_3H_7D]^- + B_2H_6 \qquad 4.8a$$

structure of $[B_4H_{11}]^-$ is chosen to parallel that which can be inferred for its isoelectronic analogue $B_4H_{10}\cdot L$, the ligand L being replaced by D^-. The first identified product of Lewis base attack upon B_4H_{10} is $[H_2BL_2][B_3H_8]$ [19] which can sometimes rearrange to $BH_3\cdot L$ + $B_3H_7\cdot L$, depending upon the ligand, so that initial wingtip, 2,4-, attack is prefered over 1,3- ligation. This structural parity is comparable to that known to exist between $[B_2H_7]^-$ and LBH_2-H_μ-BH_3 (L=NH3 [20], $MeNH_2$ [20], Me_3N [20b], Et_2O [11d]).

At higher temperatures $[B_3H_8]^-$ and B_2H_6 react to form a selection of higher hydride anions[13b] and in **4.8b** it is shown how


$[B_3H_8]^-$ + ½ B_2H_6 ⇌ $[\ ]^-$ $\xrightarrow{-H_2}$ $[B_4H_9]^-$ **4.8b**

$[B_4H_{11}]^-$ might be able to decompose by hydrogen elimination to commence cage-growth. A test of whether or not $[B_4H_{11}]^-$ exists and eliminates hydrogen rapidly would be to produce $[B_4H_9]^-$ from the reaction of MD (suggest KD c.f. KH + B_6H_{11} [33]), or perhaps $Li[DBEt_3]$, with B_4H_{10} where an H/D ratio >1 in the product gas would indicate the transient formation of $[B_4H_{11}]^-$. Possibly related to **4.8b** is protonation of $K[B_4H_9\cdot PMe_3]$ [21] which presumably proceeds via $\{B_4H_{10}\cdot PMe_3\}$ (this being isoelectronic to $[B_4H_{11}]^-$). This gives 30% hydrogen elimination to $B_4H_8\cdot PMe_3$ although 70% decomposes to the cleavage products BH_3PMe_3 and $B_3H_7\cdot L$.

4.3.4 Heptahydrotetraborate(1-)[22] and Nonahydrotetraborate(1-)[13f,23]

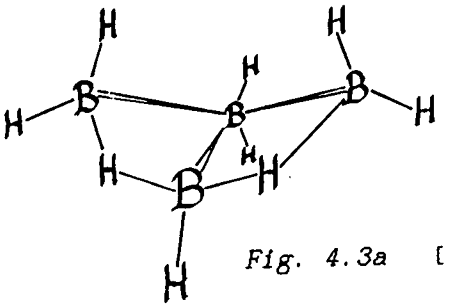


Fig. 4.3a $[B_4H_9]^-$

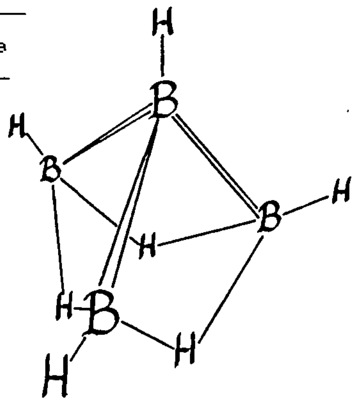


Fig. 4.3b $[B_4H_7]^-$

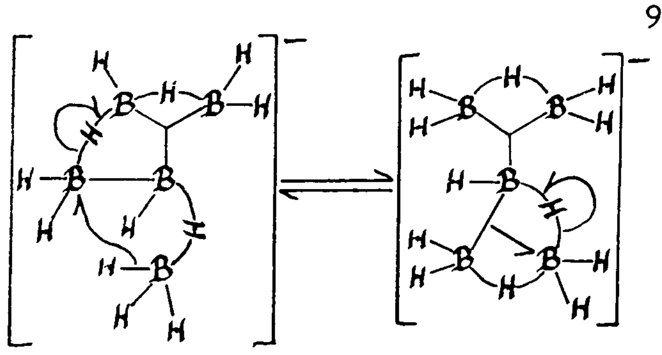
The only salt of the nido B_4 species so far reported in the literature is $[H_2B(NH_3)_2][B_4H_7]$, prepared by the action of an at least two fold excess of ammonia on B_5H_9. It is stable indefinitely <0°C but, after a short induction period, at 25°C it decomposes violently producing, amongst other things, aminoboranes so that an interaction of the cation and anion may be responsible for initiating the reaction. On comparing this anion with the other nido anions, it is possible that replacement of $[H_2B(NH_3)_2]^+$ by another less reactive cation, such as alkali metal or tetraalkylammonium, might confer greater stability on $[B_4H_7]^-$ than it at first appears to have. This is also suggested by its molecular symmetry which is similar to that of highly stable B_5H_9.

There has been little study of the chemistry of $[B_4H_7]^-$ and it is not known whether or not it will react with other boranes. However, since the other well studied nido anions $[B_5H_8]^-$, $[B_6H_9]^-$ $[B_9H_{12}]^-$ and $[B_{10}H_{13}]^-$ will all abstract a BH_3 fragment from B_2H_6, one suspects that $[B_4H_7]^-$ will react likewise giving $[B_5H_{10}]^-$. Such a reaction is potentially useful for producing ^{10}B base labled B_5H_9 if one can abstract hydride from $[B_5H_{10}]^-$; $[Ph_3C][BF_4]$ is suggested for such hydride abstractions since it will react this way with $B_5H_9 \cdot PMe_3$, isoelectronic to $[B_5H_{10}]^-$, but not with B_5H_9 [22c].

The Na^+, K^+, $[Me_4N]^+$ and $[Ph_3PMe]^+$ salts of $[B_4H_9]^-$ are stable for short periods at room temperature but the lithium salt decomposes above -63°C and they all break down giving hydrogen as the only volatile product. The identity of the solid residue is not known but one interesting possibility is that it contains some $[B_4H_7]^-$ since, as noted in chapter 3, B_4H_{10} hydrogen eliminates to give $\{B_4H_8\}$ and the above anions are their respective conjugate bases.

$[B_4H_9]^-$ reacts with B_2H_6 [33] according to **4.9**. The suggested mechanism assumes that $[B_4H_9]^-$ can be regarded as a hydride adduct of $\{B_4H_8\}$ and that the hydrogen atom derived from the inserted

$[B_4H_9]^- + ½\ B_2H_6 \rightleftharpoons$



$\rightleftharpoons [B_5H_{12}]^-$ **4.9**

hydride anion is the most basic site in the molecule, as considered likely in secton 4.3.1. This reaction is reversed when one attempts to desolvate the potassium etherates of $[B_5H_{12}]^-$ by prolonged exposure to dynamic vacuum and so **4.9** is represented as an equilibrium.

4.3.5 Octahydropentaborate(1-) [22b,24,36c]

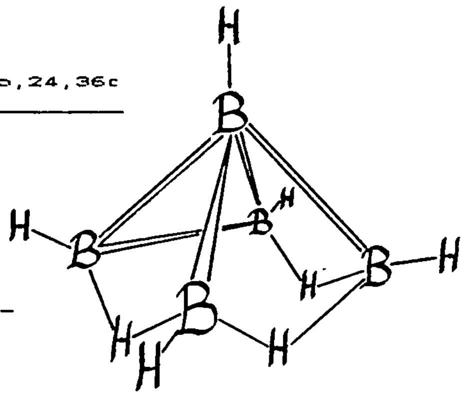
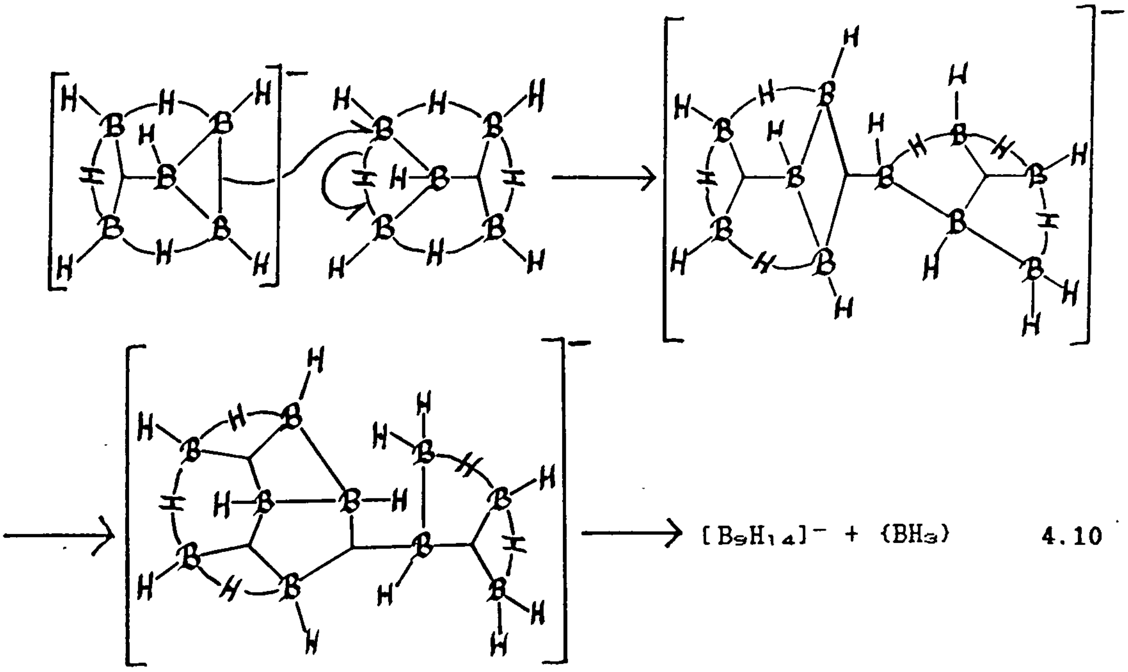


Fig. 4.4 $[B_5H_8]^-$

Although the $[n\text{-}Bu_4N]^+$ salt is more stable than the alkali metal salts of this anion they all decompose similarly - the potassium salt breaks down slowly at 20°C to 27-36% $[B_9H_{14}]^-$, as well as $[B_3H_8]^-$ and $[BH_4]^-$, but whether or not any hydrogen is evolved has not been reported[25a]. This process is much accelerated (then starting at -10°C) by the addition of just 5% B_5H_9 and, because the products are so similar to those from the reaction of $[B_5H_8]^-$ and B_5H_9, it is proposed that the two mechanisms are closely related. Thus the decomposition of an activated complex $[B_{10}H_{16}]^{2-}$ is suggested to be the RDS.

If $[B_5H_8]^-$ is mixed with excess B_5H_9 [26b] at low temperatures an unidentified species is observed in the ^{11}B NMR spectrum which on warming disappears as $[B_9H_{14}]^-$ appears. This is thought to be the intermediate involved in the reaction of NaH or KH with 1·8 equivalents of B_5H_9, optimised to yield >60% $[B_9H_{14}]^-$. The other products in the $B_5H_9/[B_5H_8]^-$ reaction are H_2, $[BH_4]^-$, B_2H_6, $[B_3H_8]^-$ and $[B_{11}H_{14}]^-$ although $[B_6H_{11}]^-$, which does not accumulate, can also be observed during the reaction. As a result these species are all thought to derive from secondary reactions, after **4.10**, since $[B_6H_{11}]^-$ is produced in the reaction of $[B_5H_8]^-$ with {BH_3} and the minor anionic products could all be produced in the decomposition of $[B_6H_{11}]^-$.



$\longrightarrow [B_9H_{14}]^- + \{BH_3\}$ **4.10**

A possible initial structure for $[B_{10}H_{17}]^-$ is shown in **4.10** and is taken to be that of a B_5H_9 mono-adduct. $[B_5H_8]^-$ is well known to act as a Lewis base (c.f. B_6H_{10}, also with one unbridged basal bond) toward such diverse species as B_2H_6 [23a,26a,3] (reaction **4.17**), DCl [24c], Me_2BCl [26b], R_3(Si/Ge/Sn/Pb)Cl [26c] and R_2PCl [26d], where a bridge-substituted derivative of B_5H_9 is the initial product. Because of its likely complexity no mechanism is suggested for the rearrangement of $[B_5H_8{\rightarrow}B_5H_9]^-$ to an isomer that could feasably eject {BH_3}. However, simple arrow-pushing shows that $[B_6H_9{\rightarrow}B_4H_8]^-$ might be one possible transient structure so that the reaction of $[B_6H_9]^-$ and $B_4H_8{\cdot}L$ could well give products similar to the $B_5H_9/[B_5H_8]^-$ reaction. The earlier experiment of Savory and Wallbridge[25a], who reacted a 1:1 mixture of NaH and B_5H_9 to obtain $[B_9H_{14}]^-$, is probably the same reaction.

Comparing the $B_5H_9/[B_5H_8]^-$ reaction to the chemistry of 1:2'-$[B_5H_8]_2$ [27] it can now be inferred that at least two of its reactions proceed via a hypho B_{10} species. 1:2'-$[B_5H_8]_2$ reacts with Me_2S to give 77% $B_9H_{13}\cdot SMe_2$ (isoelectronic to $[B_9H_{14}]^-$) and presumably, $BH_3\cdot SMe_2$. One assumes that B_5H_8-$B_5H_8\cdot SMe_2$ forms initially which, if it can rearrange to a single cage unit, is a hypho B_{10} adduct. 1,2'-$[B_5H_8]_2$ also reacts with Li[$HBEt_3$] in THF (without hydrogen evolution) to give 94% $[B_9H_{14}]^-$ as well as $BH_3\cdot$THF, $Et_3B\cdot$THF and Li[BH_4] (ie. {BH_3} + [$HBEt_3$]$^-$) so that one suspects the same $[B_{10}H_{17}]^-$ as in **4.10** is being generated by rearrangement of 1:2'-$[B_5H_9][B_5H_8]^-$.

4.3.6 Decahydropentaborate(1-)[131,23d,33] and Nonahydropentaborate(2-)[28]

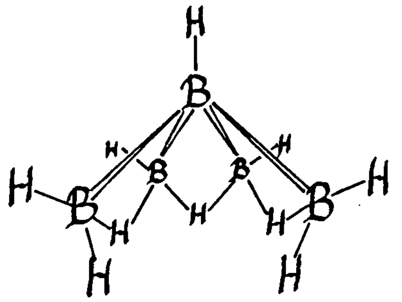


Fig. 4.5a $[B_5H_{10}]^-$

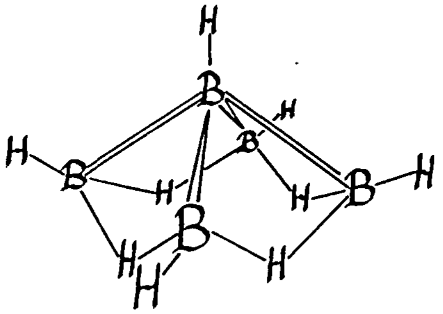


Fig. 4.5b $[B_5H_9]^{2-}$

$[B_5H_9]^{2-}$ has only recently been prepared so that its chemistry has not yet been thoroughly explored. However, its ^{11}B NMR indicates a square pyramidal structure like the nido-B_5 species (only it is thought to be flatter and more open) and it suffers minimal decomposition after one week at room temperature. Protonation with HCl gives 38% B_5H_{11}.

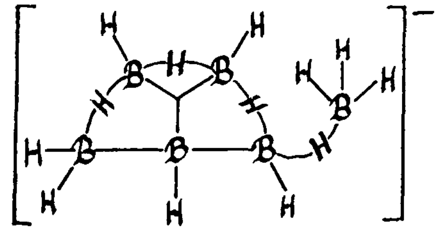
There has been surprisingly little work published on $[B_5H_{10}]^-$ and, although the ^{11}B NMR of this species consists of two doublets in a 4:1 area ratio (like all the other B_5 anions), it is interpreted as the spectrum of a fluxional anion with the stationary structure in *fig. 5a* (Ref. 22c, footnote 7). The lithium salt is stable in Et_2O at 0°C for about a day but attempting to remove the solvent brings about decomposition liberating B_5H_9 and H_2 [13f].

The reaction between $[B_5H_{10}]^-$ and B_2H_6 does not appear to have been attempted yet, however they may be expected to react according to **4.11a** for the reasons set out below:-

$[B_5H_{10}]^- + \frac{1}{2} B_2H_6 \longrightarrow [B_6H_{13}]^-$ **4.11a**

a) In the low temperature reaction of equimolar quantities of B_5H_9 and $Li[BH_4]$ Savory and Wallbridge[29] observed a species at -78°C with the ^{11}B NMR spectrum δ=-13·4 (J=114Hz br.d, 3·9B), -29·1 (br.s, 2B), -60·2 (J=110Hz br.d,1B)ppm which did not return the starting B_5H_9 on pumping. However, warming the solution started a reaction which returned 10% of the initial B_5H_9 (hydrogen atoms were shown to have exchanged with $Li[BD_4]$) and produced 30% $[B_9H_{14}]^-$, 41% B_2H_6, and substantial quantities of $[B_3H_8]^-$. The remaining ~20% starting boron was contained in unidentified species some of which were also observed in the ^{11}B NMR of the products of the B_5H_9/NaH reaction[25b,c]. Thus, although the reaction seems to be closely related to the $B_5H_9/[B_5H_8]^-$ reaction, it appears that the first product of the reaction is a $[BH_4]^-$ adduct of B_5H_9, $[B_5H_9 \cdot BH_4]^-$, **4.11b**.

$B_5H_9 + [BH_4]^- \rightleftharpoons$



4.11b

b) The only reasonably well characterised mono-adduct of B_5H_9 is $B_5H_9 \cdot PMe_3$ [30]. From its NMR spectra it is thought to be isostructural to $[B_5H_{10}]^-$ with the phosphine bound to the apex. However, it is likely that less polarisable ligands, lacking the ability to back-bond through low lying unoccupied orbitals, would attack and bind to the basal atoms of B_5H_9 [34b]. Not so well characterised is the anionic adduct $[B_5H_9\cdot CN]^-$ [31] whose ^{11}B NMR consisting of three broad singlets (δ=-22 (3B, basal), -32 (1B, basal substituted), -59 (1B, apex) ppm) is assigned to a base substituted structure, possibly fluxional, isostructural to $[B_5H_{10}]^-$. Despite the integral values, the ^{11}B NMR spectrum of $[B_5H_9\cdot CN]^-$ is strikingly similar to that of $[B_5H_9\cdot BH_4]^-$ proposed in a). Also, if one assumes that the $R\text{-}H_\mu\text{-}BH_3$ unit is comparable to $[B_2H_7]^-$, for which $\delta\approx$-25ppm [11b], then the singlet in the spectrum of $[B_5H_9\cdot BH_4]^-$ is explained. Hence, $[B_6H_{13}]^-$ is proposed to have the structure shown in **4.11b**. In this thesis the hydrogens of the BH_2 groups of $[B_5H_{10}]^-$ are thought to be the most hydridic so that its reaction with B_2H_6 is likely to proceed via the same $[B_6H_{13}]^-$.

c) B_5H_9 and Li[HBEt$_3$] react in THF to give 23% 2,3,4-$Et_3B_5H_6$ and transient $[B_5H_9\cdot HBEt_3]^-$ is thought to account for the exchange[32]. Such a reversible association would closely parallel the minor route for the fragmentation of isolectronic $B_6H_{12}\cdot PMe_3$ into B_5H_9 and $BH_3\cdot PMe_3$ [30]; the major route is fragmentation into $B_5H_9\cdot PMe_3$ + ½ B_2H_6 which bears a similar relationship to the reverse of **4.11a**. Notably, alkyl exchange fails to occur between $[B_5H_{10}]^-$ and BEt_3 in Me_2O [32]. This seems to cast doubt upon the formation of $[B_5H_9\cdot HBEt_3]^-$ but one notes that the formation of $Me_2O\cdot BEt_3$ could account for this negative result; the reaction of $[n\text{-}Bu_4N][B_5H_{10}]$ with BEt_3 in DCM would be a better test.

Finally, if one accepts the arguments for the existence of $[B_6H_{13}]^-$, this could explain the production of B_5H_9 during $[B_5H_{10}]^-$ decomposition. If the RDS is the cleavage of the anion into $[B_4H_7]^-$ and $\{BH_3\}$ (c.f. B_5H_{11}, chapter 3), then the $\{BH_3\}$ could react with another molecule of $[B_5H_{10}]^-$ to give $[B_6H_{13}]^-$.

4.3.7 Dodecahydropentaborate(1−)[23d,24a,33]

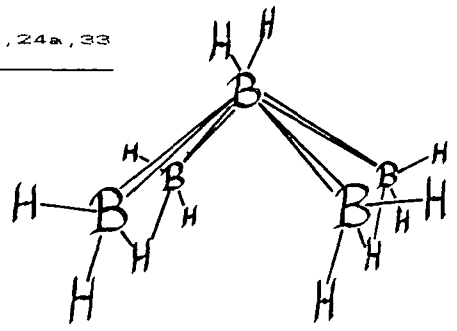
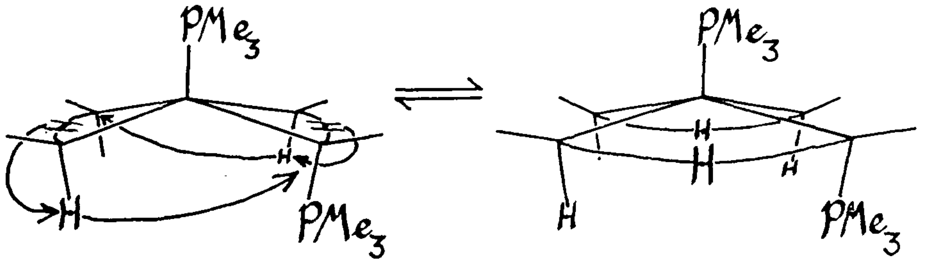
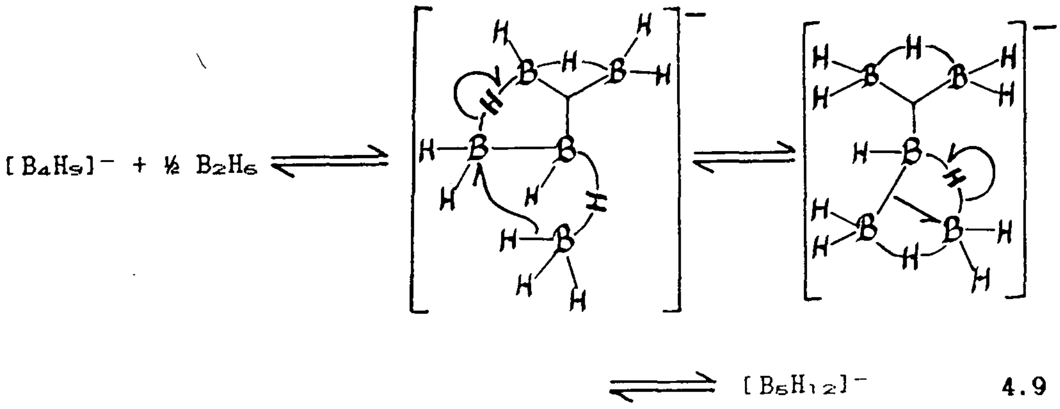


Fig. 4.6a $[B_5H_{12}]^-$

This anion is highly fluxional and all the hydrogen atoms migrate around the molecule so that the ^{11}B NMR spectrum consists of two singlet resonances in the area ratio of 4:1. This fluxionality is probably the product of two seperate mechanisms: a) the isoelectronic $B_5H_9 \cdot 2PMe_3$ [34a], in which one phosphine ligand is permanently attached to the apex, is thought to undergo hydrogen tautomerism according to **4.12**; b) in the anion's substituted derivative $[MeB_5H_{11}]^-$ [23d] the methyl group exchanges between base and apex positions thus requiring a different mechanism, probably involving boron migration as well. The topological structures in **4.9** for the reaction of $[B_4H_9]^-$ with B_2H_6 to give $[B_5H_{12}]^-$ show what this other mechanism of migration might be. **4.9** demonstrates that the accepted stationary structure of $[B_5H_{12}]^-$ could be in equilibrium with an isomer that can be



4.12



$[B_4H_9]^- + \frac{1}{2} B_2H_6 \rightleftharpoons \; \rightleftharpoons \; \rightleftharpoons [B_5H_{12}]^-$

4.9

regarded as a derivative of the arachno B_4 anion. If the pendant monoboron unit is able to migrate between the 1- and 3- positions it is clear that both boron and hydrogen will scramble. In support of this point, the 1- and 3- positions of $[B_4H_9]^-$ are seen to be equivalent on the "B NMR time scale at -20°C [33] and the X-ray structure $B_5H_9\cdot[Me_2NCH_2]_2$ [34b] (see *fig. 6b)*, which is also a hypho B_5 species, can easily be thought of as a $[B_4H_9]^-$ derivative.

