CHEMISTRY OF B_{1-} AND B_{10-} BORANES CONTAINING HALOGEN OR PSEUDOHALOGEN GROUPS

by

MICHAEL MYERS, B.Sc.

Thesis presented for the degree of

Doctor of Philosophy

to

The National University of Ireland

DEPARTMENT OF CHEMISTRY

UNIVERSITY COLLEGE

CORK

October, 1987

ABSTRACT

The research described in this thesis involved the chemistry of borane-species which contain one or more halide or pseudohalide groups. Both monoboron species e.g. $[BH_3X]^-$ and "cluster" borane species e.g. $[B_{10}H_9X]^{2-}$ and 1-Se $B_{11}H_{10}$ were studied.

The first chapter is a review of the syntheses, properties and reactions of halide and pseudohalide species containing from one to ten boron atoms.

Chapter Two is a theoretical investigation of the electronic and molecular structures of two series of boranes i.e. $[BH_3X]^-$ and $[B_{10}H_9X]^{2-}$ where X = H, Cl, CN, NCS, SCN and N_3. The calculational method used was the Modified Neglect of Differential Overlap (MNDO) method of Dewar *et al.* The results were compared where possible with experimental results such as the X-ray crystallographically determined structures of $[BH_3Cl]^-$ and $[B_{10}H_{10}]^{2-}$.

Chapter Three concerns halogenated selenaborane clusters and reports an improved synthesis of 12-Br-Se $B_{11}H_{10}$ and the first structural data for a simple non-metal containing selenaborane cage with the X-ray crystallographically determined structure of 12-I-Se $B_{11}H_{10}$. Finally, an indepth n.m.r. study of $Se_2B_9H_9$ is also reported together with attempts to halogenate this compound.

The last two chapters are based on single boron systems. Chapter Four concerns the synthetic routes to amine-boranes and -cyanoboranes from $[BH_4]^-$ and $[BH_3CN]^-$ substrates. This chapter discusses some difficulties encountered when polyamines were used in these reactions. The characterisation of an unusual ketone isolated from some of these reactions, the X-ray crystallographically determined structure of 4-dimethylamino-pyridine-cyanoborane and a new route to pyrazabole dimeric species are also discussed.

The final chapter reports on work carried out at producing BH_2X (X = H, CN) adducts of aminophosphines. Three routes were attempted to generate P-B and N-B bonded species with varying degrees of success. Some unusual products of these reactions are discussed including $[Ph_2(O)\ PPPh_2]$ $[Ph_2NH]_2$, the structure of which was determined by X-ray crystallography.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS

The completion of a Ph.D requires, from the very first day, the help and cooperation of many people. It would be impossible for me to mention everyone whose knowledge, assistance and company I have called upon these past four years. I would like to take this opportunity to say 'Thank You' to all those.

However, there are some people I would especially like to acknowledge. Firstly, my long-suffering and almost extremely patient Supervisor, Dr. Trevor Spalding. His expert guidance, enthusiasm, frequent reassurances on chemical matters and wise counsel on a more personal basis, made my research years more enjoyable and interesting. Although there were occasions when it did not seem so, I am very grateful to him for his help with production of this thesis. I would also like to express my gratitude to the other members of the academic staff for their interest and helpful comments, in particular Professor Brian Hathaway. A special word of thanks to Dr. Paul Brint for his assistance with the computer calculations. I would also like to thank Dr. Reed (University of Edinburgh), Dr. Kennedy (University of Leeds) for "B n.m.r. spectra and Professor George Ferguson (University of Guelph) for the X-ray structures.

Many hands and minds are needed to maintain the easy life for us postgrads. To: Helen, Barry and Mrs Duggan for microanalyses; Pat O'Connell for n.m.r.s.; Ollie, Johnny and Tony for repair work; Dave for liquid nitrogen; Jimmy, Liam and Dan for supplies of all sorts and the office staff, Eileen, Mary, Majella and especially Karen for envelopes and for typing; I would like to say thank you all for your help and wish you the best. Special thanks to Sean Downey for many "loans" of chemicals and other things ("I'll bring them back, Sean"); Derry Kearney who although he is enjoying a successful Autumn career as a footballer, is thankfully a much better glassblower. He also keeps a 'watchful eye' on 'some' of the postgrads. Then there's Mick O'Shea who helps in every way. Mick, may your Oedipus complex never falter and may the 'harpies' never get you.

I would especially like to thank Monica for her excellent typing of this thesis. Fingers crossed, that it is finally completed.

Despite the frequent ups and downs of research life and the occasional altercation I am very grateful to my fellow postgrads for their company and

especially for the illuminating coffee-breaks where we looked forward each morning to learning about the exciting happenings in "A Country Practice".

To those who started on this road with me; Nuala, Con, Noel, Orla, my lab companion for three years, and Brid, whose after-tea and Saturday company on the fourth floor meant a lot to me; I wish every good luck and happiness.

To my lab. mates Paul and Mary (who are still searching for that elusive 'f' in boron), Therese, Patrick, Periwais Faridoon and my two Thai friends Venus and Sujitra; thank you for your company and for enduring that horrible racket which I call singing. A special word of thanks to the terrible twins, Siobhan and Suzanne (the best American footballers in the department), for many good times and to Pat Hayes for his work on the clusters. And Marguerite whose presence in the lab. made every bad day more bearable and whose friendship has been one of the highlights of my years at U.C.C. She also proof-read this thesis. Thanks Marguerite. I would also like to thank all the members of the Thai community for many a kind word and friendly chats, especially Benchang (did I ever tell you you're the best cook in the world) for her trojan work on the computer.

In spite of our diligence at attempting to push back the frontiers we did manage some social occasions. I would like to thank the 'members of the bar'; Frank (the buddy, the brother), Andrew ('the height of discretion' my eye); Eileen (the great discoverer), Billy, Vinnie and most of those previously mentioned, with whom I've spent many an hour discussing the more important things in life. The games fraternity; Mick Owens, Mary C; Mary D; Noreen, Martha, David, Anthony, Jerh, Brian and the 'non-playing captain' Anita all contributed in a big way to the 'sporting life' in U.C.C. A special thanks to Sean (has the boss been up) Naughton for his illuminating conversation.

The task of writing this thesis was made light by Sharon's company in the office. I hope her "road least travelled by" brings her the happiness she deserves.

I was a year and a half on the fourth floor before I spoke to Anne Culhane. Over the past years she became my closest friend and confidante. Thanks for the many happy memories Annie. A special thanks to Linda for "words at once true and kind, or at least not untrue and not unkind".

The past year and a half would have been so much duller and lonelier without Elizabeth. Thank you for the microscopic proof-reading of this thesis but mostly for your friendship, company, tolerance when I was difficult and especially for caring.

I would also like to thank my sister Geraldine and her husband Danny for their encouragement and help and Sally who sent me off each morning in the best way possible.

Writing these last few lines of my thesis means the end of my student days. Over the past twenty-one years "in school" many changes have occurred in my life. Buildings have changed, friends and comrades have come and gone, yet through it all two people have stood by my side and made all this possible. For the many willing sacrifices on my behalf, for their happiness at the highs and comfort through the lows, for their financial assistance but more than anything else for their kindness and love I want to thank my parents, Michael and Breda. I cannot even begin to describe my feelings of gratitude, there are no suitable words or expressions, so I'll just say 'Thank you both' and hope you understand what I really mean.

Michael Myers

Michael Myers

To my Mother and Father

Like a bird on a wire

Like a drunk in a midnight choir

I have tried in my way

To be free

LEONARD COHEN.

CHAPTER ONE

A REVIEW OF HALIDE AND PSEUDOHALIDE BORANES WITH ONE TO TEN BORON ATOMS

1.1 INTRODUCTION

In 1912 Alfred Stock and his collaborators[1] initiated the systematic study of borane chemistry and in so doing exposed an area of chemistry in which unprecedented problems of structure and bonding became apparent. Over a period of twenty four years this group isolated, identified and studied the chemistry of six boron hydrides (B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10} and $B_{10}H_{14}$). Their work represented a remarkable achievement at that time (1912-1936) since it was first necessary to develop techniques for handling, separating and physically characterising materials which frequently were isolated in less than millimolar quantities and often exploded on contact with air.[2]

Although this field has expanded considerably[3] and there is a rich and varied chemistry of boranes and their derivatives, several drawbacks to their development still remained such as the absence of synthetic procedures to furnish many of these materials in reasonable yields and quantities. In earlier years the syntheses of boranes were heavily dependent upon pyrolytic techniques. In recent years more rational syntheses of several boron hydrides have been achieved, sometimes using halogenated borane species.[3]

The discussion here will deal with the chemistry of halogenated and pseudohalogenated boron hydrides. Compounds will be dealt with sequentially from monoboron species to those with ten boron atoms. For cluster systems, *nido* and *arachno* compounds will be dealt with together but *closo* compounds are discussed separately (Section 1.1 1.1). Emphasis will be placed on those compounds which are chemically stable species. Highly reactive 'free' monoboron species such as BH_2X and BHX_2, which have been characterised only in the gas phase, are not included. Chapter 3 does, however, deal with some of the stable coordination complexes of these species.

1.2 MONOBORON COMPOUNDS $[X_nB\,H_{(4-n)}]^-$

The monoboron species discussed here are of the type $[X_nBH_{(4-n)}]^-$, where X may be F, Cl, Br, I, CN and SCN and n may be 1, 2, 3. The halide derivatives are dealt with first in group order of the periodic table followed by the pseudohalide compounds $[BH_3CN]^-$, $[BH_3NC]^-$, $[BH_2(CN)_2]^-$ and $[BH_3SCN]^-$.

1.2.1 *Synthesis and Properties of Monoboron Halide Compounds*

Prior to a report in 1985 by Shore and co-workers[4] the only $[BH_3X]^-$ species isolated were $[BH_3F]^-$[5] and $[BH_3I]^-$[6], although $[BH_3Cl]^-$ and $[BH_3Br]^-$ were reported to have been observed in solution in the presence of other borohydride derivatives.

Muetterties and co-workers[5] reported that an ethereal solution of borane reacted almost quantitatively with potassium fluoride (1).

$$R_2O \cdot BH_3 + K[F] \xrightarrow[R.T.]{R_2O} K[BH_3F] + R_2O \qquad (1)$$

R_2O = 1,2-dimethoxyethane

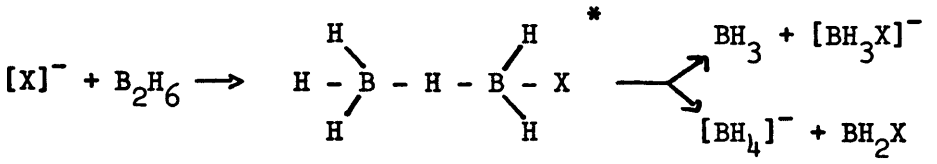
These authors noted that the hydrolytic stability of $[BH_3F]^-$ was poor in neutral solution. The infrared spectrum exhibited B-H stretching as a strong 2330, 2400 cm^{-1} doublet with a shoulder at about 2380 cm^{-1}.

In a study carried out using ion cyclotron resonance spectroscopy[7] the gas phase species $[BH_3X]^-$ were observed from the ion-molecule reactions of a number of anions, $[X]^-$, with diborane (2)

$$[X]^- + B_2H_6 \longrightarrow \begin{cases} [BH_4]^- + BH_2X & 2(a) \\ [BH_3X]^- + BH_3 & 2(b) \end{cases}$$

Ab initio calculations were carried out to determine the importance of the relative thermodynamic stabilities of the two sets of products (2(a) and 2(b)) on the product distribution. The reactions of the anions with diborane could be divided into three broad categories (i) those producing $[BH_4]^-$ only, (ii) those producing both $[BH_4]^-$ and $[BH_3X]^-$ in varying proportions and (iii) those producing $[BH_3X]^-$ only. The authors claimed that reactions of anions with B_2H_6 could be interpreted as occurring through a common intermediate, $[B_2H_6X]^-$ complex (Scheme 1).

Scheme 1 - Pathway of Reaction of $[X]^-$ with B_2H_6



The decomposition path depended upon the position of the central hydrogen atom in the B–H–B linkage, which in turn is dictated by the electronic properties of the X-substituent. When X is strongly electron donating the central hydrogen atom is displaced towards the boron to which X is not bound (Figure 1) thus facilitating decomposition to $[BH_4]^-$ and BH_2X. Conversely, when X is an electron withdrawing group the central hydrogen atom is displaced towards the boron to which X is bonded (Figure 2) thus favouring dissociation to $[BH_3X]^-$ and BH_3

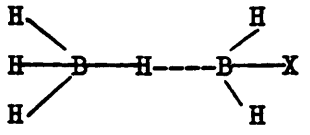


Figure 1

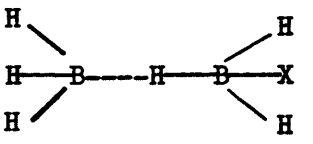


Figure 2

Finally, substituents which are neither intrinsically good electron withdrawing nor electron donating groups yield intermediates in which the central hydrogen atom remains close to the centre of the bond giving rise

to a mixture of products. According to this classification, fluorine must be regarded as a more electron donating than withdrawing substituent on boron since 95% of the products of $[F]^-$ and diborane are $[BH_4]^-$ and BH_2F.

During attempts to grow crystals of $[PPN][B_2H_7]$ from dichloromethane solutions, Shore and co-workers[4] isolated crystals of $[PPN][BH_3Cl].CH_2Cl_2$. This product was apparently the result of prolonged reaction between $[B_2H_7]^-$ anion and the solvent, resulting in the replacement of some of the $[BH_4]^-$ of $[B_2H_7]^-$ by chloride. Tensimetric titration of $[PPN][Cl]$, $[Bu_4N][Cl]$ and $[Et_4N][Cl]$ with B_2H_6 at -78°C indicated the reaction stoichiometry (3)

$$[E]^+ + [Cl]^- + \tfrac{1}{2}B_2H_6 \longrightarrow [E][BH_3Cl] \qquad (3)$$

$$[E]^+ = [PPN]^+,\ [Bu_4N]^+,\ [Et_4N]^+$$

In each case a plot of vapour pressure versus the mole ratio of B_2H_6 to $[E][Cl]$ gave a break in the curve at (mmol of B_2H_6)/(mmol of $[E][Cl]$) = 0.5. Corresponding tensimetric titrations of $[Me_4N][Cl]$, $[PPN][Br]$, $[Bu_4N][Br]$ and $[PPN][F]$ with diborane showed no evidence for reaction.

As solids, $[BH_3Cl]^-$ salts were stable under inert atmosphere at room temperature but decomposed rapidly on exposure to air. Solutions of $[BH_3Cl]^-$ salts were generally handled at low temperatures to avoid anion dissociation. The disproportionation of $[BH_3Cl]^-$ in solution as a function of temperature was followed by ^{11}B n.m.r. spectroscopy. Disproportionation was clearly evident above -50°C and became more pronounced at higher temperatures. No intermediate species were detected but $[BH_2Cl_2]^-$ and $[B_2H_7]^-$ were observed in a 1:1 reaction. The overall disproportionation reaction is (4).

$$3[BH_3Cl]^- \longrightarrow [BH_2Cl_2]^- + [B_2H_7]^- + [Cl]^- \qquad (4)$$

The ^{11}B n.m.r. spectra of samples allowed to stand at room temperature for over 24 hours also showed the presence of $[B_3H_8]^-$, probably formed by the decomposition of $[B_2H_7]^-$.[8,9] The infrared spectrum of $[BH_3Cl]^-$ exhibited absorptions at 2210 (m), 2299 (s) and 2340 (s) cm^{-1}.

The X-ray crystallographically determined structure of [PPN][BH_3Cl] is illustrated in Figure 3.

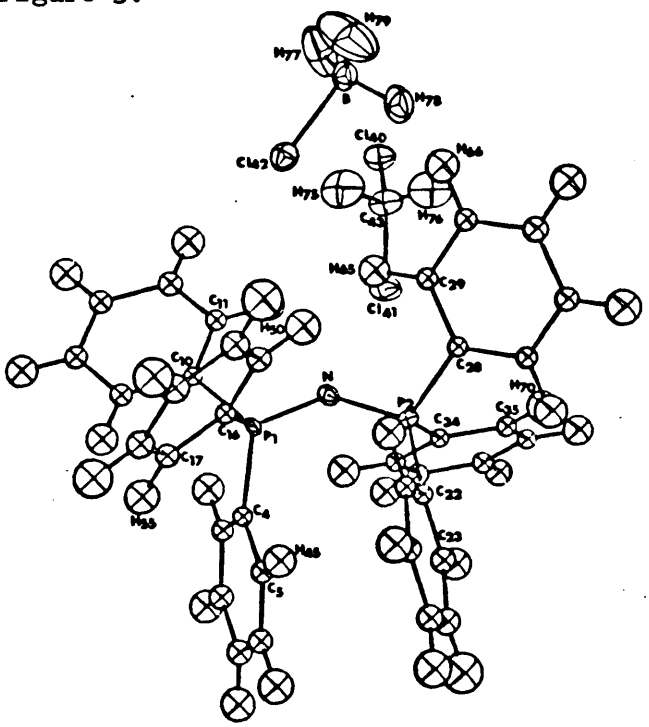


Figure 3: Molecular Plot of [PPN][BH_3Cl]

Gavrilova *et al*[10] studied the interaction of tetrabutylammonium borohydride with iodine (5).

$$[Bu_4N][BH_4] + nI_2 \xrightarrow[C_6H_6]{20^\circ C} [Bu_4N][BH_{4-n}I_n] + nHI \qquad (5)$$

The authors noted that these compounds dissociated in benzene solution and that the degree of dissociation increased in the series $[Bu_4N][BI_4] < [Bu_4N][BHI_3] < [Bu_4N][BH_2I_2] < [BU_4N][BH_3I]$. The latter was found to dissociate completely to diborane and $[Bu_4N][I]$.

1.2.2 *Pseudohalide Compounds* $[BH_3X]^-$ *and* $[BH_2X_2]^-$ *X = CN, NC, SCN, NCS*

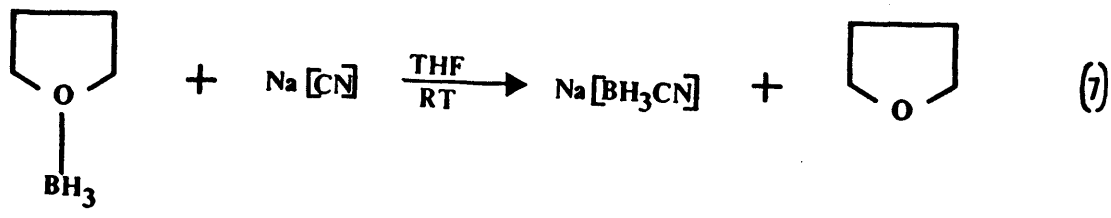
1.2.2.1. *Introduction and Synthesis*

The remarkable hydrolytic stability of cyanoborohydride compared to boro hydride has established it as one of the more important hydride reagents in organic reductions.[11,12,13] However, due to its toxicity this potential[14] was not realised until recently.[15]

The first reported synthesis of a cyanoborohydride was in 1951 when Wittig and Raff prepared the lithium salt by the reaction of $Li[BH_4]$ and excess HCN under pressure (6).

$$Li[BH_4] + HCN\ (excess) \xrightarrow[\substack{Et_2O \\ pressure}]{100^\circ C} Li[BH_3CN] + H_2 \qquad (6)$$

The relative commercial inaccessibility of lithium cyanoborohydride by an inconvenient literature synthesis and the economic disadvantages inherent to all lithium compounds, led to the preparation of the corresponding sodium salt by Wade *et al*[16] in 1970 by a somewhat similar reaction. This method, which furnished the product in 91% yield, involved the dropwise addition of a 16.7% HCN solution to $Na[BH_4]$ in THF at room temperature. Hui[11] reported that excellent yields of sodium cyanoborohydride were obtained by stirring equimolar quantities of borane-THF complex with sodium cyanide at room temperature (7)



(7)

Sodium cyanoborohydride has also been prepared by Gyori and Emri[17] by a method which avoids the use of HCN (8).

$$2\ Na[BH_4] + Hg(CN)_2 \xrightarrow[3\ hour\ reflux]{THF} 2Na[BH_3CN] + Hg^{\circ} + H_2\uparrow \qquad (8)$$

Due to the much greater solubility of $Na[BH_3CN]$ over $Na[BH_4]$ in THF, the product is easily isolated from the reaction solution. Similar redox reactions have been suggested to take place with other mercury (II) compounds such as $Hg[Cl]_2$, $Hg[F]_2$, $Hg[Ac]_2$ and $Hg[SCN]_2$ etc., but details have not yet appeared.

In 12M HCl, potassium cyanoborohydride is rapidly hydrolysed to boric acid (9).

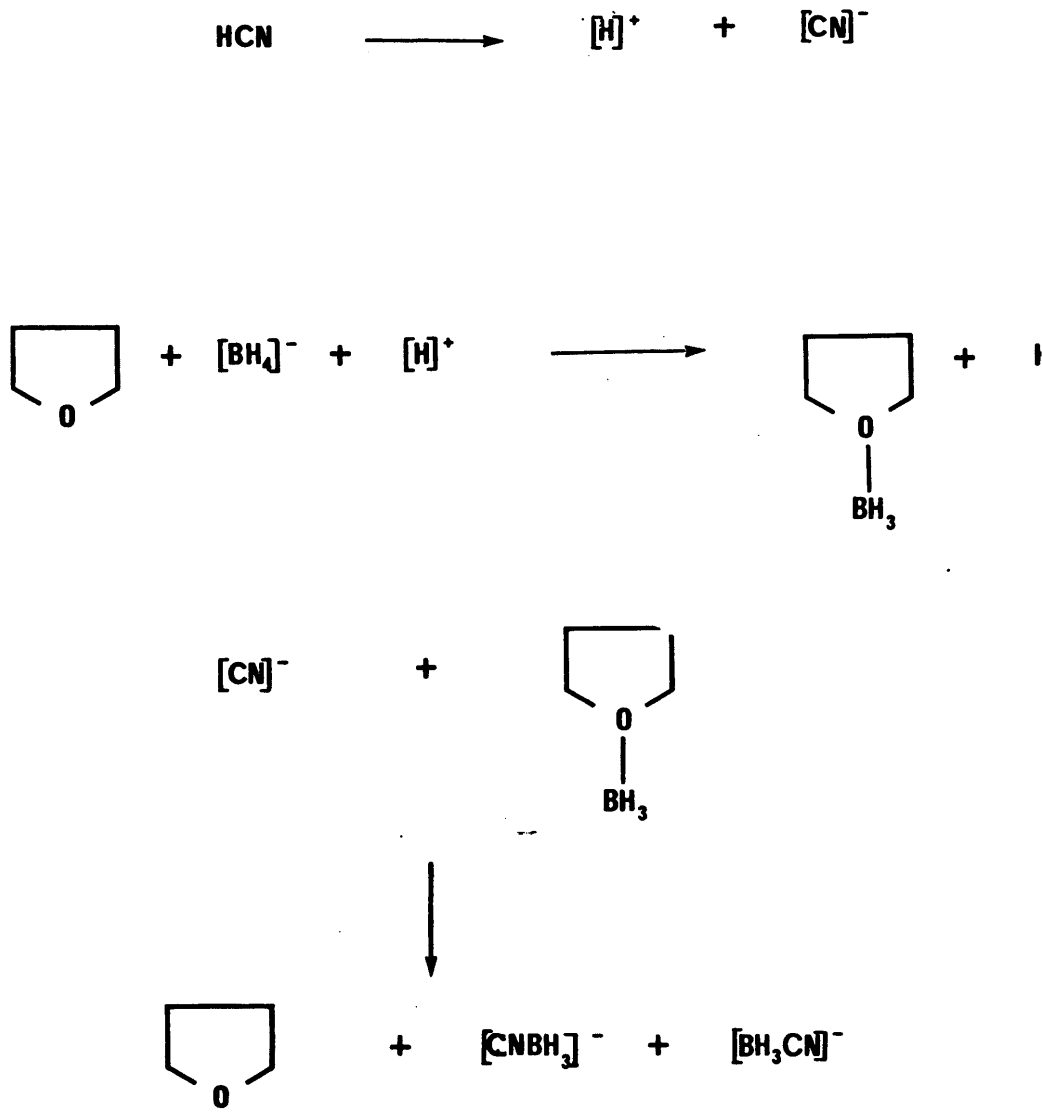
$$K[BH_3CN] + 3H_2O + HCl \longrightarrow H_3BO_3 + HCN + K[Cl] \qquad (9)$$

In initially neutral solution, cyanoborohydride hydrolysis is very slow (0.5% in 24 hours). Addition of a small amount of acid (0.016 mmol of $[H]^+$ to 4.1 mmol of $[BH_3CN]^-$ in H_2O) will induce decomposition. However, if the aqueous solution is cooled to $0^{\circ}C$, the addition of the same amount of acid will cause no immediate decomposition.

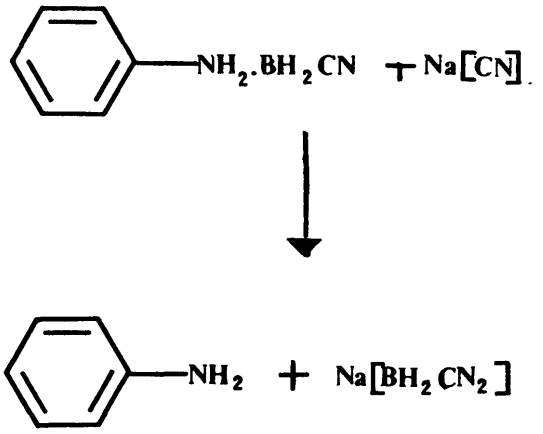
The isocyanide isomer $[BH_3(NC)]^-$ is prepared in the same manner as the cyanide analogue,[16] but the reaction solution is never heated above room temperature. Examination of this reaction solution showed that it contained both $[BH_3CN]^-$ and $[BH_3NC]^-$ isomers. Removal of the THF solvent at room temperature, under vacuum, allowed the isomer mixture to be separated. The ratio of $[BH_3CN]^-$:$[BH_3NC]^-$ was deduced by infrared spectroscopy and by aqueous decomposition experiments to be 4:1. In normal reaction conditions, i.e. prolonged reflux in THF there is no evidence for the presence of isocyanide in the isolated product.

The existence of isomeric forms of cyanoborohydride is explained by the reaction sequence outlined in Scheme 2.

Scheme 2



Further replacement of hydride by cyanide to synthesise $[BH_2(CN)_2]^-$ was reported in 1984 by Spielvogel *et al.*[18] The disubstituted anion was prepared as the sodium (9) and tetrabutylammonium salts.



(9)

These very hygroscopic salts were characterised by elemental analysis, ^{11}B n.m.r. and infrared spectroscopy. Hui[11] reported the synthesis and properties of the thiocyanate derivative $Na[BH_3SCN]$. This was prepared by passing diborane into a solution of anhydrous sodium thiocyanide (10).

$$\tfrac{1}{2}B_2H_6 + Na[SCN] \xrightarrow{\text{monoglyme}} Na[BH_3SCN] \qquad (10)$$

Addition of dioxane to the filtered solution precipitated the product as $Na[BH_3SCN].(C_4H_8O_2)_2$. Evidence for the isomeric isothiocyanate isomer was also detected in the infrared spectrum.

1.2.2.2. *Spectral Properties*

A comprehensive infrared and Raman spectroscopic analysis of cyanoborohydride anion was reported by Berschied and Purcell.[19] This study assigned thirteen bands as stretching, bending or rocking modes. Table 1 lists the major B-H, cyanide, isocyanide, thiocyanate and isothiocyanate stretching bands for the substituted borohydride anions. In this table

it is seen that the isocyanide absorption at 2070 cm^{-1} in $Na[BH_3NC]$ is significantly lower than those for mono- (2179 cm^{-1}) and di- (2200 cm^{-1}) substituted cyanoborohydride anions. The presence of both isomeric forms for thiocyanate derivative is indicated by bands at 2180 (SCN) and 2080 (NCS) cm^{-1} in the infrared spectrum.

Table 1

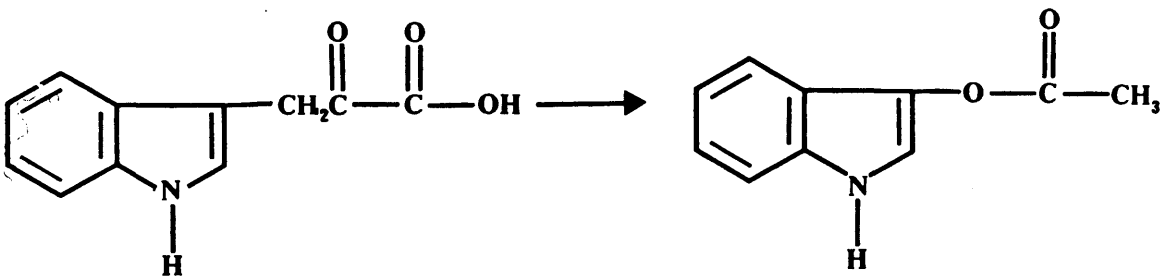
Infrared Data[a] for $Na[BH_3X]$ and $Na[BH_2X_2]$

X	ν_{BH}	ν_X
CN	2390	2180
	2350	
	2320	
	2240	
NC	2350	2070
	2290	
$(CN)_2$	2380	2200
	2250	
SCN	2380	2180
	2330	
	2290	
NCS		2080

[a] Frequency in cm^{-1}

1.2.2.3 *Reductions with* $Na[BH_3X]$ *and* $Na[BH_2X_2]$ X = CN, SCN

Considerable attention has been devoted to the application of modified boron hydrides as selective reducing agents for organic functional groups.[20-22] However, since this area of research is not of major interest in this thesis, only brief reference will be made to it here. Sodium cyanoborohydride readily reduces aldehydes, ketones and carboxylic acids such as substituted pyruvic acids (to α-amino acids) e.g. 3-indolylpyruvic acid to tryptophan (11).



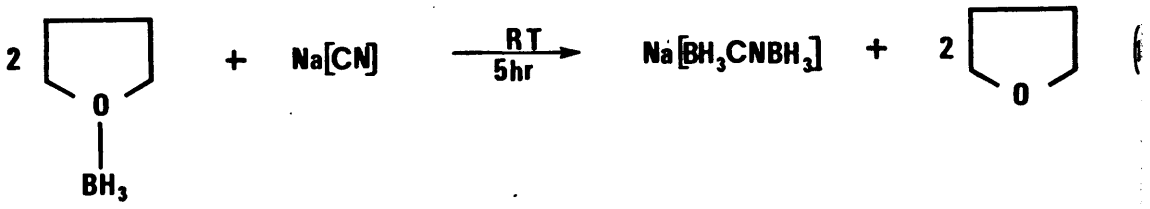
(11)

In general the order of increasing reducing ability in pseudohaloborohydrides is $[BH_2(CN)_2]^- < [BH_3CN]^- < [BH_3SCN]^-$. The greater electron withdrawing ability of cyanide relative to thiocyanate makes $Na[BH_3SCN]$ a stronger reducing agent than $Na[BH_3CN]$.

1.3 DIBORON COMPOUNDS $[B_2H_6X]^-$ AND B_2H_5X

1.3.1 $[B_2H_6X]^-$

To date no halogenated compounds of the type $[B_2H_6X]^-$ have been isolated. However, calculations by Sapse and Osoris[23] on the $[B_2H_6F]^-$ anion indicated a bent structure with a bridging fluorine atom would be the preferred form. A cyanide analogue, $[BH_3CNBH_3]^-$, was first prepared by Muetterties and co-workers in 1961[5,24] by the room temperature reaction of sodium cyanide with borane -THF in a 1:2 stoichiometry (12).



Wade *et al*,[6] later reported that unless a considerable excess of borane-THF complex or longer (75 hours) reaction times were used, significant amounts of $[BH_3CN]^-$ and $[BH_3NC]^-$ are isolated with the product. The presence of these impurities is readily detected by ^{11}B n.m.r. and infra-red spectroscopy of the THF reaction solution or by the infrared spectrum of the isolated product.

The ^{11}B n.m.r. spectrum of $[BH_3CNBH_3]^-$ consists of two quartets, one well defined and the other broadened,[5,16] at -62.3 and -41.8 ppm respectively (^1J (^1H-^{11}B) = 94Hz). The integrated intensities of the two quartets are in the ratio 3:2 (BC:BN). Wade *et al*[16] claimed that the disagreement between this intensity ratio and that expected for the boron atoms (1:1) was probably a result of different relaxation times for the two boron sites.

The B-H vibrations for $[BH_3CNBH_3]^-$ at 2270 and 2225 cm^{-1} are compatible with both $[BH_3CN]^-$ (2240 cm^{-1}) and $[BH_3NC]^-$ (2290 cm^{-1}) but the cyanide absorption is shifted to a higher frequency (2260 cm^{-1}) than either of the monoboron species, (2180 and 2070 cm^{-1} respectively). This strong sharp band at 2260 cm^{-1} is characteristic of a bridging cyanide group.

1.3.2 B_2H_5X

Terminally substituted diborane derivatives are well known. In 1933 Stock[2] prepared B_2H_5Br by direct bromination of diborane at 100°C (13).

$$B_2H_6 + Br_2 \xrightarrow{100^\circ C} B_2H_5Br + HBr \qquad (13)$$

The bromo derivative was also prepared by Schlesinger *et al*[25] by the equilibration of BBr_3 with diborane in an exchange reaction. A similar equilibration using BCl_3 prepared chlorodiborane. An alternative preparation is the reaction of hydrogen iodide or hydrogen bromide with diborane to produce B_2H_5I and B_2H_5Br, respectively.

Both the bromo- and the chloro- derivative are rapidly hydrolysed (14).

$$B_2H_5Cl + 6H_2O \longrightarrow 2B(OH)_3 + HCl + 5H_2 \qquad (14)$$

In a Wurtz-like coupling reaction between B_2H_5I and sodium amalgam, tetraborane (10) has been prepared (15).[26]

$$2B_2H_5I + 2Na \longrightarrow 2NaI + B_4H_{10} \qquad (15)$$

The terminal nature of the bromine atom in B_2H_5Br was confirmed by Gaines and Schaeffer who used ^{11}B n.m.r. techniques.[27] Table 2 lists the ^{11}B n.m.r. signals for the chloro-, bromo- and iodo- derivatives.

Table 2

^{11}B n.m.r. data for B_2H_5X, X = Cl, Br, I

X	δ_B ppm	$^1J(^{11}B\ ^1H)$ Hz	Assignment
Cl	23.0	167	BH_2
	7.7	139	BHX
Br	18.9	163	BH_2
	12.2	141	BHX
I	7.8	172	BH
	18.1	144	BHX

1.4 TRIBORON COMPOUNDS

1.4.1 *Synthesis of* $[B_3H_7X]^-$

The first reported synthesis of a $[B_3H_7X]^-$ species was in 1961 by Aftandillan and co-workers[5] who prepared $[B_3H_7CN]^-$. The authors claimed the cleavage of tetraborane (10) by cyanide ion (16) led to the cyano-haptahydrotriborate anion but no supporting spectroscopic data was reported.

$$2B_4H_{10} + 3[CN]^- \longrightarrow 2[B_3H_7CN]^- + [BH_3CNBH_3]^- \qquad (16)$$

Halogenated analogues, $[B_3H_7X]^-$ (X = Cl, Br, I), were first reported by Ryschkewitsch and Miller in 1975 (17).[28]

$$[Bu_4N][B_3H_8] + HX \xrightarrow{CH_2Cl_2} [Bu_4N][B_3H_7X] + H_2 \qquad (17)$$

X = Cl, Br, I.

Later, Jacobsen and Morris,[29] found that reaction of $[Bu_4N]^+$ or $[(Ph_3P)_2N]^+$ salts of $[B_3H_8]^-$ with mercurous chloride, in noncoordinating solvents such as dichloromethane, generated the $[B_3H_7Cl]^-$ anion (18).

$$2[Bu_4N][B_3H_8] + Hg_2Cl_2 \xrightarrow[R.T.]{CH_2Cl_2} 2[Bu_4N][B_3H_7Cl] + Hg + H_2 \qquad (18)$$

The reaction mixture also contained a second species, $[B_3H_6Cl_2]^-$, present as an impurity. This anion is also the result of a reaction of $[B_3H_7Cl]^-$ with mercurous chloride (19).

$$2[B_3H_7Cl]^- + Hg_2Cl_2 \longrightarrow 2[B_3H_6Cl_2]^- + H_2 + Hg \qquad (19)$$

Previously a 25% yield of $[B_3H_6Cl_2]^-$ had been achieved by the reaction of $[Bu_4N][B_3H_8]$ and hydrochloric acid in dichloromethane.[29]

The brominated analogue, $[B_3H_7Br]^-$, was obtained from the reaction between $[B_3H_8]^-$ and mercurous bromide. However, dichloromethane solutions of the tetrabutylammonium salt quickly decomposed to give tetraborane (10). There was no evidence for the dibrominated product. The reaction between mercurous iodide and the octahydrotriborate anion in dichloromethane yielded tetraborane (10) as the major product, with no evidence for the presence of an iodinated borane salt. The treatment of dichloromethane solutions of $[(Ph_3P)_2N][B_3H_8]$ with mercurous fluoride was thought to produce $[B_3H_7F]^-$ as the major product along with a number of uncharacterised impurities but attempts to isolate pure samples of this product were unsuccessful.[29]

Jacobsen and Morris,[29] observed that the chloride substituent of $[B_3H_7Cl]^-$ was very labile and could be readily substituted by ions such as $[SCN]^-$, (20).

$$[B_3H_7Cl]^- + Ag[SCN] \xrightarrow[R.T.]{CH_2Cl_2} [B_3H_7NCS]^- + Ag[Cl] \qquad (20)$$

45%

The isoselenocyanate analogue, $[B_3H_7NCSe]^-$, was similarly prepared. The reaction of $[B_3H_7Cl]^-$ with silver cyanide which originally had been thought to generate $[B_3H_7CN]^-$, has recently been shown by X-ray diffraction methods, to afford the substituted silver complex, $[Ag\{B_3H_7(NC)\}_2]^-$. The reaction of the dichlorinated anion, $[B_3H_6Cl_2]^-$, with silver cyanide also yielded a cyanide substituted triborane derivative, which had properties similar to $[Hg\{B_3H_7(NC)\}_2]^-$ and which was believed to be $[Ag\{B_3H_6Cl(NC)\}_2]^-$, (21).

$$2[B_3H_6Cl_2]^- + 3Ag[CN] \longrightarrow [Ag\{B_3H_6Cl(NC)\}_2]^- + [CN]^- + Ag[Cl] \qquad (21)$$

Solutions of both $[Ag\{B_3H_7(NC)\}_2]^-$ and $[Ag\{B_3H_6Cl(NC)\}_2]^-$ decomposed on standing at room temperature, depositing silver.

1.4.2 *Spectroscopic Properties*

The infrared spectra of $[B_3H_7Cl]^-$, $[B_3H_6Cl_2]^-$ and $[B_3H_7Br]^-$ are very similar. A larger, higher energy shift, relative to the B-H stretching modes in $[B_3H_8]^-$ was observed for bromine substitution than for chlorine substitution (Figure 4). Dichlorination (Figure 5) affected a further shift of these absorptions to a still higher energy.

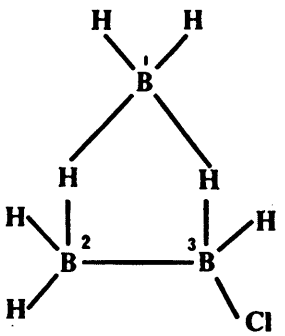


Figure 4: $[B_3H_7Cl]^-$

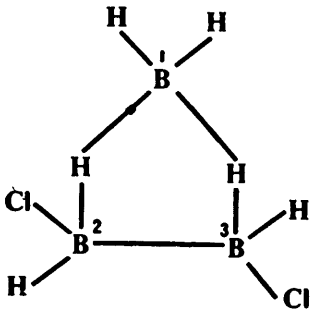


Figure 5: $[B_3H_6Cl_2]^-$

Table 3 lists the B-H frequencies for Cl, Br and Cl_2 substituted octahydroborate anions.

A strong band at 2160 cm^{-1} in the infrared spectrum of $[B_3H_7NCS]^-$ is assigned to NCS assymetric stretch and is indicative of nitrogen coordinated thiocyanate. X-ray diffraction studies have shown that, like both $H_3N.BH_2NCS$[31] and $B_{10}H_{13}(NCS)$[32] which are B-N bonded isothiocyanates, $[B_3H_7NCS]^-$ is also B-N coordinated.[33]

Table 3

B-H Infrared Absorptions[a] of $[B_3H_7X]^-$ and $[B_3H_6X_2]^-$

X = H, Cl, Br

H	Cl	Br	Cl_2
2450 (s)	2480 (s)	2490 (s)	2515 (s)
2400 (s)	2425 (s)	2430 (s)	2455 (s)
2300 (sh)	2300 (sh)	2300 (sh)	
2130 (m)			
2080 (m)			

[a] Frequencies in cm^{-1}

^1H n.m.r. data for mono- and disubstituted halide and pseudohalide heptahydrotriborate anions were reported by Arunchaiya and Morris.[34] The $^1H\{^{11}B\}$ n.m.r. spectra of $[B_3H_7Cl]^-$ in CD_3CN and $CDCl_3$, recorded with broad band irradiation or continuous wave specific frequency irradiation of the ^{11}B resonances are shown in Figures 6 and 7.

In CD_3CN, the $^1H\{^{11}B$, broad band$\}$ spectrum showed a single proton resonance at δ = 1.46 ppm. The spectrum resulting from irradiation of the unsubstituted B (1) and B (2) (Figure 6(c)) showed a coupling pattern comprising of a partly relaxed 1:1:1:1 quartet which results from the remaining coupling of the seven equivalent hydrogens to the boron atom, B (3) with an apparent coupling constant, $^1J(^1H-^{11}B(3))$ of 180 Hz. In $CDCl_3$, the $^1H\{^{11}B\}$ n.m.r. spectrum showed more extensive quadrupolar relaxation.

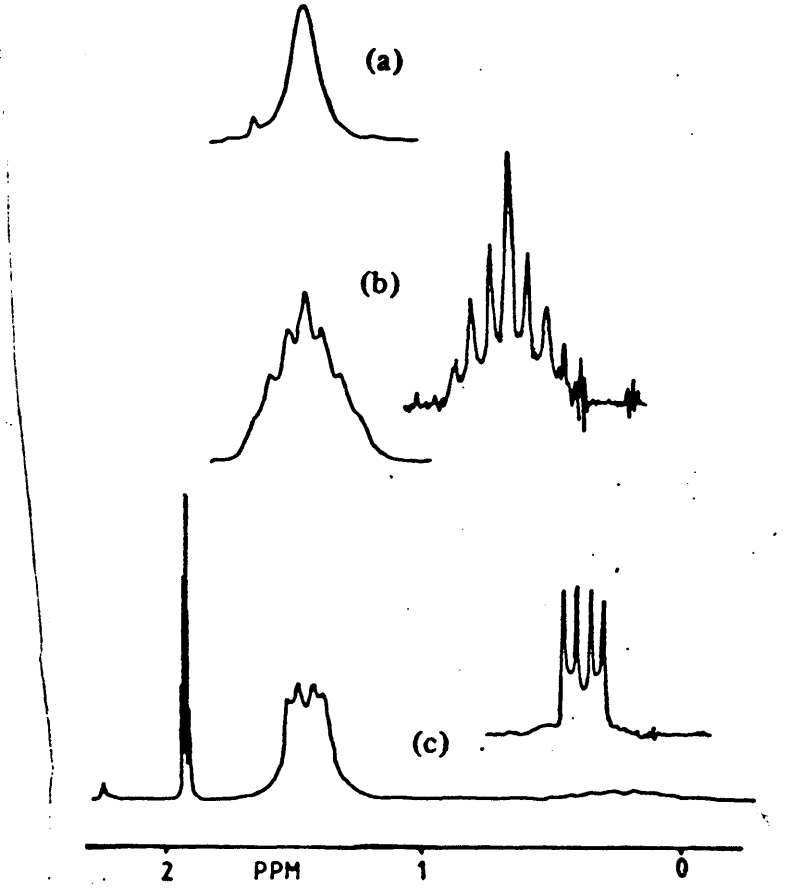


Figure 6: 360 MHz $^{1}H\{^{11}B\}$ NMR spectra of $[B_3H_7(Cl)]^-$ in CD_3CN; (a) Broad band irradiated; (b) Irradiation of the substituted boron, B(3); (c) Irradiation of the unsubstituted borons, B(1, 2).

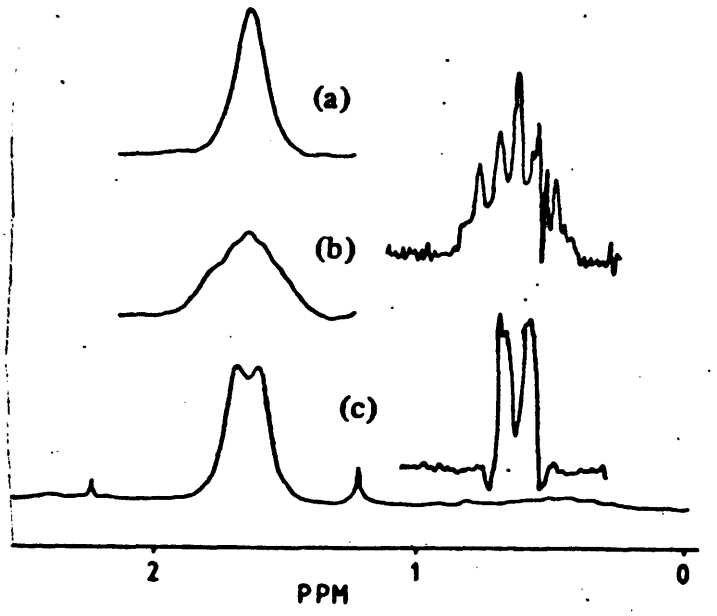


Figure 7: 360 MHz $^{1}H\{^{11}B\}$ NMR spectra of $[B_3H_7(Cl)]^-$ in $CDCl_3$; (a) Broad band irradiated; (b) Irradiation of the substituted boron, B(3); (c) Irradiation of the unsubstituted borons, B(1, 2).

The $^{1}H\{^{11}B\}$ n.m.r. spectra of $[B_3H_6Cl_2]^-$ (Figure 5) in $CDCl_3$ obtained with off-resonance or continuous wave specific frequency irradiation of the ^{11}B resonances are shown in Figures 8 (a-c).

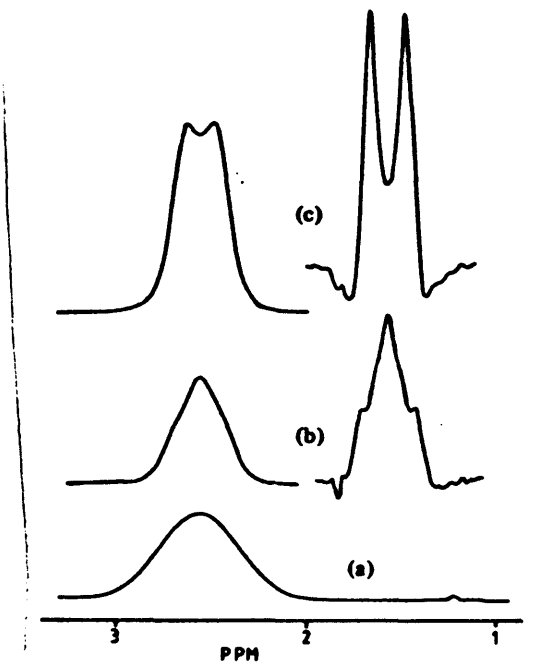


Figure 8: 360 MHz $^{1}H\{^{11}B\}$ NMR spectra of $[B_3H_6(Cl)_2]^-$ in $CDCl_3$

The $^{1}H\{^{11}B$, off-resonance$\}$ spectrum exhibited a broad band (δ = 2.57 ppm). The proton spectrum resulting from irradiation of the unique unsubstituted boron atom, B (1), (Figure 8(b)) showed a signal with fine structure corresponding to coupling to the two remaining boron atoms, B (2) and B (3). The ^{1}H n.m.r. data recorded at 360 MHz for the derivatives and other substituted triborate anions such as $[B_3H_7NCS]^-$ (Figure 9(a)) and $[B_3H_6Cl(NCS)]^-$ (Figure 9(b)) are listed in Table 4.

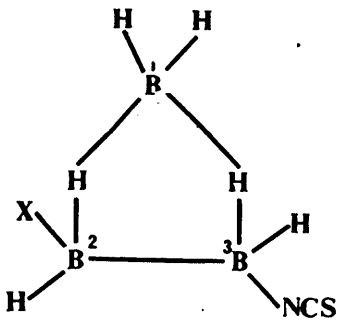


Figure 9: $[B_3H_6X(NCS)]^-$ a, X = H; b, X = Cl

Table 4

^1H n.m.r. Data for Octahydrotriborate (1-) Derivatives

Anion	δ_H/ppm	$J(^1H-^{11}B)$ (Hz)	Solvent
$[B_3H_8]^-$	+0.175	$^1H-^{11}B$ = 32.17 $^1H-^{11}B$ = 10.96	CD_3CN
$[B_3H_7Cl]^-$	+1.46	H-B(3) = 18.0 H-B(1,2) = 25.0	CD_3CN
$[B_3H_7Cl]^-$	+1.63		$CDCl_3$
$[B_3H_7NCS]^-$ [a]	+1.4		CD_3CN
$[B_3H_6Cl_2]^-$	+2.57	H-B(1) = 65	$CDCl_3$
$[B_3H_6Cl(NCS)]^-$	+2.30		$CDCl_3$
$[Ag\{B_3H_6Cl(NCS)\}_2]^-$	+2.24		$CDCl_3$

[a] at 303K and 220K

The ^{11}B n.m.r. spectrum of $[B_3H_7Cl]^-$ at 32.08 MHz consisted of two multiplets with unresolved fine structure due to ^{11}B-^{1}H and ^{11}B-^{11}B couplings. The two unsubstituted boron atoms (B(1) and B(2)) have low field resonances at δ - 16.3 ppm with the substituted boron atom having a high field resonance at δ - 22.2 ppm. This is in keeping with previously reported ^{11}B n.m.r. spectra for neutral B_3H_7L adducts.[35,36]

The ^{11}B n.m.r. spectrum of $[B_3H_6Cl_2]^-$ displayed a low field resonance due to B(1) and a high field resonance for B(2) and B(3). Jacobsen and Morris,[29] initially suggested that this shift of the B(1) resonance supports the contention that both chlorines are substituted on B(1), because the shift was similar to that observed in BH_2Cl and $BHCl_2$ adducts.[37] However, in a later paper, the chlorines are depicted as being trans-substituted on B(2) and B(3). The ^{11}B n.m.r. data for the octahydrotriborate derivatives are listed in Table 5.

Table 5

32.08 MHz ^{11}B n.m.r. Data for $[B_3H_7X]^-$ and $[B_3H_6X_2]^-$

X = Cl, Br, NC, NCS, F

Compound	δ (ppm) B(2), B(3)[a]	δ (ppm) B(1)[a]	J ^{11}B-^{1}H (Hz)[d]
$[B_3H_7Cl]^-$ [c]	-16.3	-22.2	42.0
$[B_3H_6Cl_2]^-$ [c]	-13.4	- 5.3	35.4
$[B_3H_7Br]^-$ [b]	-12.2	-28.9	
$[B_3H_7NC]^-$ [e]	- 9.6	-36.6	41.0
$[B_3H_7NCS]^-$ [c]	-13.2	-33.5	38.0
$[B_3H_7F]^-$ [c]	-17.6	-15.4	38.5

[a] Shifts expressed relative to BF_3 Negative shifts are high field.
[b] Solvent, CD_2Cl_2. [c] Solvent, $CDCl_3$. [d] 115.5 MHz line narrowed data.
[e] Solvent, CD_3CN.

The use of 2D boron-boron coordination n.m.r. spectroscopy (^{11}B-^{11}B COSY) has been shown to give valuable information relating to boron atom connectivities.[38-42] Meina *et al* in 1986[42] reported an ^{11}B-^{11}B COSY study on halogenated and pseudohalogenated octahydrotriborate compounds.[43-45] All the monosubstituted triborane derivatives had ^{11}B n.m.r. spectra which comprised two signals of relative intensities 2:1, and correlations occurred between these in all cases. In the disubstituted triboranes, the symmetrical $[B_3H_6Cl_2]^-$ anion showed a correlation between the resonances of the unsubstituted boron and the two substituted boron atoms (Figure 10). Each of the unsymmetrical disubstituted anions exhibited ^{11}B n.m.r. spectra which comprised of three resonances of relative intensities 1:1:1 (Figure 11).

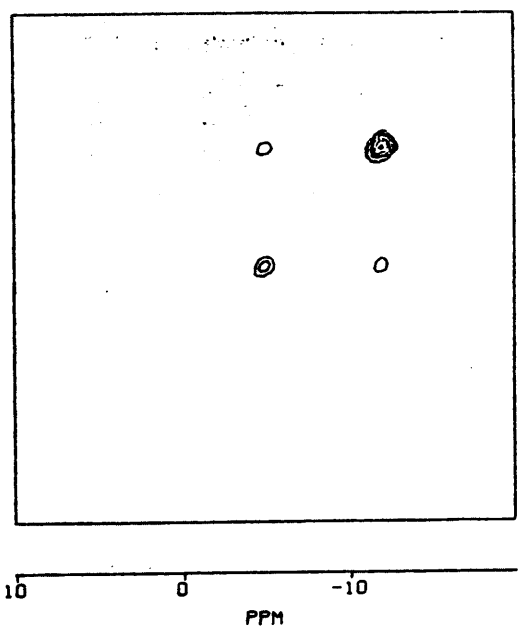


Figure 10 ^{11}B COSY n.m.r. of $[B_3H_6Cl_2]^-$

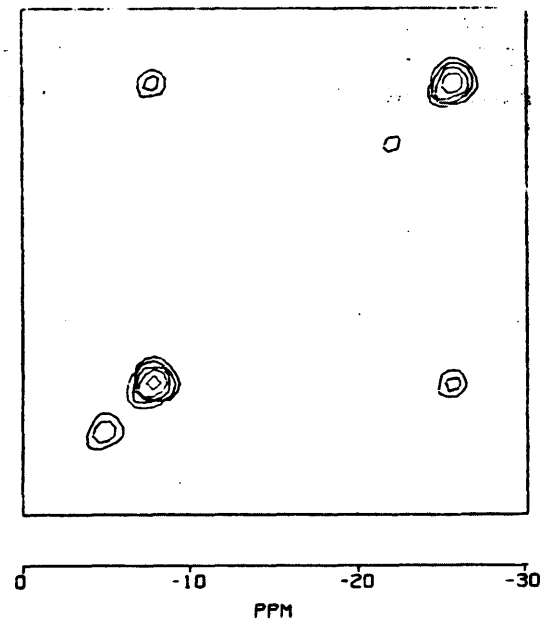
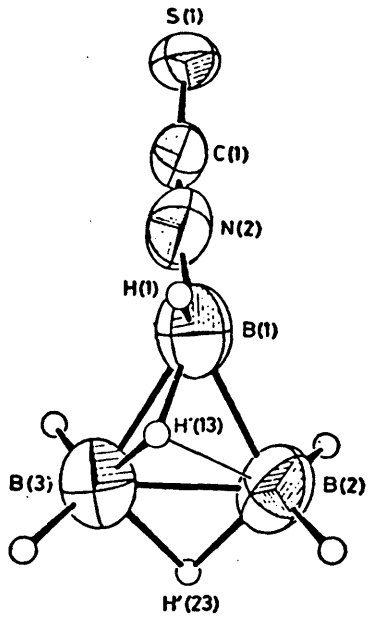


Figure 11 ^{11}B COSY n.m.r. of $[B_3H_6Cl(NCS)]^-$

Solid State Studies

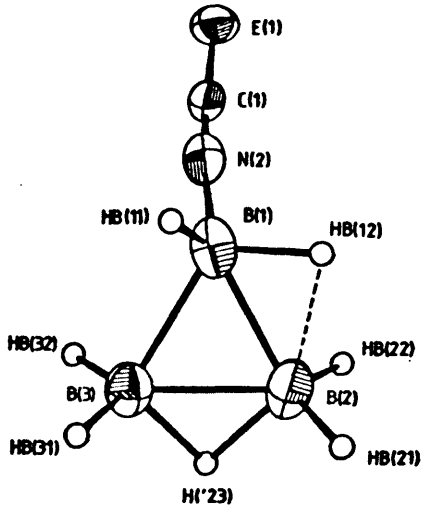
Andrews *et al* initially published an X-ray crystallographically determined structure of $[(Ph_3P)_2N][B_3H_7(NCS)]$ (Figure 12) with a μ_3-H bridge.[1] But in a later paper,[33] the structure was amended to that in Figure 13, using data collected at low temperature (185K).

The strongly bridging μ_2-H (13) between B(1) and B(3) and weakly linked to B(2) (Figure 12) is changed to a weak, semibridging interaction between B(2) and B(3). The different interpretations of the μ-H position were related to the fact that the X-ray data were collected at different temperatures, which affected the data especially for the μ-H position. The latter type structure is also observed for $[B_3H_7NCSe]^-$.



Projection of the structure of the $[B_3H_7NCS]^-$ anion. Molecular parameters include B(1)–B(2) 1.802(9), B(1)–B(3) 1.780(9), B(2)–B(3) 1.758(8), B(1)–H'(13) 1.151(15), B(3)–H'(13) 1.182(20), B(2)–H'(13) 1.639(13), B(2)–H'(23) 1.367(20), B(3)–H'(23) 1.479(13), and B(1)–N(2) 1.510(7) Å.

Figure 12



Perspective view of the anions of 1 and 2, with atomic numbering scheme. Thermal ellipsoids are constructed at the 30% probability level (using data from 1 (LT)), except for H atoms which have an artificial radius of 0.1 A for clarity. For 1 E = S, for 2 E = Se.

Figure 13

In both structures, the BNCS and BNCSe fragments are nearly linear with bond distances, B(1)-B(2), 1.802 Å, B(1)-B(3), 1.780 Å; and B(2)-B(3), 1.758Å. All terminal B-H bonds are of expected length (mean 1.10 Å). The B-N, N-C and C-S bonds are 1.51, 1.17 and 1.54 Å respectively.

1.4.3 *Chemical Stability and Reactions*

The halogen substituted salts, $[B_3H_7X]^-$, are thermally and hydrolytically rather unstable. However, the isothiocyanate, $[B_3H_7NCS]^-$ is stable and the $[Bu_4N]^+$ or $[(Ph_3P)_2N]^+$ salts show negligible decomposition when stored at room temperature in air for a period of months. Solutions of $[B_3H_7CN]^-$ in chlorinated hydrocarbons quickly decomposed, depositing a black solid, whereas solutions in acetonitrile appeared to be stable. Salts of $[B_3H_6Cl_2]^-$ and $[B_3H_6Cl(NCS)]^-$ deteriorated slowly and survived several days exposure to air.

Substituted $[B_3H_7X]^-$ (X = Cl, Br) ions have been used to synthesise higher boranes, such as pentaborane (9) by a thermal decomposition route (22).[5]

$$5[Bu_4N][B_3H_7Br] \xrightarrow{100^\circ C} 3B_5H_9 + 4H_2 + 5[Bu_4N][Br] \qquad (22)$$

Shore[3] isolated tetraborane (10) and the monobrominated analogue (10-15% each) from the reaction of $[Bu_4N][B_3H_7Br]$ and boron tribromide. Ryschkewitsch and Miller[28] reportedly prepared pentaborane (9) (36.8%) from a reaction of $[Bu_4N][B_3H_7Br]$ under vacuum. No evidence for pentaborane (11) was detected in the products.

1.5 TETRABORANE SPECIES

1.5.1 $[BH_3CN\ B_3H_7]^-$

The reaction of dichloromethane solutions of $[B_3H_7Cl]^-$ with $[Bu_4N][BH_3CN]$ yielded the bridged-cyanide ion $[BH_3CN\ B_3H_7]^-$ as the major product, along with small amounts of $[BH_3CNBH_3]^-$ and $[BH_3CNBH_2CN]^-$ which were identified by their ^{11}B n.m.r. spectra (23).[5,40]

$$[B_3H_7Cl]^- + [Bu_4N][BH_3CN] \longrightarrow [BH_3CNB_3H_7]^- + [Bu_4N][Cl] \quad (23)$$

The formation of $[BH_3CNBH_2CN]^-$, which is also an oxidation product of $[BH_3CN]^-$, was claimed to arise from a reaction involving a small amount of dissolved mercury salts in the solution of $[B_3H_7Cl]^-$. The presence of $[BH_3CNBH_3]^-$ was rationalised by the fact that some B_3H_7L adducts undergo cleavage[41-43] by excess ligand to yield BH_3L and $B_2H_4L_2$ as decomposition products (24).

$$B_3H_7L + L\ (\text{excess}) \longrightarrow BH_3L + B_2H_4L_2 \quad (24)$$

A similar reaction using $[(Ph_3P)_2N][B_3H_7X]$ (X = Cl, CN) yielded the $[(Ph_3P)_2N]^+$ salt of $[BH_3CNB_3H_7]^-$. The structure of this species appeared to consist of separate B_3^- and B- units linked by the CN- ion in a similar manner to $[BH_3CNBH_3]^-$.

The ^{11}B n.m.r. spectrum of $[BH_3CNB_3H_7]^-$ showed the usual low field resonance due to B(1) and B(2) (δ - 9.9 ppm) and a high field resonance due to B(3) (δ - 36.1 ppm), along with a well defined quartet at δ - 43.8 ppm [$^1J_{(^{11}B-^1H)}$ = 93Hz] consistent with the BH_3CN moiety. The latter compares with the chemical shift of δ - 41.8 ppm [$^1J_{(^{11}B-^1H)}$ = 90Hz] in free cyanoborohydride.[18] The infrared spectrum of $[BH_3CNB_3H_7]^-$ showed B-H stretching modes due to the B_3H_7 moiety along with bands at 2375 and

2345 cm^{-1} due to the B-H stretching of the BH_3- group. The strong sharp band at 2255 cm^{-1} is characteristic of a bridging cyanide and is also similar to that reported for $[BH_3CNBH_3]^-$ (2260 cm^{-1}).[16] The $[BH_3CNB_3H_7]^-$ salts were of comparable stability to those of $[B_3H_7NCS]^-$.

Jacobsen and Morris[46] examined the hydrolytic stabilities of $[B_3H_7NCS]^-$ and $[BH_3CNB_3H_7]^-$. The $[(Ph_3P)_2N]^+$ salt of $[B_3H_7NCS]^-$ was found to be stable to pH 4, at which point free thiocyanate ion could be detected by infrared spectroscopy. In contrast, $[(Ph_3P)_2N][BH_3CNB_3H_7]$ was found to be stable to pH 1 but hydrolysis occurred when solutions of the salt in acetonitrile were treated with 12M HCl.

1.5.2 *B_4H_9Br*

In 1982 Toft *et al*[47] reported that when the butylammonium salt of $[B_3H_7Br]^-$ is reacted with BBr_3 (25) the principal products are 2-BrB_4H_9, B_4H_{10}, 2-BrB_5H_8 and B_2H_6 (each in 10-15% yields).

$$[Bu_4N][B_3H_7Br] + BBr_3 \xrightarrow[-78^oC]{CH_2Cl_2} 2\text{-}BrB_4H_9 + B_4H_{10} + 2\text{-}BrB_5H_8 + B_2H_6 \quad (25)$$

Other volatile products, B_2H_5Br, 1-BrB_5H_8 and B_5H_9, were obtained in smaller amounts (1-5%). The reaction described above is an alternative to that of B_4H_{10} with Br_2 over an 18 hour period at -15°C.[48] The ^{11}B (Figure 14) and ^1H n.m.r. (Figure 15) spectra for 2-BrB_4H_9 were recorded at 96.2 and 300 MHz respectively.

The ^{11}B spectra (Figure 14) are consistent with the previously assigned 19.3 MHz spectra,[48] with the exception that the resonances due to B(2) and B(4) no longer overlap in the coupled spectrum and that those for B(3) are found at -39.4 ppm instead of -34.7 ppm.

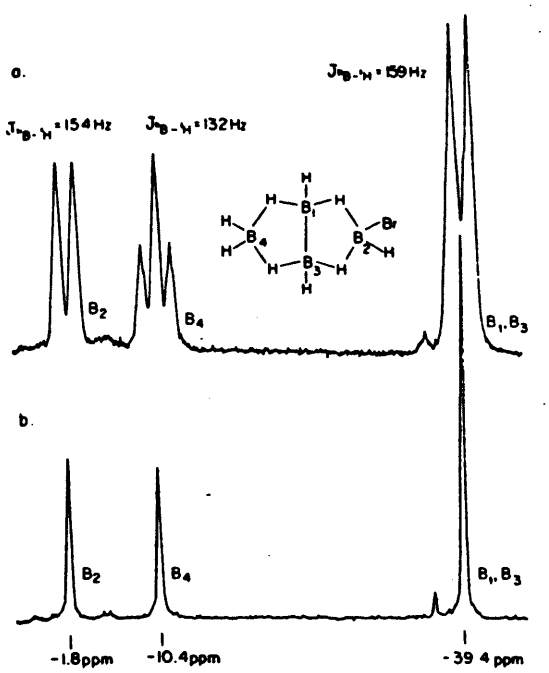


Figure 14: 96.27-MHz boron-11 NMR spectra of 2-BrB_4H_9 in CD_2Cl_2 at -20 °C: (a) proton coupled; (b) proton decoupled.

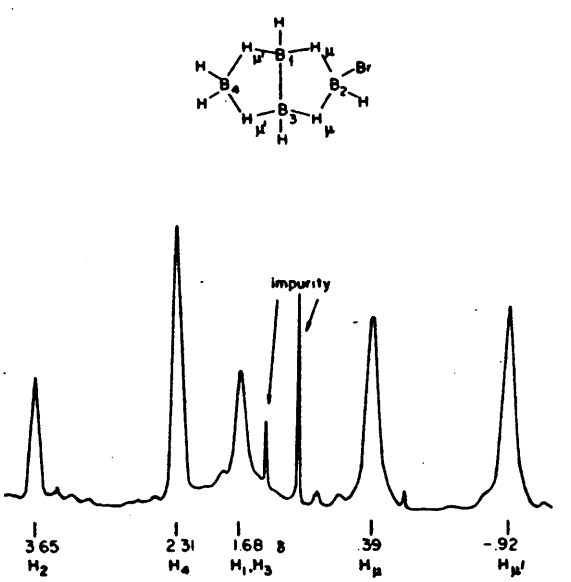


Figure 15: 300-MHz proton NMR spectrum of 2-BrB_4H_9 in CD_2Cl_2 at -20 °C, with the boron-11 broad band decoupled.

1.6 PENTABORANE COMPOUNDS

1.6.1 *Synthesis*

Figgis and Williams[49] prepared the first chloro- and bromo- mono-substituted pentaborane derivatives, 1-XB_5H_8, (Figure 16) in 1959 (26).

$$B_5H_9 + X_2 \longrightarrow 1\text{-}XB_5H_8 + HX \qquad (26)$$

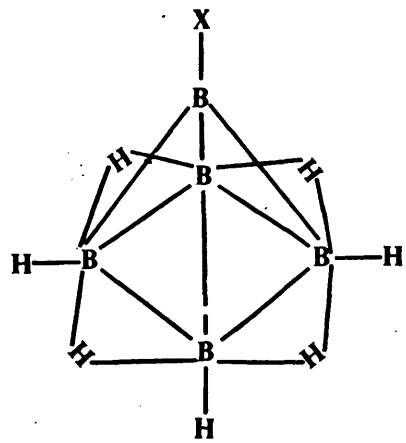


Figure 16 1-XB_5H_8 X = Cl, Br

Onak and Dunks[50] isolated 2-ClB_5H_8, in 8.2% yield, from a halogen exchange reaction between 1-BrB_5H_8 and $AlCl_3$ (27)

$$1\text{-}BrB_5H_8 \xrightarrow{AlCl_3} 2\text{-}ClB_5H_8 \qquad (27)$$

8.2%

Side products of this reaction included B_5H_9, BCl_3, $HBCl_2$, B_2H_6 and HCl. Several attempts to synthesise 2-BrB_5H_8 *via* 1-BrB_5H_8 and $AlCl_3$ or from reaction of BCl_3 and 1-BrB_5H_8 resulted only in the recovery of starting

materials. Gaines[51] reported on alternative synthesis of 1-ClB_5H_8 in 1966 using a catalysed reaction. Prior to this, attempts to produce 1-chloropentaborane, in carbon disulphide, in the presence of aluminium chloride furnished only microquantities of a chloropentaborane contaminated with carbon tetrachloride.[52] Duplication of this reaction on a larger scale resulted in explosions.[53] When no catalyst is used in Gaines' synthesis 2-ClB_5H_8 is the predominant isomer produced but the yields never exceed 30%.

Very high yields of bromo- and iodo- pentaborane were obtained without either catalyst or solvent by Hall *et al.*[54] The optimum reaction conditions for the iodo-derivative (7 95% yield) were 14 days at 75°C with 25% excess pentaborane (9), for the bromo derivative complete reaction occurs in 6-8 hours at room temperature with a 10% molar excess of pentaborane (9). If an excess of halogen is present polyhaloboranes are usually formed.

Burg and Sandhu[55] studied the reversible conversion of 1-BrB_5H_8 to 2-BrB_5H_8 catalysed by hexamethylenetriamine. After 20 hours at 35°C in a sealed tube, 48.5% conversion had taken place.

In 1985, Taylor and Wallbridge[56] reported the synthesis of $Na[B_5H_9CN]$ from the reaction of pentaborane (4) with sodium cyanide (27).

$$B_5H_9 + Na[CN] \xrightarrow[-30^\circ \text{ to } 10^\circ C]{\text{monoglyne}} Na[B_5H_9CN] \qquad (27)$$

The product is isolated in the form of a dioxanate. When excess pentaborane (9) is used, another reaction occurs which yields predominantly the $[B_9H_{14}]^-$ anion. When sodium cyanoborohydride is used instead of $[CN]^-$ no intermediates of the type $Na[B_5H_9CN]$ are detected and the major product is again $[B_9H_{14}]^-$.

1.6.2 *Spectral Properties*

^{11}B n.m.r. spectra have been recorded by Onak *et al*[57] for both 1- and 2- chloro- and bromo- substituted and 1- iodopentaboranes. Table 6 lists the chemical shift values for these compounds.

Substitution of a hydrogen by a halogen at the apex ($1\text{-}XB_5H_8$) or at the base ($2\text{-}XB_5H_8$) of pentaborane generally results in a downfield chemical shift for the so attached boron. The only known exception is 1-iodopentaborane.[58] The magnitude of the shift for various directly attached substituents is not unusual when compared to other boron systems.[58-63] However, the unique boron diagonally opposite the B-X substituent is located at an unusually high field.[58,64] Onak and Dunks[50] at first attributed this to a long range effect similar to that found in substituted benzenes.[65] The same authors revised this theory in a later publication[57] in which they claimed that considering the complexities inherent in rationalising chemical shifts in boron compounds, other factors could contribute to the observed shift.

The ^{1}H n.m.r. spectra of substituted pentaboranes reveal the following trends: (i) the signal for the proton bonded to the apical boron is shifted upfield upon basal substitution (alkyl groups are more effective in this than the known halogen derivatives); (ii) upon halogen substitution at the apex the signal for the basal protons is shifted to a slightly lower field. Double resonance of the ^{11}B nuclei resolved the two types of bridge hydrogens in 2-chloro- and 2-bromopentaborane, but because the number of each kind is identical an absolute assignment was not possible.