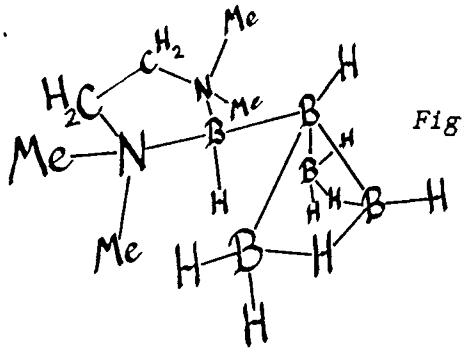


Fig. 4.6b $B_5H_9\cdot[Me_2NCH_2]_2$

Another way of picturing $[B_5H_{12}]^-$ is as a hydride adduct of B_5H_{11} since, along with $[B_5H_{10}]^-$, it is also produced in the reaction of B_5H_{11} with KH[33]. This view point is strengthened by reaction **4.13b** which is thought to be hydride transfer[33].

$$B_5H_{11} + [B_6H_{11}]^- \longrightarrow [B_5H_{12}]^- + B_6H_{10} \qquad \textbf{4.13}$$

$K[B_5H_{12}]$ in etherial solution starts to decompose at -10°C giving an unidentified white solid and B_5H_9. Also it is noted that during the preparation of $[B_5H_{12}]^-$ this anion does not react with excess B_2H_6. Therefore the reverse of **4.9** is probably not the RDS during decomposition because no B_2H_6 is formed. Instead hydrogen elimination, **4.14**, is prefered here as the first step.

$$[B_5H_{12}]^- \longrightarrow [B_5H_{10}]^- + H_2 \qquad \textbf{4.14}$$

This proposal is supported by the protonation of $[B_5H_{12}]^-$ which gives B_5H_{11}. Also, the reaction of B_4H_{10} with $\{BH_3\}$ (see 3.3.3, p. 55) to give B_5H_{11} may be expected to proceed via $\{B_4H_{10}\cdot BH_3\}$ which eliminates H_2. Lastly, the decomposition of $[B_5H_{10}]^-$, the product of **4.14**, itself decomposes giving B_5H_9.

4.3.8 Hexahydrohexaborate(2-)[18b,35], Nonahydrohexaborate(1-)[24c,36] and Undecahydrohexaborate(1-)

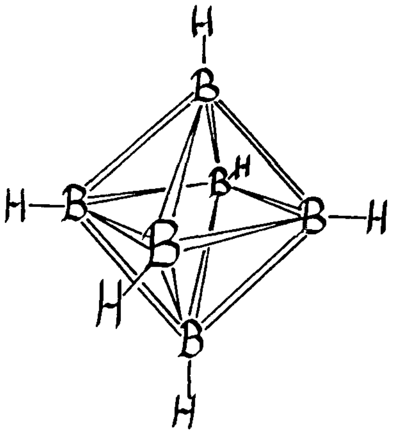


Fig. 4.7a $[B_6H_6]^{2-}$

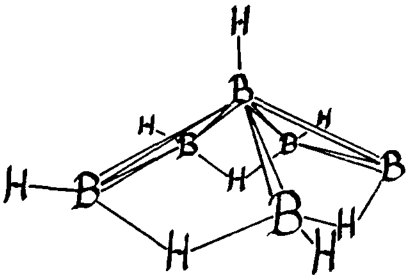


Fig. 4.7b $[B_6H_9]^-$

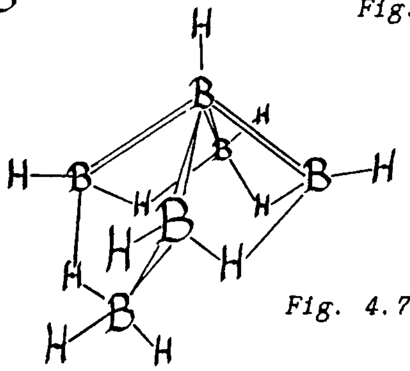


Fig. 4.7c $[B_6H_{11}]^-$

Little is known of the chemistry of $[B_6H_6]^{2-}$ with respect to its reactions with other boron hydrides. However, it is reported[18a] that both $[B_3H_8]^-$ and Et_3NBH_3 convert it to $[B_{12}H_{12}]^{2-}$, although no experimental details are given.

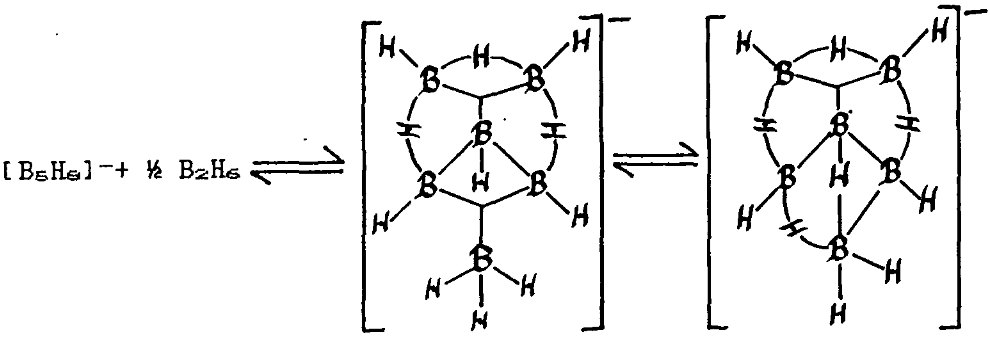
The chemistry of $[B_6H_9]^-$ seems to be rather similar to that of $[B_5H_8]^-$, although not so well explored, because of the Lewis base properties conferred by the unbridged basal B-B bonds. Exactly analogous to the preparation of $[B_6H_{11}]^-$, **4.17**, $[B_6H_9]^-$ reacts with B_2H_6, **4.19**, to give $[B_7H_{12}]^-$; as should be expected, it seems that $[B_6H_9]^-$ is a stronger Lewis base than B_6H_{10}, one manifestation of this being that it will form a complex with BF_3 [36c], $[B_6H_9 \cdot BF_3]^-$, whereas B_6H_{10} will not[37]. Also similar to and simpler than the $B_5H_9/[B_5H_8]^-$ reaction is the recently reported[26b] reaction of $K[B_6H_9]$ and B_6H_{10} to give $[B_{11}H_{14}]^-$ and B_2H_6 (and

$$[B_6H_9]^- + B_6H_{10} \longrightarrow [B_{12}H_{19}]^- \xrightarrow{-H_2} [B_{12}H_{17}]^- \xrightarrow{-(BH_3)} [B_{11}H_{14}]^- \qquad \textbf{4.15}$$

H_2?). The reaction path in **4.15** is prefered here over the alternative where the complex eliminates {BH_3} first giving the transient $[B_{11}H_{16}]^-$. The reason for this is that $[B_{11}H_{16}]^-$ is known to favour fragmentation by {BH_3} ejection (to $[B_{10}H_{13}]^-$) over hydrogen elimination below -0° (see 4.3.11, **4.24**). Lastly, a 0.1M solution of $K[B_6H_9]$, although more stable than its nido B_5 homologue, decomposes slowly over two weeks at room temperature yielding $[B_{11}H_{14}]^-$ and $[BH_4]^-$ as the principal products[26*]. It seems that this is most easily interpreted if, like the $B_6H_{10}/[B_6H_9]^-$ reaction, a bimolecular activated complex is formed that dissociates according to **4.16**.

$$2[B_6H_9]^- \longrightarrow [B_{12}H_{18}]^{2-} \longrightarrow [B_{11}H_{14}]^- + [BH_4]^- \qquad \mathbf{4.16}$$

$[B_6H_{11}]^-$ is prepared by the reaction of $[B_5H_8]^-$ and B_2H_6, **4.17**.



4.17

Although at -125°C the anion is assigned the static structure in *fig.4.7c* by NMR experiments, the spectra at -25°C are indicative of a molecule with mirror plane symmetry so that both representations in **4.17** are probably valid. Whilst the anion is formally arachno it is not isostructural to its neutral counterpart B_6H_{12}. However it does appear to be isostructural with $B_6H_{10}\cdot PPh_3$ [36] so that it is perhaps better thought of as a hydride adduct of B_6H_{10}. This might explain why the anion cannot be produced in the deprotonation of B_6H_{12} with KH[33], although all the B_6H_{12} is consumed. If $[B_6H_{13}]^-$ is formed instead of $[B_6H_{11}]^-$ (c.f. B_5H_{11}+KH gave both $[B_5H_{12}]^-$ and $[B_5H_{10}]^-$), one might expect to see the same products from this reaction as from that between B_5H_9 and $[BH_4]^-$ - unfortunately the products are not reported[33].

$[B_6H_{11}]^-$ reacts slowly with B_2H_6 if excess is used in the anion's preparation where H_2, B_5H_9, B_6H_{10} and $B_{10}H_{14}$ are amongst the final products[33]. Geanangel, Johnson and Shore[39a] have developed the reaction of $Li[B_5H_8]$ with one equivalent of B_2H_6 (presumably via $[B_6H_{11}]^-$) to yield up to 25% B_6H_{10} per mole of $[B_5H_8]^-$ along with 5% $B_{10}H_{14}$ and some $Li[BH_4]$ and B_5H_9. This led Gaines[39b] to propose a hypho B_7 transient hydride which fragmented as shown in **4.18** and this parallels the fragmentation suggested in

$$[B_6H_{11}]^- + \tfrac{1}{2} B_2H_6 \longrightarrow [B_7H_{14}]^- \longrightarrow B_6H_{10} + [BH_4]^- \qquad \textbf{4.18}$$

this chapter for $[B_6H_{13}]^-$, **4.11b**, p. 99 . This reacton might in its turn explain the route of $[B_6H_{11}]^-$ decomposition where after 12-14 hrs at room temperature the $[Ph_3PMe]^+$ and $[n\text{-}Bu_4N]^+$ salts are destroyed giving $[B_6H_9]^-$ as a major product. Whilst it is tempting to imagine that this is due to hydrogen elimination from $[B_6H_{11}]^-$, one notes that B_6H_{12} (see 3.3.7, p. 68) does not eliminate hydrogen and that the neutral species and the next higher homologue, $[B_7H_{12}]^-$, decompose by loss of (BH_3), **4.19**. Consequently the RDS for this reaction may be expected to be the reverse of **4.17**, perhaps followed by **4.18**, to give B_6H_{10} which is deprotonated by another anion present.

4.3.9 B_7 and B_8 Anionic Boron Hydrides

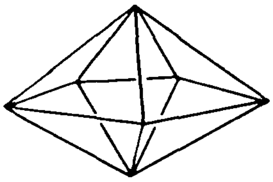


Fig. 4.8a $[B_7H_7]^{2-}$

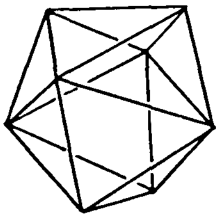


Fig. 4.8b $[B_8H_8]^{2-}$

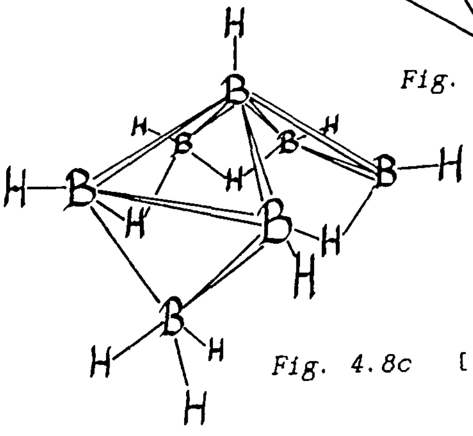


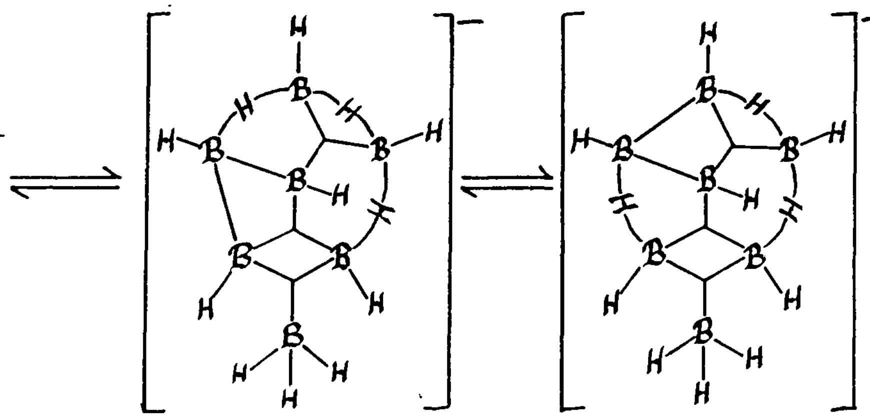
Fig. 4.8c $[B_7H_{12}]^-$

$[B_7H_7]^{2-}$ [35] has received some study through theoretical interest. However, it is the least stable of the closo cages and its reactions with other boron hydrides do not seem to have been studied; the situation is similar for the somewhat more stable closo $[B_8H_8]^{2-}$ [35,40]. Salts, probably consisting of a mixture of $[B_8H_{11}]^-$ and $[B_8H_{13}]^-$, can be prepared by the action of Na or NaH upon B_8H_{12} [41] but neither anion has been isolated nor has their reactivity toward other boranes been studied. Like their neutral counterparts (B_8H_{12} and B_8H_{14}, see chapter 3), it is conceivable that they are important intermediates in hitherto unexplained cage-growth reactions; further study would be valuable since not even their structures have been deduced. It may be that $[B_8H_{13}]^-$ decomposes by hydrogen elimination (c.f. B_8H_{14}, i-B_9H_{15}, $[B_{10}H_{15}]^-$, $[B_{11}H_{16}]^-$) and that $[B_8H_{11}]^-$ reacts with diborane to give $[B_9H_{14}]^-$ (c.f. B_8H_{12}, $[B_9H_{12}]^-$, $[B_{10}H_{13}]^-$).

$[B_7H_{12}]^-$ is produced in the reaction of $[B_6H_9]^-$ and B_2H_6 [26a,33], **4.19**, and, since $[B_6H_9]^-$ is a major decomposition product (the others are not reported[33]) of $[Ph_3PMe][B_7H_{12}]$ above -70°C in DCM, the reaction is thought to be reversible. Although the NMR spectra have not been assigned, $[B_7H_{12}]^-$ is thought to be isostructural to its anionic carborane analogue $[C_2B_5H_{10}]^-$ [42]. If excess B_2H_6 is used during $[B_7H_{12}]^-$ preparation then, as with $[B_6H_{11}]^-$, further reactions ensue yielding 15% $B_{10}H_{14}$ amongst other products. However, B_7H_{11} is not a stable species, if it exists at all, so that a reaction similar to **4.18** would not seem likely. Also one begins to wonder what the reactive site of the

$[B_6H_9]^-$

$+ \frac{1}{2} B_2H_6$



4.19

anion is; like B_6H_{10}, it still has one basic basal B-B bond and so a complex related to the unstable $[B_6H_9 \cdot 2BX_3]^-$, X=Cl or F, might be expected to form. On the other hand, perhaps the terminal hydrogens of the pendant BH_3 moiety are basic enough to form an adduct, $[B_6H_9 \cdot BH_2\text{-}H_\mu\text{-}BH_3]^-$.

4.3.10 Nonahydronanaborate(2−)[40,43], Dodecahydrononaborate(1−)[45] Tetradecahydrononaborate(1−)[46]

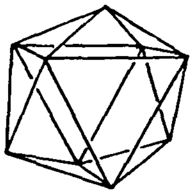


Fig. 4.9a $[B_9H_9]^{2-}$

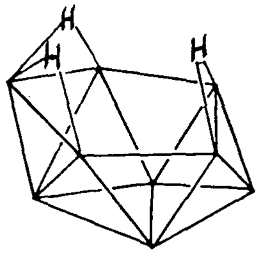


Fig. 4.9b $[B_9H_{12}]^-$

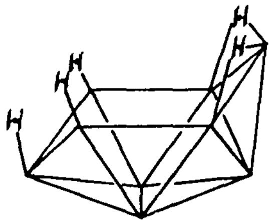


Fig. 4.9c $[B_9H_{14}]^-$

The $[B_9H_9]^{2-}$ anion has been noted to maintain its comparatively rigid D_{3h} symmetry up to at least 200°C in DMSO (ref. 40, footnote 29) so that its thermal stability up to 600°C is not surprising. Although the mechanism of its formation in the pyrolysis of $[B_3H_8]^-$ salts is unknown either of two routes would seem to be good contenders for this pathway:-

a) Cage closure of a more open B_9 species. Since slow pyrolysis of $[B_3H_8]^-$ gives B_5H_9 and this borane reacts with both $[BH_4]^-$ and $[B_3H_8]^-$ [25c] to produce substantial quantities of $[B_9H_{14}]^-$ there is certainly scope for such a reaction. One would expect this route to $[B_9H_9]^{2-}$ to parallel the formation of $[B_{10}H_{10}]^{2-}$ from $[B_{10}H_{14}]^{2-}$, via $[B_{10}H_{12}]^{2-}$, by two consecutive hydrogen elimination steps, **4.20**. However, this clearly requires a base of

$$[B_9H_{13}]^{2-} \xrightarrow{-H_2} [B_9H_{11}]^{2-} \xrightarrow{-H_2} [B_9H_9]^{2-} \qquad \textbf{4.20}$$

some description to produce the dianions because $[B_{12}H_{12}]^{2-}$ is the major product from $[B_9H_{14}]^-$ pyrolysis and the only product from $[B_9H_{12}]^-$ pyrolysis. Although neither B_9 dianion has yet been prepared, the presence of the free base Et_3N may be the reason for the relatively high claimed yields of $[B_9H_9]^{2-}$ during $[Et_4N][B_3H_8]$ pyrolysis[8] (47% by ^{11}B NMR, salts not isolated) compared to the pyrolysis of alkali metal triborohydrides. An alternative is that Et_3N might be able to encourage cage-closure by formation of $[B_9H_{12}\cdot NEt_3]^-$ (c.f. $[B_{10}H_{13}]^- + L \rightarrow [B_{10}H_{13}\cdot L]^-$). If $[B_9H_{12}\cdot NEt_3]^-$ can eliminate H_2 giving $[B_9H_{10}\cdot NEt_3]^-$, this nido adduct would be expected to fragment to $[B_9H_9]^{2-}$ and $[Et_3NH]^+$ like its B_{10} counterpart (see 4.3.12).

b) Exscission of a BH_3 fragment from a nido B_{10} species. Mongeot et al[9] state that Et_3NBH_3 reacts rapidly with $[B_9H_9]^{2-}$ to give $[B_{10}H_{10}]^{2-}$ which may most reasonably be expected to proceed via $[B_{10}H_{12}]^{2-}$ (or $[B_{10}H_{12}\cdot NEt_3]^{2-}$; the higher closo cages are prone to attack or substitution by electrophiles[44]). If this process could be reversed this might account for $[B_9H_9]^{2-}$ formation. In this respect when Wilks[49] pyrolysed several $[B_{10}H_{12}]^{2-}$ salts he found that $[B_{10}H_{10}]^{2-}$ was not the only product but that there was also a compound with the properties of a "bowl-like" cage, christened stapho-$[B_{10}H_{10}]^{2-}$. This might be explained by **4.21**

$$2[B_{10}H_{12}]^{2-} \xrightarrow{BH_3\ \text{transfer}} [B_9H_9]^{2-} + [B_{11}H_{15}]^{2-} \longrightarrow [B_9H_9]^{2-} + [B_{11}H_{13}]^{2-} + H_2 \qquad 4.21$$

where it is assumed that $[B_{10}H_{12}]^{2-}$ reacts with $\{BH_3\}$ in the same fashion as $[B_{10}H_{13}]^-$, **4.24**.

$[Ph_3PMe][B_9H_{12}]$ starts to decompose at 118-20°C and the only product reported from pyrolysis of the $[Et_4N]^+$ salt is $[B_{12}H_{12}]^{2-}$ [7]. $[Me_4N][B_9H_{12}]$ reacts slowly with B_2H_6 [46d] at room temperature to give >0.5 moles of $[B_{10}H_{13}]^-$ per mole of $[B_9H_{12}]^-$ and also some $[B_{11}H_{14}]^-$. This is entirely explained by **4.22** because $[B_{10}H_{15}]^-$

$[B_9H_{12}]^- + ½\ B_2H_6 \longrightarrow [B_{10}H_{15}]^-$ 4.22

eliminates H_2 at room temperature, **4.25b**, and $[B_{10}H_{13}]^-$, like $[B_9H_{12}]^-$, reacts with B_2H_6 to give $[B_{11}H_{14}]^-$, **4.24**, p.111 . It is also noted here that $[B_9H_{12}\cdot Py]^-$ has been prepared by deprotonating $B_9H_{13}\cdot Py$ [46b] and it is predicted that anionic adducts can be prepared, like $[B_{10}H_{13}\cdot L]^-$, by direct reaction of $[B_9H_{12}]^-$ and the ligand - caveat; the compound originally thought to be $[EtNH_3][B_9H_{12}\cdot NH_2Et]$[46b] is in fact $\mu_{7,8}$-EtNH-4-EtNH$_2$-B_8H_{11} [45d].

The skeleton of $[B_9H_{14}]^-$ is derived from i-B_9H_{15} (see 3.3.9) and is isostructural to $B_9H_{13}\cdot L$ [47] (L=Me_2S, Me_3N,$[NCS]^-$,$[H_3BCN]^-$) so that it may be thought of as a hydride adduct of $\{B_9H_{13}\}$. However, ^{11}B NMR indicates that there may also be an [n-$B_9H_{14}]^-$ [46c] produced by deprotonating n-B_9H_{15} with liquid ammonia but brief warming of this to room temperature isomerises it to the usual [i-$B_9H_{14}]^-$. The pyrolysis of $[Et_4N][B_9H_{14}]$ [7,48], which commences at about 198°C, gives predominantly $[B_{12}H_{12}]^{2-}$. Although the mechanism is unknown, it would be worthwhile establishing the kinetics of this reaction since, if $[B_9H_{14}]^-$ behaves like i-B_9H_{15}, the RDS would be expected to be hydrogen elimination and the pyrolysis would be first order. The reactions of this anion with other boron hydrides or Lewis bases do not appear to have been studied.

4.3.11 Dodecahydrodecaborate(2-)[49], Tridecahydrodecaborate(1-)[50] Tetradecahydrodecaborate(2-)[49b,50d,54] and Pentadecahydrodecaborate(1-)[54a,55]

Little has been published concerning $[B_{10}H_{12}]^{2-}$ and it does not seem to have been reliably structurally characterised although one can assume that the cage's skeletal geometry will resemble that of $[B_{10}H_{13}]^-$. Pyrolysis of the alkali metal salts of the dianon

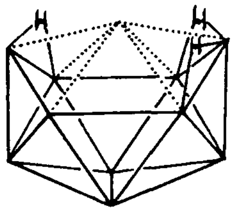


Fig. 4.10a $[B_{10}H_{13}]^-$

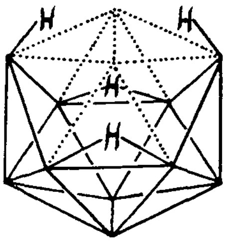


Fig. 4.10b $[B_{10}H_{14}]^{2-}$

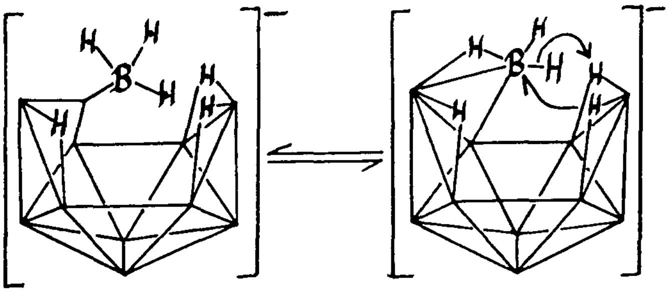
gives $[B_{10}H_{10}]^{2-}$ as a major product, presumably via **4.23**, and the possible nature of the other products is commented upon in 4.3.10.

$$[B_{10}H_{12}]^{2-} \longrightarrow [B_{10}H_{10}]^{2-} + H_2 \qquad \textbf{4.23}$$

The boron skeleton of $[B_{10}H_{13}]^-$ is outwardly similar to that of $[B_{10}H_{14}]^{2-}$, however the former is formally nido whilst the latter is arachno (missing vertices illustrated in *fig. 10*). Pyrolysis of $[Et_4N][B_{10}H_{13}]$ gives 10% $[B_{12}H_{12}]^{2-}$ (no $B_{10}H_{10}]^{2-}$ is reported) but that of $[Et_3NH][B_{10}H_{13}]$ gives 31% $[B_{10}H_{10}]^{2-}$, some $[B_{12}H_{12}]^{2-}$ and $B_{10}H_{14}$ [51] and is clearly quite different. An interaction with the cation is the probable cause of this where a proton transfer, producing free Et_3N and $B_{10}H_{14}$, seems simplest. The formation of $[B_{10}H_{12}]^{2-}$ could perhaps be the reason why the free base causes $[B_{10}H_{10}]^{2-}$ production in $[Et_3NH][B_{10}H_{13}]$ pyrolysis. However, the known reaction of $[B_{10}H_{13}]^-$ with ligands to give $[B_{10}H_{13}\cdot L]^-$ [50b] is prefered here, L=$EtNH_2$, Et_2NH, Et_3N, Ph_3P, Py and pyrolidine. $[B_{10}H_{13}\cdot L]^-$ is isoelectronic to the arachno B_{10} anions, is also probably isostructural to $[B_{10}H_{14}]^{2-}$ and so, similarly, may be expected to eliminate H_2(c.f. $B_{10}H_{14}$ + excess $Et_3N \rightarrow B_{10}H_{12}\cdot 2\ NEt_3$ + H_2; one presumes via ($B_{10}H_{14}\cdot NEt_3$) which loses H_2) giving $[B_{10}H_{11}\cdot L]^-$. This species is discussed further in 4.3.12 but may well dissociate into $[B_{10}H_{10}]^{2-}$ and $[LH]^+$.