Mass spectral data for $1\text{-}BrB_5H_8$ and $1\text{-}IB_5H_8$ were reported by Hall *et al*[66] including the ionisation potentials of the parent molecules and appearance potentials of $[B_5H_8]^+$ ions. The ionisation potentials of the iodo-

Table 6

^{11}B n.m.r. Chemical Shifts Values and Coupling Constants for B_5H_8X isomers[a]

Compound	Boron Environment	δ[b]	$^1J_{(^{11}B-^1H)}$
1-ClB_5H_8	B(1)	30.6	
	B(2,3,4,5)	14.5	ca 160
2-ClB_5H_8	B(1)	51	174
	B(2)	-0.5	
	B(3,5)	12.5	177
	B(4)	22.0	178
1-Br B_5H_8	B(1)	36.4	
	B(2,3,4,5)	12.5	161
2-Br B_5H_8	B(1)	53.5	180
	B(2)	11[c]	
	B(3,5)	15[c]	ca 170
	B(4)	20[c]	ca 170
1 I-B_5H_8	B(1)	55.0	
	B(2,4,5)	11.8	160

[a] all spectra were recorded at 12.8 MHz

[b] δ ppm relative to BF_3OEt_2

[c] represents an approximate value for the designated types of boron atoms. Overlapping of resonances make individual assignments difficult.

and bromo-substituted pentaboranes are more than 1 e.v. lower than pentaborane (4), i.e. $I_p(B_5H_8I) = 9.20 \pm 0.1$ e.v.

1.6.3 *Mechanism of Rearrangement and Substitution*

It is recognised that 2-substituted pentaboranes (Figure 17) are thermodynamically more stable than the corresponding 1-substituted derivatives.[63,67-72]

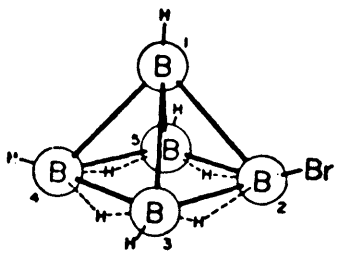


Figure 17: $2\text{-}BrB_5H_8$

Gaines has suggested that in the absence of a strong Lewis acid the chlorination of pentaborane lending to $2\text{-}ClB_5H_8$ is a radical reaction. This assumption on the uncatalysed chlorination of pentaborane is supported by the following observations. First, when the bromination of pentaborane is carried out in the presence of strong ultraviolet irradiation, the reaction proceeds about one hundred times faster than usual,[71] and the ratio of $2\text{-}BrB_5H_8$:$1\text{-}BrB_5H_8$ increases from the value (0.049) reported by Burg and Saudhu[69] to 1.2 (although the total yield of bromo-pentaboranes decreases to about 45% based on bromine). Second, attempts to chlorinate pentaborane with ICl and ICl_3 resulted in the formation of $1\text{-}IB_5H_8$ in yields greater than 90% in both cases.

In contrast to these results, halogenations with bromine and iodine, under the same conditions, furnish 1-halopentaboranes almost exclusively and in high yields. These reactions can be envisaged as occurring *via* heterolytic cleavage of the halogen followed by electrophilic displacement of a proton from the 1-position in pentaborane, by the positive halogen. This concept is similar to the chlorination reaction in the presence of aluminium chloride, a strong heterolytic Friedel-Crafts catalyst.

The reaction between aluminium chloride and 1-bromopentaborane to give 2-chloropentaborane was the first observed halogen exchange-rearrangement reaction in a borane cluster. Onak and Dunks[50] initially suggested that the mechanism for exchange involved a bridged intermediate or transition state analogous to the structure of the aluminium chloride dimer, but the low yield of product near the decomposition temperature (*ca* 158-160°C) of 1-BrB_5H_8 suggested a fragmentation-exchange-recombination sequence.

1.7 HEXABORANE COMPOUNDS

Chlorohexaborane (Figure 18) was synthesised by the reaction of K $[B_6H_9]$ and chlorine gas (28)

$$K[B_6H_9] + Cl_2 \xrightarrow[-80^{\circ}C]{(CH_3)_2O} B_6H_9Cl + K\,Cl \qquad (28)$$

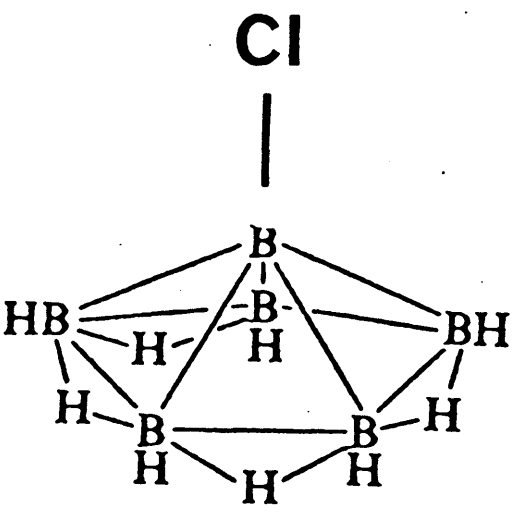


Figure 18 B_6H_9Cl

Bromohexaborane was isolated in 71% yield from the room temperature reaction of hexaborane (10) and BBr_3. Previous to this, BrB_6H_9 had been prepared in 10% yield by the reaction of hexaborane (10) with bromine.[73] Iodohexaborane was isolated in 78% yield from the condensation of excess B_6H_{10} into a tube containing BI_3. A side product of this reaction was $B_{13}H_{19}$ and upto 40% yield of this compound was achieved by increasing the reaction time. Heating the reaction mixture yielded trace amounts of $B_{13}H_{18}I$, which was detected by mass spectrometry.

Reactions of hexaborane (10) with either BF_3 or BCl_3 failed to produce any halogenated cluster compounds.[74-76] Cooling the reaction to -95°C or heating to 60°C for one week yielded either starting materials or caused decomposition of hexaborane.[77,78]

1.7.1 *Reactions*

Lewis basicity decreases through the series B_6H_{10} > B_6H_9I > B_6H_9Br > B_6H_9Cl as determined by the rate and extent of reaction of these compounds with boron trihalides. This agrees with the predicted availability of electron density at the unbridged basal B–B bond in these compounds.

1.8 OCTABORANE COMPOUNDS

One interesting side product formed in low yield from the reaction of $B_9H_{13}(SMe_2)$ with $[(Ph_3P)_2N][NCS]$ (29) was the eight boron cluster $[(Ph_3P)_2N][B_8H_{12}NCS]$.[79]

$$B_9H_{13}(SMe_2) + [NCS]^- \longrightarrow [B_9H_{13}NCS]^- + Me_2S + [B_8H_{12}NCS]^- \qquad (29)$$

This compound represents the first example of a stable anionic eight boron cluster and may be regarded as a derivative of the unknown $[B_8H_{13}]^-$ anion.[80]

1.8.1 *Spectral Analysis*

The ^{11}B spectrum of $[B_8H_{12}(NCS)]^-$ (Figure 19) comprises five doublets of relative area 1, one doublet of relative area 2 and a triplet of area 1.

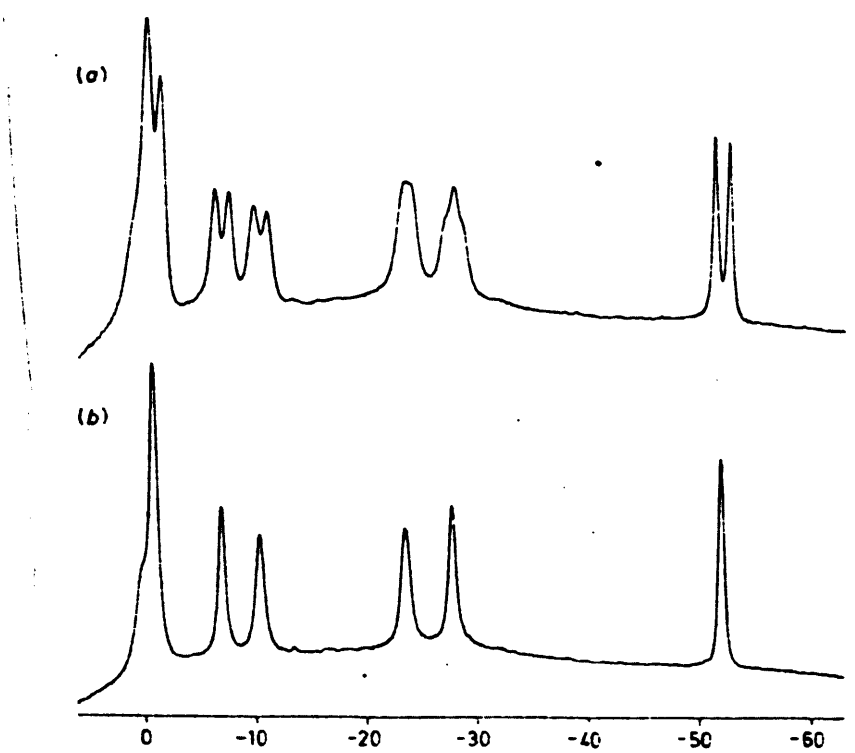


Figure 19 ^{11}B (a) and $^{11}B\{^1H\}$ (b) n.m.r. spectra (115.5 MHz) of $[B_8H_{12}NCS]^-$

The ^{1}H spectrum showed a complex pattern of overlapping 1:1:1:1 quartets due to terminal hydrogens on boron, and in addition, two resonances of relative area 2:1 at -2.1 and 3.0 ppm which may be assigned to bridging hydrogens. ^{1}H n.m.r. spectra with specific frequency boron decoupling confirmed the assignements of the ^{11}B spectrum. The n.m.r. data are consistent with the structure (Figure 20) with no plane of symmetry.

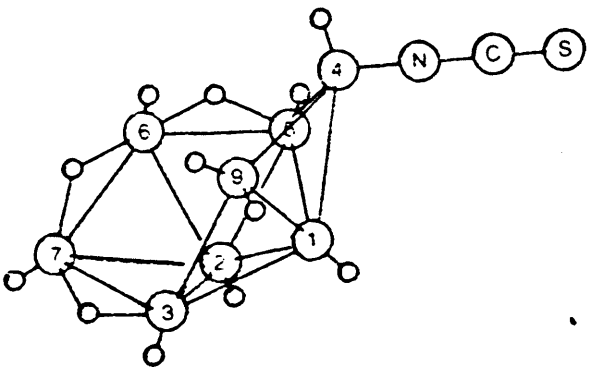


Figure 20 Proposed Structure of $[B_8H_{12}NCS]^-$

Jacobsen *et al*[79] suggested that the compound is also structurally similar to the neutral derivatives $B_8H_{12}(NMe_3)$ and $B_8H_{12}(NCCH_3)$,[81] whose ^{11}B n.m.r. spectra have been recorded at 19.3 MHz[80] and is also structurally related to the known derivative, $[(Et_2NH)B_8H_{11}(H_2NEt)]$.[82]

1.9 NONABORANE COMPOUNDS

1.9.1 *Synthesis*

The first halogenated B_9- clusters were prepared in 1969.[84] Treatment of $B_9H_{13}(SMe_2)$ with bromine generated 56.2% of $B_9H_{12}Br(SMe_2)$ and 2.9% of the dibrominated derivative, $B_9H_{11}Br_2(SMe_2)$. Subsequently, Nelson[85] reported that the $[B_9H_{12}]^-$ anion reacted with mercury halides to give the halogenated *nido* anions, $[B_9H_{10}Cl_2]^-$, $[B_9H_{11}Cl]^-$ and $[B_9H_{11}Br]^-$ as well as neutral $B_{18}H_{22}$. Jacobsen *et al*[86] reported the preparation of *arachno* $[B_9H_{13}Cl]^-$ in 34% yield by an unusual addition reaction of $[(Ph_3P)_2N][B_9H_{12}]$ and HCl (30)

$$[(Ph_3P)_2N][B_9H_{12}] + HCl \xrightarrow[3\ hrs]{R.T.} [(Ph_3P)_2N][B_9H_{13}Cl] \qquad (30)$$

The authors noted that the successful synthesis of $[B_9H_{13}Cl]^-$ was dependent on the choice of counter ions; $[(Ph_3P)_2N]^+$ gave $[B_9H_{13}Cl]^-$ but with $[Bu_4N]^+$ only *anti*- $B_{18}H_{22}$ was isolated. Possible reasons for this difference in reactivity were discussed.[85]

Muetterties and Knoth[83] prepared $[B_9H_{13}NCS]^-$ in 1965. On recrystallisation of a sample of $[B_{10}H_{12}NCS]^-$ from water vigorous hydrogen evolution occurred,[5] and the only anionic species isolated from this aqueous solution was $[B_9H_{13}NCS]^-$. Muetterties and Knoth[5] reported that this anion could also be prepared in high yield by the reaction of decaborane with an aqueous dioxane solution of potassium thiocyanate. An alternative preparation in 1984 by Jacobsen *et al*[79] involved the use of $B_9H_{13}(SMe_2)$ (31).

$$B_9H_{13}(SMe_2) + [NCS]^- \xrightarrow[reflux]{C_2H_4Cl_2} [B_9H_{13}NCS]^- + Me_2S \qquad (31)$$

45%

The iso selenocyanate and cyanoborohydride derivatives have also been prepared.[83]

1.9.2 *Spectral Properties*

Jacobsen *et al*[79] reported high field ^{11}B and ^{1}H n.m.r. spectra for $[B_9H_{13}NCS]^-$ (previously reported low field spectra had failed to resolve some of the boron signals). In the ^{11}B n.m.r. spectrum five doublets were observed, similar to the corresponding signals in neutral $B_9H_{13}L$ species, with the exception that the resonance associated with the substituted boron atom, B(4), was a singlet. Selective irradiation at the ^{1}H resonance of the bridged hydrogens resulted in sharpening of resonances due to B(6) and B(8), B(5) and B(9), and B(4) in $[B_9H_{13}(NCS)]^-$. The suggested cage structure is shown in Figure 21 and has been confirmed by a single crystal X-ray diffraction study.

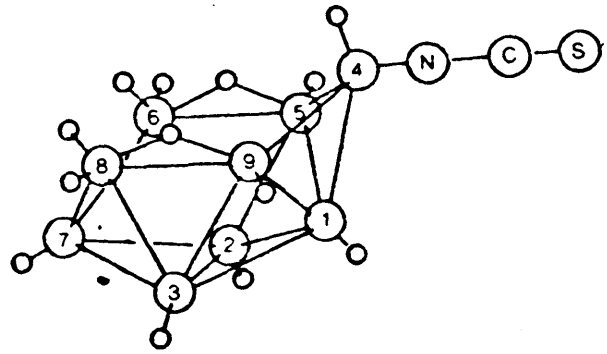


Figure 21 Suggested Structure of $[B_9H_{13}NCS]^-$

The ^{11}B data was interpreted as suggesting that the ion was fluxional and further evidence was obtained from ^{1}H spectra. A variable temperature ^{1}H n.m.r. study of the fluxional process was reported.

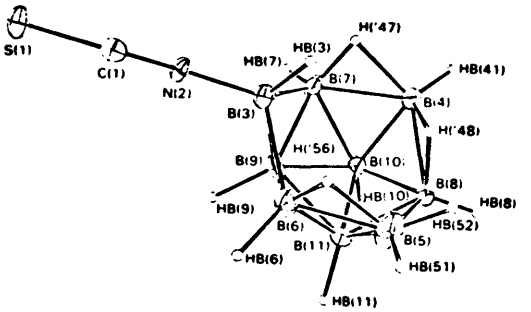
At room temperature the presence of a single signal for five bridging hydrogens (δ - 1.4 ppm) was observed. Thus rapid intramolecular exchange of the two bridging hydrogens with two *endo*-hydrogens from B(6) and B(8) and the single terminal hydrogen was occurring. At temperatures below 233K the appearance of a bridging hydrogen resonance (δ - 3.3 ppm) showed the presence of only two bridging hydrogens. In addition a new resonance of relative intensity 2 appeared at -0.41 ppm, indicating two hydrogens in an *endo*-terminal environment. At 203K another terminal hydrogen signal was observed (δ - 0.6 ppm). The intramolecular exchange between the bridging hydrogens, the two *endo*-terminal hydrogens, and the terminal hydrogen at B(4) was sufficiently slowed to indicate a coalescence temperature near 243K, but the static structure was not fully achieved above 203K.

The ^{11}B n.m.r. spectrum of $[B_9H_{13}Cl]^-$ is fully consistent with an anion that is fluxional at room temperature and parallels the results for $[B_9H_{13}NCS]^-$.

1.9.3 *Structure of* $[(Ph_3P)_2N][B_9H_{13}NCS].0.5CH_2Cl_2$

The cage structure of the $[B_9H_{13}NCS]^-$ anion, inferred from high field and variable temperature n.m.r. was similar to that of $B_9H_{13}(NCCH_3)$, proposed by Wang *et al*,[87] in which there were μ- 4, 7 and μ - 5, 6 hydrogen atoms, in contrast to the parent species $[B_9H_{14}]^-$[88] which has μ- 3, 6 and μ- 3, 7 hydrogen atoms. The solid state structure of $[B_9H_{13}NCS]^-$ was determined as its $[(Ph_3P)_2N]^+$ salt.[89] Andrews and Walsh initially determined the structure from a data set collected at room temperature (α-form) but this study failed to locate all the borane hydrogen atoms. On repeating the experiment with a different crystal at low temperature (185K) a second crystalline modification (β-form) was

unexpectedly encountered. Solution and refinement of this structure allowed all the borane hydrogens to be located. The cage of the $[B_9H_{13}NCS]^-$ anion (β-form) has an *arachno* architecture with hydrogen atoms bridging the 4,7; 4, 8; and 5, 6 B-B connectivities and a BH_2 group at position 5. B(3) also carries two terminal functions, *exo*-polyhedral NCS and *endo*-polyhedral HB(3) (Figure 22).



A perspective view of the anion.

Figure 22 Structure of $[B_9H_{13}NCS]^-$ (β-form)

The discovery of the third hydrogen bridge [between B(4) and B(8)] in the β-form was unexpected; although such an arrangement had been observed[90,91] in *commo*- $B_{15}H_{23}$ which contains a similar B_9H_{13} fragment. Bridging μ- 4, 7 and μ- 5, 6 are also found in $B_9H_{13}(NCCH_3)$[87] and μ- 3, 6 and μ - 3, 7 in $[B_9H_{14}]^-$.[88] It appears then that the n.m.r. data reported, where only two bridging hydrogens were observed, do not coincide with the solid state structural data in which three bridging hydrogens are noted. No explanation for this was given by the authors.

1.9.4 *Reactions*

Meina and Morris[92] have reported ion exchange reactions between the isothiocyanate $[B_9H_{13}NCX]^-$ anion (X = S, Se) and $[Cu(PPh_3)_2][BH_4]$ which produce $[Cu(PPh_3)_2][B_9H_{13}NCX]$ salts in high yield.

1.10 DECABORANE COMPOUNDS

1.10.1 *Synthesis*

Of all the boron hydrides, decaborane stands out as the most widely studied in terms of its reaction chemistry. Stock,[2] reported the isolation of two dihalo-decaboranes from the reaction of the halogen and decaborane in a sealed tube. These compounds analysed as a dibromodecaborane and a diiododecaborane.[3] By means of a preliminary X-ray crystal structure determination, Schaeffer[93] showed that the iodine atoms were in the 2- and 4- positions in agreement with Lipscomb's predictions[81] from molecular orbital theory for the electrophilic substitution preferences of decaborane.

Two patents[94,95] were published concerning the properties of a dichlorodecaborane (m.p. 115-122°C) and a monochlorodecaborane (m.p. 40-55°C). The preparation in both cases involved the use of chloroform or 1,1-dichloroethane in the presence of aluminium chloride. The structure of neither compound was reported. A bromodecaborane and a dibromodecaborane were also prepared by a similar reaction using ethylene bromide or bromoform (32).

$$2B_{10}H_{14} + H\text{-}CBr_3 \longrightarrow B_{10}H_{13}Br + B_{10}H_{12}Br_2 + CH_4 \qquad (32)$$

In an attempt to prepare fluorodecaboranes, Hillman and Mangold[96] reacted 1,1-difluoroethane with aluminium chloride and decaborane. However, the product of the reaction was a mixture of 1- and 2-chlorodecaborane. Fluorodecaboranes were subsequently prepared by a sealed tube reaction of decaborane and hexafluorobenzene at 100°C.

Alternative approaches to halodecaboranes using the conditions of Friedel-Crafts substitution (34)[97] (iodination,[98-104] bromination,[90,92,105-] chlorination[94,96]) had been reported by 1968 and gave rise to mixtures of 1- and 2- isomers.

$$B_{10}H_{14} + X_2 \xrightarrow{AlCl_3} 1\text{-}X\ B_{10}H_{13} + 2\text{-}X\ B_{10}H_{13} + HX \qquad (34)$$

X = Cl, Br, I

Another route was that of Hermanek and co-workers by the reaction of 6,9-*bis*(dimethylsulphide)decaborane with hydrogen halides (35) furnishing 5- and 6- halodecaboranes.[104,107,108]

$$5\text{-}X\ B_{10}H_{13} \xleftarrow{HX} 6,9\text{-}(SMe_2)_2B_{10}H_{12} \xrightarrow{HCl} 6Cl\text{-}B_{10}H_{13} \qquad (35)$$

(X = F, Br, I)

Whereas the separation of mixtures 1- and 2- isomers was easily achieved by fractional recrystallisation from organic solvents the separation by recrystallisation of mixtures of 5- and 6- isomers was very difficult. Hence, for a pure sample of 6-bromodecaborane, Hermanek and co-workers had to use chromatographic separation techniques. In general, the following order of descending R_F values was noted:

$$6\text{-}XB_{10}H_{13} > 5\text{-}XB_{10}H_{13} > 1\text{-}XB_{10}H_{13} > 2\text{-}XB_{10}H_{13}$$

In 1974, Sprecher *et al*[109] reported the synthesis of all the monohalodecaborane isomers (X = Cl, Br, I) in high yields by a convenient room temperature reaction (36)

$$B_{10}H_{14} + X_2 \xrightarrow[R.T.]{AlCl_3,\ CS_2} X\text{-}B_{10}H_{13} + HX \qquad (36)$$

^{11}B n.m.r. analysis showed that the 94% yield of monobromodecaboranes consisted of 80% $2\text{-}BrB_{10}H_{13}$ and 20% $1\text{-}BrB_{10}H_{13}$.

The 5,10-dihalodecaboranes (X = Br, I) were synthesised by Dupont *et al* from $Me_2SnB_{10}H_{12}$ (37).[110]

$$Me_2SnB_{10}H_{12} + 2X_2 \xrightarrow{-78^{\circ}C} Me_2SnX_2 + B_{10}H_{12}X_2 \qquad (37)$$

The bromination reaction was very efficient (70-80% yields) but the iodination reaction was less clean and also afforded $B_{10}H_{14}$, $B_{10}H_{13}I$ and $B_{10}H_{11}I_3$. The analogous chlorine reaction requires much more forcing conditions and leads mainly to decaborane with only traces of chlorinated products.

Two syntheses of mono-isothiothiocyanatodecaborane, (NCS) $B_{10}H_{13}$, have been published. The first[117] involved the reaction of 6,9-*bis* (dimethylsulphide)decaborane with mercuric thiocyanate (38)

$$2(6,9\text{-}[Me_2S]\ B_{10}H_{12}) + Hg[SCN]_2 \longrightarrow 2(NCS)\ B_{10}H_{13} + 2Me_2S + Hg^{\circ} \qquad (38)$$

It was suggested, on the basis of infrared structural data, that the NCS ligand bonded to the boron cage at B(6).

An alternative approach was reported by Lipscomb and Kendall in 1973 (39).[112]

$$B_{10}H_{14} + HCl + Na[SCN] \xrightarrow[R.T.]{Monoglyme} (NCS)\ B_{10}H_{13} + Na[Cl] + H_2 \qquad (39)$$

Sublimation of the crude product furnished the isothiocyanate in 27% yield. Again, preference was expressed for substitution at B(8).[113,114] In a later note[115] the reaction of decaborane with metal thiocyanate in ethereal medium was described as (40)

$$X\ R_2O + [M][SCN] + B_{10}H_{14} \longrightarrow H_2 + [M][B_{10}H_{12}(NCS)(OR_2)_x] \qquad (40)$$

The behaviour of thiocyanate ion in this reaction contrasts sharply with that of aqueous $[BH_4]^-$, NH_3, $[OH]^-$ and $[CN]^-$ which react with decaborane to give $[B_{10}H_{14}]^{2-}$, $[B_{10}H_{13}NH_3]^-$, $[B_{10}H_{13}OH]^{2-}$ and $[B_{10}H_{13}CN]^{2-}$, respectively.[114-116] Moreover, it was found that the addition of $[B_{10}H_{13}]^-$ salts to aqueous solutions of $[CN]^-$, $[BH_4]^-$ and $[OH]^-$ gave $[B_{10}H_{13}CN]^-$, $[B_{10}H_{14}]^{2-}$ and $[B_{10}H_{13}OH]^{2-}$, respectively.

1.10.2 *Spectral Properties*

Using ^{11}B n.m.r. spectroscopy, Williams and Onak,[117] established the monoiodecaborane isomers as 1-$IB_{10}H_{13}$ and 2-$IB_{10}H_{13}$. Other early work was reported by Sedmera *et al*[118] [5-$XB_{10}H_{13}$ (X = F, Br, I) and 6-$ClB_{10}H_{13}$] and Williams and Pier[119] [all the 1- and 2- $XB_{10}H_{13}$ (X = Cl, Br, I) isomers].

In 1974, using ^{11}B-^{11}B double resonance techniques, Sprecher *et al*[109] assigned chemical shift values for all the possible isomers of monohalogenated decaboranes (Cl, Br, I). These authors found a trend of increasing shielding at the substituted atom in the order of σ (B-Cl) < σ (B-Br) < σ (B-I). This trend was explicable in terms of the anisotropic susceptibility of the halogen atom and an induced paramagnetic shielding at the substituted boron atom. Sprecher and Aufderheide,[120] showed that the changes in the ^{11}B n.m.r. chemical shifts of decaborane on halogen substitution are additive parameters which can be used to predict chemical shift values in dihalogenated decaboranes. The authors recorded the chemical shifts for dichloro- and diiododecaborane isomers as well as for some mixed dihalodecaboranes such as 2-chloro, 9-bromo decaborane and 1-chloro, 6-bromodecaborane.

1.10.3 *Solid State Structural Data*

X-ray crystallographically determined structures have been reported for a number of halodecaboranes and also for 6-(NCS)$B_{10}H_{13}$.[112] Sequiera and Hamilton[121] published the structure of 1-$IB_{10}H_{13}$ in 1967. Figure 23 illustrates this structure.

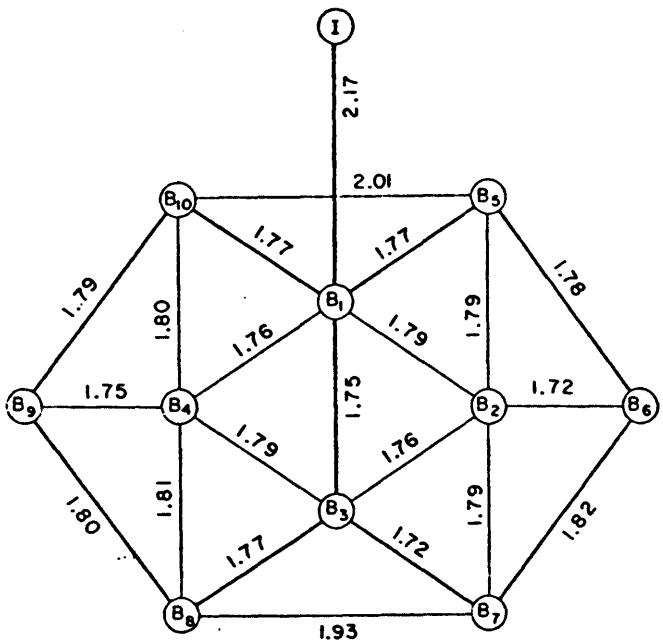


Figure 23 Structure and Bond Distances for 1-$IB_{10}H_{13}$

A comparison with the bond distances in $B_{10}H_{14}$,[122,123] and $B_{10}H_{13}$ (C_2H_5),[124] suggested that there are no important differences in B-B bond lengths among these structures except perhaps for the long B_5-B_{10} (1.96) Å, $B_{10}H_{13}$ (C_2H_5); and (2.01) Å, $B_{10}H_{14}$; and B_7-B_8 bonds (2.01), $B_{10}H_{14}$ and (1.98) Å. $B_{10}H_{13}$ (C_2H_5).

The structure of $B_{10}H_{13}$(NCS) is illustrated in Figure 24.

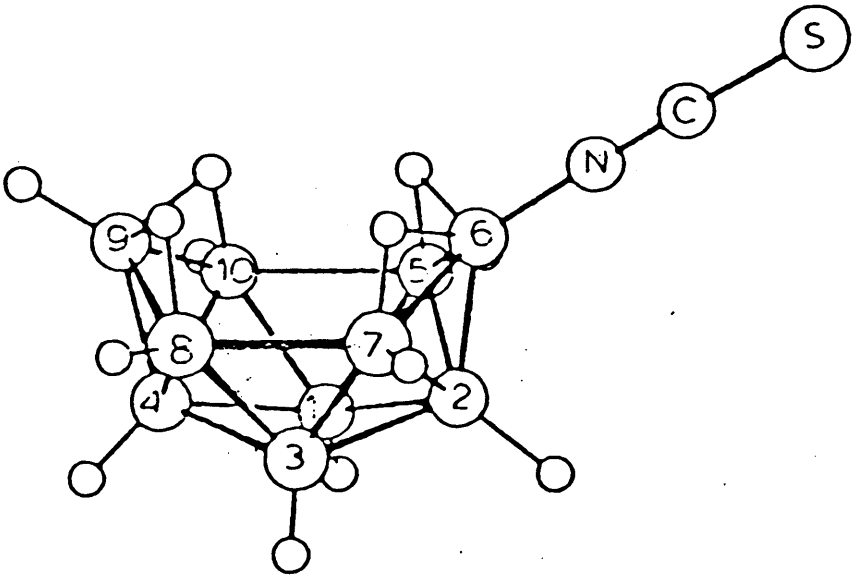


Figure 24 Structure of $B_{10}H_{13}$ (NCS)

Dupont *et al*[110] reported the structure of 5,10-$Br_2B_{10}H_{12}$ (Figure 25).

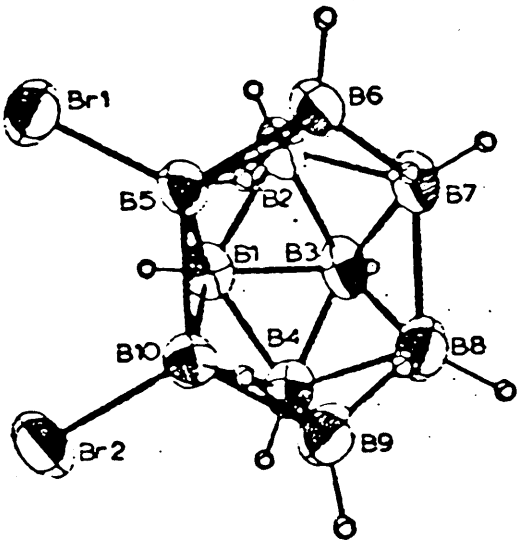


Figure 25 Structure of 5,10-$Br_2B_{10}H_{12}$

Spalding and co-workers[125] obtained anisotropic mass spectra of 2-$ClB_{10}H_{13}$, 6-$ClB_{10}H_{13}$ and 2-$IB_{10}H_{13}$ using high resolution measurements. The parent molecular ion appeared to be more stable with the 2-chloro-substituent than with the 6-chloro- but for both compounds the base peak was $[M-3H_2]^+$. In contrast, the base peak for the iodo- compound was $[M^+]$, though $[M-3H_2]^+$ was almost as abundant.

1.10.4 *Reactions of Halodecaboranes*

Plesek and co-workers[126] found a marked difference in the reactivity of the 5- and 6- halodecaborane isomers to dialkylsulphides. The 6-$ClB_{10}H_{13}$ compound reacted extremely slowly with the evolution of HCl and formation of 6,9-$(SR_3)_2B_{10}H_{12}$ (R = Me, Et) (40)

$$6\text{-}ClB_{10}H_{13} + 2R_2S \longrightarrow HCl + 6,9\text{-}(SR_2)_2B_{10}H_{12} \qquad (40)$$

However, the 5-halo-derivatives reacted smoothly with evolution of hydrogen (41)

$$5\text{-}XB_{10}H_{13} + 2R_2S \longrightarrow H_2 + 5\text{-}X,\ 6,9\text{-}(SR_2)_2B_{10}H_{11} \qquad (41)$$

a-d

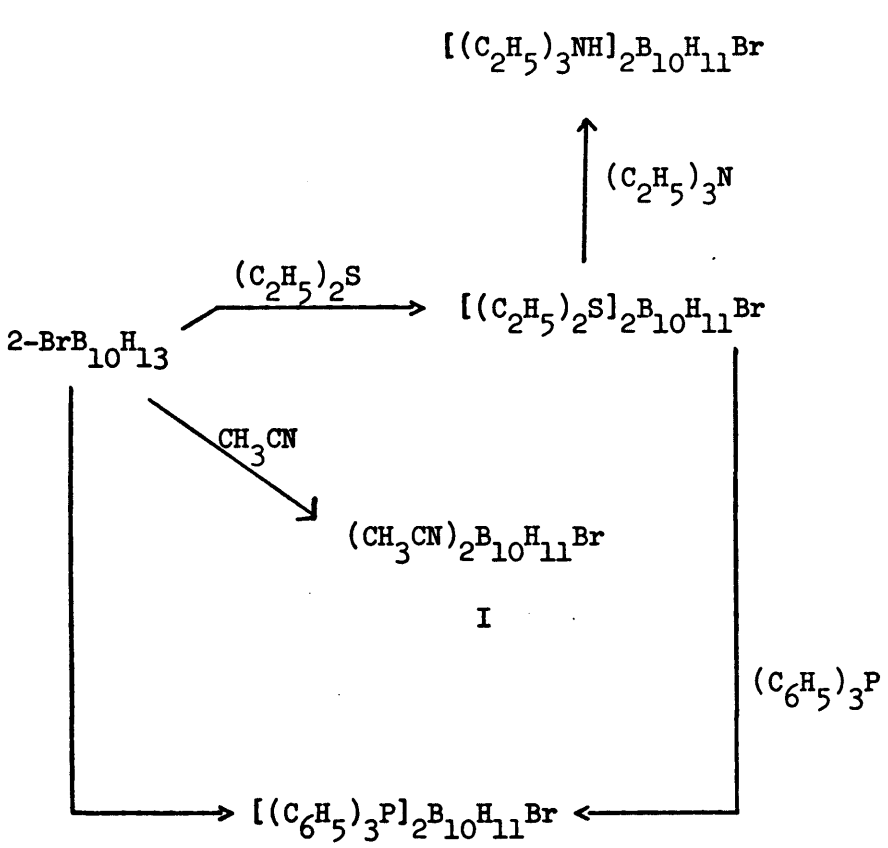
a, X = F, R = CH_3; b, X = Br, R = CH_3;

c, X = I, R = CH_3; d, X = Br, R = CH_2CH_3

This difference in reactivity is due to the fact that disubstitution at the 6-position is not possible for 6-$ClB_{10}H_{13}$.

Heying and Naar-Colin[127] reacted 2-$BrB_{10}H_{13}$ with various donor ligands (Scheme 3)

Scheme 3 Reactions of 2-$BrB_{10}H_{13}$



Acetonitrile reacted readily in benzene to give compound I in 61% yield. Subsequent ligand displacement reactions are exemplified by the conversion of *bis* (diethylsulphide)-2-bromodecaborane to the *bis* (triphenylphosphine) derivative by treatment with triphenylphosphine at room temperature. This compound is also prepared, in 67% yield, by the spontaneous and rapid reaction of 2-$BrB_{10}H_{13}$ with the phosphine in ether.

1.11 HALOGENATED AND PSEUDOHALOGENATED *CLOSO* BORANES DERIVED FROM $[B_nH_n]^{2-}$ (n = 6 to 12)

1.11.1 *Synthesis*

In 1964, Muetterties and co-workers[128] reported that the reactions of $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ with elemental halogens (X = Cl, Br, I) proceeded readily in the dark and usually lead to multiple substitutions. If more forcing conditions are used complete halogenation to $[B_{10}X_{10}]^{2-}$ and $[B_{12}X_{12}]^{2-}$ was observed (Figure 26)

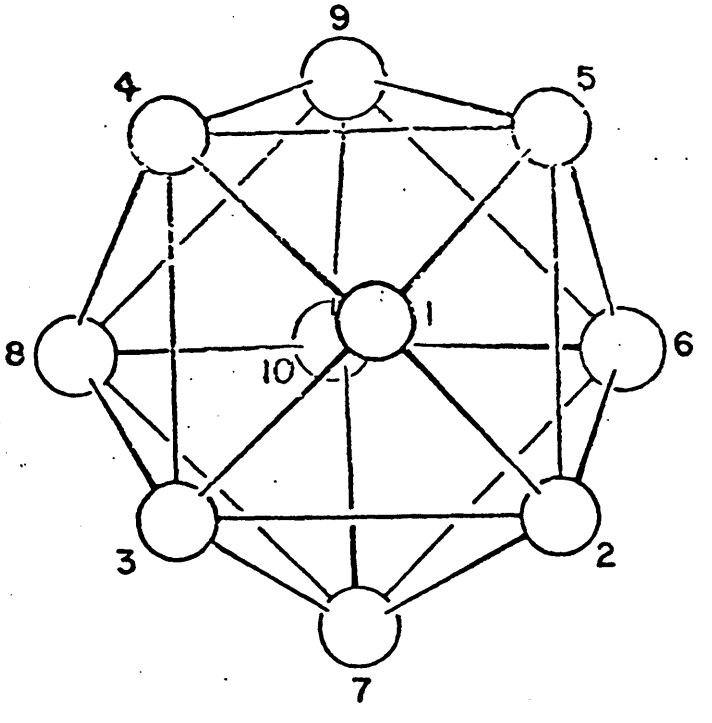


Figure 26

The use of elemental fluorine, even when diluted in aqueous media, resulted in extensive decomposition. However, $[B_{12}F_{11}OH]^{2-}$ has been isolated from the reaction of $[B_{12}H_{12}]^{2-}$ with fluorine in water. The order of reactivity for both halogens and boranes is $Cl_2 > Br_2 > I_2$ and $[B_{10}H_{10}]^{2-} > [B_{12}H_{12}]^{2-}$. This is the expected order if it is assumed that reactions occur by an electrophilic substitution mechanism. Conversely in a reaction

that has been described as an acid-catalysed nucleophilic substitution reaction, salts of $[B_{12}H_{12}]^{2-}$ were treated with anhydrous HF or HCl to generate $[B_{12}H_{6-8}F_{6-4}]^{2-}$ and $[B_{12}H_{11}Cl]^{2-}$.[128] Silver salts of polychlorinated B_{10} and B_{12} anions are soluble in water and in a variety of other solvents. Heating these solutions, even to reflux temperatures, does not cause precipitation of silver chloride. Also, the fully halogenated B_{10} and B_{12} *closo* anions are more stable to attack by acids and bases than the unsubstituted anions. Very few reactions have been reported which involve cleavage of the boron halogen bonds in these systems. Chlorine reacts with $[B_{10}I_{10}]^{2-}$ to give $[B_{10}Cl_8I_2]^{2-}$ but $[B_{12}I_{12}]^{2-}$ does not exchange under the same conditions.[129] The boron-halogen bonds of $[B_{12}Cl_{12}]^{2-}$, $[B_{12}Br_{12}]^{2-}$ and $[B_{10}Cl_{10}]^{2-}$ are, however, labilised by ultraviolet irradiation. Trofimenko[130,131] achieved the replacement of upto nine hydrogens by cyanide and one or two hydrogens by cyanide or azide groups, in aqueous solutions irradiated with 235.7 n.m. light.

Reactions (42) and (43) demonstrate that under free radical conditions (u.v. irradiation or elevated temperatures) the boron-carbon bonds of B-COOH groups can be replaced by B-Cl bonds.[128]

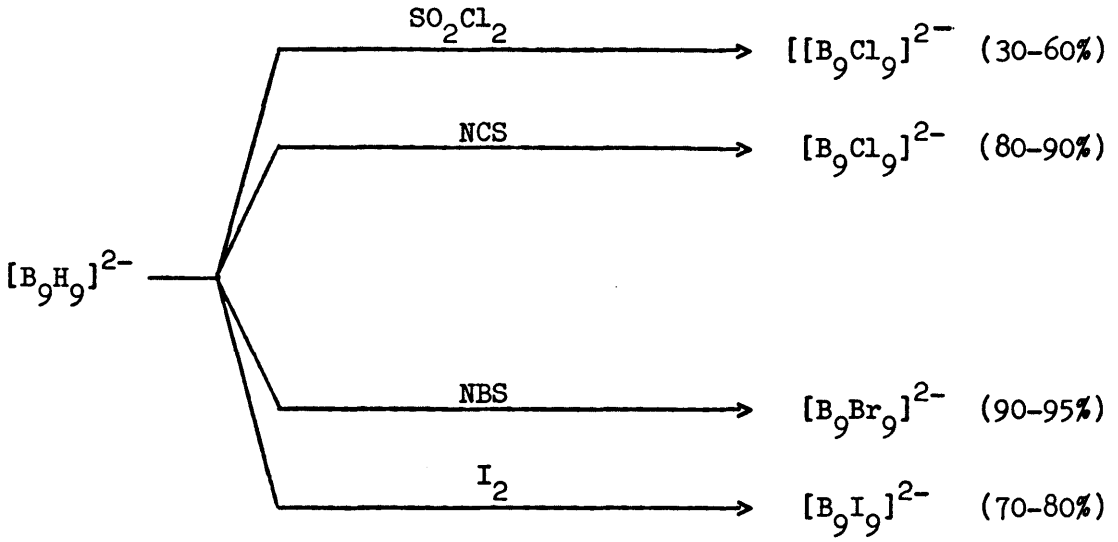
$$[B_{10}Cl_8(COOH)]^{2-} + Cl_2 \xrightarrow[\text{or } 150^\circ C]{\text{h.v.}} [B_{10}Cl_{10}]^{2-} \qquad (42)$$

$$[B_{12}Br_{11}(COOH)]^{2-} + Cl_2 \xrightarrow[\text{or } 150^\circ C]{\text{h.v.}} [B_{12}Br_{10}Cl_2]^{2-} \qquad (43)$$

Brominations of $[B_6H_6]^{2-}$,[132] $[B_8H_8]^{2-}$,[133] $[B_9H_9]^{2-}$ and $[B_{11}H_{11}]^{2-}$ have been carried out using sodium hypobromite. The method avoids acidic conditions which cause hydrolytic degradations. From these reactions, products having the anion compositions $[B_6Br_6]^{2-}$, $[B_8H_2Br_6]^{2-}$, $[B_9H_3Br_6]^{2-}$ and $[B_{12}H_3Br_9]^{2-}$ have been isolated.

More recent preparations include the work of Wong and Kabbani[134] where tetrabutylammonium salts of $[B_9H_9]^{2-}$ were fully halogenated by reaction with a variety of reagents in dichloromethane under nitrogen atmosphere (Scheme 4). The air and hydrolytic instability of $[B_9H_9]^{2-}$ precludes per halogenation under protic conditions.

Scheme 4 Halogenation of $[B_9H_9]^{2-}$



The same authors reported[135] that the addition of a large excess (20 equivalents) of sulphuryl chloride afforded the neutral B_9Cl_9 cluster in 30-40% yield in addition to $[B_9Cl_9]^{2-}$. The neutral products were easily isolated by extraction with hexane or by sublimation to give pure B_9Cl_9 without contammination from other perchlorinated boron clusters, (B_9Cl_9 had been first prepared by Lanthies and Massey in 1970[136]).

Muetterties and co-workers[137] prepared octachlorononaborane-9, B_9Cl_8H by degradation of the acid form of $[B_{10}Cl_{10}]^{2-}$. The crystalline acid $(H_3O)_2B_{10}Cl_{10}\cdot 5H_2O$ undergoes a reversible dehydration under vacuum to a dihydrate at 150°C (44).

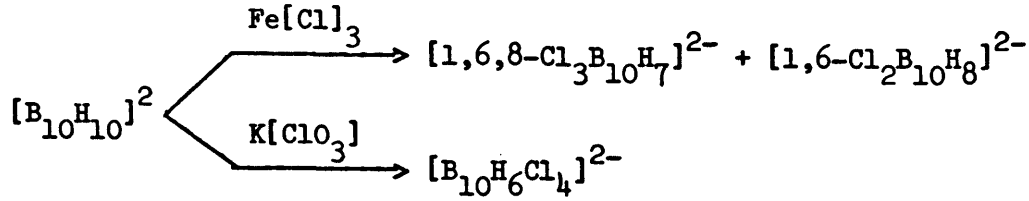
$$(H_3O)_2R_{10}Cl_{10}\cdot 5H_2O \longrightarrow 3H_2O + (H_3O)_2\ B_{10}Cl_{10}\cdot 2H_2O \qquad (44)$$

An irreversible decomposition occurs at 200° and red crystals of B_9Cl_8H sublime from the reaction zone.

In 1923, Morrison and co-workers,[138] re-examined the thermal decomposition of $(H_3O)_2B_{10}Cl_{10}$ under dynamic vacuum. The major nine-vertex products were found to be $H_2B_9Cl_7$, HB_9Cl_2 and B_9Cl_9. At ambient temperature any differences in the ^{11}B n.m.r. chemical shifts of the halogen-substituted boron atoms in HB_9Cl_8 were unresolved at 28.9 MHz. The decomposition reaction also led to a variety of other products, e.g. $B_{10}Cl_{10}$, $B_{11}Cl_{11}$ and $B_{12}Cl_{12}$. Mass spectrometric evidence indicated the existence of boron halides, B_nCl_n where n = 13-20. In aqueous solution, B_9Cl_8H is reduced to the dianion, $[B_9Cl_8H]^{2-}$.

The thermal decomposition of $[Et_3NH]_2[B_{10}Br_{10}]$ was also studied by Saulys and Morrison,[139] as an alternative to the oxidative decomposition reaction of $[(H_3O)]_2\ [B_{10}Cl_{10}]$, to determine if it would prove a viable synthetic route for the preparation of substituted boron subhalides. At temperatures near 430°C the trialkylammonium salt was found to decompose yielding predominantly the neutral compound, $CH_3B_9Br_8$. The decomposition was radical in nature. By varying the reaction conditions, the authors also isolated other alkylated boron sub bromide, $C_2H_5B_9Br_8$, $(CH_3)_2B_9Br_7$, and $CH_3(C_2H_5)B_9Br_7$, along with B_9Br_9, but in smaller amounts than the chloro-analogue. Curtis *et al*[140] reported some by-products of oxidative coupling of $[B_{10}H_{10}]^{2-}$ using $FeCl_3$ and $KClO_3$ (Scheme 5).

Scheme 5 Reactions of $[B_{10}H_{10}]^{2-}$



The reactions take place by a radical mechanism and none of the by-products were ever isolated in greater than 8% yield, irrespective of the experimental conditions. A protonated species, such as $[B_{10}H_{11}]^-$ was postulated as a key intermediate. Such an intermediate has also been considered in the nucleophilic halogenation of polyhedral boranes.[5]

Salts of the polyhalogenated *closo* ions are generally more stable, thermally and hydrolytically, than the unsubstituted analogues. This particularly is obvious in the cases of $[B_6Br_6]^{2-}$ and $[B_8Br_6H_2]^{2-}$ which are stable towards aqueous acid, whereas $[B_6H_6]^{2-}$ and $[B_8H_8]^{2-}$ are not.[135-137] The following order of stability to oxidation was established by voltammetry: $[B_{12}Cl_{12}]^{2-}$, $[B_{12}Br_{12}]^{2-} > [B_{12}Br_6H_6]^{2-} > [B_{12}H_{11}I]^{2-}$.[138,139]

1.11.2 *Mechanistic Studies*

Mechanistic studies of the rates of iodination of $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ ions have been reported. The first three iodi ations of $[B_{10}H_{10}]^{2-}$ with elemental iodine are kinetically indistinguishable. However, $[B_{10}H_7I_3]^{2-}$ reacts more slowly. For the less reactive $[B_{12}H_{12}]^{2-}$ it is possible to kinetically distinguish the first two iodinations; with $[B_{12}H_{11}I]^{2-}$ reacting 69 times slower than $[B_{12}H_{12}]^{2-}$. Comparison of the rates of reaction of iodine with deuterated analogues resulted in a kinetic isotope effect of 2.9 for $[B_{12}H_{12}]^{2-}$ versus $[B_{12}D_{12}]^{2-}$ and 2.3 for $[B_{12}H_{11}I]^{2-}$ versus $[B_{12}D_{11}I]^{2-}$. The reaction is not apparently slowed by the substitution of D_2O for H_2O as solvent.

1.12 REFERENCES

1. A. Stock; Massenez, *Chem. Ber.*, 1912, 45, 3529.
2. A. Stock, "Hydrides of Boron and Silicon", Cornell University Press, Ithaca, New York, 1933.
3. S.G. Shore, "Systematic Approaches to the Preparation of Boron Hydrides and their Derivatives". A.C.S. Symposium Series, 1983, 232, 1.
4. S.H. Lawrence, S.G. Shore, T.F. Koetzle, J.C. Huffman, C. Wei and R. Bau; *Inorg. Chem.*, 1985, 24, 3171.
5. V.D. Aftandilian, H.C. Miller and E.L. Muetterties, *J. Am. Chem. Soc.*, 1961, 83, 2471.
6. M. Sugie, H. Takeo and C. Matsumura; *J. Mol. Struct.*, 1985, 131.
7. O. Eisentein, M. Kayser, M. Roy and T.B. McMahon; *Can. J. Chem.*, 1985, 63, 281.
8. S.G. Shore, S.H. Lawrence, M.I. Watkins and R. Bau; *J. Am. Chem. Soc.*, 1982, 104, 7669.
9. L.V. Titov, L.A. Gavrilova, K.V. Titova and V.Y. Rosolovskii; *Bull. Acad. Sci.*, USSR Div. Chem. Sci. (Engl. Transl.), 1978, 27, 1504; Izv. Akad. Nauk SSR., Ser. Khim., 1978, 27, 1722.
10. L.A. Gavrilova, L.V. Titov and V.Y. Rosolovskii; *Russ. J. Inorg. Chem.*, (Engl. Transl.), 1981, 26, 955; Zh. Neorg. Khim., 1981, 26, 1769.
11. B.C. Hui; *Inorg. Chem.*, 1980, 19, 3185.
12. C.F. Lane; *Synthesis*, 1975, 135.
13. R.O. Hutchins and N.R. Natale; *Org. Prep. Proced. Int.*, 1979, 11, 201.
14. G. Drefahl and E. Keil; *J. Prakt. Chem.*, 1958, 6, 80.

15. R.F. Borch and H.D. Durst; *J. Am. Chem. Soc.*, 1969, 91, 3996.

16. R.C. Wade, E.A. Sullivan, J.R. Berschied and K.F. Sullivan; *Inorg. Chem.*, 1970, 9, 2146.

17. B. Gyori and G. Emri; *J. Chem. Soc., Chem. Commun.*, 1983, 1303.

18. B.F. Spielvogel, F.U. Ahmed, M.K. Das and A.T. McPhail; *Inorg. Chem.*, 1984, 23, 3263.

19. J.R. Berschied and K. Purcell; *Inorg. Chem.*, 1970, 9, 624.

20. R.F. Borch, M.D. Bernstein and H. Dupont-Durst; *J. Am. Chem. Soc.*, 1971, 93, 2897.

21. (a) G.R. Pettit and D.M. Piatak; *J. Org. Chem.*, 1962, 27, 217;
(b) R. Paul and N. Joseph; *Bull. Soc. Chem. Fr.*, 1952, 550;
(c) H.C. Brown and E.J. Mead, *J. Am. Chem. Soc.*, 1953, 75, 6263.

22. (a) H. Nöth and H. Reyes, *Chem. Ber.*, 1963, 93, 1078;
(b) J.H. Bullman and I.W. McDowell, *J. Org. Chem.*, 1961, 26, 1437;
(c) S.G. White and H.C. Kelly; *J. Am. Chem. Soc.*, 1970, 92, 4203 and references therein.

23. A.M. Sapse and L. Osorio, *Inorg. Chem.*, 1984, 23, 627.

24. M.C. Jackson and H.C. Miller; U.S. Patent, 1961, 2, 992, 885.

25. H.I. Schlesinger, H.C. Brown and A.B. Burg; *J. Am. Chem. Soc.*, 1931, 53, 4321.

26. E.L. Muetterties; "The Chemistry of Boron and its Compounds", Wiley, New York, 1967, 249.

27. D.F. Gaines and R.F. Schaeffer, *J. Phys. Chem.*, 1964, 68, 955.

28. G.E. Ryschkewitsch and V.A. Miller; *J. Am. Chem. Soc.*, 1975, 97, 6258.

29. G.B. Jacobsen and J.H. Morris, *Inorg. Chem. Acta.*, 1982, 54, 207.

30. S.J. Andrews and A.I. Welch, unpublished work.

31. J.R. Pippal and R.N. Grimes, *Inorg. Chem.*, 1979, 18, 252.

32. J.R. Pippal and R.N. Grimes; *Inorg. Chem.*, 1979, 18, 263.

33. S.J. Andrews and A.J. Welch; *Inorg. Chim. Acta.*, 1984, 88, 153.

34. M. Arunchaiya and J.H. Morris; *Inorg. Chim. Acta.*, 1985, 103, 31.

35. (a) G. Kodama, R.N. Parry and J.C. Carter, *J. Am. Chem. Soc.*, 1959, 81, 3354;

(b) W.R. Deever and D.M. Ritter; *Inorg. Chem.*, 1968, 7, 1036;

(c) R.T. Paine and R.W. Parry; *Inorg. Chem.*, 1972, 11, 268;

(d) A.R. Dodds and G. Kodama; *Inorg. Chem.*, 1976, 15, 741.

36. (a) W.N. Lipscomb; *Adv. Inorg. Nucl. Chem.*, 1959, 1, 117;

(b) M.A. Rigg, E.F. Wituki and R.C. Greenough; *Inorg. Chem.*, 1967, 6, 395;

(c) G. Kodama; *Inorg. Chem.*, 1975, 14, 452.

37. D.J. Pasto and P. Balasubramaniyan; *J. Am. Chem. Soc.*, 1959, 81, 6164.

38. W.C. Hutton, R.N. Grimes and T.L. Venable; *J. Am. Chem. Soc.*, 1982, 104, 4716.

39. T.L. Venable, W.C. Hutton and R.W. Grimes; *J. Am. Chem. Soc.*, 1984, 106, 29.

40. D. Reed, *J. Chem. Res. S.*, 1984, 198.

41. G.B. Jacobsen, D.G. Meina, J.H. Morris, C. Thomson, S.J. Andrews, D. Reed, A.J. Welch and D.F. Grimes; *J. Chem. Soc., Dalton Trans.*, 1985, 1645.

42. D.G. Meina, J.H. Morris and D. Reed; *Polyhedron*, 1986, 5, 1639.

43. G.B. Jacobsen and J.H. Morris; *Inorg. Chim. Acta.*, 1982, 59, 207.

44. M. Arunchaiya, J.H. Morris, S.I. Andrews, D.A. Welch and A.I. Welch; *J. Chem. Soc., Dalton Trans.*, 1984, 2525.

45. D.G. Meina and J.H. Morris; *J. Chem. Soc., Dalton Trans.*, 1986, 2645.

46. S.I. Andrews, A.I. Welch, G.B. Jacobsen and J.H. Morris; *J. Chem. Soc., Chem. Commun.*, 1982, 749.

47. M.A. Toft; J.B. Lench; F.L. Himpsl and S.G. Shore; *Inorg. Chem.*, 1982, 21, 1952.

48. J. Dobson and R. Schaeffer; *Inorg. Chem.*, 1965, 4, 593.

49. B. Figgis and J. Williams, *Spectrochim Acta.*, 1959, 15, 331.

50. T. Onak and G. Dunks; *Inorg. Chem.*, 1964, 3, 1060.

51. D.F. Gaines; *J. Am. Chem. Soc.*, 1966, 88, 4528.

52. I. Shapiro and H. Landesman; *J. Chem. Phys.*, 1960, 33, 2590.

53. Pentaborane forms shock sensitive mixtures with carbon tetrachloride: "Pentaborane", Callery Chemical Co. Technical Bulletin, CT-1300, 1961 and references therein.

54. L.H. Halls, V.V. Subbanna and W.S. Koski; *J. Am. Chem. Soc.*, 1964, 86, 3969.

55. A.B. Burg and J.S. Sandhu; *J. Am. Chem. Soc.*, 1965, 87, 3787.

56. J.G. Taylor and M.G.H. Wallbridge; *Polyhedron*, 1985, 4, 321.

57. T. Onak, G.R. Dunks, I.W. Searcy and J.Spielman; *Inorg. Chem.*, 1967, 6, 1465.

58. T. Onak, H. Landesman, R.E. Williams and I. Shapiro; *J. Phys. Chem.*, 1959, 63, 1533.

59. R.E. Williams, H.D. Fisher and C.O. Wilson; *J. Phys. Chem.*, 1960, 64, 1563.

60. W.D. Phillips, H.C. Miller and E.L. Muetterties; *J. Am. Chem. Soc.*, 1959, 81, 4496.

61. H. Noth and H. Vahrenkamp; *Chem. Ber.*, 1966, 99, 1049.

62. R.E. Williams and T.Onak; *J. Am. Chem. Soc.*, 1964, 86, 3159.

63. R.L. Williams, J. Dunstan and N.J. Blay; *J. Chem. Soc.*, 1960, 5006.

64. T. Onak; *J. Am. Chem. Soc.*, 1961, 83, 2584.

65. (a)H.Spieseche and W.G. Schneider; *J. Chem. Phys.*, 1961, 35, 731;

65. (b) P.C. Lauterbur; *J. Am. Chem. Soc.*, 1961, 83, 1846.

66. L.H. Hall, V.V. Subbanna and W.S. Koski; *J. Am. Chem. Soc.*, 1964, 86, 3964.

67. T. Onak and F.J. Gerhort; *Inorg. Chem.*, 1962, 1, 742.

68. W.V. Haigh, L.J. Edmonds and A.F. Stang; *J. Am. Chem. Soc.*, 1963, 85, 831.

69. A.B. Burg and J.S. Sandhu; *J. Am. Chem. Soc.*, 1965, 87, 3787.

70. T. Onak, L.R. Friedman, J.H. Hartsuck and W.N. Lipscomb; *J. Am. Chem. Soc.*, 1966, 88, 3439.

71. L.B. Friedman and W.N. Lipscomb; *Inorg. Chem.*, 1966, 5, 1752.

72. E.A. Hasely; Ph.D. Dissertation, The Ohio State University, 1956.

73. V.T. Brice, H.D. Johnson and S.G. Shore; *J. Chem. Soc., Chem Commun.*, 1972, 1128.

74. P.J. Dolenz, D.C. Moody and R.N. Schaeffer; *J.Am. Chem. Soc.*, 1973, 95, 6629.

75. E.L. Muetterties, "The Chemistry of Boron and its Compounds", Wiley, New York, 1967, 333.

76. G.L. Brubaker; Ph.D. Thesis, The Ohio State University, 1971.

77. J. Rathbe and R. Schaeffer; *Inorg. Chem.*, 1974, 13, 3008.

78. H.D. Johnson, V.T. Price and S.G. Shore; *Inorg. Chem.*, 1973, 12, 689.

79. G.B. Jacobsen, J.H. Morris and D. Reed; *J. Chem. Soc., Dalton*, 1984, 415.

80. J. Dobson and R. Schaeffer; *Inorg. Chem.*, 1968, 7, 402.

81. W.N. Lipscomb; *J. Inorg. Nucl. Chem.*, 1959, 11, 1.

82. R. Lewin, P.G. Simpson and W.N. Lipscomb; *J. Am. Chem. Soc.*, 1963, 85, 478; *J. Chem. Phys.*, 1963, 39, 1532.

83. E.L. Muetterties and W.H. Knoth; *Inorg. Chem.*, 1965, 4, 1498.

84. B. Stibr, J. Plesek and S. Hermanek; *Collect. Czech. Chem. Commun.*, 1969, 34, 3241.

85. C.K. Nelson; *Diss. Abst. Int. B.*, 1983, 43, 2549.

86. G.R. Jacobsen, D.G. Meina, J.H. Morris, C. Thomson, S.J. Andrews, D. Reed, A.J. Welch and D.F. Grimes; *J. Chem. Soc., Dalton*, 1985, 1645.

87. F.E. Wang, P.G. Simpson and W.N. Lipscomb, *J. Chem. Phys.*, 1961, 35, 1335.

88. N.N. Greenwood, J.A. McGinneky and J.D. Owen; *J. Chem. Soc., Dalton*, 1972, 986.

89. S.J. Andrews and A.J. Welch; *Acta Cryst.*, 1985, (4), 1208.

90. L. Barton; *Top. Cusr. Chem.*, 1982, 100, 169.

91. J.C. Huffman and R. Schaeffer, Personal Communication to N.N. Greenwood, Liversedge Lecture of the Royal Society of Chemistry, 1984.

92. D.G. Meina and J.H. Morris; *J. Chem. Soc., Dalton*, 1985, 1903.

93. R. Schaeffer; *J. Am. Chem. Soc.*, 1957, 2725.

94. P.R. Wunz; U.S. Patent, 1982, 3046 086.

95. S.L. Clark and D.A. Fidler, U.S. Patent, 1961, 3 010783.

96. M. Hillman and D.J. Mangold; *Inorg. Chem.*, 1965, 4, 1356.

97. J. Stuchlik, S. Hermanek, J. Plesek and B. Stibr; *Collec. Czech. Chem. Commun.*, 1970, 35, 339.

98. R. Schaeffer, J.N. Schoolery and R. Jones; *J. Am. Chem. Soc.*, 1958, 80, 2670.

99. M. Hillman; *J. Am. Chem. Soc.*, 1960, 82, 1096.

100. L.T. Zacharkin and V.N. Kalinin; *Z. Obsc. Chim.*, 1966, 36, 2160.

101. M.H. Wallbridge, J. Williams and R.L. Williams; *J. Chem. Soc.*, 1967, 132.

102. U.S. Patent, 2 990 239 (1961); *Chem. Abst.*, 1961, 55, 27812.

103. U.S. Patent, 3 010 783 (1961); *Chem. Abst.*, 1962, 56, 82957.

104. J. Plesek, B. Stibr and S. Hermanek; *Collect. Czech Chem. Commun.*, 1966, 31, 4744.

105. A. Tippe and W.C. Hamilton; *Inorg. Chem.*, 1969, 8, 454.

106. J.P. Pipal and R.N. Grimes; *Inorg. Chem.*, 1977, 16, 3151.

107. J. Plesek, S. Hermanek and F. Hanousek; *Collect. Czech. Chem. Commun.*, 1968, 33, 699.

108. B. Stibr; Thesis.Institute of Chemical Technology, Prague, 1968.

109. R.F. Sprecher, B.E. Aufderheide, G.W. Luther and J.C. Carter; *J. Am. Chem. Soc.*, 1974, 96, 4404.

110. T.J. Dupont, R.E. Loffredo, R.C. Haltiwanger, C.A. Turner and A.D. Norman; *Inorg. Chem.*, 1978, 17, 2062.

111. B. Stibr, J. Plesek, F. Hanousek and S. Hermanek; *Collect. Czech. Chem. Commun.*, 1971, 35, 1794.

112. D.S. Kendall and W.N. Lipscomb; *Inorg. Chem.*, 1973, 12, 2915.

113. E.L. Muetterties, *Inorg. Chem.*, 1963, 2, 647.

114. J.M. Reddy and W.N. Lipscomb; *J. Am. Chem. Soc.*, 1959, 81, 754.

115. W.H. Knoth and E.L. Muetterties; *J. Inorg. Nucl. Chem.*, 1961, 20, 66.

116. L.E. Benjamin, S.F. Stafiej and E.A. Takacs; *J. Am. Chem. Soc.*, 1963, 85, 2674.

117. R.E. Williams and T.P. Onak; *J. Am. Chem. Soc.*, 1964, 86, 3159.

118. P. Sedmera, F. Hanousek and Z. Samek; *Collect. Czech. Chem. Commun.*, 1967, 2169.

119. R.E. Williams and E. Pier; *Inorg. Chem.*, 1965, 4, 1357.

120. R.F. Sprecher and B.E. Aufderheide; *Inorg. Chem.*, 1974, 13, 2287.

121. A. Sequeira and W.C. Hamilton; *Inorg. Chem.*, 1967, 6, 1281.

122. J.S. Kasper, C.M. Lucht and D. Harker; *Acta. Cryst.*, 1950, 3, 346.

123. E.B. Moore, R.E. Dickerson and W.N. Lipscomb; *J. Chem. Phys.*, 1957, 27, 209.

124. A. Perloff; *Acta. Cryst.*, 1964, 17, 332.

125. N.N. Greenwood, T.R. Spalding and D. Talyorson; *J. Inorg. Nucl. Chem.*, 1980, 42, 317.

126. B. Stibr, J. Plesek and S. Hermanek; *Collect. Czech. Chem. Commun.*, 1969, 34, 194.

127. T.L. Heying and C.Naar-Colin; *Inorg. Chem.*, 1964, 3, 282.

128. W.H. Knoth, H.C. Miller, J.C. Saner, J.H. Balthis, Y.T. Chia and E.L. Muetterties; *Inorg. Chem.*, 1964, 3, 159.

129. E.L. Muetterties and W.H. Knoth; "Polyhedral Boranes", Dekker, New York, 1968, 110.

130. S. Trofimenko and H.N. Cripps; *J. Am. Chem. Soc.*, 1965, 87, 653.

131. S. Trofimenko; *J. Am. Chem. Soc.*, 1966, 88, 1899.

132. W.R. Klanberg; cited in footnote 17 of F. Klanberg and E.L. Muetterties, 137.

133. F. Klanberg, D.R. Eaton, L.J. Guggenberger and E.L. Muetterties; *Inorg. Chem.*, 1971, 6, 1271.

134. E.H. Wang and R.M. Kabbani; *Inorg. Chem.*, 1980, 19, 451.

135. R.M. Kabbani and E.H. Wong; *J. Chem. Soc., Chem. Commun.*, 1978, 462.

136. G.F. Lauthier and A.G. Massey; *J. Inorg. Nucl. Chem.*, 1970, 32, 1807.

137. J.A. Forstner, T.E. Maas and E.L. Muetterties; *Inorg. Chem.*, 1964, 3, 155.

138. D.A. Saulys, N.A. Kutz and J.A. Morrison; *Inorg. Chem.*, 1983, 22, 1821.

139. D.A. Saulys and J.A. Morrison; *Inorg. Chem.*, 1980, 19, 3057.

140. Z.B. Curtis, C. Young, R. Dickerson, K. Kalei and A. Koczmarczyk; *Inorg. Chem.*, 1973, 13, 1760.

CHAPTER TWO

A THEORETICAL ASSESSMENT OF $[BH_3X]^-$ *AND* $[B_{10}H_9X]^{2-}$ *SERIES (X = H, Cl, CN, SCN, NCS,* N_3*)*

2.1 *Introduction*

Modified Neglect of Differential Overlap (MNDO) calculations were used to provide insight into the electronic structure and bonding of $[BH_3X]^-$ and $[B_{10}H_9X]^{2-}$ species for which X = H, Cl, CN, SCN, NCS, and N_3. Where possible the calculated results are compared with experimentally determined data e.g. X-ray crystallographically determined structures of $[BH_3Cl]^-$, $[B_{10}H_{10}]^{2-}$ and $[B_{10}H_7Cl_3]^{2-}$.

The choice of M.N.D.O. calculations devised by Dewar and Thiel,[1,2] for this study is a logical one. M.N.D.O. has been shown to produce geometries and heats of formation in good agreement with experiment. For many boranes and carbaboranes numerous *ab initio* calculations[3,4] have suffered from a neglect of electron correlation which is effectively built in to the M.N.D.O. calculation through its parameterisation and *ab initio* calculations with a reasonable basis set (e.g. 4-31G etc.)could not be performed on such large molecules as the B_{10} - species studied here. The experimental chemist usually approaches the bonding of boranes and related compounds from the rules developed by Wade[5] which accounts for the correspondence between cluster bonding units. The calculational methods here are a theoretical basis for these rules. The M.N.D.O. program[6] accepts an approximate geometry and calculates an optimised minimum-energy geometry from it, provided certain precautions are taken to avoid initial pseudo or minima geometries. A facility exists for maintaining certain aspects of the symmetry of the molecule during the calculation. If totally unsymmetrical variation is allowed the calculation generally converges on slightly assymetric geometries.

The effect on the molecular and electronic character of the species $[BH_4]^-$ and $[B_{10}H_{10}]^{2-}$ of halogen and pseudo halogen substitution is discus-

sed. In the case of the *closo* cluster systems the possible sites for electrophilic substitution of the cage are also analysed. In all non *ab initio* studies it is advantageous to compare results from a series of related compounds. This has been the approach adopted here for the series $[BH_3X]^-$ and $[B_{10}H_9X]^{2-}$.

2.2 *Results and Discussion*

2.2.1 $[BH_3X]^-$ *Species*

2.2.1.1. *Molecular Structures*

To date, of the $[BH_3X]^-$ compounds for which calculations were performed, only $[BH_3Cl]^-$ has been structurally characterised (by X-ray crystallographic techniques). However, the structures of many metal $-BH_4$ compounds have been published as well as structures of neutral ammonia-pseudo-haloborane adducts e.g. $H_3N.BH_2CN$[7] and $H_3N.BH_2NCS$[8]. Eisentein *et al*[9] in 1985 reported *ab initio* calculations for $[BH_3X]^-$ species with X = H, F and CN using a 4-31G basis set. Both the M.N.D.O. and 4-31G calculations produce the expected tetrahedral geometry a round boron (C_3V symmetry) for all the $[BH_3X]^-$ amines. The calculated and where available, experimental bondlengths are shown in Figures 1 to 6. In all cases the angles around boron are very close to the tetrahedral angle (109°). In all six compounds the B-H bondlengths are approximately the same; the shortest is 1.17 Å in $[BH_3Cl]^-$ and the longest 1.19 Å in $[BH_3CN]^-$. These B-H bondlengths compare well with X-ray crystallographically determined bondlengths e.g. $[H\,Ga\,(BH_4)_2]$ which has terminal B-H bondlengths of 1.20 Å (Figure 7)[10].