At 0°C, in etherial solution, $[B_{10}H_{13}]^-$ and $^{10}B_2H_6$ exchange boron so that a fluxional transient hydride has been proposed [50c], $[B_{11}H_{16}]^-$. However, $Na[B_{10}H_{13}]$ and B_2H_6 react[52] at 45°C to give

$[B_{10}H_{13}]^- + \frac{1}{2} B_2H_6 \rightleftharpoons$



$\xrightarrow{-H_2} [B_{11}H_{14}]^-$ 4.24

$[B_{11}H_{14}]^-$ so that it seems $[B_{11}H_{16}]^-$ can eliminate H_2, **4.24**. This will also be the reaction underlying the formation of $[B_{11}H_{14}]^-$ when $B_{10}H_{14}$ and $[BH_4]^-$ react in etherial media at 40°C [13c,52]; $[B_{10}H_{15}]^-$ and B_2H_6 will be the initial products [55] but $[B_{10}H_{15}]^-$ will rapidly lose H_2 at this temperature. The structure shown for $[B_{11}H_{16}]^-$ in **4.24** assumes that the basic site of $[B_{10}H_{13}]^-$ is the unbridged B-B bond in the open face as in $[B_5H_8]^-$ and $[B_6H_9]^-$. Whilst the arachno B_{11} species has not been isolated, one isomer of the isoelectronic $Me_4C_4B_7H_9$ has this cage geometry [53] - lacking three H_μ of course; $[B_{11}H_{15}]^{2-}$, from $[B_{10}H_{12}]^{2-} + \frac{1}{2} B_2H_6$, might be more stable c.f. $[B_{10}H_{14}]^{2-}$ vs $[B_{10}H_{15}]^{2-}$.

An aqueous solution of $[B_{10}H_{14}]^{2-}$ is only 10-20% decomposed after four weeks but pyrolysis of $[Ph_3PMe]_2[B_{10}H_{14}]$ [51] gives 75% $[B_{10}H_{10}]^{2-}$. By comparison, a freshly prepared solution of $[B_{10}H_{15}]^-$ in glyme is completely decomposed to $[B_{10}H_{13}]^-$ within 12 hrs at room temperature whilst the pyrolysis of $[Et_4N][B_{10}H_{15}]$ gives very nearly the same results as $[Et_4B][B_{10}H_{13}]$ pyrolysis[51]. Thus it seems that for the decomposition of both arachno B_{10} anions hydrogen elimination is the RDS, **4.25**. Neither of these anions has been tested for reactions with other boranes or Lewis bases.

$[B_{10}H_{14}]^{2-} \longrightarrow [B_{10}H_{12}]^{2-} + H_2$ 4.25a

$[B_{10}H_{15}]^- \longrightarrow [B_{10}H_{13}]^- + H_2$ 4.25b

4.3.12 Decahydrodecaborate(2-) and the Mechanism of Cage-Closure

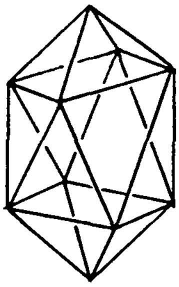


Fig. 4.11a $[B_{10}H_{10}]^{2-}$

This anion is nowadays most easily prepared by the pyrolysis of tetraalkylammonium borohydrides as discussed in section 4.2. However it can also be prepared by the action of Et_3N upon $B_{10}H_{12}\cdot2L$ [56] (L = Et_3N or Me_2S). The reaction is first order in the adduct, but independent of Et_3N, and the cage-closure mechanism is known to follow the geometry in *fig. 11b* - revealed by the reaction of 1,2,3,4-$D_4B_{10}H_{10}$ with Et_3N [56b]. This leads to the conclusion that the RDS for this reaction is dissociation of the bis-adduct to form $\{B_{10}H_{12}\cdot L\}$, the same species as is thought to be important in the reaction of acetylenes with $B_{10}H_{14}$ to give ortho-carboranes[57]. The next step in cage-closure is thought to be deprotonation of the mono-adduct. In this respect, the report that deprotonation of the substituted derivative of $B_{10}H_{12}\cdot L$, 5-Me_2S-9-C_6H_{11}-$B_{10}H_{11}$ [58], with NaH gives 93% $[2\text{-}C_6H_{11}\text{-}B_{10}H_9]^{2-}$ seems to confirm this point of view; this reaction obeys the geometrical constraint in *fig. 11b*. It must, however, be stressedthat this is not the reactive isomer of $\{B_{10}H_{12}\cdot L\}$ since the unsubstituted 5-Me_2S-$B_{10}H_{12}$ has been prepared[59] and its rate of cage-closure, on reaction with Et_3N, is three orders of magnitude slower than $B_{10}H_{12}\cdot2SMe_2$ [56c].

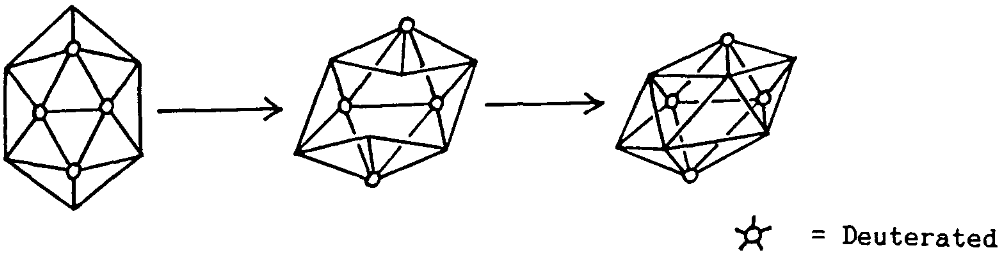


Fig. 4.11b Geometry of $B_{10}H_{14}$ cage-closure

Other clues to the mechanism of cage-closure may be obtained by now considering the reverse reaction. The basic requirement for opening $[B_{10}H_{10}]^{2-}$ is to react it with a Lewis base under strongly acidic conditions[4,5,9e]; the highest yielding example of this claimed to date is the reaction of $[Et_4N]_2[B_{10}H_{10}]$ with Ph_2PMe and HCl[5] to give 95% $B_{10}H_{12}\cdot 2\,PMePh_2$. A special case of this type of reaction is to distil water from a solution of $[H_3O]_2[B_{10}H_{10}]$ which gives $B_{10}H_{13}OH$ [60]. To understand this reaction it is first noted that, when pH<4, $[B_{10}H_{10}]^{2-}$ exchanges hydrogen with D_2O [60a], principally at the apical 1- and 10- positions[44e]. This is thought to proceed via a fluxional intermediate, $[HB_{10}H_{10}]^-$ [44c]; the stationary structure of $[HB_{10}H_{10}]^-$ may well be related to that of $[Ph_4P][HB_6H_6]$ [61] in which the face to which the extra proton is bound has the longest B-B distances. It is also noted that although $[B_{10}H_{10}]^{2-}$ is very resistant toward Lewis base attack [56d], it is open to nucleophilic substitution in strong acid conditions[44c]. The sequence of events during cage-opening is expected to be an initial protonation to give $[HB_{10}H_{10}]^-$, followed by Lewis base attack to $[B_{10}H_{11}\cdot L]^-$ and then another protonation before final production of $B_{10}H_{12}\cdot 2L$. Reversing this order, **4.26**, provides a possible pathway for cage-closure.

$$B_{10}H_{12}\cdot 2\,L \underset{+L}{\overset{-L}{\rightleftharpoons}} (B_{10}H_{12}\cdot L) \xrightarrow{+L} [LH][B_{10}H_{11}\cdot L] \xrightarrow{-L}$$

$$[LH][B_{10}H_{11}] \xrightarrow{+L} [LH]_2[B_{10}H_{10}] \qquad 4.26$$

Finally $[B_{10}H_{10}]^{2-}$ reacts with excess Et_3NBH_3 at 185°C [7] to give 66% $[B_{12}H_{12}]^{2-}$. As with $[B_9H_9]^{2-}$, addition of a BH_3 unit (an electrophile) to the cage is again suspected, giving $[B_{11}H_{13}]^{2-}$; since this does not pyrolyse rapidly at 185°C there must be further reaction, see 4.3.13.

4.3.13 Undecahydroundecaborate(2-)[40,43], Tridecahydroundecaborate(1-)[13b c, 40, 52, 62] and Tetradecahydroundecaborate(1-)

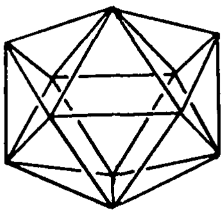


Fig. 4.12a $[B_{11}H_{11}]^{2-}$

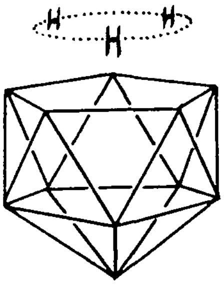


Fig. 4.12b $[B_{11}H_{14}]^{-}$

$[B_{11}H_{11}]^{2-}$ is prepared by the pyrolysis of $Cs_2[B_{11}H_{13}]$, **4.27**,

$$[B_{11}H_{13}]^{2-} \longrightarrow [B_{11}H_{11}]^{2-} + H_2 \qquad \textbf{4.27}$$

and although this reaction begins slowly at 150°C it is not brisk until ~230°C. Whilst this anion is thermally stable to 400°C, the yield of **4.27** is much diminished if CsCl or $Cs[BH_4]$ is present and it seems that these salts bring about the disproportionation of $[B_{11}H_{11}]^{2-}$ into $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$.

The structure of $[B_{11}H_{14}]^{-}$ is clearly an icosahedral fragment. The ^{11}B NMR, consisting of two doublets in the ratio of 10:1, is thought to demonstrate that the bridging hydrogens tautomerise so rapidly that all three can be thought of as a freely rotating single unit; $[B_{11}H_{13}]^{2-}$ is probably of a similar geometry. There is some disagreement as to the conditions under which $[B_{11}H_{14}]^{-}$ will add a BH_3 [5,13b,9] unit (usually in the form of Et_3NBH_3). However, the fact that $B_{10}H_{14}$ and $Na[BH_4]$ react in refluxing diglyme to give about 60% $[B_{12}H_{12}]^{2-}$ [63] (when at lower temperatures they have already been noted to give $[B_{11}H_{14}]^{2-}$) shows fairly clearly that a mono-boron unit can be inserted into a nido B_{11} skeleton. The possible mechanism for $[B_{12}H_{12}]^{2-}$

formation is discussed below in terms of $\{BH_3\}$ addition to $[B_{11}H_{13}]^{2-}$. This is because it would be necessary to include a deprotonation step in a cage-growth scheme starting from $[B_{11}H_{14}]^-$ (unless $[B_{11}H_{14}]^- + [BH_4]^- \rightarrow [B_{12}H_{16}]^{2-} + H_2$) and it is not possible to predict where this would occur. Also, in the $B_6H_{10}/[B_6H_9]^-$ reaction, **4.15**, $[B_{12}H_{17}]^-$ probably dissociates to $[B_{11}H_{14}]^-$ and $\{BH_3\}$ but, since $[B_{11}H_{13}]^{2-}$ may be expected to be a stronger Lewis base than $[B_{11}H_{14}]^-$ and the open face will be less hindered by bridging hydrogens, an arachno B_{12} species formulated $[B_{11}H_{13}\cdot BH_3]^{2-}$ should be more stable.

The reaction pathway between $[B_{11}H_{13}]^{2-}$ and $\{BH_3\}$ is obviously expected to be that in **4.28** and a parallel for each step can be

$$[B_{11}H_{13}]^{2-} + \{BH_3\} \longrightarrow [B_{12}H_{16}]^{2-} \xrightarrow{-H_2} [B_{12}H_{14}]^{2-} \xrightarrow{-H_2} [B_{12}H_{12}]^{2-} \qquad 4.28$$

found amongst the B_{10} and B_{11} lower homologues. However, the structures of the transient $[B_{12}H_{16}]^{2-}$ and $[B_{12}H_{14}]^{2-}$ are not known and to predict these one can look to isoelectronic carboranes as models. For $[B_{12}H_{14}]^{2-}$ the nido carboranes $[R_2C_2B_{10}H_{11}]^-$ [64] which have the structure shown in *fig. 12c* might

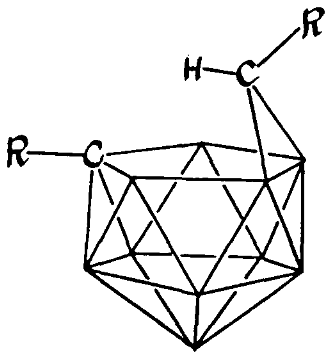


Fig. 4.12c $[R_2C_2B_{10}H_{11}]^-$

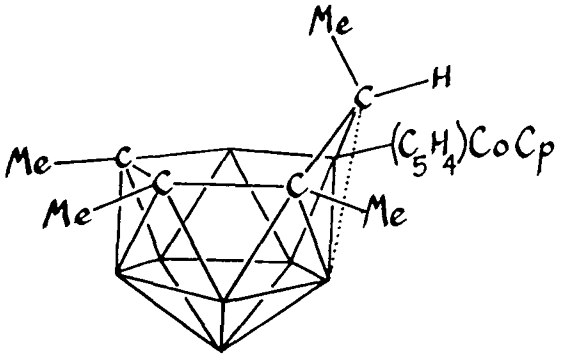


Fig. 4.12d $[(CpCoC_5H_4)Me_4C_4B_8H_9]^-$

be good candidates. It must be pointed out that the known anion $[B_{12}H_{15}]^-$ is almost certainly not structurally related since this has a transoid, edge-fused octaboran-(12)-yl hexaborane-(10) skeleton[65]. A model for $[B_{12}H_{16}]^{2-}$ might be found in the known structure of $[(CpCoC_5H_4)Me_4C_4B_8H_9]^-$ [66] (see *fig. 12d*) although the validity of this will be strictly limited since this carborane lacks three of the bridging hydrogens present in the suspected transient boron hydride anion.

4.4 Conclusions

In this chapter it has become clear that the pyrolysis of $[Et_4N][BH_4]$ is a valuable, if little understood, route to higher polyboron cages. It may be that a continuation of the analysis of anionic cage-growth reactions presented here could offer some insight into this reaction's mechanism and how it might be more usefully controlled. Because such species as $[B_{10}H_{13}\cdot NEt_3]^-$, cf. $B_{10}H_{12}\cdot 2L$, could be present during the reaction some studies were conducted, in this laboratory, to see if carboranes could be prepared directly from the copyrolysis of $[Et_4N][BH_4]$ and acetylenes[67] (MeCCMe and PhCCPh) in an autoclave at 185°C. However, the major product from such reactions was a brown oily material which did not seem to show any B-H coupling in the ^{11}B NMR so that carboranes were not thought to have been produced. An alternative approach to carboranes related to such reactions might be to pyrolyse $[Et_4N][[H_3BR]$ [68a,b], R=alkyl[68c] or perhaps alkenyl[68d]; it might be necessary to copyrolyse the salt with Et_3NBH_3 because the reaction of $[H_3BR]^-$ and Et_3NBH_2R could be too sterically hindered to allow cage growth via a $[B_2H_7]^-$ derivative. If cage growth does occur in such a reaction it might be useful, firstly, as a probe of the mechanism and, secondly, species such as R-B_5H_8 might be produced, similar to $[B_3H_8]^-$ pyrolysis. If R= alkenyl and could avoid reduction early in the reaction, pyrolysis of R-B_5H_8 will give monocarbahexaborane-(9) derivatives[69a]. If R=

alkyl and R-B_6H_9 were produced it seems that its pyrolysis can also give give the same carboranes[69b].

As far as the chemistry of the anions is concerned it is clear, just from the sheer number already known, that they are more easily prepared and studied under controlled conditions than are their neutral counterparts. Thus they may offer a greater prospect of providing planned synthetic routes to higher cages. One line of research that could prove particularly fruitful would be to study their reactions with the Lewis acids {B_3H_7} and {B_4H_8}; this could, for instance, provide new and efficient routes to the presently little understood B_8 species or perhaps to linked cages.

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Chapter 5 A Study of the Hydrolysis of Magnesium Diboride Under Acidic Conditions

5.1 Introduction

In this chapter the reactions of magnesium diboride, MgB_2, with protic acids (mainly orthophosphoric acid) are studied in detail. The results presented here confirm those of Timms and Phillips[2] and show that MgB_2 reacts with 7M H_3PO_4 to give B_4H_{10}, B_5H_9 and B_6H_{10} as the major volatile boron hydride products. Apart from traces of $B_{10}H_{14}$, no other neutral boranes are produced in this reaction although anionic species, including $[B_{12}H_{12}]^{2-}$, $[B_{10}H_{10}]^{2-}$ and $[B_9H_{14}]^-$ are now also thought to be formed in yields comparable with those of the neutral boranes. The yield of boranes from MgB_2 hydrolysis has never been reported to exceed 16%. However, it was decided to try and develop this reaction into a practical synthesis on the grounds that:-

a) The preparation of boranes from MgB_2 and H_3PO_4 requires only simple apparatus and moderate conditions compared to their presently preferred multi-stage synthesis from B_2H_6 and $[BH_4]^-$.
b) The starting materials are safe and easily handled.
c) MgB_2 can be prepared quite easily in the thermite reaction of Mg with the appropriate proportions of elemental boron or B_2O_3.

The primary aim of this project was to study the reaction of MgB_2 with acids under a wide range of conditions to see if any systematic ways of increasing the yield and/or controlling the distribution of boranes produced could be found. The selection of systems studied in this project, their experimental details and the techniques used are described in section 5.2. In section 5.3.1 the patterns of borane production observed in this work are discussed and some inferences drawn concerning the later stages of the reaction's mechanism. Section 5.3.2 is concerned with the involatile boron compounds produced during MgB_2 hydrolysis, including the polyboron anions whose formation was observed for the first time in this situation. Section 5.3.3 comments briefly on some attempts to find a one-pot synthesis of carboranes in this project. Lastly, section 5.3.4 speculates upon the earlier stages of the mechanism of MgB_2 hydrolysis.

5.2 Experimental Section

5.2.1 General Method

The commercially available single phase MgB_2 (Strem, 98%, delivered under Ar) was used in all experiments. Three 50g batches were purchased and these were labelled (B1, B2, and B3) so that variable reactivity of the MgB_2 samples could be taken into account. The MgB_2 was a very fine, low density, black powder and when examined under a hand lens was noted to contain small metallic flecks - probably elemental Mg. An attempted microanalytical assay by oxygen combustion gave B=8·9%, Mg=44·28% and Si=0·36%, calc. B=47·07%, Mg=52·93%; this was clearly incorrect. The result was probably due to incomplete combustion giving very fine, insoluble particles of higher borides or boron; c.f. the same assay with commericial 95% boron gave a similar low analysis at only B=63·30%. Instead the MgB_2 was examined by its Debye-Scherrer X-ray powder photograph from which it was deemed acceptable since the only lines not attributable to MgB_2 were those of Mg and MgO - an excess of Mg is often used in the preparation of MgB_2 (by direct combination of the elements) to inhibit formation of higher borides. 88-93% H_3PO_4 (Koch-Lite Ltd.) was used without further purification.

The apparatus used during the reaction is illustrated in *fig. 5.1*. The powder addition apparatus was first charged with ~3·6g (78mmol) MgB_2 in a dry box. For this a tared, long-handled weighing boat was used taking care that none of the MgB_2 was accidentally spilt into either stopper. The remainder of the

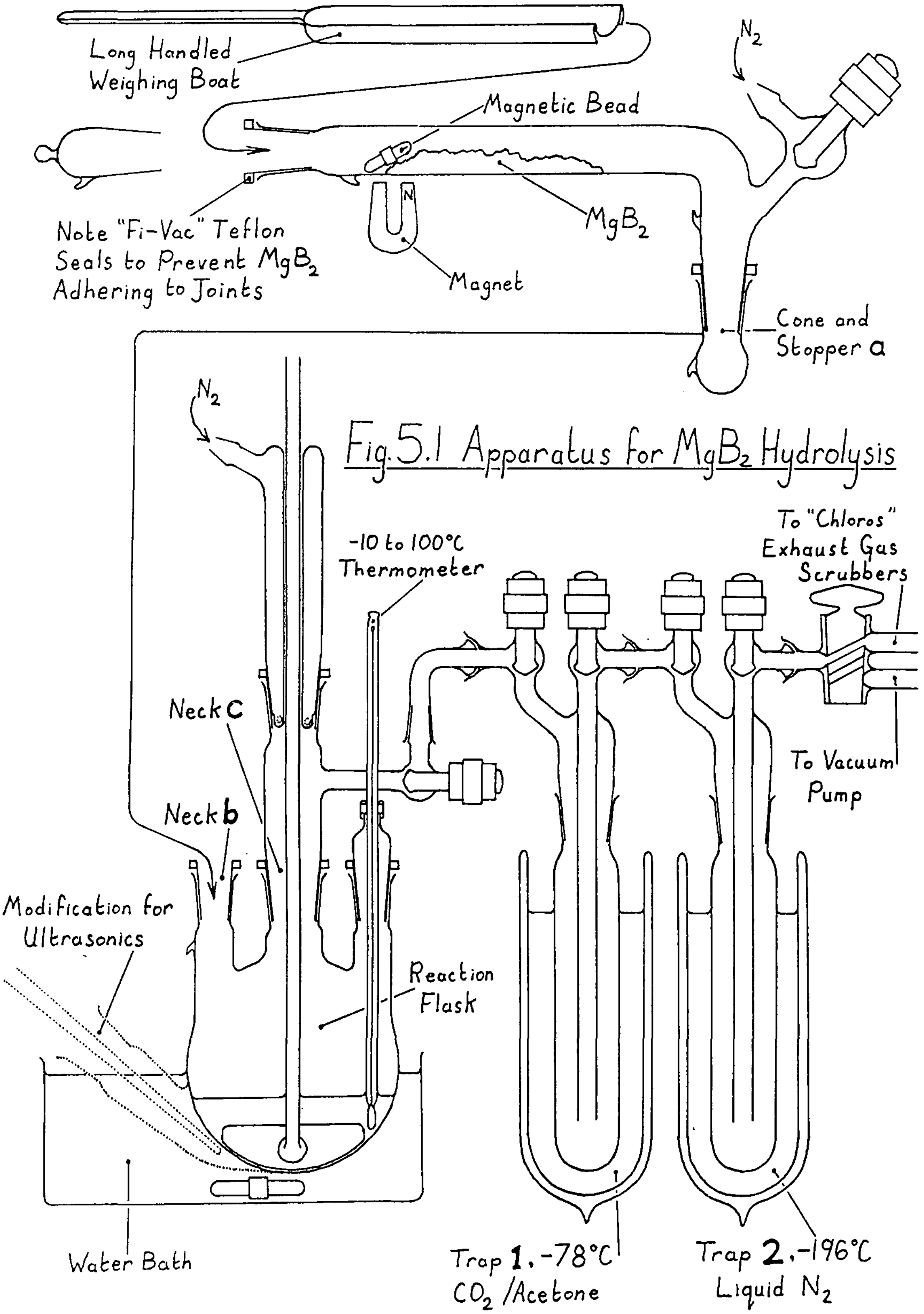


Fig. 5.1 Apparatus for MgB_2 Hydrolysis

apparatus was flushed with N_2 and the traps sealed from the reaction flask. The 500ml reaction flask was then charged with 52ml of water and 42ml of concentrated phosphoric acid (~0·66 mol, >8 fold excess of approx. 7M H_3PO_4); if a greater volume or concentration of acid was used, or >4g MgB_2 added to it, troublesome foam effectively prevented addition of all the powder. The acid was warmed to the desired temperature, ca. 65°C, and stirred under a flow of N_2 to degas.