2.2.1.2. *The $[BH_3Cl]^-$ Anion*

The experimentally determined B-Cl bondlength in $[BH_3Cl]^-$ was 2.003 (5) Å[11]. However, Shore *et al* reported that some of this "long" B-Cl bond distance can be ascribed to problems with the crystallographic determination since there was incorporation of approximately 19% $[B_2H_7]^-$ into the $[BH_3Cl]^-$ site, which led to unusual difficulties in the structural refinement. (As discussed in Chapter One, during attempts to grow a single crystal of $[PPN][B_2H_7]$, prolonged exposure of the $[B_2H_7]^-$ anion to the mother liquor $[(C_2H_5)_2O/CH_2Cl_2]$ resulted in the formation of crystals of $[PPN][BH_3Cl]$ CH_2Cl_2. Crystallisation of the $[BH_3Cl]^-$ salt from solutions containing the precursor, $[B_2H_7]^-$, resulted in the presence of the impurity). Two of the

Bondlengths

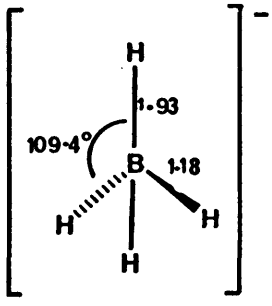


Figure 1: $[BH_4]^-$

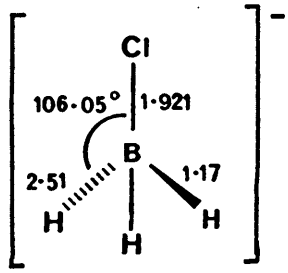


Figure 2: $[BH_3Cl]^-$

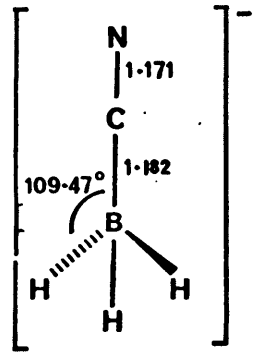


Figure 3: $[BH_3CN]^-$

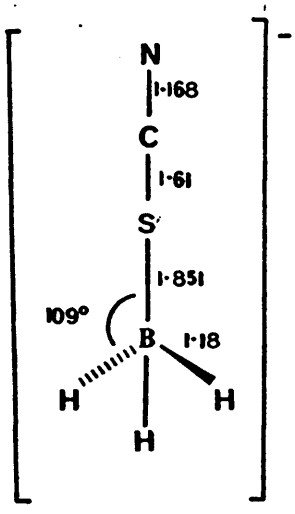


Figure 4: $[BH_3SCN]^-$

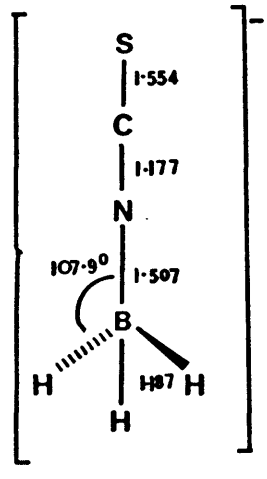


Figure 5: $[BH_3NCS]^-$

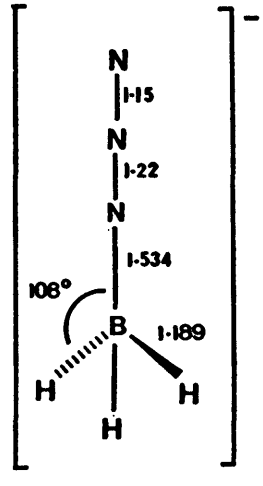


Figure 6: $[BH_3N_3]^-$

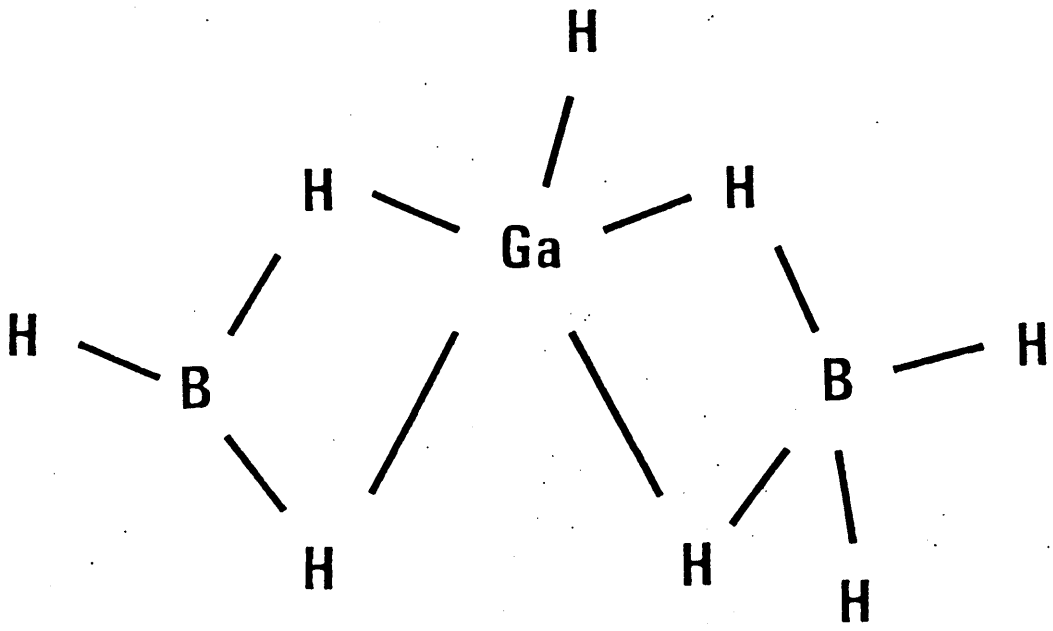


Figure 7: Structure of $[HGa(BH_4)_2]$

experimentally determined B-H bondlengths in $[BH_3Cl]^-$ are comparable to those calculated by M.N.D.O. but one is longer at 1.380 Å. This may be due to the incorporation of $[B_2H_7]^-$ and could be associated with the bridging hydrogen bond (Figure 8). Single crystal structural determination of $[B_2H_7]^-$ in 1982 by Shore and Lawrence[12] reported the B_1-H_1 bridged bondlength as 1.27(5) Å. More recently calculations by Sapse and Osario[13] using 6-31G[14] and 6-31G** [15] basis sets reported the bridging bond distance as 1.33 and 1.34 Å respectively. These values are very similar to the long B-H bondlengths in $[BH_3Cl]$. The experimentally determined terminal B-H bondlengths for $[B_2H_7]^-$ are 1.03(5) Å while the calculated values are 1.21 Å; the latter correspond more closely with the B-H values in the $[BH_3X]^-$ series above.

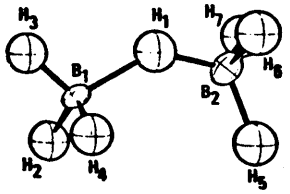


Figure 8: $[B_2H_7]^-$

2.2.1.3. *Comparison of Calculations on $[BH_3CN]^-$, BH_2CN and Experimentally Determined Results for $H_3N.BH_2CN$*

The structure of $H_3N.BH_2CN$ has been reported by Spielvogel and coworkers[7] (Figure 9). *Ab initio* calculations have been reported for $[BH_3CN]^-$ and the unknown species, BH_2CN. The relevant bondlengths and bondangles for these compounds are listed in Table 1.

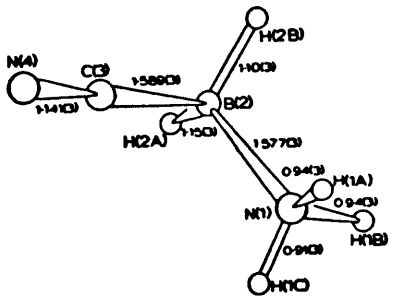


Figure 9: $H_3N.BH_2CN$,

TABLE 1. *Bondlengths and Bond Angles*

	MNDO $[BH_3CN]^-$	4-31G $[BH_3CN]^-$	X-Ray $H_3N.BH_2CN$	4-31G BH_2CN
B-C[a]	1.517	1.613	1.589(3)	1.533
B-H[a]	1.182	1.229	1.15 (3)	1.177
C-N[a]	1.171	1.155	1.141(3)	1.147
<HBC[b]	109.5	108.8	108(1)	119.0

a bondlengths in Angstroms; b bond angles in degrees.

The results in Table 1 show good agreement between both the MNDO and 4-31G calculations and the experimental measurements. With the exception of the B-C bondlengths from the MNDO calculations, there is a slight overestimation in the calculated values relative to the experimentally determined results. However, these differences are not significant and are typical of the differences found between MNDO calculated and X-ray crystallographically determined data.[1,2]

On comparison of the 4-31G calculations for $[BH_3CN]^-$ and BH_2CN all the B-H, B-C and C-N bonds in the latter are shorter. The order of shortening is B-C (0.08 Å) > C-N(0.008 Å) > B-H (0.052 Å). The HBC bond angles for the four coordinate boron species are all within one degree of 109°. The unknown BH_2CN species adopts a planar geometry with a HBC angle of 119° (Figure 10).

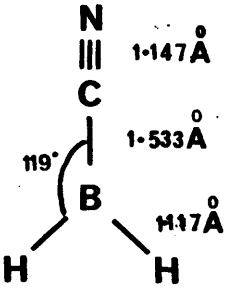


Figure 10: BH_2CN

The B-CN moiety in $[BH_3CN]^-$ was calculated by MNDO to be linear (< BCN 180°). This was also the case with the *ab initio* calculations and found in the experimentally determined structures of cyanoborane adducts such as ammonia-cyanoborane[7] and 4-dimethylaminopyridine-cyanoborane (Chapter Four, *vide infra*).

2.2.1.4. *Comparison of* $[BH_3X]^-$ *(X = NCS, SCN,* N_3*) Species with Available Experimental Results*

The structure of ammonia-isothiocyanatoborane has been determined by X-ray crystallographic techniques (Figure 11).[8] The preparation of $[BH_3SCN]^-$ has been reported by Hui,[17] but to date azidoborohydride has not been reported in the chemical literature. *Ab initio* calculations have not been reported for any of the above three species. The experimentally determined bond-lengths and bond angles for $H_3N.BH_2NCS$ and the MNDO calculated values for $[BH_3NCS]^-$ $[BH_3SCN]^-$ and $[BH_3N_3]^-$ are listed in Table 2.

TABLE 2. *Bondlengths and Bond Angles*

	X-Ray	MNDO		
	$H_3N.BH_2NCS$	$[BH_3NCS]^-$	$[BH_3SCN]^-$	$[BH_3N_3]^-$
B-X[a]	1.534(8)[c]	1.507[c]	1.81[d]	1.543[c]
B-H	1.15 (4)	1.187	1.177	1.185
C-N	1.137(8)	1.176	1.162	
N-N				1.220
C-S	1.627(6)	1.554	1.613	
N-N				1.150
<HBX[b]	109(3)[c]	107.9[c]	145.7[d]	163.5[c]

[a] Bondlengths in Angstroms; [b] Bond Angles in Degrees; [c] X=N, [d] X=S

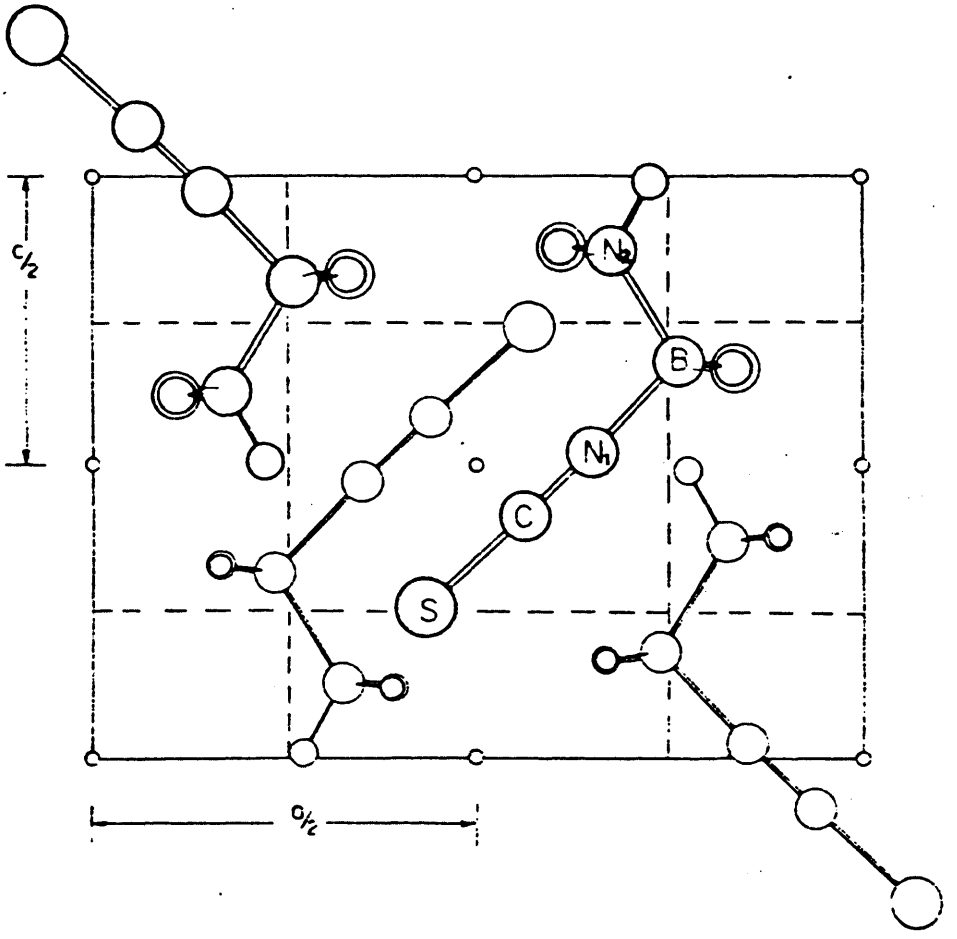


Figure 4 : The structure of $H_3N.BH_2NCS$ in projection along the b axis

Overall, the experimental and calculated data are comparable. The largest difference is 0.07 Å in the carbon-sulphur bonds, with the longer bondlength in $H_2N.BH_2NCS$. However, since this is reversed for the carbon-nitrogen bondlengths it appears to be a feature of the bonding in the isothiocyanate groups rather than a calculational one. The C-S bondlength in $[BH_3NCS]^-$ is shorter (1.554 Å) than in $[BH_3SCN]^-$ (1.613 Å) reflecting greater double bond-character in the former. Complete B-X-Y-Z linearity does not occur in any of the three pseudohalide species here according to the MNDO calculations. In $[BH_3NCS]^-$ the B-N-C angle is 180° but the N-C-S angle is 30° giving a slightly bent geometry as depicted in Figure 12.

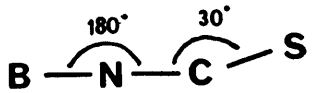


Figure 12: B-N-C-S

This is in contrast with the experimentally determined structures of isothiocyanates such as $H_3N.BH_2NCS$[8], $B_{10}H_{13}NCS$[17] where B-N-C is 177.5(6)° and 171.06(6)° respectively. Furthermore, in more recently analysed isothiocyanates such as $[B_3H_7NCS]^-$ [18,19] (Figure 13) the B-N-C-S moiety is linear with angles B-N-C of 173.7(3)° and N-C-S of 178.1(3)°. The structure of $[B_9H_{13}NCS]^-$ was reported in 1985 (Figure 14)[20] and the B-N-C-S moiety also attains linearity. However, the isoelectronically related methylisothiocyanate is also bent,[21] such that the CH_3-N-C angle is 142° and the N-C-S angle is 180°.

The boron-sulphur bonded compound $[BH_3SCN]^-$ is more distorted. The B-S-C angle is 146° and the S-C-N angle 168° thereby achieving the geometry depicted in Figure 15.

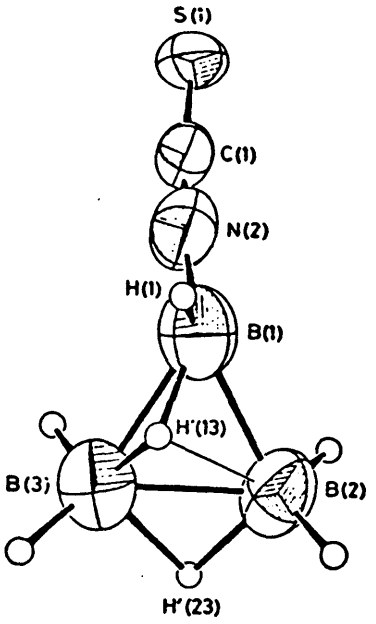


Figure 13: $[B_3H_7NCS]^-$

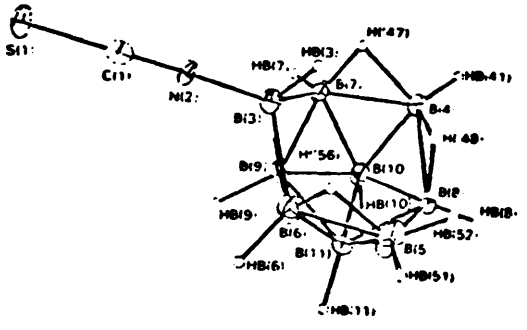


Figure 14: $[B_9H_{13}NCS]^-$

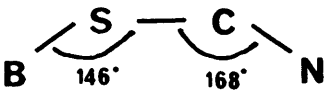


Figure 15: B-SCN

Finally, azidoborohydride is also distorted both at B-N-N (163.5°) and N-N-N (28°) Figure 16).

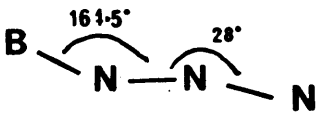


Figure 16: $B-N_3$

2.2.1.5. *Bonding in* $[BH_3X]^-$ *Series*

2.2.1.6. *Molecular Orbital Correlation Diagram*

From the results of the molecular orbital calculations on the $[BH_3X]^-$ series a correlation diagram showing the eigenvector energy values can be drawn. The molecular orbitals which are predominantly B-H or B-X bonding are correlated in Figure 17. The energies of the lone pair orbitals on the halide and pseudo-halide groups and the essentially non-boron containing molecular orbitals are illustrated in this diagram by dashed lines.

The bonding in $[BH_4]^-$ is most straightforward and will be discussed first. The four B-H bonding molecular orbitals, a_1g and t_1u, are at -14.94 and -5.41 e.v. respectively, in the tetrahedral symmetry. Replacement of hydride by halide or pseudohalide reduces the local symmetry around the boron atom to C_3v. For the chloride and cyanide derivatives the t_1u molecular orbitals of $[BH_4]^-$ become an a and e set. The e molecular orbital pair is at a lower energy than a symmetry molecular orbital in $[BH_3Cl]^-$ but this is reversed in $[BH_3CN]^-$. For the thiocyanate, isthiocyanate and azide deriv-

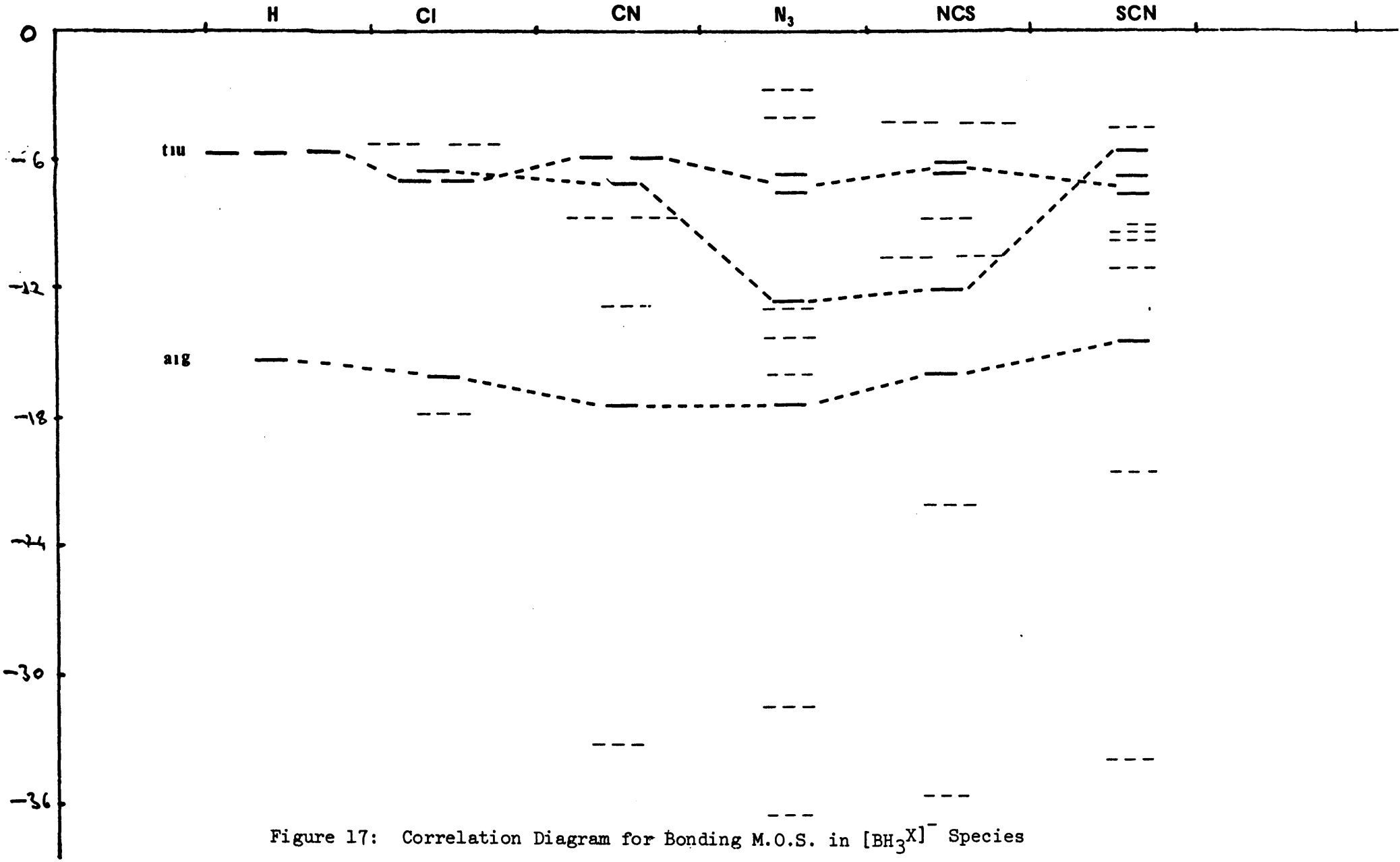


Figure 17: Correlation Diagram for Bonding M.O.S. in $[BH_3X]^-$ Species

atives the t_1u set is split into three singly degenerate levels. In all cases replacement of hydride results in the B-H and B-X molecular orbitals being at a lower energy level than their equivalents in the borohydride anion. The other molecular orbitals present are either lone pair in character ($[BH_3Cl]^-$) or for the pseudohalide derivatives they can be ascribed to lone pairs on either nitrogen or sulphur or σ and π bonds between carbon, nitrogen and sulphur atoms.

2.2.1.7. *Localised Bonding Schemes*

The results of the MNDO localised bonding calculations show that all terminal boron-hydrogen bonds in the series are twocentre-two electron bonds in which boron supplies approximately 40% of the orbital composition and hydrogen the remaining 60% (Table 3). Moreover, this not affected by replacement of hydride by either halide or pseudohalide for B-X bonding.

All the B-X bonds are approximately twocentre-two electron bonds. However, the number of centres does vary from 2.01 for the boron-nitrogen bond in $[BH_3N_3]^-$ to 1.58 for the boron-nitrogen bond in $[BH_3NCS]^-$. The X-Y and Y-Z bonding in the pseudohalide groups is interesting. The carbon-nitrogen bond in $[BH_3CN]^-$ consists of three (σ and 2π) bonds with bond indices of 2.03 (σ) and 1.94 (π) respectively. There is also a lone pair molecular orbital on nitrogen (Figure 18). All of the other bonds in the pseudo halide groups are essentially between two centres (Table 3). There are lone pair orbitals on nitrogen atoms in $[BH_3N_3]^-$ (the nitrogen attached to boron and the terminal nitrogen atom of the azide group, Figure 19) and $[BH_3SCN]^-$ but none in $[BH_3NCS]^-$. There are three sulphur lone pair orbitals in the B-N-C-S derivative and two in the B-S-C-N isomer (Figures 20 and 21).

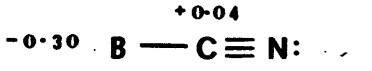


Figure 18: -0.30 + 0.04 -0.38

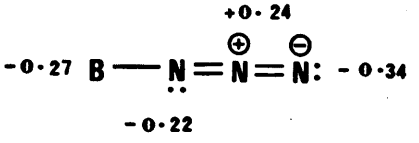


Figure 19: Bonding in $B-N_3$

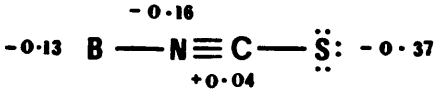


Figure 20: Bonding in B-NCS

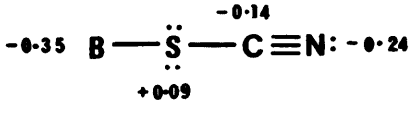


Figure 21: Bonding in BSCN

TABLE 3. *Number of Centres and Orbital Composition in $[BH_3X]^-$ Species*

No. of Centres	Compound	Atom	% Composition	Atom	% Composition
1.96	$[BH_4]^-$	B	41	H	59
1.62	$[BH_3Cl]^-$	B	25	Cl	75
1.98		B	44	H	56
1.00		Cl	100		
1.82	$[BH_3CN]^-$	B	34	C	66
2.0		B	44	H	56
2.03		C	50	N	50
1.94		C	40	N	60
1.00		N	100		
1.58	$[BH_3NCS]^-$	B	24	N	76
2.01		B	44	H	56
2.09		C	45	N	53

TABLE 3 (Contd.)

No. of Centres	Compound	Atom	% Composition	Atom	% Composition
1.85		C	64	S	36
1.19		S	92		
1.90	$[BH_3SCN]^-$	B	34	S	66
2.0		B	44	H	56
1.86		S	36	C	64
2.03		C	52	N	48
1.97		C	45	N	55
1.0		N	100		
1.0		S	100		
2.01	$[BH_3N_3]^-$	B	31	N	64
2.00		B	44	H	56
1.91		N	60	N	40
1.75		N	72	N	24
1.00		N	100		

2.2.1.8. *Atom Charges*

The atom charges in $[BH_4]^-$ are -0.32 on boron and -0.17 on hydrogen. In $[BH_3Cl]^-$ the polarity of the B-X bond is reversed with -0.47 on chlorine and -0.11 on boron. The polarity of the B-H bond is also altered in $[BH_3Cl]^-$ with the hydrogen atoms having a charge of -0.11. In cyanoborohydride the charge on boron is -0.3 while carbon is slightly positively charged (+ 0.04) (Figure 18). As expected nitrogen is the most negative atom in $[BH_3CN]^-$ (-0.38). In the other pseudohalides there is one positively charged atom in each (Figures 19 to 21); the middle nitrogen in $[BH_3N_3]^-$ (+0.24); the carbon atom in $[BH_3NCS]^-$ which has the same charge as the carbon atom in $[BH_3CN]^-$ (+0.4) and the sulphur atom $[BH_3SCN]^-$ (+0.09). The boron sulphur bond in $[BH_3SCN]^-$ is the most polar of the six B-X bonds in the $[BH_3X]^-$ series.

2.2.1.9. *Heats of Formation*

M.N.D.O. calculations provide Heat of Formation data for the $[BH_3X]^-$ compounds (Table 4). Chloroborohydride is apparently the most thermodynamically stable of the series. However, Shore and coworkers[11] reported that the $[BH_3Cl]^-$ salts were stable under inert atmosphere at room temperature but decomposed rapidly on exposure to air. Heating [PPN][BH_3Cl] to 200°C with continuous removal of volatiles resulted in the recovery of $B_2H_6.CH_2Cl_2$ and a small amount of hydrogen. The stability of $[BH_3Cl]^-$ in solution is temperature dependent with higher temperatures promoting both anion disproportionation and diborane evolution. Both $[BH_4]^-$ and $[BH_3CN]^-$ appear to be chemically more stable and survive periods of longer exposure to air and moisture than $[BH_3Cl]^-$. Due to the electron withdrawing character of cyanide relative to hydride,[22,23] cyanoborohydride is stable in aqueous acid down to pH3. Borohydride does not have this pronounced acid stability.

The calculations also predict that $[BH_3SCN]^-$ ($\Delta H^\circ F$ -44.13 KCal mol^{-1}) is slightly more stable than $[BH_3NCS]^-$ ($\Delta H^\circ F$ -38.45 KCal mol^{-1}). A review by Lappert and Pyszora[24] of the known pseudohalides of group III and IV

TABLE 4. *Heats of Formation for* $[BH_3X]^-$

$H_3B - X$ -X	ΔH^oF $KCalmol^{-1}$
-H	-35.9
-Cl	-85.6
-CN	-40.8
-NCS	-38.45
-SCN	-44.13
$-N_3$	+12.6

elements (excluding carbon) found that only isothiocyanates (X-NCS) occurred. In most cases the isothiocyanate was thermally more stable and could be formed from the thiocyanate.[25] Lappert and Pyszora[26,27] prepared and examined a number of boron derivatives and concluded on the basis of infrared stretching frequencies that they were indeed isothiocyanates. Furthermore, compounds such as 6-$B_{10}H_{13}NCS$[28,29] and $(t\text{-BuNBNCS})_4$ [30] are known to be isothiocyanates, as are more recently prepared compounds such as $[B_3H_7NCS]^-$ [18,19] and $[B_9H_{13}NCS]^-$[20], whose structures have been resolved by single crystal X-ray analysis. Thus it would appear that, in general, under commonly encountered chemical conditions the B-NCS bond is preferred to B-SCN. However, the calculations refer to isolated anions and do not take into account e.g. preparative methods, counter ion effects etc. Bearing this in mind and the relatively small $\Delta H^\circ F$ difference for B-NCS compared to B-SCN it is perhaps not surprising that Hui[16] has reported the synthesis and characterisation of $[BH_3SCN]^-$ as the sodium salt. Sodium thiocyanate borohydride was obtained in high yield by passing diborane into a solution of anhydrous sodium thiocyanate (1).

$$\tfrac{1}{2}B_2H_6 + Na[SCN] \xrightarrow{\text{monoglyme}} Na[BH_3SCN] \qquad (1)$$

The product was identified as the thiocyanate by the infrared stretching frequency at 2180 cm^{-1} (SCN). However, Hui also reports an absorption at 2080 cm^{-1} which corresponds to an isothiocyanate absorption, but does not give the relative concentration of each.

Azidoborohydride is the only member of the $[BH_3X]^-$ to have a positive heat of formation(+12.2 KCal mol^{-1}). To date pure azidoborohydride has not been isolated.

2.2.2 $[B_{10}H_9X]^{2-}$ Series

Only the parent compound of the $[B_{10}H_9X]^{2-}$ series i.e. X=H, has been structurally characterised experimentally.[32] However, the structures of the related molecules 1, 10-$B_{10}H_8(N_2)_2$[33] and $[(CH_3)_4N]_2[B_{10}H_7Cl_3]$[34] have also been reported.

2.2.2.1. $[B_{10}H_{10}]^{2-}$

The M.N.D.O. (free variation) calculation for $[B_{10}H_{10}]^{2-}$ converged on a geometry of almost exactly $D_{4}d$ symmetry. The calculated bondlengths and the experimental values are listed in Table 5. The calculation tends to slightly overestimate the boron-boron bondlengths between the two B_4 squares and also the B-H bondlengths, but all other bondlengths agree within 0.05 Å with the X-ray crystallographically determined values. The slight asymmetry (deviation from $D_{4}d$ symmetry) is typical of free varied M.N.D.O. calculations and is not significant. The B-H and B-B bondlengths for 1, 10-$B_{10}H_8(N_2)_2$ (Figure 22) and $[(CH_3)_4N]_2$ $[B_{10}H_7Cl_3]$ (Figure 23) are also listed in Table 5 together with B-N and B-Cl values. In Table 5, Ba-Be refers to bonds between apical boron Ba and equatorial (ring) boron-atoms Be; likewise Be-Be and B ring-B ring refer to the inter (B4)-B ring bonds. Apart from the slight overestimation in the calculated values agreement between the theoretical and experimental results is very good.

Further comparisons with experimental data from $Cu_2[B_{10}H_{10}]$ (Be-Be 1.82; Ba-Be 1.73; B ring-B ring 1.86 Å)[35]; the photoisomer of $[B_{20}H_{12}]^{2-}$ (Be-Be 1.79; Ba-Be 1.68; Bring-Bring 1.83 Å);[36] the normal isomer of $[B_{20}H_{18}]^{2-}$ (Be-Be 1.81; Ba-Be 1.70; Bring-Bring 1.84 Å)[37] and $[B_{20}H_{17}NO]^{3-}$ (Be-Be 1.82; Ba-Be 1.72; Bring-Bring 1.87 Å)[38] may be made and confirm the validity of the results obtained from the MNDO calculations.

The bonding in $[B_{10}H_{10}]^{2-}$ consists of ten terminal twocentre-two electron B-H bonds and eleven cluster bonds (as determined in a less sophis-

TABLE 5. *B–H and B–B Bondlengths* [a]

Bond	$[B_{10}H_{10}]^{2-}$ calc.	$[B_{10}H_{10}]^{2-}$ Expt.	1.10-$B_{10}H_8(N_2)_2$ [b] Expt.	$[B_{10}H_7Cl_3]^{2-}$ [c] Expt.
Be-Be	1.90	1.81(3)	1.881(3)	1.875(3)
Ba-Be	1.72	1.68(3)	1.668(3)	1.707(3)
Bring-Bring	1.82	1.815(5)	1.799(3)	1.775(3)
B-H	1.17	1.11(7)	1.075(2)	

a Bondlengths in Angstroms

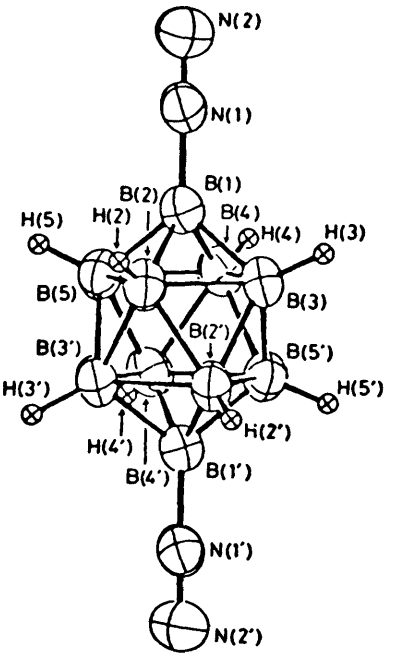


Figure 22: 1,10-$[B_{10}H_8(N_2)_2]$

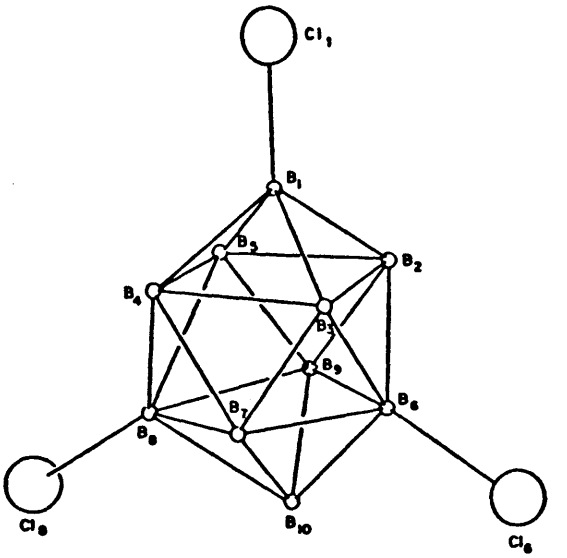


Figure 23: $[B_{10}H_7Cl_3]^{2-}$

ticated way by Wade's Rules[5]). The calculated molecular orbital energies, their symmetries and assignements are given in Figure 24. The eleven cluster bonding molecular orbitals are divided into four "radial" (S^{σ}, $P^{\sigma/\pi}$ from -35 to -15 e.v.) and seven "tangential" (D^{π} and F^{π} from -10 to -1 e.v.) type orbitals[2,39,40]. The calculations place ten orbitals between -20 and -13 e.v. and these correspond to the terminal B-H bonds. The four radial orbitals are assigned as a_1, b_2 and e_1, the former relates to S^{σ} and the latter three to P^{σ} according to Stones' classification.[41] The seven tangential orbitals are assigned as e_3, a_1, e_2 and e_1 with the lower energy five orbitals classified as D^{π} and the higher energy pair (-0.89 e.v.) as F^{π}.

2.2.2.1.1 *Localised Bonding in* $[B_{10}H_{10}]^{2-}$

Boron-hydrogen bonding in $[B_{10}H_{10}]^{2-}$ consists of two-centre two-electron bonds. As expected in systems such as $[B_{10}H_{10}]^{2-}$ where delocalisation occurs, the boron-boron cluster bonds are more complex and are basically three centre bonds. The three boron atoms directly involved in the bonding supply approximately 30% each of the orbital composition.

2.2.2.1.2. *Atom Charges: Electrophilic Substitution*

Electrophilic substitution reactions of boranes have been previously analysed by Lipscomb and coworkers[42] in terms of the atomic charges in the molecule in their ground state. For the $[B_{10}H_{10}]^{2-}$ cluster there is a correlation between the B- site of electrophilic substitution and the negative charge carried by that site. The negative charge at the apical boron atoms (-0.32) is greater than twice that at the equatorial positions (-0.12) (Figure 25) and the apical positions are substituted first, thereafter substitution could occur in any one of the eight equatorial positions. This prediction is borne out by the experimental results for example in the preparation of 1, 10-$B_{10}H_8(N_2)_2$[33] which involves "$N2^+$" attack (Figure 22).

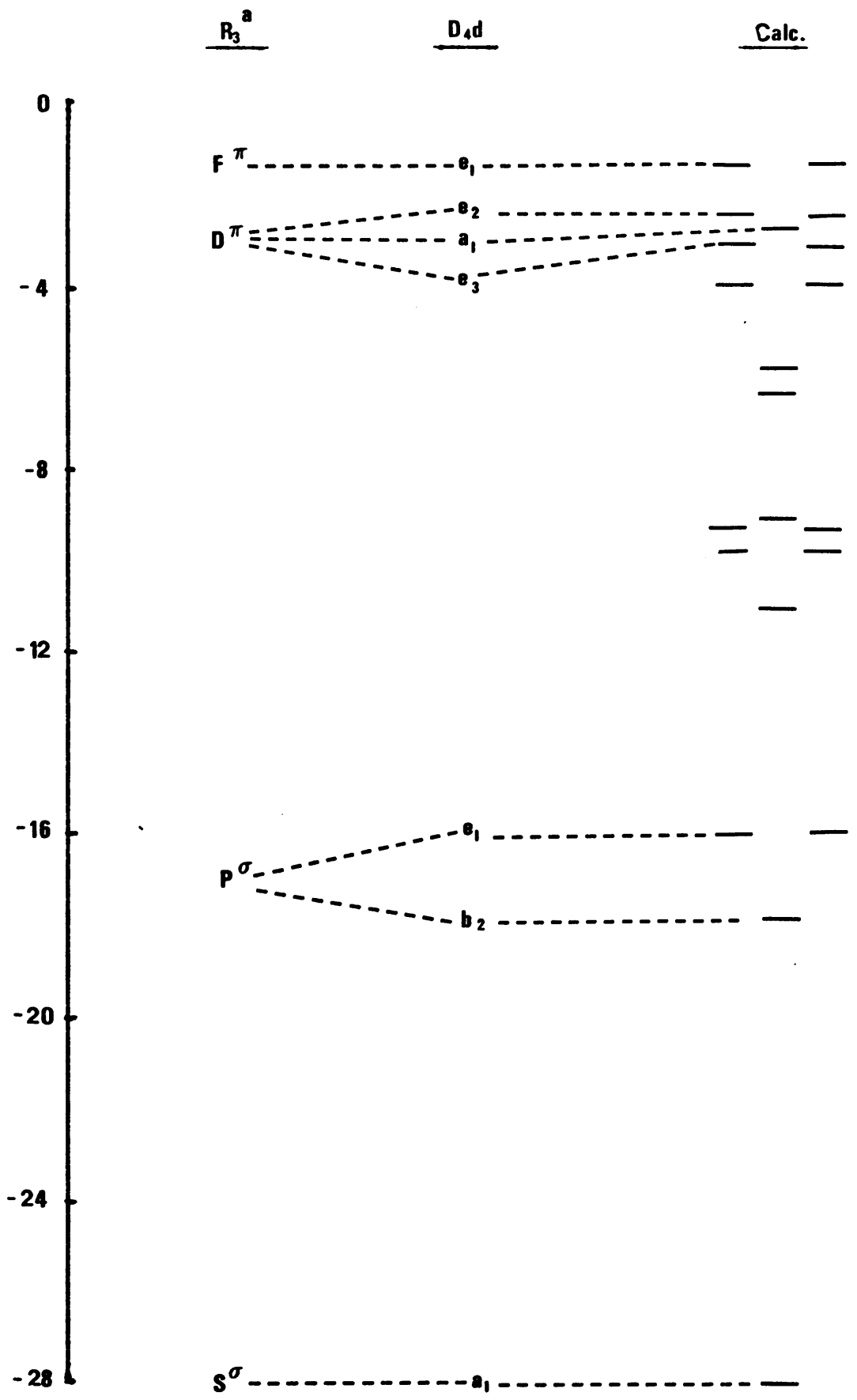


Figure 24: Orbital Energy Levels and Assignements for $[B_{10}H_{10}]^{2-}$
[a] Spherical Symmetry Label

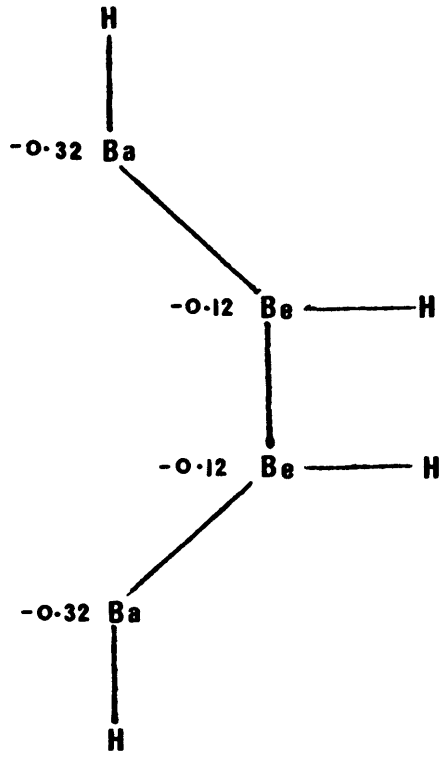


Figure 25: Atomic Charges in $[B_{10}H_{10}]^{2-}$

However, for electrophilic halogenation of $[B_{10}H_{10}]^{2-}$ the results cannot be easily correlated with the above predictions because fast sequential substitution occurs which obscures information on the site(s) of attack. Kinetic data[43] have shown that it is impossible to distinguish between the rates of the first three iodinations of $[B_{10}H_{10}]^{2-}$. According to the MNDO predictions, substitution to give $[B_{10}H_7Cl_3]^{2-}$ should occur at the 1- and 10- apical positions first, with the third chlorine bonded to any one of the eight equatorial boron atoms. However, Scarborough and Lipscomb[34] have reported that the structure of the trichloro derivative $[B_{10}H_7Cl_3]^{2-}$ is the 1,6,8 $-Cl_3$ -isomer (Figure 23) with C_2V symmetry. This apparent contradiction can be resolved since the reaction leading to $[B_{10}H_7Cl_3]^{2-}$ (2)[44].

$$K_2\,[B_{10}H_{10}] \xrightarrow[[Me_4N]X]{FeCl_3(\text{excess})} [Me_4N]_2\,[B_{10}H_7Cl_3] + K[X] \qquad (2)$$

most probably proceeds by a free radical mechanism.

2.2.2.2. $[B_{10}H_9Cl]^{2-}$

In general the bonding picture in $[B_{10}H_9Cl]^{2-}$ is very similar to that in $[B_{10}H_{10}]^{2-}$. The eleven cluster bonding molecular orbitals are retained, there are ten two centre-two electron bonds (nine B-H and one B-Cl) and in addition there are three chlorine lone pair orbitals. The orbital energies for $[B_{10}H_9Cl]^{2-}$ are shown in Figure 26. With the exception of the chlorine 3s lone pair orbital (at -16.5 e.v., shown by a dashed line in Figure 26) the four orbitals of lowest energy are the radial cluster orbitals (S^{σ}, $P^{\sigma/\pi}$). Just as in $[B_{10}H_{10}]^{2-}$ the seven orbitals of highest energy are the tangential cluster orbitals. Replacement of hydrogen by chlorine reduces the symmetry from D_4d in $[B_{10}H_{10}]^{2-}$ to C_4V. Hence the e_2 pair of cluster molecular orbitals are split in $[B_{10}H_9Cl]^{2-}$. The chlorine 3py, 3pz lone

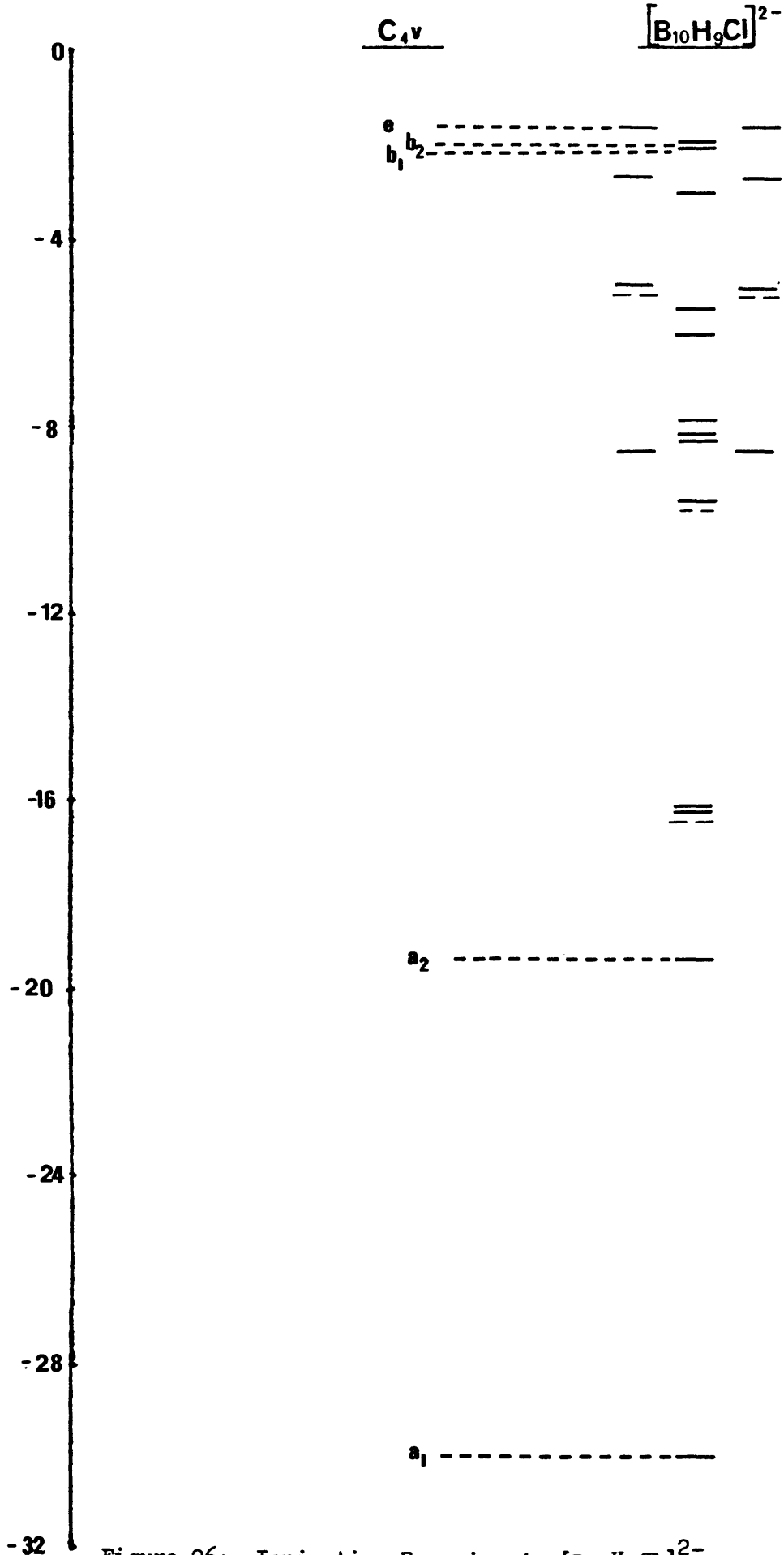


Figure 26: Ionisation Energies in $[B_{10}H_9Cl]^{2-}$

pairs are found at an energy below the seven highest cluster orbitals (-5.2 e.v.) and among the B-H bonding orbitals.

The B-H bondlengths in $[B_{10}H_9Cl]^{2-}$ are approximately the same as those in $[B_{10}H_{10}]^{2-}$, with a slight reduction in the apical B-H bondlength (1.158 Å) opposite the chlorine atom. The calculated B-Cl bondlength at 1.85 Å corresponds exactly with the apical B-Cl bondlength in $[B_{10}H_7Cl_3]^{2-}$ (1.85(2) Å). The equatorial boron-chlorine bondlengths are longer (B6-Cl6, 1.93(2)Å; B8-Cl8, 1.95 (2)Å). Table 6 lists the relevant bondlengths in $[B_{10}H_9Cl]^{2-}$.

There is very little evidence from the MNDO calculations for any chlorine-cluster π type interaction (1-2%) in the e pair of orbitals of $P^{\sigma/\pi}$ type. There is, however, evidence in orbitals of D^{π} type for some π B-Cl antibonding character (approximately 8%) and also in the H.O.M.O.e pair at -1.1 e.v. (approximately 7%).

2.2.2.2.1. *Localised Bonding in* $[B_{10}H_9Cl]^{2-}$

The localised bonding picture of $[B_{10}H_9Cl]^{2-}$ is very similar to that in $[B_{10}H_{10}]^{2-}$.

2.2.2.2.2. *Atom Charges: Electrophilic Substitution*

The distribution of atomic charges in $[B_{10}H_9Cl]^{2-}$ is depicted in Figure 27. The charges on the apical boron-hydrogen bond and the equatorial boron-hydrogen bonds are very similar to those in $[B_{10}H_{10}]^{2-}$. In the boron-chlorine bond the negative charge on the boron atom is only -0.18, with chlorine charged at -0.30. Thus according to the MNDO calculations, electrophilic substitution at boron in $[B_{10}H_9Cl]^{2-}$ is most likely to occur at the apical site opposite the chlorine atom. However, no data on the substitution of $[B_{10}H_9Cl]^{2-}$ exists.

TABLE 6. *Bondlengths in* $[B_{10}H_9Cl]^{2-}$ [a]

Bond	$[B_{10}H_9Cl]^{2-}$
Be - Be	1.90
Ba - Be	1.72
Bring- Bring	1.82
B - H	1.17
B - Cl	1.85

[a] Bondlengths in Angstroms

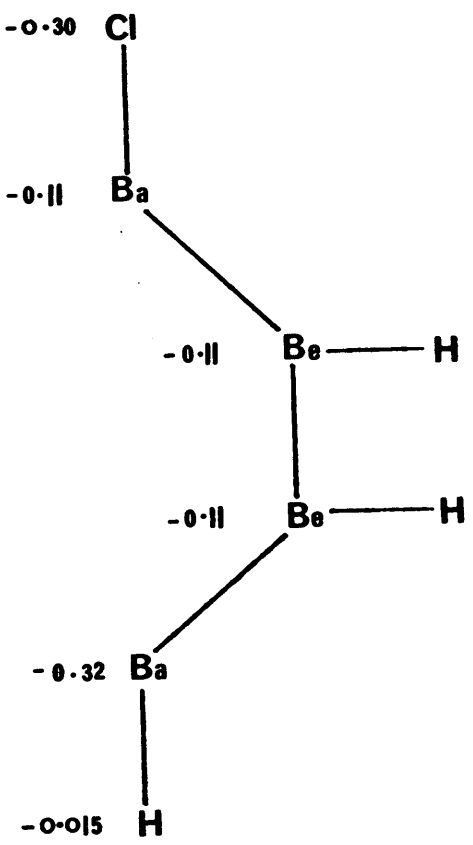


Figure 27: Charge Distribution in $[B_{10}H_9Cl]^{2-}$

2.2.2.3. $[B_{10}H_9(CN)]^{2-}$

The boron-hydrogen and cluster bonding in $[B_{10}H_9(CN)]^{2-}$ are very similar to both $[B_{10}H_{10}]^{2-}$ and $[B_{10}H_9Cl]^{2-}$ and require little further comment. The boron-carbon bondlength (1.486 Å) is significantly shorter than that in both ammonia-cyanoborane (1.589(3)Å) and *cyclo*(hexacyanoborane) (1.559(6)Å). The C≡N bondlength of 1.171 Å is, however, longer than in both of the latter compounds. Although this tends to suggest that there is some extra (possibly π type) bonding interaction between the cyanogroup and the cluster cage at the expense of the carbon-nitrogen bonding, but analysis of the molecular orbitals reveals that apart from a slight interaction in the e pair of orbitals of $P^{\sigma/\pi}$ type, $[B_{10}H_9(CN)]^{2-}$ is essentially a B_{10} cluster cage with a non-interacting cyanide substituent.

A correlation diagram showing the relationship of the cluster bonding molecular orbitals in the group of $[B_{10}H_9X]^{2-}$ series reported here is illustrated in Figure 28. Apart from a slight stabilisation in energy, the four radial cluster orbitals of $[B_{10}H_9(CN)]^{2-}$ are equivalent to those in $[B_{10}H_{10}]^{2-}$. With the exception of the orbitals equivalent to the e_2 pair in $[B_{10}H_{10}]^{2-}$, which in $[B_{10}H_9(CN)]^{2-}$ are split and a reversal in the energies of the a_1 and e_3 pair, the tangential orbitals are equivalent to those in $[B_{10}H_{10}]^{2-}$. The carbon-nitrogen σ bonding and π bonding orbitals are shown by dashed lines in Figure 28.

An analysis of the bond angles reveals that the B-C≡N group is linear, Figure 29.

Figure 29: B-C-N Bond Angle

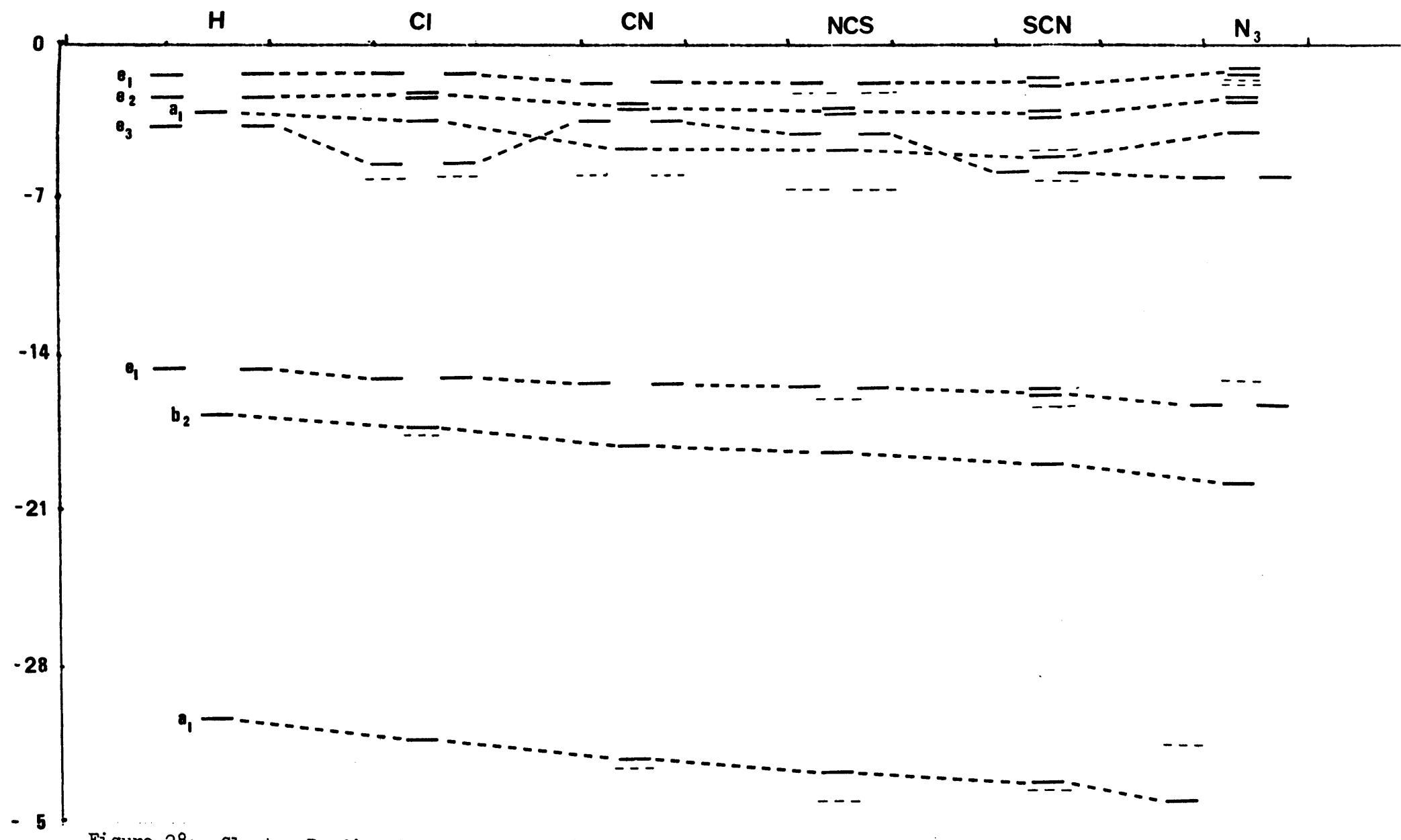


Figure 28: Cluster Bonding Correlation for $[B_{10}H_9X]^{2-}$

2.2.2.3.1. *Localised Bonding*

As with $[B_{10}H_9Cl]^{2-}$ replacement of hydrogen in $[B_{10}H_{10}]^{2-}$ by a cyanide group does not affect the localised $B_{10}H_9X$- bonding picture significantly. The boron-carbon bond is a two centre-two electron bond and the three carbon-nitrogen bonds (σ and 2π) are also two centre-two electron systems. The remaining filled molecular orbital in $[B_{10}H_9(CN)]^{2-}$ is a nitrogen lone pair orbital.

2.2.2.3.2. *Atom Charges: Electrophilic Substitution*

The atomic charge distribution in $[B_{10}H_9(CN)]^{2-}$ is illustrated in Figure 30. The apical boron to which the cyanide group is bonded is the most negative boron atom (-0.32) but the other apical boron is very similarly charged (-0.30). Thus on the basis of charges, electrophilic substitution at boron could take place at either of the apical sites. However, the presence of the cyanide group introduces another factor and it is possible that the positively charged carbon atom (+ 0.14) of the cyanide group could repel an attacking electrophile. Therefore, it seems likely that electrophilic substitution at boron in $[B_{10}H_9(CN)]^{2-}$ would occur preferentially at the apical boron atom opposite the cyanide group.

The B-C≡N system is quite planar and although the charge distribution suggests a more correct representation may be $B-C^{+}=N^{-}$, the bonding analysis indicates that the former is the better description.

2.2.2.4. $[B_{10}H_9(NCS)]^{2-}$

The eleven cluster bonding molecular orbitals in $[B_{10}H_9(NCS)]^{2-}$ have the same pattern as in $[B_{10}H_9(CN)]^{2-}$, albeit with a very slight stabilisation in energy (Figure 28). The orbitals are readily identified and mixing with NCS -based orbitals is not a significant factor. Also, boron-hydrogen in $[B_{10}H_9(NCS)]^{-}$ is unaffected by isothiocyanate substitution. The calcul-

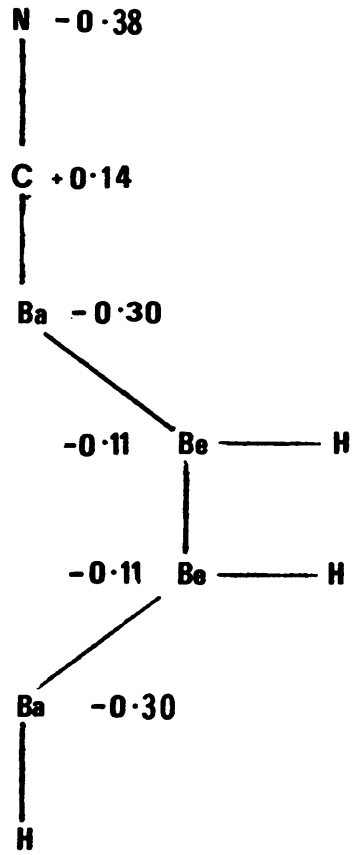


Figure 30: Charge Distribution in $[B_{10}H_9(CN)]^{2-}$

ated boron nitrogen bondlength (1.461 Å) is quite similar to that in $B_{10}H_{13}NCS$ (1.43 Å)[33] but short in comparison with that in ammonia-isothiocyanatoborane (1.534 (8))[8]. The shortened bond in $[B_{10}H_{13}(NCS)]^{2-}$ suggests the possibility of some π interaction between the B_{10}-cage and the isothiocyanate group and this is partly substantiated on analysis of the molecular orbitals. There is a slight (2-3%) boron-nitrogen π bonding interaction in the $P^{\sigma/\pi}$ molecular orbital.

Both the calculated N-C (1.172 Å) and C-S (1.560 Å) bond distances are shorter than the corresponding ones in $B_{10}H_{13}NCS$ (1.615 (5) Å)[14] and $H_3N.BH_2NCS$ (1.627(6)Å)[8]. On comparison with $[B_9H_{13}(NCS)]^-$[20] the bondlengths in $[B_9H_{13}(NCS)]^-$ are, B-N, 1.531(19); N-C, 1.182 (15) and C-S, 1.568 (12) Å. One of the more interesting features of the molecular structure of $[B_{10}H_9(NCS)]^{2-}$ is that the B-NCS moiety is linear. This is consistent with experimental results for $B_{10}H_{13}NCS$ (B(6)-N-C, 171.0(6)°; N-C-S, 178.1(6)°) $H_3N.BH_2NCS$ (B-N-C, 177.5 (6)°; N-C-S, 179.2 (5)° and is also consistent with the B-NCS bond angles in both $[B_3H_7(NCS)]^-$ and $[B_9H_{13}(NCS)]^-$. However, the result for $[B_{10}H_9(NCS)]^{2-}$ is at variance with the calculated findings for $[BH_3NCS]^-$ which showed a slight (30°) deviation from linearity at N-C-S.

2.2.2.4.1. *Localised Bonding*

The localised bonding in B-H and the B_{10}-cage unit in $[B_{10}H_9(NCS)]^{2-}$ is the same as for all the previous molecules in the $[B_{10}H_9X]^{2-}$ series. The MNDO calculation shows that all bonds in the B-NCS moiety are two centre-two electron bonds. The localised bonding picture also shows that there are three lone pair orbitals on sulphur and none on nitrogen which gives the bonding in the linear B-NCS group as in Figure 31.

B —— N ≡ C —— S:

Figure 31: Bonding in B-NCS

2.2.2.4.2. *Atom Charges: Electrophilic Substitution*

The charge distribution in $[B_{10}H_9(NCS)]^{2-}$ is depicted in Figure 32. The sulphur atom is the most negatively charged atom (-0.50) in the molecule and could possibly be susceptible to some electrophilic attack, however, as far as the boron atoms are concerned, the apical boron atom opposite the heteroatomic group is the most likely site for further electrophilic substitution.

2.2.2.5. $[B_{10}H_9(SCN)]^{2-}$

The overall bonding picture in $[B_{10}H_9(SCN)]^{2-}$ is very similar to that in the isothiocyanate derivative. Unlike $[B_{9}H_{11}(NCS)]^{2-}$, the thiocyanate derivative is bent at the boron-sulphur bond, but the SCN group itself is linear (Figure 33).

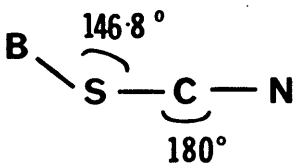


Figure 33: Bond Angles in BSCN

The structure is less symmetrical and the molecular orbitals are more complicated because of mixing. (This was not a significant feature in $[B_{10}H_9(NCS)]^{2-}$ which had symmetry: C_4V). The orbitals which are essentially cluster orbitals are shown in the molecular orbital correlation diagram (Figure 28).

The pattern of these orbitals is slightly altered from that for $[B_{10}H_9(NCS)]^{2-}$. The highest energy pair of both the four radial and seven tangential orbitals are slightly split, although the energy gap is less than 0.5 e.v. Also, the pattern of the tangential orbitals with e_3 and a parentage (from $[B_{10}H_{10}]^{2-}$) is the same as the chloride and the parent $[B_{10}H_{10}]^{2-}$ species (*i.e.* a above e in energy).

The bondlengths in the B-SCN group are shown in Figure 34.

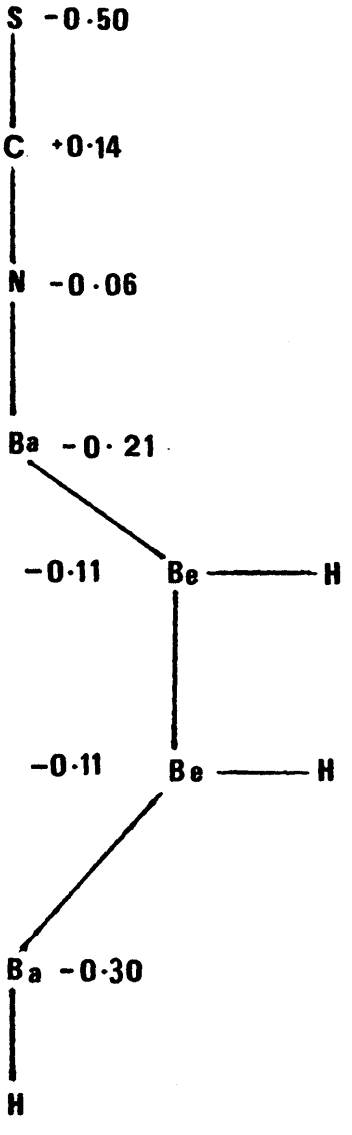


Figure 32: Charges in $[B_{10}H_9(NCS)]^{2-}$

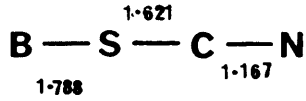


Figure 34: Bondlengths in B-SCN

On comparison with the isothiocyanate group in $[B_{10}H_9(NCS)]^{2-}$, the carbon-sulphur bond in that compound (1.560 Å) is 0.006 Å shorter than in the NCS group. As against that, however, the carbon-nitrogen bond in SCN (1.172 Å) is 0.005 Å longer than in the isothiocyanate group (*vide infra*).

2.2.2.5.1. *Localised Bonding*

The localised bonding picture of the BSCN group (Figure 35) indicates the presence of two sulphur and one nitrogen lone pairs. The boron-sulphur bond is a two centre-two electron bond but the carbon-sulphur bond is more of a single bond than in $[B_{10}H_9(NCS)]^{2-}$ and the three carbon-nitrogen bonds are more readily identifiable as one σ and two π bonds. This accounts for the longer carbon-sulphur and shorter carbon-nitrogen bondlengths than in $[B_{10}H_9(NCS)]^{2-}$

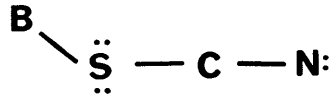


Figure 35: Bonding in BSCN

The presence of lone pair orbitals on the sulphur atom bonded to boron results in a non-linear B-SCN moiety (< BSC 146.2°).

2.2.2.5.2. *Atom Charge: Electrophilic Substitution*

The charge distribution in $[B_{10}H_9(SCN)]^{2-}$ is illustrated in Figure 36. The boron atom bonded to the sulphur atom is the most negative atom in the compound and hence may be the site of electrophilic attack. However, it is possible that the positive sulphur atom would repel such an attack in which

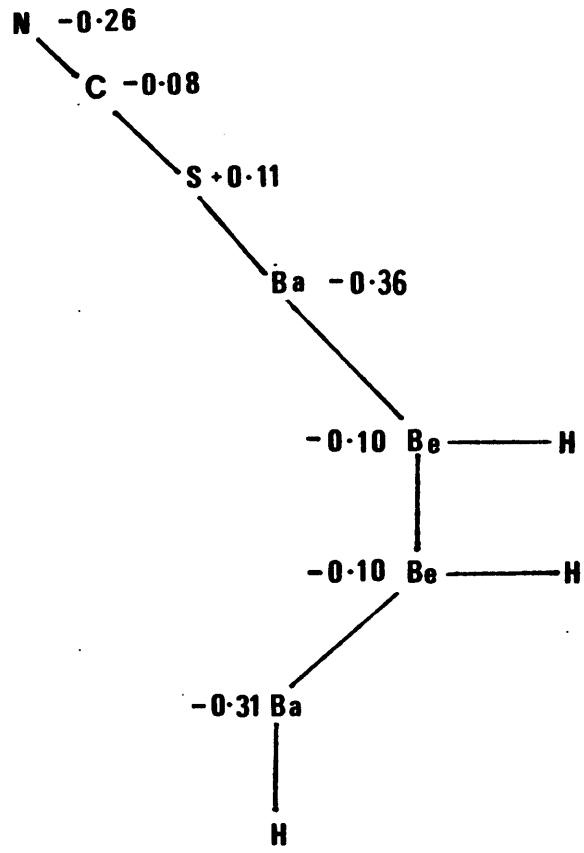


Figure 36: Charges in $[B_{10}H_9(SCN)]^{2-}$

case the next most negative boron atom is that in the apical position opposite the thiocyanate group.

2.2.2.6. $[B_{10}H_9(N_3)]^{2-}$

The cluster cage bonding in $[B_{10}H_9(N_3)]^{2-}$ is similar to those in the rest of the $[B_{10}H_9X]^{2-}$ series. However, like the thiocyanate derivative above the azido group is bent (Figure 37) giving an assymmetry to the molecule (C_1) and causing a mixing of the components in the molecular orbitals. This makes all assignements more difficult than for the previous members of the series. Of the eleven cluster bonding molecular orbitals it is possible to identify the radial cluster orbitals but the seven higher energy cluster orbitals are very mixed and split by the assymmetry. Since there are no experimental results to compare with the predicted structure of $[B_{10}H_9(N_3)]^{2-}$ thus calculated cannot be tested. The bondlengths in the $B-N_3$ moiety are also illustrated in Figure 37.

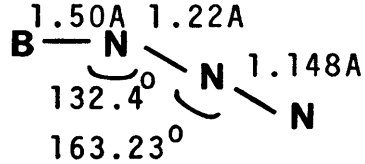


Figure 37: Bondlengths and Bond Angles in BN_3

The boron-nitrogen bondlength is approximately 0.04 Å longer than that in $[B_{10}H_9(NCS)]^{2-}$ (1.46 Å). In hydrazoic acid, HN_3 and methylazide, CH_3N_3, the *endo* nitrogen-nitrogen bondlengths are longer (1.24 and 1.26 Å, respectively) while the *exo* nitrogen-nitrogen bondlengths are shorter (1.13 and 1.10 Å respectively). These species are also bent at the R-N-N moiety (R = H, CH_3) (Figures 38 and 39)

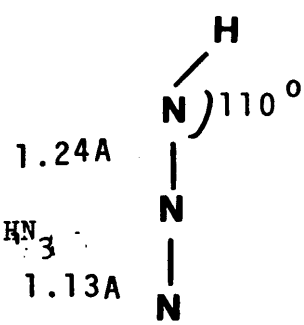


Figure 38: HN_3

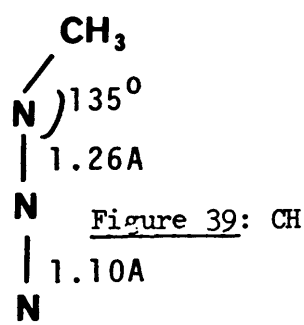


Figure 39: CH_3N_3

2.2.2.6.1. *Localised Bonding*

As in the case of the thiocyanate derivative the presence of a lone pair on the nitrogen atom bonded to boron results in the $B-N_3$ portion being bent. There is also a lone pair on the terminal nitrogen of the azido group. The boron-nitrogen bond is a two centre-two electron bond.

Localised bonding in the azido group consists of a σ and π bond in each of the two nitrogen-nitrogen bonds.