Once the equipment had been set up the powder addition apparatus was connected to a nitrogen line, stopper a removed, and cone **a** swiftly joined to the reaction flask at neck **b**. The tap to the traps was now reopened and the entire apparatus flushed with N_2 for ~2 mins to expel any remaining traces of air. The following procedures were carried out as quickly as possible to minimise the amount of water condensed in trap **1** and also because the MgB_2 became clumped and awkward to handle after lengthy exposure to the moist vapours from the reaction flask. A strong magnet was used to manipulate a magnetic bead inside the apparatus with which <u>very</u> small piles of MgB_2 were pushed into the reaction flask at a quick and steady pace. The acid was stirred very vigorously but the rate of powder addition was soon limited when foam filled about two thirds of the volume of the flask; this foam seemed to become more persistent as the reaction progressed. The reaction flask temperature usually exceeded that of the water bath by ~4°C because the reaction was exothermic. Since water condensed in neck **b** a deposit of MgB_2 built up in this region during powder addition. It was essential to periodically dislodge the damp MgB_2 to prevent a catastrophically large lump unexpectedly falling into the acid; this problem was minimised when neck **b** was vertical. When adding the last of the MgB_2 the powder addition apparatus could be completely emptied by tapping it at the closed end to dislodge any adhering powder. Following this the bead was rinsed in the acid and used to help wash down any tenacious MgB_2 from around neck **b**. After powder addition, which took ~75 mins, the apparatus was flushed with N_2 for 15 mins to ensure that the reaction was complete and that all volatiles transfered to the traps. The traps were then sealed from the reaction flask and evacuated ready for analysis of the boranes.

The reaction flask was allowed to cool and a very fine dark brown, nearly black, residue settled out leaving a yellow solution. Later in the cooling colourless, plate-like crystals precipitated. Frequently a few colourless, needle-like crystals formed around neck c and although there were never enough to collect and analyse they were thought to have been $B_{10}H_{14}$ (see below).

One of the sealed traps was transfered to the vacuum line shown in *fig. 5.2* and the whole system evacuated to <0.01 mmHg; trap 1 was cooled to -198°C to ensure that any B_4H_{10} that might have collected there was not lost. All the apparatus was sealed from the line, except for the trap and manometer, and the volatiles collected from the reacton were allowed to expand slowly into the line via the water scrubbing tube. Periodically the boranes were condensed into the small weighing ampoule before continuing to empty the trap. As the trap approached room temperature iced water was placed around it; this was to prevent any water in the trap volatilising rapidly enough to make the P_2O_5 in the water scrubbing tube excessively hot, possibly causing decomposition of the boranes. It was because of this effect that two traps were used during the reaction. During early exploratory reactions only one trap at -198°C had been used and, whilst drying the volatiles by the above procedure, fine, colourless, needle-like crystals were seen to form at the end of the water scrubbing tube. The mass spectrum of these crystals was identical to that of $B_{10}H_{14}$ and it was suspected that they were produced by the copyrolysis of B_4H_{10} and B_6H_{10} passing over the hot P_2O_5 (see p. 67 , 3.3.6, **3.19**). In later experiments, when all the B_6H_{10} stopped in trap **1** and most of the B_4H_{10} continued to trap **2**, no further $B_{10}H_{14}$ was seen in the water scrubbing tube.

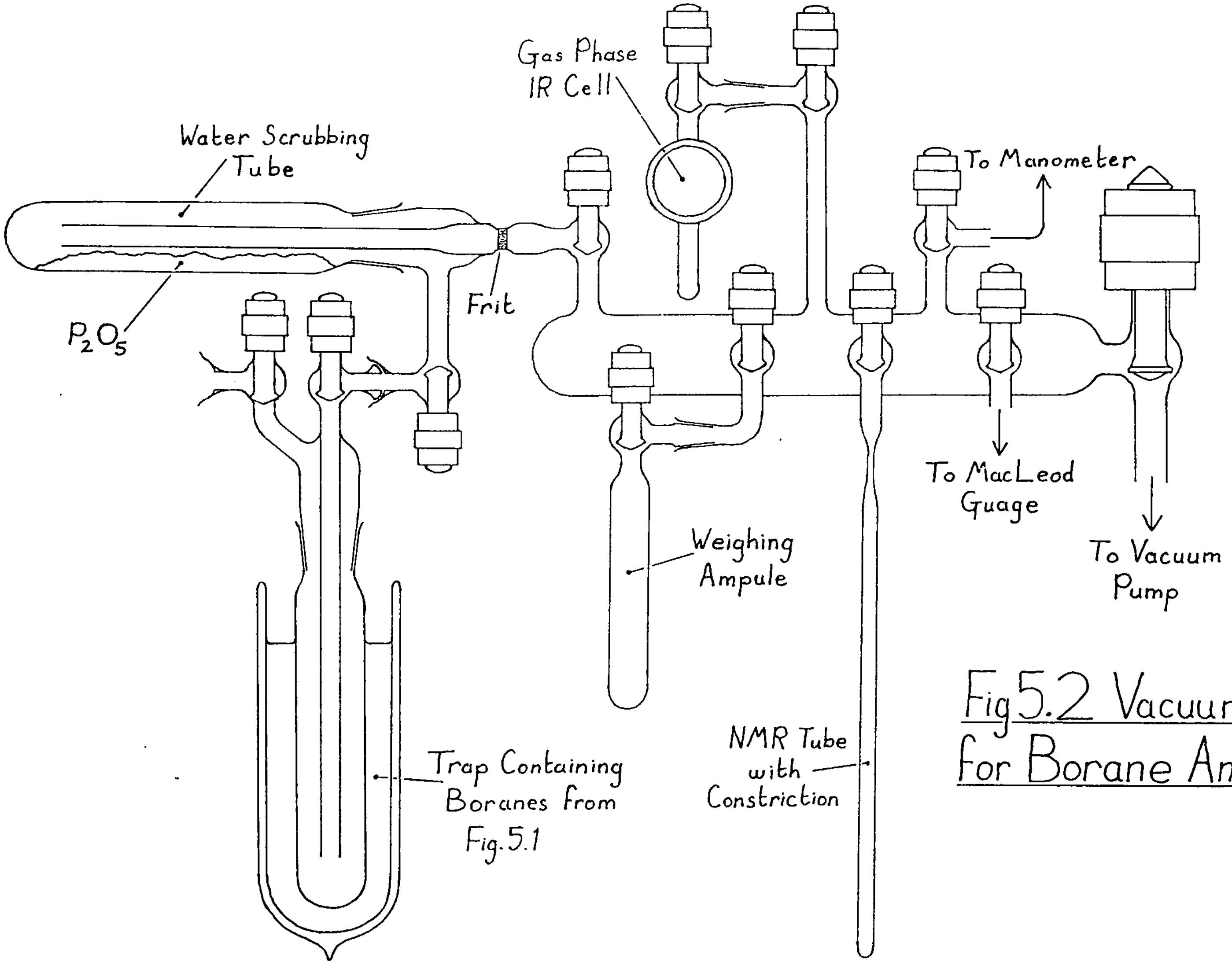


Fig 5.2 Vacuum Line for Borane Analysis

Once the trap's volatile contents had been transfered to the weighing ampoule, a little white rime was often observed in the bottom of the trap, some of which sublimed to form needles further up the tube. The component which sublimed was probably $B_{10}H_{14}$. That which would not sublime was probably $B(OH)_3$ although it seemed unlikely that there would be a high enough temperature or time enough for hydrolysis of the boranes to occur in the trap. Instead, the $B(OH)_3$ could have come directly from the reaction flask since it has a significant vapour pressure in steam[16] (enhanced by acid) due to the formation of hydrates.

After the trap had been emptied both it and the water scrubber were sealed from the line. The volatiles were next sealed into the tared ampoule which was detached from the line, warmed to ambient temperature, weighed and recooled as rapidly as possible to prevent decomposition of the boranes. The ampoule was reattached to the line so that the IR spectrum could be taken and finally the boranes were condensed into the NMR tube. Once the above process had been repeated with both traps, the IR spectrum of the mixed boranes from both traps was taken. If the sample was lost through accident, before the ^{11}B NMR could be taken, the proportions of the different components could still be worked out from the IR

5.2.2 Analysis of the Volatiles

Only infra-red and ^{11}B nuclear magnetic resonance spectroscopy were used to examine the volatiles from MgB_2 hydrolysis but both techniques lent themselves to the requirements of this project on the grounds that:-

a) they were fast and non-destructive.

b) no further processing was required so that spurious experimental artifacts from, say, cothermolysis were unlikely to give confusing results.

c) the entire yield could be examined at once, unambiguously giving the relative yields of the different boranes.

I.R. spectra were obtained with a Perkin-Elmer 577 using a 10cm pathlength gas cell with NaCl windows. The gas cell was filled by opening just it and the weighing ampoule to the vacuum line and allowing the condensed boranes to come to ambient temperature. After this the cell was sealed and the remaining boranes returned to the ampoule. The pressure in the vacuum line was noted on each such occasion and if it was <1·0 cmHg the entire sample was condensed into the cell to give a strong spectrum. *Fig. 5.3* shows some representative spectra obtained during the project and *Table 5.1* gives the peak positions which agree well with the literature[1]. Whilst these spectra were a useful check for volatile contaminants, they also showed clearly that no B_2H_6 was produced during MgB_2 hydrolysis because B_2H_6 has a very intense broad band centered on 1600cm^{-1} as well as a strong sharp absorption around 1280cm^{-1}, neither of which were ever seen. Another important purpose for these spectra was as security against accidental loss of the sample before the ^{11}B NMR spectrum could be taken. This is because, by adapting the work of McCarty, Smith and McDonald[18], a quantitative measure of the proportions of the different boranes present in the gas could be made. However, since such accuracy was not required, it was sufficient just to use the experimental relationship that the H_μ bands for B_5H_9 and B_6H_{10} are of about the same intensity whilst that for B_4H_{10} is about four times greater when all three gases have the same partial pressure.

All ^{11}B NMR spectra were taken on a Bruker AC 250 MHz machine using a $BF_3 \cdot OEt_2$ external standard. The total borane yield from any one experiment was dissolved in 0·5ml of d_6-benzene, sealed in a 5mm o.d. NMR tube and the spectra run at room temperature. The relative molar concentrations of the boranes were obtained by integration of the proton decoupled spectrum, see *fig. 5.4*, where

Table 5.1 Peak Assignments for *fig. 5.3*/cm^{-1}

	Trace a	Trace b	Trace c	
	B_4H_{10}	B_5H_9	$(B_4H_{10}+B_5H_9)$	B_6H_{10}
Terminal Hydrogens		2610(s)		2630 to
	2590(s)			2590
	2500(s,sh)		2500	
Bridging Hydrogens	2150(m)		2150	
				1940
		1810(m,br)	1810	
				1555
				1486
		1448(m,sh)		
		1429(m)		
		1411(s,sh)	1411	
	1410(m)			
	1140(m)		1140	
		1130(w,sh)		
	1075(w)			
		1049(w)		
				1019
	972(m)		972	
		900(s)	900	Not well
				886 resolved
	864(w)			
	851(m,sh)		851	
	839(w)			
				752
				752
				690

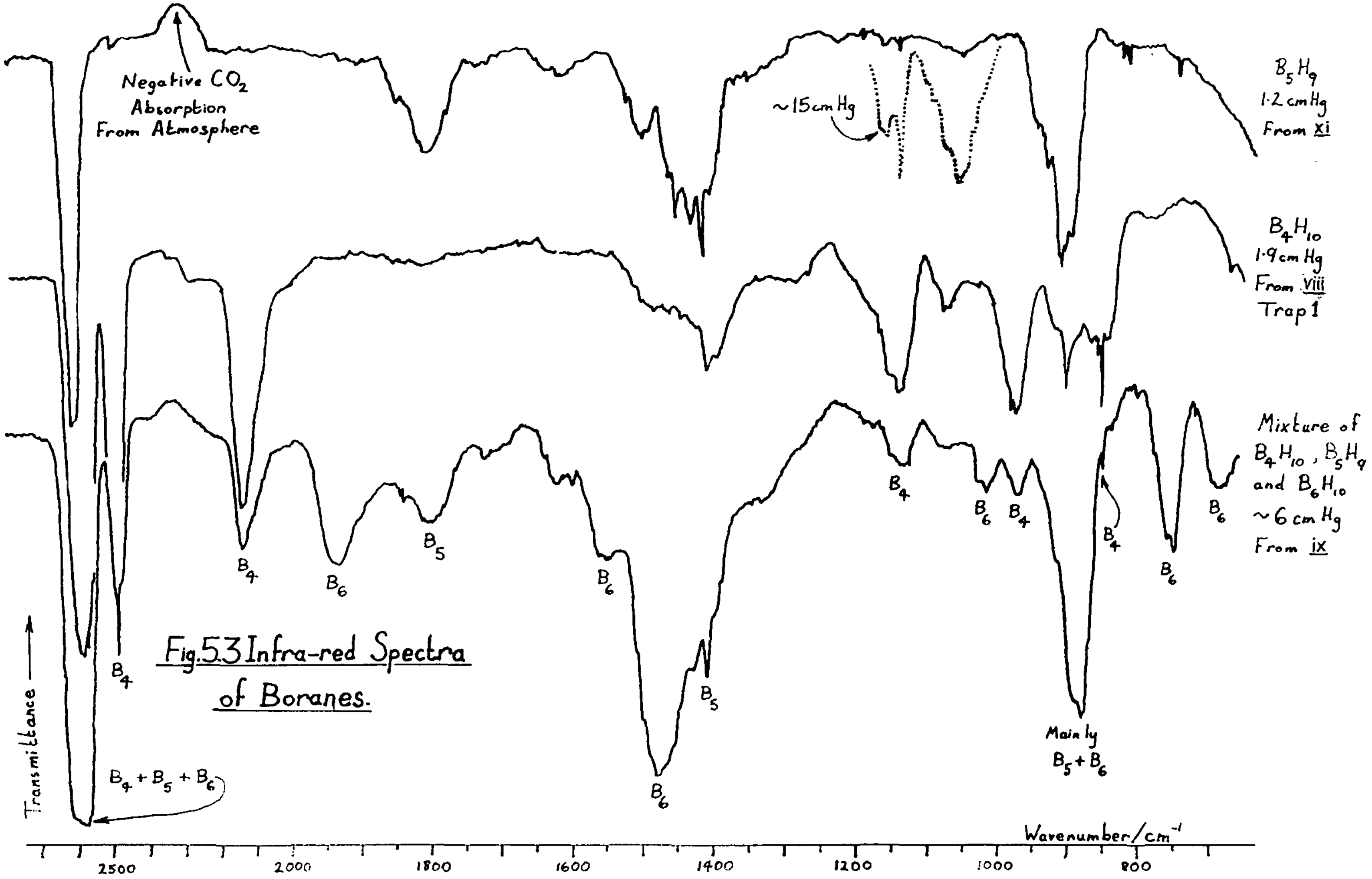


Fig. 5.3 Infra-red Spectra of Boranes.

$[B_4H_{10}]_{REL}$=(sum of both signals)÷4, $[B_5H_9]_{REL}$=(signal from basal borons)÷4 and $[B_6H_{10}]_{REL}$=(signal from basal borons)÷5; the apical signals from the nido boranes were not resolved from one another and thus could not be used. The proton coupled spectrum was always taken to confirm peak assignments but the decoupled spectrum was used to calculate relative concentrations because:-

a) the relevant signals were more clearly resolved.

b) despite a varying NOE for the different signals used, the curving base line inevitably distorted the integral of a decoupled signal less than a coupled signal.

The curve of the base line (very prominent in the weak spectrum in *fig. 5.9*, p.154) was an experimental artifact from the probe which was unfortunately made of boron nitride and, possibly, the borosilicate glass of the NMR tube. It is an extremely broad signal spreading from +100 to -100 ppm and could be removed numerically by subtracting a stored blank. However, this technique was not practical during this project because the wide range of total borane yields prevented recording all spectra under necessarily identical conditions, i.e. same number of scans, temperature, volume of solvent and, preferably, the same tube.

The boiling points of B_4H_{10}, B_5H_9 and B_6H_{10} at atmospheric pressure are 18, 60 and 108°C respectively so that on two occasions (5.2.3, experiments **viii** and **ix**) the boranes were dissolved in toluene and their spectra run at 20 and at -30°C to ensure that they were not significantly partitioned between the solution and gas phases. The spectra at both temperatures were identical so it was thought that the integrals were giving a true picture of each borane's relative concentration. Samples were always stored in liquid nitrogen because even keeping them overnight at -30°C led to some decomposition - evidenced by the appearance of a white, flakey precipitate.

5.2.3 Specific Experimental Conditions

For a listing of the results from all the experiments in 5.2.3 for which the yields and proportions of B_4H_{10}, B_5H_9 and B_6H_{10} were measured see *Table 5.2.*, p.158.

1. Early Attempt to Obtain Reproducible Results Under a Set of Standard Conditions

3·600g (78·4mmol) MgB_2 from B1 was reacted with 7M H_3PO_4 using the method described in section 5.2.1. The product boranes gave a combined pressure of 27mmHg in the vacuum line and the ^{11}B NMR spectrum shown in *fig. 5.4, trace a*. Unfortunately the boranes from this reaction were not weighed because techniques were still being acquired for handling these dangerous compounds. However, a scaling factor, $\bar{C}$=0·016 mmol/mmHg (Average of 8 results, σ=0·003), was calculated from later experiments to convert the pressure measurements into a reasonable estimate of the total molar yield of boranes, M. Integration of the ^{11}B NMR spectrum showed that the ratio of the relative molar concentrations of B_4H_{10}, B_5H_9 and B_6H_{10} (which were the only boranes present) was 0·47:0·17:0·36 respectively and thus the yields could be calculated:-

$$0{\cdot}016 \times 27 \times \left\{ \begin{array}{l} 0{\cdot}47 = 0{\cdot}208\text{mmol } B_4H_{10} \equiv 0{\cdot}833\text{mmol boron} \equiv 0{\cdot}53\% \\ 0{\cdot}17 = 0{\cdot}075\text{mmol } B_5H_9 \equiv 0{\cdot}377\text{mmol boron} \equiv 0{\cdot}24\% \\ 0{\cdot}36 = 0{\cdot}160\text{mmol } B_6H_{10} \equiv \underline{0{\cdot}957}\text{mmol boron} \equiv 0{\cdot}60\% \end{array} \right.$$

$$2{\cdot}167\text{mmol boron}$$

∴ Total percentage boron converted from MgB_2 to boranes =

$$100 \times \frac{2{\cdot}167}{2\text{x}78{\cdot}4} = 1{\cdot}4\%$$

Notably this gives a B_5H_9/B_4H_{10} molar ratio (B_5/B_4) of ~0·4.

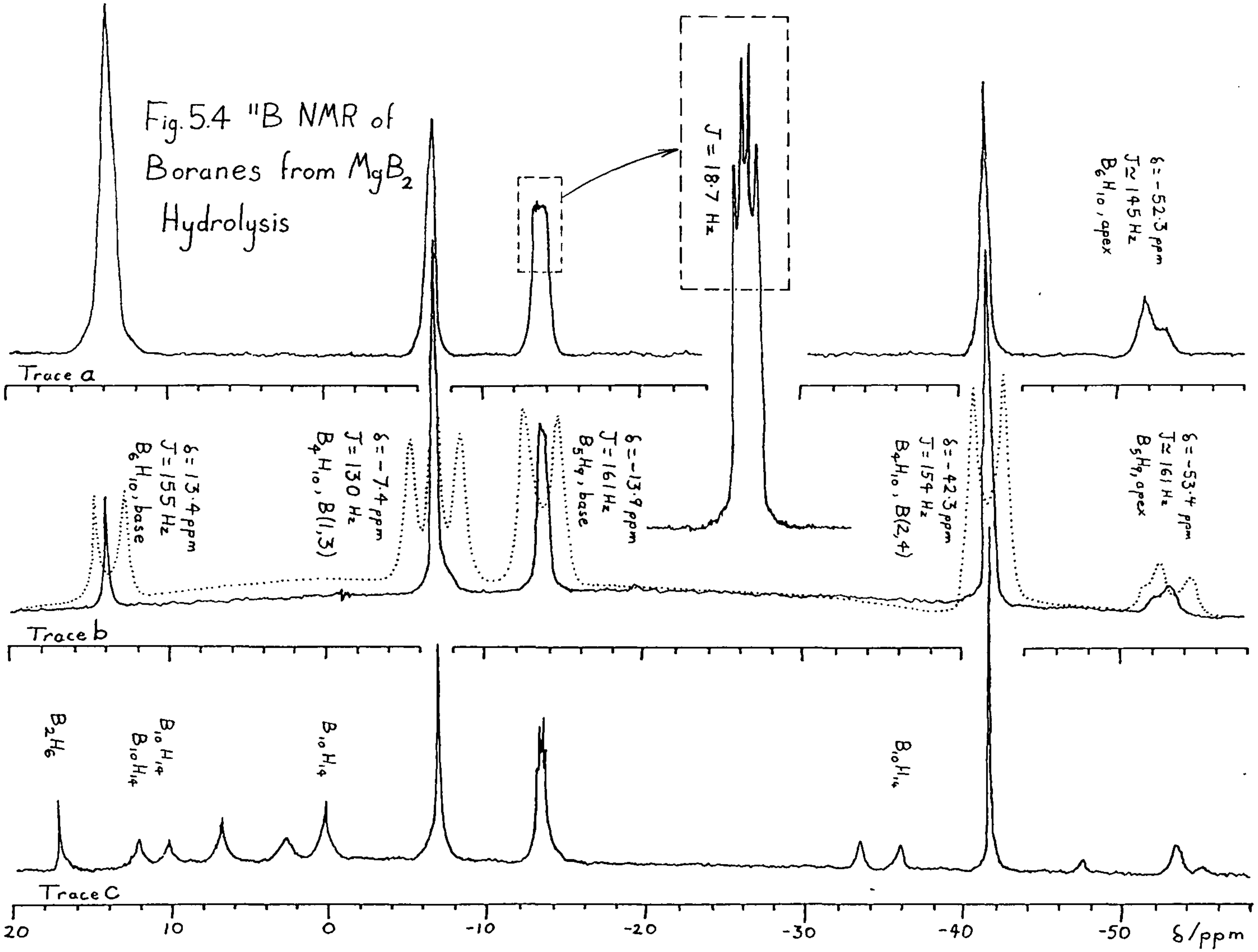


Fig. 5.4 ^{11}B NMR of Boranes from MgB_2 Hydrolysis

ii. Standard Conditions for MgB_2 Hydrolysis by 7M H_3PO_4

3·603g (78·5mmol) MgB_2 from B3 was reacted with 7M H_3PO_4 using the method described in 5.2.1. After the reaction trap 1 contained 1·2mg boranes, consisting of mainly B_5H_9 and B_6H_{10}, which gave a pressure of 1mmHg in the vacuum line; trap 2 contained 13·8mg of mixed B_4H_{10} and B_5H_9 which gave a pressure of 17mmHg in the vacuum line. Integration of the ^{11}B NMR spectrum, *fig. 5.4 trace b*, showed that B_4H_{10}, B_5H_9 and B_6H_{10} had been produced in the ratio 0·64:0·26:0·10 respectively so that the total molar yield of boranes, M, could be calculated and thus the total percentage of boron converted from MgB_2 to boranes:-

$$M = \frac{1{\cdot}2 + 13{\cdot}8}{[(0{\cdot}64 \times 53{\cdot}24)+(0{\cdot}26 \times 63{\cdot}05)+(0{\cdot}1 \times 74{\cdot}86)]} = 0{\cdot}259\text{mmol}$$