2.2.2.6.2. *Atom Charges: Electrophilic Substitution*

The charge distribution in $[B_{10}H_9(N_3)]^{2-}$ is depicted in Figure 40. Just as in the previous five members of the $[B_{10}H_9X]^{2-}$ series the most likely position of electrophilic substitution at the $[B_{10}H_9(N_3)]^{2-}$ cage is at the apical atom opposite the azido-substituent.

The furthest nitrogen from the boron cluster in the azido group is the most negative atom in the molecule (-0.34). The possibility exists of some electrophilic attack here but there would also be repulsion by the positively charged (+0.25) adjacent nitrogen atom. The charge separation in the azido group agrees with the localised bonding and leads to the bonding description illustrated in Figure 41.

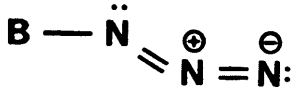


Figure 41: Bonding in BN_3

This coincides with the conventional description of azide substituents e.g. HN_3 and CH_3N_3.

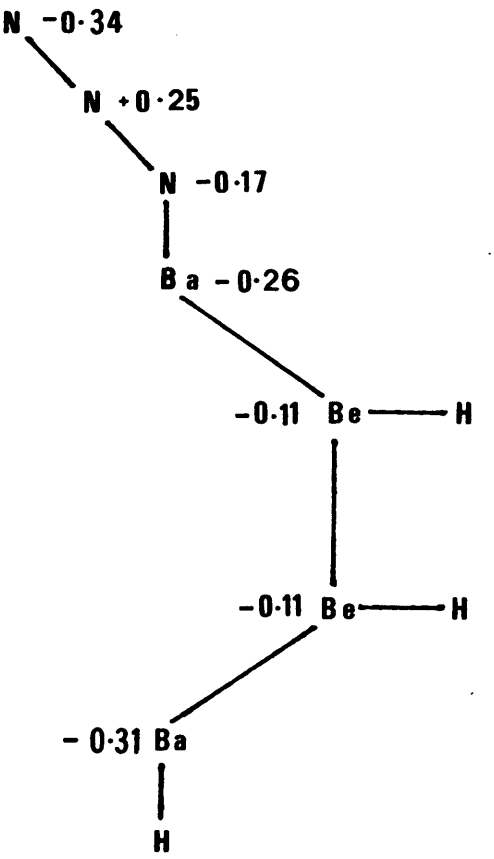


Figure 40: Charges in $[B_{10}H_9(N_3)]^{2-}$

2.2.2.7. *Heats of Formation*

The MNDO calculated Heats of Formation for the $[B_{10}H_9X]^{2-}$ series is listed in Table 7. As with the previous series, the chloride derivative appears to be the most stable. Also, the cyanide derivative is very similar to the parent molecule. However, the stabilities of the thiocyanate and isothiocyanate derivatives are reversed from the monoboron series, with $[B_{10}H_9(NCS)]^{2-}$ more stable than $[B_{10}H_9(SCN)]^{2-}$.

2.2.3. *Conclusions*

The MNDO calculations reported here are the first for the series $[BH_3X]^-$ and $[B_{10}H_9X]^{2-}$ (X = H, Cl, CN, SCN, NCS, N_3). The validity and accuracy of the calculations is supported by the favourable comparisons with experimental data such as the solid state structures of $[BH_3Cl]^-$ and $[B_{10}H_{10}]^{2-}$, etc. Thus the calculations would appear to provide a sound theoretical assessment of hitherto unknown compounds such as $[BH_3(N_3)]^-$, $[B_{10}H_9N_3]^{2-}$, and $[B_{10}H_9(SCN)]^{2-}$.

In the monoboron series, $[BH_3X]^-$, all six molecules are tetrahedral. Replacement of hydride by halide or pseudohalide causes very little variation in boron-hydrogen bonding. For the pseudohalide derivatives, B-CN is linear but the other three (B-SCN, B-NCS, B-N_3) are not.

In the $[B_{10}H_9X]^{2-}$ series the cluster cage bonding remains very consistent with that in the parent $[B_{10}H_{10}]^{2-}$. The rest of the bonds are basically two centre-two electron bonds. The variations in the X substituents are not very significant to cluster cage bonding in this series.

Only B-NCS is linear of the pseudohalide derivatives with the others all distorted.

During the course of the present research it was envisaged that the synthesis of members of the $[B_{10}H_9X]^{2-}$ series would be attempted *via* $[B_{10}H_9Cl]^{2-}$. However, reactions of $[B_{10}H_{10}]^{2-}$ with various chlorinating agents afforded polyhalogenated products and further reactions could not be attempted.

TABLE 7. *Heats of Formation in* $[B_{10}H_9X]^-$ *Series*

X	$\Delta H^\circ F$ K Cal mol^{-1}
H	-58.44
Cl	-94.46
CN	-59.16
NCS	-64.18
SCN	-53.57
N_3	-2.85

2.3 EXPERIMENTAL

The MNDO program was used as supplied by Quantum Chemistry Program Exchange without alteration. All MNDO calculations were run with complete free variation of all geometry parameters (≈ 70 parameters).

2.4 REFERENCES

1. M.S. Dewar and W. Thiel, *J. Am. Chem. Soc., 1977,* 99, *5231.*
2. M.S. Dewar and M.L. McKee, *Inorg. Chem., 1978,* 17, *1569.*
3. N.N. Lipscomb in *'Boron Hydride Chemistry'*, E.L. Muetterties (Ed.), *Academic Press, New York, 1975,* Ch. 2.
4. S.K. Lambiris, D.S. Marynick and W.W. Lipscomb; *Inorg. Chem., 1978,* 17, *3706.*
5. K. Wade; *Adv. Inorg. Chem., Radiochem., 1976,* 18, *1.*
6. W. Thiel, *Quantum Chemistry Programme Exchange, 1978,* 11, *353.*
7. A.T. McPhail, K.D. Onan, B.F. Spielvogel and P. Wisian-Neilson; *J. Chem. Res. (M), 1978,* 8, *2601.*
8. D.S. Kendall and W.N. Lipscomb; *Inorg. Chem, 1973,* 12, *2920.*
9. O. Eisenstein, M. Kayser, M. Roy and T.B. McMahon, *Can. J. Chem., 1985,* 63, *281.*
10. M.T. Barlow, C.J. Dain, A.J. Downs, G.S. Laurenson and D.W.H. Rankin; *J. Chem. Soc., Dalton, 1982, 597.*
11. S.H. Lawrence, S.G. Shore, T.F. Koetzle, J.C. Huffman, C. Wei and R. Bau; *Inorg. Chem., 1985,* 24, *3171.*
12. S.G. Shore and S.H. Lawrence, *J. Am. Chem. Soc., 1982,* 104, *7669.*
13. A.M. Sapse and L. Osorio; *Inorg. Chem., 1984,* 23, *627.*
14. W.J. Hehre, R. Ditchfield and J.A. Pople; *J. Chem. Phys., 1972,* 56, *2257.*
15. P.C. Harihanan and J.A. Pople; *Theor. Chim. Acta., 1973,* 28, *213.*
16. B.C. Hui; *Inorg. Chem., 1980,* 19, *3185.*
17. D.K. Kendall and W.N. Lipscomb; *Inorg. Chem., 1973,* 12, *2915.*
18. S.J. Andrews, A.J. Walsh, G.B. Jacobsen and J.H. Morris; *J. Chem. Soc., Chem. Commun., 1982, 749.*
19. S.J. Andrews and A.J. Welch; *Inorg. Chim. Acta, 1984,* 88, *153.*
20. S.J. Andrews and A.J. Welch; *Acta Cryst., 1985,* C41, *1208.*
21. G.I. Beard and B.P. Daiely; *J. Am. Chem. Soc., 1949,* 79, *929.*

22. R.C. Wade, E.A. Sullivan, J.R. Berschied and K.F. Purcell; *Inorg. Chem., 1970,* 9, 2147.

23. M.M. Kreevoy and J.E. Hutchins; *J. Am. Chem. Soc., 1969,* 91, *3996.*

24. M.F. Lappert and H. Pyszora; *Adv. Inorg. Chem. Radiochem., 1966,* 9, *133.*

25. S.F. Assony; *Org. Sulphur Compounds, 1961, 1,* 326.

26. M.F. Lappert and H. Pyszora; *J. Chem. Soc., 1963, 1744.*

27. M.F. Lappert and H. Pyszora; *J. Chem. Soc., 1965, 4256.*

28. D.S. Kendall and W.N. Lipscomb; *Inorg. Chem., 1973,* 12, *2915.*

29. R. Stibr, J. Plesek, F. Hanousek and S. Hermanek; *Collect. Czech. Chem. Commun., 1971,* 36, *1794.*

30. P.T. Clarke and H.M. Powell, *J. Chem. Soc. B, 1966, 1172.*

31. J.T. Gill and S. Lippard, *Inorg. Chem., 1975,* 14, *1975.*

32. T. Whelan, R.P. Brint, T.R.Spalding, W.S. McDonald and D.R. Lloyd; *J. Chem. Soc., Dalton, 1982, 2469.*

33. F. Scarborough and W.N. Lipscomb; *Inorg. Chem., 1972,* 11, *369.*

34. R.D. Dobrott and W.W. Lipscomb; *J. Chem. Phys., 1962,* 37, *1779.*

35. B.G. de Boer, A. Zalkin and D.H. Templeton; *Inorg. Chem., 1969,* 7, *1085.*

36. C.H. Schwalbe and W.W. Lipscomb; *Inorg. Chem., 1971,* 10, *151.*

37. C.H. Swhwalbe and W.N. Lipscomb; *Inorg. Chem., 1971,* 10, *160.*

38. P. Brint, E.F. Healy, T.R. Spalding and T. Whelan; *J. Chem. Soc., Dalton Trans., 1981, 2515.*

39. K.W. Pelin, T.R. Spalding and R.P. Brint; *J. Chem. Res., (S), 1982,120.*

40. A.J. Stone; *Inorg. Chem., 1981,* 20, *563.*

41. D.A. Dixon, D.A. Klein, T. A. Halgre, J.N. Hall and W.N. Lipscomb; J. Hui; *Chem. Soc., 1977,* 99, *6226.*

42. R.L. Middaugh in *"Boron Hydrides"*, W.W. Lipscomb (Ed.), p. 297.

43. A. Kaczmarczyak; *Private Communication* to W.N. Lipscomb.

44. F.A. Cotton and G.A. Wilkinson; *"Advanced Inorganic Chemistry", 1962,* J. Wiley and Sons, p. 253.

CHAPTER THREE

HALOGENATED SELENABORANE CLUSTERS

3.1 INTRODUCTION

The work reported in this chapter relates to halogenated clusters containing eleven or twelve cluster atoms, at least one of which is a selenium atom. The first report of a Group VI element inserted into a polyhedral borane framework was in 1967 when Muetterties and coworkers prepared the $[S\ B_9H_{12}]^-$ by the quantitative reaction of decaborane with ammonium polysulphide in aqueous solution (1)[1].

$$B_{10}H_{14} + [S]^{2-} + 4H_2O \longrightarrow [S\ B_9H_{12}]^- + [B(OH)_4]^- + 3H_2 \qquad (1)$$

The preparation of $[Se\ B_{10}H_{11}]^-$ by Todd and coworkers in 1976[2] was the first insertion of a selenium atom into a borane cluster (2).

$$B_{10}H_{14} + Na_2\ [Se_4] \xrightarrow[H_2O]{Liq\ NH_3} Na\ [Se\ B_{10}H_{11}] \qquad (2)$$

The present chapter deals mainly with the chemistry of halogenated selenaboranes which were prepared either by initial halogenation of decaborane (14) (3).

$$B_{10}H_{14} + X_2 \xrightarrow[CS_2,\ R.T.]{AlCl_3} X\text{-}B_{10}H_{13} + HX \qquad (3)$$

followed by insertion of a selenium atom into the borane cage.(4).

$$X\text{-}B_{10}H_{13} + [Se]^{2-} \xrightarrow[H_2O,\ R.\ T]{NH_3(liq)} [X\text{-}Se\ B_{10}H_{10}]^- \qquad (4)$$

or by direct halogenation of the selenaborane 1-Se $B_{11}H_{11}$ (5).

$$1\text{-}Se\ B_{11}H_{11} + X_2 \xrightarrow{AlCl_3} X\text{-}Se\ B_{11}H_{10} + HX \qquad (5)$$

Some chemistry of *closo* systems based on the 1-Se $B_{11}H_{11}$ cluster are dealt with first followed by *nido* Se $B_{10}H_{12}$ and $Se_2B_9H_9$ compounds.

3.1.1. *Closo Systems based on 1-Se $B_{11}H_{11}$*

Friesen and Todd[3] reported the preparation of Se $B_{11}H_{11}$ (18%) by reaction of $[B_{11}H_{14}]^-$ with sodium bi-selenite in a water-heptane mixture (6).

$$[B_{11}H_{14}]^- + Na[HSeO_3] \xrightarrow{H_2O/C_7H_{16}} Se\text{-}B_{11}H_{11} \qquad (6)$$

Se $B_{11}H_{11}$ has been halogenated under conditions which are commonly used for Friedel-Crafts electrophilic substitution to furnish the 12-substituted-Se $B_{11}H_{10}X$ (X = Cl, Br, I) (7).[4]

$$Se\ B_{11}H_{11} + X_2 \xrightarrow{AlCl_3} 12 - X - Se\ B_{11}H_{10} + HX \qquad (7)$$

X = Cl, (50%); Br (22%); I (40%).

The chlorine derivative was prepared by the addition of chlorine to Se $B_{11}H_{11}$ in dichloromethane, with $AlCl_3$ present as a catalyst. The mixture was initially reacted at -45°C and then allowed to warm to room temperature. Both the bromine and iodine derivatives were prepared by the addition of Se $B_{11}H_{11}$ to a mixture of dichloromethane, $AlCl_3$ and halogen and then refluxed for 14 and 6 hours respectively. The bromo-derivative was isolated in a yield which was notably lower than either the chloro- or iodo-compound. Part of the present work involved an attempt to improve the yield of Br-Se $B_{11}H_{10}$ by varying the reaction conditions. Substitution was shown to have taken place at the 12- position by ^{11}B n.m.r. spectroscopy (Figure 1).

The spectra consisted of three signals with relative intensities and multiplicities of 1(s) : 5 (d) : 5(d). An analogous pattern had previously been observed in the ^{11}B n.m.r. spectrum of 12 - Br-S $B_{11}H_{10}$ [5]. The unique 12-boron atoms in halogenated selenaboranes had chemical shifts of 24.0(Cl), 20.2 (Br) and 4.9 (I) ppm. Compared to the chemical shift of 24.1 (H) p.p.m. in Se $B_{11}H_{11}$ there is a noticeable shift to a higher field on going from Cl to I. This trend with changing halogen substitution has also been

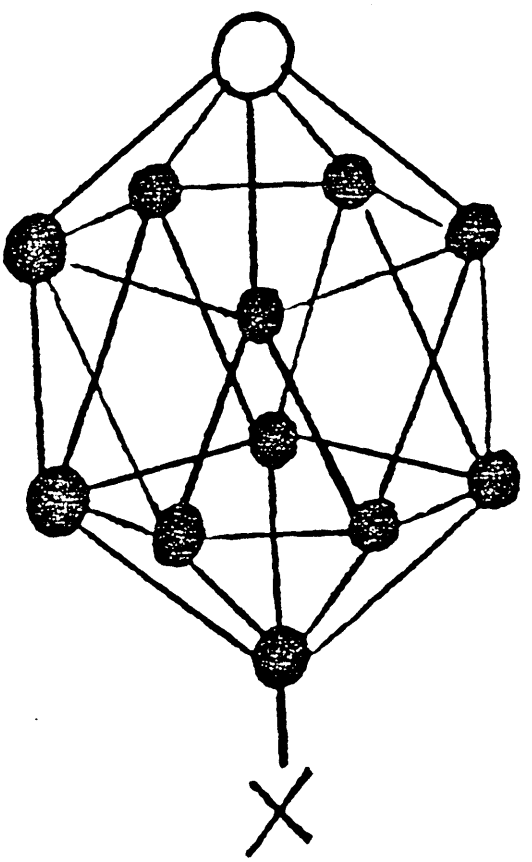


Figure 1:

12-X-$SeB_{11}H_{10}$ (proposed structure).

observed for BX_3 and $[BX_4]^-$ compounds for X = Cl, Br, I. As part of the characterisation of these compounds the photoelectron spectra (p.e.s.) of Se $B_{11}H_{11}$ (Figure 2) and 12- Br Se $B_{11}H_{10}$ (Figure 3) were recorded

The spectra were rather featureless and hence difficult to interpret even with the aid of MNDO molecular orbital calculations performed on the analogous sulphur compounds. The spectrum of the bromoselenaborane was very similar to that of 10- Br - S B_9H_8 (Figure 4). In particular, the first band, which was assignable to ionisation from orbitals with large bromine p character, was split by spin-orbit coupling.

In 1985 Ng *et al*[6] reported halogen exchange between B-haloderivatives of *closo* -2, 4- $C_2B_5H_7$ and tetra-alkylammonium halides, *e.g.* (8).

$$\begin{array}{l} \text{5-Br } C_2B_5H_6 + [Bu_4N]\,F \\ \qquad\qquad \downarrow \\ \text{5-F } C_2B_5H_6 + [Bu_4N]\,Br \end{array} \qquad (8)$$

The authors reported that these exchanges occurred when the reagent "halide" ion is smaller than the "leaving" halide. In the present work the use of this exchange reaction with 12-I-Se $B_{11}H_{10}$ and $[Bu_4N]$ F was envisaged in order to prepare the fluorinated species, 12F -1-Se $B_{11}H_{10}$. A study of further halogenation to produce X_2-Se $B_{11}H_9$, *etc.*, species was also envisaged.

There is a notable lack of structural data for Group VI heteroboranes including selenaboranes. The previously reported data for Se $B_{11}H_{11}$ showed the molecule to have crystallographic $\bar{3}\cdot$ symmetry with the one selenium atom and the eleven BH sites scrambled over the twelve positions of an icosahedron (Figure 5). Also, the X-ray crystallographic analysis of $[Et_4N]$ [7-Se $B_{10}H_{11}$] showed the anion to be disordered.[5] Thus no bond-length and bond angle data for simple selenaboranes had been reported in the literature to data. It was hoped that the presence of the iodine atom in

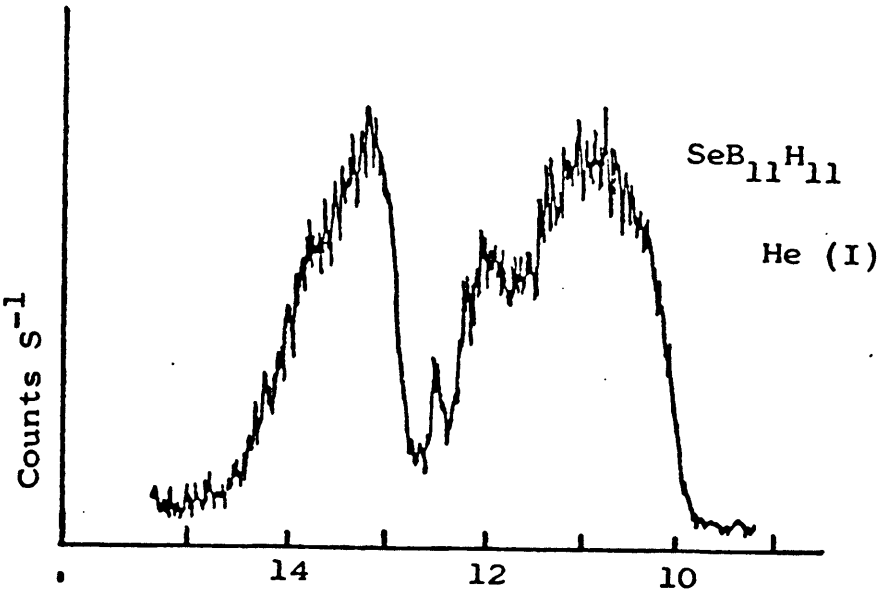


Figure 2: p.e.s. of Se B_{11} H_{11}

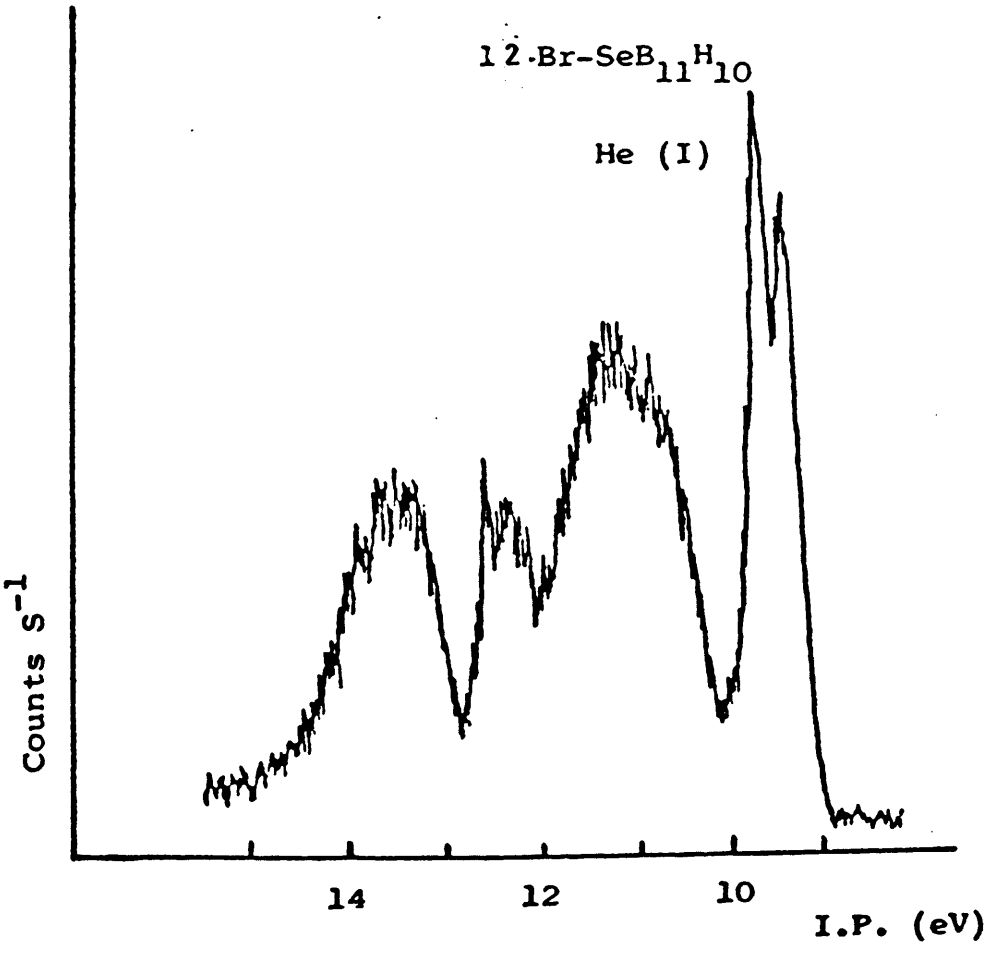


Figure 3: p.e.s. of 12 Br Se B_{11} H_{10}

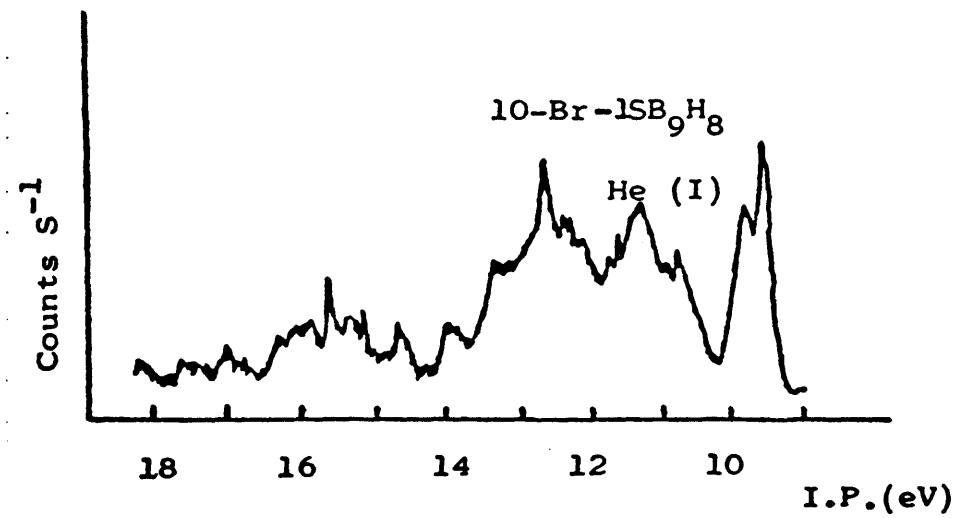


Figure 4: p.e.s. of 10 - Br - 1 - S B_9 H_8

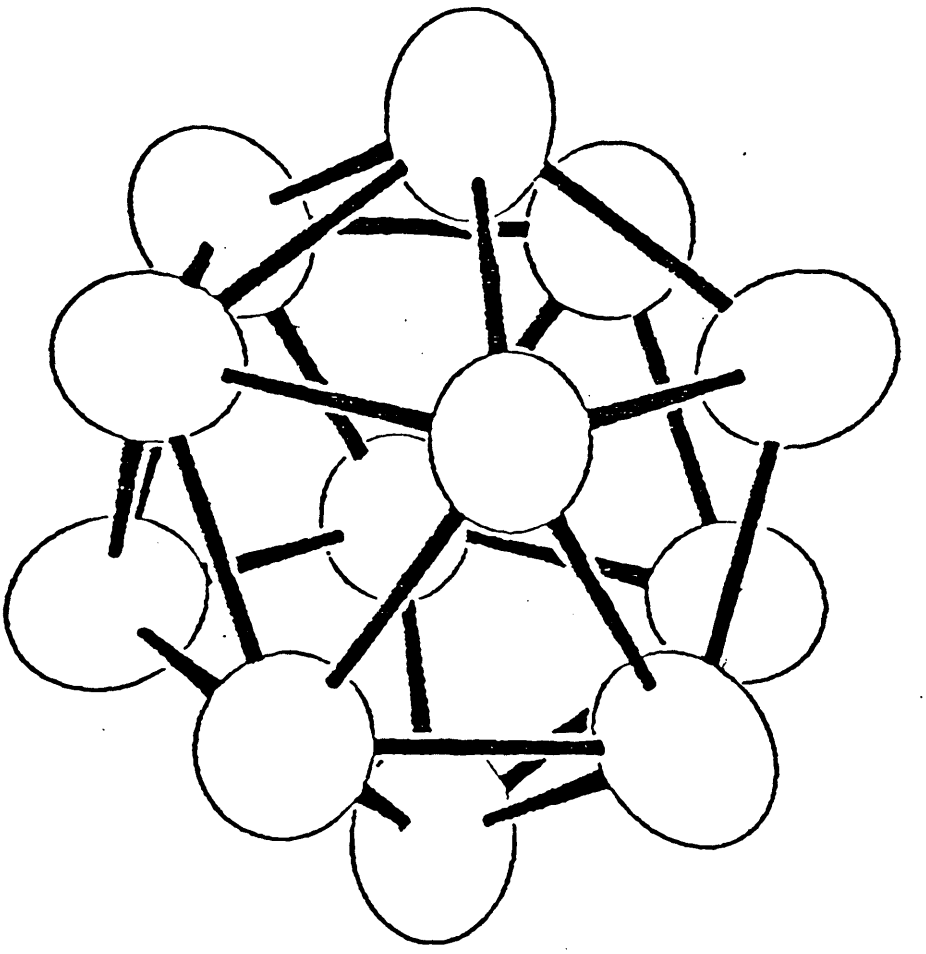


Figure 5:

Structure of $SeB_{11}H_{11}$

The molecule has crystallographic $\bar{3}$ symmetry with the one Se and eleven B-H sites scrambled over twelve apical positions.

12-I- Se $B_{11}H_{10}$ would "order" the system such that an X-ray crystallographic analysis would furnish the required data.

3.1.2 *Nido* Systems Based on 7 -Se $B_{10}H_{12}$ and Se_2 B_9H_9

Todd and coworkers[2] reported that $Na_2[Se_4]$ reacts in aqueous ammonia with decaborane to form the [Se $B_{10}H_{11}$]$^-$ anion (7).

$$B_{10}H_{14} \xrightarrow[NH_3(aq)]{Na_2[Se_4]} [Se\ B_{10}H_{11}]^- \qquad (7)$$

The anion was isolated as the tetramethyl-ammonium salt (70%). Based on ^1H and ^{11}B n.m.r. spectra the structure of [Se $B_{10}H_{11}$]$^-$ was proposed to contain selenium in an open face position (Figure 6).

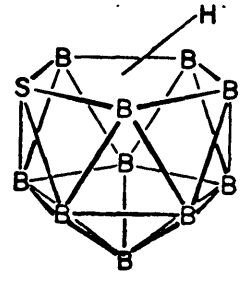
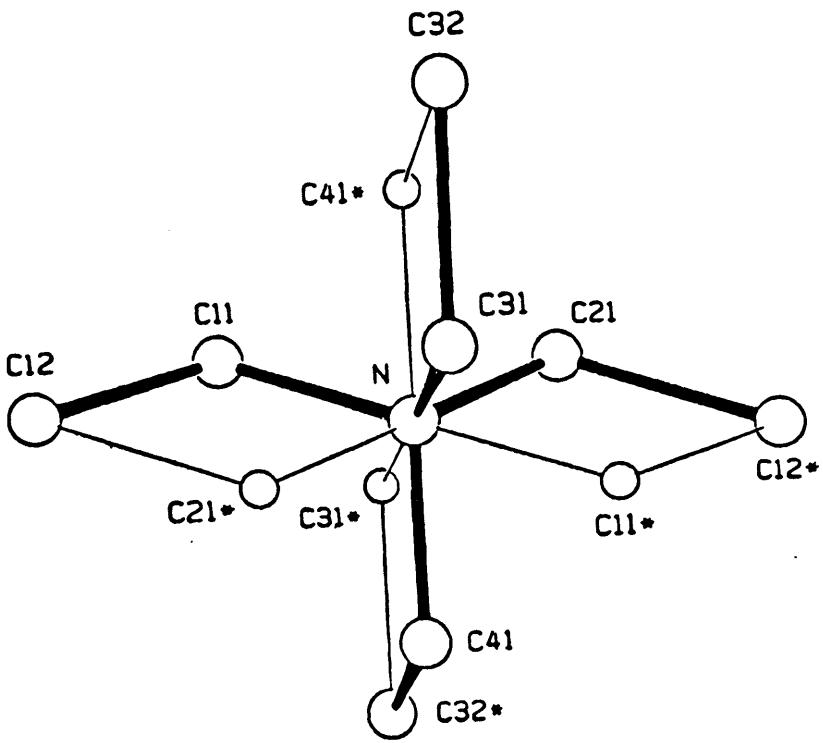


Figure 6: Proposed structure of $[SeB_{10}H_{11}]^-$

An X-ray crystallographic study of $[Et_4N]$ $[SeB_{10}H_{11}]$ showed both the cation and the anion to be disordered.[7] The non-hydrogen atoms of the $[SeB_{10}H_{11}]^-$ cage were scrambled over twelve "sites" with the selenium atom scrambled unequally (Figure 7). However, from an analysis of the ^{11}B-^{11}B COSY spectrum of the $[SeB_{10}H_{11}]^-$ anion it was concluded that the structure was indeed that of the $[7\text{-}SeB_{10}H_{11}]^-$ anion.[7] In order to obtain detailed structural data it was envisaged that the preparation of a halogenated derivative [X-7-Se $B_{10}H_{10}$]$^-$ possibly by a reaction analogous to (7), might produce a more ordered system and allow a complete structural analysis.

Specific positional labelling of the $[X\text{-}SeB_{10}H_{10}]^-$ species could also be achieved by degradation of the X-$SeB_{11}H_{10}$ compounds. Degradation using sodium ethoxide would possibly generate [X-Se $B_{10}H_{10}$]$^-$. Stereospecific



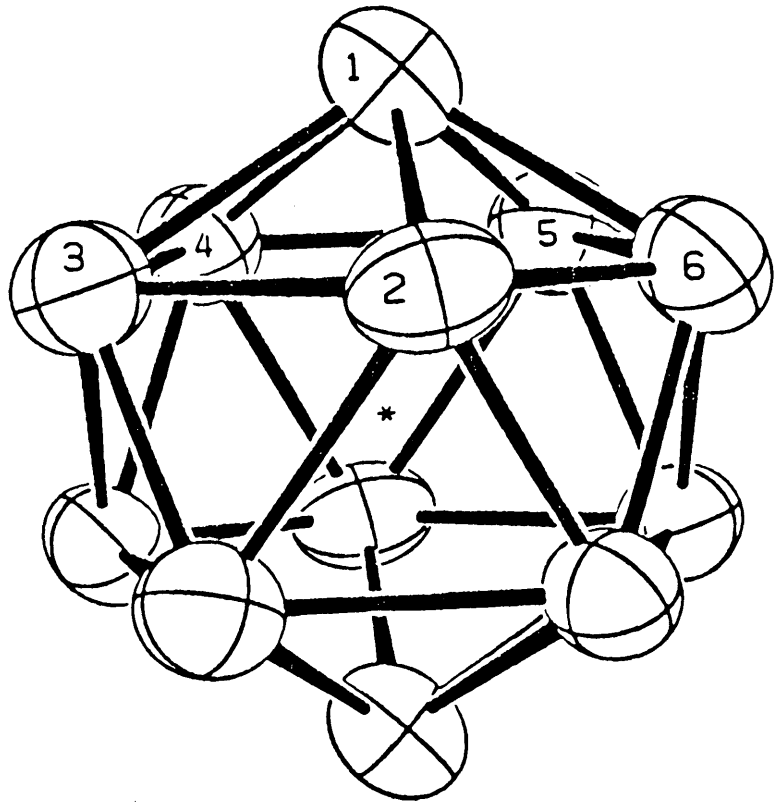


Figure 7: X - ray Crystallographic Structure of $[Et_4N]$ $[Se\ B_{10}\ H_{11}]$

degradation has been reported for carboranes $C_2B_{10}H_{12}$ [8] for $PhSB_{11}H_{10}$ [1] and also for a sample of 1-$SeB_{11}H_{11}$ which was specifically deuterated in the six sites, B(7)-B(12) only [7] (Scheme 1). The degradation thus appeared to be stereospecific and involved the removal of a boron atom which had been attached to selenium i.e. one of B(2) to B(6).

3.1.3 *$Se_2B_9H_9$*

Todd and coworkers[2] reported the formation of $Se_2B_9H_9$ as an unexpected minor product during the synthesis of $[SeB_{10}H_{11}]^-$. The authors suggested that during the synthesis of $[SeB_{10}H_{11}]^-$ in strong aqueous base some of the decaborane was converted to $[B_9H_{14}]^-$ (8).

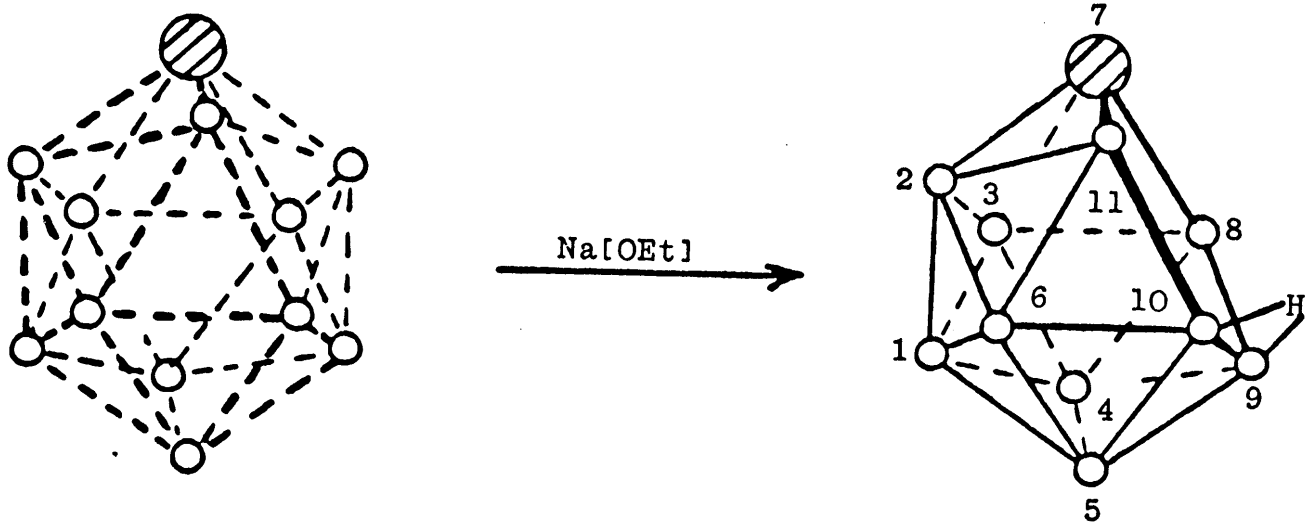
$$B_{10}H_{14} \xrightarrow{[OH]^-} [B_9H_{14}]^- + B(OH)_3 \qquad (8)$$

which then reacted with the polyselenide reagent to give $Se_2B_9H_9$. In a later paper, Todd and coworkers[9], outlined a synthesis of $Se_2B_9H_9$ from decaborane by the *in situ* generation of the $[B_9H_{14}]^-$ anion followed by reaction with potassium polyselenide solution (9).

$$B_{10}H_{14} \xrightarrow[H_2O]{KOH} K[B_9H_{14}] \xrightarrow[Se]{KOH} \underset{86\%}{Se_2B_9H_9} \qquad (9)$$

Base and Stibr[10] also reported the synthesis of $Se_2B_9H_9$ from the reaction between decaborane and $Na_2[SeO_3].5H_2O$ in tetrahydrofuran. The proposed structures of this species contained both selenium atoms in an open face (Figures 8 and 9) with the selenium atoms either bonded to each other or separated by boron atoms. However, it was not possible to differentiate these on the basis of ir. and ^{11}B n.m.r. spectroscopy. Hence, it was envisaged that a halogenated derivative (*e.g.* Br-Se B_9H_8) which may be prepared either by a reaction involving degradation of X-$B_{10}H_{13}$ *via* (9), or by direct halogenation of $Se_2B_9H_9$ would facilitate further structural study.

Scheme 1: Degradation of [7, 8, 9, 10, 11, 12 - D_6 - I - Se B_{11} H_5]



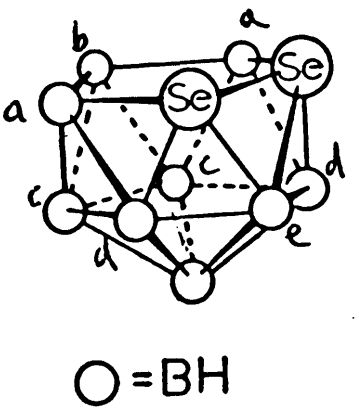


Figure 8: Proposed Structure of $Se_2 B_9 H_9$ (i)

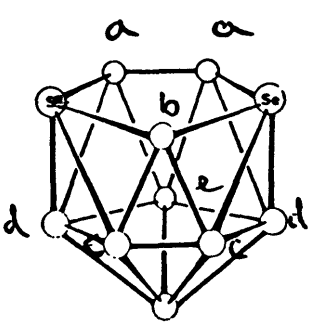


Figure 9: Proposed Structure of $Se_2 B_9 H_9$ (ii)

3.2. RESULTS AND DISCUSSION

3.2.1. *Closo* SeB_{11} -*Cluster Systems*

3.2.1.1. *Structural Study of 12-I-Se* $B_{11}H_{10}$

It was hoped that the replacement of a hydrogen atom by halogen to give a 12-X-Se $B_{11}H_{10}$ derivative of Se $B_{11}H_{11}$ would result in a crystallographically ordered system which would be susceptible to structural analysis. Thus 12-I-Se $B_{11}H_{10}$ was prepared according to the literature method[4] and crystals suitable for an X-ray diffraction study were grown from a dichloromethane: hexane mixture (70:30) and sent to Professor G. Ferguson, University of Guelph, Canada. The results of the analysis are reported below. The structure of 12-I-Se $B_{11}H_{10}$ was determined as $P_{21/n}$ (No 14) (Figure 10). The only reported structural data for a *closo* -selenaborane is that for the metallo species [2, 2-$(PPh_3)_2$-1, 2-SePt $B_{10}H_{10}$]. CH_2Cl_2,[12] however, comparisons may be made with *closo* [2, 2-$(1\text{-}SB_9H_8)_2$] [13] and *closo*-$[Se_3B_{11}H_9]^{2-}$ which has an *exo* polyhedral Se_3 chain.[14]

The Se-B bond distances in 12-I-Se $B_{11}H_{10}$ range from 2.112(9) Å (Se-B(5) to 2.144(10) Å (Se -B (3)). Spalding and coworkers[14] reported two Se-B bond distances in the *closo* platinoselena-borane system (Figure 11) of 2.210(6) and 2.198(7) Å for Se-B(1) and Se-B(4) respectively whereas for bonds to B(8) and B(9) the Se-B distances are 2.098(9) and 2.101(7) Å respectively. However, B(1) and B(4) are also attached to Pt. The *exo* polyhedral Se-B bonddistances in $[Se_3B_{11}H_9]^{2-}$ are 2.016(15) and 2.023 (16)Å which are slightly shorter than in the iodoselenaborane. If the difference in covalent radii of Se and S which is generally taken to be 0.11-0.13 Å, is borne in mind the Se-B distances in 12-I-Se $B_{11}H_{10}$ are comparable with the S-B distance of 1.930(8) Å in *closo* - [2, 2^1 $(1\text{-}SB_9H_8)_2$].

The range of boron-boron bond distances in 12-I-$SeB_{11}H_{10}$ is 1.715(12) to 1.934(13) Å. This is quite comparable to the ranges in *closo* -$[SeB_{11}H_9]^{2-}$ and the thiaborane dimer which are in the ranges 1.738(20)-2.091(21) and

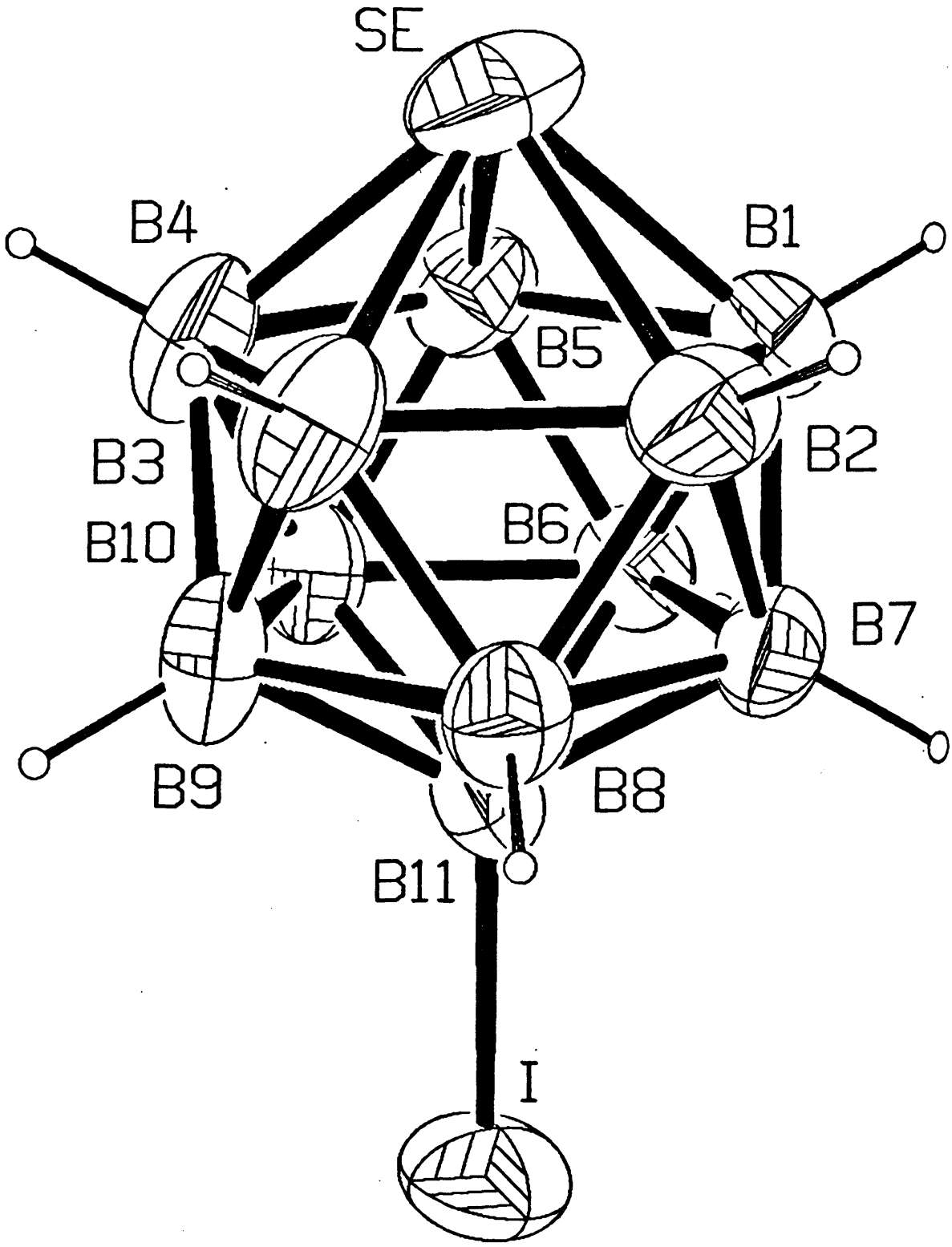


Figure 10: Structure of 12 - I - Se B_{11} H_{10}

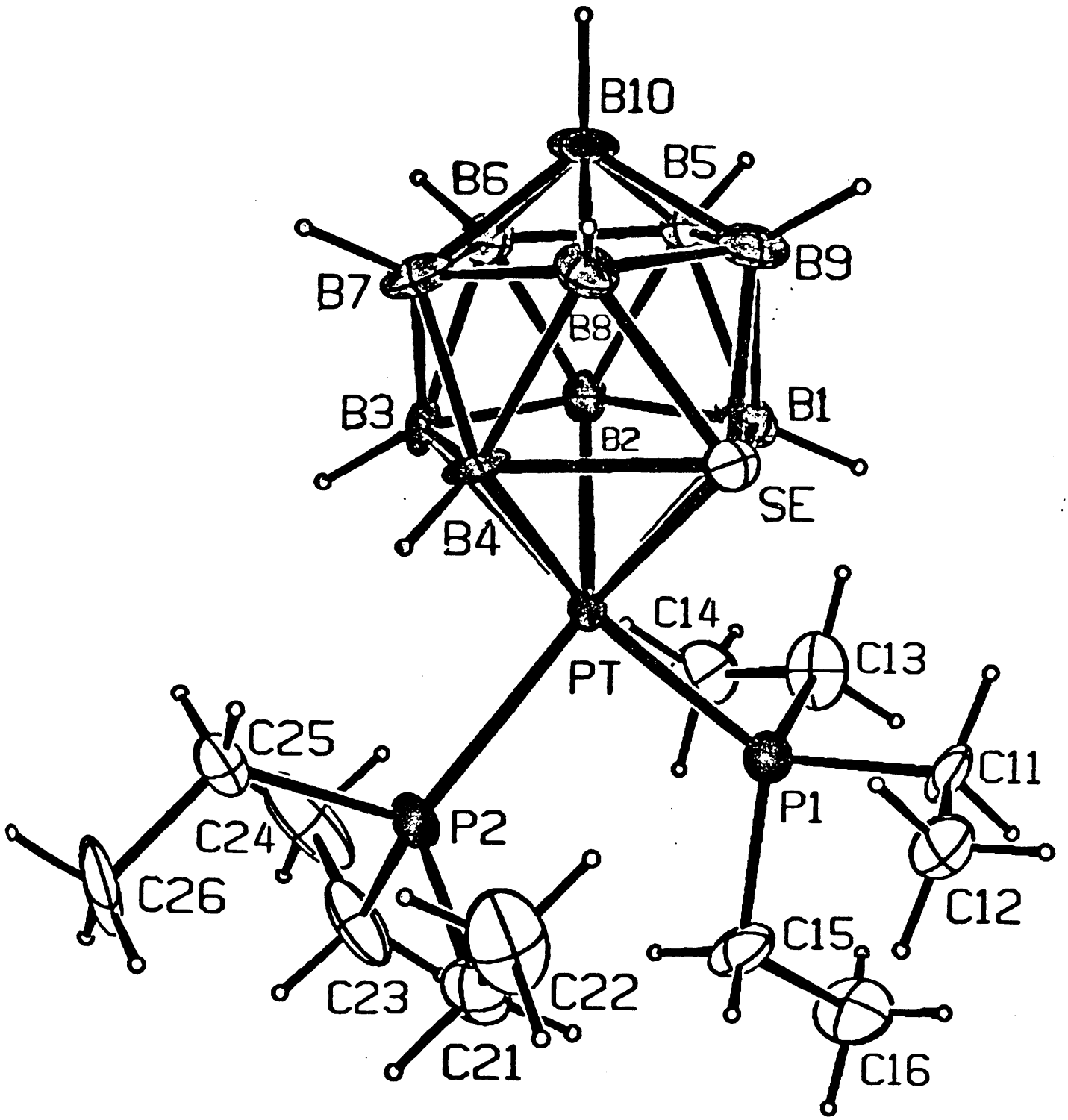


Figure 11a Structure of [2,2 - $(PPh_3)_2$ - 1, 2 - Se Pt B_{10} H_{10}]

1.689(8) to 1.940(4) Å. The B-B bond distance range in [2, 2-$(PPh_3)_2$ -1, 2- $SePtB_{10}H_{10}$]· CH_2Cl_2 is 1.702-1.965 Å while in *nido*- [7- (μ^5-C_5H_5) -7, 8, 12 - $CoSe_2$- B_9H_9][9] the range is 1.708(7)- 2.007(7) Å.

The B-I bond distance of 2.167(7) Å in 12-I- Se $B_{11}H_{10}$ is comparable to that in I $B_{10}H_{13}$ (2.152 (13) Å) the structure of which was reported by Sequeira and Hamilton in 1967.[15]

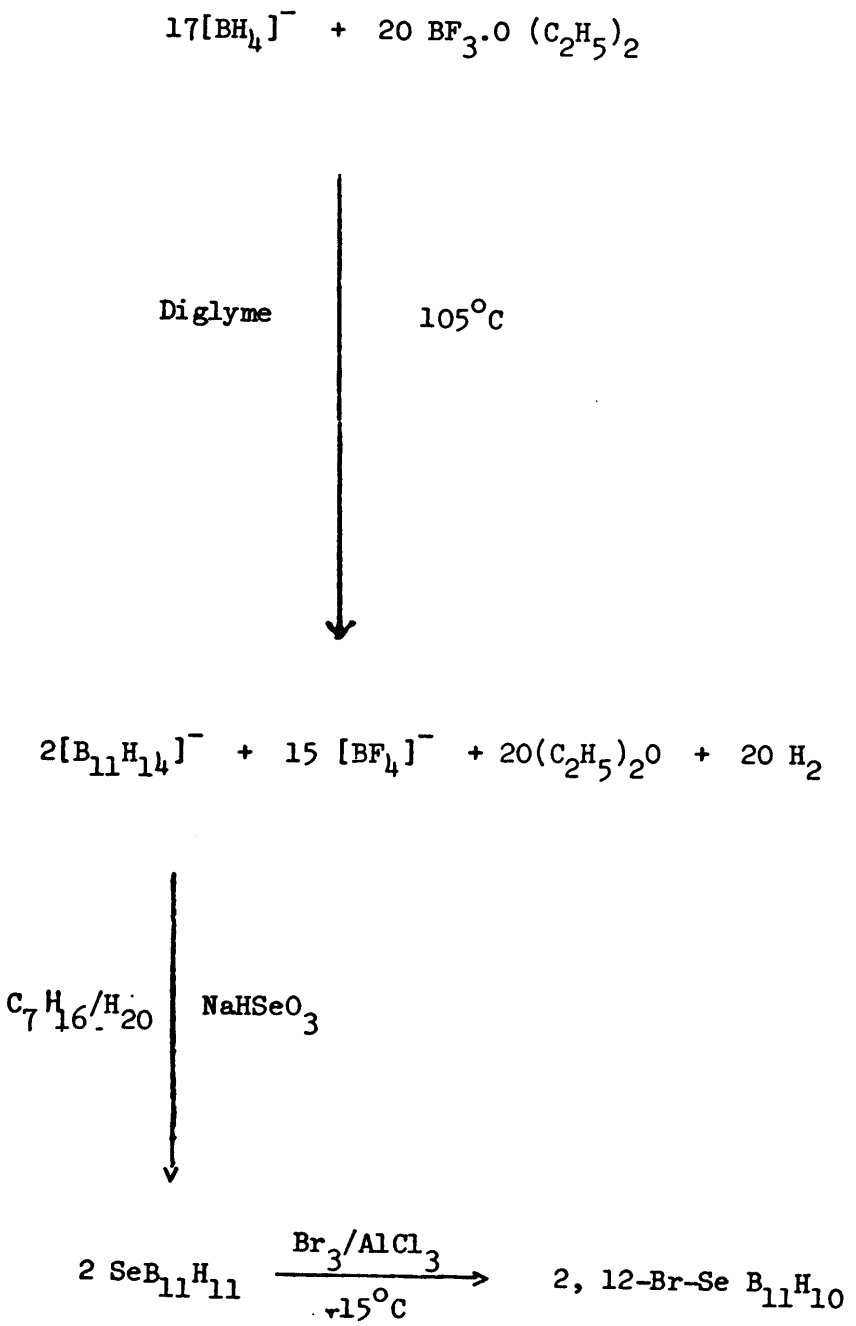
3.2.1.2. *Preparation of 12-Br-Se $B_{11}H_{10}$*

One objective in the present work on *closo* selenaboranes was to improve the yield of 12-Br-Se $B_{11}H_{10}$ since the previously reported yield was only 22%. Scheme 2 outlines the general pathway to 12-Br-Se $B_{11}H_{10}$ from borohydride. Tetraethylammonium-tetradecahydroborate was prepared according to the literature synthesis of Dunks and Ordonez.[16] The conversion of $[B_{11}H_{14}]^-$ anion to Se $B_{11}H_{11}$ was carried out using the procedure of Todd and Friesen (Equation 4)[3]. However, benzene was used as the extracting solvent instead of heptane and the yield was improved (25% c.f. 18%). The $SeB_{11}H_{11}$ was characterised by its infrared and mass spectra. The original preparation of 12-Br-Se $B_{11}H_{10}$[4] (reflux for 14 hours) (12) was modified as follows.

$$\text{Se } B_{11}H_{11} + Br_2 \xrightarrow[CH_2Cl_2]{AlCl_3} \text{12-Br-Se } B_{11}H_{10} + HBr \qquad (12)$$

First, bromine was solidified by cooling to -15°C then one equivalent of Se $B_{11}H_{11}$ and powdered aluminium chloride catalyst were added. The reaction mixture was allowed to warm slowly to 0°C and maintained at this temperature for 2 hrs before being warmed to ambient temperature. The crude product was isolated by evaporation of the dichloromethane *in vacuo* (85% yield). The mass spectrum of the crude product indicated the presence of both mono- and di-brominated SeB_{11} products. T.l.c. analysis (eluent dichloromethane: hexane, 2: 1) suggested approximate ratios 6:1 respectively. In a second modification of the above reaction dichloromethane was added when the

Scheme 2:


17[BH4]⁻ + 20 BF3.O (C2H5)2
Diglyme
105°C
2[B11H14]⁻ + 15 [BF4]⁻ + 20(C2H5)2O + 20 H2
C7H16/H20
NaHSeO3
2 SeB11H11
Br3/AlCl3
-15°C
2, 12-Br-Se B11H10

mixture reached room temperature and the mixture refluxed for 14 hours. T.l.c. analysis indicated 80% conversion to 12-Br-Se $B_{11}H_{10}$ with less than 10% of the dibrominated product. From this reaction 12-Br-Se $B_{11}H_{10}$ was isolated by sublimation onto a water cooled probe in 63.4% yield and characterised by its infrared spectrum and melting point.

3.2.1.3. *Attempted Synthesis of 12-F-Se $B_{11}H_{10}$*

As discussed in the introduction to this Chapter, Ng *et al*[6] reported that halogen exchange can take place in *closo* carboranes when the "reagent" halide is smaller than the "leaving" halide. (Reaction 8, Section 3.1). However, it should be noted that the evidence for these reactions was obtained from ^{11}B n.m.r. studies and that the isolation of the fluorinated species was not reported. An exchange reaction was attempted in the present work using 12-I-Se $B_{11}H_{10}$ and a solution of tetrabutylammonium fluoride in THF (10).

$$\text{12-I-Se } B_{11}H_{10} + [Bu_4N]F \xrightarrow{\text{THF}} \text{12-F-Se } B_{11}H_{10} + [Bu_4N]\,I \quad (10)$$

After 5 days stirring equimolar quantities of the reagents at room temperature there was no evidence (t.l.c., eluent, dichloromethane: hexane; 2:1) for reaction (10). The addition of excess $[Bu_4N]F$ resulted in a distinct colour change from yellow to dark green and the appearance of two new spots on the t.l.c. plate. However, attempts at isolation of a product by dissolution of the crude material in water and extraction with either dichloromethane or benzene proved unsuccessful. A mass spectrum of the residual solid indicated that no volatile borane containing material was present.

3.2.1.4. *Formation of Polychlorinated Derivatives of Se $B_{11}H_{11}$*

The polychlorination of $SeB_{11}H_{11}$ using the conditions of Friedel-Crafts electrophilic substitution was attempted (11).

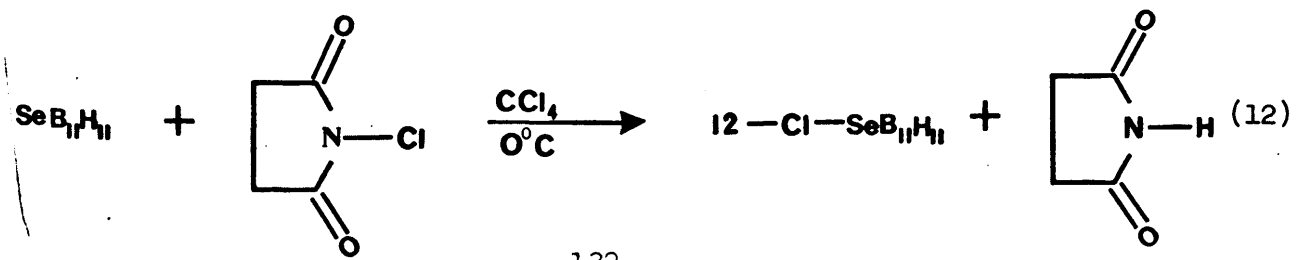
$$SeB_{11}H_{11} + nCl_2 \xrightarrow[AlCl_3]{CH_2Cl_2} Se\,B_{11}H_{(11-X)}\,Cl_X + X\,HCl \quad (11)$$

with a $SeB_{11}H_{11}$: Cl_2 ratio of 1:5. After the usual work-up procedures the chlorinated selenaboranes were separated by preparative t.l.c. (eluent, dichloromethane: cyclohexane, 70:30). Three bands were separated of which two provided analysable quantities.

The lower band which was the dichlorinated product was isolated in 4.3% and melted at 117-119°C. The infrared spectrum showed B-H stretching frequencies at 2655 and 2555 cm^{-1}. The 115 MHz ^{11}B n.m.r. Spectrum (Figure 12) exhibited two singlets at 5.2 and + 25.6 ppm which are ascribable to B-Cl bonds. However, the spectrum shows that this species is in fact a mixture of two dichlorinated isomers which were not separable on the chromatographic plate. It is not possible to completely assign these signals. However, the previously recorded ^{11}B n.m.r. spectrum of 12-Cl-Se $B_{11}H_{10}$ exhibited a B-Cl resonance at + 24.0 ppm. Taking the expected shift to a higher field into account for the presence of a second chlorine atom it appears likely that one of the chlorine atoms is substituted at position 12.

The upper band was isolated as a white crystalline solid (19.37%) and melted at 248-250°C. The infrared spectrum of this species showed B-H stretching frequencies at 2645 and 2530 cm^{-1}. The 115 MHz ^{11}B n.m.r. spectrum consisted of just five signals (Figure 13). Four of these were doublets which collapsed to singlets on proton decoupling (Figure 14). The remaining signal at _4 p.p.m. was a singlet in both spectra and is assigned to the B-Cl bond. The $^{11}B - {}^{11}B$ COSY n.m.r. spectrum (Figure 15) was also recorded. However, these spectra indicate that degradation had taken place and that the product was in fact [5-Cl-7-Se $B_{10}H_{10}]^-$.

In an attempt to achieve a more convenient synthesis of 12-Cl-$SeB_{11}H_{10}$, a reaction between $SeB_{11}H_{11}$ and N-chlorosuccinimide was attempted (12).



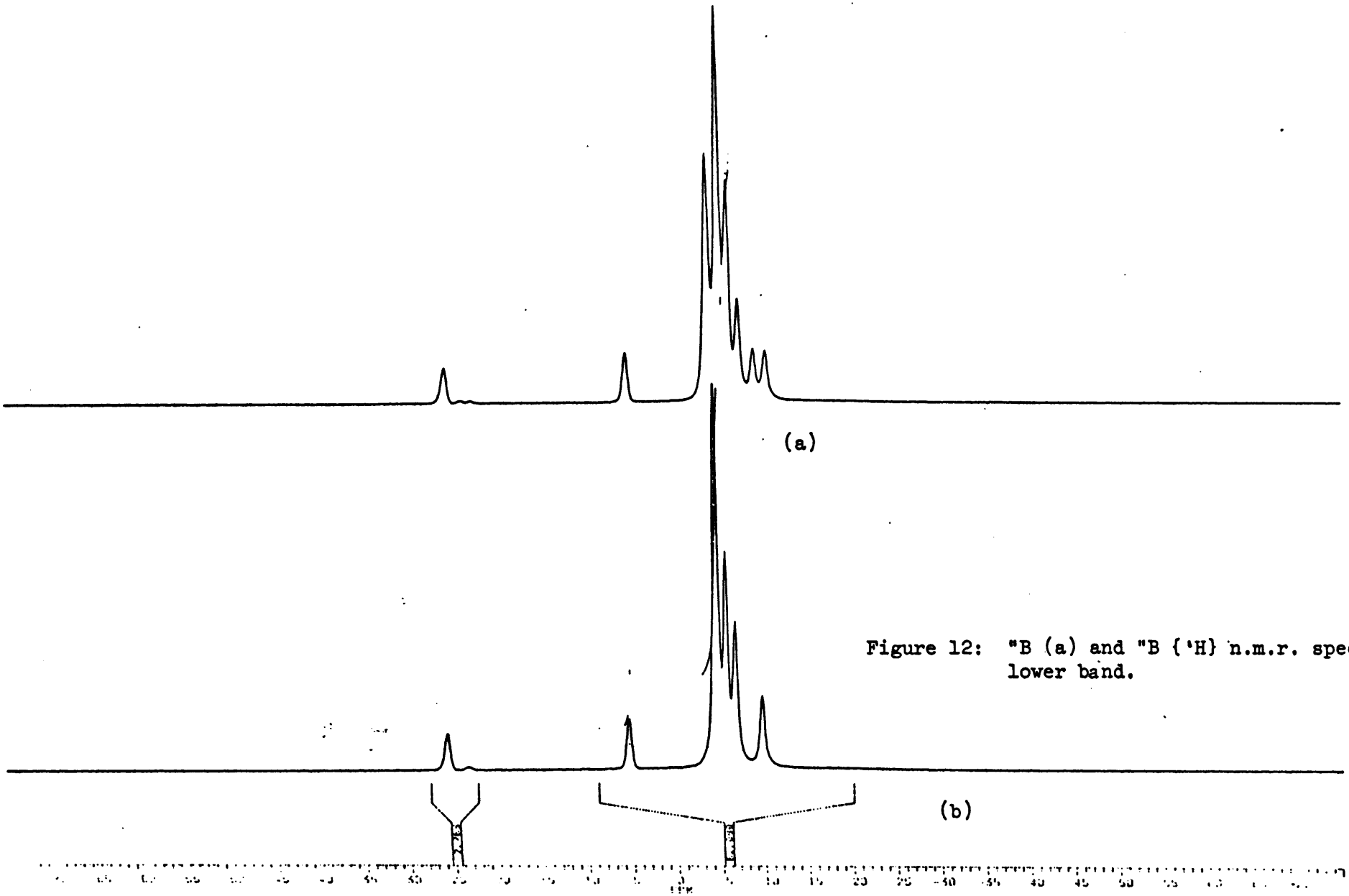


Figure 12: ^{11}B (a) and $^{11}B\{^1H\}$ n.m.r. spectra of lower band.

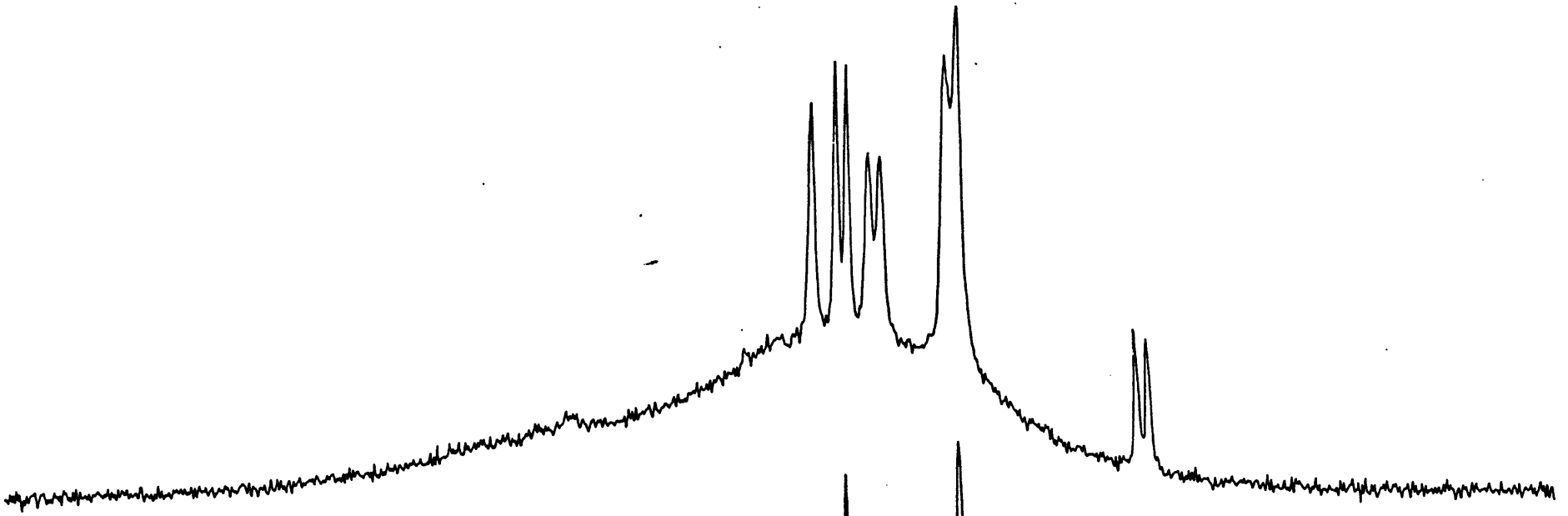


Figure 13: ^{11}B n.m.r. spectrum of [5 - Cl- 7 - Se B_{10} H_{10}]$^-$

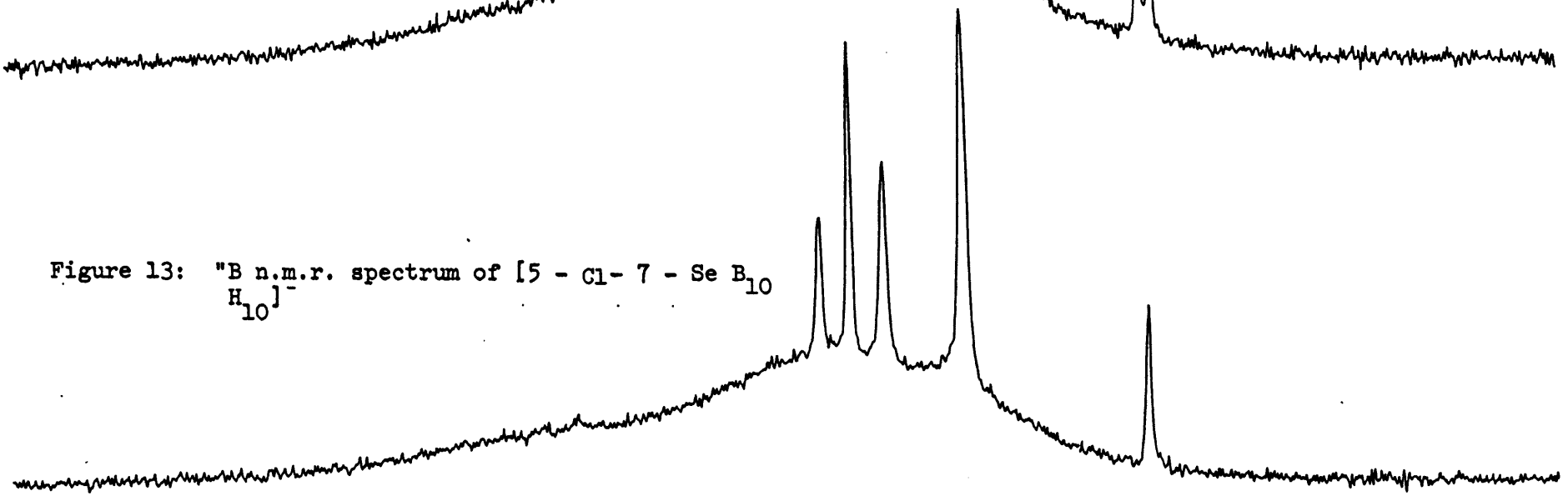


Figure 14: ^{11}B {^1H} n.m.r. spectrum of [5 - Cl- Se B_{10} H_{10}]$^-$

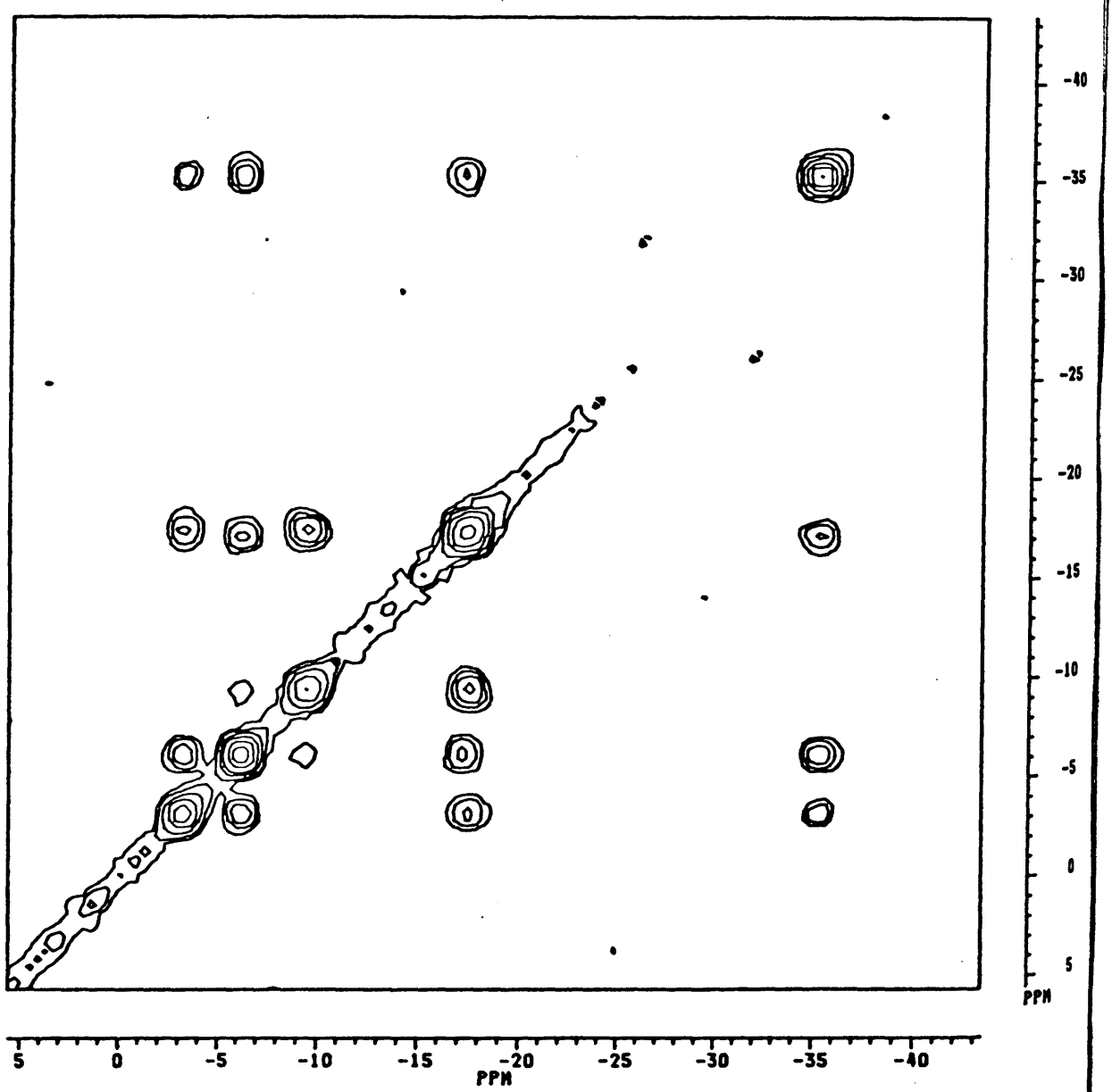


Figure 15: $^{11}B - ^{11}B$ COSY n.m.r. spectrum of $[5 - Cl - 7 - Se\ B_{10}\ H_{10}]^-$

However, on completion of the reaction, only Se $B_{11}H_{11}$ (85% recovery) was isolated.