$$\therefore\ 0{\cdot}259 \times \begin{cases} 0{\cdot}64 = 0{\cdot}166\text{mmol } B_4H_{10} \equiv 0{\cdot}633\text{mmol boron} \equiv 0{\cdot}42\% \\ 0{\cdot}26 = 0{\cdot}067\text{mmol } B_5H_9 \equiv 0{\cdot}337\text{mmol boron} \equiv 0{\cdot}21\% \\ 0{\cdot}10 = 0{\cdot}026\text{mmol } B_6H_{10} \equiv \underline{0{\cdot}154}\text{mmol boron} \equiv 0{\cdot}10\% \end{cases}$$

$$1{\cdot}154\text{mmol boron}$$

∴ Total percentage boron converted from MgB_2 to boranes =

$$100 \times \frac{1{\cdot}15}{2 \times 78{\cdot}5} = 0{\cdot}74\%$$

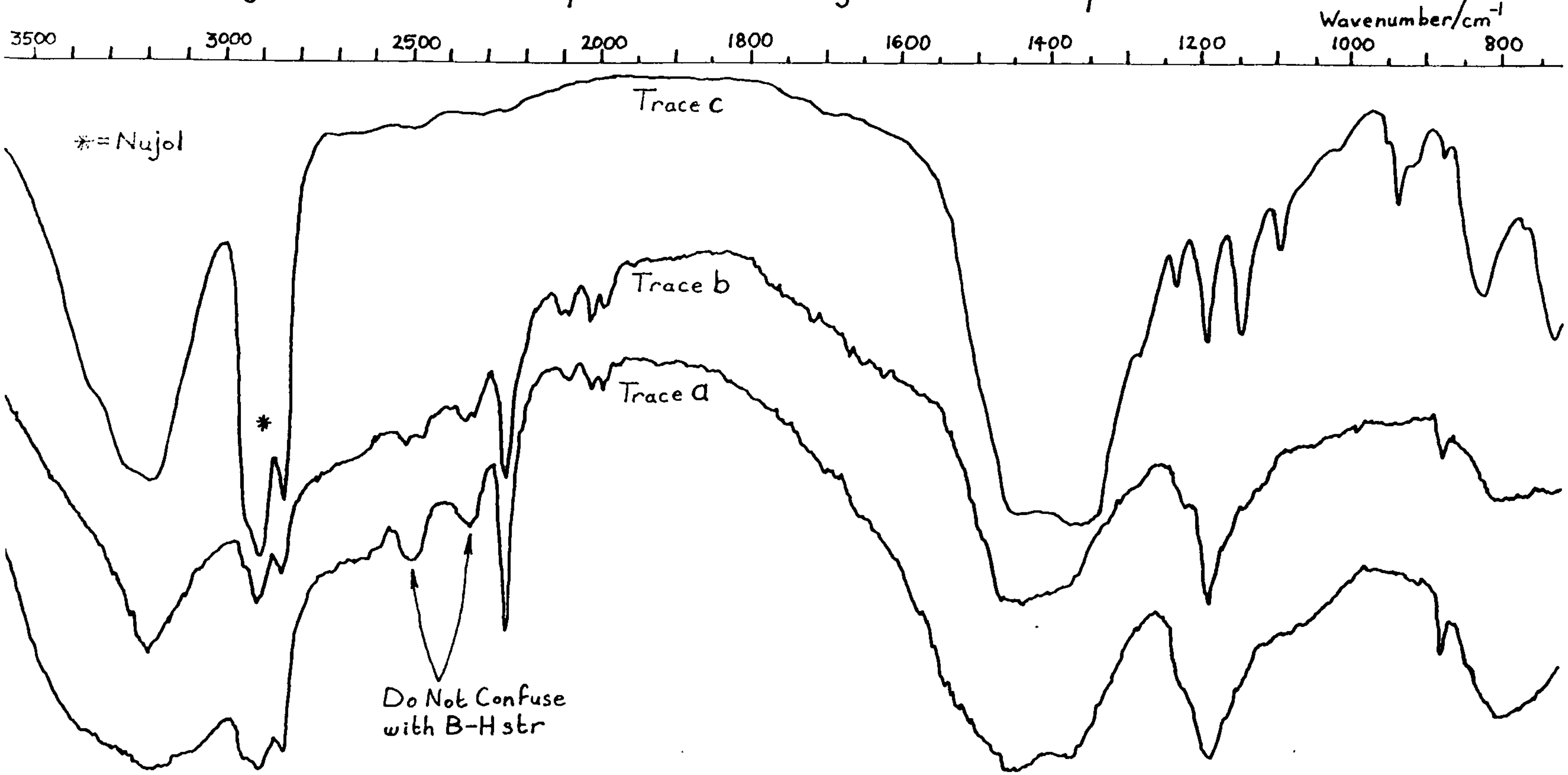
Again B_5/B_4 is ~0·4.

In this reaction the colourless, plate-like precipitate in the reaction flask was also examined. The acid solution was diluted with water until all the precipitate had dissolved and then filtered through a pad of "Hi-flo Supercell" silica on a glass sinter to remove the fine, dark, insoluble residue. The clear yellow filtrate was heated at 90°C and 1cmHg pressure to reduce it to between 50 and 80ml in volume after which cooling reprecipitated the colourless plates. These were filtered off and washed sparingly with cold distilled water. Further concentration of the above acid solution down to the limit of around 15ml, when a thick treacle remained, failed to precipitate any other solids. Notably if both the insoluble residue and soluble precipitate were filtered from the acid solution directly after completing a hydrolysis and a little conc. H_3PO_4 was added to the filtrate more of the plate-like crystals precipitated. Thus it seemed that the formation was pH dependant.

The crude precipitate, about 2·2g, was recrystallised from the minimum amount of distilled water to give a waxy, plate-like solid whose IR spectrum, *fig. 5.5 trace a*, is almost identical to that of orthoboric acid, $B(OH)_3$ *fig. 5.5 trace b*. A 1.125g sample of the recrystallised precipitate, which had been air dried, was placed in an oven at 90°C for four days. After this its mass was reduced to 0·770g and it had the IR spectrum in *fig. 5.5 trace c;* microanalysis gave B=23·43%, H=2·39%, Mg, P, N, C absent and O (by difference) = 74·18% and it seems that the sample had mainly deydrated to metaboric acid, HBO_2 calc. B = 24·67%, H = 2·29%.

After removing the $B(OH)_3$ from the yellow acid solution it was decided to see if any organically soluble species could be extracted from the remaining ~50ml. Extraction with toluene gave only a very small amount of an oily material (B-H str ~2570cm^{-1}) which could perhaps have been $B_{10}H_{14}$. However, shaking the acid solution with ether (100ml) produced a three phase system: the top etherial layer, ~60ml, was clear and bright yellow; the middle layer was yellow/brown, viscous and translucent whilst the bottom phosphoric acid layer was almost colourless but also viscous and translucent. It was later observed that although 7M H_3PO_4 was immiscible with Et_2O, 88% H_3PO_4 reacted with Et_2O liberating gas and leaving a single phase. This reaction was thought to be acid catalysed cleavage of ether to ethene and EtOH; the alcohol could then have esterified the acid and this was perhaps responsible for the second phase in the extraction above. The top two layers were taken, neutralised with sodium hydrogen carbonate powder (diluting

Fig.5.5 Infra-red Spectra from Crystalline Precipitate



with water when necessary) and evaporated to dryness leaving a large amount of faintly yellow solid which was ground to a fine powder. Washing this with EtOH gave a yellow solution which, on driving off most of the alcohol, left a dark yellow gum - prolonged heating at 100°C and 1cmHg finally gave a friable powder but this proved highly hygroscopic. The IR spectrum of the gum is shown in *fig. 5.6 trace a* and the ^{11}B NMR of the powder dissolved in water is shown in *fig. 5.7 trace a*.

iii. **Repeat of ii. with Further Examination of the Anionic Hydrolysis Products**

3·555g (77·4mmol) MgB_2 from B3 was reactd with 7M H_3PO_4 using the method described in 5.2.1 except that nitrogen was flushed through system for 100 mins after completing MgB_2 addition to the acid to check that the reaction was totally completed in ii. The combined contents from traps 1 and 2 gave identical IR and NMR spectra to ii and the total percentage of boron converted from MgB_2 to boranes was 0·77% showing that the results from these techniques were reasonably reproducible.

On this occasion the fine, dark, insoluble residue was also examined. After diluting the resultant acid solution from MgB_2 hydrolysis to ~150ml (to redissolve the $B(OH)_3$) it was filtered through a porosity 4 glass sinter which caught nearly all the insoluble residue. This material was then placed in conc. 88% H_3PO_4 for a month, to leach out any remaining traces of MgB_2, before being filtered and liberally washed with distilled water. After heating in an oven at 90°C for several days 0·45g of powder remained and its Debye-Scherrer X-ray powder photograph was taken; the two most prominent lines were d = 1·76-8 and 2·05-8Å although all the lines were weak and diffuse.

Returning to the yellow resultant acid solution, the last traces of the dark, insoluble residue were removed by filtration through a silica pad before concentrating it to precipitate the $B(OH)_3$ as in **ii**. The acid solution was again diluted to 100ml after which it was extracted with ether (3x30ml) to give a two phase system consisting of an upper, bright yellow, etherial solution and a lower, pale yellow, phosphoric acid solution. The ether extract was taken, divided exactly in two and then the ether was removed from each half under reduced pressure to leave a few white crystals in a small amount of yellow gum. Setting one half of the extract aside, the yellow gum in the other was carefully washed from the white crystals with 0·5ml portions of ether from a Pasteur pipette and the deep yellow solution decanted. The white crystals were characterised as $B(OH)_3$ from their strong, broad, triangular-shaped absorption centered on 3200cm^{-1} and discarded. 5ml of saturated $[Me_4N]Cl(aq)$ was added to the 5ml of deep yellow etherial washings and this immediately caused a dense, pale yellow precipitate to develop. This was stirred for a further 30 mins before the precipitate was filtered off, washed liberally with water and dried at reduced pressure and 60°C. The yield was 44·4mg of salts and the IR and ^{11}B NMR spectra are shown in *fig. 5.6 trace b* and *fig. 5.7 trace b* respectively.

The remaining half of the ether extract was now redissolved in 20ml of water and mildly basified with $Na[HCO_3]$ powder. This solution was evaporated to dryness leaving a white solid which was ground to a fine powder and thoroughly washed with ether. The nearly colourless etherial washings were concentrated to 5ml in volume and treated with $[Me_4N]Cl$ as above to yield 10·6 mg of off-white salts. The IR and ^{11}B NMR spectra of this material are shown in *fig. 5.6 trace c* and *fig. 5.7 trace c.*

Finally the acid solution remaining from the ether extraction was concentrated to 50ml in volume and to this was added another 60ml of ether. In the three phase system that now developed the top ether layer was completely colourless, the middle layer (~40ml) was yellow and viscous and the bottom phosphoric acid layer was almost colourless. The top two layers were taken,

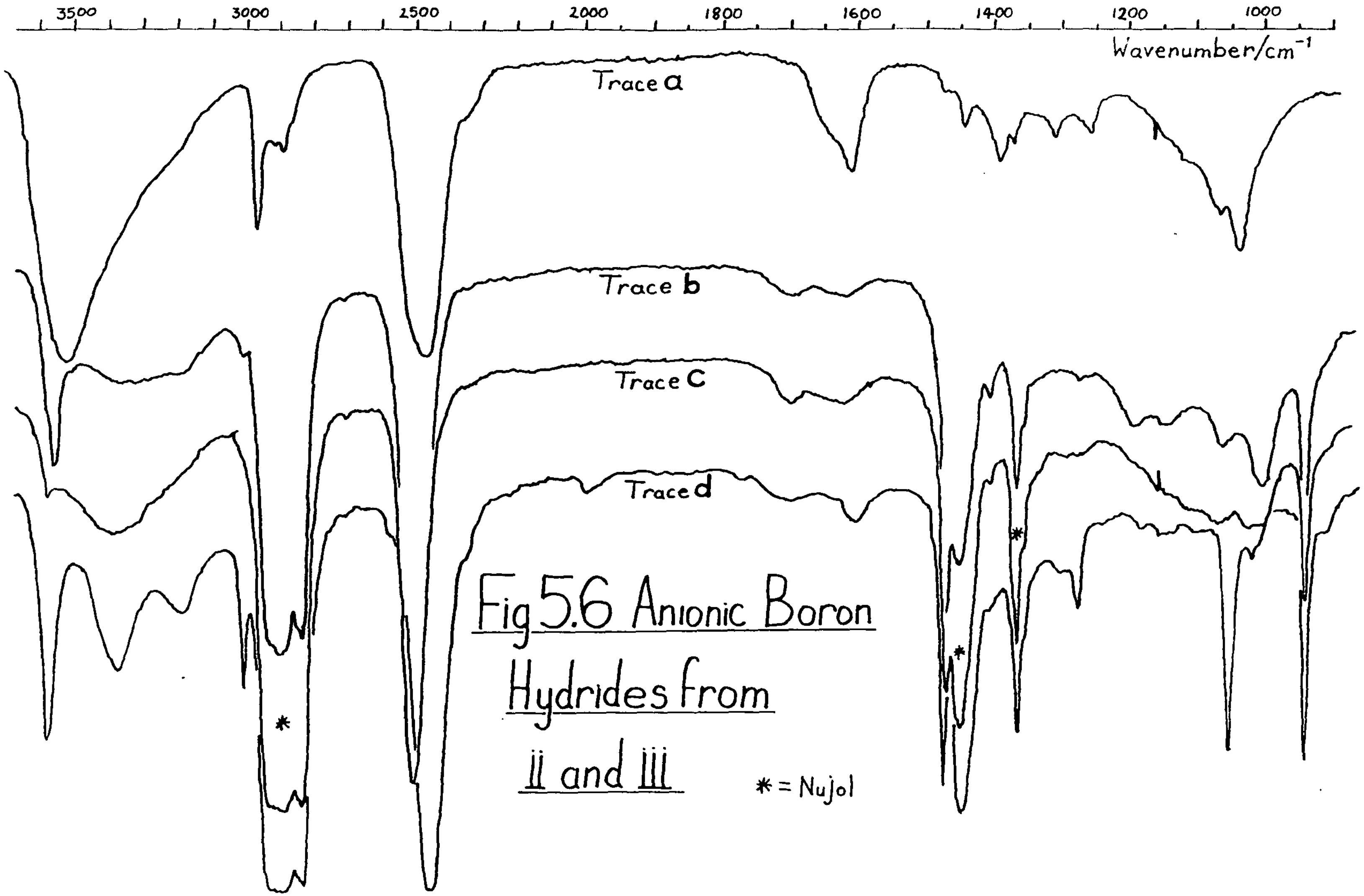
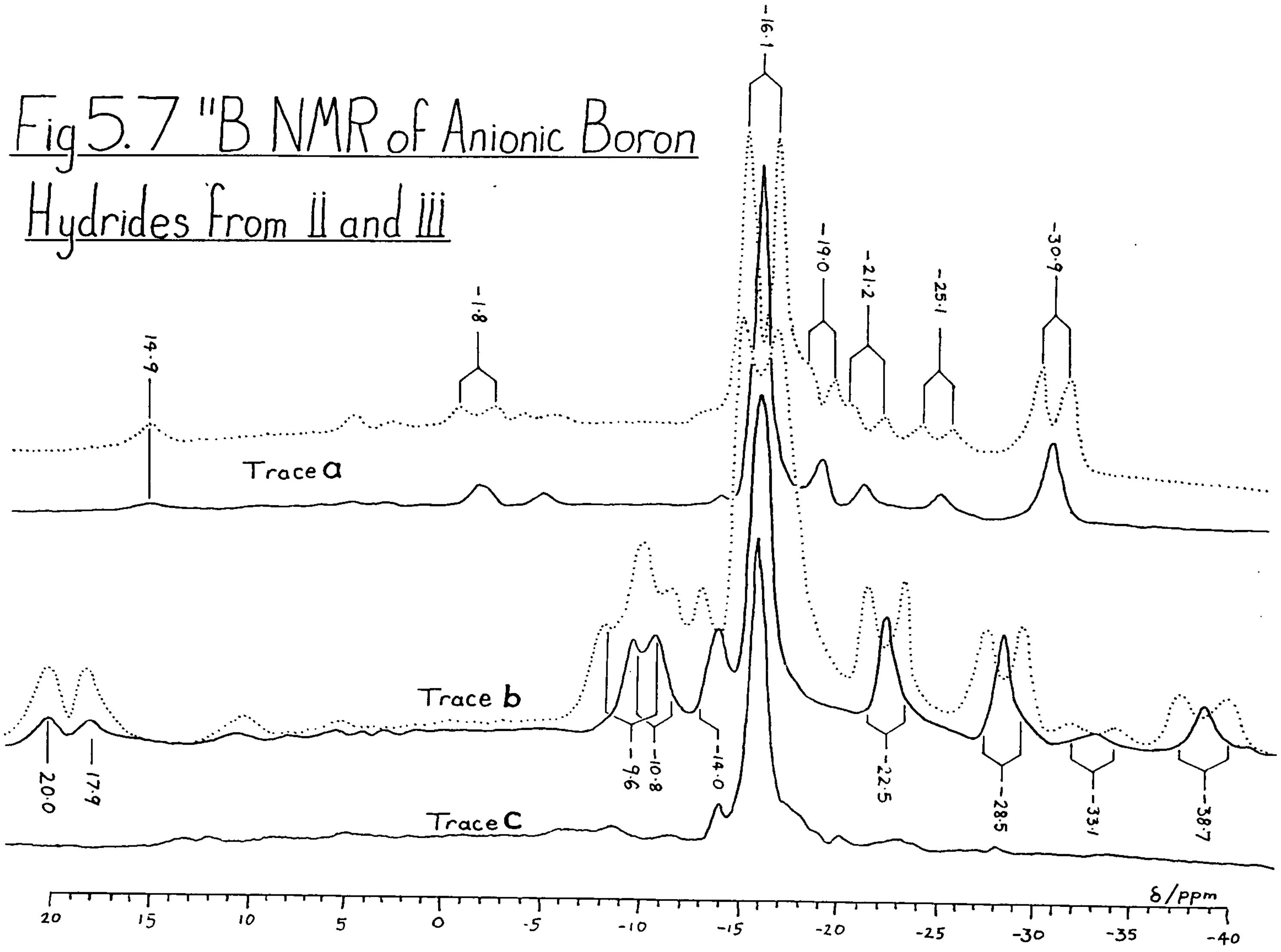


Fig 5.6 Anionic Boron Hydrides from ii and iii

* = Nujol

Fig 5.7 ^{11}B NMR of Anionic Boron Hydrides from II and III



neutralised and this solution evaporated to dryness, as in **ii**, to obtain a white solid which was ground to a fine powder. This powder was then liberally washed with ether and the washings treated with $[Me_4N]Cl$ as above to obtain 12·2mg of precipitated salts. This material's IR spectrum is shown in *fig. 5.6 trace d* but because of its low solubility in both acetonitrile and acetone only poor ^{11}B NMR spectra were obtained. A signal around -16ppm indicated the presence of some $[B_{12}H_{12}]^{2-}$.

iv. Hydrolysis of MgB_2 by 7M H_3PO_4 at Reduced Pressure

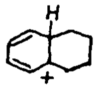
The apparatus in *fig. 5.1* was slightly modified to allow a small leak of N_2 into the reaction flask during the reaction and a manometer and needle valve were connected in series from the waste gas exhaust to a pump. Otherwise, the experiment was conducted as in 5.2.1. 3·510g (76·4mmol) MgB_2 from B1 was added to 7M H_3PO_4 as usual but the reaction temperature was lowered to 50°C (because of excessive foaming) and the needle valve was continuously adjusted to maintain the pressure inside the apparatus between 15 and 17mmHg. The combined volatiles from traps 1 and 2 gave a pressure of 30mmHg in the vacuum line and the ^{11}B NMR spectrum was identical to that obtained in **i** so that the total borane yield was calculated to be 1·6%.

v. Hydrolysis of MgB_2 by 7M H_3PO_4 with Added Anti-foaming Agent

3·605g (78·5mmol) MgB_2 from B3 was reacted with 7M H_3PO_4 using the method described in 5.2.1 except that five drops of anti-foaming agent (BDH Ltd) were added to the acid before starting the experiment. Although this had no apparent effect upon the troublesome foam the borane yield had risen slightly (compared to **ii** and **iii** - standard reactions using B3) to 0·92% but B_5/B_4 had fallen to ~0·2. The anionic borane salts (43·4mg) were isolated by ether extraction of the resultant acid solution and were then precipitated with [Me_4N]Cl, as described in iii. Their ^{11}B NMR spectrum was identical to that in *fig. 5.7 trace b.*

vi. Hydrolysis of MgB_2 by 7M H_3PO_4 Including a Second Hydrocarbon Phase

Two reactions were performed here; one with added tetrahydronaphthalene (THN), to see if the second phase affected borane production, and one with added benzene to see if the boranes could be copyrolysed in the conditions of the hydrolysis to give $B_{10}H_{14}$.

3·676g (80·0mmol) MgB_2 from B1 was reacted with 7M H_3PO_4 using the method described in 5.2.1 except that 20ml of THN (distilled from P_2O_5 and K[MnO_4] under 3cmHg at 98-100°C) were mixed with the acid. Although the volatiles from this experiment were accidentally lost before the ^{11}B NMR spectrum could be taken, IR showed that the total yield of boranes and their relative proportions were roughly comparable to i. During the reaction it was noted that the THN had the useful property of completely suppressing the foam so that the rate of powder addition was only limited by the extremely rapid evolution of non-condensible gas (presumably H_2). However, after the reaction, the THN layer was brown and congealed on cooling. This was later found to be the product of its reaction with H_3PO_4 (perhaps via ) so that it is suggested that any future such reaction requiring an involatile hydrocarbon might use trans-decalin. Also, it is noted that adding five drops of THN to the standard reaction conditions i-iii only suppressed foaming for about a minute after which the foam returned.

In the reaction with 20ml of benzene added to the acid, the volatiles were not studied because it would have been difficult to separate them from the benzene. Instead traps 1 and *2* in *fig.*

5.1 were replaced by an iced-water reflux condenser fitted to neck *c*, and connected directly to the exhaust gas scrubber. The addition of 3·431g (74·7mmol) MgB_2 from **B1** to the acid was then conducted similarly to the method described in 5.2.1. After the reaction the precipitates were filtered from the resultant solutions and the yellow benzene phase separated from the H_3PO_4 under N_2 to be dried over P_2O_5. The organic solution was then filtered from the drying agent and the benzene driven off under reduced pressure to leave a yellow oil with $B(OH)_3$ (identified by IR) suspended in it. The oil was diluted with a little cyclohexane, decanted from the $B(OH)_3$ and the cyclohexane driven off to return the oil. Stored for 3 days under N_2, many large needle-like crystals were seen to form, both in the oil and on the dry upper surfaces of the flask, and several were >5mm in length. The mass spectrum and ^{11}B NMR of the crystals showed them to be pure $B_{10}H_{14}$ as expected from B_4H_{10}/B_6H_{10} copyrolysis (see 3.3.6, p.67). In line with this, $B_{10}H_{14}$ (and B_2H_6) also seemed to be produced if the borane samples were left to stand at room temperature see *fig. 5.4 trace c*. This spectrum shows the same sample as in *trace a* only it has been kept at ambient temperature for two weeks and whilst the resonances for B_6H_{10} have disappeared those for $B_{10}H_{14}$ are now visible.

vii. Hydrolysis of MgB_2 by 88% H_3PO_4

3·595g (78·3mmol) MgB_2 from **B2** was reacted with 90ml 88% (~16M) H_3PO_4 using a similar method to that described in 5.2.1. 20ml of THN had to be added to the acid to destroy the now extremely persistent foam. The borane products obtained directly from this reaction were conveniently almost dry, due to the low vapour pressure of water over such concentrated acid. The total borane yield was unremarkable at 0·96%, but there was very little B_6H_{10} and B_6/B_4 had risen to 1·3.

viii. Hydrolysis of MgB_2 by 100% Fused H_3PO_4

3·593g (78·2mmol) MgB_2 from B2 was reacted with 100g (1·02mol) pure molten H_3PO_4 (Koch-Lite, m.p.=38-42°C) using a similar method to that described in 5.2.1. The MgB_2 was added to the acid over 2 hrs but the reaction was very slow and had to be left for another 18 hrs to complete. A continous current of dry N_2 was passed through the apparatus to avoid the risk of air suck-back through the exhaust gas scrubbers if the temperature of the reaction flask should drop slightly. A very powerful stirrer was required for this experiment because, apart from the foam being very long lived (but easy enough to control because of the slowness of reaction), an almost solid grey mud remained in the reaction flask after 20 hrs. The MgB_2 was definitely completely consumed here because addition of 30ml of water to the mud liberated no further gases.