3.2.2 *Nido B_{10} Cluster Systems*

3.2.2.I Attempted Synthesis of $[Br\text{-}Se\ B_{10}H_{10}]^-$

The method of synthesis of the $[Br\text{-}Se\ B_{10}H_{10}]^-$ anion which was attempted was similar to that reported for the non-halogenated analogue (reaction 7). Bromodecaborane (the 1- and 2- isomers were used in separate experiments) was reacted with sodium polyselenide in aqueous ammonia, during workup the product was isolated as the tetralkylammonium salt. The reaction sequence is outlined in Scheme 2.

Scheme 3: *Synthesis of $[Et_4N]$ $[Se\text{-}Br\ B_{10}H_{10}]$*

$$Br\text{-}B_{10}H_{11} \xrightarrow[\text{liq. } NH_3]{Na_2[Se_4]} Na[Br\text{-}Se\ B_{10}H_{10}] \xrightarrow{[Et_4N]\,Cl} [Et_4N][Br\text{-}Se\ B_{10}H_{10}] + Na[Cl]$$

The yellow crystalline solid which resulted was stable to air and water, insoluble in hydrocarbons but soluble in methanol. The infrared spectrum exhibited strong alkyl C-H absorptions at 2960 and 2870 cm^{-1} as well as strong B-H stretching absorption at 2530 cm^{-1}. The 115.5 MHz ^{11}B n.m.r. spectrum was recorded in methanol (Figure 16) and showed fourteen signals (when 1-Br $B_{10}H_{13}$ was used). The relative ratios and numbers of signals indicated the presence of three or possibly four products. A comparison of the chemical shifts for the non-halogenated anion, $[7\text{-}Se\ B_{10}H_{11}]^-$ suggested the presence of this species as well as brominated derivatives. Thus some loss of bromine appeared to have occurred during the reaction with the polyselenide.

A comparison of the ^1H coupled and decoupled ^{11}B n.m.r. spectra suggested the presence of at least two brominated products { two signals at -20.1 and

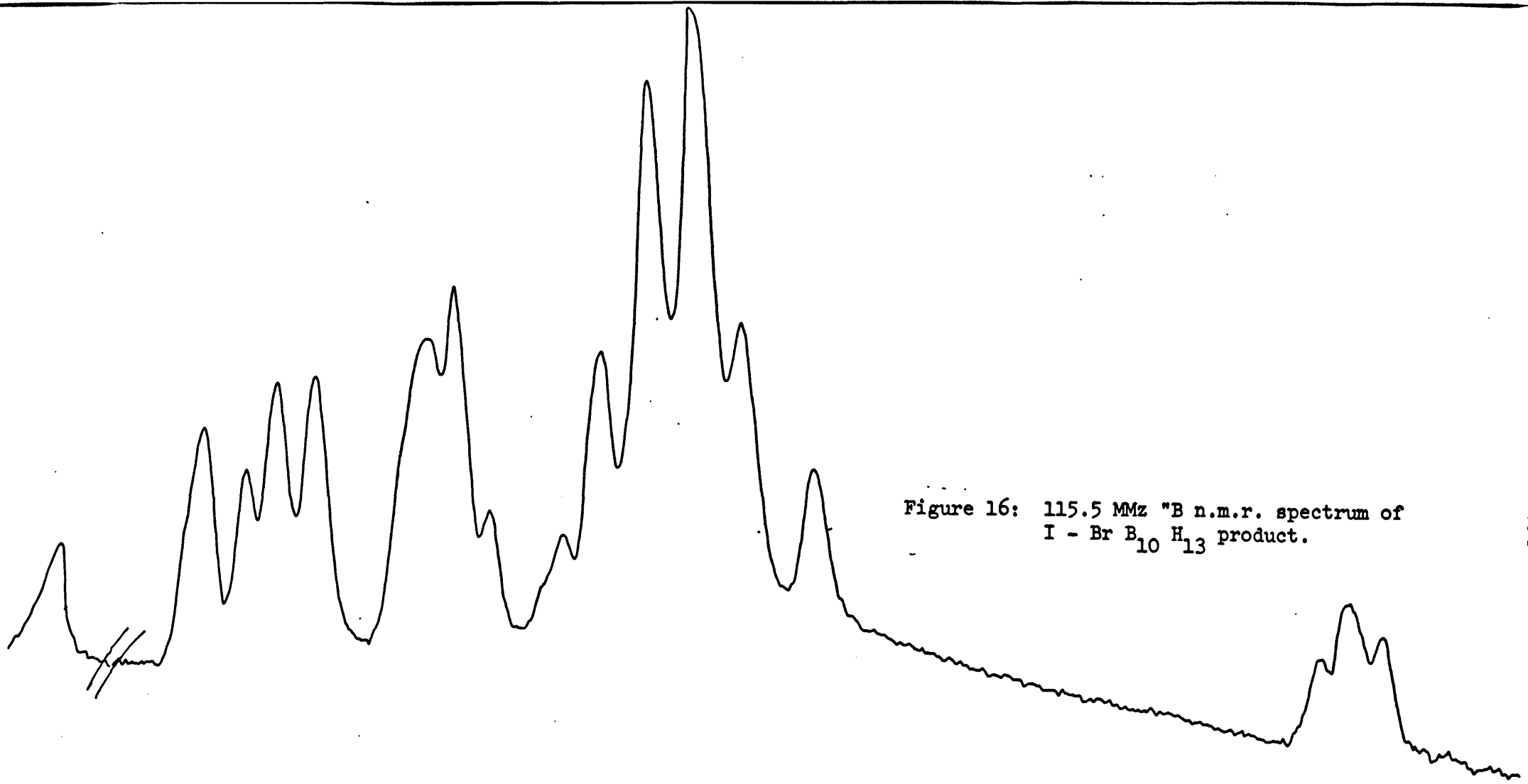


Figure 16: 115.5 MMz ^{11}B n.m.r. spectrum of I - Br $B_{10}H_{13}$ product.

+ 19.8 p.p.m. were singlets in both spectra }. The chemical shift of the B-Br atoms at + 19.8 p.p.m. is very close to the B-Br signal for 12-Br-Se $B_{11}H_{10}$ (+ 20.2 p.p.m.).[4] When 2-Br $B_{10}H_{13}$ was reacted with the polyselenide, the ^{11}B n.m.r. spectrum of the product (Figure 17) was similarly complex. However, unlike the spectrum for the product of the 1-Br $B_{10}H_{13}$ reaction, this spectrum did not contain any signals above -3.0 p.p.m. Sprecher *et al*[16] assigned the B-Br resonances in 1-Br $B_{10}H_{13}$ and 2-Br $B_{10}H_{13}$ as + 2.0 and + 45.6 p.p.m. respectively. The absence of these signals in the products obtained here indicate that the starting bromodecaboranes are not present in the final products.

It appears that although the reaction of decaborane with sodium polyselenide generated high yields of the single isomer, [7-Se $B_{10}H_{11}]^-$,[7] the reaction with bromodecaborane afforded a mixture of products which included [Se $B_{10}H_{11}]^-$ and isomers of [Br-Se $B_{10}H_{10}]^-$.

3.2.2 *Attempted Synthesis of Br-Se $B_{10}H_{12}$*

In an attempt to obtain a pure Br-Se $B_{10}H_{12}$ isomer the crude product from the reaction between 1-Br $B_{10}H_{13}$ and sodium polyselenide was protonated (13).

$$[Et_4N]\,[Br\text{-}Se\ B_{10}H_{10}] \xrightarrow[CH_3CN]{HCl} Br\text{-}Se\ B_{10}H_{12} + [Et_4N]\,Cl \qquad (13)$$

The product of this reaction was initially purified by sublimation and then recrystallised from hexane. The infrared spectrum of the purified material showed a strong B-H stretching frequency centred at 2520 cm^{-1}. There were no alkyl C-H absorptions present in the spectrum. Both the ^{11}B and ^{11}B { ^{1}H} n.m.r. spectra (Figures 18 and 19) exhibited sharp well-resolved signals but once again there was a mixture of products, but the n.m.r. spectral evidence showed that $SeB_{10}H_{12}$ was not one of them.

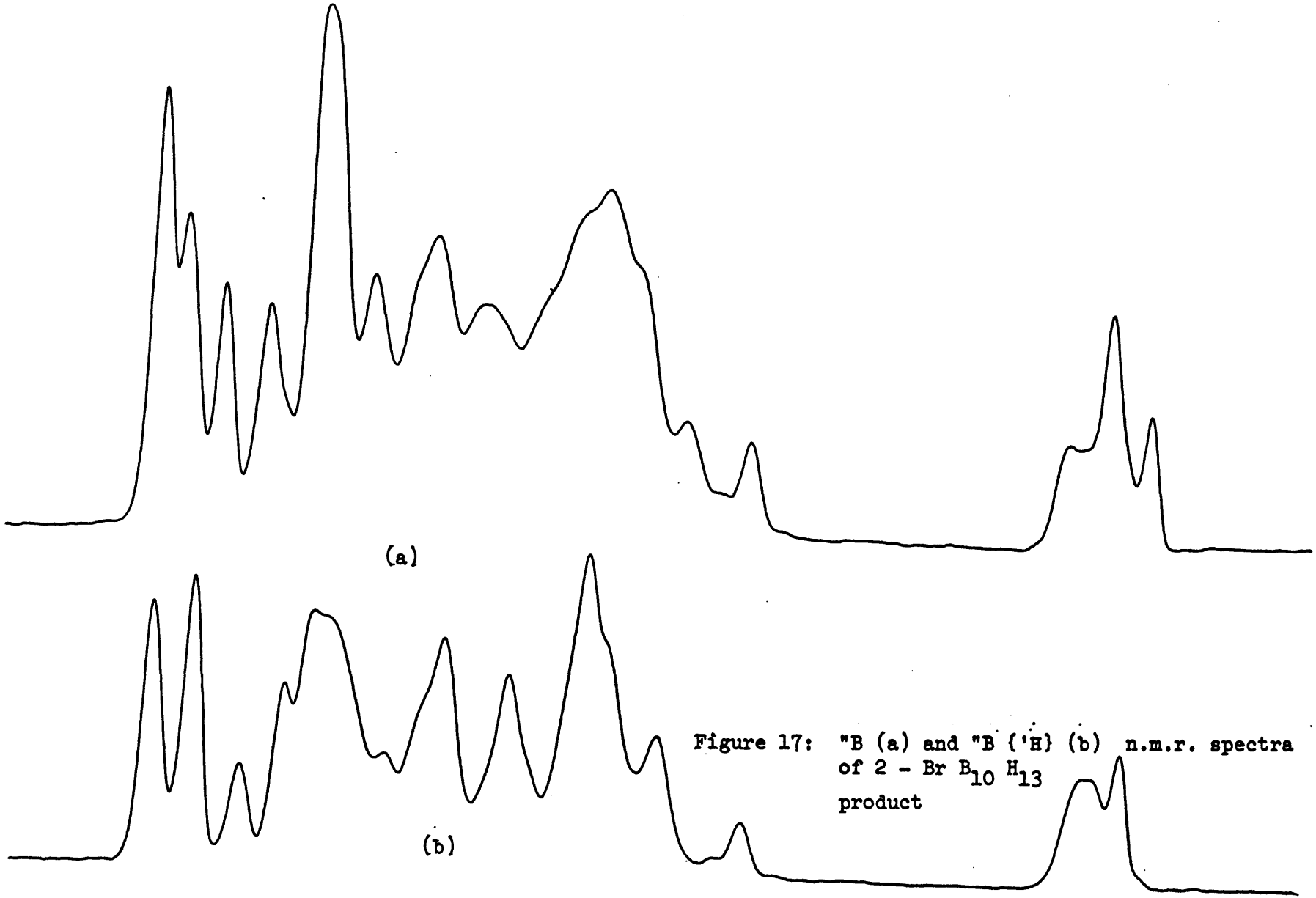


Figure 17: ^{11}B (a) and $^{11}B\{^1H\}$ (b) n.m.r. spectra of 2 - Br $B_{10}H_{13}$ product

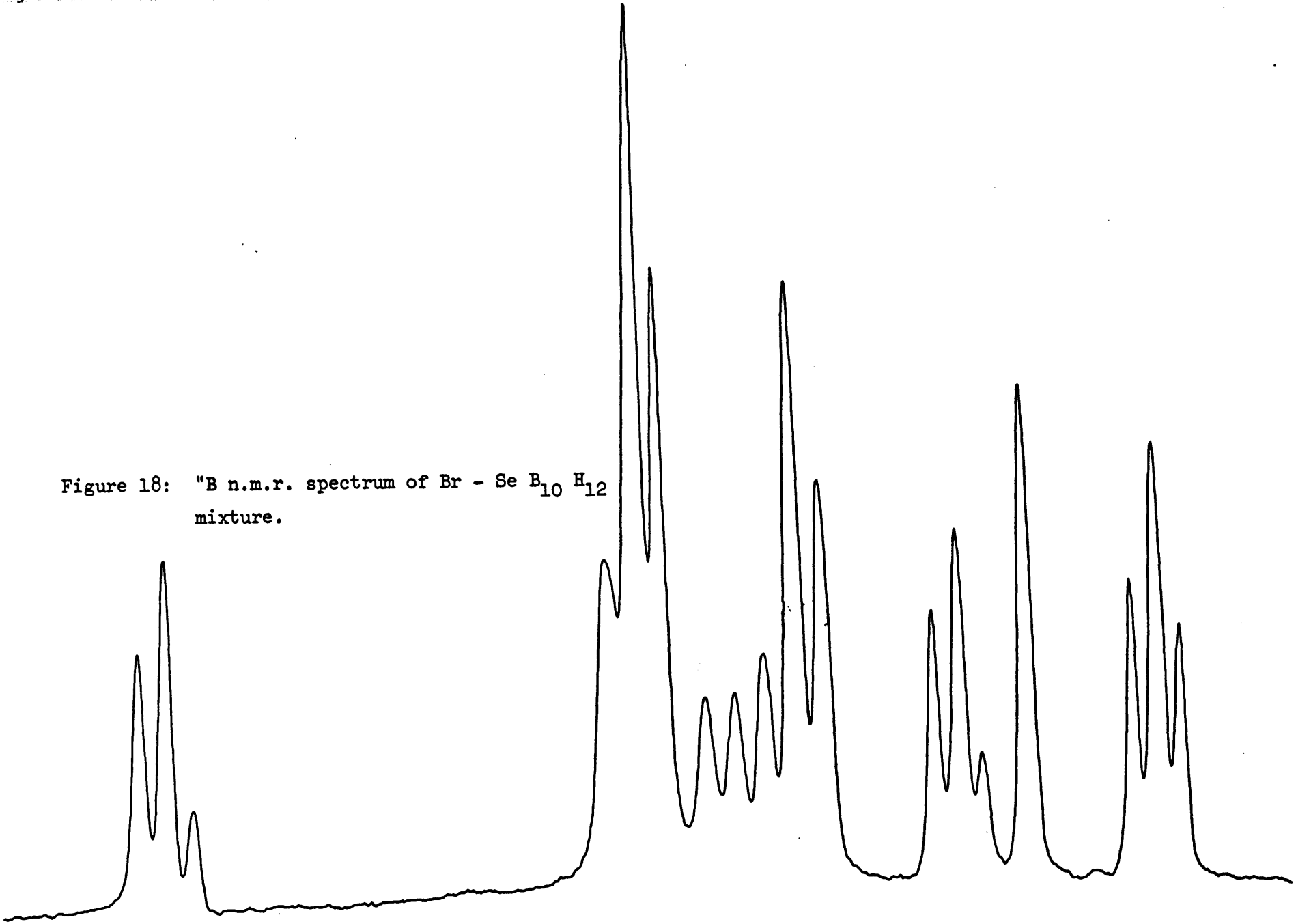
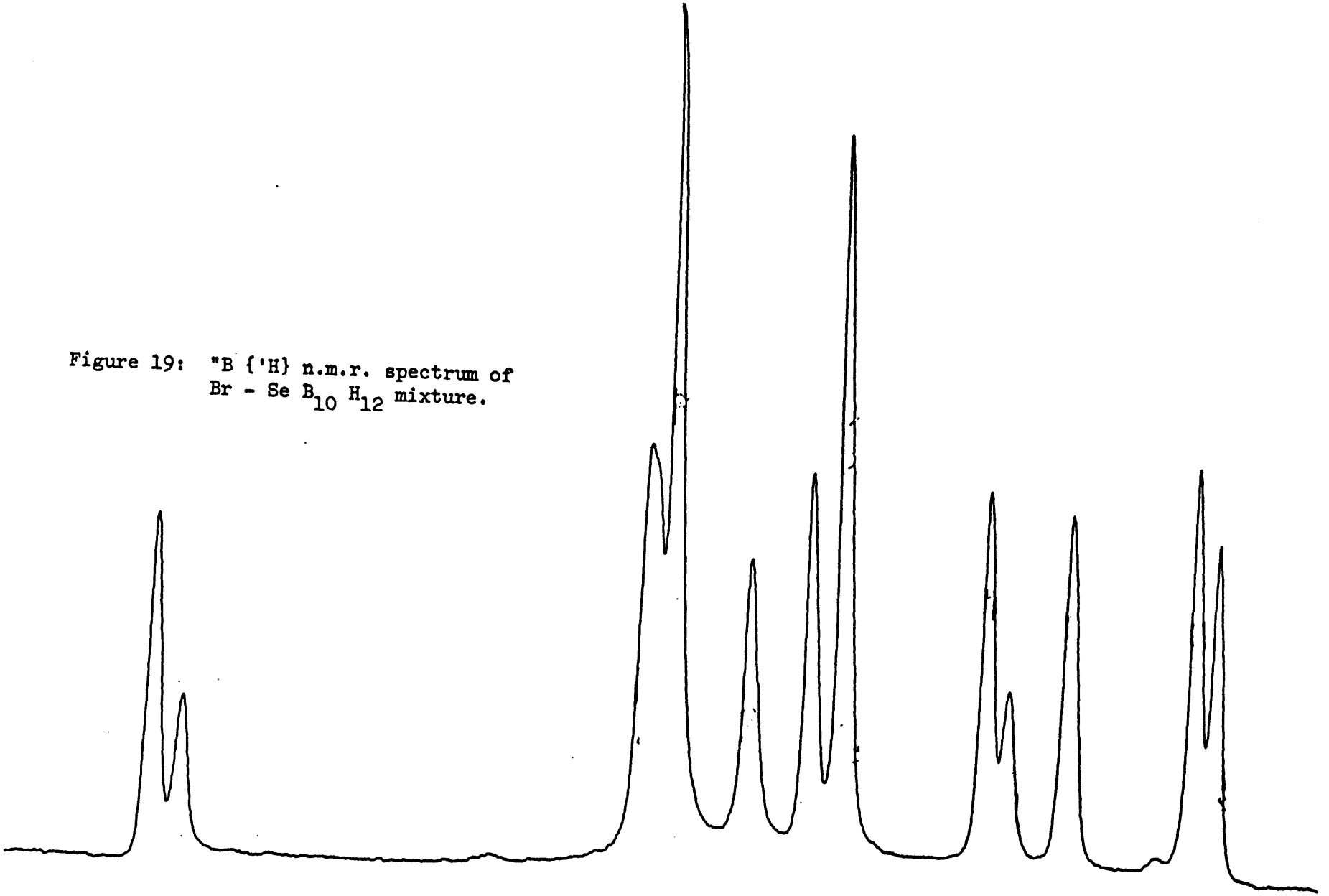


Figure 18: ^{11}B n.m.r. spectrum of Br - Se $B_{10}H_{12}$ mixture.

Figure 19: ^{11}B {^{1}H} n.m.r. spectrum of Br - Se $B_{10}H_{12}$ mixture.



The ^{11}B n.m.r. spectrum of the brominated product consisted of twelve signals including two B-Br signals at -19.9 and + 18 p.p.m. It therefore appears that the product of the protonation reaction (13) is a mixture of at least two neutral brominated species.

3.2.3. *Nido* X-Se_2 B_9H_8 *Systems (X = H, Br)*

As noted earlier in the introduction to this Chapter, several authors have reported syntheses of $Se_2B_9H_9$[9,10]. However, to date its structure has not been established in detail although it is isoelectronic with the known *nido* $[B_{11}H_{13}]^{2-}$. Since a study of the structure of 12-I-Se $B_{11}H_{10}$ had proved successful a similar experiment was envisaged with $Se_2B_9H_9$. Two routes to Br-$Se_2B_9H_8$ were attempted.

In a separate experiment to solve the structure of $Se_2B_9H_9$ detailed ^{11}B- ^{11}B COSY 2D n.m.r. spectra were obtained by Dr. J.D. Kennedy, (University of Leeds) and are discussed here.

3.2.3.1 $Se_2B_9H_9$

Se_2 B_9H_9 was prepared in 23.5% yield by the reaction between decaborane and KOH and potassium polyselenide, (9), characterisation was by melting point (339-340°C), infrared (2595, 2555 cm^{-1}, both B-H) and mass spectroscopy (M/Z cut off at 272, $^{82}Se_2$ $^{11}B_9$ $^{1}H_9$ = 272). Further evidence for the molecular composition was obtained from both 1D. and 2D ^{11}B n.m.r. spectroscopy. Todd and coworkers[2] originally proposed an 11-atom cage structure from ^{11}B n.m.r. evidence (Figure 8) in which the selenium atoms were bonded to each other. However, the same authors[3] proposed a different structure for the analogous S Se B_9H_9 (Figure 9) in which the heteroatoms were separated by boron atoms. Moreover, either structure could be assigned the XY B_9H_9 molecules based on the infrared and n.m.r. data presented by Todd and coworkers. In an attempt to elucidate the structure of Se_2 B_9H_9 further n.m.r. studies were undertaken. The ^{11}B $\{^{1}H\}$ n.m.r. spectrum of $Se_2B_9H_9$ recorded

at 115.5 MHz (Figure 20) is comparable to that recorded at 70.6 MHz by Todd and coworkers. Table 1 lists the chemical shifts for $Se_2 B_9H_9$ (115.5 and 70.6 MHz) and S Se B_9H_9. There is a shift of 1.1 p.p.m. to a lower field in each of the signals reported here compared to those reported by Todd and coworkers.[3] The intensities of the three spectra are in the ratios 3:4:1:1 due to accidental overlap of the signals of some of the boron atoms. Even the line narrowed ^{11}B spectrum of $Se_2 B_9H_9$ (Figure 21) failed to fully resolve the signals appearing at 1.1 p.p.m. but succeeded in splitting the signal at -1.5 p.p.m. into two signals at -1.4 and -1.7 p.p.m. in the ratio 2:2. The 2D COSY n.m.r. spectrum (Figure 22) was somewhat more informative and allows some tentative assignements of the n.m.r. signals to be made.

The low frequency signal at -35.2 p.p.m. is the easiest to assign and in the signal for Bf (in both Figure 8 and 9) not only on the basis of the shift value but also on the number of COSY correlations. From the COSY spectrum it is seen that this boron atom is not bonding with that giving the signal at -8.9 p.p.m. Since the signal at -8.9 p.p.m. is of intensity 1 it can be assigned to Bb in either Figure 8 or 9. The signal at +1.1 p.p.m. of intensity 3 is bonded to Bf and could be assigned Bd and Be, whose signals may overlap. Finally, the signal of intensity 4 at -1.5 p.p.m. may be assigned to the four boron atoms Ba and Bc. The COSY spectrum could be interpreted to suggest that Bf is bonded to some atoms which give this signal (Bc) but not to the others (Ba) but this is not certain. Interestingly this signal is the only one which was split in the line narrowed spectrum (Figure 21) showing the slightly different environment of the two pairs of boron atoms. It is clear that although the COSY n.m.r. spectrum allows some assignements to be made it does not distinguish between the possible structures for $Se_2 B_9H_9$.

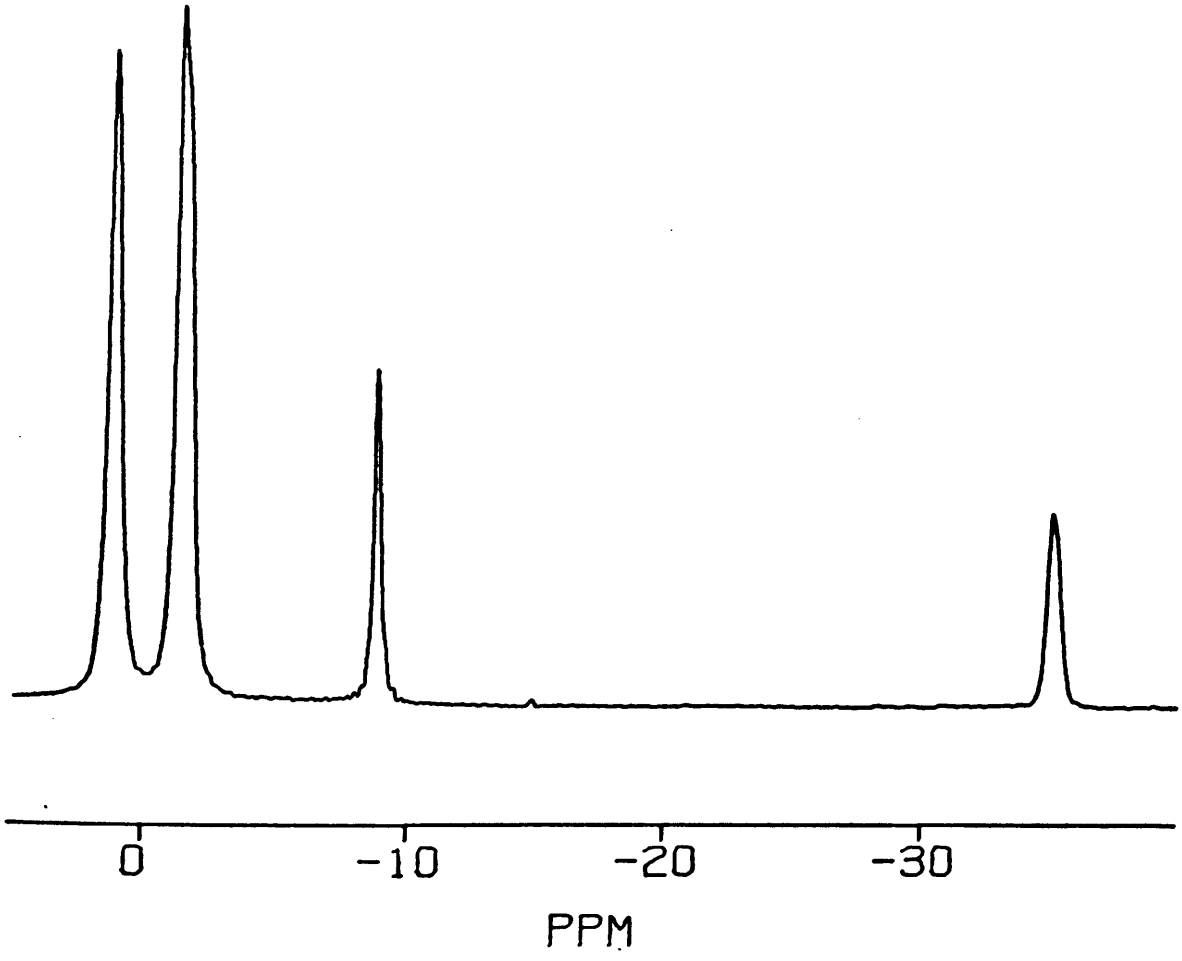


Figure 20: ^{11}B {^{1}H} n.m.r. spectrum of $Se_2 B_9 H_9$

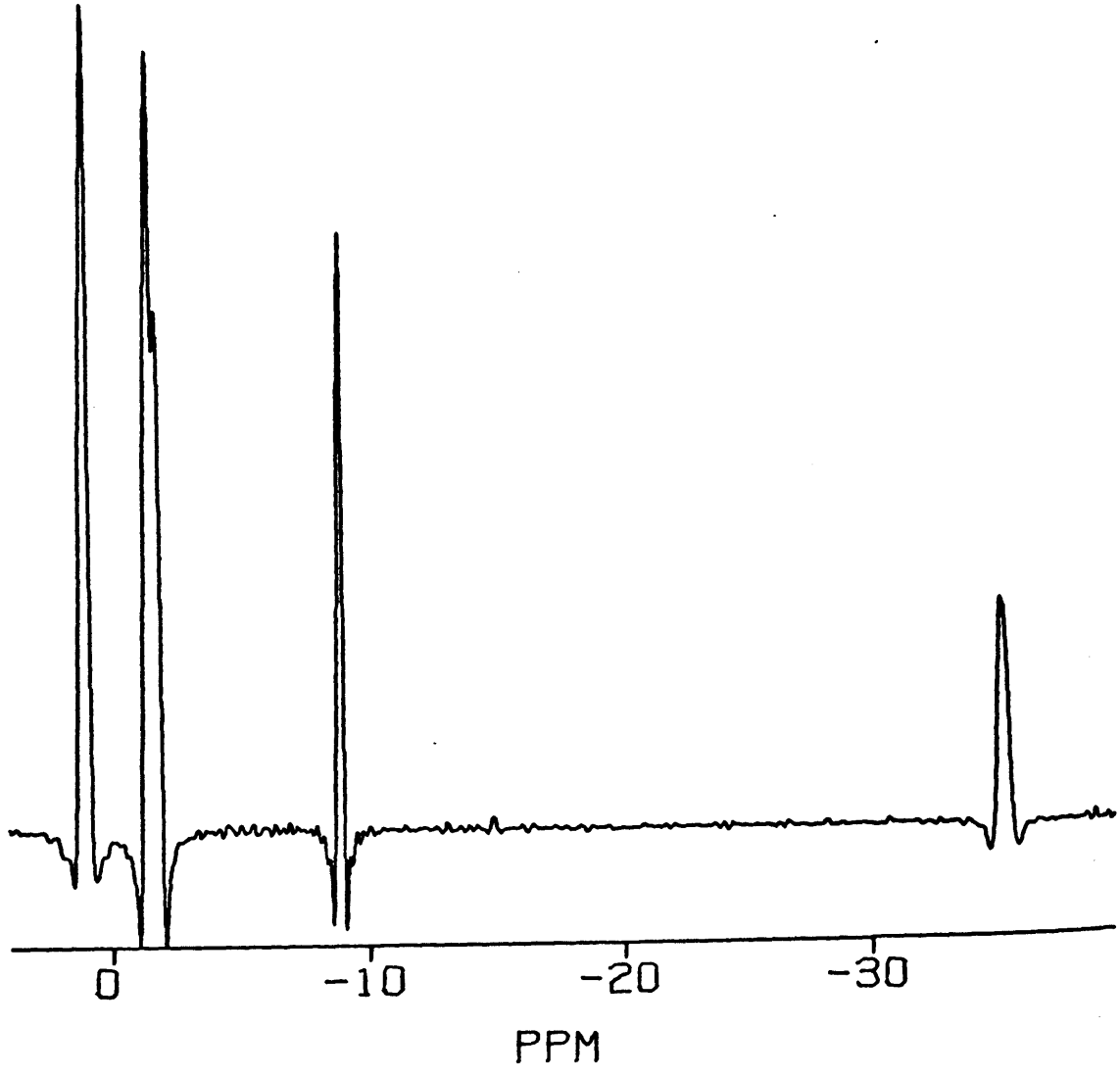


Figure 21: ^{11}B $\{^1H\}$ n.m.r. spectrum of $Se_2 B_9 H_9$ (line narrowed)

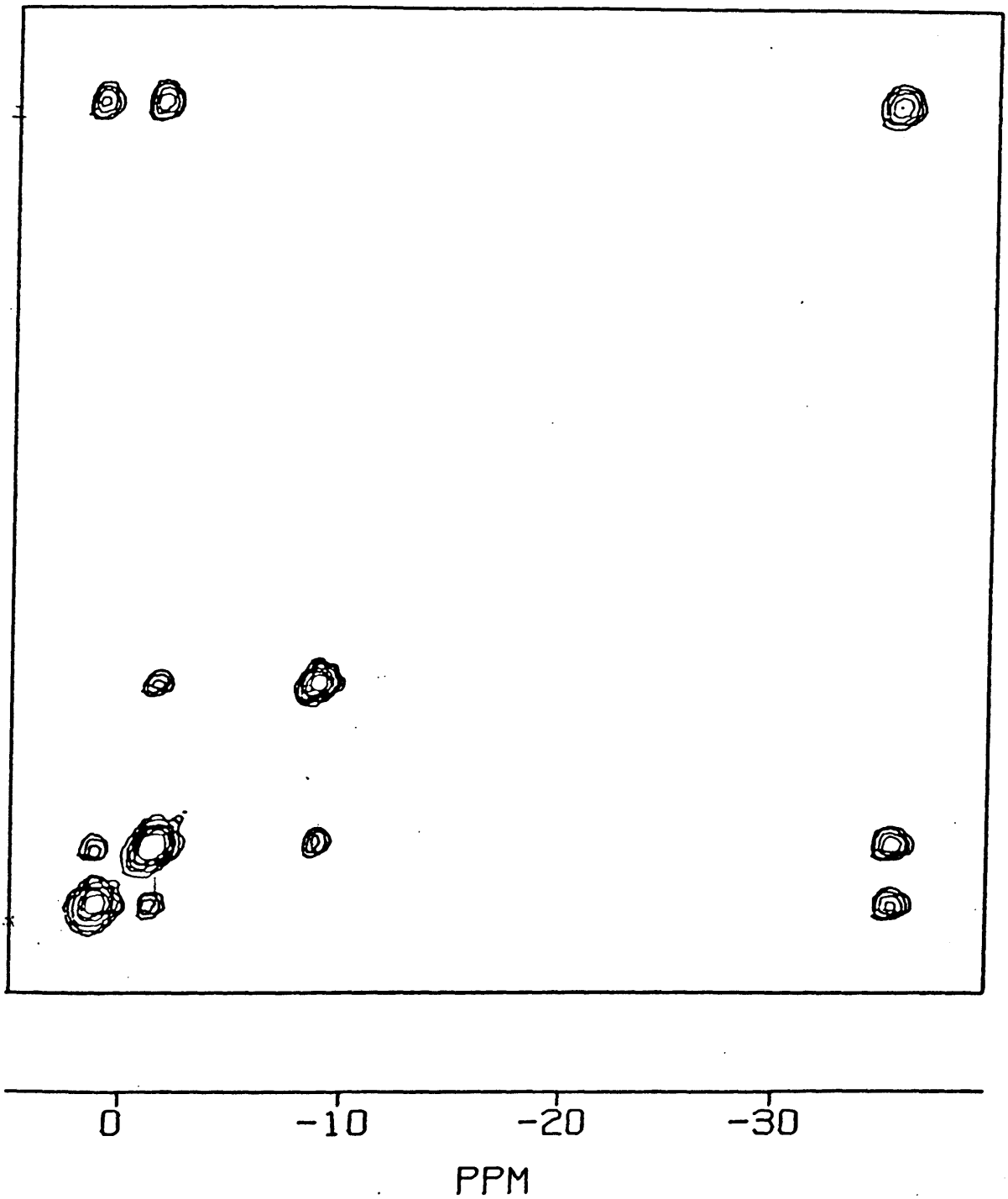


Figure 22: ^{11}B - ^{11}B COSY n.m.r. spectrum of $Se_2 B_9 H_9$

3.2.3.2 *Attempted Synthesis of Br-Se_2 B_9H_8*

The bromination of Se_2 B_9H_9 was attempted by three routes; (i) using Friedel-Crafts conditions, (ii) using N-bromo succinimide as the halogenating agent and (iii) *via* degradation of 2-bromodecaborane (14).

$$2\text{-Br } B_{10}H_{13} + KOH + Na_2[Se_4] \xrightarrow[R.T.]{H_2O} Br\text{-}Se_2B_9H_8 + B(OH)_3 \qquad (14)$$

However both methods (i) and (ii) resulted in the recovery of unchanged Se_2 B_9H_9, but method (iii) resulted in generation of the product. Proof of this was obtained from the mass spectrum which showed M/Z cut off at 352 (^{80}Br ^{82}Se $^{11}B_9$ $^{1}H_8$ = 352). However, the relative conversion was too small (3 %) to make this a synthetically viable route to Br-Se_2 B_9H_8.

TABLE 1. *"B N.m.r. Data" for B_9 Clusters* [a]

δ $Se_2B_9H_9$ 115.5 MHz	δ Se_2 B_9H_9 70.6 MHz	δ S Se B_9H_9 70.6 MHz	Intensities
-35.2	-36.3	-36.2	1
-8.95	- 9.7	-10.5	1
-1.5	- 2.6	- 2.6	4
+1.1	- 0.1	- 1.1	3

[a] Signals in p.p.m.

3.2.4. *Conclusions*

The results in this chapter are significant in that they provide the first accurate data on the boron-selenium bond length from the X-ray crystallographically determined structure of 12-I-Se $B_{11}H_{10}$. Other work on *nido* B_{11} systems includes an improved synthesis of 12-Br-Se $B_{11}H_{10}$ and the polychlorination of Se $B_{11}H_{11}$.

This chapter also includes the attempted synthesis of $[Br\text{-}Se\ B_{10}H_{10}]^-$. The preparation of the non-halogenated analogue $[Se\ B_{10}H_{11}]^-$ is straightforward but it is reported here that the presence of the halogen atom leads to the formation of a complex mixture of isomeric species inseparable by chromatography.

Finally, an indepth n.m.r. study using 2D ^{11}B- ^{11}B COSY spectroscopy on $Se_2B_9H_9$ is reported in an attempt to elucidate the structure of this species.

3.3. EXPERIMENTAL

Tetramethylammonium-tetradecahydroundecaborate[11]

A solution of predried sodium borohydride (60g, 1.59 mol) was prepared in a 2 litre flask, fitted with a mechanical stirrer, containing 500 ml diglyme. Two acetone filled scrubbers to remove gaseous boranes were also attached to the flask. The contents of the flask were heated and at 105°C boron-trifluoride etherate (250 ml, ·204 mol) was added at the rate of 40 ml/hour from a pressure equalised dropping funnel. On completion of the addition (26 hours), the reaction mixture was allowed to attain ambient temperature. The solution was filtered through a bed of celite in a sintered glass funnel and the resulting Na $[BF_4]$ solid material washed twice with 50 ml portions of diglyme. The combined diglyme filtrates were evaporated to an oil by heating under vacuum. The oil was taken up in 500 ml of H_2O and added in one portion to a solution of tetraethylammonium iodide (100g, 0.475 mol) in 200 ml H_2O. The resulting solution was allowed to stand for 15 mins and filtered by suction. The filter cake was then dissolved, with slight degassing in 300 ml acetone and heated to reflux temperature. Water was added until cloudiness was apparent and the solution allowed to cool slowly to room temperature and then further cooled to 10°C overnight. The pale yellow crystals were filtered to furnish tetraethylammonium-tetradecahydroundecaborate (14.1g, 28.56%). The mother liquid was evaporated to half the original volume and water added until the solution was cloudy. The solution was cooled as above and filtration isolated a further 1.8g (3.7%) of $[Et_4N]$ $[B_{11}H_{14}]$. Total percentage yield was 32.3%. ν max (KBr): 2940 (vs); 2850 (vs); 2500 (br, vs); 1450 (br, S); 1380 (w); 1350 (w); 1245 (w); 1190 (w); 1080 (s); 1010 (m); 940 (m); 860 (m); 840 (m); 740 (w) cm^{-1}. Analysis: calcd. for $C_8H_{34}NB_{11}$: C, 36.50; H, 12.93; N. 5.32; B, 45.25%. Found: C, 36.36; H, 12.88; N, 5.17; B, 44.63%.

Se $B_{11}H_{11}$

Tetraethylammonium-tetradecahydroundecaborate (24g, 9 10^{-3}mol) and sodium biselenite (2.0g, 1.4x 10^{-2}mol) were reacted in a water-heptane mixture (250 ml, 3:2) by stirring at room temperature for 24 hrs. The product was isolated from the heptane layer which was changed four times during the course of the reaction. Recrystallisation of the crude solid, from evaporation of the combined heptane layers, in dichloromethane yielded Se $B_{11}H_{11}$ (0.36g, 22.4%) as large crystals. m.p. >360°. (lit. 390-395 (decomp))[3] νmax (KBr): 2585; 2565; 2530; 2515 (all s, B-H) cm^{-1}. Mass spectrum cut-off at M/Z 214 ($^{82}Se\ ^{11}B_{11}\ ^{1}H_{11}$ = 214)

12-Br-Se $B_{11}H_{10}$ *Method (i)*

Bromine (0.20g, 1.26 x 10^{-3} mole) was solidified by cooling to -15°C in an ice-salt bath. $B_{11}H_{11}Se$ (0.27g, 1.26 x 10^{-3} mol) and 5 mg of powdered aluminium were added at this temperature. The mixture was slowly allowed to reach 0°C and maintained at this temperature for 2 hours and then warmed to ambient temperature. Mass spectral analysis of the product showed it to be a mixture of about 30% unreacted Se $B_{11}H_{11}$, 60% 12-Br-Se $B_{11}H_{10}$ and 10% of a dibrominated product. Preparative chromatography (hexane: benzene eluent (3:1)) isolated 12-Br-Se $B_{11}H_{10}$ (0.155g, 41.6% mol) m.p. 284-286°C (lit. 284-287)[4] .νmax (KBr) 2615; 2570; (both s, B-H) cm^{-1}. Mass spectrum cut off at M/Z 294 ($^{80}Br^{82}Se\ ^{11}B\ ^{1}H_{11}$ = 294).

Method (ii)

The reaction was repeated using the same quantities except that when the mixture had reached room temperature dichloromethane was added and the reaction mixture refluxed for 14 hrs. Mass spectral and chromatographic analysis indicated about 80% conversion to 12-Br Se $B_{11}H_{10}$ with less than 10% each of the unreacted Se $B_{11}H_{11}$ and the dibrominated species. P.l.c. separation followed by sublimation onto a water cooled probe at 90° afforded 12-Br-Se-$B_{11}H_{10}$ (0.236g, 63.4%) which analysed as above.

12-I-Se $B_{11}H_{10}$

To a solution of iodine (1.5g, 6×10^{-3} mol), dichloromethane (15.0 cm^3) and aluminium trichloride (0.5g, 3.7×10^{-3} mol). Se $B_{11}H_{11}$ (1g, 4.8×10^{-3} mol) was added and the resulting solution refluxed for 20 hours. The dichloromethane was evaporated *in vacuo* and ensuing solid sublimed at 110°C under vacuum to afford pale, purple crystals of 12-I-Se $B_{11}H_{10}$ (0.17g, 10.73%). Benzene extraction of remaining solid furnished a further (0.24g, 15.15%) of solid which analysed chromatographically (t.l.c., eluent: C_6H_{14} : CH_2Cl_2, 70:30) as the sublimed material. Recrystallisation of the combined product afforded 12-I-Se $B_{11}H_{10}$ (0.34g, 21.89%) as colourless crystals; a sample of which were sent for X-ray crystallographic structural analysis m.p. 213-215 (lit. 213-215°C) [4]. ν max (KBr) 2600 (s); 2570(s); 2555(s); 1020 (w); 990 (w); 965 (w); 932 (m); 928 (sh); 902 (m); 860 (m); 815 (s); 795 (s); 770 (w); 740 (sh); 725 (m); 690 (w) cm^{-1}.

Crystallography

A colourless small block crystal of I-Se $B_{11}H_{10}$ having approximate dimensions of 0.36 X 0.44 X 0.51 m.m. was mounted on a glass fiber in a random orientation. Data collection was performed on an Enraf-Nonius CAD4 computer controlled kappa axis diffractometer equipped with a graphite crystal, incident beam monochromator.

Cell constants and an orientation matrix for data collection were obtained from least squares refinement, using the setting angles of 25 reflections in the range $8 < \theta < 16°$, measured by the computer controlled diagonal slit method of centering. The monoclinic cell parameters. The space group was determined to be $P_{21/n}$ (No. 14). A total of 2848 reflections were collected of which 2493 were unique and most systematically absent. As a check on crystal and electronic stability three representative reflections were measured every 240 min. The intensities of these standards remained constant within experimental error, throughout the data collection.

Lorentz and polarisation corrections were applied to the data. The linear absorption coefficient is 58.71 cm^{-1} for Mo-K radiation. Relative transmission coefficients ranged from 0.10732 to 0.19201 with an average value of 0.15974.

The structure was solved using the Patterson heavy-atom method which revealed the position of two atoms. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded.

TABLE 1. *Molecular Dimensions Bond Lengths (Å)*

I	B11	2.167(7)	B4	B5	1.902(13)
Se	B1	2.118(8)	B4	B9	1.742(12)
Se	B2	2.132(9)	B4	B10	1.772(12)
Se	B3	2.144(10)	B5	B6	1.780(12)
Se	B4	2.119(10)	B5	B10	1.785(13)
Se	B5	2.112(9)	B6	B7	1.781(11)
B1	B2	1.894(12)	B6	B10	1.796(11)
B1	B5	1.911(12)	B6	B11	1.763(11)
B1	B6	1.763(11)	B7	B8	1.774(11)
B1	B7	1.762(11)	B7	B11	1.757(11)
B2	B3	1.934(13)	B8	B9	1.787(10)
B2	B7	1.743(11)	B8	B11	1.760(11)
B2	B8	1.769(12)	B9	B10	1.774(11)
B3	B4	1.862(12)	B9	B11	1.774(11)
B3	B8	1.741(11)	B10	B11	1.767(10)
B3	B9	1.715(12)			

TABLE 2. *Bond Angles* (°)

B1	Se	B2	52.9(3)	Se	B2	B3	63.4(5)
B1	Se	B3	92.5(3)	Se	B2	B7	111.6(5)
B1	Se	B4	93.1(3)	Se	B2	B8	111.1(5)
B1	Se	B5	53.7(3)	B1	B2	B3	107.0(5)
B2	Se	B3	53.8(3)	B1	B2	B7	57.8(4)
B2	Se	B4	92.8(3)	B1	B2	B8	106.3(6)
B2	Se	B5	92.3(3)	B3	B2	B7	104.4(6)
B3	Se	B4	51.8(3)	B3	B2	B8	55.9(5)
B3	Se	B5	91.9(3)	B7	B2	B8	60.7(5)
B4	Se	B5	53.4(4)	Se	B3	B2	62.8(4)
Se	B1	B2	63.9(4)	Se	B3	B4	63.4(4)
Se	B1	B5	63.0(4)	Se	B3	B8	111.7(5)
Se	B1	B6	111.8(5)	Se	B3	B9	112.5(5)
Se	B1	B7	111.5(5)	B2	B3	B4	108.3(6)
B2	B1	B5	108.3(6)	B2	B3	B8	57.3(5)
B2	B1	B6	106.2(6)	B2	B3	B9	107.4(6)
B2	B1	B7	56.8(4)	B4	B3	B8	108.0(5)
B5	B1	B6	57.8(5)	B4	B3	B9	58.1(5)
B5	B1	B7	106.2(6)	B8	B3	B9	62.3(5)
B6	B1	B7	60.7(5)	Se	B4	B3	64.8(4)
Se	B2	B1	63.2(4)	Se	B4	B5	63.1(4)

TABLE 2. (Continued)

Se	B4	B9	112.5(5)	B1	B6	B11	109.0(5)
Se	B4	B10	112.1(5)	B5	B6	B7	111.2(5)
B3	B4	B5	108.8(6)	B5	B6	B10	59.9(5)
B3	B4	B9	56.7(5)	B5	B6	B11	108.9(6)
B3	B4	B10	105.8(5)	B7	B6	B10	107.7(5)
B5	B4	B9	106.8(6)	B7	B6	B11	59.4(4)
B5	B4	B10	58.0(5)	B10	B6	B11	59.5(4)
B9	B4	B10	60.6(5)	B1	B7	B2	65.4(5)
Se	B5	B1	63.3(4)	B1	B7	B6	59.7(4)
Se	B5	B4	63.5(4)	B1	B7	B8	112.0(5)
Se	B5	B6	111.4(5)	B1	B7	B11	109.3(5)
Se	B5	B10	112.0(5)	B2	B7	B6	112.2(6)
B1	B5	B4	107.5(5)	B2	B7	B8	60.4(5)
B1	B5	B6	56.9(4)	B2	B7	B11	110.0(6)
B1	B5	B10	105.8(5)	B6	B7	B8	108.3(5)
B4	B5	B6	105.6(6)	B6	B7	B11	59.8(4)
B4	B5	B10	57.4(5)	B8	B7	B11	59.8(4)
B6	B5	B10	60.5(5)	B2	B8	B3	66.9(5)
B1	B6	B5	65.3(5)	B2	B8	B7	59.0(5)
B1	B6	B7	59.6(4)	B2	B8	B9	111.7(6)
B1	B6	B10	111.8(6)	B2	B8	B11	108.7(6)

TABLE 2. (Continued)

B3	B8	B7	111.7(6)	B5	B10	B9	110.7(6)
B3	B8	B9	58.1(4)	B5	B10	B11	108.6(5)
B3	B8	B11	108.2(5)	B6	B10	B9	107.9(5)
B7	B8	B9	108.0(5)	B6	B10	B11	59.3(4)
B7	B8	B11	59.6(4)	B9	B10	B11	60.1(4)
B9	B8	B11	60.0(4)	I	B11	B6	119.8(5)
B3	B9	B4	65.2(5)	I	B11	B7	120.9(5)
B3	B9	B8	59.6(5)	I	B11	B8	121.6(5)
B3	B9	B10	112.4(6)	I	B11	B9	121.6(5)
B3	B9	B11	108.7(6)	I	B11	B10	119.9(5)
B4	B9	B8	111.4(6)	B6	B11	B7	60.8(4)
B4	B9	B10	60.5(5)	B6	B11	B8	109.7(5)
B4	B9	B11	109.3(6)	B6	B11	B9	109.3(5)
B8	B9	B10	108.1(6)	B6	B11	B10	61.1(5)
B8	B9	B11	59.2(4)	B7	B11	B8	60.6(4)
B10	B9	B11	59.7(4)	B7	B11	B9	109.3(5)
B4	B10	B5	64.6(5)	B7	B11	B10	110.1(5)
B4	B10	B6	110.6(6)	B8	B11	B9	60.7(4)
B4	B10	B9	58.8(5)	B8	B11	B10	109.7(5)
B4	B10	B11	108.3(5)	B9	B11	B10	60.1(4)
B5	B10	B6	59.6(5)				

12-Cl-Se $B_{11}H_{10}$ *Method I*

To a solution of Se $B_{11}H_{11}$ (0.2g, 0.0001 mol) in 5 ml carbontetrachloride, N-chlorosuccinimide (0.13g, 0.0001 mol) was added and the reaction stirred at 0°C. The reaction was allowed to attain ambient temperature after 2 hrs and thus maintained for a further 16 hrs. Filtration of unreacted solid material, followed by evaporation of the solvent *in vacuo*, afforded Se $B_{11}H_{11}$ (0.17g, 85% recovery) as a crystalline solid. There was no evidence for reaction on infrared and chromatographic analysis.

Method 2

A mixture of Se $B_{11}H_{11}$ (0.8g, 4×10^{-3} mol), $AlCl_3$ (0.36g, 2.7×10^{-3} mol) and 9 ml dichloromethane were frozen to -190°C. Chlorine gas (1.4g, 0.02 mol) was added. The reaction was allowed to proceed at -45°C with stirring for 4 hrs. Subsequently the mixture was brought to ambient temperature and maintained thus for a further 16 hrs. Evaporation of the solvent followed by recrystallisation of the crude solid from benzene afforded 0.32g, of a mixture of products. These were initially identified by a mass spectrum of the solid as 12-Cl-Se $B_{11}H_{10}$, Cl_2-Se $B_{11}H_9$ and Cl_3-Se $B_{11}H_8$. Preparative chromatography (eluent, dichloromethane: cyclohexane, 70:30) separated the three products. However, the amount of the trichlorinated species obtained was too little for analytical purposes. The lower of the other two bands was isolated as a white solid (0.04g, 4.3%) and identified as a mixture of Cl_2-Se $B_{11}H_9$ isomers. m.p. 117-119°C. ν max (KBr) 2655 (s) 2555 (s); (B-H) cm^{-1}. The remaining band was isolated as a white crystalline solid (0.18g, 19.37%) and identified as [5-Cl-7-Se $B_{10}H_{10}]^-$. m.p. 248-250°C. ν max (KBr) 2645 (s); 2520 (s) (B-H) cm^{-1}.

Attempted Synthesis of 12-F-Se $B_{11}H_{10}$

A solution of tetrabutylammonium fluoride (0.66 ml, 6 X 10^{-4} mol) in THF was added to a solution of 12-I Se $B_{11}H_{10}$ (0.22g, 6 x10^{-4} mol) in 10 ml THF and reaction mixture stirred at room temperature. After 5 days there was no evidence that reaction had taken place. Addition of excess $[Bu_4N]$ [F] resulted in a distinct colour change from yellow to dark green. Chromatographic analysis (t.l.c.: eluent, 100% CH_2Cl_2) showed the presence of new products; extractions with either benzene/water or dichloromethane/ water did not, however, afford any borane containing material. Mass spectral analysis of the residual solid found no evidence for the presence of borane.

Bromodecaborane

A solution of bromine (2.5g, 0.031 mol) in 5 ml carbon disulphide was added dropwise from a pressure equalised dropping funnel to a solution of decaborane (2.0g, 0.016 mol) and $AlCl_3$ (0.1g, 7.5x10^{-4} mol) in 25 ml carbon-disulphide at -10°C. The reaction was allowed to attain ambient temperature and stirred for a further 30 minutes. The carbon disulphide was evaporated and the residue extracted three times with refluxing hexane. (3 X 30 ml portions). The combined hexane portions were kept at 4°C to promote precipitation of the brominated species. The 2-Br isomer (2.23g, 67.7%)[14] separated, first from the solution as colourless crystals. m.p. 105-106°C (lit 106-107°C). ν max (KBr) 2590 (v.s.); 1850 (w); 1560 (w); 1510 (w); 1495 (w); 1460 (w); 1400 (w); 1040 (w); 995 (m); 945 (m); 920 (m); 880 (m); 865 (m); 820 (m); 790 (s); 755 (m); 710 (m); 660 (w) cm^{-1}. Mass spectrum cut-off at M/Z 203 ($^{80}Br\ ^{11}B_{10}\ ^{1}H_{13}$ = 203).

Continued fractional recrystallisation of the mother liquor resulted in the isolation of 1-Br $B_{10}H_{13}$ (0.75g, 22.9%) as colourless crystals. m.p. 90-92°C (lit. 92-93°C)[15]. Infrared and mass spectra were as above.

Tetraethylammonium bromoselenadecaborane $[Et_4N]$ $[Br\text{-}Se\ B_{10}H_{10}]$

Ammonia (60 ml) was condensed into a reaction flask which was maintained at -78°C by an acetone-liquid nitrogen bath. Sodium metal (0.3g, 0.013g. atom) was added in small chips followed by elemental selenium (2.0g, 0.025g, atom) from a solid addition tube over a 15 minute period. The addition of the selenium resulted in sputtering due to the vigorous reaction caused by formation of sodium polyselenide. The reaction was stirred for 2 hours while warming slowly until the ammonia was evaporated to a volume of approximately 25 ml. Deoxygenated water (60 ml) was added and the reaction solution stirred for 10 minutes before 2-bromodecaborane (1.17g, 0.005 mol) was added gradually over 15 minutes from the addition tube. The reaction mixture was further stirred for 22 hours at room temperature. An insoluble material, containing $Se_2B_9H_9$, was removed from the solution by filtration. Excess saturated aqueous tetraethylammonium iodide solution was added to the filtrate and the ensuing precipitate collected by filtration and thoroughly washed with water. Extraction of the crude solid with three 50 ml portions of acetone, followed by evaporation of the combined solvent, afforded a mixture of products containing tetraethylammonium bromo-selenadecaborane (1.9g, 80.55%) as a yellowish crystalline solid. ν max (KBr) 2960 (s); 2870 (m); 2530 (br, s); 1380(m); 1165 (m); 1105 (w); 1050 (w); 1030 (m); 990 (w); 920 (w); 900 (w); 880 (w); 840 (s); 790 (m); 740 (s); 570 ((m) cm^{-1}. δB $\{^1H\}$ (Me OD, 115 MHz) -35.5; -34.9; -20.1; -17.5; 16.1; -14.87; -14.46; -13.63; -10.45; -9.32; -5.30; -3.35; -2.3; + 19.8 p.p.m.

Bromoselenadecaborane $Br\text{-}Se\ B_{10}H_{11}$

Crude tetraethylammonium bromoselenadecaborane (1.9g, 0.0046 mol) was dissolved in a minimum of acetonitrile and filtered to remove impurities. The filtrate was poured into a 250 ml separating flask followed by 20 ml concentrated hydrochloric acid. The resulting solution was extracted with 150 ml portions of a diethylether : hexane (1:2) mixture until no further

solid was obtained on evaporation of the extract. The solutions were combined and evaporated to dryness. Sublimation of the crude solid onto a water cooled probe followed by recrystallisation from hexane afforded a mixture of products containing bromoselenadecaborane (0.74g, 55%). ν max (KBr) 2550 (s); 1440 (s); 1190 (m); 1070 (w); 1000 (m); 975 (m); 930 (w); 910 (w); 880 (m); 830 (w); 810 (m); 765 (w); 750 (w); 730 (w); 635 (m) cm^{-1}. δ B {^{1}H} (Silanon-C, 115 MHz) -26.12; -25.22; -19.98; -17.38; -16.44; -10.34; -8.94; -6.38; -3.03; -1.76; + 17.90; + 19.18; ppm. Mass spectrum cut-off at M /Z 284 ($^{80}Br^{82}Se^{11}B_{10}{}^{1}H_{10}$ = 284).

$Se_2B_9H_9$

A solution containing the $[B_9H_{14}]^-$ anion was prepared by the addition of decaborane (0.75g, 0.006 mol) and potassium hydroxide (1.1g, 0.018 mol) to 16.5 mls H_2O and the mixture was stirred until completely colourless. Concentrated hydrochloric acid was added dropwise until a neutral solution was formed.

A polyselenide solution was prepared by the addition of powdered selenium (1.51g, 0.009 mol) and potassium hydroxide (1.13g, 0.02 mol) to 7 ml H_2O. The resulting solution was refluxed for 20 minutes. When the polyselenide solution had cooled to ambient temperature, the solution containing the $[B_9H_{14}]^-$ was added as rapidly as possible resulting in the immediate precipitation of a white solid. $B_9H_9Se_2$ was isolated by successive extractions with 25 ml portions of hexane until no further solid was obtained on evaporation of the hexane. $Se_2B_9H_9$ (0.38g, 23.4%) was obtained as a white crystalline solid.m.p. 339-340°C (lit 340-342°C). Analysis: Calcd: H, 3.43%. Found: H, 3.50% ν Max (KBr) 2595 (vs); 2555 (vs); 1400 (w); 990 (s); 965 (m); 895 (m); 880 (w); 855 (w); 820 (w); 785 (m); 760 (m); 730 (m); 695 (w) cm^{-1}. δ ^{11}B {^{1}H} (115 MHz); 1.1 (s); -1.52 (s); -8.85(s); -35.2 (s) p.p.m. An ^{11}B- ^{11}B COSY n.m.r. was also obtained for $Se_2B_9H_9$ Mass.

spec. cut off at M/Z 272 ($^{82}Se_2\ ^{11}B_9\ ^{1}H_9$ = 272).

Br-$Se_2B_9H_8$

(i) A solution containing the $[Br\ B_{10}H_{13}]^-$ ion was similarly prepared by the addition of 2-bromodecaborane (0.23g, 0.001 mol) and potassium hydroxide (0.21g, 0.003 mol) to 3 ml H_2O. In accordance with the above procedure, concentrated hydrochloric acid was added until the solution was neutral. This solution was then added to a polyselenide solution prepared from powdered selenium (0.28g, 0.003 mol) potassium hydroxide (0.21g, 0.003 mol) and 1.28 ml H_2O and reacted as above. Mass spectral analysis of the solid from hexane extractions showed that Br-$Se_2B_9H_8$ (M/Z = 352, $^{80}Br-^{82}Se_2\ ^{11}B_9\ ^{1}H_8$ = 352), was present as was $Se_2B_9H_9$ (M/Z 272, $^{80}Se_2\ ^{11}B_9\ ^{1}H_9$ = 272). The ratio of the brominated to the non-brominated species was determined from peak intensities to be ~ 1:10. However, the ratio of conversion was too small for the product to be isolated.

(ii) A solution of bromine (0.12g, 7.6×10^{-4} mol) in 2 ml dichloromethane was added dropwise from a pressure equalised dropping funnel to a stirring solution of $Se_2B_9H_9$ (0.1g, 3.8×10^{-4} mol) and $AlCl_3$ (0.1g, 7.5×10^{-4} mol) in 10 ml dichloromethane, cooled to 10°C by an ice-water bath. When the addition was completed the reaction was allowed to attain ambient temperature and further stirred for 1 hour. The dichloromethane was removed *in vacuo* and the solid residue extracted three times with refluxing hexane. The combined hexane extracts were evaporated to dryness under reduced pressure. Chromatographic (t.l.c. eluent C_6H_{14}: C_6H_6, 3:1) and mass spectral analysis revealed that the product was > 95% $Se_2\ B_9H_9$.

(iii) Attempts to brominate $B_9H_9Se_2$ using N-bromosuccinimide also resulted in recovery of the starting material.

3.4. REFERENCES

1. W.R. Hertler, F. Klanberg and E.L. Muetterties; *Inorg. Chem, 1967, 6, 1696.*
2. J.L. Little, G.D. Friesen and L.J. Todd; *Inorg. Chem., 1977, 16, 869.*
3. G.D. Friesen and L.J. Todd; *J.Chem. Soc., Chem. Commun., 1978, 349.*
4. J.A. MacCurtain; *M.Sc. Thesis, University College Cork, 1984.*
5. J. Plesek and S. Hermanek; *J. Chem. Soc., Chem. Commun., 1975, 127.*
6. B. Ng, T. Onak, T. Banıelus, F. Gomez and E.W.Di Stefano; *Inorg. Chem., 1985, 24, 4091.*
7. D. Reed, G. Ferguson, O. Ní Dhubhghaill and T.R. Spalding; *in press.*
8. M.F. Hawthorne, D.C. Young, P.M. Garrett, D.A. Owen, S.G. Scherwin, F.N. Tebbe and P.A. Wegner; *J. Am. Chem. Soc., 1968, 80, 862.*
9. G.D. Friesen, A. Barriola, P. Daluga, P. Ragatz, J.C. Huffman and L.J. Todd; *Inorg. Chem., 1980, 19, 459.*
10. K. Base and I. Stibr; *Chem. Ind., 1978, 631.*
11. G.B. Dunks and K.P. Ordonez; *Inorg. Chem., 1978, 14, 1514.*
12. G. Ferguson, M. Parvez, J.A. MacCurtain, O. Ní Dhubhghaill, T.R. Spalding and D. Reed; *J. Chem. Soc., Dalton Trans., 1987, 699.*
13. W.R. Pretzer and R.W. Rudolph; *J. Chem. Soc., Chem. Commun, 1974, G 29;* W.R. Pretzer, T.K. Hilty and R.W. Ruldolph; *Inorg. Chem., 1975, 14, 2459.*

14. G.D. Friesen, J.L. Little, J.C. Huffman and L.J. Todd; *Inorg. Chem., 1979, 18, 755.*

15. A. Sequiera and W.C. Hamilton; *Inorg. Chem., 1967, 6, 1281.*

16. G.B. Dunks and K.P. Ordonez; *Inorg. Chem., 1978, 17, 1514.*

17. R.F. Sprecher, B.E. Aufderheide, G.W. Luther and J.C. Carter; *J. Am. Chem. Soc., 1974, 96, 4404.*

18. J. Stuchlik, S. Hermanek, J. Plesek and B. Stibr; *Collect. Czech. Chem. Commun, 1970, 35, 339.*

CHAPTER FOUR

REACTIONS OF BORANE AND CYANOBORANE WITH AMINES AND PHOSPHINES

4.1 INTRODUCTION

4.1.1 *Synthesis of Amine-Boranes* [$(R_nNH_{3-n}).BH_3$]

There have been a large number of amine-boranes of the general formula $R_nNH_{(3-n)}.BH_3$ reported in the chemical literature.[1-4] Several synthetic methods have been developed for reactions in both the gas and liquid phases. Although reactions in non-aqueous solvents are usually preferred nowadays, the first reported amine-borane, $Me_3N.BH_3$, was prepared by the gas phase reaction of Me_3N and $BH_3.CO$, (1).[1]

$$(CH_3)_3N + BH_3.CO \longrightarrow (CH_3)_3N.BH_3 + CO \qquad (1)$$

This reaction involved high vacuum techniques which imposed limitations on the quantities of amine-boranes available.

An investigation of the reaction of lithium borohydride and the methylammonium chlorides, $[Me_nNH_{4-n}]Cl$, in 1948 by Schaeffer and Anderson[2] first led to the synthesis of gramme quantities of amine-boranes in reasonable yields. Trimethylammonium chloride and lithium borohydride reacted rapidly and smoothly at room temperature in diethyl ether to produce trimethylamine-borane (I) in 86% yield, (2).

$$(CH_3)_3NH[Cl] + Li[BH_4] \xrightarrow[R.T]{Et_2O} \underset{\text{I}}{(CH_3)_3NBH_3} + Li[Cl] + H_2 \qquad (2)$$

Another high yield method developed for the synthesis of amine-boranes was the transamination reaction (3).

$$(CH_3)_3N.BH_3 + R_3N \longrightarrow R_3N.BH_3 + (CH_3)_3N \qquad (3)$$

Trimethylamine-borane was specifically chosen since trimethylamine may be periodically pumped away or readily distilled from a reaction

mixture. Using an excess of R_3N produced the required amine in almost quantitative yields.

An alternative synthetic method involved the reduction of an appropriate boron compound using hydrogen or borohydride, (4).[5,6,7]

$$(C_2H_5)_3N.BCl_3 \xrightarrow{3H_2} (C_2H_5)_3N.BH_3 + 3HCl \qquad (4)$$

Possibly the most convenient synthesis to date was that devised by Nainan and Ryschkewitsch,[8] in 1969. In a general synthesis, borane adducts were prepared in yields usually ranging from 85% to 95% by the reaction of sodium borohydride, an appropriate donor molecule and iodine in an ether solvent, typically 1,2-dimethoxyethane (glyme), (5).

$$R_3N + Na[BH_4] + \tfrac{1}{2}I_2 \xrightarrow{\text{glyme}} R_3N.BH_3 + Na[I] + \tfrac{1}{2}H_2\uparrow \qquad (5)$$

This method has been used to synthesise ammonia-borane, borane adducts of aliphatic amines (RNH_2, R_2NH, R_3N, di- and tri-amines), aromatic amines and substituted pyridines. It has also been extended to synthesise phosphine-boranes. In a typical experiment, iodine in 1,2-dimethoxyethane is added dropwise to a 15-20% excess of sodium borohydride and a 7-10% excess of amine in the same solvent. The most likely reaction pathway is initial hydride abstraction followed by the trapping of the liberated borane by the amine, (6).

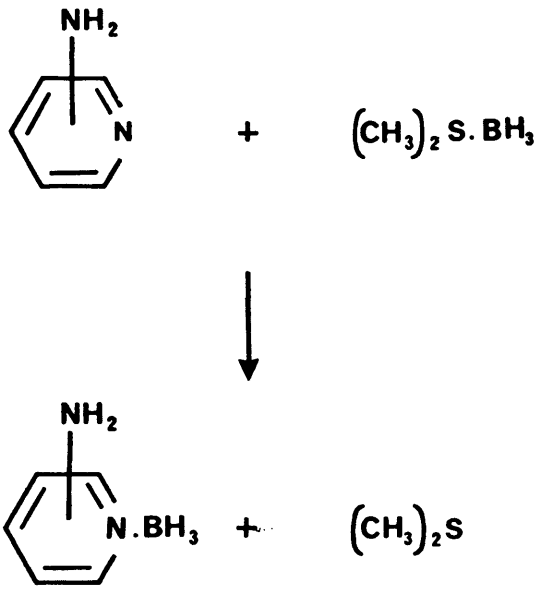
$$[BH_4]^- + \tfrac{1}{2}I_2 \longrightarrow BH_3 + HI$$

$$BH_3 + H_{3-n}NR_n \longrightarrow H_{3-n}NR_n.BH_3 \qquad (6)$$

Whether HI reacts directly with an additional mole of $[BH_4]^-$ or whether it is temporarily trapped by the amine does not affect the eventual result since ammonium salts react with borohydrides to form amine-boranes, see equation (2).

As expected, organic diamines formed 1:2 adducts with most boranes and, in general, the amine-borane structure is preferred to an ionic $[L_2BH_2][BH_4]$ formulation. For example, the reaction of ethylenediamine with diborane in ether solvent yielded $H_3B.H_2N(CH_2)_2NH_2.BH_3$[9] rather than $[H_2N(CH_2)_2NH_2BH_2][BH_4]$ as evidenced from the ^{11}B n.m.r. spectrum[10] which showed a single boron signal split into a 1:3:3:1 quartet characteristic of BH_3 groups.

It is known that the reactions of mixed aromatic-aliphatic diamines with boranes occur through the aromatic nitrogen rather than the NR_2- substituent. This is exemplified in the displacement of borane from dimethylsulphide-borane by 2-, 3-, and 4- aminopyridines (7).[11]



(7)

It has been claimed that intramolecular hydrogen bonding between the borane and the amino substituent in the 2- and 4- substituted species (Fig. 1) causes a stronger diamagnetic field around the boron atom, which in turn shifts the ^{11}B signal further upfield compared to that for pyridine-borane. The structure of 3-aminopyridine-borane precludes the possibility of hydrogen bonding and so the ^{11}B spectrum of this species is approximately the same as that of pyridine-borane.