This experiment gave the highest total yield of volatile boranes (2·0%) consisting of just B_5H_9 and B_4H_{10} with $B_5/B_4 \simeq 1{\cdot}6$. Additionally, 2·4mg (0·13%) $B_{10}H_{14}$ was recovered from trap 1.

This reaction was also repeated but with a current of hydrogen flowing through the apparatus. Emptying the traps after 8 hrs yielded 28·7mg B_4H_{10} and B_5H_9 and continued collection for another 16 hrs yielded a further 11·2mg. The total yield and relative proportions of B_5H_9 and B_4H_{10} were the same as with the experiment conducted under N_2.

ix. Hydrolysis of a Suspension of MgB_2 by 100% Fused $H_4P_2O_7$

The apparatus in *fig. 5.1* was modified in this experiment by replacing the powder addition apparatus by a graduated pressure equalising dropping funnel containing distilled water. 3·531g (76·9mmol) MgB_2 from B2, mixed with 25·0g (140mmol) $H_4P_2O_7$ (Koch-Lite, m.p.=58-61°C), was placed in the reaction flask and heated to 70°C under N_2; MgB_2 and molten $H_4P_2O_7$ do not react. With powerful stirring, the water was very slowly added to the acid a drop at a time, waiting for the initial rapid rate of gas evolution to slow significantly before adding another drop. This procedure gave a reassuringly sedate rate of reaction up ~0·5ml added water. However, on adding one further drop the reaction accelerated drastically over a few seconds during which time the foam expanded to fill the reaction flask and the temperature exceeded the thermometer scale. This fast reaction did not produce an explosion probably only because the foam froze. After this, adding a further 10ml of water produced no such similar uncontrollable event and gas evolution progressed smoothly until the reaction was completed.

Whilst the total borane yield, 0·94%, was unremarkable the relative proportions of the boranes were comparable to those obtained from the standardised MgB_2 hydrolysis in 7M H_3PO_4, **i-iii**, and the fact that B_6H_{10} was produced at all, when the similar reaction with 100% H_3PO_4, **viii**, produced none, was unexpected. Consequently, the results from this experiment were viewed with doubt. It was not possible to devise a safer technique for this reaction.

x. Hydrolysis of MgB_2 by 7M H_3PO_4 Under Ultrasonic Irradiation

In this experiment the reaction flask was modified, as shown in *fig. 5.1*, by the addition of a new side arm through which a titanium 5mm microtip ultrasonic horn was inserted; the apparatus was made gas tight by a flexible rubber seal around the wide portion of the horn where it fitted into the ultrasound generator housing. The 20MHz "Sonicator" was set to continuous mode and run at 25% maximum power throughout MgB_2 addition. Apart from the adaptations necessary for ultrasonic irradiation, the experiment was conducted as described in 5.2.1 where 3·584g (78·0mmol) MgB_2 from B3 was reacted with 7M H_3PO_4. Two effects of ultrasonics during the experiment should be noted: firstly, it raised the temperature of the reaction solution by 15-20°C so that the temperature of the water bath had to be adjusted accordingly; secondly, it completely suppressed the previously unavoidable foam. This meant that powder addition was easily completed within 3/4 hour.

The total percentage yield of boranes had more than doubled (compared to the standard reactions **ii** and **iii** also using MgB_2 from B3) and, whilst the B_4H_{10} and B_5H_9 yields had doubled with $B_5/B_4 \simeq 0{\cdot}3$, the B_6H_{10} yield had increased by a factor of 4·6. 109·4mg of anionic borane salts were isolated by ether extraction of the resultant acid solution followed by their precipitation with $[Me_4N]Cl$ as described in **iii**. The ^{11}B NMR of the salts was identical to that in **iii** (see *fig. 5.7 trace b*), therefore their yield had increased by a factor of 2·5.

xi. Hydrolysis of MgB_2 by 100% Fused H_3PO_4 Under Ultrasonic Irradiation

This was an attempt to repeat **viii** but including the adaptations for ultrasonic irradiation described in **x**. As in **x** the foam was conveniently completely suppressed. However, after the addition of just 1·038g (22·6mmol) MgB_2 from B2 to the molten H_3PO_4 the ultrasonic effect ceased and this was later found to be because the ultrasonic horn had become cracked and pitted. The experiment was not repeated because of the cost of the accident (£100 per horn) although it may be that it was caused by the age of the horn and not the conditions under which it was used. The reaction gave 0·65% of solely B_5H_9. It may be that this low yield was caused by incomplete reaction of the boride or experimental error incurred by the small quantities of B_5H_9 studied. This experiment could be valuably repeated and although the yield seemed to be low the rate of gas evolution still appeared to be very much faster than the unirradiated **viii**.

xii. Hydrolysis of MgB_2 by H_3PO_4 in Hexamethyl Phosphoric Triamide (HMPT)

The same apparatus was used for this experiment as in **ix**. A suspension of 3·546g (77·2mmol) MgB_2 from B2, in a solution of 50·g (0·51mol) crystalline H_3PO_4 dissolved in 60ml HMPT ($(Me_2N)_3PO$), was prepared without any apparent reaction occuring. When the reaction flask had reached 65°C water was slowly added to the suspension from a dropping funnel causing brisk gas (H_2?) evolution. However, when the volatiles were examined there were no boranes present. The solution from the reaction was not examined since the solvent is highly carcinogenic. In retrospect this is unfortunate because the anionic boron hydrides formed under the standard conditions of **ii** and **iii** had not been discovered at the time.

xiii. Hydrolysis of MgB_2 by $(PhO)_2P(O)OH$ in THN

The same apparatus was used for this experiment as in **ix**. A suspension of 2·200g (50·1mmol) MgB_2 from B2, in a solution of 22·83g (91·2mmol) $(PhO)_2P(O)OH$ in 90ml THN, was prepared without any apparent reaction occuring; unlike H_3PO_4, $(PhO)_2P(O)OH$ did not react with THN. Water was slowly added to the suspension and after about 1 hr, when 2·0ml (110mmol) water had been introduced, the rate of gas (H_2?) evolution rapidly dropped to a very slow trickle; since there was a slight excess of boride present this is probably due to the much slower reaction of water with MgB_2 (see 2.3, p.34).

Only a low (0·34%) yield of boranes was produced here but, interestingly, this consisted of just B_6H_9 and B_6H_{10} in the relative proportions of 4:1. The involatile products of this reaction all precipitated from the THN solution and were washed with toluene to remove as much of the THN as possible.

Dissolution of these solids in EtOH and filtration removed most of the $B(OH)_3$ and the recovered solids had a quite sharp B-H stretch at 2495cm^{-1}. This sample was completely soluble in Et_2O but no way was found to separate the diphenyl phosphate salts from the boron hydride species so that these were not examined any further.

xiv. Hydrolysis of MgB_2 by 7M H_3PO_4 in the Presence of Iron

3·654g (79·6mmol) MgB_2 from B3 was reacted with 7M H_3PO_4 in which 0·470g (8·4mmol) iron filings had previously been dissolved, using the method described in 5.2.1. The total borane yield, 0·72%, was approximately the same as the standard reactions **ii** and **iii** with $B_5/B_4 \simeq 0{\cdot}4$ but very little B_6H_{10} was produced.

xv. Hydrolysis of MgB_2 by 7M H_3PO_4 in the Presence of Nickel

The procedure for this experiment was the same as in **xiv** except that ~1g (3·5mmol) $NiSO_4 \cdot 7H_2O$ was added to the acid. 3·501g (76·2mmol) MgB_2 from B2 was reacted with the acid giving a 0·55% total borane yield. Although no standard reaction was performed for B2, the total borane yield was comparatively low and, whilst the distribution of the individual boranes was roughly similar to **i-iii**, the proportion of B_6H_{10} seemed somewhat reduced (see *Table 5.2*).

xvi. Hydrolysis of MgB_2 by 7M H_3PO_4 in the Presence of the Tetramethylammonium Cation

The procedure for this experiment was the same as in **xiv** except that ~0·9g (8·2mmol) $[Me_4N]Cl$ was added to the acid. 3·602g (78·4mmol) MgB_2 from B3 was reacted with the acid giving a 0·45% total borane yield (significantly lower than 0·75% for the standard reactions **ii** and **iii**) consisting almost entirely of B_4H_{10} and B_5H_9 with $B_5/B_4 \simeq 0{\cdot}4$ and only a trace of B_6H_{10}.

After the reaction, apart from the $B(OH)_3$ and boride residue normally expected, there was also a small amount of fine powder which floated on top of the resultant acid solution. The acid solution was diluted to redissolve the $B(OH)_3$ and the new powder and the boride residue were filtered into a porosity 4 filter stick. After drying in vacuo the solid in the filter stick was broken up and thoroughly washed with acetonitrile (3 x 20ml) which was filtered off having dissolved the new precipitate. The solvent was removed from the yellow washings at reduced pressure and the IR and ^{11}B NMR spectra of the resultant 43·4mg of solid are shown in *fig. 5.8 trace a* and *fig. 5.9 trace a* respectively. A further 15·9mg of anionic borane salts was isolated from the acid solution still remaining by ether extraction and was then precipitated with $[Me_4N]Cl$ as described in iii. The IR and ^{11}B NMR spectra of this second batch of salts are shown in *fig. 5.8 trace b* and *fig. 5.9 trace b* respectively.

xvii. Hydrolysis of MgB_2 Mixed with Metallic Magnesium by 7M H_3PO_4

Before starting the reaction 3·550g (77·3mmol) MgB_2 from B2 was mixed with 7·5g (309mmol) powdered Mg but othewise the experiment was conducted using the method described in 5.2.1. During the reaction the acid solution became a lot more viscous than under the standard conditions and this, combined with the obviously far larger amount of hydrogen produced here, made foaming particularly awkward. A greater volume of acid is recommended for any repeat of this experiment. Since no standard reaction was studied for B2 comparisons are difficult and, whilst the total borane yield of 1·3% is unexceptional, B_5/B_4 does seem to be a little low at ~0·2.

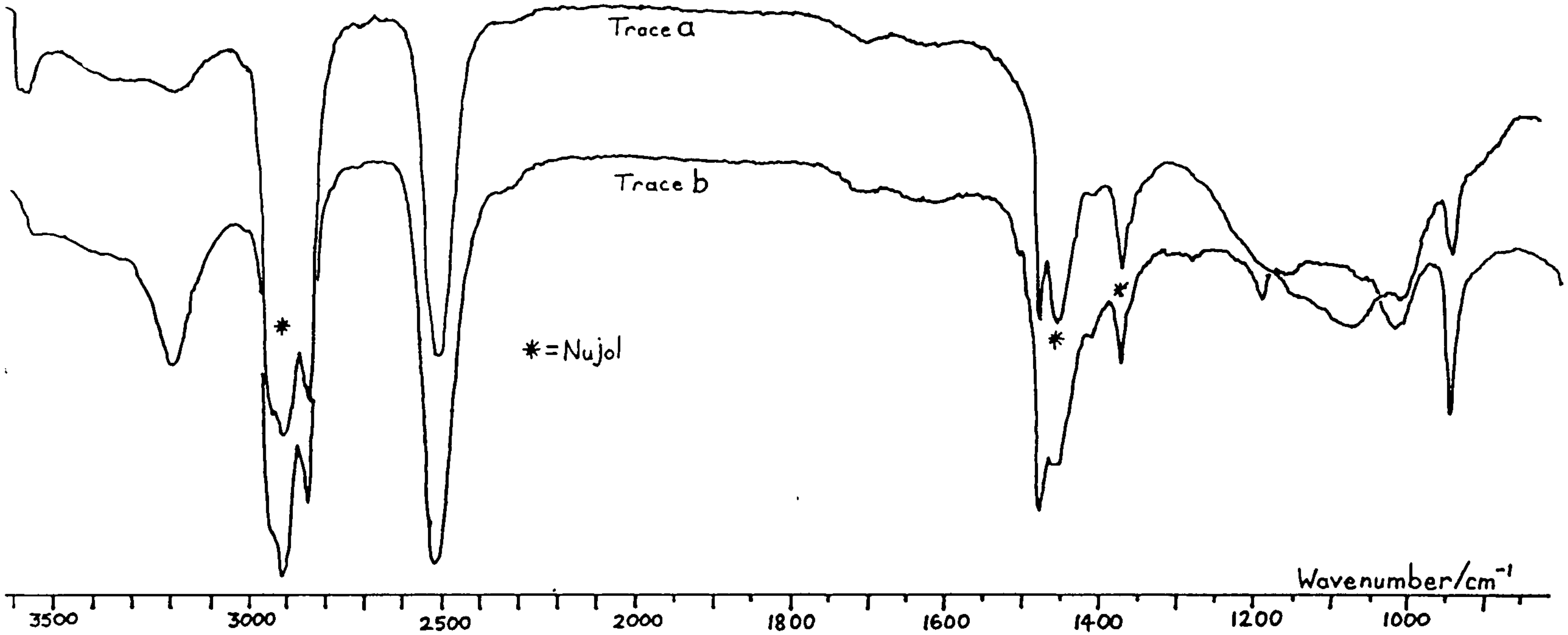
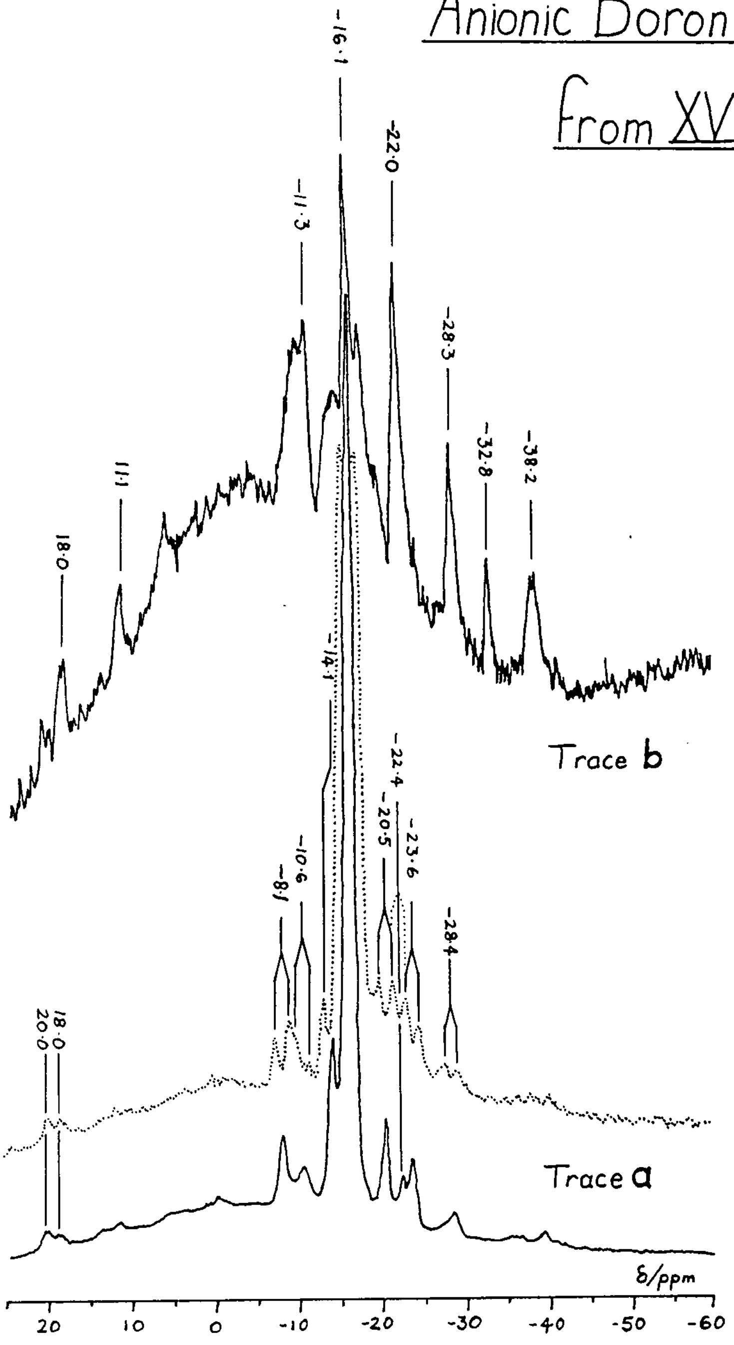


Fig 5.8 Anionic Boron Hydrides from XVII

Fig. 5.9 ^{11}B NMR of Anionic Boron Hydrides from XVII



xviii. Attempted Carborane Formation: Hydrolysis of MgB_2 by 7M H_3PO_4 in the Presence of Phenyl Acetylene

The apparatus for this reaction was the same as in *fig. 5.1* except that a double-walled reflux condenser was placed between the reaction flask and traps 1 and *2*. Apart from the 7M H_3PO_4, 1·0ml of phenyl acetylene dissolved in 20ml of benzene was placed in the reaction flask and to this was added 3·611g (78·6mmol) MgB_2 from B1 using the method described in 5.2.1. Since benzene escaped from the reaction flask with the boranes the yield of volatiles could not be measured. However, ^{11}B NMR showed them to consist of just B_4H_{10} and B_5H_9 with $B_5/B_4 \approx 0{\cdot}3$ - presumably all the B_6H_{10} is returned to the reaction flask. After the reaction, the benzene layer was separated, dried and concentrated to a yellow oil. Two-dimensional and three-dimensional COSY ^{11}B NMR were used to search for carboranes in this material but showed that $B_{10}H_{14}$ was the only boron hydride contained in it.

xix. Attempted Carborane Formation: Hydrolysis of MgB_2 by 7M H_3PO_4 in the Presence of Phenyl Acetylene and Diethyl Sulphide

In this experiment the traps in *fig. 5.1* were not used, but instead, iced-water and CO_2/acetone reflux condensers were connected in sequences between neck *c* and the exhaust gas scrubbers. Apart from the 7M H_3PO_4, 20ml benzene with 1ml phenyl acetylene and 1ml diethyl sulphide dissolved in it were placed in the reaction flask. Using the method described in 5.2.1, 3·489g (76·0mmol) MgB_2 from B2 was added to this mixture and after completing the reaction the organic phase was isolated as in <u>xviii</u>. It was expected that $B_{10}H_{14}$ would be produced here under similar conditions to <u>xviii</u> and so it was hoped that the Et_2S would catalyse carborane formation. However, ^{11}B NMR of the benzene solution showed $B_{10}H_{14}$ to be the only boron hydride present.

xx. Attempted Carborane Formation: Hydrolysis of MgB_2 by Fused H_3PO_4 Under a Solution of Phenyl Acetylene in Diethyl Sulphide

The apparatus was set up as in **xix** and 7·2g (73·5mmol) crystalline H_3PO_4, 50ml of Et_2S and 3·20g (31·4mmol) phenyl acetylene were placed in the reaction flask. To this was added 3·553g (77·3mmol) MgB_2 from B2 but without much apparent reaction; during this phase of the experiment the original droplets of molten H_3PO_4 combined with the MgB_2 to form large sticky globules - it is noted that ultrasonics would have broken these up into a much more homogeneous dispersion. The powder addition apparatus was now replaced by a dropping funnel and 5ml of water was slowly added to the reaction mixture over 1hr during which time brisk gas evolution occured. The reaction was left to complete for a further 2hrs.

After the reaction the organic phase was isolated and the Et_2S driven off under reduced pressure to give a brown oil. A pale yellow oil (strong absorptions at 1684, 1268 and 762cm^{-1} but no B-H stretch) distilled from the remaining gum at 90°C under dynamic high vacuum. The residue contained boron hydrides with a B-H stretch at 2520cm^{-1} and these could be further purified by column chromatography on silica using a dichloromethane eluant. Collecting the fraction with $R_f \approx 0{\cdot}8$ removed a major impurity with a strong broad absorption at 1460cm^{-1}. ^{11}B NMR of the resultant gum gave doublets at $\delta=+5{\cdot}1$, $-14{\cdot}2$, $-15{\cdot}7$, $-20{\cdot}6$, $-25{\cdot}9$ and $-38{\cdot}1$ ppm. This material was not further examined because its lack of volatility indicated that it did not contain any neutral carboranes and the resonances at $-14{\cdot}2$, $-20{\cdot}6$ and $-38{\cdot}1$ ppm were probably those of the anionic boron hydrides observed in experiments **ii**, **iii**, and **xvi**.

xxi. Attempted Carborane Formation: Hydrolysis of MgB_2 by p-Toluene Sulphonic Acid in Diethyl Sulphide Solution in the Presence of Phenyl Acetylene

The apparatus was set up as in **xix** and 28·61g (151mmol) p-Me-$C_6H_4SO_3H \cdot H_2O$, 50ml of Et_2S and 3·20g (31·4mmol) phenyl acetylene were placed in the reaction flask; the acid was completely soluble in this system. 3·640g (79·3mmol) MgB_2 from B2 was added to the reaction flask at 60°C during which time some gas was evolved; the water in the hydrated acid was probably responsible for this reaction. After this the powder addition apparatus was replaced by a dropping funnel and a further 3ml water was added to the mixture over 1hr. When the reaction had finished the Et_2S was distilled from the reaction flask under reduced pressure leaving a mass of grey solid. This was broken up and thoroughly washed with toluene. Driving off the toluene from the washings left a brown oil which was treated exactly like the similar oil obtained in **xx**; the same pale yellow oil distilled from this residue at 90°C under dynamic high vacuum as in **xx**. The material collected by chromatography at $R_f \approx 0 \cdot 8$ possessed a strong B-H stretch at 2520cm^{-1} but this time the ^{11}B NMR spectrum displayed only a single doublet resonance around -16ppm.

5.3 Results and Discussion

5.3.1 Discussion of the Boranes Produced During MgB_2 Hydrolysis

For a review of MgB_2 hydrolysis the reader is directed to part 2.3 of this thesis and the refs. therein. The results of all the experiments for which the borane yield and distribution were determined are shown in *table 5.2*.

Comparing the total borane yields in *table 5.2* to those obtained by previous workers in this area they are clearly in the low end of the range expected from magnesium diboride although not

Table 5.2 Borane Yield and Distribution Data

Reaction Number	Conditions of MgB_2 Hydrolysis	Bottle Number	Amount of MgB_2 /mmol	Mass of Boranes /mg	M, Total Molar yield of Boranes/mmol	Pressure of mixed Boranes/mmHg	Scaling factor, C[e]/ mmol/mmHg	Total Borane Yield, %	Rel, Molar Yield			B_5H_4	Yield, %		
									B_4H_{10}	B_5H_9	B_6H_{10}		B_4H_{10}	B_5H_9	B_6H_{10}
i,	7M H_3PO_4 standard	B1	78·4		0·443[a]	27		1·4	0·47	0·17	0·36	0·36	0·53	0·24	0·60
ii,	7M H_3PO_4 standard	B3	78·5	15·0	0·259	18	0·0144	0·74	0·64	0·26	0·10	0·41	0·42	0·21	0·10
iii,	7M H_2PO_4 standard	B3	77·4	15·4	0·266	18	0·0148	0·77	0·64	0·26	0·10	0·41	0·44	0·22	0·10
iv,	7M H_3PO_4, reduced pressure	B1	76·4		0·492[a]	30		1·6	0·47	0·17	0·36	0·36	0·71	0·32	0·77
v,	7M H_3PO_4, anti-foaming agent	B3	78·5	18·8	0·328	22	0·0149	0·92	0·72	0·16	0·12	0·22	0·66	0·15	0·11
vi,	7M H_3PO_4 + 20ml THN[b]	B1	80·0		0·449[a]	27		1·3	0·60	0·20	0·20	0·33	0·67	0·28	0·34
vii,	88% H_3PO_4 + 20ml THN	B2	78·3		0·328[a]	20		0·96	0·43	0·56	0·01	1·3	0·36	0·59	0·01
viii,	100% Fused H_3PO_4 under N_2	B2	78·2	42·7	0·670	37	0·0181	2·0	0·38	0·62	nil	1·6	0·65	1·35	nil
	100% Fused H_3PO_4 under H_2	B2	78·4	39·9	0·670			2·0	0·36	0·64	nil	1·8	0·62	1·37	nil
ix,	100% Fused $H_4P_2O_7$ + 10·5ml H_2O	B2	76·9		0·328[a]	20		0·94[d]	0·66	0·27	0·07	0·41	0·56	0·29	0·09
x,	7M H_3PO_4, Ultrasonics	B3	78·0	35·6	0·597	26	0·0230	1·7	0·60	0·19	0·21	0·32	0·86	0·35	0·46
xi,	100% Fused H_3PO_4, Ultrasonics	B2	22·6	3·3	0·052			0·65[c]	trace	1·0	nil	$+\infty$	trace	0·65	nil
xiii,	Suspension in $(PhO)_2P(O)OH$/THN+2ml H_2O	B2	50·1	4·1	0·063	4·5	0·0140	0·34	nil	0·80	0·20	∞	nil	0·27	0·07
xiv,	7M H_3PO_4 with added Iron	B3	79·6	14·3	0·253	16	0·0158	0·72	0·69	0·29	0·02	0·42	0·45	0·24	0·02
xv,	7M H_3PO_4 with added Nickel[b]	B2	76·2		0·197[a]	12		0·55	0·68	0·24	0·08	0·35	0·37	0·13	0·04
xvi,	7M H_3PO_4 with added $[Me_4N]Cl$	B3	78·4	9·3	0·167	10·5	0·0176	0·45	0·74	0·26	trace	0·35	0·32	0·13	trace
xvii,	MgB_2/Mg added to 7M H_3PO_4[b]	B2	77·3		0·449[a]	27		1·3	0·68	0·16	0·16	0·24	0·79	0·23	0·28

$\Sigma C = \overline{0{\cdot}1584}$

$\therefore C = 0{\cdot}016, \quad \sigma = 0{\cdot}003$

a, calculated from M=C x pressure, ±15%

b, only approximate distribution of boranes; determined from IR spectrum

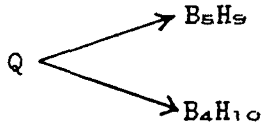
c, value probably too low (see text)

d, reaction very violent, suspect not all the boranes were caught in the traps

e, C=M÷Pressure

exceptionally low. The best method for increasing the borane yield from this reaction is to use the MgB_2/Mg alloy of composition Mg_3B_2 instead of the single phase MgB_2. However, other factors - such as lower purity, lower crystallinity and the general processing - can also increase the yield. It would have been too time consuming to have prepared our own boride and the parameters controlling borane yield have not been precisely defined. Thus it was decided not to aim for the highest possible yield immediately but instead to look for new factors that might improve the yield from commercially available MgB_2. If any particularly promising effects emerged using MgB_2 it seemed probable that these would also apply to the more productive Mg_3B_2. It was hoped that the quite large batches of MgB_2 purchased would give reasonably reproducible results. Whilst it is clear from the results of **ii** and **iii** that samples of MgB_2 taken from the same batch do give repeatable results, comparison of these two experiments with **i** shows that both borane yield and distribution vary when the samples are taken from different batches.

The ^{11}B NMR spectra in *fig. 5.4* show that the three boranes in a fresh sample from MgB_2 hydrolysis are quite clearly and unambiguously identifiable. Although the yields are low in the standard experiments **i-iii** the results are in broad qualitative agreement with those of Timms and Phillips[2] who hydrolysed MgB_2 in 8M H_3PO_4. One of the most notable results from the work in this thesis is that for the eleven experiments using 7M H_3PO_4 the pentaborane to tetraborane ratio always ranges about the average $B_5/B_4=0{\cdot}34$ ($\sigma=0{\cdot}06$). Whilst the relative and absolute B_6H_{10} yields were seen to vary with the batch of MgB_2 used and differed markedly from those of Timms and Phillips, these authors' value of $B_5/B_4=0{\cdot}29$ for MgB_2 hydrolysis in 8M H_3PO_4 agrees well with the values in table *5.2*. Furthermore, these authors' value for B_5/B_4 ranged between $0{\cdot}06$ and $0{\cdot}17$ (average $0{\cdot}10$, $\sigma=0{\cdot}04$) when Mg_3B_2 was hydrolysed in 8M H_3PO_4. An interpretation of this may be that B_5H_9 and B_4H_{10} share a common intermediate, Q, not far back along the pathway to their formation, 5.1. Also it seems that the



5.1a

5.1b

presence of excess Mg in the magnesium boride alloy Mg_3B_2 favours **5.1a** and this may be the reason why B_5/B_4 was rather low in **xvii** when a mixture of MgB_2 and Mg was added to 7M H_3PO_4. It would be worthwhile testing whether or not this is the effect of Mg^{2+} already in the acid solution by performing a hydrolysis, similar to the standard conditions of **i-iii**, but with a large quantity of Mg dissolved in the acid prior to starting the reaction.

The reaction of MgB_2 with 100% fused H_3PO_4, **viii**, was slow but no reaction at all occured between MgB_2 and the very similar 100% fused $H_4P_2O_7$ until water was added, **ix**. In molten H_3PO_4 12·5% of the acid condenses to form $H_4P_2O_7$ and water[3], 5.2, but in molten

$$2\ H_3PO_4 \rightleftharpoons H_2O + H_4P_2O_7 \qquad k \propto 4x10^{-3} \qquad 5.2$$

$H_4P_2O_7$, although the acid reorganises to 17·2% H_3PO_4, 42·5% $H_4P_2O_7$ and the remainder to other higher polyphosphoric acids, there is essentially no free water present. Thus, water is an integral part of the reaction of phosphoric acids with MgB_2, i.e. it is definitely a hydrolysis. This point is supported by the reactions of MgB_2 with H_3PO_4 in HMPT, **ii**, and with $(PhO)_2P(O)OH$ in THN, **xiii** which did not start until water was added; in a 25% solution of H_3PO_4 in ethylacetate the acid is monomeric and 5.2 does not occur - the situation is probably the same in HMPT. This observation leads to the suggestion that the high B_5/B_4 in **vii**, **viii** and **xi**, in which 88% and 100% H_3PO_4 were used, was the result of the low water concentration and not of the high acid concentration or low pH; the reaction with $H_4P_2O_7$, **ix**, is discounted here because the reaction conditions were uncontrollable and the product distribution was very similar to that expected from a reaction in 7M H_3PO_4. B_5/B_4 is thought to be dependant upon water availability because B_4H_{10} was completely absent in the boranes from the reaction of water with a suspension of MgB_2 in a THN solution of $(PhO)_2P(O)OH$, **xiii**. In this initially anhydrous and quite hydrophobic system the acid was relatively dilute and delivery of water to the boride surface was very probably the rate limiting step. Also the low water activity in the reaction of MgB_2 with molten H_3PO_4 could be the cause of the relatively high borane yields.

Another important inference from the reactions in highly concentrated H_3PO_4 is that B_2H_6 is not produced at all during MgB_2 hydrolysis. Although B_2H_6 might hydrolyse in 7M H_3PO_4 it can be prepared in high yield from the reaction of $[BH_4]^-$ with polyphosphoric acid[4] and so it is unlikely that it would have remained below detectable limits in **vii**, **viii** or **xi** if it formed at all. On the other hand, detection of $B_{10}H_{14}$ in **viii** shows that it is almost certainly a minor direct product from MgB_2 hydrolysis; on most other occasions when this borane was observed its formation could be accounted for by B_6H_{10}/B_4H_{10} copyrolysis but here no B_6H_{10} formed and B_2H_6, the other copyrolysis product, was still absent.

Although the relative and absolute yields of B_6H_{10} vary with the source of the MgB_2, its very low yield in the reaction with 88% H_3PO_4, **vii**, and absence with 100% H_3PO_4, **viii** and **xi**, seems to be significant. B_6H_{10} rapidly exchanges H_μ with D_2O [5] and this was thought to proceed via $[B_6H_{10}D]^+$ because salts of this cation have been prepared in the low temperature reaction of B_6H_{10} and HCl [6]. The formation of $[B_6H_{11}]^+$ should be encouraged in strong acid and its production is here suggested to be the cause of the disappearance of B_6H_{10} from amongst the volatile boranes generated by MgB_2 hydrolysis in very concentrated H_3PO_4. This is because the cation should be more soluble than the neutral borane and so open to solvolysis. In this respect it is possible that $[B_6H_{11}]^+$ is the precursor (Q in 5.1) of both B_5H_9 ad B_4H_{10} because the first step in the cation's solvolysis would be expected to be formation of an adduct, $[B_6H_{11}\cdot L]^+$, 5.3, where L could be H_2O or

$$B_6H_{10} + H^+ \rightleftharpoons [B_6H_{11}]^+ \xrightarrow{L} [B_6H_{11}\cdot L]^+ \qquad 5.3$$

$[H_2PO_4]^-$. This species would be isoelectronic to B_6H_{12} and might behave analogously. For instance, solvolysis of the neutral borane with Me_2O gives ~75% B_5H_9 and B_2H_6 [7] and so $[B_6H_{11}\cdot L]^+$ may be able to react similarly as in 5.4. On the other hand, the rapid

$$[B_6H_{11}]^+ + L \longrightarrow B_5H_9 + [H_2BL_2]^+ \qquad 5.4$$

hydrolysis of B_6H_{12} gives B_4H_{10} quantitatively[7] and a related reaction for $[B_6H_{11}\cdot L]^+$ may compete with 5.4 to give B_4H_{10}, this alternative being favoured by dilute aqueous acid. A test of this hypothesis would be to shake B_6H_{10} with a range of concentrations of H_3PO_4.

Timms and Phillips[2] reported that the borane yield from Mg_3B_2 hydrolysis decreased when high purity boron was used in its manufacture and so it was decided to test a few metal cations for catalytic effects. Iron and nickel were chosen because both will precipitate borides when the cation is added to solutions of $[BH_4]^-$ [8]. Thus it seemed reasonable to suppose that they might interact with the surface of the boride during hydrolysis. In the case of added iron, **xiv**, the total borane yield was not very different from the standard reactions, **ii** and **iii**, but the proportion of B_6H_{10} in the volatiles was significantly reduced. In the case of added nickel, **xv**, the borane distribution was unremarkable although the total yield was, perhaps, rather low; the significance of this was not easy to judge without a standard for B2. Whatever the cause of these effects they do not seem to be specifically related to the fact that they are transition metal cations. This is because addition of the bulky, but non-complexing and fairly inert, $[Me_4N]^+$, **xvi**, gave by far the most pronounced effects where the total yield decreased by a factor of ~0·6 and only a trace of B_6H_{10} was produced. The original reason that $[Me_4N]^+$ was added to the reaction mixture was to try and trap any anionic polyboron intermediates as insoluble precipitates (see 5.3.2, p.166). However, since the first several stages of hydrolysis must necessarily occur at the surface of the boride, it may be that the effects of $[Me_4N]^+$ were caused by its interacting with the fragmenting surface. This is because the boron sublattice in MgB_2 can be regarded as an infinite polyboron anion (see 2.2.2, p. 24) and the cation may be able to bind electrostatically to it during hydrolysis - perhaps hindering access of reactants from the solution or the escape of products.

The use of ultrasonics during MgB_2 hydrolysis was one of the most promising techniques tested in this project for increasing the borane yield. Ultrasonics[9] alter the progress of a reaction in three main ways:-

a) The high temperature/pressure regime inside the cavitation bubbles causes species present as vapour to react differently.
b) The collapse of cavitation bubbles produces extremely high pressures and these may force a reaction.
c) These two effects may cause a reaction at the gas/liquid interface.

The root cause of all the large scale effects of ultrasonics known to date is cavitation; a consequence of ultrasonic irradiation in the reaction of a solid with a liquid is that the solid is rapidly broken up into a dispersion of very fine particles. This is because the surface of the solid acts as a nucleation site for cavitation bubbles and the shock of their collapse shatters the solid. This implies that in the sonicated hydrolysis of MgB_2 any changes in the reaction pathway will be most pronounced on or near the surface of the boride particles.

The first visible effect of ultrasonics upon MgB_2 hydrolysis in 7M H_3PO_4, **x**, was suppression of the otherwise troublesome foam. This may account for the disproportionately large increase in the yield of B_6H_{10}, compared to B_4H_{10} and B_5H_9, because it would reduce the contact time of the B_6H_{10} with the acid and so inhibit 5.3. However the more than doubled total borane yield is likely to have a more fundamental cause. The principal volatiles inside the cavitation bubbles will be H_2 and water vapour and it is thought that ultrasonics enhance a reaction of H_2 with the boride or a dissolved species. This is preferred here over a reaction involving water because low water activities have already been associated with higher yields. If H_2 increases the borane yield then this might explain the higher productivity of Mg_3B_2 or of MgB_2 mixed with powdered Mg (see 2.3, p.35); reaction <u>xvii</u>, which attempted to repeat the latter, was inconclusive. Another experiment which attempted to test this hypothesis was the reaction of MgB_2 with molten H_3PO_4, <u>viii</u>, which was conducted under a flow of N_2 as well as under H_2. The results from both experiments were identical but it is possible that the foam prevented contact between the molten acid and the gas above it. A better test would be to perform the experiment under the influence of ultrasonic irradiation which would have the doubled advantages of destroying the foam and probably actively increasing the exchange of gases between the liquid and atmosphere above it.

No boranes were produced in <u>xii</u> and this is thought to be the consequence either, of HMPT being a strong enough Lewis base to cleave the boranes, or of HMPT being a common solvent for boranes and water causing rapid hydrolysis; c.f. hydrolysis of B_5H_9 in damp dioxan is very fast[10]. Reaction <u>xiii</u> avoided this second problem and produced just B_5H_9 and B_6H_{10} although why the yield should have been comparatively so low is not understood. It is notable that just over 2 moles H_2O per mole MgB_2 were required to complete this reaction. Further investigation of non-aqueous systems could prove valuable because, as <u>xiii</u> shows, they may well be useful for controlling the distribution of boranes obtained.

5.3.2 Discussion of the Involatile Products of MgB_2 Hydrolysis

The X-ray powder photograph of the dark, insoluble boride residue obtained in the standard experiment **iii**, showed clearly that it contained no unreacted MgB_2. Moreover, comparison to the powder photographs of MgB_4 and MgB_7 [11] (MgB_7 originally denoted MgB_6) showed that neither of these was present. Although the lines for the residue were all weak and diffuse, its powder photograph did show quite a marked similarity to that for an, as yet uncharacterised, higher magnesium boride prepared in the high temperature reaction of amorphous boron and magnesium (chap. 2, ref. 40). The weight of residue recovered constituted >10% of the weight of MgB_2 used in the hydrolysis and it seems unlikely that it was an impurity in the starting material since its strongest line was not visible in the powder photograph of a sample of MgB_2. This implies that it was a product although samples of MgB_2 can be prepared which dissolve completely in aqueous acids, leaving no residue. The origins of this material are unknown but might be resolved by a study of MgB_2 prepared in the laboratory under known conditions.

The $B(OH)_3$ recovered from the standard reaction **iii**, only contained about a quarter of the total amount of boron from the MgB_2. Whilst it is possible that as much as 40% of the starting boron could have ended up in the insoluble residue (assuming it is a higher boride or even a form of elemental boron), at least 25% still remained in the acid solution. This might be in the form of various mixed anhydrides of phosphoric and boric acids[3], e.g. borophosphate anion or solvated boron phosphate. However, Duhart[11] reported that the reaction of MgB_2 with 1M HCl at 15°C converted 21·5% of the starting boron to an unidentified, dissolved reducing species and the unrecovered boron in **ii** might be in a similar form.

The boron hydride species recovered by ether extraction of the resultant acid solution from the standard experiment **iii** were precipitated with [Me_4N]Cl and so it seems that they were anionic. Consequently the largest doublet signal in the ^{11}B NMR spectrum of these salts, $\delta = -16{\cdot}1$, was assigned to $[B_{12}H_{12}]^{2-}$ (see *fig. 5.7, trace b*) although no suitable assignment for the other peaks could be suggested from the spectra of the known anions. The anions obtained in **ii** were isolated from the ether extract using a method not involving precipitation with [Me_4N]Cl, and had a completely different ^{11}B NMR spectrum (see *fig. 5.7 trace a*). The only major doublet in this spectrum, apart from that for $[B_{12}H_{12}]^{2-}$, was observed at $\delta = -30{\cdot}9$ppm and this, along with the smaller doublet $\delta = -1{\cdot}8$ppm, was assigned to $[B_{10}H_{10}]^{2-}$. All the other occasions on which the ether extracts were examined involved precipitating the anions with [Me_4N]Cl but since $[Me_4N]_2[B_{10}H_{10}]$ is water soluble (chap. 4, ref. 1) this anion was not observed again. In any future study of the anionic products from MgB_2 hydrolysis it is recommended that other counter ions which give less water soluble salts with $[B_{10}H_{10}]^{2-}$ e.g. $[Et_4N]^+$, Cs^+, should be tested.

It is highly unlikely that anionic species could have formed from a neutral precursor under the strongly acidic conditions used in this project. Instead it would seem reasonable to suggest that they were generated directly from the fragmentation of the anionic boron sublattice of the boride. This also suggests that the direct precursors of the neutral boranes are discrete borane anions. For this reason the standard reaction was repeated with a small quantity of [Me_4N]Cl added to the acid solution, **xvi**, to see if any anionic intermediates could be trapped as insoluble salts; as above with the ether extraction of the acid solutions, replacing $[Me_4N]^+$ with $[Et_4N]^+$ or Cs^+ in this experiment could be more informative. The ^{11}B NMR spectrum of the $[Me_4N]^+$ salts precipitated during MgB_2 hydrolysis are shown in *fig. 9 trace a*. The doublets at $\delta = -10{\cdot}6$, $-14{\cdot}1$, $-16{\cdot}1$, $-22{\cdot}4$ and $-28{\cdot}4$ppm are all clearly visible in *fig. 5.7 trace b*, but three new doublets, of about equal intensity, can now also be seen at $\delta = -8{\cdot}1$, $-20{\cdot}5$ and

-23·6ppm. These are assigned to $[B_9H_{14}]^-$ [12] but this anion is unlikely to be an intermediate in the formation of the smaller neutral boranes because protonation of $[Et_4N][B_9H_{14}]$ in polyphosphoric acid gives 40% B_2H_6 as well as the boranes observed in MgB_2 hydrolysis[13].

Although no intermediates seem to have been trapped using the above procedure the acid solution from **xvi** was still extracted with ether and treated with $[Me_4N]Cl$ as in **iii**. More anionic species precipitated and the ^{11}B NMR spectrum of this small sample is shown in *fig. 5.9 trace b.* It seems that most of the peaks here have already been observed in *fig. 5.7 trace b* as minor peaks but now they are the predominant signals with only relatively small amounts of $[B_{12}H_{12}]^{2-}$ present. This result is somewhat surprising since these unidentified boron hydrides did not precipitate during the reaction. One interpretation of this is that these species were protonated in the acidic reaction solution but deprotonated in the aqueous $[Me_4N]Cl$ solution and so precipitated. A class of compound that might be able to fit this behaviour is a hydroxyhydroborate which would have to be a zwitterion in acid, $^+H_2O{-}B_pH_q^-$, but an anion in neutral solution, $[HO{-}B_pH_q]^-$. This would explain the hydroxy stretch in the IR spectra of all the anionic boron hydrides isolated during this project, *figs. 5.6 and 5.8*, and is consistent with the isolation of $[HB(OH)_3]^-$ from the hydrolysis of Mg_3B_2 in water (chap. 2, ref.36). Whatever these species may be they do not appear to be stable in the presence of mild base. This was demonstrated in **iii** where the soluble salts in the ether extract were treated with aqueous $Na[HCO_3]$ before precipitation with $[Me_4N]Cl$ and ^{11}B NMR (*fig. 5.7 trace c*) showed that $[B_{12}H_{12}]^{2-}$ was now almost the only boron hydride recovered. The yield of $[B_{12}H_{12}]^{2-}$ was 0·57% so that the production of anionic boron hydrides is at least as important as borane production in MgB_2 hydrolysis.

5.3.3 Discussion of Attempts to Develop a One-Pot Carborane Synthesis

Experiments **xviii** to **xxi** were attempts to produce carboranes in situ without having to isolate the potentially dangerous boranes. B_4H_{10} [17] and B_5H_9 [18] will react directly with acetylenes to form carboranes (albeit under more severe conditions) although B_6H_{10} [19] gives only a very low yield of $Me_2C_2B_6H_6$ in its thermal reaction with MeCCMe. Thus, **xviii** tested whether simple inclusion of an acetylene in the reaction mixture would bring about carborane formation. This approach failed, although it should be noted that an alternative acetylene to PhCCH might have given different results; PhCCH was used because of its availability and conveniently low volatility.

Since the conditions of MgB_2 hydrolysis could be chosen to favour $B_{10}H_{14}$ production (**vi** and **xvii**) Et_2S, as well as PhCCH, was placed in the reaction flask in **xix** to try to catalyse ortho-carborane formation[20]. This particular Lewis base was chosen as the catalyst for several reasons: Et_2S has a high enough boiling point for a reflux condenser to return it to the reaction flask; Et_2S is a fairly weak Brønsted base and so is probably not completely protonated and deactivated under the acidic conditions used; Et_2S is also quite a weak Lewis base and it was hoped that it would not interfere with production of $B_{10}H_{14}$ by irreversibly cleaving B_6H_{10} and B_4H_{10} before they could react. As with **xviii**, $B_{10}H_{14}$ was the only boron hydride observed in the organic phase of **xix**.

The failure of **xix** to produce carboranes was thought to be due to the Et_2S being too soluble in the aqueous acid. Consequently experiment **xx**, in which one could be sure that free Et_2S was present, was attempted. Molten H_3PO_4 was used in this experiment, instead of 7M H_3PO_4, because it was suspected that the Et_2S would act as a common solvent for water and boranes causing the rapid hydrolysis of the latter; even so it would be worth attempting a similar reaction with 7M H_3PO_4 because the $B_{10}H_{14}$ yield is so low when 100% H_3PO_4 is reacted with MgB_2, viii. This experiment also failed to give carboranes and the boron hydrides that were produced seemed to be the anionic species already discussed in 5.3.2. The last attempt to prepare carboranes in situ, xxi, was designed to avoid the clumsy multi-phase mixture in xx but this too failed to give carboranes.

The experiments discussed above indicate that it will probably not be easy to design a system in which the boranes produced in MgB_2 hydrolysis are consumed as they form by reaction with acetylenes to give carboranes. As a result, this project concentrated on increasing the borane yield from MgB_2 hydrolysis where, if carboranes were required, the boranes would have to be isolated and reacted with acetylenes using methods already reported in the literature.

5.4.3 Discussion of the Mechanism of MgB_2 Hydrolysis

Although the early stages of the mechanism are not yet open to experimental examination some speculation is offered here as to what may be happening. Duhart[11] found that MgB_2 was completely consumed in its reaction with 1M HCl at 15°C after 4 hrs but that the reaction of MgB_2 with water under the same conditions took between 20 days and one month to complete. The electronic structure of MgB_2 has been discussed in section 2.2.2, p.23, and it was found that it probably approached the extreme $Mg^{2+}(B^-)_2$. Thus, because acid so increased the rate of the reaction, protonation of the boron sublattice, 5.5, is a good candidate for the first step in the reaction.

$$MgB_2 + HA \longrightarrow MgA_2 + 2\text{"BH"} \qquad 5.5$$

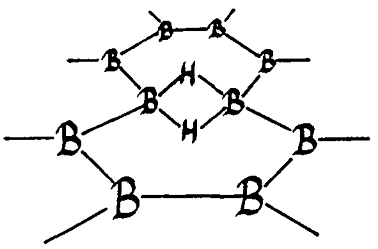


Fig. 5.10 Possible feature on the surface of hydrolysing MgB_2

The bond angles and lengths of the boron sublattice (see *fig. 2.5a*, p.22), B-B = 1·78Å and ∠(B-B-B) = 120° (chap. 2, ref. 40) are very similar to those of B_2H_6, B-B = 1·770Å and $\angle(H_T\text{-}B\text{-}H_T)$ = 121·8° [14]. Also it is noted that the $B\text{-}H_\mu\text{-}B$ links in B_2H_6 are mathematically equivalent to a protonated π-bond and so it is possible that the transient "BH" in 5.5 contains structures like that shown in *fig. 5.10*. However, to obtain stable boranes from the partially protonated uppermost layers of the boron sublattice, $[B_pH_{p-m}]^{m-}$ it is clear that further hydrogen must somehow be added. It is suggested that this is why water is necessary for the reaction of MgB_2 with protic acids to give boranes. For the production of B_4H_{10} this process may be represented by 5.6.

$$7\text{"BH"} + 9\ H_2O \longrightarrow B_4H_{10} + 3\ B(OH)_3 + 3\ H_2 \qquad 5.6$$

However, 5.6 will be in competition with more complete hydrolysis of the boron sublattice, 5.7; this is thought to be the reason why

$$\text{"BH"} + 3\ H_2O \longrightarrow B(OH)_3 + 2\ H_2 \qquad 5.7$$

the reaction of MgB_2 with molten H_3PO_4, **viii**, gave the highest borane yield in this project since very little free water would have been present.