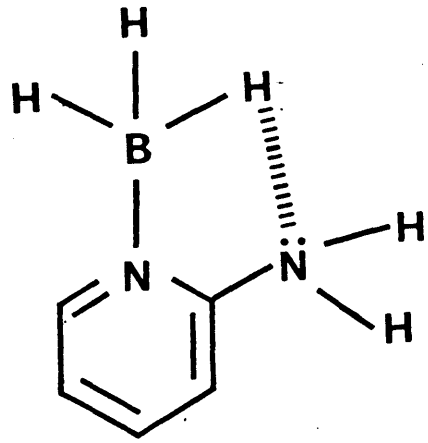


Figure 1: Intramolecular Hydrogen Bonding in 2-Aminopyridine-borane

4.1.2 *Structures of Amine-Boranes*

It is rather surprising that although solid state structures of adducts such as *bis*(borane) aminophosphane adducts are known,[12] none have

been reported for simple amine-borane adducts. However, accurate measurements of the boron-nitrogen bond distance and the dipole moment have been made in the gas phase by Cassoux and co-workers[13] on ^{15}N-enriched trimethylamine-borane in a microwave spectroscopic study. The adducts previously studied in the gas phase, each containing a normal isotopic distribution, were $(CH_3)_2NH.BH_3$,[14] $(CH_3)_3N.BF_3$[15] and $(CH_3)_3N.BH_3$.[16] The bond lengths calculated for each of these were not very precise. Three gas-phase structure studies had been reported for $(CH_3)_3N.BH_3$ with bond lengths reported as 1.62 ± 0.01 Å,[16] 1.65 ± 0.02 Å,[18] and a study by Odom and co-workers[19] who reported the bond length as either 1.609 Å or 1.637 Å, with preference expressed for the 1.609 Å value. Using the double substitution procedure,[17] Cassoux and co-workers calculated the B - N bond distance to be 1.63 ± 0.01 Å.

Other B - N bond distances have been calculated including that in borazine, $B_3N_3H_6$, the bond length of which was reported as 1.435 ± 0.002 Å, from an electron diffraction study.[20] For amino boranes, B - N bond lengths vary from 1.379 ± 0.06 Å in Cl_2BNMe_2 (electron diffraction)[21] to 1.485 ± 0.022 Å in $F_2BN(SiH_3)_2$ (electron diffraction).[22] However, these are extreme values and the remainder fall in the range 1.41-1.45 Å.[23] It is evident from these values that no π bonding is present in amine-boranes. However, in the aminoboranes for which the B - N bond distance is typically 0.2 Å shorter than in amine-boranes, there is a substantial degree of π bonding in the B - N bond.

4.1.3 *Reactions of Amine-Boranes*

The reactions of amine-boranes dealt with here are divided into two main sections. The first of these deals with reactions in which the N - B is retained and the second in which the N - B bond is broken.

4.1.3.1. *Retention of the N - B bond*

Although it has been shown that amine-boranes are thermally and hydrolytically reasonably stable,[24] intramolecular decomposition as depicted in (8) was reported in early studies of amine-borane chemistry[25] and is one of the best known reactions of these compounds.

$$R_3N.BH_3 \xrightarrow{\Delta} R_2N\text{-}BH_2 + RH \qquad (8)$$

In some instances, amine-boranes have been known to polymerise thermally. Heating 2-aminopyridine-borane causes cyclisation to a borazine structure (9).[11] It is claimed by Martin and co-workers that the juxtaposition of NH_2 and the BH_3 groups allow the borane molecule to easily migrate to the amine position and subsequently form the borazine ring.

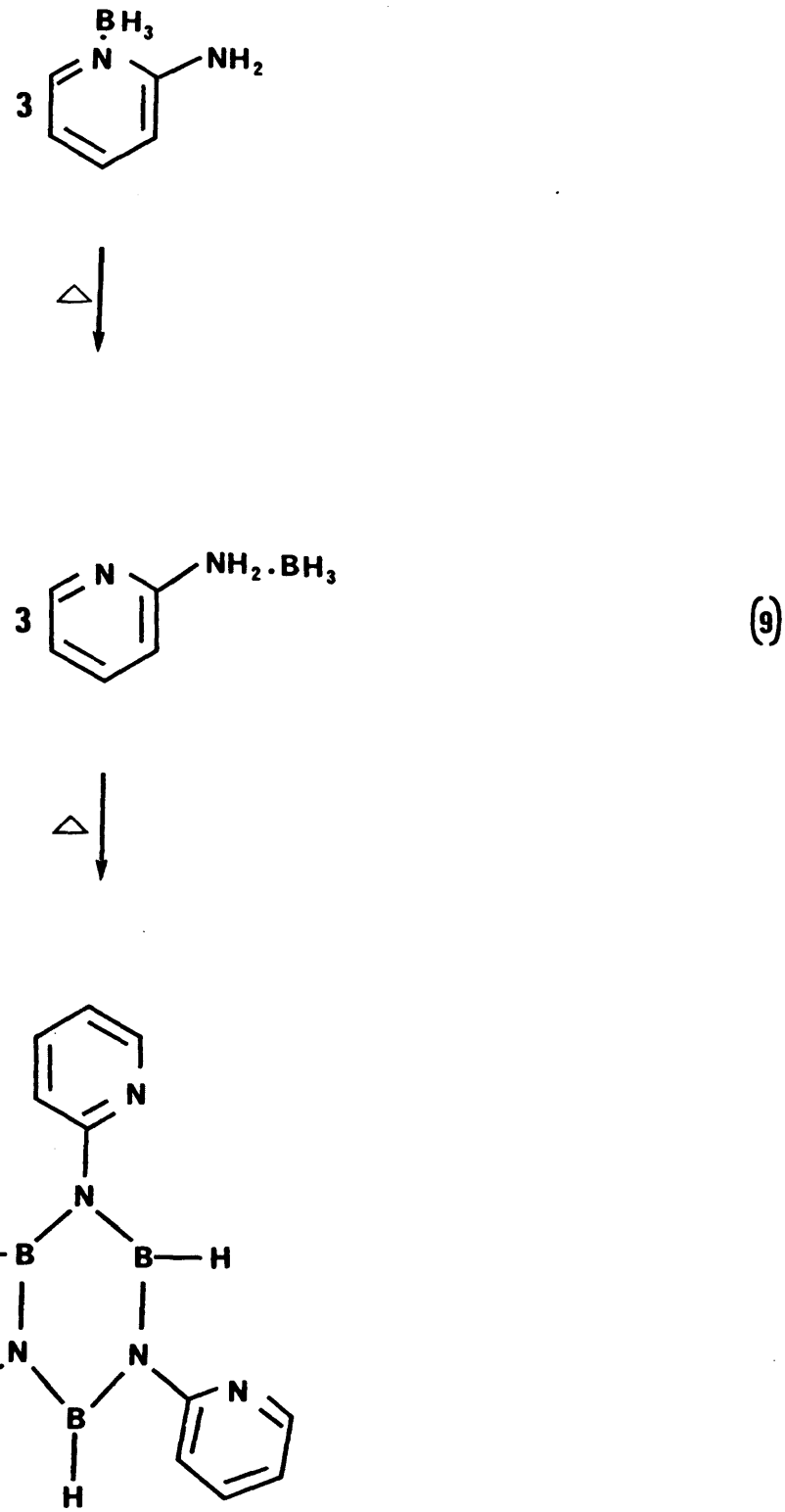
Muetterties and Miller[26] found that the most versatile preparation of $[H_2BD_2]^+$ cations is the reaction at elevated temperatures of base-borane adducts, $D.BH_3$, with onium salts, [DH][X], (10).

$$D.BH_3 + [DH][X] \xrightarrow{100\text{-}180^{\circ}C} [H_2BD_2][X] + H_2 \qquad (10)$$

In one, rather complicated, example of this type of reaction, the amine, R_3N, is heated with $[(C_2H_5)_3NH]_2B_{12}H_{12}$ and triethylamine-borane (11) and the displaced triethylamine is removed by distillation.

$$\begin{array}{l} [(C_2H_5)_3NH]_2B_{12}H_{12} + 2(C_2H_5)_3N.BH_3 + 4R_3N \\ \qquad\qquad\qquad\qquad \downarrow \\ [H_2B(NR_3)_2]_2B_{12}H_{12} + 4(C_2H_5)_3N + 2H_2 \end{array} \qquad (11)$$

Borane cations of amines, phosphines, arsines and sulphides have all been prepared in this fashion, e.g. H_2BTMED, $H_2B[P(CH_3)_3]_2$, $H_2B[As(CH_3)_3]_2$ and $H_2B[S(CH_3)_2]_2$.[26]



(9)

4.1.3.2. *Halogenation Reactions*

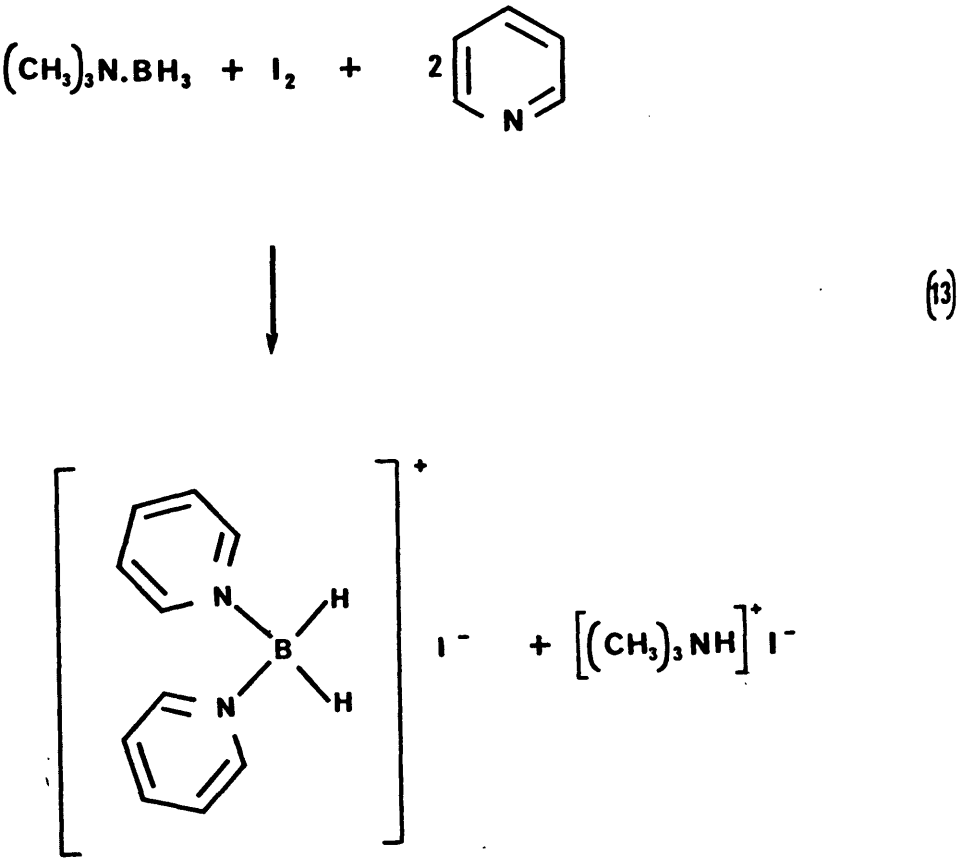
Amine-boranes can be halogenated at the boron atom. These reactions are discussed in detail in section 4.2.

4.1.3.3. *Cleavage of B - N bond*

Many important reactions of amine-boranes involve cleavage of the boron-nitrogen bond. An example of this is the reaction with certain Lewis bases (12).[27]

$$LiH + (CH_3)_2N.BH_3 \longrightarrow Li[BH_4] + (CH_3)_3N \qquad (12)$$

Bis(pyridine) boronium salts have been synthesised in quantitative yields from the reaction of pyridine, iodine and trimethylamine-borane, (13).[28,29]



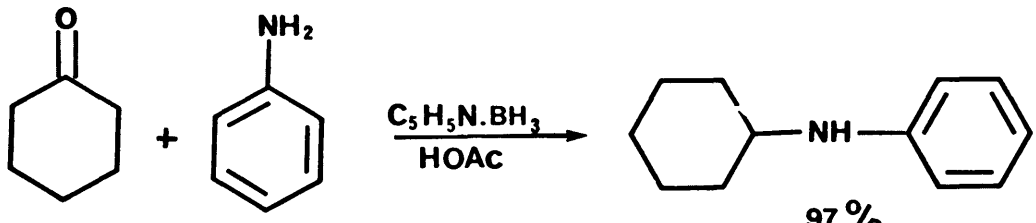
(13)

It was shown that with borane as the reference acid, the base strength of trimethylphosphine was greater than the base strength of trimethylamine. Removal of a volatile amine, such as trimethylamine, therefore provides a convenient method for the essentially quantitative preparation of a variety of phosphine- and amine-boranes (15).[30]

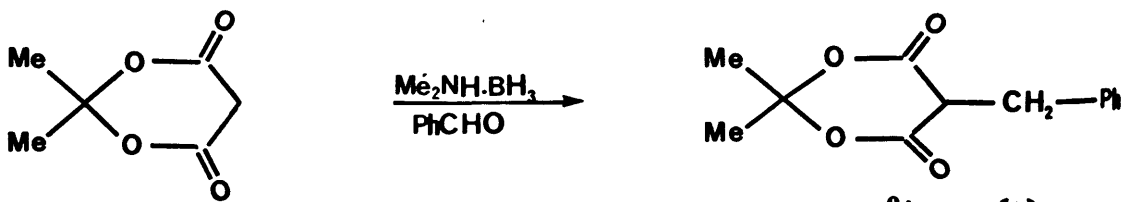
$$(n\text{-}C_4H_9)_3P + (CH_3)_3N.BH_3 \longrightarrow (CH_3)_3N + (n\text{-}C_4H_9)_3P.BH_3 \quad (15)$$

4.1.4.1. *Amine-boranes as reducing agents*

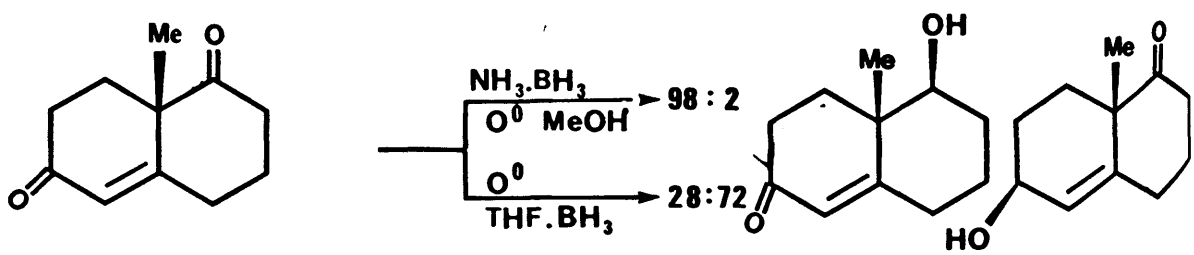
Amine-boranes are versatile reducing agents. Greatly overshadowed in the past by their more popular relatives (e.g. borane-THF,[31] borane-methyl sulphide,[32] sodium borohydride,[33] and sodium cyanoborohydride[34]), amine-boranes are currently receiving greater attention.[35] These reagents, which may be used under protic and aprotic conditions, show a wide range of reactivity and diversity, examples of which are shown below, (16-20).


O
NH2
C5H5N.BH3
HOAc
NH
97 %

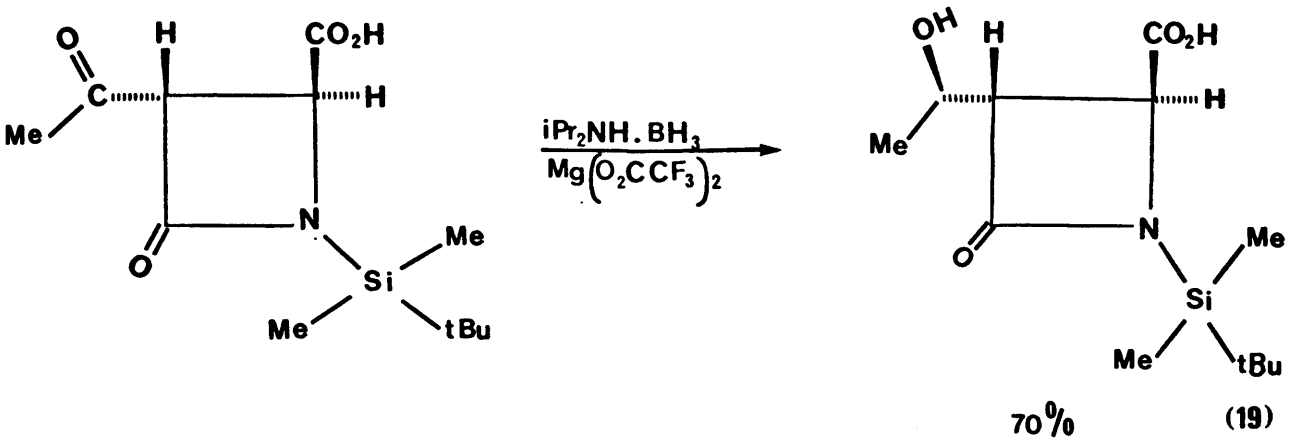
(16)


Me
Me
O
O
O
O
Me2NH.BH3
PhCHO
CH2—Ph
94 %

(17)

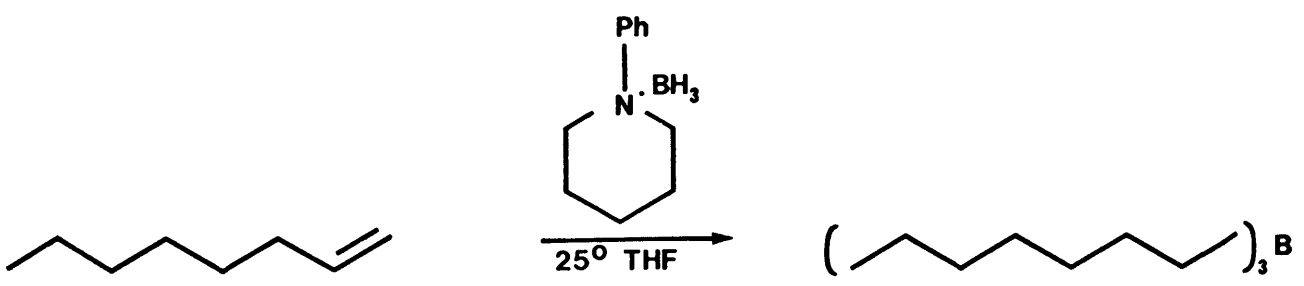

Me
O
NH3.BH3
O0 MeOH
98 : 2
O0
THF.BH3
28:72
OH
Me
O
HO

(18)


O
H
CO2H
C
H
Me
N
O
Me
Si
Me
tBu
iPr2NH.BH3
Mg(O2CCF3)2
OH
H
CO2H
Me
H
N
O
Me
Si
Me
tBu

70%

(19)

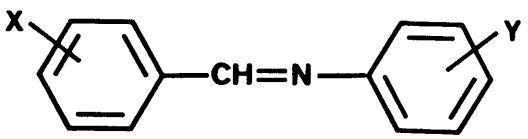

Ph
N.BH3
25° THF
)3B

100%

(20)

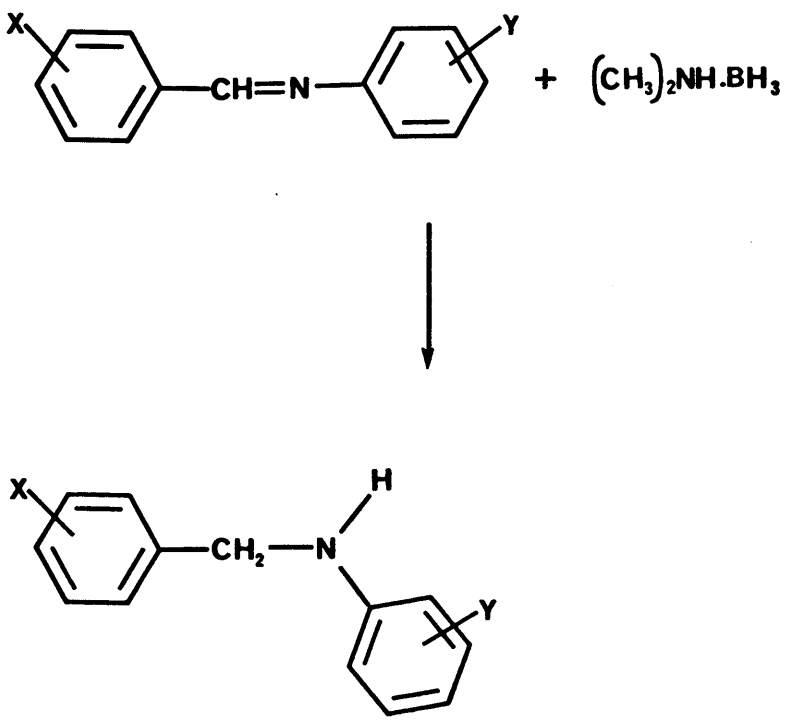
4.1.4.2. *Reduction of Imines*

The effect of $Me_2NH.BH_3$ on the imine linkage as in compound II and derivatives thereof with X and Y = chloro, nitro, hydroxy, methoxy, carboxy, carbalkoxy and sulfanamido, was studied in 1961 by Billman and McDowell.[41]



II

These compounds were readily converted to the corresponding amines (21).



(21)

Yields of these secondary amines were generally good, typically around 90%. The ease and speed of such reductions are comparable to, or better than, similar reactions with sodium borohydride or lithium aluminium hydride. An interesting advantage in the use of amine-boranes is their ability to reduce in acidic media which is not possible with the anionic hydrides.

4.1.5 *Summary*

The most convenient laboratory synthesis of amine-boranes appears to be the method of Nainan and Ryschkewitsch (5). In this preparation, the reaction is carried out in a single step and does not require the synthesis of amine-hydrochlorides as in the method of Schaeffer and Anderson (2).

Amine-boranes, though first synthesised over thirty years ago, are undergoing a revival of current interest because of their reducing abilities. In recent years, chemical suppliers, such as the Aldrich Chemical Company, have been promoting the use of amine-boranes as selective and effective reducing agents in organic synthesis.

4.2 AMINE-HALOBORANES

4.2.1 *Introduction*

The adduct of trifluoroborane with ammonia, $H_3N.BF_3$, was one of the first boron-nitrogen compounds to be recognised.[42] The heat of the gas phase reaction was experimentally determined by Bauer and co-workers[43] to be 175.56 kJ mol^{-1}.

Niedenzu and Dawson,[44] questioned the validity of early reports of the formation of addition compounds of ammonia with trihalogeno-boranes other than BF_3. In contrast to BF_3, the heavier halogeno-boranes are readily susceptible to aminolysis of the boron-halogen bonds and the resulting triaminoborane, $B(NH_2)_3$, readily decomposes with the elimination of ammonia and the formation of polymeric materials.[45] However, a wide range of amines have been found to yield isolable addition compounds of the amine-borane type with trihalogenoboranes.

4.2.2 *Synthesis of Amine-Haloboranes* $R_nH_{(3-n)}N.BH_yX_{(3-y)}$

Like the amine-boranes, these have been synthesised by a variety of methods. Compounds of the general formula $R_nH_{(3-n)}N.BH_yX_{(3-y)}$ have been prepared for y = 1 or 2 with X = F, Cl, Br or I. Some examples of mixed halo-compounds, such as $Me_3N.BHFI$[46] are known also.

4.2.2.1. *Halogenation of Amine-boranes with Halogens or Hydrogen Halides*

Geanangel and co-workers,[47,48] have investigated the halogenation of amine-boranes using carefully controlled addition of halogens or hydrogen halides. These reactions were monitored by proton nmr since the chemical shift of the amine alkyl protons changes significantly with B-halogenation.

The bromination of trimethylamine-borane (22) and the fluorination and chlorination of t-butylamine-borane (23) by these methods produce yields greater than 50% in each step.

$$(CH_3)_3N.BH_3 \xrightarrow{Br_2} (CH_3)_3N.BH_2Br \xrightarrow{Br_2} (CH_3)_3N.BHBr_2 \xrightarrow{Br_2} (CH_3)_3N.BBr_3 \qquad (22)$$

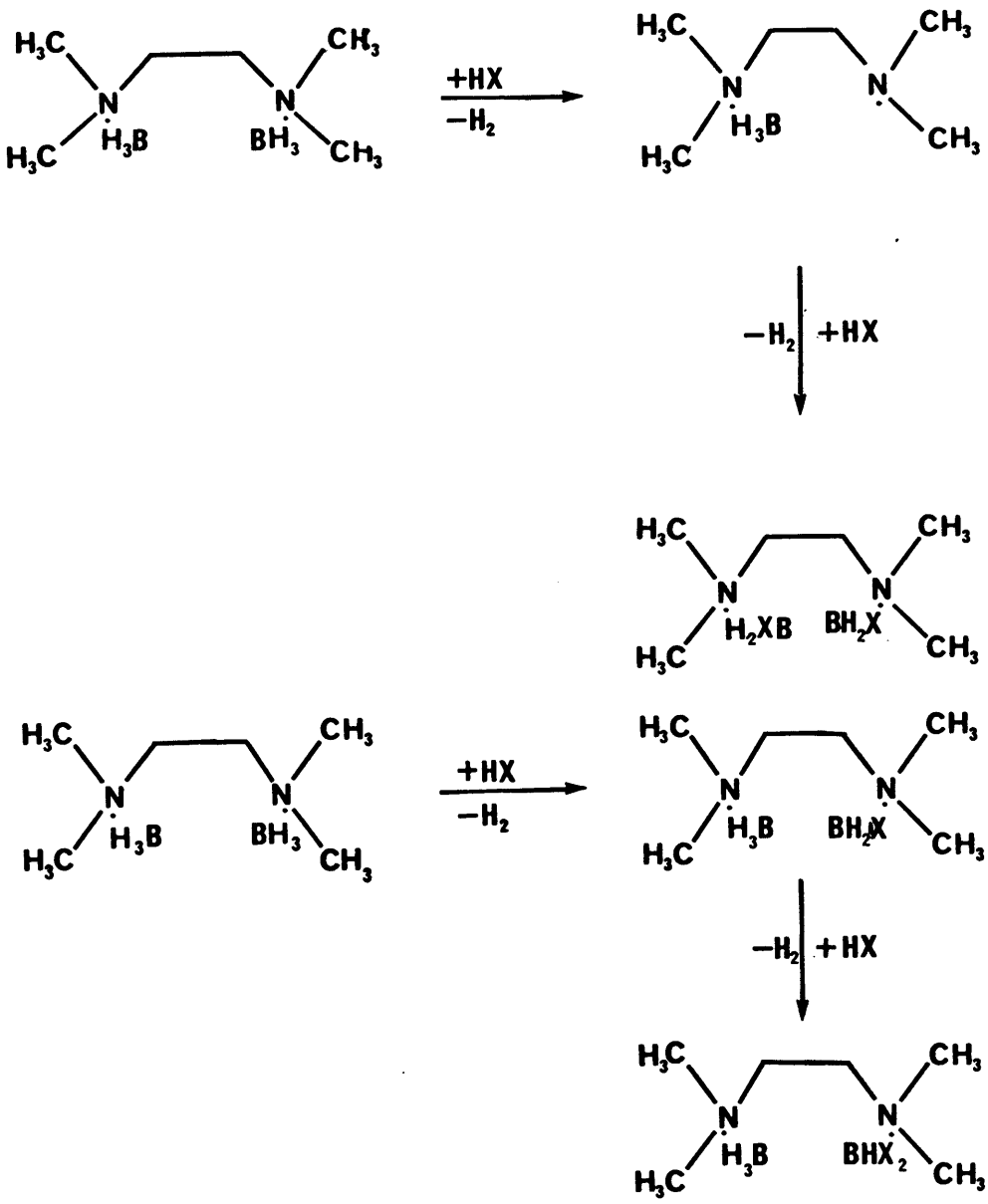
$$(CH_3)_3CNH_2.BH_3 \xrightarrow[-H_2]{+HX} (CH_3)_3CNH_2.BH_2X \xrightarrow[-H_2]{+HX} (CH_3)_3CNH_2.BHX_2 \xrightarrow[-H_2]{+HX} (CH_3)_3CNH_2.BX_3 \xrightarrow[-H_2]{+HX} [(CH_3)_3CNH_3][BX_4] \qquad (23)$$

(X = F, Cl) (X = F)

This halogenation method was most successful for relatively large scale reactions (20 mmol) in somewhat dilute solutions, since these conditions reduce the number of alternative products formed.

B-halogenation of N,N,N',N'-Tetramethylethylenediamine-*bis*borane has been carried out by Hu and Geanangel[49] also using hydrogen halides or halogens. Successive halogenation was considered to proceed *via* (24) rather than (25) on electronic grounds. It is clear from this that the inductive effect caused by halogens on boron makes the remaining hydrogens less sesceptible towards electrophilic attack.

In a further study on the reactions of diamines, Geanangel and Van Paaschen[50] reacted ethylenediamine, piperazine and triethylenediamine with $(CH_3)_3NBH_2F$, $(CH_3)_3N.BHF_2$ and $(CH_3)_3N.BF_3$. All the products from the diamines, which could be characterised, were found to contain only one BH_3 group. Ethylenediamine was found to displace less trimethylamine than either of the other diamines, making isolation and purification of the products more difficult.



4.2.2.2. *Reaction with Alkyl-Halides*

The general equation for the reaction of amine-boranes with alkyl halides is (26).

$$(\text{amine}).BH_3 + RX \longrightarrow (\text{amine}).BH_2X + RH \qquad (26)$$

The ease with which these reactions proceed depends on both the amine-borane and the halide. Evidence has been presented by Ryschkewitsch and

Miller[51] that the substitution of hydrogen by halogen may proceed by either a polar or free-radical pathway. Polar reactions are observed with organic halides such as chlorotriphenylmethane. It is claimed that reactivity increases with increasing stability of the carbonium ion. The proposed reaction pathway is hydride abstraction from the borane adduct by a carbonium ion paired with halogen ion, followed by formation of the boron-halogen bond to yield the neutral halogenated boron adduct (27).

$$R_3N.BH_3 + [(C_6H_5)_3C][Cl] \longrightarrow [R_3N.BH_2]^+ + [Cl]^- + (C_6H_5)_3CH$$
$$\longrightarrow R_3N.BH_2Cl + (C_6H_5)_3CH \qquad (27)$$

Supporting evidence for this mechanism came from a study of the solvent and the way the structure of the reactants influenced the reaction rate and by the isolation of the intermediates.

In contrast to the reaction with chlorotriphenylmethane, amine-boranes react with alkyl halides such as $1,2\text{-}Cl_2C_2H_4$ or CCl_4 or CCl_3Br by a free radical chain mechanism which can be initiated by benzoylperoxide (28).[51]

$$R^{\cdot} + (\text{amine}).BH_3 \longrightarrow RH + (\text{amine}).BH_2^{\cdot}$$
$$(\text{amine}).BH_2^{\cdot} + RCl \longrightarrow (\text{amine}).BH_2Cl + R^{\cdot} \qquad (28)$$

R· is a radical derived by abstraction of halogen from the halocarbon. The yields of such reactions are generally high, for example the chlorination of dimethylsulphide-borane by CCl_4 (29),[52] gives dimethylsulphide-chloroborane in quantitative yield.

$$(CH_3)_2S.BH_3 + CCl_4 \xrightarrow[20\ hr]{reflux} (CH_3)_2S.BH_2Cl + CHCl_3 \qquad (29)$$

4.2.2.3. *Chlorination with Sodium Hypochlorite*

Kelly and coworkers[53] have found that numerous tertiary-alkylamine-boranes undergo successive β-chlorination on treatment with aqueous sodium hypochlorite. The trend in the second-order rate constants in the trimethylamine-borane system at pH 8.5 is k $Me_3N.BH_3$ > k $Me_3N.BH_2Cl$ > k $Me_3N.BHCl_2$. The activity of tertiary amine-boranes towards hypochlorite contrasts with that of some secondary amine-boranes[54] which have been proposed to undergo quantitative hydride oxidation followed by chlorination of the free amine.

4.2.2.4. *Reaction of BCl_3 with Amine-boranes*

Ratajczak[55] has shown that direct reaction of BCl_3 with amine-boranes is a convenient synthesis of mono, di and trihalogenoborane adducts, (30), (31), (32).

$$(C_2H_5)_3N.BH_3 + BCl_3 \longrightarrow (C_2H_5)_3N.BCl_3 + \tfrac{1}{2}B_2H_6 \qquad (30)$$

$$3(C_2H_5)_3N.BH_3 + BCl_3 \longrightarrow 3(C_2H_5)_3N.BH_2Cl + \tfrac{1}{2}B_2H_6 \qquad (31)$$

$$3(C_2H_5)_3N.BH_3 + 2BCl_3 \longrightarrow 3(C_2H_5)_3N.BHCl_2 + B_2H_6 \qquad (32)$$

The exact outcome of the reaction depends on the stoichiometric quantities of triethylamine-borane and boron trichloride used in the reaction. Triethylamine-monochloroborane may also be prepared by reaction of triethylamine-borane and triethylamine-dichloroborane (33).

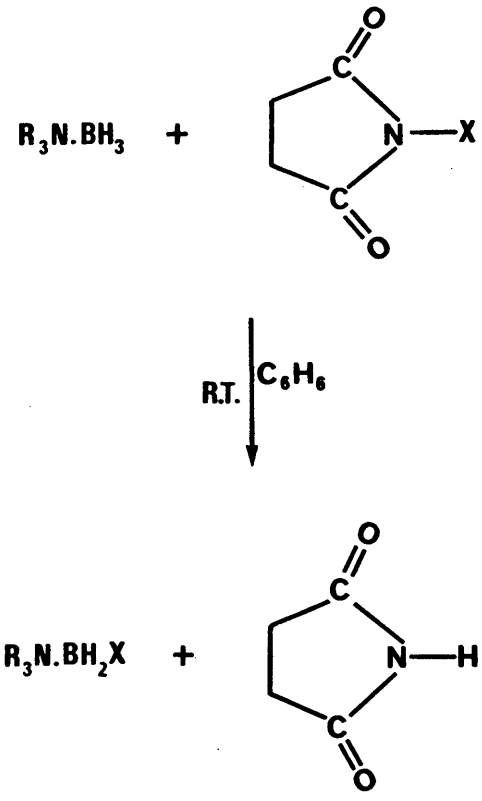
$$(C_2H_5)_3N.BHCl_2 + (C_2H_5)_3N.BH_3 \longrightarrow 2(C_2H_5)_3N.BH_2Cl \qquad (33)$$

Triethylamine-dichloroborane is also prepared by a 3 : 1 reaction of triethylamine-monochloroborane with boron trichloride (34).

$$3(C_2H_5)_3N.BH_2Cl + BCl_3 \longrightarrow 3(C_2H_5)_3N.BHCl_2 + \tfrac{1}{2}B_2H_6 \qquad (34)$$

4.2.2.5. *Reaction of N-halosuccinimide with Amine-Boranes*

The reaction of N-bromo- or N-chlorosuccinimide with amine-boranes in benzene (35).[56]



(35)

affords a convenient method for preparing amine-haloboranes under relatively mild conditions. Typical yields of product are 60-75%. Although allylic and benzylic bromination is well established as a free-radical chain reaction[57] in which the bromine atom functions as the chain carrier,[58] it is unlikely that this is the case for amine-boranes. The reasons are (i) there is no detectable induction time and (ii) the reaction proceeds rapidly without irradiation or added peroxide. An ionic mechanism has been proposed instead, (36) and (37). The N-halosuccinimide serves as a source of a low steady-state concentration of halogen.

$$X_2 + H\text{-}BH_2.\ NR_3 \longrightarrow HX + X - BH_2\ NR_3 \qquad (36)$$

4.2.2.6. *Halogenation with Metal Halides*

Metal salts, such as mercury (II) and silver (I) compounds, are important reagents for the synthesis of B-monosubstituted amine-boranes (38),[59] (X=Cl, Br),

$$(CH_3)_3N.BH_3 + 2Hg[X]_2 \longrightarrow (CH_3)_3N.BH_2X + Hg_2[X]_2 + HX \quad (38)$$

Average yields were of the order of approximately 90% using $Hg[Br_2]$. All of the available data are consistent with the hypothesis that mercury (II) halides react with amine-boranes by a polar mechanism involving hydride transfer via a transition state.[60] Gyori and Emri[61] have postulated that, in view of the above results and others described for $Hg[Cl_2]$,[62] similar redox reactions may also take place with other Hg (II) compounds [e.g. $Hg[F_2]$, $Hg[OAc]_2$, $Hg[SCN]_2$, etc.], although to date, no evidence for this has been reported.

4.2.3 *Summary*

From the synthesis described above it is apparent that B-halogenation of amine-boranes and diamine-*bis* boranes generally gives good yields irrespective of the methods employed. The use of alkyl halides, mercury (II) halides and N-halogens reduces the inherent difficulties associated with the use of anhydrous hydrogen halides and halogens. Chlorination using aqueous sodium hypochlorite offers an alternative synthetic pathway without the need for dry conditions.

4.2.4. *Structures of Amine-Haloboranes*

To date no structural data have been reported for $R_nH_{(3-n)}N.BH_yX_{(3-y)}$ compounds from either solid state or gas phase studies. Gas phase data for $(CH_3)_3N.BF_3$ were reported.[63] This compound which is undissociated at room temperature was calculated to have a boron-nitrogen bond length of 1.636 ± 0.04 Å.

4.2.5 *Reactions of Amine-Haloboranes*

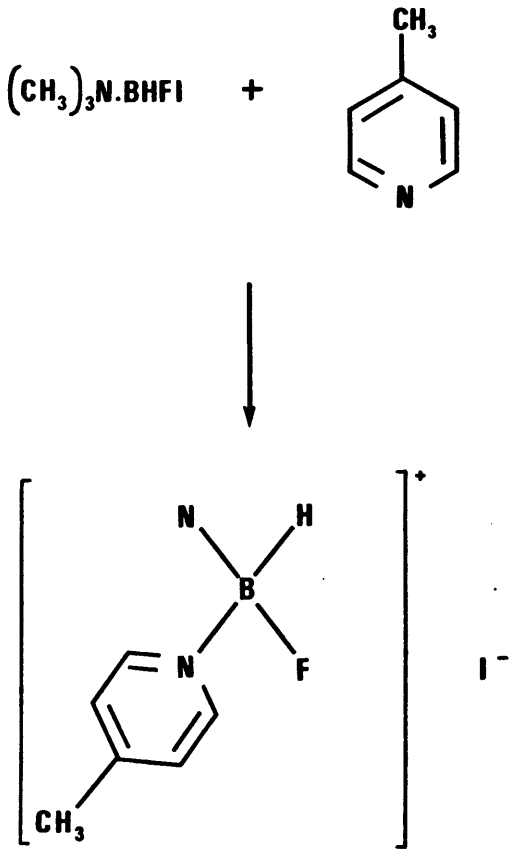
Ryschkewitsch[46] has claimed that the most versatile route to boron cations is the displacement of halide from a haloborane by a neutral donor (39).

$$D' + DBH_2Y \longrightarrow [D'DBH_2][Y] \qquad (39)$$

This reaction was first formally developed by Nöth and coworkers for displacement of chloride[64,65] for instances where D' and D are amines. Subsequent extensions of the technique were made by Ryschkewitsch[66,67] and Miller[68,69] who applied the displacement reaction to amine-iodoboranes and to introduce a large variety of donors D' into the coordination sphere of the cations.

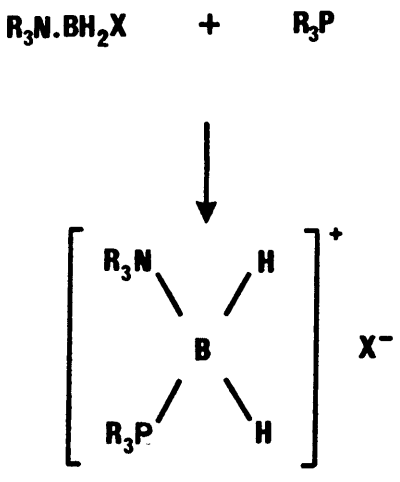
Halide displacement from the adduct follows the expected order $[I]^- > [Br]^- > [Cl]^-, [F]^-$. Since the rate of reaction with a given haloborane adduct does depend on the nature of the displacing donor, the reaction appears to be of S_N2 type, at least in noncoordinating solvents like benzene or carbon tetrachloride and in instances where electronic stabilisation of a trigonal cationic[66,67] intermediate is not possible. Adducts of tertiary alkyl amines are less reactive than those of primary or secondary amines, or of pyridine derivatives, especially when chloride or bromide are displaced, or when the displacing donor has itself a large steric requirement.[71] Finally, the readiness with which substitution of halide occurs on neutral adducts of haloboranes is also influenced by other electronegative substituents on boron. Progressive substitution of hydrogen by halogen tends to deactivate the molecule toward displacement of halide. Thus trimethylamine-diiodoborane is practically inert toward trimethylamine whereas the monoiodo adduct reacts readily with cation formation.[72] This decrease in reactivity makes it difficult to prepare ions of the type DD'BHX by the displacement route, since the more drastic reaction conditions required to promote the competitive displacement of one neutral donor by the

other.[73] An exception is the reaction of $(CH_3)_3N.BHFI$ with 4-methylpyridine (40), which takes place under mild conditions and leads to the assymetric cation.[74]



(40)

Loss of the donor originally attached to boron is a possible complication even under mild reaction conditions when two different neutral donors are to be attached. It is then advisable to start with the stronger donor already attached to boron and displace halide with the weaker one. Thus, mixed amine-phosphine cations are best prepared from amine-haloboranes rather than from phosphine-haloboranes (41),



(41)

the reverse procedure generally leading to mixtures. This problem is particularly awkward when dealing with polydentate amines or phosphines.[75] Here favourable ring closure by the chelating donor leads to displacement of the original donor, as, for example, of trimethylamine in the reaction of $(CH_3)_3N.BHBr_2$ with tetramethylethylenediamine,[76] or in the reaction of $(CH_3)_3N.BH_2I$ with N-dimethylpiperazine, which even gives the strained bicyclic norbornane homorph.[77]

4.3 AMINE-CYANOBORANES

4.3.1 *Introduction*

The known chemistry of amine-boranes and the convenient synthesis of sodium cyanoborohydride (42)[62]

$$2Na[BH_4] + Hg[CN]_2 \xrightarrow[\Delta \ 3\ hrs]{THF} 2Na[BH_3CN] + Hg^{o} + + H_2 \qquad (42)$$

led to the synthesis of a series of amine-cyanoboranes. These adducts have been used as intermediates in the synthesis of boron analogues of the α-amino acids. They are also biologically active species in their own right and the result of such studies is discussed later.

4.3.2 *Synthesis of Amine-Cyanoboranes*

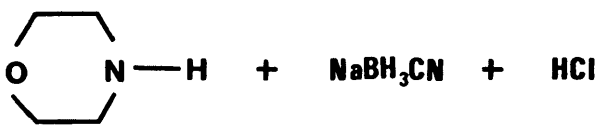
Many of the reactions leading to amine-cyanoborane synthesis are analogous with those previously discussed for amine-boranes. Spielvogel and coworkers[78] have prepared primary, secondary and tertiary aliphatic and aromatic amine-cyanoboranes by the reaction of sodium cyanoborohydride and amine-hydrochlorides in refluxing THF (43)

$$Na[BH_3CN] + amine.HCl \xrightarrow[65^{o}C]{THF} amine.BH_2CN\ (III - VIII) + H_2 + Na[Cl] \qquad (43)$$

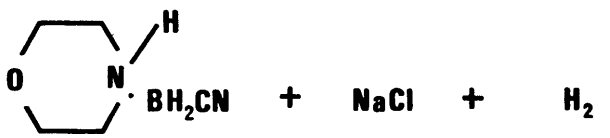
(amine = Me_3N (III); Me_2NH (IV); $MeNH_2$ (V); C_5H_5N (VI); $PhNH_2$ (VII); $pMeC_6H_4NH$ (VIII).)

Yields of products ranged from 48% ($MeNH_2$) to 90% ($p\text{-}MeC_6H_4NH_2$), with the exception of VI, which could not be solidified, all of the above are white, crystalline solids, readily purified by either recrystallisation or sublimation.

In a similar reaction Kelly et al[79] have prepared morpholine-cyanoborane, IX, in 29% yield by the reaction of sodium cyanoborohydride with HCl and morpholine (44).



(44)



IX

The reaction of I_2 with sodium cyanoborohydride in the presence of a donor L would be expected to generate LBH_2CN addition compounds. Martin and coworkers[80] have investigated such reactions (45) and (46).

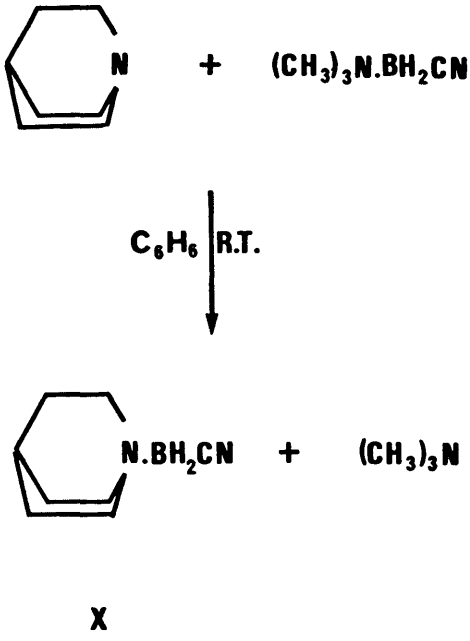
$$n\,Na[H_3BCN] + \frac{n}{2}\,X_2 \longrightarrow n\,Na[X] + [BH_2CN] + \frac{n}{2}\,H_2 \qquad (45)$$

$$nL + [BH_2CN]_n \longrightarrow nLBH_2CN \qquad (46)$$

(L = Lewis-base)

The addition of the Lewis base is delayed until the halogen has fully reacted with the cyanoborohydride. Typical yields are in the region of 25%, with no appreciable difference if chlorine or bromine are used in lieu of iodine.

Displacement reactions which are a feature of amine-borane chemistry may also be used in the synthesis of amine-cyanoboranes. The displacement of trimethylamine from trimethylamine-cyanoborane has been utilised by Geanangel *et al*[81] in their synthesis of quinuclidine-cyanoborane, X, (47).



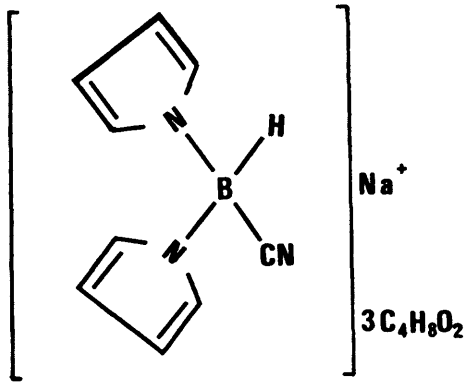
X

(47)

The yield of white crystalline solid was 87%. The pronounced donor ability and favourable steric disposition of quinuclidine render it an excellent displacing agent, moreover, the triethylamine can be periodically pumped away from the reaction mixture.

4.3.3 *Amine-Aminocyanoboranes*

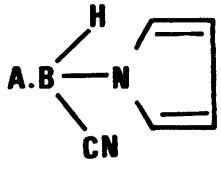
Gyori and Emri[82] have synthesised several amino-cyano (pyrrolyl) borane complexes containing a chiral boron, from the reaction of sodium cyanohydridopyrrolyl borate - dioxanate, $NaBH(NC_4H_4)_2CN.3C_4H_8O_2$, XI, with amine hydrochloride, (48).



\+ A.HCl (48)

XI

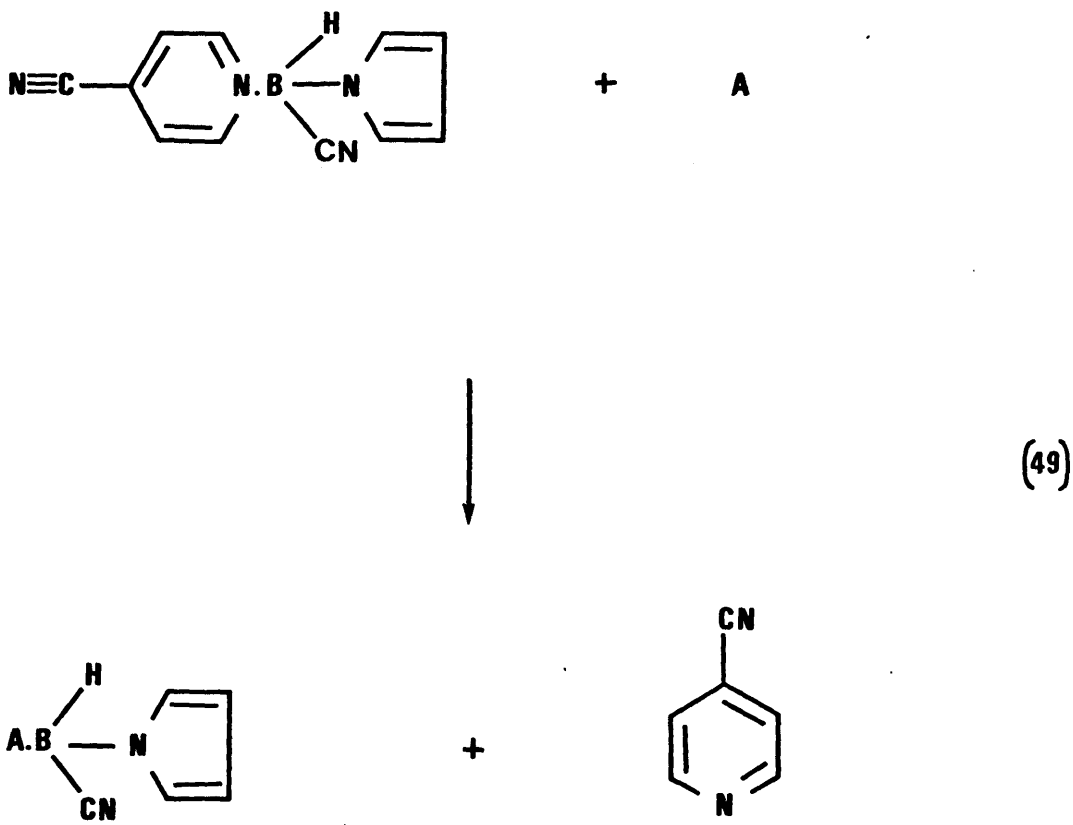
T.H.F R.T.



\+ $3C_4H_8O_2$ +

\+ NaCl

Base displacement reactions from the 4-cyanopyridine complex ^{4}-$CNC_5H_4N.BH(NC_4H_4)CN$, XII, were also reported (49). They concluded that the cyano-pyrrolyl-borane is, like borane,[83] a soft (or borderline) Lewis Acid.



(49)

(A = amine)

4.3.4 *Reactions of Amine-Cyanoboranes*

Kelly and coworkers[53] have described the mechanism of hydrolysis of amine-cyanoboranes in alkaline solution, (50).

$$R_2NH.BH_2\text{-}CN + 2H_2O + 2[OH]^- \longrightarrow R_2NH + [B(OH)_4]^- + 2H_2 + [CN]^- \quad (50)$$

It was found that cyanoborane adducts of $(CH_3)_3N$ and N-methyl-morpholine reacted very slowly and at rates independent of alkali up to 0.09 M $[OH]^-$. In oxidation studies with iodine only 2% of the cyanoborane was oxidised in 10 minutes at 20°C. This contrasts with the rapid oxidation of analogous borane adducts. A similar decrease in reactivity has also been observed on substitution by chloride for hydride in borane adducts.[84]

Although amine-boranes and sodium cyanoborohydride are known to be effective and selective reducing agents, they have not as of yet been utilised in that field. Thus, reactions of amine-cyanoboranes have been limited to their use in the synthesis of amine-carboxyboranes and the corresponding ester and amide derivatives.

The conversion of amine-cyanoboranes to amine-carboxyboranes via an N-ethylnitrilium intermediate is shown in (51).

$$(CH_3)_3N.BH_2CN \xrightarrow{[Et_3O][BF_4]} [(CH_3)_3N.BH_2CNEt][BF_4] \quad (51)$$

XIII → XIV

XIV → (Na OH) → XV

XV → (HCl) → XVI

XVI: $(CH_3)_3N.BH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH$

XV: $(CH_3)_3N.BH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_2CH_3$

This reaction sequence was first reported by Spielvogel *et al.*[85] Compound XVI, is the protonated boron analogue of the dipolar amino acid betaine, $(CH_3)_3\overset{+}{N} - \overset{O}{\overset{\|}{C}} - O^-$. The use of triethyloxonium tetrafluoroborate, $[Et_3O][BF_4]$,[86] is critical to the synthesis. The N-ethylnitrilium salt, XIV, was not isolated but instead converted *in situ* to the N-ethylamide, XV.

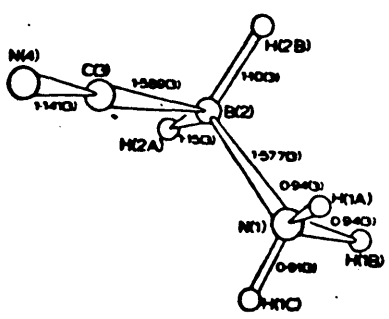
Ammonia-carboxyborane, $H_3NBH_2CO_2H$,[87] XVII which is the B analogue of glycine, $H_3NCH_2CO_2H$, was the first of the borane-analogues to contain hydrogen bonded directly to nitrogen. Ammonia-carboxyborane may be prepared by an amine exchange reaction, (52).

$$\underset{\text{XVI}}{(CH_3)_3N.BH_2CO_2H} + NH_{3(liq)} \longrightarrow \underset{\text{XVII}}{H_3N.BH_2CO_2H} + (CH_3)_3N \qquad (52)$$

Typical yields of XVII were 50-55%. Longer reaction periods did not increase the amounts of product.

Ammonia-carboxyborane, which may be considered the parent of the class of boron analogues of the α-amino acids, has like its glycine counterpart, the ability to form peptide linkages and to be incorporated into proteins. The structure of ammonia-carboxyborane (Fig. 2) has been established by single crystal X-ray analysis.[87]

Figure 2: *Ammonia Carboxyborane*



Spielvogel *et al*[88] have also synthesised a series of esters derived from boron analogues of amino acids, having the general formulation, amine.BH_2COOR. Trimethylamine-carbethoxyborane,

$(CH_3)_3N.\ BH_2COOCH_2CH_3$,

XVIII is isolated in 34% yield from reaction (12). Trimethylamine-carbomethoxyborane, XIX,[89] was prepared in 82% yield by condensing $(CH_3)_3N.BH_2COOH$ and methanol with dicyclohexylcarbodiimide (DCC) at room temperature for 1 week, (53).

$$\underset{\text{XVI}}{(CH_3)_3N.BH_2-\overset{\overset{O}{\|}}{C}-OH} + CH_3OH \xrightarrow[CH_2Cl_2]{DCC} \underset{\text{XIX}}{(CH_3)_3N.BH_2-\overset{\overset{O}{\|}}{C}-OCH_3} + (C_6H_{11}NH)_2CO \qquad (53)$$

DCU

An extension of the reaction period to two weeks led to an increase in the yield of XIX to 98%.

The trimethylsilyl derivative, $(CH_3)_3N.BH_2COO\ Si(CH_3)_3$, XX, was prepared via lithiation of $(CH_3)_3N.BH_2COOH$ and subsequent reaction of the lithium salt, XXI with trimethylsilylchloride, (54).

$$\underset{\text{XVI}}{(CH_3)_3N.BH_2-\overset{\overset{O}{\|}}{C}-OH} \xrightarrow[Et_2O]{nC_4H_9Li} \underset{\text{XX}}{(CH_3)_3N.BH_2-\overset{\overset{O}{\|}}{C}-OLi} \qquad (54)$$

$$\underset{\text{XXI}}{(CH_3)_3N.BH_2-\overset{\overset{O}{\|}}{C}-O-Si(CH_3)_3}$$

The silyl ester was isolated in 58% yield as a clear moisture sensitive liquid that solidifies on standing. Ammonia-carbomethoxyborane, $H_3N.BH_2COOCH_3$, XXII, was prepared in 49% yield by an amine exchange reaction involving $(CH_3)_3N.BH_2COOCH_3$ and excess liquid ammonia, (55).

$$(CH_3)_3N.BH_2 - \overset{O}{\overset{\|}{C}} - O\,CH_3 \quad + \quad NH_{3(liq)}$$

XXI

2 weeks | R.T. (55)

$$H_3N.BH_2 - \overset{O}{\overset{\|}{C}} - O\,CH_3 \quad + \quad (CH_3)_3N$$

XXII

4.3.5. *Biological Activity of the Borane-Adducts*

Both amine- and phosphine-cyanoboranes and carboxyboranes have been shown to possess interesting biological properties. For example they are known to be hyperlipidemic agents in mice, i.e. they lowered serum cholestrol and triglyceride levels significantly.[90] These compounds appear to inhibit lipid synthesis in the early stages. The ability to lower serum cholestrol levels appears to correlate with the suppression of the regulatory enzyme of cholestrol synthesis, β-hydroxy - β-methyl glutaryl - CoA reductase activity. The reduction of serum triglycerides correlates with the ability of the borane to suppress liver fatty acid synthetase activity. It was noted by Spielvogel and coworkers[91] while studying the effects of the α-aminoboron analogues on tumor cell metabolism, that these agents interfered with oxidative phosphorylation processes of mitochondria, inhibited lysosomal enzymatic hydrolytic activities and elevated cyclic adenosine monophosphate levels. Since commercially available anti-inflammatory agents, phenylbutazone salicylates and indomethacin have similar effects on cellular metabolism, the boron analogues were tested for anti-inflammatory activity in rodents. Initial studies showed that these boron analogues can be used at safe therapeutic doses. Administration of $(CH_3)_2NH.BH_2CN$ resulted in at least 50% inhibition of carrageenan-induced edema in mouse footpads. Administration of $(CH_3)_3N.BH_2CN$ caused 80% inhibition of the writhing reflex, which is similar to inflammation pain. In the induced arthritic screen in rats, three weeks dosing of $C_5H_5N.BH_2CN$ caused >80% inhibition, with $(CH_3)_3N.BH_2CN$ causing 96% inhibition. A positive correlation with *in vivo* anti-arthritic activity is seen in the ability of these boron analogues to elevate levels of cyclic adenosine monophosphate, which account for the ability of these agents to block lysosomal enzyme release and prostaglandin synthesis and release. The exact mechanism by which these boron analogues cause elevation in cyclic

adenosine monophosphate levels is not fully understood and requires further study. Toxicity and side-effects do not appear to be problems using boron analogues at the required therapeutic dose.

4.4 PHOSPHINE-BORANES

4.4.1 *Introduction*

As early as 1890, Besson synthesised $H_3P.BCl_3$, the first compound to contain a discrete P - B bond.[92] In 1948 Gamble and Gilmont[93] reported the preparation of $H_3P.BH_3$. However the first systematic studies of phosphine-boranes were not until 1953.[94] The unexpected thermal and chemical stability of $(CH_3)_3P.BH_3$ and its homologues, as well as the formation of unusual cyclic and polymeric phosphine-boranes were of particular interest. Structural studies[95-101] have shown that phosphine-boranes are similar to their nitrogen analogues. However, their comparatively peculiar properties such as inertness to oxygen and moisture and sometimes even to strong acid and base, are claimed to result from the low polarities and polarisibilities of the P - B and B - H bonds rather than from structural consequences.[102-107]

4.4.2. *Synthesis of Phosphine-Boranes*

4.4.2.1. *Amine-Displacement*

Most of the synthetic routes for the preparation of amine-boranes are applicable to the synthesis of phosphine-boranes. Indeed, since phosphorus is a much stronger base towards borane than nitrogen, the displacement of a volatile amine from an amine-borane is a viable synthetic pathway to phosphine-boranes, (56)

$$R_3P + R_3N.BH_3 \longrightarrow R_3P.BH_3 + R_3N \qquad (56)$$

With an excess of phosphine, quantitative yields may be obtained.

4.4.2.2. *Iodine Method*

The reaction of $(C_6H_5)_3P$, $Na[BH_4]$ and iodine in monoglyme (57)

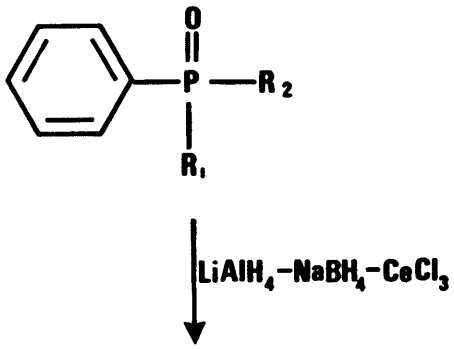
$$(C_6H_5)_3P + Na[BH_4] + \tfrac{1}{2}I_2 \xrightarrow[\text{monoglyme}]{\text{reflux}} (C_6H_5)_3P.BH_3 + Na[I] + \tfrac{1}{2}H_2 \quad (57)$$

XXIII

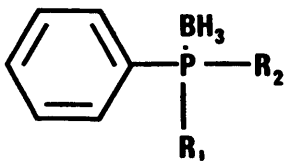
yields triphenylphosphine-borane (XXIII) almost quantitatively.[108] Mixed phosphine-boranes may be prepared similarly. For example, dimethylphenylphosphine-borane is prepared in 92% yield from $(C_6H_5)(CH_3)_2P$ with the above synthetic procedure.

4.4.2.3 *From Phosphine-Oxides*

In 1985, Imamoto *et al*,[109] reported a novel synthesis of phosphine-boranes from phosphine-oxides. This one-pot synthesis employed a novel reagent system, $Li[AlH_4]$ - $Na[BH_4]$ - $Ce[Cl]_3$. In THF at room temperature, under N_2, various phosphine oxides reacted smoothly (58)



(58)



to produce phosphine-boranes in yields of 75-95%.

4.4.3. *Bonding in Phosphine-Boranes*

It has been shown in a large number of physical and preparative studies on phosphine-boranes, with a great variety of substituents of

phosphorus and boron,[93,94] that the P - BX_3 group is greatly influenced by the electronic effect of those substituents. In a study on adduct stability Mente and Mills,[110] reported that $Me_3P.BH_3$ is less stable than the corresponding tribromo adduct but more stable than the trichloro and trifluoro adducts.

Generally, species containing aromatic R groups, such as triphenylphosphine borane have been found to be particularly stable. In fact, $(C_6H_5)_3P.BH_3$ was unchanged after six months in air and was recovered unchanged from attempted oxidation with alkaline hydrogen peroxide. It was also reported to resist 3MHCl at 150° for three hours.[111]

Earlier studies on the bonding properties of phosphine-boranes have included valence-bond[112,113] and molecular orbital descriptions.[92-101] It was suggested from these studies that the reduced polarity of the B-H bond and the apparent non-hydridic character of BH_3 are due to the contributions of phosphorus d-orbitals and the BH_3 group orbitals. An increase in P-B bond order and a transfer of negative charge from hydrogen to boron and phosphorus was also postulated.[110] Experimental evidence such as the comparatively high P-B rotational barriers,[108,109] slightly reduced P-B bond lengths and compressed C-P-C bond angles,[108,109] has been noted. However, dipole moment studies[114-117] leave no doubt that phosphine-boranes are molecules of high overall polarity and this also becomes obvious from other gross physical properties; such as low solubilities in organic solvents and high melting points.

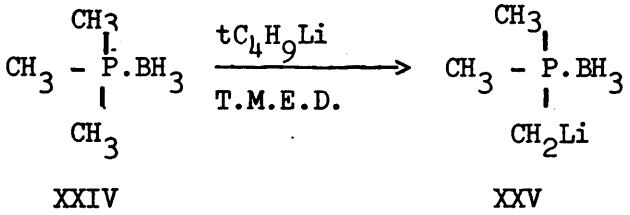
4.4.4. *Reactions of Phosphine-Boranes*

Like their nitrogen counterparts, phosphine-boranes undergo reactions which involve retention of, or cleavage of, the phosphorus-boron bond. These reactions, as well as the use of phosphine-boranes as hydroborating agents are discussed below.

4.4.4.1. *Phosphorus-boron bond retention*

In 1980, Schmidbaur *et al*[118] reported the synthesis of forty-five compounds from trimethyl phosphine-borane and dimethylchlorophosphine-borane. Use of $(CH_3)_2PCl.BH_3$ allowed further substitution and reaction to take place at the P-Cl bond.

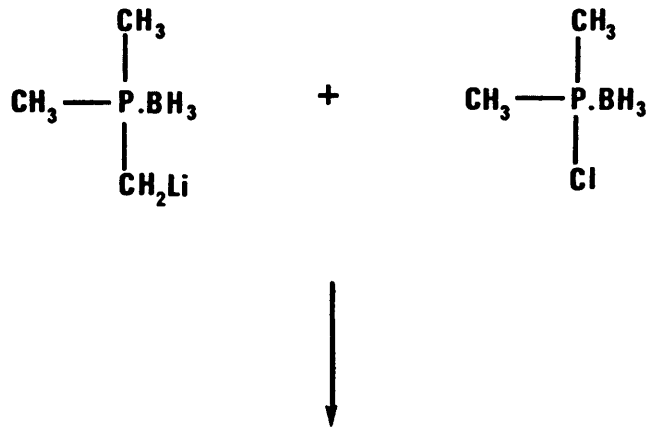
The metalation of $(CH_3)_3P.BH_3$, XXIV in the presence of tetramethyl-ethylenediamine (59)



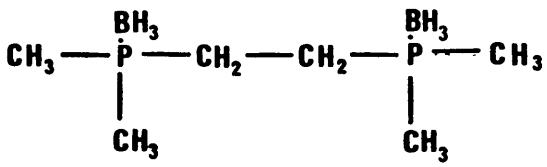
(59)

XXIV XXV

formed XXV which undergoes a coupling reaction with $(CH_3)_2PCl.BH_3$ to produce XXVI,(60).

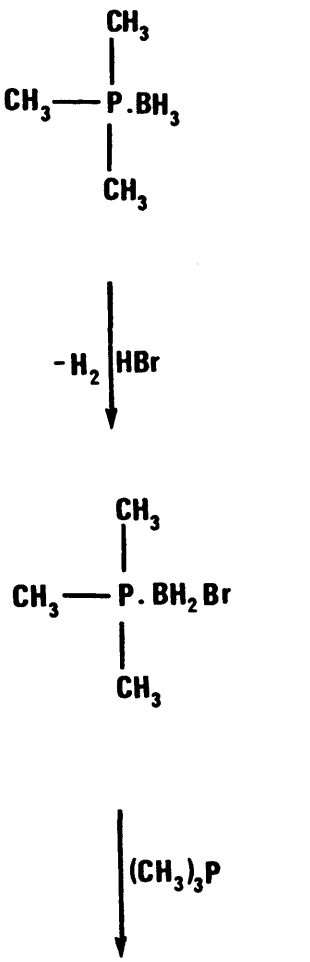


(60)

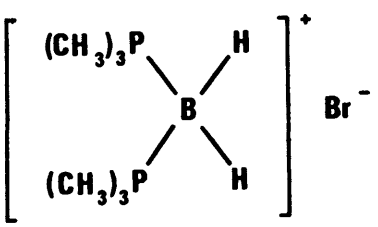


XXVI

The introduction of a second trialkylphosphine moiety at the boron atom in phosphine-boranes leads to the unsymmetrical cation XXVII, (61).

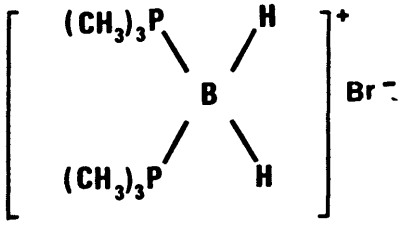


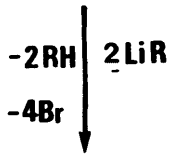
(61)



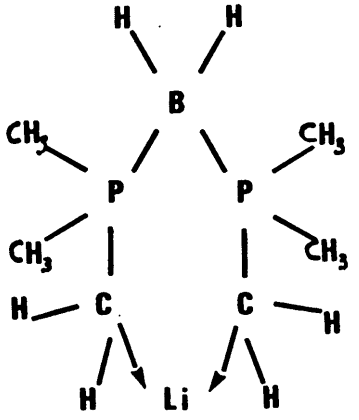
XXVII

Metalation of XXVII yields the lithium complex, XXVIII, (62).



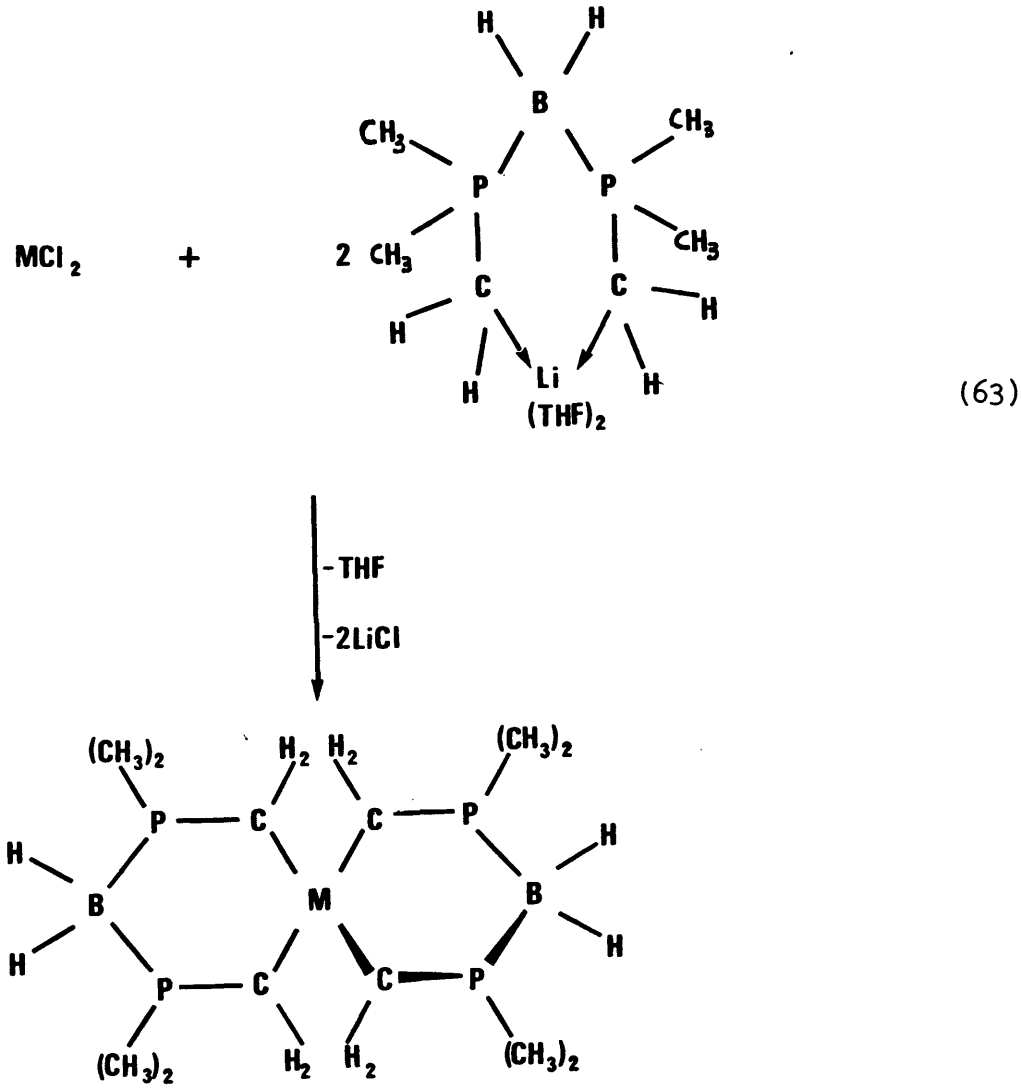


(62)



XXVIII

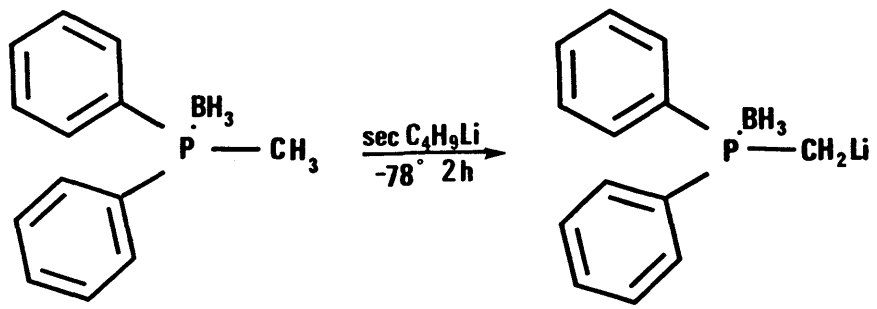
Further reaction of XXVII with metal halides leads to the synthesis of the crystalline sublimable solids, XXIX and XXX, (63).



(63)

The reaction of other metals, such as Au, with XXVIII were also reported.

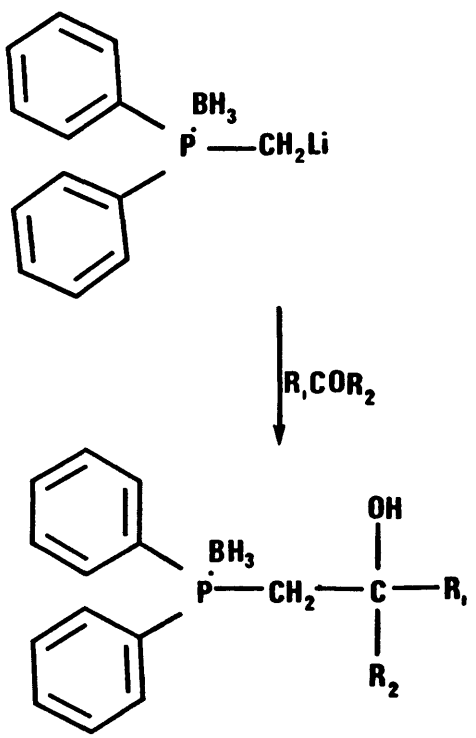
The reactivity of phosphine-boranes has also been studied in some detail by Inamoto *et al.*[109] Metalation of the methyl group in diphenylmethylphosphine-borane XXXI by *sec*-butyllithium in THF at -78°C, (64)[115] produced the lithium salt, XXXII.



(64)

XXXI XXXII

The carbanion of XXXII reacted with carbonyl compounds to give the addition product, XXXIII, in high yields where R^1 = n-C_3H_7 - (92%); $C_6H_3(CH_2O_2)$ (96%); and $C_6H_4NO_2$ (85%) and R^2 = H (65).

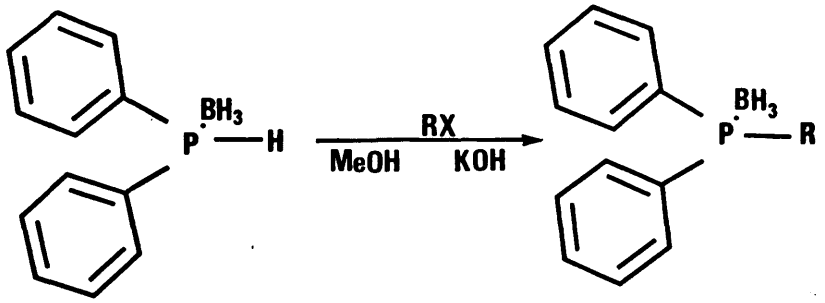


(65)

XXXIII

The carbanion reagent also underwent oxidative coupling promoted by copper copper(II) salts[119,120] without impairment of the borane functionality.

An extensive study of the chemistry of diphenylphosphine-borane, XXXIV was also undertaken. At room temperature, in the presence of KOH, XXXIV reacted rapidly with alkyl halides to yield the phosphine-borane derivatives, XXXV, (66).



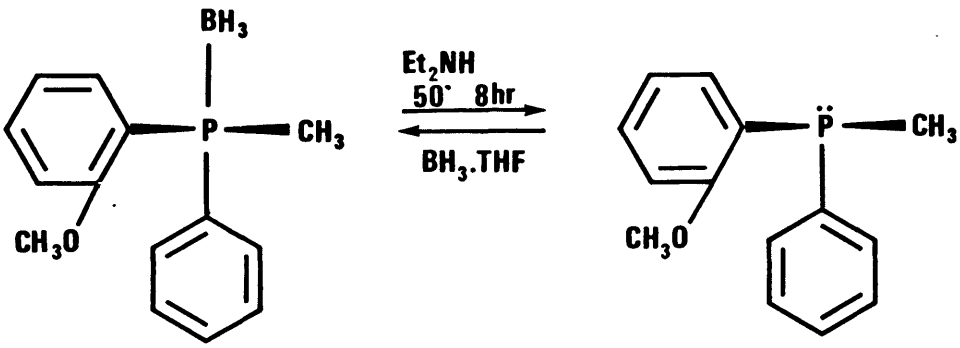
(66)

XXXIV XXXV

Further replacement of hydrogen in XXXIII by aldehydes and α, β - unsaturated carbonyl compounds is also possible.

4.4.4.2. *Cleavage of the Phosphorus-boron bond*

The BH_3 group in phosphine-boranes can be removed by reaction with an amine such as diethylamine. This reaction has been proven to proceed in a stereospecific manner with retention of configuration. For example (S) - (o-methoxyphenyl) methylphenylphosphine-borane, XXXVI, is converted quantitatively to the optically active phosphine XXXVII, (67).[121]

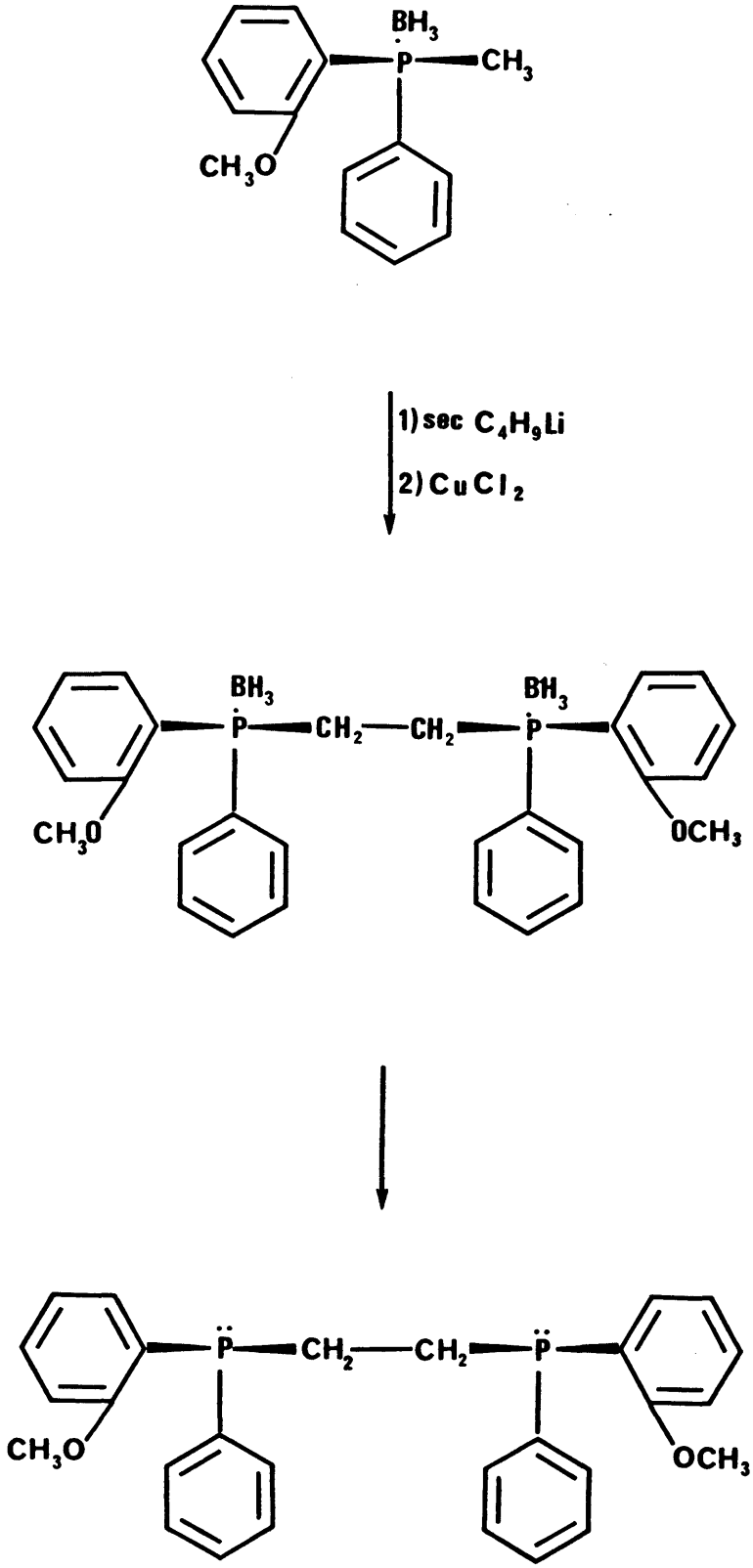


(67)

XXXVI XXXVII

This reaction is completely reversible by the action of $THF.BH_3$ at room temperature on XXXVII,

It is particularly noteworthy that in the above reaction sequences the BH_3 group acts both as an activating group and a protecting group. That is, it activates the adjacent methyl group as well as the P - H bond to deprotonation with a strong base, at the same time it protects the labile phosphine group. On the basis of these results, Minamoto *et al,* have developed a route to optically pure 1, 2- ethanediyl *bis* [(o-methoxyphenyl) phenylphosphine], XXXVIII (68) which is an extremely useful ligand in catalytic assymetric hydrogenation. Typical yields of XXXVIII are > 80% which compare favourably with other synthetic routes.[121]


BH3
P
CH3
CH3O
1) sec C4H9Li
2) CuCl2
BH3
P
CH2
CH2
P
BH3
CH3O
OCH3
P
CH2
CH2
P
CH3O
OCH3

(68)

XXXVIII

4.4.4.3. *Phosphine-boranes as Hydroborating Agents*

Alkenes are normally hydroborated by use of either $Me_2S.BH_3$ or $THF.BH_3$ adducts.[122,123] However, these complexes are sensitive to oxygen and moisture and their use involves special storage and handling techniques.[123] Triphenylphosphine-borane is a crystalline solid (mp 189°C) which is stable in air and can be recovered unchanged after attempted oxidation with alkaline hydrogen peroxide.[115] It is unaffected by 3M HCl at 150°C for 3 hrs., but will exchange the hydrogen atoms attached to boron for deuterium or halogen.[124] Pelter *et al*[115] found that $(C_6H_5)P.BH_3$ can hydroborate oct-1-ene but that the reaction was incomplete (75%) even after 16 hrs. reflux in 1,2- dimethoxyethane. However, addition of methyliodide (3 mol. equiv.) led to efficient hydroboration to the octylboron, (XXXIX), (69).

$$(C_6H_5)_3P.BH_3 + 3\ CH_3\text{-}(CH_2)_5\text{-}CH = CH_2 + MeI \xrightarrow[\text{Reflux}]{} (CH_3 - (CH_2)_7)_3B + [Ph_3P\ Me][I] \qquad (69)$$

XXXIX

The optimum conditions are 6 hr. reflux in THF or 2hr. reflux in 1,2-dimethoxyethane (95%) yield.

A further method for activation of triphenylphosphine-borane for hydroboration would be to oxidise the triphenylphosphine to triphenylphosphine oxide. However, since oxidising conditions are incompatible with the survival of borane, Pelter *et al* chose instead to study the formation of triphenylphosphine sulphide. It is known,[125,126] that trialkyl and triarylphosphines react exothermically with elemental sulphur, at different rates depending on the sulphur allotrope used.[127] Sulphur (S_8) was added in a

stoichiometric ratio of one sulphur to one triphenylphosphine-borane (70).

$$(C_6H_5)_3P.BH_3 + 3\ C_8H_{16} + \frac{1}{8}\,S_8 \longrightarrow (C_8H_{17})_3B + Ph_3P{=}S \qquad (70)$$

This proved to be even more efficient for hydroboration than (8) resulting in a 92% yield of product in 2 hrs. (reflux THF) or 1 hr. (glyme). Using these conditions cyclohexene was also 97% hydroborated.

4.5 PHOSPHINE-HALOBORANES $R_nH_{(3-n)}P\ BH_y\ X_{(3-y)}$

4.5.1 *Introduction*

As previously mentioned $H_3P.BCl_3$[92] was the first compound known to contain a discrete phosphorus-boron bond. Since then complexes of BX_3 (X=F, Cl, Br, I) with phosphines have been extensively investigated.[128-13] In contrast, however, relatively little work has been done on complexes containing $BH_yX_{(3-y)}$ groups.[137-141]

4.5.2 *Synthesis of Phosphine-Haloboranes*

Previously, direct combination of BX_3 groups (X=F, Cl, Br, I) and phosphines, both in the gas state and in solution, produced adducts such as $Ph_3P.BX_3$, $MePh_2P.BX_3$,[142,143] $PhPH_2.BX_3$ and $Ph_2PH.BX_3$,[143] and $Me_3P.BX_3$.[144] However, phosphine-haloboranes of the type $(CH_3)_3P.BH_yX_{(3-y)}$ (X=Cl, Br, I and y = 0, 1, 2) were synthesised in 1977 by Sisler and Mathur.[137] Trimethylphosphine-monobromoborane (91.4%) and trimethylphosphine-monoiodoborane (100%) were prepared by the reaction of trimethylphosphine-borane and excess HBr and HI (71), (X= Br, I).

$$(CH_3)_3P.BH_3 + HX_{(excess)} \longrightarrow (CH_3)_3P.BH_2X + H_2\uparrow \qquad (71)$$

Monochlorination of trimethylphosphine-borane did not go to completion even after prolonged reaction with HCl.

Trimethylphosphine-dibromoborane (94.2%) was the only soluble dihaloborane adduct from the direct combination of trimethylphosphine-borane with Cl_2, Br_2 or I_2 (72).

$$(CH_3)_3P.BH_3 + Br_2 \xrightarrow{C_6H_6} (CH_3)_3P.BH\ Br_2 + H_2 \qquad (72)$$

Only the monoiodoborane adduct was formed from the reaction with iodine, even after 12 hours at 80°C. Attempts to prepare $(CH_3)_3P.BHCl_2$ resulted in a mixture of products. Direct chlorination of $(CH_3)_3P.BH_3$ produces the trichloro-adduct in very high yield, while the tribromo-adduct is likewise synthesised in 91% yield.

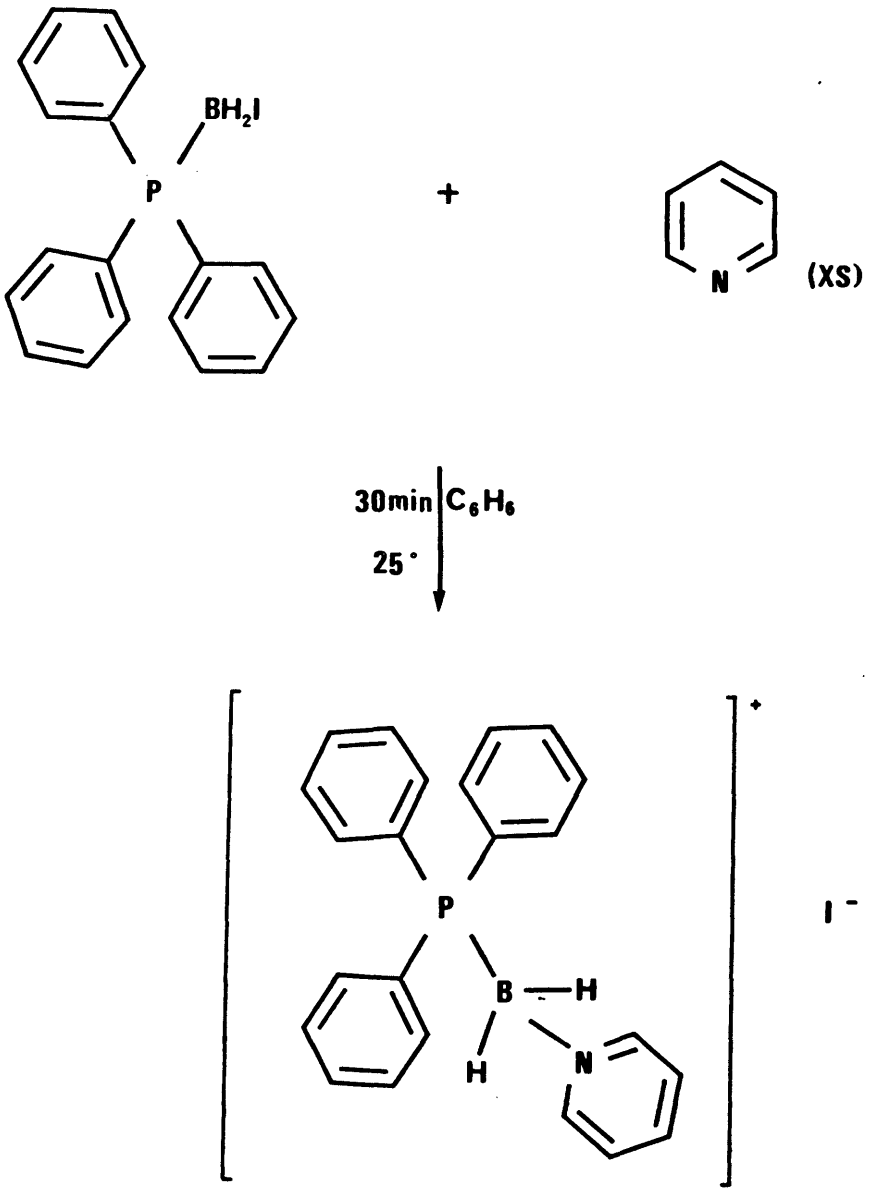
4.5.3 *Physical Properties of Phosphine-Haloboranes*

Extensive study of the proton n.m.r. data of $(CH_3)_3P.BH_nX_{3-n}$ (n = 0, 1, 2, 3) by Sisler and Mathur[137] led to the following general conclusions. (i) The order of deshielding of the methyl protons by B-X groups is B-I > B-Br > B-Cl > B-H. (ii) A comparison [140] of chemical shifts of the methyl protons in the two series $(CH_3)_3N.BH_nX_{3-n}$ and $(CH_3)_3P.BH_nX_{3-n}$ shows that the methyl protons in phosphorus compounds are considerably less deshielded than the methyl protons in their nitrogen analogues. (iii) The replacement of a hydrogen atom by a halogen on boron in the phosphorus compound causes less deshielding of the methyl proton than a similar substitution in the nitrogen compound. (iv) The value of the C-H-^{31}P coupling constant increases as the size or the number of halogen atoms bonded to the boron atom is increased in the series $(CH_3)_3P.BH_nX_{3-n}$.

Odom *et al* [142] reported a detailed spectroscopic study of the properties of phosphine-trifluoroboranes and compared those findings to related compounds such as $H_3P.BH_3$. The dipole moment was found from Stark splittings to be 3.73 ± 0.30 . for $H_3P.BF_3$. The phosphorus-boron bond length was calculated as 1.921 ± 0.07 Å. This bond length is the same within experimental error as that for $H_3P.BH_3$(1.937 ± 0.005 Å),[146] but longer than in $F_3P.BH_3$ (1.836 ± 0.006 Å),[140] and approximately equal to those of the methylphosphine-boranes (~ 1.91 Å).[147,148]

4.5.4 *Reactions of Phosphine-Haloboranes*

The reactions of phosphine-haloboranes are nowhere near as well documented as those of their borane counterparts. Martin and coworkers[149] have reported reactions such as (73).



(73)

to compare the displacement of iodide by amines and phosphines. From a similar study of $(CH_3)_3N.BH_2I$, Ryschkewitsch[143] has concluded that displacement of iodide from boron was faster than displacement of amine or

phosphine. This is due, to a large extent, to the weakness of the boron-iodine bond relative to the boron-nitrogen or boron-phosphorus bonds.

4.6 PHOSPHINE-CYANOBORANES

4.6.1 *Synthesis*

Using a synthesis similar to that for triphenylphosphine-borane,[8] Martin and coworkers[142] synthesised a series of phosphine-cyanoboranes. Yields of approximately 50% were obtained from the reaction of a concentrated monoglyme solution of triphenylphosphine and $(BH_2CN)_n$. However, an attempted synthesis of triphenylphosphine-cyanoborane by the reaction of sodium cyanoborohydride with $Ph_3P.HBr$ in THF produced no detectable quantities of product, even after refluxing the reaction mixture for one week in THF.

Das and Roy[150] using the synthesis outlined in (74) prepared the following phosphine-cyanoboranes.

$$n\ Na[BH_3CN] + \frac{n}{2}\ I_2 \xrightarrow{\text{Monoglyme}} n\ Na[I] \downarrow + (BH_2CN)_n + \frac{n}{2}\ H_2 \uparrow \qquad (74)$$

$$n\ R_3P + (BH_2CN)_n \longrightarrow n\ R_3P.BH_2CN$$

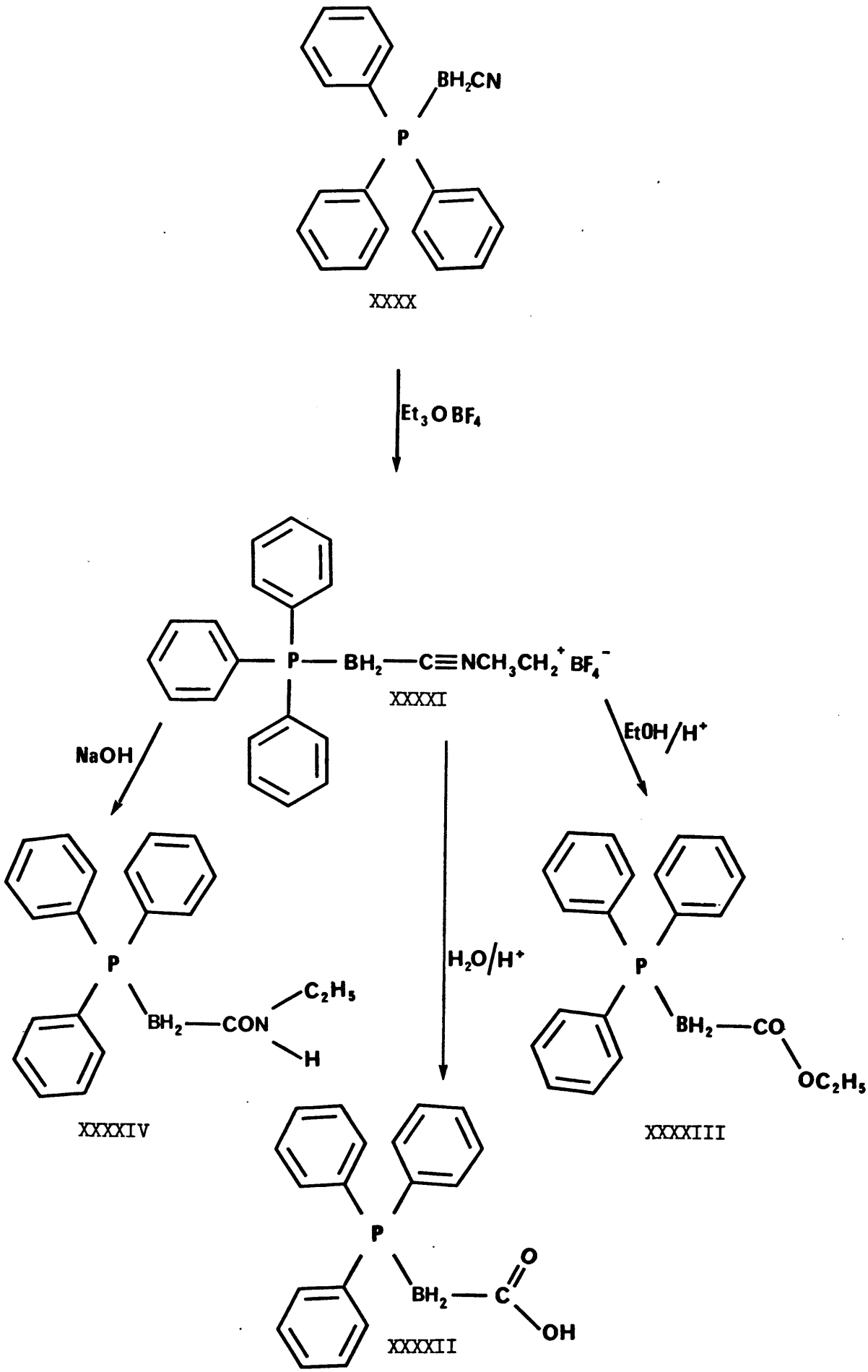
R = *n*-C_4H_9 (70%); n-C_6H_{13} (50%); *cyclo*-C_6H_{11} (65%); n-C_6H_{17} (55%); and $R_3 = (C_6H_5)_2(4\text{-}CH_3C_6H_4)$ (54%).

The reaction is slow and requires two days stirring. The authors claimed that THF, which was found to be a good solvent for triphenylphosphine-cyanoborane, is inefficient here.

4.6.2 *Reactions of Phosphine-Cyanoboranes*

Using analogous routes to those outlined for amine analogues, Wisian-Nelson *et al*[149] synthesised a series of phosphine carboxy borane derivatives containing the triphenylphosphine unit. This series and typical yields of products are outlined in Scheme 1.

Scheme 1


BH2CN
P
XXXX
Et3O BF4
P— BH2—C≡NCH3CH2+ BF4−
XXXXI
NaOH
EtOH/H+
H2O/H+
P
BH2—CON
C2H5
H
XXXXIV
P
BH2—CO
OC2H5
XXXXIII
P
BH2—C
O
OH
XXXXII

4.7 ARSINE-BORANES

4.7.1 *Introduction*

The discovery[2] of stable boron-phosphorus compounds, e.g. $H_3P.BCl_3$,[92] $Me_3P.BH_3$,[94] etc., and trimers and tetramers based on the $[(CH_3)_2P.BH_2]_n$ and the $[(CH_3)_2PB(CH_3)_2]_n$ units (where n = 3, 4) raised the question as to whether analogous boron-arsenic compounds could be prepared.[151] In a study of such compounds, Stone and Burg[152] reported the preparation and properties of several arsine-borane monomers and polymers. Generally As-B compounds are similar to the corresponding P - B compounds, however arsenic-boron bonds are generally weaker than those of the analogous phosphorus compounds.

4.7.2. *Synthesis of Arsine-Boranes*

The synthesis of trimethylarsine-borane (XXXXV, (75) is carried out

$$2(CH_3)_3As + B_2H_6 \longrightarrow 2(CH_3)_3As.BH_3 \qquad (75)$$

XXXXV

in the gas phase, by direct combination of the reactants, on a high vacuum system.[153] Other arsine-boranes prepared are the trihalide-adducts, $Me_3As.BX_3$ (X=Cl, Br)[154] and triiodo-adduct $Me_3As.BI_3$,[155] all using vacuum line and inert atmosphere techniques.[156]

4.7.3. *Physical Properties of Arsine-Boranes*

Mente and Mills[144] have calculated the enthalpy of reaction for trimethylarsine and borane as -49.6 K cal mol^{-1}.

As noted for the series $Me_3P.BX_3$ (X = H, F, Cl. Br), Mente and Mills[144] found that $Me_3As.BX_3$ (X = H, Cl, Br) also had small saturation vapour pressure at room temperature. The sequence of adduct stability for the

Me_3As adducts was established as $Me_3As.BBr_3 > Me_3As.BH_3 > Me_3As.BCl_3$. In a mass spectral analysis of these compounds it was found that most of the ion current was carried by ions derived from the Me_3As or BX_3 units.[130]

4.7.4 *Comparison of Arsine- and Phosphine-Boranes*

From experiments involving successive displacement of bases, Mente and Mills[144] obtained the following sequences of adduct stability: $Me_3P.BH_3 > Me_3As.BH_3$; also $Me_3P.BCl_3 > Me_3As.BCl_3 > Me_3Sb.BCl_3$; and $Me_3P.BBr_3 \approx Me_3As.BBr_3 > Me_3Sb.BBr_3$. These sequences are in accord with the order determined with gas-phase calorimetry.[157] The general trend of Lewis-base strengths, predicted by Hewitt and Holliday in 1953[94] on the basis of melting points of the respective borane-adducts, was found to correspond exactly with the results of the gas phase displacement reactions of Mente and Mills.

4.8 RESULTS AND DISCUSSION

The work presented here is divided into two main sections, one dealing with borane and cyanoborane derivatives of N-donor systems and the other with some P-donor derivatives. The first section includes subsections dealing with a comparison of some of the methods for preparing amine-boranes and cyanoboranes, an X-ray crystallographic study of 4-$Me_2NPy.BH_2CN$, a new route to pyrazaboles and the isolation of an unexpected product, (Ph(CO)(C_6H_{11}). The second section deals with the methods of preparation of $Ph_3P.BH_2CN$ and some of its reactions.

4.9.1 *Section I: Subsection (i)*

4.9.1.1. *Comparison of Synthetic Methods for Adducts of Amines*

The general synthetic routes to borane adducts of amines were discussed earlier (Section 4.1.1). From a study of these preparations a number of general comments pertaining to the present work can be made. First, the procedure of Schaeffer and Anderson,[2] method (a), involving the reaction between amine-hydrochlorides and sodium borohydride, and a later version reported by Spielvogel and coworkers[77] using sodium cyanoborohydride was found to be successful only for the synthesis of monoamine adducts (76).

$$[R_1\ R_2\ R_3\ NH]\ [Cl] + Na[BH_3X] \xrightarrow[\text{T.H.F.}]{\text{Reflux}} R_1\ R_2\ R_3N.BH_2X + Na[Cl] + H_2 \qquad (76)$$

X= H, CN

The borane adducts prepared in this way were all isolated in high yield and in some cases were of analytical purity. The cyanoborane adducts were generally achieved in lower yields (see Section 4.3.2. for discussion of this). However, when either sodium borohydride or cyanoborohydride was reacted with diamine- (LV, LVI and LVII) and triamine- (LI) hydrochlorides, no borane

containing products were isolated, irrespective of reaction conditions (See Experimental Section).

A more widely applicable rate was that devised originally by Nainan and Ryschkewitsch[8] and modified by Martin and coworkers[79] for cyanoborane derivatives. Both of these syntheses involve the reaction of amine with iodine and either borohydride or cyanoborohydride in monoglyme (77).

$$R_1\ R_2\ R_3N + Na[BH_3X] + \tfrac{1}{2}I_2$$

Reflux ↓ Monoglyme

$$R_1\ R_2\ R_3N.BH_2X + Na[I] + \tfrac{1}{2}H_2 \qquad (77)$$

X=H, CN

The difference between the two methods is that the former (b(i)), involves the addition of an iodine solution to a mixture of the amine and borohydride in monoglyme. Then the borane complex being generated reacts immediately with the more strongly coordinating amine to form the adduct. In the latter method, (b(ii)) the borane-monoglyme complex is prepared separately prior to the addition of the amine. Both methods b(i) and b(ii), produced borane and cyanoborane adducts of simple monoamines in good yields, with the yield of the cyanoborane adduct less than that of the borane derivative e.g. $(C_6H_{11})_2NH.BH_2X$ (X = H, 95.6%; CN, 87%). However, only the latter method afforded reasonable yields of adducts of more complex amines. Moreover, the use of method b(i) in the attempted syntheses of borane and cyanoborane adducts of diamines (3, 5-dimethylpyrazole) triamines (1, 3-*bis* aminopropylamine) and tetramines (N, N^1 - *bis* -(3- aminopropyl)-piperazine) generated an unusual product, cyclohexylphenylketone, which is discussed below.

4.9.1.2. *Amine-boranes*

The amine-boranes prepared in this work are listed in Table I. Their empirical formulae were confirmed by C, H, N and B chemical analysis. Both

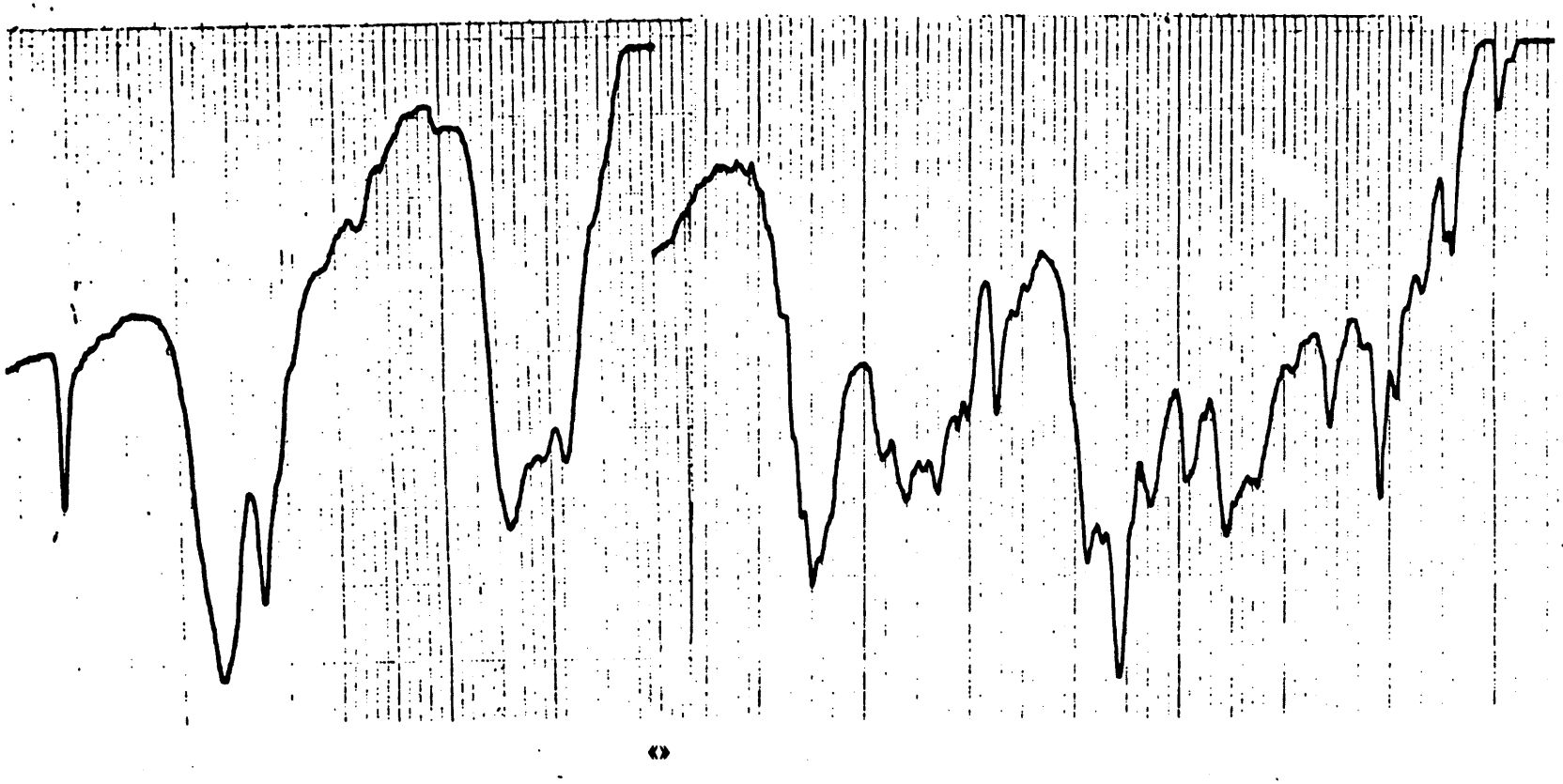


Figure 3: Infrared Spectrum of Dicyclohexylamine-borane.

adducts of tertiary amines were liquids while those of the primary and secondary amines were solids.

Each of the amine-boranes has characteristically strong B-H absorptions in the region of 2250 to 2400 cm^{-1} in the infrared spectrum. The spectrum of dicyclohexylamine-borane is typical and also shows N-H and C-H absorptions (Figure 3). The B-H stretching frequencies for the amine-boranes are also listed in Table I.

TABLE I: *Amine-borane Data*

Compound	M.P.	b.p.	ν_{B-H}	Method Yield/%		
				a	b(i)	b(ii)
$(CH_3)_3CNH_2.BH_3$	96-98		2380(s); 2360(sh); 2340(sh); 2320(m); 2270(m).	90.5	93.6	
$(C_6H_{11})_2NH.BH_3$	101-102		2380(s); 2340(w); 2320(w); 2270(m);	98.9	95.6	
$(C_2H_5)_3N.BH_3$		42-44 (0.02mm)	2350(br,s); 2230(s)			
$(C_4H_9)_2NH.BH_3$	25-26		2370(s); 2360(sh); 2330(w); 2280(m).		68.2	
$(C_4H_9)_3N.BH_3$		120 (1.5mm)	2380-2320(br, v.s.) 2280(s)			63.8

The ^{11}B chemical shifts for amine-boranes of the type $R_{3-n}H_n.BH_3$ are typically found in the region from -5 to -24 p.p.m. and the shielding of the boron atom increases with increasing values of n.[157] This effect is reflected in the difference of approximately 3 p.p.m. between the primary amine adduct, t-butylamine-borane ($\delta^{11}B$-24.6 p.p.m.) and the secondary amine adduct, dicyclohexylamine-borane ($\delta^{11}B$ -21.6 p.p.m.). Other data for ^{1}H and

δ C are given in the experimental section below.

4.9.1.3. *Amine-cyanoboranes*

The cyanoborane adducts that were prepared were white, crystalline solids which were soluble in ethanol, benzene, THF and halogenated hydrocarbons. Each was thermally stable and had melting points as follows: 196-197° (dicyclohexylamine-cyanoborane); 153-154° (aniline-cyanoborane) and 126-128°C (4-dimethylamino-pyridine-cyanoborane). The infrared spectra were characterised by N-H; B-H, C-H, C ≡ N absorption frequencies. Table 2 lists the B-H and C≡ N stretching frequencies together with the preparative methods employed and the yields obtained. The infrared spectrum of dicyclohexylaminocyanoborane is typical and is illustrated in Figure 4.

TABLE 2: *Infrared Data, Preparative Methods and Yields for Amine-Cyanoboranes*

Adduct	ν B-H	ν C≡N	Method Yield /%		
			a	b(i)	b(ii)
$(C_6H_{11})_2NH.BH_2CN$	2460(s h); 2430(w); 2360(s); 2310(s); 2280(s); 2230(w).	2180(S)	45.8	86.9	
$C_6H_5NH_2.BH_2CN$	2400(s); 2365(m); 2305(s h).	2180(M)	78.88	82.4	
$^4Me_2\ C_5H_4N.BH_2CN$	2400(s); 2360(s h); 2280(s h); 2245(s);	2210(M)			24.8

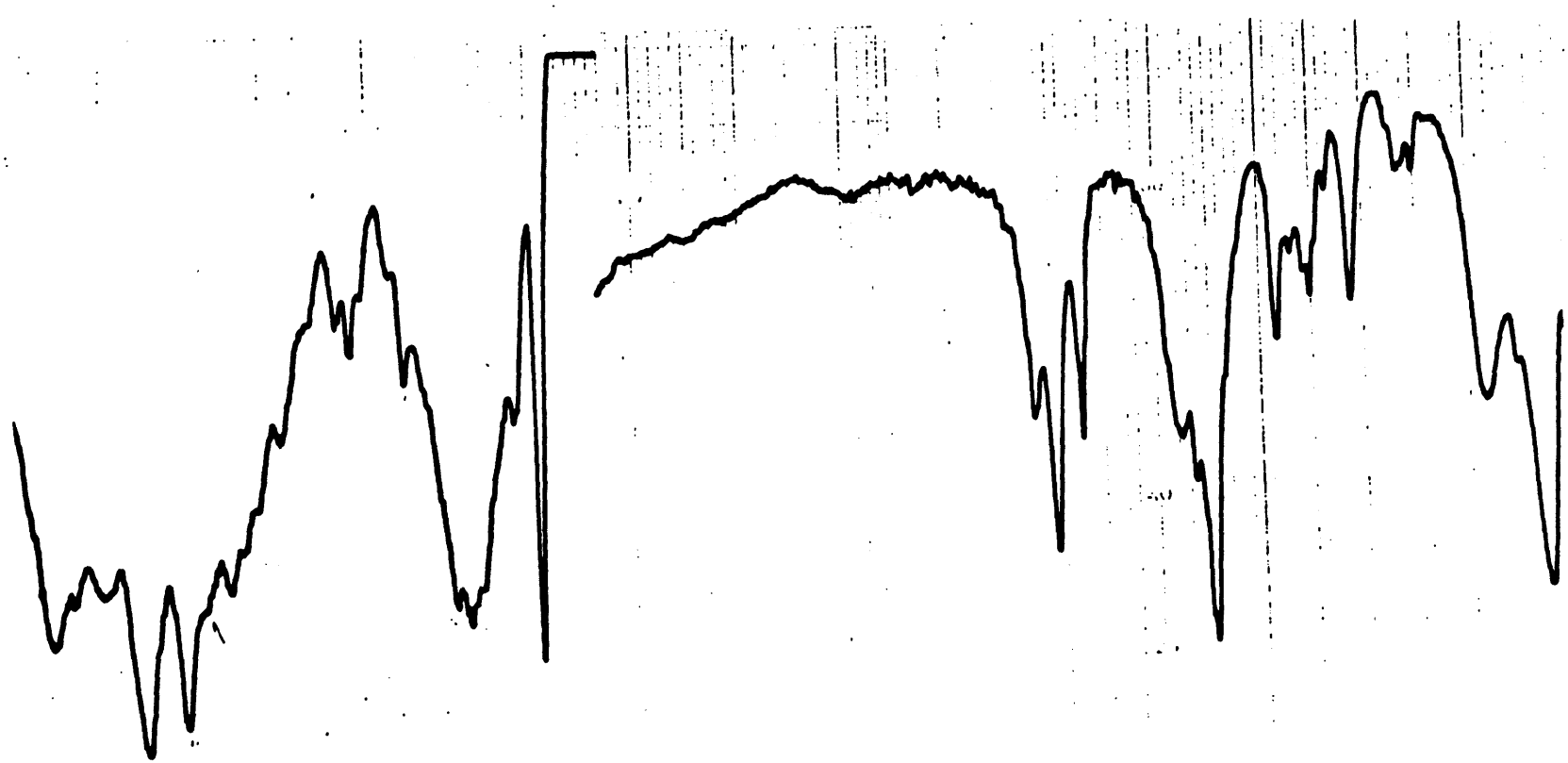


Figure 4: Infrared Spectrum of Dicyclohexylamine-cyanoborane

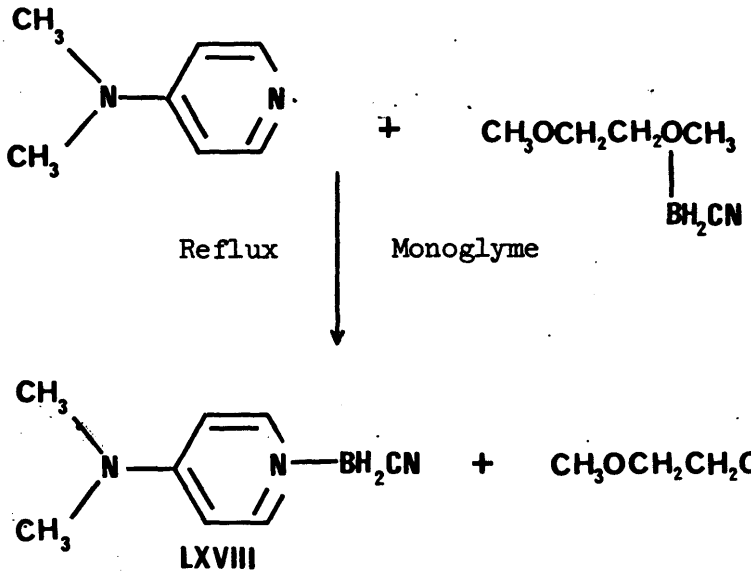
In a study of the isomers $Me_3N.BH_2CN$ and $Me_3N.BH_2NC$, Vidal and Ryschkewitsch[158] compared the C ≡ N stretching frequencies and found that the isocyano absorption at 2 135 cm^{-1} was at least 50 cm^{-1} lower than the cyano group frequency which ranged from 2180 to 2280 cm^{-1}. The CN frequency for both LXVI and LXVII is 2180 cm^{-1} while that for LXVIII is 2210 cm^{-1} which precludes the possibility of the isocyano isomer being present. Moreover it is expected that the cyano linkage is probably formed because of the thermodynamic preference of the boron-carbon over the boron-nitrogen bond; demonstrated by the ease with which both $Me_3N.BH_2NC$ and $Na[BH_3NC]$[159] isomerise to $Me_3N.BH_2CN$ and $Na[BH_3CN]$ respectively. Furthermore, in view of the experimental conditions used in the synthesis of amine-cyanoboranes i.e prolonged refluxing in either THF or monoglyme, it is unlikely that the isocyanoborane adduct would be isolated.[77, 84, 86, 87, 160] Wade *et al*[159] reported that, in the synthesis of $Na[BH_3NC]$, the isocyanoborohydride isomer is only isolated if the solvent is removed from the reaction mixture at room temperature and no heat is applied to the system at any stage. Even then the isocyano isomer is only the minor product as shown by quantitative infrared analysis which gave a ratio of 4 : 1 for cyano : isocyano isomers.

The ^{11}B chemical shifts for aniline-cyanoborane (δB -13.34 p.p.m.) and dicyclohexylamine-cyanoborane (-40.1 p.p.m.) are somewhat disparate. However, those values are comparable with reported signals for trimethylamine-cyanoborane (-15.1 p.p.m.),[161] quinuclidine-cyanoborane (δB -15.2 p.p.m.)[38], 2-methylpyridine-cyanoborane (-36.3 p.p.m.)[80] and Pyridine-cyanoborane (δB -34.9 p.p.m.)[79]. The upfield shift for the cyanoborane adducts over the borane adducts e.g. dicyclohexylamine-borane (δB -21.6 p.p.m.) and trimethylamine-borane (δB -8.1 p.p.m.)[162] is due to the replacement of hydride by cyanide in the borane group.

4.9.2 *Subsection (ii)*

4.9.2.1. *4- Dimethylamino-cyanoborane LXVIII*

The successful synthesis of 4-dimethylaminopyridine-cyanoborane, LXVIII was highly dependent on the method used. When method b(ii) was employed the product was isolated in 24.8% yield (78).



(78)

Use of method b(i), involving the addition of a solution of iodine to a mixture of 4-dimethylaminopyridine and sodium cyanoborohydride in monoglyme, generated only a complex mixture from which no pure products could be isolated. Furthermore, no replacement of hydride by cyanide was achieved when 4-dimethylaminopyridine-borane was refluxed with mercuric cyanide in THF.

Crystals of LXVIII suitable for X-ray crystallographic study were grown from acetonitrile solution and sent to Professor George Ferguson, Chemistry Dept., University of Guelph, Canada. Professor Ferguson completed a successful solution of the structure (See Experimental Section) The results of this study are discussed below. Figure 5 is an ORTEP view of compound LXVIII.

Not surprisingly, the cyanoborane group is coordinated to the pyridine nitrogen since this is more basic than the dimethylamino nitrogen. Such

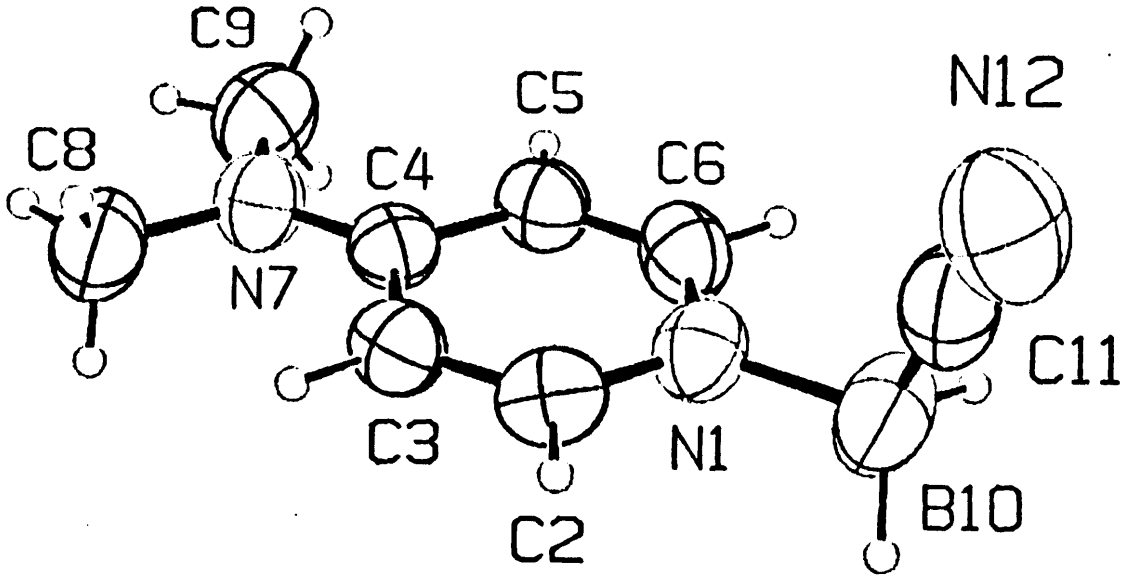
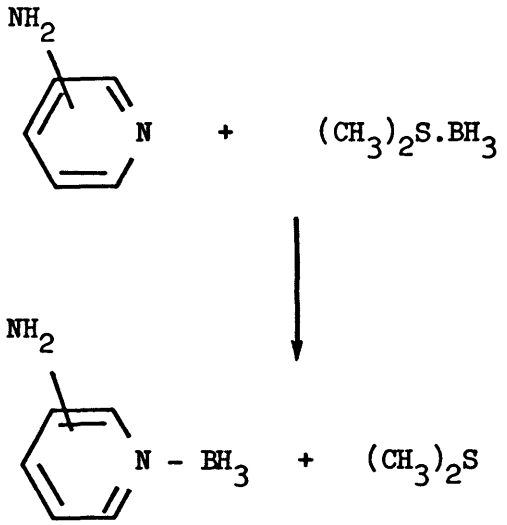


Figure 5: Structure of 4-Dimethylaminopyridine-cyanoborane

behaviour was suggested by Martin and coworkers[11] in their study of the reactions of 2-,3-, and 4- aminopyridines with dimethylsulphide-borane (79).



(79)

Likewise, the coordination of 4-dimethylaminopyridine to transition metals also occurs through the pyridine nitrogen. An example of this was previously reported by Ferguson and coworkers in 1982[166] when they published the structure of chloro(3-dimethylamino)-1- formyl -2, 2-dimethylpropyl -C, N) - (4-(dimethylamino)pyridine) palladium (Figure 6)

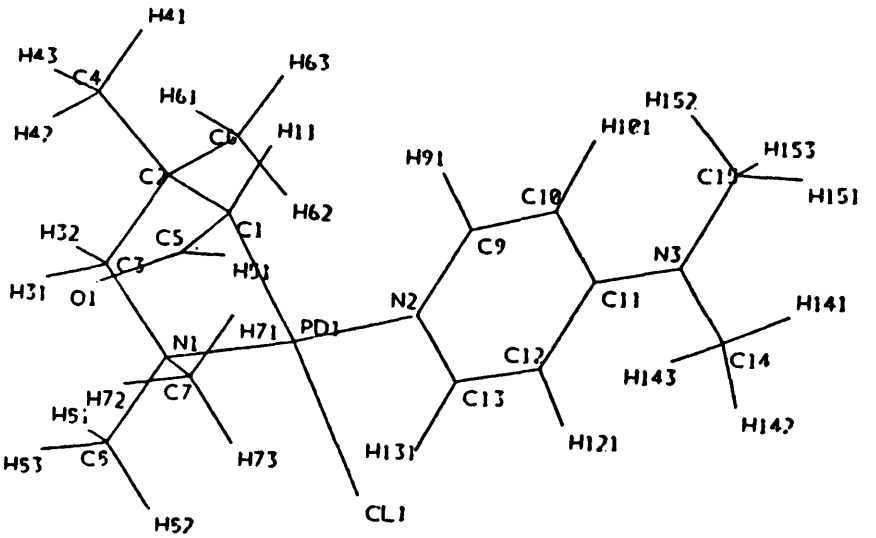


Figure 6: *Structure of Chloro-(3-dimethylamino)- I -formyl I -2, 2-dimethylpropyl -C,N) - (4-(dimethyl-amino)pyridine) Palladium (II)*

The single crystal X-ray structural analysis of LXVIII not only confirmed that the pyridine nitrogen coordinates the BH_2CN group but showed, also, that the aromatic character of the pyridine ring is somewhat disrupted to give an essentially planar molecule with a more localised bonding structure which could be represented as in Figure 7. The torsional angle for atoms N7 -C4 -C5 -C6 is 179.7 (3)°.

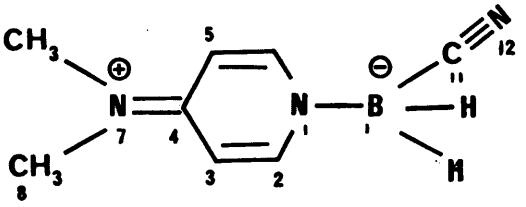


Figure 7: *4-Dimethylaminopyridine-cyanoborane*

This may be compared to the corresponding value in 4-dimethylamino-pyridine (Figure 8) of 111.36 (3)° which is closer to the "expected" RR_2N - angle of 109° in ammonia based structures.

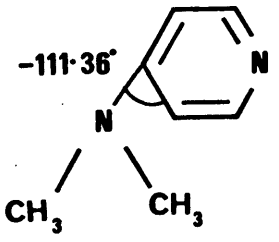


Figure 8: *4-Dimethylaminopyridine*

In the aforementioned palladium complex the corresponding angle is 163.3°.

In 1978, Spielvogel and coworkers[164] reported the structure of ammonia-cyanoborane (Figure 9). Table 3 lists a comparison of these comparable bondlengths.

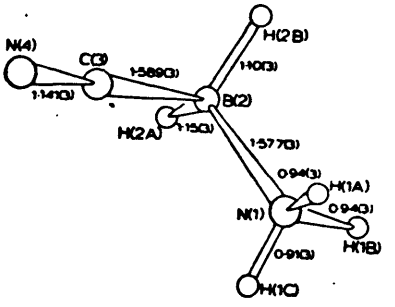


Figure 9: *Ammonia-cyanoborane*

TABLE 3: *Comparison of Bondlengths in (LXII) and Ammonia-Cyanoboranes*

Bond	*LXII* A^o	*Ammonia-cyanoborane* A^o
B - H		1.12 (3)
B - N	1.574 (3)	1.577(3)
B - C	1.573 (2)	1.589(3)
C ≡ N	1.130 (2)	1.141(3)

There are slight reductions in the bond lengths of LXVIII over those in ammonia cyanoborane, the most significant of these is the boron-carbon linkage which is 0.016 $\overset{o}{A}$ shorter in compound LXVIII. However, this could be attributed to experimental error. In ammonia-cyanoborane the (ammonia) N(1)-B(2)-C(3) and B(2) -C(3)-N(4) (cyano) angles are 107.6 (2) and 179.6 (3)^o respectively. In compound (LXII), the corresponding angles N(1) -B(10)-C(11) and B(10)-C(11)-N(12) are 108.6(2) and 179.9(2)^o respectively.

In 1975, McPhail and McFadden,[165] published an X-ray crystal structure characterisation of *cyclo*(hexacyanoborane), $(BH_2CN)_6$ (Figure 8).

The average B-C and B-N bond lengths were 1.561 (6) and 1.565(6)Å respectively which are shorter than the corresponding bond lengths in both compound (LXII) and ammonia cyanoborane.

Table 4 compares the relative bond lengths of compound LXVIII and 4-dimethylaminopyridine. Comparison of bond lengths C2-C3 and C5-C6 (1.375(2) and 1.381(2) Å respectively) and C3-C4 and C4-C5 (1.403(2) and 1.404 (2) Å respectively) with the equivalent bonds in LXVIII, C2-C3 (1.355(3)Å); C5-C6 (1.353(4) Å) and C3-C4 (1.414(2) Å); C4-C5 (1.404(3)Å) clearly shows the changed electronic character of 4-dimethylaminopyridine when coordinated to cyanoborane. Further proof of the localised bonding in LXVIII is obtained from a comparison of C4-N7 bond-lengths. In 4-dimethylaminopyridine this is typical of a conventional carbon-nitrogen single bond at 1.367(3) Å.[166] In the adduct, LXVIII this C4-N7 bondlength is reduced by 0.032 Å to 1.355 (3) Å which approaches a C = N linkage (e.g. 1.144(3) Å)[167]. Furthermore, the nitrogen-boron bondlength, N1-B10 of 1.574 (4) Å in LXVIII shorter than that in trimethylamine-borane (1.638 Å)[13] and other B-N bonds in amine-borane adducts of 1.65 Å in $(CH_3)_3N.B(CH_3)_3$ and 1.636 Å in $(CH_3)_3N.BF_3$. However, the observed B-N bond length in LXVIII does not reasonably imply that there is a significant amount of π bonding present, since the B-N value in ammonia-cyanoborane (1.577 (3) Å) is very similar. On comparison of B-N bondlengths with borazine, which is recognised as having π bond character the value of 1.44 (3) Å [168] in borazine is 0.13 Å shorter than in LXVIII.

Table 4 also lists a comparison of the bondlengths in LXVIII with the previously mentioned aminopyridine coordinated palladium complex.[163] As is evident from the data in Table 4 the bondlengths are more similar

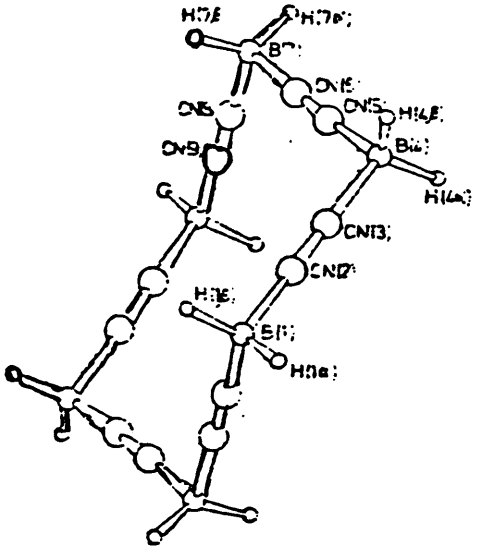
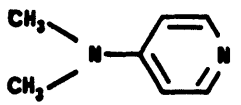
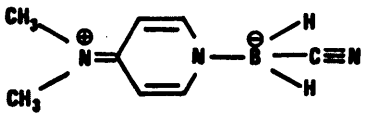


Figure 8: *Cyclo*(hexacyanoborane)

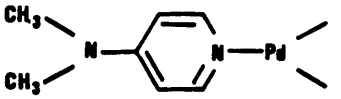
TABLE 4 *Bond Distances in Angstroms*



4 Dimethylamino-pyridine



4-Dimethylaminopyridine-cyanoborane



Chloro-(3-dimethylamino)-1-Formyl-2,2-dimethylpropyl-C,N) -(4-(dimethylamino) pyridine)-Palladium (II)

Atom I	Atom 2	Distance	Atom I	Atom 2	Distance	Atom I	Atom 2	Distance
N1	C2	1.335	N1	C2	1.345	N1	C2	1.353
N1	C6	1.337	N1	C6	1.342	N1	C6	1.353
			N1	B10	1.574			
C2	C3	1.575	C2	C3	1.355	C2	C3	1.355
C3	C4	1.403	C5	C4	1.412	C3	C4	1.412
C4	C5	1.404	C4	C5	1.404	C4	C5	1.413
C4	N1	1.367	C4	N7	1.335	C4	N7	1.346
C5	C6	1.381	C5	C6	1.353	C5	C6	1.264
N7	C8	1.452	N7	C8	1.449	N7	C8	1.451
N7	C9	1.452	N7	C9	1.448	N7	C9	1.468
			B10	C11	1.573			
			C11	N12	1.130			

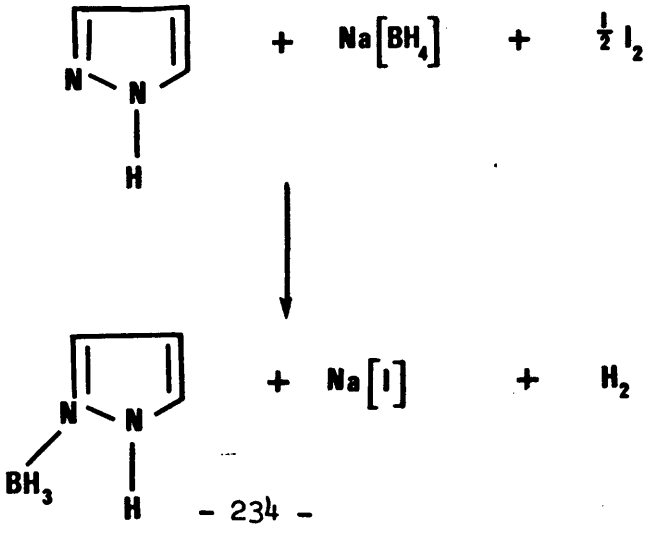
especially in the region of the pyridine ring system. The C2-C3, C3-C4, and C4-C5 bondlengths are the same in both compounds with a difference of 0.01 Å between the C5-C6 bondlengths. The C4-N7 bondlengths in the transition metal complex at 1.346 (4) Å is 0.011 Å longer than that in compound LXVIII and possesses the same single bond character as 4-dimethylamino-pyridine. However, differences are apparent in the dimethylamino to the pyridine ring moiety. Apart from the C4-N7 disparity the N7-C9 bondlength in LXVIII (1.448 (4) Å) is significantly shorter than that in the palladium complex (1.468 (6) Å). However, the difference between the N7-C8 bondlengths in both compounds is just 0.002 Å.

The C ≡ N bondlength in both compound LXVIII (1.130(3) Å) and ammonia-cyanoborane (1.141(3) Å) are shorter than the value listed for a C ≡ N bondlength (1.144 (4) Å) listed by Greenwood and Earnshaw.[167] This may be due to greater back-bonding from the boron atom which in LXVIII has a formal negative charge.

4.9.3 *Subsection (iii)*

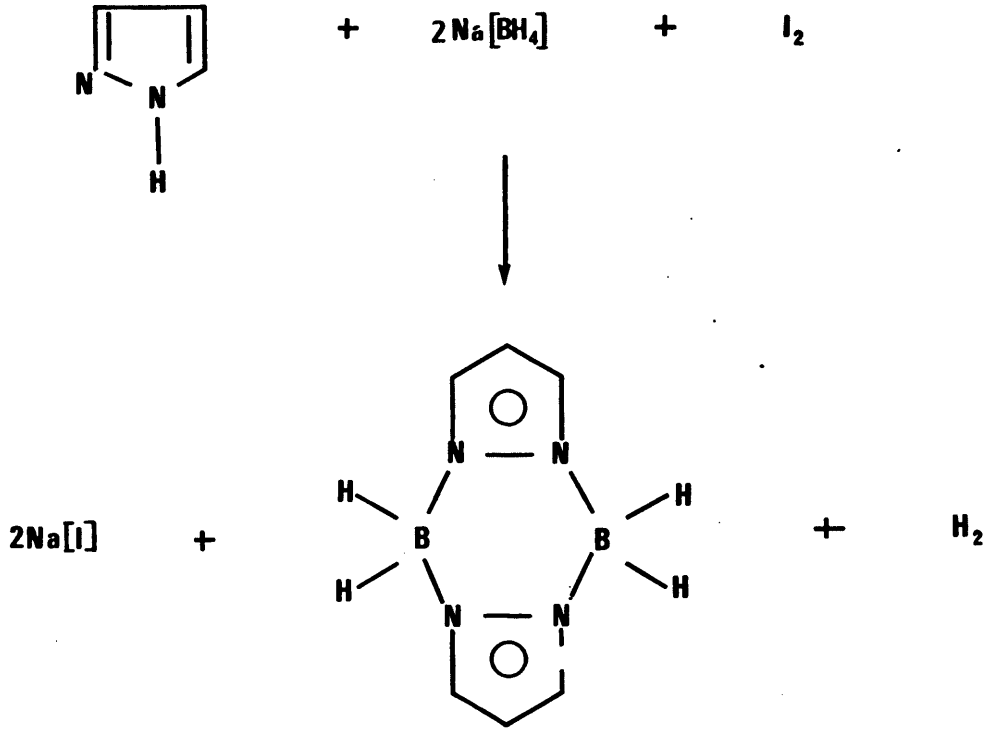
4.9.3.1. *Borane-Pyrazole Chemistry*

The reactions of pyrazoles with borane or cyanoborane generated by reaction method b(i) were potentially interesting for two reasons. First, to see if the reactions between pyrazoles and borane would furnish the monomeric species (80).



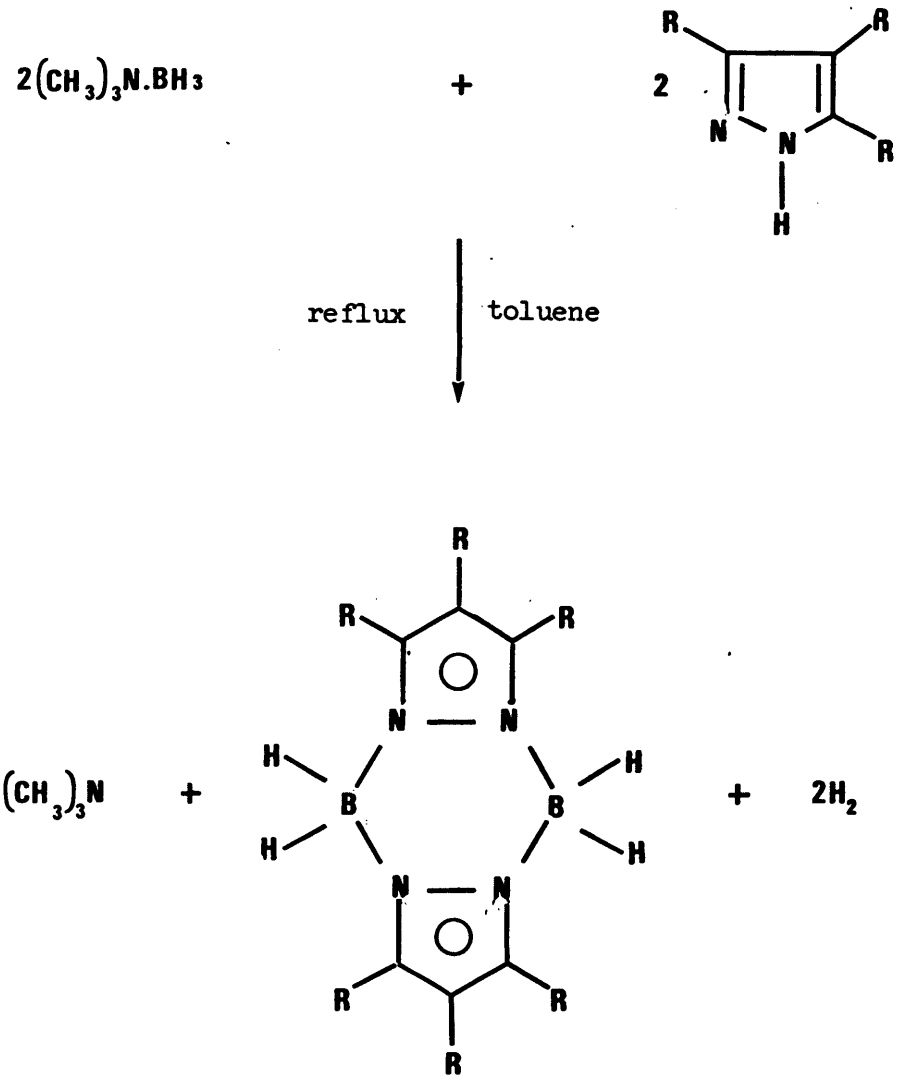
(80)

or whether dimerisation would occur to form pyrazaboles{ dimeric (1-pyrazolyl) boranes} (81).



(81)

The second point of interest was to attempt to prepare the first B-CN containing derivatives of (80) or (81). In the case of (80), the borane adducts had been previously prepared by Noth and Wrackmeyer.[169] Pyrazaboles such as in (81) had been prepared by Trofimenko from the reaction of pyrazoles with trimethylamine-borane in refluxing toluene (82)[170]

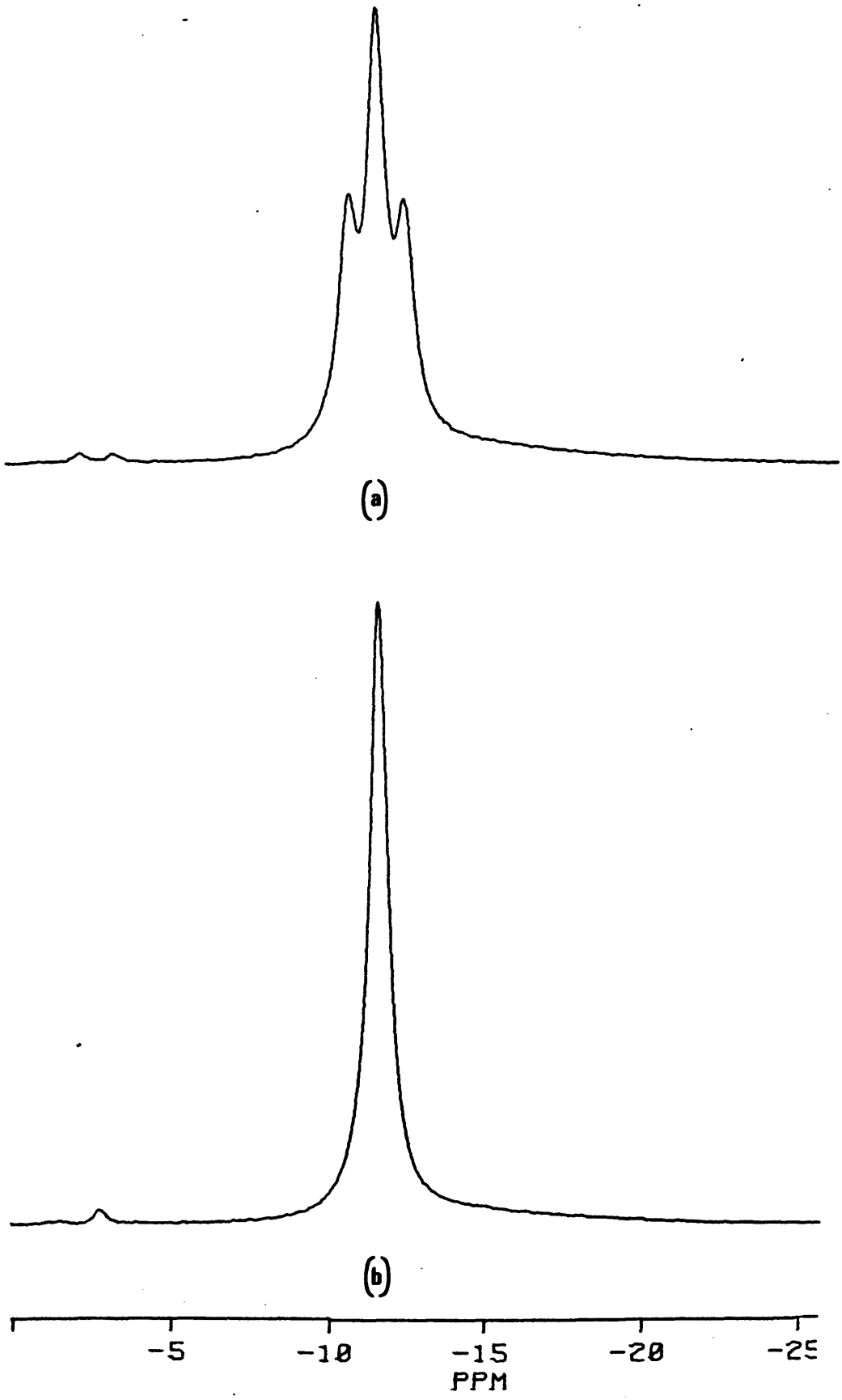

2(CH3)3N.BH3
+
2
R
R
N
N
R
H
reflux
toluene
(82)
2(CH3)3N
+
R
R
R
N
N
H
B
B
H
H
H
H
N
N
R
R
R
+
2H2

4.9.3.2. *Reaction of Pyrazoles with Borane*

The parent pyrazole (a) and two C-substituted derivatives were used in the present work. The derivatives were C-substituted (b) 3, 5-dimethylpyrazole and (c) 3-phenyl, 5-methylpyrazole. Both pyrazole and 3,5-dimethylpyrazole reacted readily, via method b(i), to yield pyrazabole species in high yields (80.1 and 80.8% respectively). These compounds were characterised by analysis, melting points, infrared and n.m.r. spectroscopy. Both pyrazabole and its tetramethyl C-substituted derivative were isolated as colourless crystals with melting points (80-81 and 172-74°C) respectively. They are unaffected by air and moisture and are soluble in halogenated hydrocarbons, THF, monoglyme and benzene.