It was pointed out in 5.3.1, p. 161 , that B_2H_6 (and thus $[BH_4]^-$ and probably $\{BH_3\}$) does not form in MgB_2 hydrolysis and so cannot be involved in the formation of the boranes which are actually generated. It is also unlikely that a triborane is involved in borane formation here because $[Me_4N][B_3H_8]$ reacts with polyphosphoric acid to give, amongst other boranes, some B_6H_{12} and a trace of B_2H_6. Instead it seems more likely that the boranes evolved in MgB_2 hydrolysis derive directly from small fragments cut out of the boron layers. If this is correct then there would have to be a mechanism for delivering the extra hydrogen atoms to $[B_pH_{p-m}]^{m-}$, bound to the boride surface, before a stable borane, $[B_pH_{p-m}H_{2n}]^{m-}$, could be generated. For this reason it is suggested that single protons can migrate over the surface of the hydrolysing boron sublattice in an analogous fashion to the tautomerisation of the bridging hydrogens in B_6H_{10}. The configuration in *fig. 5.10* may however be a more stable environment for protons on this surface.

It was indicated in 5.3.1 that H_2 may be capable of interacting directly with the hydrolysing MgB_2 to increase the borane yield. In this respect it is noted that the boron sublattice is electronically similar to the planes of carbon atoms in graphite so that the charge of a single proton delivered to it during hydrolysis would probably be dissipated over the delocalised π-cloud. Consequently the added proton would resemble a chemisorbed hydrogen atom. This implies that anhydrous acids may be able to react with MgB_2 in the presence of H_2 and it is strongly suggested that a sonicated suspension of MgB_2 in molten $H_4P_2O_7$ under a stream of H_2 should be tested for a reaction.

Finally it is perhaps important that only a very limited range of gaseous boranes is produced in MgB_2 hydrolysis. It has been shown that B_4H_{10} and B_5H_9 may share a common precursor and that this may in fact derive from B_6H_{10}. This is probably not coincidental since the B_6 hexagons of the boron sublattice strongly suggest that a hexaborane could be the first discrete intermediate. A good candidate for this is $[B_6H_9]^-$ and its reaction with phosphoric acid solutions should be examined to see if it mimics the products of MgB_2 hydrolysis. In support of $[B_6H_9]^-$ being the first species cut from the boron sublattice en route to the boranes, attention is drawn to the work of Brice et al[15]. They found that protonation of $[n\text{-}Bu_4N][B_6H_9]$ (either as the dry salt or in Me_2O solution) with anhydrous HCl did not give a quantitative yield of B_6H_{10}. Instead, only about 50% of the boron in the salt was recovered as volatiles and these consisted of a 3:1 mixture of B_5H_9 and B_6H_{10} respectively.

5.4 Conclusion

The hydrolysis of MgB_2 in acidic media has been studied under a wide range of conditions to see if any methods could be found for improving the borane yield from this reaction and/or controlling which boranes were obtained. The two most useful techniques found were to conduct the hydrolysis of MgB_2 in 7M H_3PO_4 under the influence of ultrasonics and to react MgB_2 with 100% fused H_3PO_4. Both of these improvements to the reaction more than doubled the borane yield compared to a standard. Also ultrasonics improved the B_6H_{10} yield preferentially and the reaction using molten H_3PO_4 gave B_5H_9 as the major product. In none of the experiments conducted during this project did the borane yield exceed 2%. However, it is hoped that the methods used here can be extended to the more productive Mg_3B_2. This has often been reported to give yields >10% and if the above effects are cumulative it might be possible to boost this to >30%.

It has been observed that in the reactions of different samples of MgB_2 with 7M H_3PO_4 under varied conditions the ratio of B_5H_9 to B_4H_{10} evolved is remarkably constant at ~0·3. This value rose to >1·2 and the yield of B_6H_{10} fell to zero when 88% or 100% H_3PO_4 was used. This, combined with other evidence, led to the proposal of a mechanism in which B_5H_9 and B_4H_{10} were thought to derive from cleavage of B_6H_{10} by the acid solution. Also, $[B_6H_9]^-$ was proposed to be the first species released from the boride's surface on the pathway to the boranes.

The anion $[B_{12}H_{12}]^{2-}$ has been found to be as important a boron hydride product as the volatile boranes. Also produced in lesser quantities are $[B_{10}H_{10}]^{2-}$, $[B_9H_{14}]^-$ and several unidentified species which it is thought could be hydroxyhydroborates. Other experiments have shown that it is possible to react B_6H_{10} with B_4H_{10} as they are produced during MgB_2 hydrolysis to give $B_{10}H_{14}$, and there are many well established, high yielding reactions for converting this borane to carboranes. However, attempts to synthesise carboranes in situ failed.

The yields of boranes in this project have been low. Even so the work presented in this thesis shows that further study of the acidic hydrolysis of magnesium diboride could still provide a valuable and simple route to boranes.

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Appendix 1 Kinetics for the Pyrolyses and Copyrolysis of $\mathrm{B_2H_6}$ and $\mathrm{B_4H_{10}}$

For clarity the concentration terms are abbreviated as follows:

$[\mathrm{B_2H_6}] \equiv \mathrm{B_2}$, $[\{\mathrm{BH_3}\}] \equiv B$, $[\{\mathrm{B_3H_9}\}] \equiv B_3$, $[\{\mathrm{B_3H_7}\}] \equiv B_3'$

$[\mathrm{B_4H_{10}}] \equiv \mathrm{B_4}$, $[\{\mathrm{B_4H_8}\}] \equiv B_4'$, $[\mathrm{B_5H_{11}}] \equiv \mathrm{B_5}$, $[\mathrm{H_2}] \equiv \mathrm{H}$

The reactions below are analysed by stationary state kinetics.

i) Pyrolysis of $\mathrm{B_2H_6}$ Assuming Homolytic Fission of $\mathrm{B_2H_6}$

$$\mathrm{B_2H_6} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\{\mathrm{BH_3}\}$$

$$\mathrm{B_2H_6} + \{\mathrm{BH_3}\} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \{\mathrm{B_3H_9}\} \tag{3.3}$$

$$\{\mathrm{B_3H_9}\} \xrightarrow{k_3} \{\mathrm{B_3H_7}\} + \mathrm{H_2} \qquad \text{RDS} \tag{3.4}$$

$$\mathrm{B_2H_6} + \{\mathrm{B_3H_7}\} \xrightarrow{k_4} \mathrm{B_4H_{10}} + \{\mathrm{BH_3}\} \tag{3.5}$$

$$\therefore \frac{dB}{dt} = 2k_1\mathrm{B_2} - k_{-1}B^2 - k_2\mathrm{B_2}B + k_{-2}B_3 + k_4\mathrm{B_2}B_3' = 0$$

$$\frac{dB_3}{dt} = k_2\mathrm{B_2}B - k_{-2}B_3 - k_3B_3 = 0$$

$$\frac{dB_3'}{dt} = k_3B_3 - k_4\mathrm{B_2}B_3' = 0$$

$$\therefore B = (2K_1)^{1/2}\mathrm{B_2}^{1/2} \qquad B_3 = \frac{k_2}{k_{-2}+k_3}(2K_1)^{1/2}\mathrm{B_2}^{3/2},$$

$$B_3' = \frac{k_2k_3}{k_4(k_{-2}+k_3)}(2K_1)^{1/2}\mathrm{B_2}^{1/2}$$

where $K_1 = k_1/k_{-1}$

$\therefore$ The rate of $\mathrm{B_2H_6}$ consumption =

$$\frac{-d\mathrm{B_2}}{dt} = k_1\mathrm{B_2} - k_{-1}B^2 + k_2\mathrm{B_2}B - k_{-2}B_3 + k_4\mathrm{B_2}B_3'$$

$$= k_1B_2 - 2k_1B_2 + \left[k_2 - \frac{k_2k_{-2}}{k_{-2}+k_3} + \frac{k_2k_3}{k_{-2}+k_3}\right](2K_1)^{1/2}B_2^{3/2}$$

$$= \frac{2k_2k_3}{k_{-2}+k_3}(2K_1)^{1/2}B_2^{3/2} - k_1B_2$$

Thus, the mechanism is unsatisfactory because the derived rate expression contains a first order term in addition to the experimentally established 3/2 order of reaction.

ii) Mechanism of B_2H_6 Pyrolysis Proposed by Long
(chap. 2, refs. 1a and b)

$2\ B_2H_6 \xrightarrow{k_1} \{B_3H_9\} + \{BH_3\}$ 3.2 where $k_{-1} = 0$

$B_2H_6 + \{BH_3\} \xrightarrow{k_2} \{B_3H_9\}$ 3.3 where $k_{-2} = 0$

$2\{B_3H_9\} \xrightarrow{k_3} 3\ B_2H_6$

$\{B_3H_9\} \xrightarrow{k_4} \{B_3H_7\} + H_2$ RDS 3.4

$\{B_3H_7\} + B_2H_6 \xrightarrow{k_5} B_4H_{10} + \{BH_3\}$ 3.5

$$\therefore \frac{dB}{dt} = k_1B^2 - k_2B_2B + k_5B_2B_3' = 0$$

$$\frac{dB_3}{dt} = k_1B_2^2 + k_2B_2B - k_3B_3^2 - k_4B_3^2 = 0$$

$$\frac{dB_3'}{dt} = k_4B_3 - k_5B_2B_3' = 0$$

$$\therefore B = \frac{k_4}{k_2}\left(\frac{2k_2}{k_3}\right)^{1/2} + \frac{k_1B_2}{k_2} \qquad B_3 = \left(\frac{2k_2}{k_3}\right)^{1/2}B_2 \qquad B_3' = \frac{k_4}{k_5}\left(\frac{2k_2}{k_3}\right)^{1/2}$$

$\therefore$ The rate of B_2H_6 consumption =

$$\frac{-dB_2}{dt} = k_1B_2^2 + k_2B_2B - 3k_3B_3^2 + k_5B_2B_3'$$

$$= 2(k_1-3k_2)B_2^2 + 2k_4\left(\frac{2k_2}{k_3}\right)^{1/2}B_2$$

This rate expression quite clearly does not satisfy the experimental order of reaction.

iii) Mechanism shown in Chapter 3 for B_2H_6 Pyrolysis

$$2\ B_2H_6 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \{B_3H_9\} + \{BH_3\} \qquad 3.2$$

$$B_2H_6 + \{BH_3\} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \{B_3H_9\} \qquad 3.3$$

$$\{B_3H_9\} \xrightarrow{k_3} \{B_3H_7\} + H_2 \qquad \text{RDS} \qquad 3.4$$

$$B_2H_6 + \{B_3H_7\} \xrightarrow{k_4} B_4H_{10} + \{BH_3\} \qquad 3.5$$

$$\therefore \frac{dB}{dt} = k_1\mathrm{B}_2^2 - k_{-1}BB_3 - k_2\mathrm{B}_2B + k_{-2}B_3 + k_4\mathrm{B}_2B_3' = 0 \qquad a$$

$$\frac{dB_3}{dt} = k_1\mathrm{B}_2^2 - k_{-1}BB_3 + k_2\mathrm{B}_2B - k_{-2}B_3 - k_3B_3 = 0 \qquad b$$

$$\frac{dB_3'}{dt} = k_3B_3 - k_4\mathrm{B}_2B_3' = 0 \qquad c$$

$$\therefore \frac{B_3}{\mathrm{B}_2} = \frac{k_1\mathrm{B}_2 + K_2B}{k_{-1}B + k_{-2} + k_3} = \frac{k_1\mathrm{B}_2 - k_2B}{k_{-1}B - k_{-2} - k_3} \qquad \Rightarrow B = \left(\frac{k_{-2}+k_3}{k_2}K_1\right)^{1/2}\mathrm{B}_2^{1/2}$$

(from b) (combining a and c)

$$\text{and } B = \frac{k_1\mathrm{B}_2^2 + (k_{-2}+k_3)B_3}{k_{-1}B_3 + k_2\mathrm{B}_2} = \frac{k_1\mathrm{B}_2^2 - (k_{-2}+k_3)B_3}{k_{-1}B_3 - k_2\mathrm{B}_2}$$

(combining a and c) (from b)

$$\Rightarrow B_3 = \left(\frac{K_1k_2}{k_{-2}+k_3}\right)^{1/2}\mathrm{B}_2^{3/2}$$

$$\therefore B_3' = \frac{k_3B_3}{k_4\mathrm{B}_2} = \frac{k_3}{k_4}\left(\frac{K_1k_2}{k_2+k_3}\right)^{1/2}\mathrm{B}_2^{1/2}$$

∴ The rate of B_2H_6 consumption =

$$\frac{-d\mathrm{B}_2}{dt} = k_1\mathrm{B}_2^2 - k_{-1}BB_3 + k_2\mathrm{B}_2B - k_{-2}B_3 + k_4\mathrm{B}_2B_3'$$

$$= k_1B_2^2 - k_1B_2^2 + \left[(k_{-2}+k_3)^{1/2} - \frac{k_{-2}}{(k_{-2}+k_3)^{1/2}} + \frac{k_3}{(k_{-2}+k_3)^{1/2}}\right](K_1k_2)^{1/2}B_2^{3/2}$$

$$= 2k_3\left(\frac{K_1k_2}{k_{-2}+k_3}\right)^{1/2}B_2^{3/2}$$

This rate expression fits the observed order of reaction for B_2H_6 pyrolysis

iv) **Mechanism of B_4H_{10} Pyrolysis Proposed by Greenwood Greatrex and Potter** (chap. 3, ref. 18)

$$B_4H_{10} \xrightarrow{k_1} \{B_4H_8\} + H_2 \qquad \text{RDS} \qquad 3.8a$$

$$B_4H_{10} + \{B_4H_8\} \xrightarrow{k_2} B_5H_{11} + \{B_3H_7\} \qquad 3.9$$

$$2\{B_3H_7\} \xrightarrow{k_3} \underset{\text{(Polymeric Hydride)}}{B_6H_{14-2m}} + mH_2 \qquad 3.10a$$

$$\therefore \quad \frac{dB_4'}{dt} = k_1B_4 - k_2B_4B_4' = 0 \qquad \Rightarrow \quad B_4' = \frac{k_1}{k_2}$$

$$\frac{dB_3'}{dt} = k_2B_4B_4' - k_3B_3'^{\,2} = 0 \qquad \Rightarrow \quad B_3'^{\,2} = \frac{k_2B_4B_4'}{k_3} = \frac{k_1B_4}{k_3}$$

$\therefore$ The rate of B_4H_{10} consumption =

$$\frac{-dB_4}{dt} = k_1B_4 + k_2B_4B_4' = 2k_1B_4$$

and the rate of B_5H_{11} production =

$$\frac{dB_5}{dt} = k_2B_4B_4' = k_1B_4 \qquad \Rightarrow \frac{dB_5}{dB_4} = 0{\cdot}5$$

The above kinetics are extrapolated to zero time and so the reverse of 3.8a is ignored. However, including this gives the rate expression for hydrogen inhibition

$$\frac{-d(B_4)_i}{dt} = \frac{2k_1B_4}{1+\dfrac{k_1H}{k_2B_4}}$$

v) Mechanism of B_4H_{10} Pyrolysis Proposed in This Thesis

$$B_4H_{10} \xrightarrow{k_1} \{B_4H_8\} + H_2 \qquad \text{RDS} \qquad 3.8a$$

$$B_4H_{10} + \{B_4H_8\} \xrightarrow{k_2} B_5H_{11} + \{B_3H_7\} \qquad 3.9$$

$$B_4H_{10} + \{B_3H_7\} \xrightarrow{k_3} B_{7-n}H_{17-3n-2m} + mH_2 + n\{BH_3\} \qquad 3.10b$$

$$B_4H_{10} + \{BH_3\} \xrightarrow{k_4} B_5H_{11} + H_2 \qquad 3.11$$

$$\therefore \frac{d\mathit{B}_4{}'}{dt} = k_1B_4 - k_2B_4\mathit{B}_4{}' = 0 \qquad \Rightarrow \mathit{B}_4{}' = \frac{k_1}{k_2}$$

$$\frac{d\mathit{B}_3{}'}{dt} = k_2B_4\mathit{B}_4{}' - k_3B_4\mathit{B}_3{}' = 0 \qquad \Rightarrow \mathit{B}_3{}' = \frac{k_2\mathit{B}_4{}'}{k_3} = \frac{k_1}{k_3}$$

$$\frac{d\mathit{B}}{dt} = nk_3B_4\mathit{B}_3{}' - k_4B_4\mathit{B} = 0 \qquad \Rightarrow \mathit{B} = \frac{nk_3\mathit{B}_3{}'}{k_4} = \frac{nk_1}{k_4}$$

∴ The rate of B_4H_{10} consumption =

$$\frac{-dB_4}{dt} = k_1B_4 + k_2B_4\mathit{B}_4{}' + k_3B_4\mathit{B}_3{}' + k_4B_4\mathit{B} = (3+n)k_1B_4$$

and the rate of B_5H_{11} production =

$$\frac{-dB_5}{dt} = k_2B_4\mathit{B}_4{}' + k_4B_4\mathit{B} = (1+n)k_1B_4$$

If n=1, as might be expected for a transient B_7 intermediate, then $\frac{dB_5}{dB_4} = 0{\cdot}5$. However, it was found experimentally that

$$\frac{dB_5}{dB_4} = 0{\cdot}44 = \frac{1+n}{3+n}$$

$$\therefore \quad n = \frac{(3\text{x}0{\cdot}44) - 1}{1 - 0{\cdot}44} = 0{\cdot}57$$

Also, at 40·2°C, if was found that $\frac{dH}{dt} \simeq \frac{-dB_4}{dt}$

$$\frac{dH}{dt} = k_1B_4 + mk_3B_4B_3' + k_4B_4B = (1+m+n)\ k_1B_4$$

$\therefore\ (1+m+n) \simeq (3+n) \Rightarrow m = 2{\cdot}27$

These values of m and n can now be substituted into 3.10 to give the polymer stoichiometry,

$$\text{Hydrogen:Boron} = \frac{17 - (3\text{x}0{\cdot}57) - (2\text{x}0{\cdot}27)}{7 - 0{\cdot}57} = 1{\cdot}67$$

which agrees quite well with the experimentally determined polymer stoichiometry of $BH_{1.76\pm0.08}$.

vi) Copyrolysis of B_2H_6 and B_4H_{10}

$$B_4H_{10} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (B_4H_8) + H_2 \qquad \text{RDS} \tag*{3.8a}$$

$$B_2H_6 + \{B_4H_8\} \xrightarrow{k_2} B_5H_{11} + \{BH_3\} \tag*{3.13}$$

$$B_4H_{10} + \{BH_3\} \xrightarrow{k_3} B_5H_{11} + H_2 \tag*{3.11}$$

$$\therefore\ \frac{dB_4'}{dt} = k_1B_4 - k_{-1}HB_4' - k_2B_2B_4' = 0 \qquad \Rightarrow B_4' = \frac{k_1B_4}{k_{-1}H + k_2B_2}$$

$$\frac{dB}{dt} = k_2B_2B_4' - k_3B_4B = 0 \qquad \Rightarrow B = \frac{k_1k_2B_2}{k_3(k_{-1}H + k_2B_2)}$$

$\therefore$ The rate of B_4H_{10} consumption =

$$\frac{-dB_4}{dt} = k_1B_4 - k_{-1}HB_4' + k_3B_4B = \frac{2k_1B_4}{1 + \frac{k_{-1}H}{k_2B_2}}$$

This expression reduces to $\frac{-dB_4}{dt} = 2k_1B_4$ if the partial pressure of hydrogen is low.

Appendix 2 Colloquia Lectures and Seminars Given by Invited Speakers at Durham University, 1st August 1986 to 31st July 1987

* ALLEN, Prof. Sir G. (Unilever Research) Biotechnological and the Future of the Chemical Industry	13th November 1986
BARTSCH, Dr.R. (University of Sussex) Low Co-ordinated Phosphorus Compounds	6th May 1987
* BLACKBURN, Dr.M. (University of Sheffied) Phosphonates as Analogues of Biological Phosphate Esters	17th May 1987
BORDWELL, Prof. F.G. (Northeastern Univ., U.S.A.) Carbon Anions, Radicals, Radical Anions and Radical Cations	9th March 1987
CANNING, Dr. N.D.S. (University of Durham) Surface Adsorption Studies of Relevance to Heterogeneous Ammonia Synthesis	26th November 1986
CANNON, Dr. R.D. (University of East Anglia) Electron Transfer in Polynuclear Complexes	11th March 1987
* CLEGG, Dr.W. (University of Newcastle-upon-Tyne) Carboxylate Complexes of Zinc; Charting a Structural Jungle	28th January 1987
DOPP, Prof. T. (University of Duisburg) Cyclo-additions and Cyclo-reversions involving Captodative Alkenes	5th November 1986
* DORFMULLER, Prof. T. (University of Bielefeld) Rotational Dynamics in Liquids and Polymers	8th December 1986
GOODGER, Dr. E.M. (Cranfield Institute of Technology) Alternative Fuelds for Transport	12th March 1987
* GREENWOOD, Prof. N.N. (University of Leeds) Glorious Gaffes in Chemistry	16th October 1987
* HARMER, Dr. M. (I.C.I. Chemicals & Polymer Group) The Role of Organometallics in Advanced Materials	7th May 1987
* HUBBERSTEY, Dr. P. (University of Nottingham) Demonstration Lecture on Various Aspects of Alkali Metal Chemistry	5th February 1987

* HUDSON, Prof. R.F. (University of Kent) Aspects of Organophosphorus Chemistry	17th March 1987
HUDSON, Prof. R.F. (University of Kent) Homolytic Rearrangements of Free Radical Stability	18th March 1987
* JARMAN, Dr. M. (Institute of Cancer Research) The Design of Anti Cancer Drugs	19th February 1987
* KRESPAN, Dr. C. (E.I.Dupont de Nemours) Nickel(0) and Iron(0) as Reagents in Organofluorine Chemistry	26th June 1987
* KROTO, Prof. H.W. (University of Sussex) Chemistry in Stars, between Stars and in the Laboratory	23d October 1986
* LEY, Prof. S.V. (Imperial College) Fact and Fantasy in Organic Synthesis	5th March 1987
MILLER, Dr. J. (Dupont Central Research, U.S.A.) Molecular Ferromagnets; Chemistry and Physical Properties	3rd December 1986
* MILNE/CHRISTIE, Dr.A./Mr. S. (International Paints) Chemical Serendipity - A Real Life Case Study	20th November 1986
NEWMAN, Dr.R. (University of Oxford) Change and Decay: A Carbon-13 CP/MAS NMR Study of Humification and Coalification Processes	4th March 1987
* OTTEWILL, Prof. R.H. (University of Bristol) Colloid Science a Challenging Subject	22nd January 1987
* PASYNKIEWICZ, Prof. S. (Technical University, Warsaw) Thermal Decomposition of Methyl Copper and its Reactions with Trialkylaluminium	11th May 1987
* ROBERTS, Prof. S.M. (University of Exeter) Synthesis of Novel Antiviral Agents	24th June 1987
* RODGERS, Dr. P.J. (I.C.I. Billingham) Industrial Polymers from Bacteria	12th February 1987
* SCROWSTON, Dr. R.M. (University of Hull) From Myth and Magic to Modern Medecine	6th November 1986

* SHEPHERD, Dr.T. (University of Durham) Pteridine Natural Products; Synthesis and Use in Chemotherapy	11th February 1987
* THOMSON, Prof. A. (University of East Anglia) Metalloproteins and Magnetooptics	4th February 1987
* WILLIAMS, Prof. R.L. (Metropolitan Police Forensic Science)	27th November 1987
* WONG, Prof. E.H. (University of New Hampshire, U.S.A.) Coordination Chemistry of P-O-P Ligands	29th October 1986
* WONG, Prof. E.H. (University of New Hampshire, U.S.A.) Symmetrical Shapes from Molecules to Art and Nature	17th February 1987

* Talks attended

Conferences Attended

INTRABORON VI, Warwick University	September 1986
INTRABORON VII, University of Strathclyde	September 1987