Table 5 lists the B-H stretching frequencies for both pyrazabole and 1,3,5,7-tetramethylpyrazabole. A characteristic feature of the infrared spectra of both pyrazaboles is the B-H stretching frequency. This feature is quite complex in pyrazabole itself where eight absorptions are present. The peak at 2470 cm^{-1} is the strongest and the others are of gradually decreasing intensity with the exception of the 2310, 2280 cm^{-1} pair where the higher frequency peak is the weaker of the two. Trofimenko[170] has suggested that the complexity of the B-H stretching region is inconsistent with a planar model of essentially D_2h symmetry and supports a puckered structure as indicated by molecular models.

The presence of triplet signals in the ^1H coupled ^{11}B n.m.r. spectra strongly suggested that the products were dimeric, i.e. pyrazaboles. Figures 10 and 11 illustrate the coupled and decoupled ^{11}B n.m.r. spectra for 1,3,5, 7-tetramethylpyrazabole. Table 6 lists the ^1H, ^{11}B and ^{13}C data (including results from DEPT spectroscopy) which were obtained for the pyrazabole products.



Figures 10 and 11: ^{11}B (a) and $^{11}B\{^{1}H\}$ (b) n.m.r. spectra of 1, 3, 5, 7- tetramethylpyrazabole

TABLE 5: *BH Stretching Frequencies*[a] *For Pyrazaboles*

Pyrazabole	1, 3, 5, 7 - Tetramethylpyrazabole
2470	2450
2430	
2410	
2370	2380
2310	2320
2280	2280
2250	
	2240
2240	
	2210

[a] Frequencies in cm^{-1}

TABLE 6: *Multinuclear Nm.r Data for Pyrazaboles*

Compound	δ H	δ H{^{11}B}	JH{^{11}B,^{1}H}	δC{^{1}H}	DEPT $\frac{\pi}{2}$	DEPT $\frac{3\pi}{4}$	δB	JB{^{1}H}	Assignement
Pyrazabole		3.62(s)	3.62(s)						$\underline{BH}_2$
	6.28(m)	6.28(t)	6.28(s)						$\underline{CH}$
	7.60(m)	7.60(d)							$\underline{CH}$
				105.36(d)	105.31(d)				$\underline{CH}$
				134.79(s)	134.79(s)				$\underline{CH}$
							-7.65(t	-7.65(s)	$\underline{BH}_2$
1,3,5,7, -tetra methyl pyrazabole	2.29(s)	2.29(s)							CH_3
		3.44(s)							BH_2
	5.36(s)	5.36(s)							$\underline{CH}$
				11.84(s)		11.84(s)			$\underline{CH}_3$
				105.67(s)		105.67(s)			$\underline{CH}$
				143.67(s)					$\underline{C}$-CH_3
							-11.07(t)	-11.07(s)	$\underline{BH}_2$

The ^{1}H n.m.r. spectrum of pyrazabole is shown in Figure 12 and the ^{13}C spectra for both pyrazaboles is shown in Figures 13 and 14. The spectra obtained are reasonably straight-forward and easily assignable due to the symmetrical nature of the products. Although ^{1}H and ^{13}C data had previously been reported[170] ^{11}B and $^{1}H\{^{11}B\}$ had not.

The reaction between 3-phenyl, 5-methylpyrazole, sodium borohydride and iodine in monoglyme did not lead to the expected pyrazabole derivative (Figure 15).

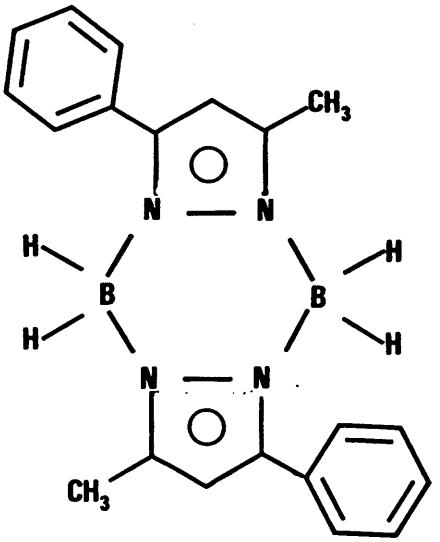


Figure 15: *1, 5-diphenyl, 3, 7-dimethylpyrazabole*

Indeed, the product which was isolated from this reaction did not contain any nitrogen. The infrared spectrum consisted of peaks corresponding to aromatic and alkyl CH stretching as well as BH stretching frequencies. The ^{1}H n.m.r. spectrum (Figure 16) consisted of aromatic signals in the region of 7.25 p.p.m. and possibly a methyl resonance at 1.41 p.p.m. The ratio of aromatic : alkyl protons was 2 : 1. One interesting feature of this spectrum was that on comparison with the ^{1}H n.m.r. spectrum of the starting 3-phenyl, 5-methylpyrazole (Figure 17) the unique heterocyclic ring CH resonance at 5.2 p.p.m. was absent in the spectrum of the product. Since this product was not a pyrazabole further reactions were not pursued. However, X-ray quality crystals of this compound were sent to Professor Ferguson of the University of Guelph for structural analysis. At the time of writing these results were not to hand.

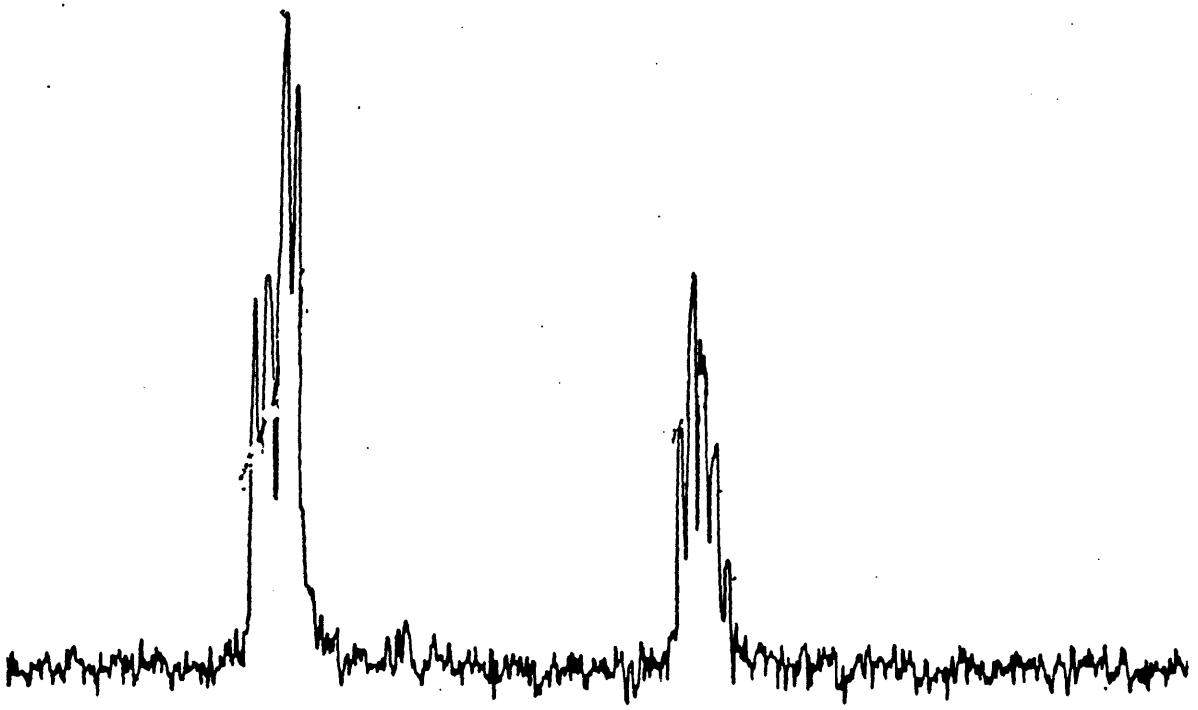


Figure 12: ^{1}H n.m.r. Spectrum of Pyrazabole

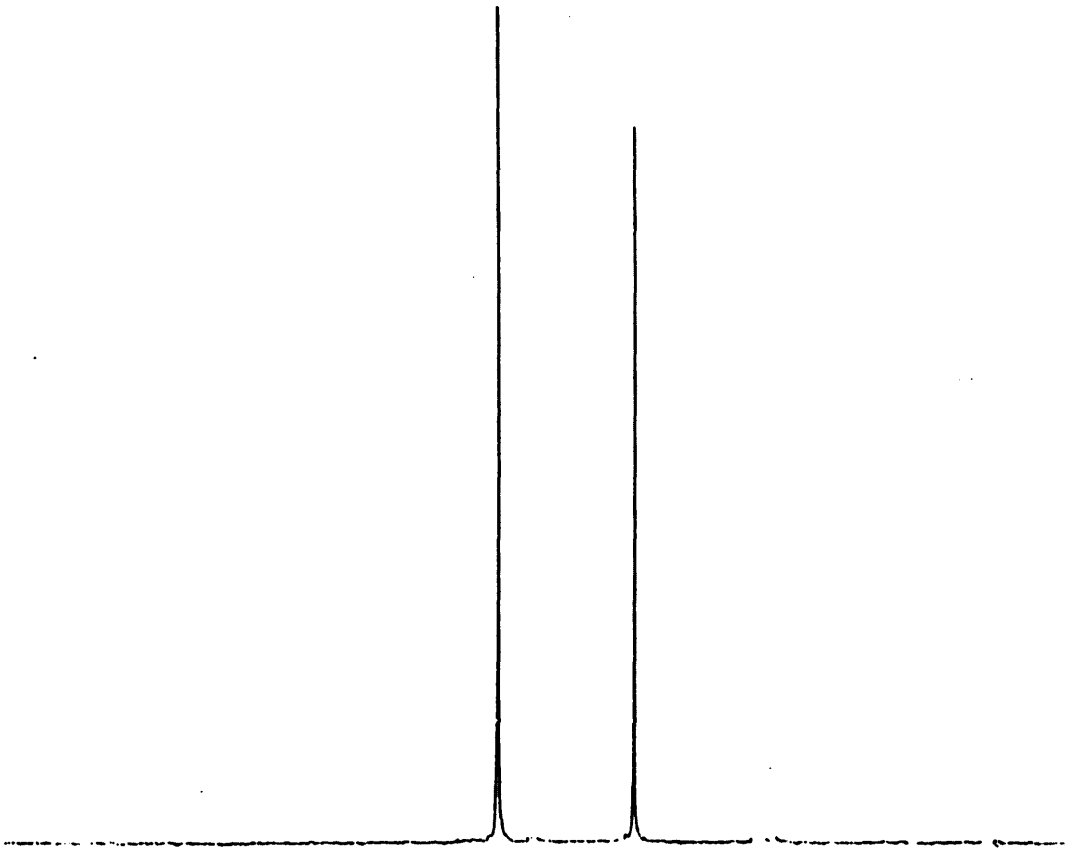


Figure 13: ^{13}C n.m.r. Spectrum of Pyrazabole

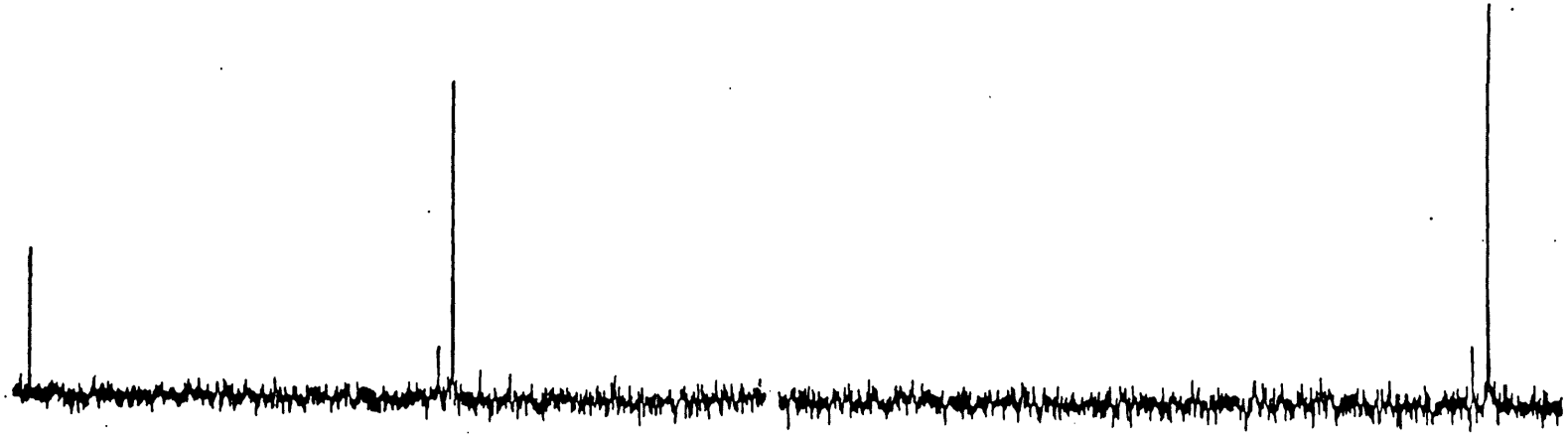
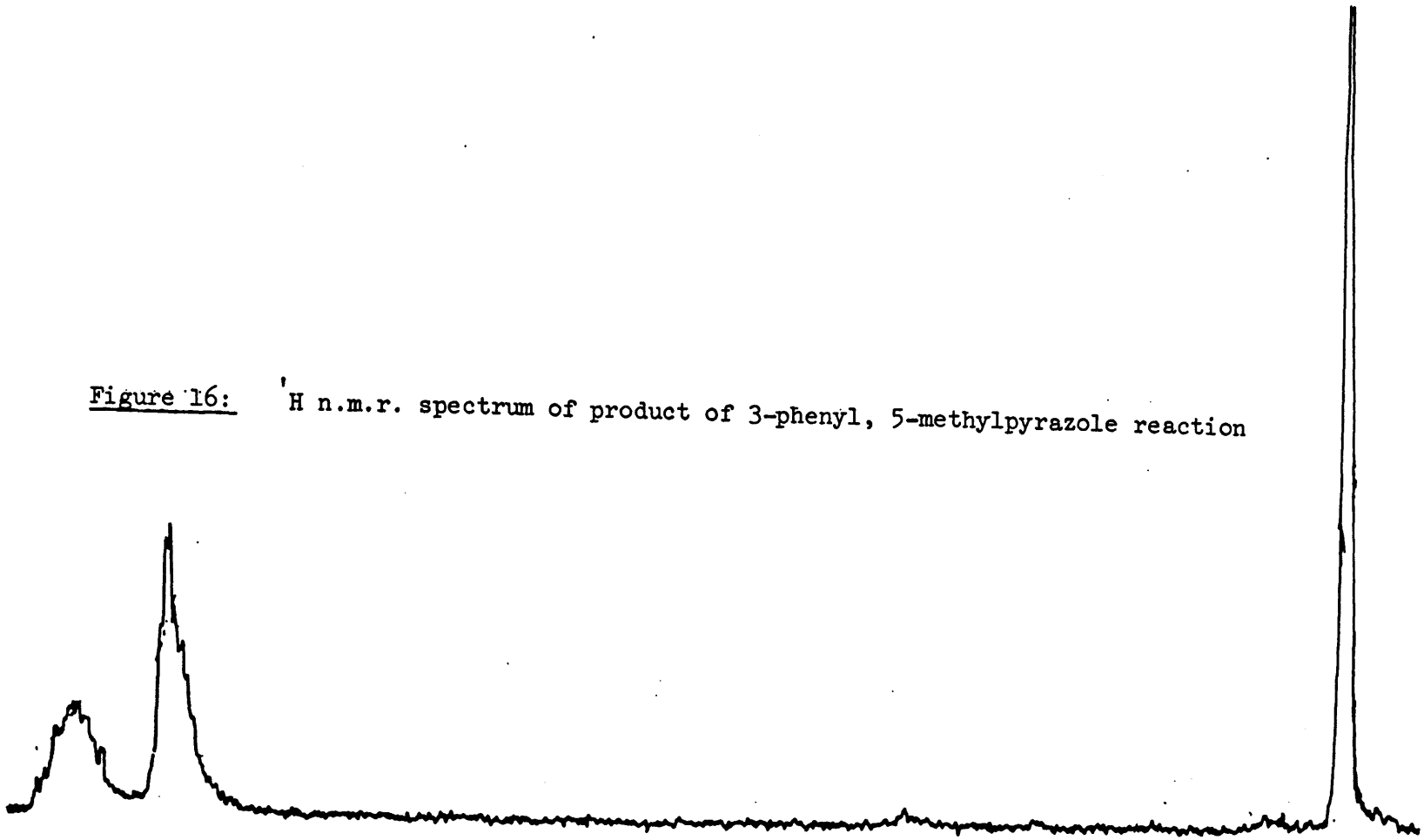


Figure 14: ^{13}C n.m.r. spectrum of 1, 3, 5, 7-tetramethylpyrazabole

Figure 16: ^1H n.m.r. spectrum of product of 3-phenyl, 5-methylpyrazole reaction



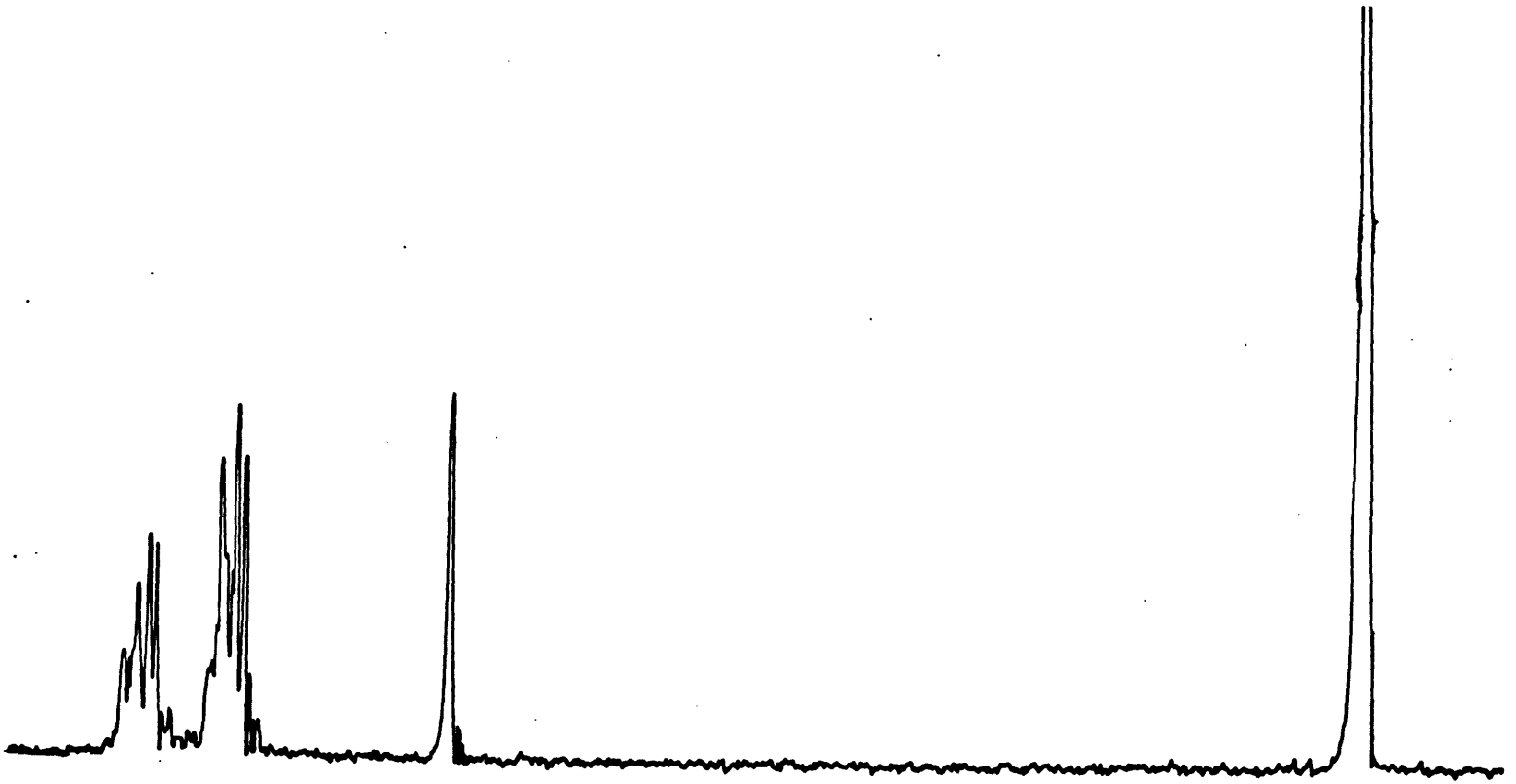
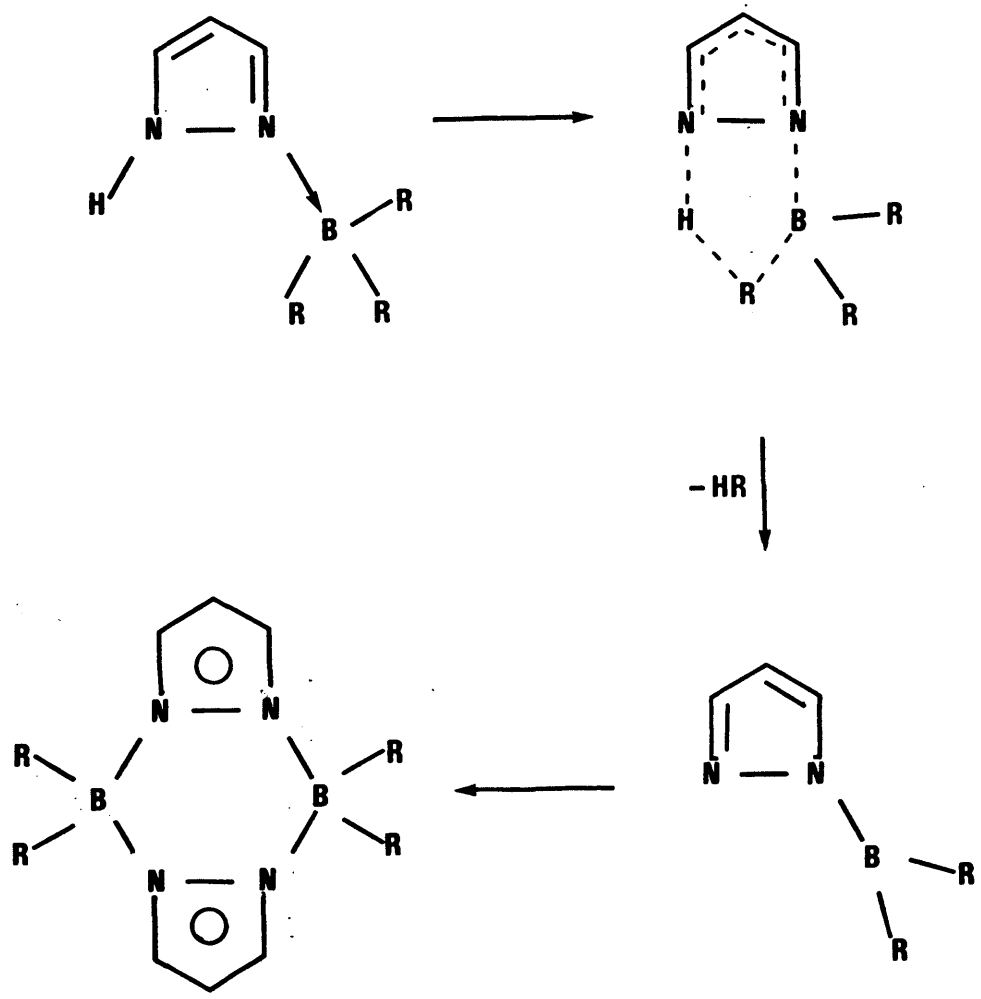


Figure 17: ^{1}H n.m.r. spectrum of 3-phenyl, 5-methyl Pyrazole

4.9.3.3. *Mechanism*

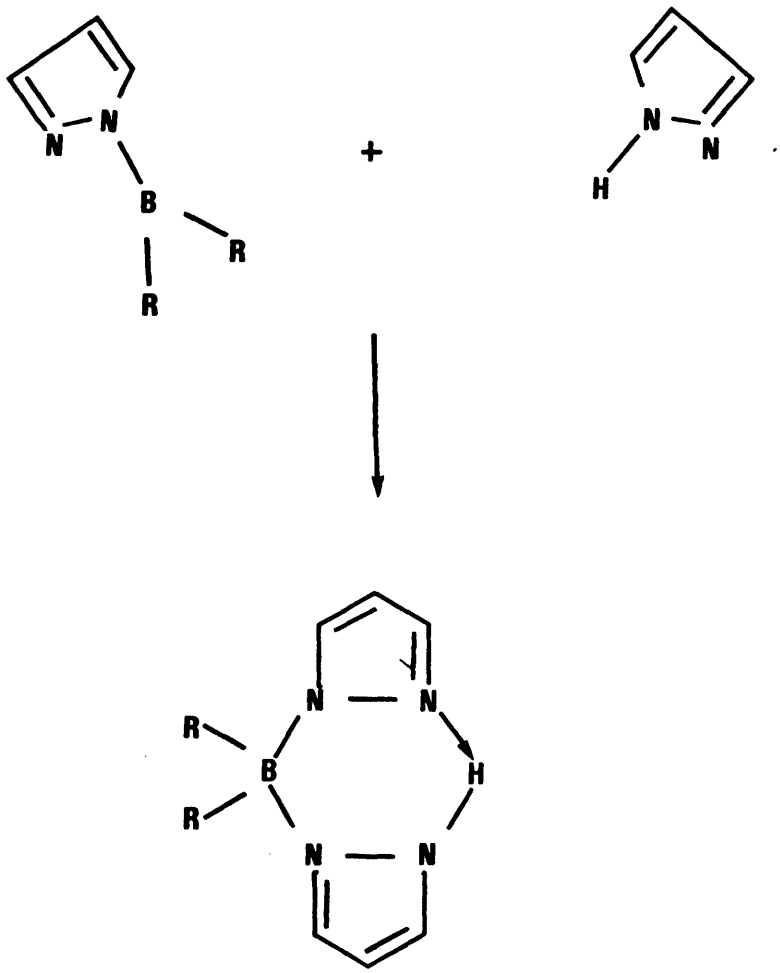
Trofimenko,[170] has commented that the geometry of pyrazole is favourable to a cyclic five-centre transition state and suggested the possible mechanism shown in Scheme 2.

Scheme 2: *Mechanism of Pyrazabole Formation*



This mechanism has been suggested to operate where BR_3 is trialkylboranes, triarylboranes and weak borane-solvent complexes such as borane -THF and borane-monoglyme.

It is also possible for the 1-dialkylborylpyrazole fragments, apart from dimerising, to react with pyrazole itself (83).

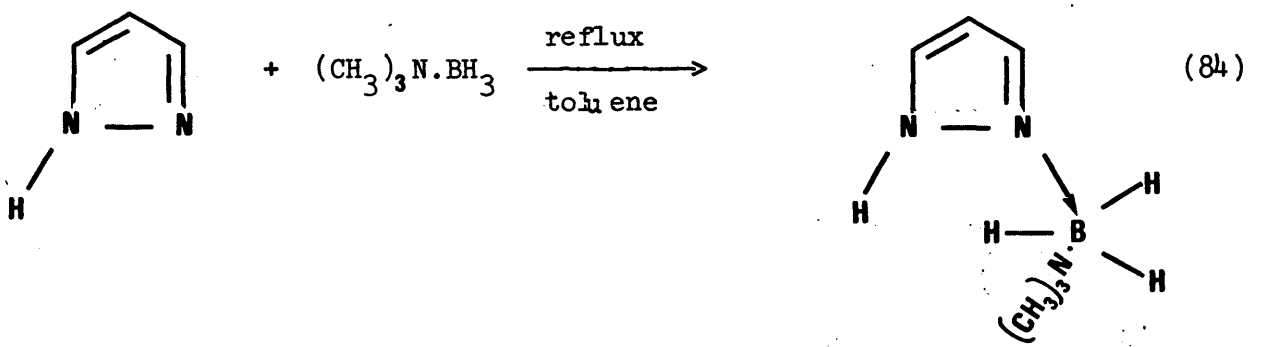


(83)

It has been shown, however, that hydrogen poly(1-pyrazolyl) borates disproportionate irreversibly at elevated temperatures to pyrazaboles and pyrazoles. Moreover, the electrophilicity of the BH_2 group surpasses that of the pyrazole hydrogen, and hence the possibility of reaction (83) above is of minor significance. The intramolecular activation by coordination suggested above is analogous to the reactions of boranes with carboxylic acids, the mechanism of which was proposed by Brown[171] and confirmed by Toporcer, Deasy and Green.[172] While the transition state in borane-

pyrazole reactions may involve a five-membered ring, electrons are relayed along the pyrazole's π system and in that sense an eight-membered ring is involved in the transition state.

A brief comparison between the reactions reported in the present work and the reactions employed by Trofimenko is in order. The previous use of trimethylamine-borane means that a strong donor molecule is involved as opposed to the weak borane-monoglyme complex used in the present work. Trofimenko[170] suggested that an equilibrium involving trimethylamine -1- pyrazolyl-borane is established (84).



(84)

The reaction (84) is driven to completion by removal of trimethylamine and hydrogen from the system and irreversible dimerisation to generate the pyrazabole. Clearly the present reaction which utilises the borane-monoglyme complex, generated *in situ* by method b(i), could proceed more efficiently since the donor strength of an ether is less than an amine.

4.9.3.4. *Attempted Preparations of B-CN Containing Pyrazaboles*

Previously B-substituted groups in pyrazaboles have been limited to alkyl and $(R_2B)_2O$ groups where R = C_2H_5, C_6H_5[173]. Due to the known potential of cyano groups for further reaction in amine-adduct chemistry the preparation of B-substituted pyrazole derivatives such as Figure 18 was attempted.

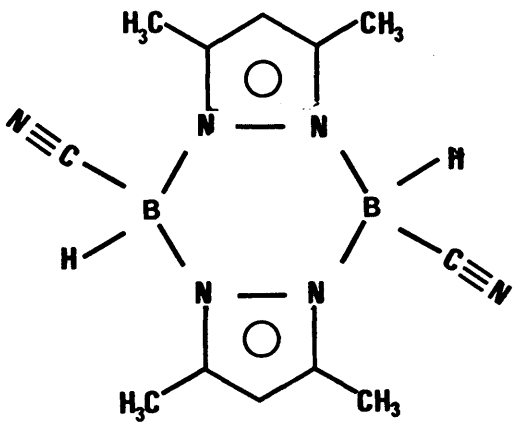


Figure 18: *1,3,5,7-tetramethyl- 4,8-dicyano pyrazabole*

The reaction of pyrazole with cyanoborane-monoglyme complex by method b(i) led to a mixture of products from which no pure products were isolated. However, the reactions of 3, 5-dimethylpyrazole with cyanoborane-monoglyme under the same conditions generated high yields of an unusual product, cyclohexylphenyl-ketone. This result is discussed in more detail in Section 4.9.4.

4.9.4 *Subsection (iv)*

4.9.4.1. *Isolation of an Unexpected Product (Cyclohexylphenylketone) from Reactions of Polyamines by Method b(i)*

A most unusual feature of the chemistry reported here was the isolation in high yields (80-90% based on amine-borane reagents) of cyclohexylphenyl ketone from certain reactions using method b(i). This ketone was produced from the following reactions irrespective of whether they were carried out at room temperature or under reflux conditions; (i) sodium borohydride and iodine with (a)N,N' -*bis* -(3-aminopropylpiperazine) or (b) 3, 3' - *bis*-aminopropylamine and (ii) the reaction of sodium cyanoboro-

hydride and iodine with 3, 5-dimethylpyrazole. Each of these reactions were carried out in monoglyme. When the reaction was completed the monoglyme solvent was removed *in vacuo* and the resulting semisolid extracted with benzene. Evaporation of the benzene and recrystallisation from ether solvents afforded cyclohexylphenyl ketone as colourless crystals. The ketone was characterised by analysis, melting point, infrared, ^{1}H and ^{13}C n.m.r. spectroscopy. Table 7 lists the major infrared absorptions.

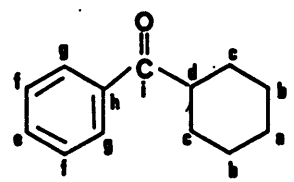
TABLE 7: *Infrared Absorptions for Cyclohexylphenylketone*

Absorption cm^{-1}	*Assignement*
3040 (W)	
3070 (M)	Ar CH
3010 (Sh)	
2930 (br,s)	
2840 (s)	CH_2
2790 (Sh)	
1665 (S)	C = O
1580 (S)	Ar CH

Full characterisation was accomplished with high field ^{1}H and ^{13}C n.m.r. and DEPT experiments. Table 8 lists the ^{1}H and ^{13}C chemical shifts and the DEPT data.

TABLE 8. ^{1}H, ^{13}C and DEPT Data for Cyclohexylphenylketone

δH ppm	Intensity	Assignement	$\delta C[^{1}H]$ ppm	DEPT $\frac{3\pi}{4}$ ppm	DEPT $\frac{\pi}{2}$ ppm	Assignement
1.19-1.54(m)	6	Ha,b	25.70	25.70(-ve)		a,b(1:2)
(m)	4	Hc	29.26	29.26(-ve)		c
3.24(t of t)	1	Hd	45.32	45.32(+ve)	45.32(+ve)	d
7.38-7.53(m)	3	He,f	128.02	128.02(+ve)	128.J2(+ve)	e
7.90(d)	2	Hg	128.34	128.34(+ve)	128.17(+ve)	f
			132.42	128.42(+ve)	132.42(+ve)	g
			136.24			h
			203.22			i



Cyclohexylphenylketone

The ^{13}C ['H] spectrum is straightforward, consisting of just nine signals. Four each for the cyclohexyl and phenyl rings and one for the carboxyl carbon. DEPT $\frac{3\pi}{4}$ and DEPT $\frac{\pi}{2}$ spectra were also recorded which aided the characterisation. In DEPT $\frac{3\pi}{4}$ spectra CH groups are seen as positive signals and CH_2 groups as negative signals. DEPT $\frac{\pi}{2}$ spectra show only signals for CH_2 groups. Figures 19, 20 and 21, illustrate these spectra.

4.9.4.2. *Discussion of the Synthesis of Cyclohexylphenylketone*

Cyclohexylphenylketone was a totally unexpected product from the reactions above. While no definitive mechanism has been established, there are a number of pertinent observations which can be made. In contrast to the reactions with monoamines, reactions with polyamines were less likely to give the expected adducts using either method (a) for example the reaction of N, N' - *bis*(3-aminopropyl) - piperazine-dihydrochloride with sodium borohydride (see Experimental Section) or method b(i) for example reactions (a) and (b) above. However, method b(ii) appeared to give the expected adducts for polyamines, for example in the preparation of 4-dimethylaminopyridine-cyanoborane.

It would be reasonable to suggest from these results that method b(i) is less consistent for polyamines and that method b(ii) should be used instead in the preparation of polyamine adducts. However, the reactions of both pyrazole and 3, 5-dimethylpyrazole leading to the dimeric pyrazabole species were both carried out using method b(i). Since both of these reactions furnished the expected adduct and the reaction of 3, 5-dimethyl-pyrazole with sodium cyanoborohydride afforded the ketone it is apparent that factors other than simply the number of amine sites may be important.

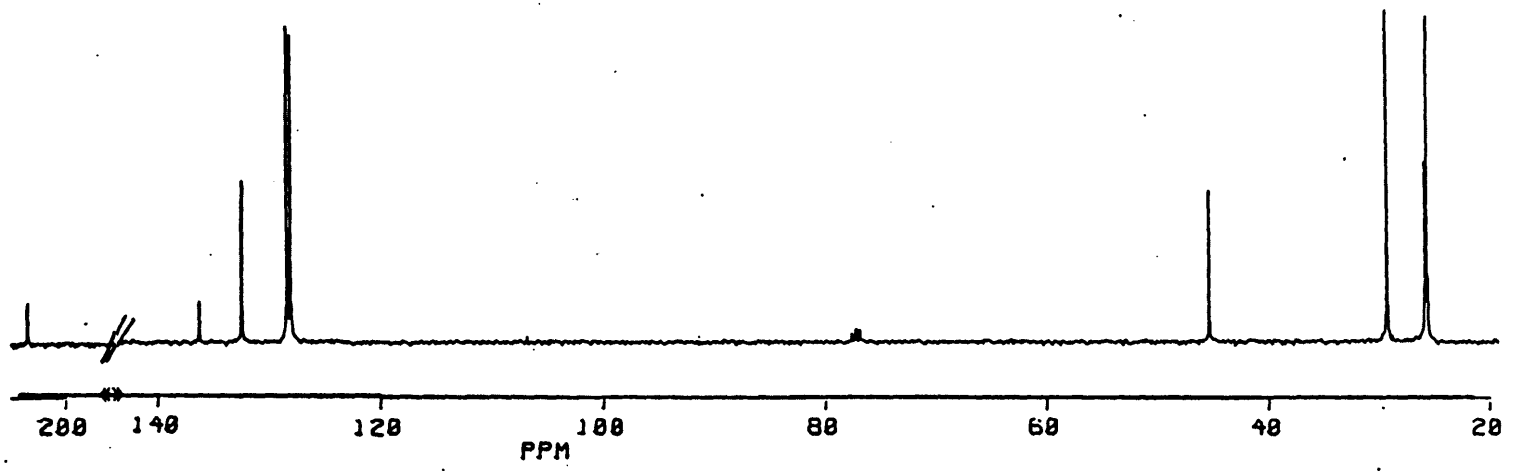
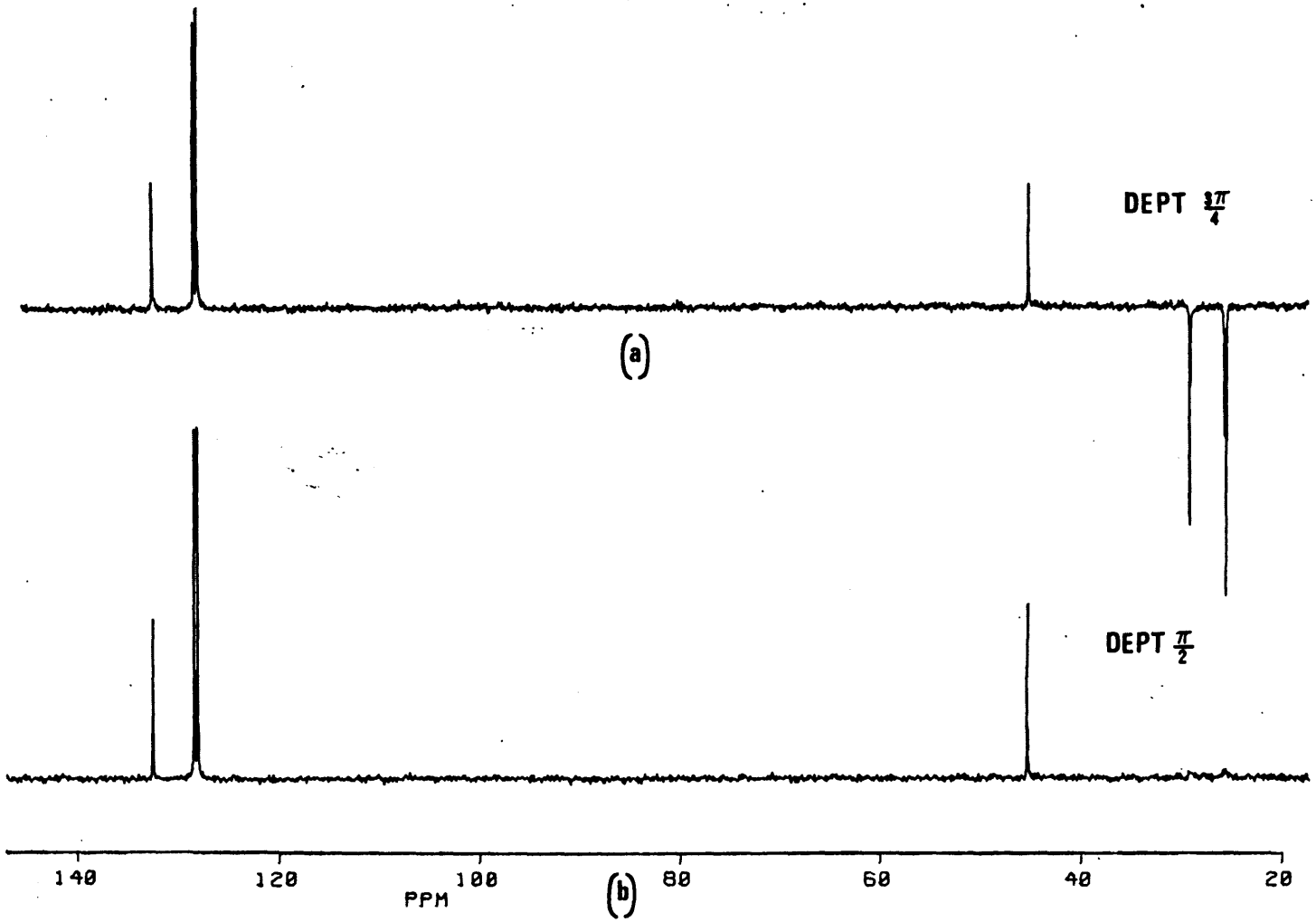


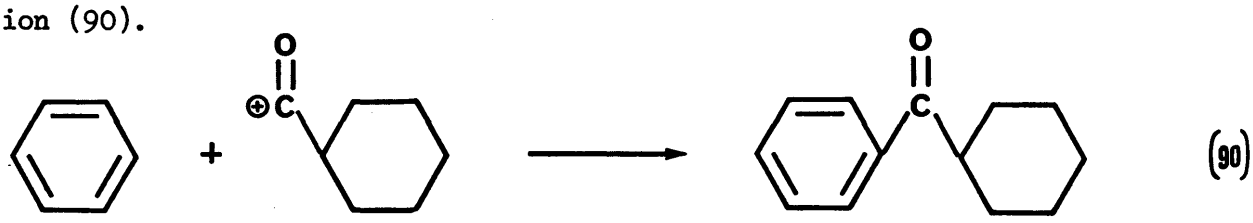
Figure 19: $^{13}C\{^{1}H\}$ n.m.r. spectrum of cyclohexylphenylketone



Figures 20 (a) and 21 (b): ^{13}C DEPT n.m.r. spectra of cyclohexyl-phenylketone

It is also relevant to note that when the ketone was produced it was the sole isolable product and no nitrogen-boron species were obtained. In some cases t.l.c. analysis of the semisolid residue indicated a complex mixture of products but this material rapidly decomposed on exposure to air and no information was obtained as to its content. In an attempt to clarify the importance of the extraction solvent an experiment using toluene for reaction (a) was carried out. However, neither the anticipated cyclohexyltolylketone nor any borane containing material were isolated after work-up and purification procedures.

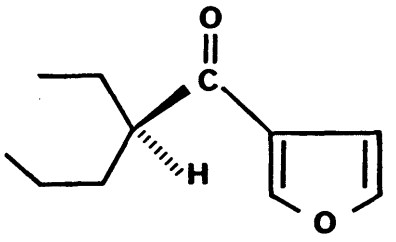
It is clear that, whatever mechanism is involved in the generation of this ketone, no $[BH_3X]^-$ or amine-borane species can be present during the formation of the ketone function since these species are known to reduce the keto function. Furthermore, the incorporation of the phenyl group suggests that the benzene extraction solvent was initially involved, possibly as a substrate for electrophilic substitution by a carbonium type ion (90).

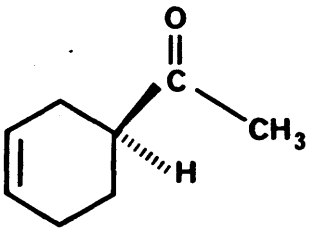


(90)

However, the failure of toluene to react similarly is inexplicable if this reaction took place. Clearly the ketone producing reaction is extremely complex and possibly of interest to organic chemists but it was not of primary interest to the work being undertaken here. It was decided not to continue with further investigation of this reaction.

One final note of interest was found in a recent edition of Aldrichimica Acta (1987)[174] which was dedicated to Professor H.C. Brown. The preparation of optically pure α-chiral ketones (Figures 22 and 23) is described, based on optically pure borane esters.[175]

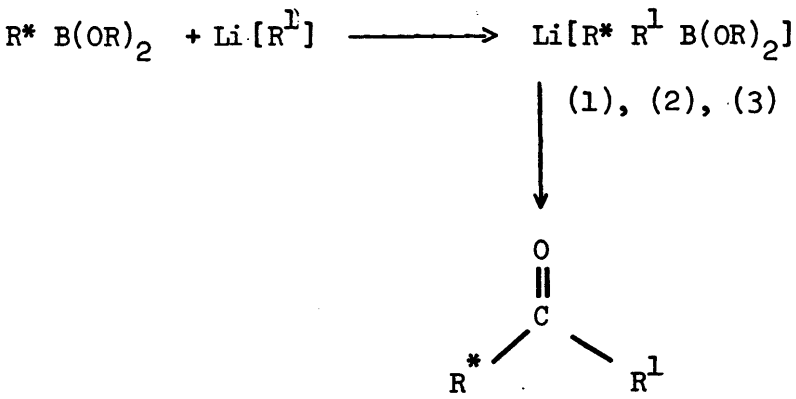




Figures 22 and 23: Optically Pure α - Chiral Ketones

Scheme 3 outlines the route to these ketones used by Brown *et al.*[175] While there is little obvious similarity between the reaction in Scheme 3 and those leading to cyclohexylphenyl ketone there may be comparable reactions taking place.

Scheme 3: Synthesis of Optically Pure α-Chiral Ketones



1) $HCl_2C{-}O{-}CH_3$ (DCME)
2) [t - B_uO]Li
3) H_2O_2, PH 8.

4.10: SECTION 2

4.10.1 *Adducts of Triphenylphosphine*

Three adducts of triphenylphosphine were prepared, namely $(C_6H_5)_3P.BH_2X$, where X = H, CN and $-\overset{O}{\overset{\|}{C}}-OCH_2CH_3$. The main purpose of this work was to improve the yield of triphenylphosphine-cyanoborane from the literature value of 34%.[149] (The Cyanoborane adduct was the precursor of the ethocarbonylborane compound). All three compounds were white, crystalline solids with well defined melting points (Table 9). A comparison of the infrared spectra in the borane region shows that replacement of hydrogen by cyanide on the ethoxy-carbonyl group shifts the B-H stretching frequencies to higher values, (Table 9)

TABLE 9: Melting Points and B-H stretching Frequencies of $(C_6H_5)_3P.BH_2X$ Adducts

X	Melting Point °C	ν B-H cm^{-1}
H	189-190	2360 (br,s)
		2240 (m)
CN	172-174	2380 (s)
		2340 (sh)
		2250 (m)
$-\overset{O}{\overset{\|}{C}}-OCH_2CH_3$	76-78	2410 (br, m)
		2350 (m)

The P-B stretching frequency has been reported to be between 750 and 550cm^{-1} with medium to strong intensity.[136] While peaks are observed in this region for the compounds studied, proper identification is difficult since there are a number of similarly intense peaks in this area in each spectrum.

The 'H n.m.r. spectra exhibited no significant differences in chemical shifts in the aryl region for the adducts. Triphenylphosphine-borane was prepared in very high yield (98%) according to the literature synthesis (method b(i)) (91)[8].

$$(C_6H_5)_3P + CH_3O(BH_3)-CH_2-CH_2-O-CH_3 \xrightarrow{\text{monoglyme}} (C_6H_5)_3P.BH_3 + CH_3-O-CH_2-CH_2-O-CH_3 \quad (91)$$

XXIII

However, when this method was applied to produce the cyanoborane adduct (92) the yield of triphenylphosphine-cyanoborane was only 36% (34% literature)[149].

$$(C_6H_5)_3P + CH_3-O(BH_2CN)-CH_2-CH_2-O-CH_3 \xrightarrow{\text{monoglyme}} (C_6H_5)_3P.BH_2CN + CH_3-O-CH_2-CH_2-O-CH_3 \quad (92)$$

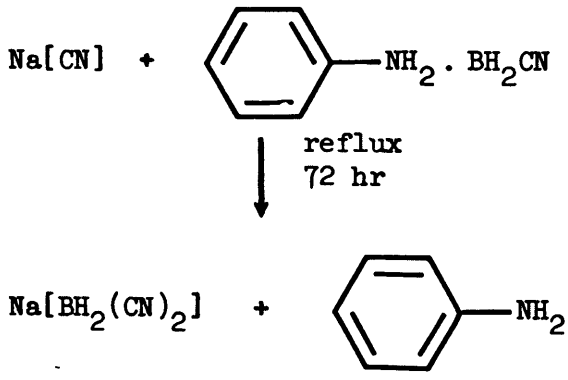
The lower yield of BH_2CN adduct compared to BH_3 adduct is also seen in the reactions of amines. For example, dicyclohexylamine-borane was isolated in 95.6% from the reaction of dicyclohexylamine with borane-monoglyme complex but when the synthesis was extended to the cyanoborane analogue the yield was reduced to 86.9%. Similarly, Martin *et al*[79] reported yields of approximately 25%. for nine amine-cyanoborane adducts prepared by method b(ii).

Spielvogel *et al*[176] have prepared a mixture of cyanoborane polymers, $(H_2BCN)_n$ (n = 4 to 10) by addition of dry HCl to a solution of $Na[BH_3CN]$

in ether. A crystal structural determination of the hexamer showed it to be a centrosymmetric chain-like macrocyclic ring.[165] (Figure 8) When Kelly and coworkers[78] reacted these cyanoborane polymers with amines the average yield of aminecyanoborane adducts was just 30%. After addition of the halogen (Cl_2, Br_2, I_2) to the sodium cyanoborohydride in monoglyme, evidence for the cyanoborane oligomers is seen in the ^{11}B n.m.r. spectrum by the broad, unresolved resonance at -43.9 to -46.9 p.p.m.[176] Some unreacted cyanoborohydride is also detected by the presence of a quartet -58.9 to -62.5 p.p.m. (from trimethylborate) in the ^{11}B spectrum. Martin *et al*[79] have reported that the addition of more halogen does not increase the yield of product. It is clear that both the generation of oligomeric species and the non-quantitative formation of cyanoborane-monoglyme play a significant role in the reduced yield of cyanoborane adducts. (These factors are not apparently significant in the synthesis of borane adducts by this method). In an effort to improve the yield of triphenylphosphine-cyanoborane two other synthetic routes were tried.

4.10.1.1. *(i) Amine-displacement Method*

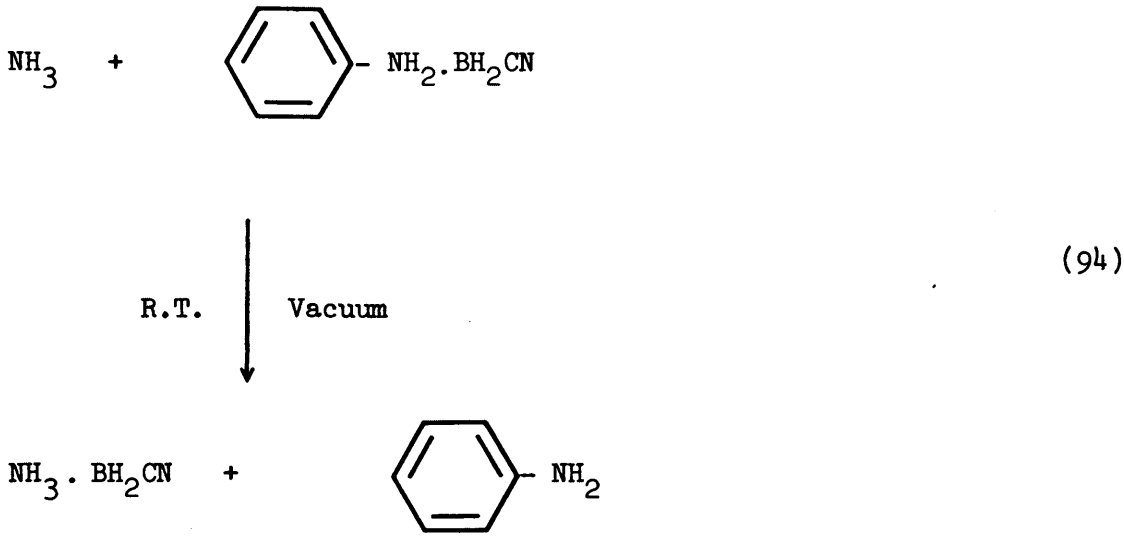
Spielvogel and coworkers in 1984[177] synthesised sodium dicycanoborohydride by the displacement of aniline from the weak cyanoborane adduct by reaction with sodium cyanide (93).



(93)

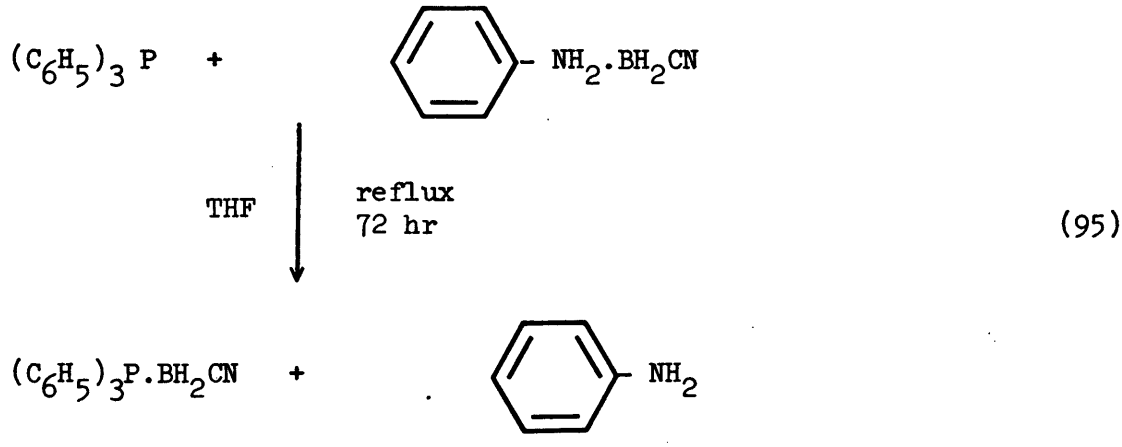
The hygroscopic $[BH_2(CN)_2]$ salt was isolated in 71% yield by the addition of dichloromethane to the crude semisolid material.

Spielvogel and coworkers[164] also prepared ammonia-cyanoborane in 81.4% by this method (94).



(94)

The reaction between triphenylphosphine and aniline-cyanoborane in THF (95) produced triphenyl phosphine-cyanoborane in 27.5% i.e. lower than the previous method.



(95)

An increased reaction time did not significantly improve the yield.

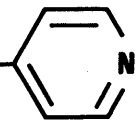
4.10.1.2. *(b) Reaction with Mercuric Cyanide*

Gyori and Emri[60] had reported the synthesis of sodium cyanoborohydride by the reaction between borohydride and mercuric cyanide (96)

$$2\ Na[BH_4] + Hg[CN]_2 \xrightarrow[\text{reflux 3 hrs}]{\text{THF}} 2\ Na[BH_3CN] + Hg^{\circ} + H_2 \qquad (96)$$

and also that amine- and sulphide-boranes reacted with mercuric cyanide to generate the corresponding amine-cyanoborane adducts (97).

$$L.BH_3 + Hg[CN]_2 \xrightarrow{\text{ether}} L.BH_2CN + Hg^{o} + HCN \qquad (97)$$

L = NC  or $(CH_3)_2S$.

In a modification of this type of reaction, two equivalents of triphenylphosphine-borane were reacted with one equivalent of mercuric cyanide (98) to afford triphenylphosphine-cyanoborane in 76.4% yield.

$$2(C_6H_5)_3P.BH_3 + Hg[CN]_2$$

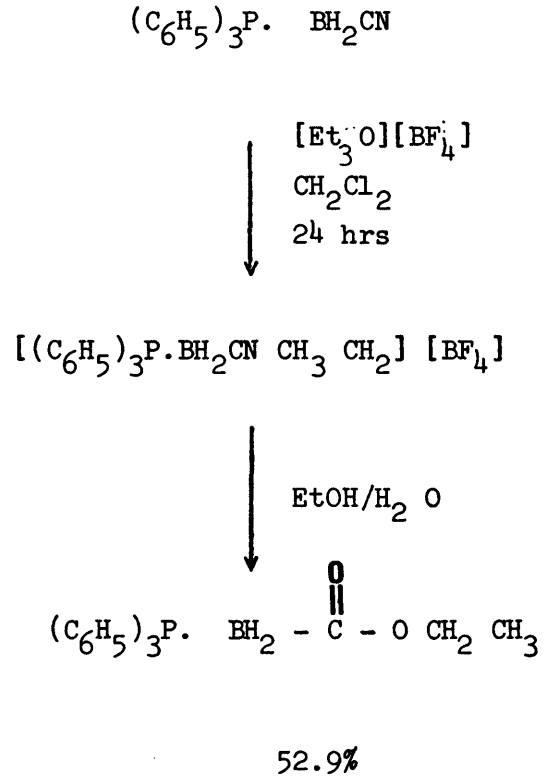
$$\xrightarrow[\text{3 hrs}]{\text{reflux, THF}} \qquad (98)$$

$$2(C_6H_5)_3P.BH_2CN + Hg^{o} + H_2$$

In terms of yield, this route was by far the most successful one to triphenylphosphine-cyanoborane and compares extremely favourably with both previous syntheses (36 and 27.5%) and the literature yield (34%). An added feature is that by using two equivalents of borane to one of mercuric cyanide the generation of HCN as a side product is avoided in contrast to reaction (97).

The conversion of the cyanoborane adduct to the ethoxycarbonylborane adduct was achieved by reaction with triethyloxonium tetrafluoroborate. This generated an N-ethylnitrilium salt which was not isolated but instead it was reacted *in situ* with aqueous ethanol to form the borane ester (Scheme 4). The yield of 52.9% compares favourably with the literature yield of 41%.[149]

Scheme 4: Synthesis of Triphenylphosphine-ethoxycarbonyborane



4.11: EXPERIMENTAL

General Methodology

All solvents were routinely distilled prior to use. Dry solvents were obtained by standard procedures according to Perrin *et al*[178]. Tetrahydrofuran (THF) was dried by initial storage over KOH pellets, followed by reflux over powdered lithium aluminium hydride. Finally, THF was distilled from the potassium-benzophenone ketyl. All reactions were carried out under dry nitrogen atmosphere. Melting points were determined on a Reichert Microscope hot stage melting point apparatus and are uncorrected. Elemental analyses were performed at the Microanalytical Laboratory, University College, Cork. Thin layer chromatography (t.l.c.) and preparative chromatography (p.l.c.) were carried out on glass supported silica gel plates using Merck silica HF_{254} and PF_{254} respectively.

Infrared (i.r.) spectra were recorded as KBr discs for solids and thin films between sodium chloride plates for liquids on a Perkin-Elmer 682 infrared spectrophotomer. Intensities are designated as, s, strong; m, medium; w, weak; and sh, shoulder. Mass spectra were recorded on an AEI Krato DB 3074 high resolution mass spectrometer at 70 e.v. (U.C.C.) or from a V.G. Micromass 7070 high resolution double focussing mass spectrometer coupled to an INCOS 2400 data system (University of Guelph, Canada).

^{1}H n.m.r. were recorded at 60 MHZ on a Hitachi-Perkin Elmer R20A (U.C.C.), at 270 MHz on a Jeol high field n.m.r. spectrometer in University College, Galway and at 360 MHZ on a Bruker WH 360 high field n.m.r. spectrometer in the University of Edinburgh. ^{13}C n.m.r. spectra were recorded at 15 MHz on a Jeol FNMFX60 Fourier transform spectrometer at 24°C and 68.75 and 90 MHz respectively on the above high field instruments. ^{31}P n.m.r. spectra were recorded at 109.25 MHZ (Galway) and

MHz (Edinburgh). ^{11}B n.m.r. were recorded at 86.55 MHz (Galway) and MHz (Edinburgh).

Deuterochloroform ($CDCl_3$) was used as solvent in all n.m.r. recordings (unless otherwise stated). Tetramethylsilane (TMS) was used as an internal standard for ^{1}H and ^{13}C n.m.r. spectra; 85% phosphoric acid and borontrifluoride-etherate were used as standards for the ^{31}P and ^{11}B n.m.r. spectra respectively. Chemical shifts are expressed in parts per million (p.p.m.); positive shifts being down field from T.M.S. Splitting patterns are designated as; s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet and m, multiplet. Single crystal X-ray crystallographic structural analyses were performed by Professor George Ferguson in the University of Guelph. Data were collected on an Enra F - Nonius CAD -4 diffractometer using graphite monochromatised MoKα radiation.

Amine Hydrochlorides: General Procedure

Hydrogen chloride gas (generated by the dropwise addition of concentrated sulphuric acid) was bubbled into a solution of amine in diethylether, at 0°C. The resulting white precipitate was isolated by vacuum filtration, washed with diethylether, dried and recrystallised from 95% alcohol.

In a typical experiment: hydrogen chloride gas (0.082 mol) was bubbled into a solution of t-butylamine (6.88 ml, 0.05 mol) in 50 ml diethylether at 0°C. Isolation and purification of the white precipitate according to the general procedure furnished t-butylamine-hydrochloride as colourless plates in quantitative yield. Analysis: calcd. for $C_4H_{12}NCl$: C, 43.83; H, 10.95; N, 12.78; Cl, 32.42%. Found: C, 43.77; H, 10.77; N, 13.01; Cl, 32.43%.

Table 10 lists the amine-hydrochlorides thus prepared, the yields obtained and the relevant analytical data.

TABLE 10

AMINE-HYDROCHLORIDES

Compound	Number	Yield	Analysis			
			C	H	N	Cl
			%			
t-butylamine-HCl	XXXVI	100	43.77 (43.83)	10.77 (10.95)	13.01 (12.78)	(32.43) (32.42)
dicyclohexylamine-HCl	XXXXVII	94	66.00 (66.20)	11.25 (11.3)	6.22 (6.43)	16.46 (16.32)
diphenylamine - HCl	XXXXXVIII	92.8	70.27 (70.07)	6.07 (5.83)	6.69 (6.81)	17.15 (17.17)
Aniline - HCl	IL	94.0	56.49 (56.47)	5.62 (5.49)	10.93 (10.90)	27.84 (27.82)
Di-n-butylamine-HCl	L	98.2	58.34 (58.35)	11.75 (11.55)	8.49 (8.51)	21.57 (21.58)
Diethylenetriamine-3HCl	LI	87.4	22.56 (22.56)	7.52 (7.52)	11.95 (11.76)	49.95 (50.11)
Triethylamine-HCl	LII	83.6	52.33 (52.36)	11.46 (11.64)	10.23 (10.23)	25.80 (25.82)
Pyrazole-HCl	LIII	94.8	34.17 (34.64)	4.84 (4.78)	26.79 (26.79)	33.72 (33.17)
Pyridine-HCl	LIV	77.2	49.47 (49.33)	10.10 (9.86)	11.20 (11.51)	29.30 (29.21)
1,2-Phenylene diamine-2HCl	LV	89	39.95 (39.77)	5.69 (5.52)	15.61 (15.46)	39.07 (39.22)

1,4-Phenylenediamine-2HCl	LVI	91.2	40.01 (39.77)	5.58 (5.52)	15.34 (15.46)	39.16 (39.22)
Epledrine-HCl	LVII	78.7	54.39 (59.48)	7.94 (7.93)	7.05 (6.93)	17.50 (17.59)
N,N^{1}-*bis*-(3-aminopropyl)-pyerazine-2HCl	LVIII	82.5	43.82 (43.79)	9.79 (9.85)	20.15 (20.43)	25.68 (25.91)

Sodium cyanoborohydride LIX: Method 1[159]

A solution of HCN gas (generated *in situ* by the dropwise addition of a solution of sulphuric acid (31.95 ml, 0.60 mol) in 124.5 ml water to a solution of potassium cyanide (39.06g, 0.60 ml) in 75 ml water) was passed through a calcium chloride drying train and into a suspension of sodium borohydride (20.0g, 0.526 ml) T.H.F. (250 ml). The reaction flask was maintained at 25°C with a water bath. Upon complete addition of the gas, the mixture was stirred for 1 hr at ambient temperature then gradually heated to reflux until hydrogen evolution ceased. The flask was allowed to cool to room temperature and the system flushed with dry N_2. Unreacted solids were removed by vacuum filtration through a bed of celite and thoroughly washed with 3 x 30 ml portions of T.H.F. The combined filtrates were then evaporated to dryness to afford sodium cyanoborohydride (15.8g, 47.7%) as a white powdery, hygroscopic solid. ν max (KBr) 2330, 2240 (br, s); 2180(s); 1620 (s); 1200 (sh); 1120 (s); 885 (m); 840 (w); 745 (w); 725 (w); 700 (w); cm^{-1}.

Method 2[60]

Mercuric cyanide (24.8 g,0.098 mol) was added quickly to a suspension of sodium cyanoborohydride (7.48 g,0.196 mol) in 250 ml tetrahydrofuran. The ensuing vigorous reaction was stirred at room temperature until hydrogen evolution had subsided and subsequently refluxed for 3 hrs. Mercury and a grey solid material separated from the cooled solution and were removed by suction filtration through a bed of celite and washed with tetrahydrofuran, under a blanket of N_2. Evaporation of the combined filtrates and drying under dynamic vacuum furnished sodium cyanoborohydride (11.27 g, 91%) whose appearance and infrared spectrum were identical to above.

Triethyloxonium tetrafluoroborate LX

Triethyloxonium tetrafluoroborate, $[(C_2H_5)_3O][BF_4]$ was prepared from borontrifluoride-etherate and epichlorohydrin according to the procedure of Meerwein.[85]

Epichlorohydrin (18.8 ml,0.024 mol) in 20 ml diethyl ether was added from a pressure equalised dropping funnel to a magnetically stirred solution of borontrifluoride etherate (40 ml,0.317 mol) in 80 ml diethyl ether. The rate of addition was chosen to maintain the reaction mixture at reflux temperature. The initially formed oil was converted into a white precipitate during rapid stirring over a 2 hr period. After the reaction had stood overnight under dry nitrogen, the diethyl ether was removed and the white solid washed three times with 50 ml portions of diethyl ether. Finally, the product was dried for 48 hrs under dynamic vacuum to furnish triethyloxonium tetrafluoroborate (45.0 g, 74.8%) as a white crystalline solid.

Triethyloxonium tetrafluoroborate is best when used immediately but may be stored in a freezer compartment or under dry nitrogen.

Amine-boranes and cyanoboranes: General Method (a)[2, 77]

A stoichiometric quantity of sodium borohydride or sodium cyanoborohydride was added to a solution of amine-hydrochloride in tetrahydrofuran. This addition resulted in vigorous hydrogen evolution and immediate precipitation of sodium chloride. After the gaseous evolution had subsided, the reaction mixture was refluxed for approx. 20 hrs typically. The sodium chloride was removed from the cooled solution by vacuum filtration through a bed of celite and thoroughly washed with 3 x 20 ml portions of T.H.F. The clear filtrates were combined and evaporated. Purification of the resulting solid typically involved precipitation from a benzene solution by the addition of hexane or recrystallisation from ethanol.

Amine and Phosphine-Boranes/Cyanoboranes: General Method (b) (i)[8]

A suspension of sodium borohydride or a solution of sodium cyanoborohydride in monoglyme was prepared. To this amine or phosphine was added followed typically by a further portion (10-23 ml) of monoglyme. The resulting solution was stirred at ambient temperature for 10 minutes. A solution of iodine in monoglyme was added dropwise from a pressure equalised dropping funnel over a period of time (usually 30-60 minutes). The subsequent reaction mixture was stirred at room temperature until the iodine colour had disappeared and then refluxed overnight. On cooling the monoglyme was removed under reduced pressure and the solid produced extracted three times with benzene portions. The crude solid from evaporation of the benzene extractions was recrystallised typically from ethanol or ethanol: glyme (2 : 1).

Method b(ii)[79]

A variation of the above synthetic method was to react sodium borohydride or sodium cyanoborohydride with iodine in monoglyme initially and then, after the iodine colour had dissipated, the amine or phosphine was added with 10-20 ml of monoglyme and the resulting mixture refluxed overnight. The workup and purification processes were as above.

The following amine and phosphine-boranes/cyanoboranes were thus prepared:

t-Butylamine-borane, LXI : Procedure (a)

Sodium borohydride (1.27g,0.033 mol) was added to a solution of t-butylamine-hydrochloride (3.7g,0.03 mol) in 40 ml THF. The slow addition of hexane to a benzene solution of the crude solid furnished t-butylamine-borane (1.85g, 90.5%) as a white, crystalline solid. m.p. 96-98°C. Analysis: calcd. for $C_4H_{14}NB$: C, 55.17; H, 16.09; N, 16.09; B, 12.64% Found: C, 54.97; H, 15.94; N, 16.20; B, 12.48% ν max (KBr): 3250 (s);

3320 (s); 2990 (sh); 2970 (m); 2870 (sh); 2400 (sh); 2300 (br,s); 1590 (s); 1470 (m); 1400 (m); 1370 (s); 1335 (s); 1225 (m); 1200 (sh); 1185 (sh); 1160 (s); 1050 (m); 975 (m); 955 (vw); 930 (w); 885 (s); 795 (w); 690 (w) cm^{-1} δ H(270 MHZ) 1.39 (s, 9H $(CH_3)_3$) p.p.m. δ B $\{^1H\}$ (86.55 MHz) - 24.6 (s, BH_3) p.p.m.

Procedure (b) (i)

t-Butylamine (18.4 ml, 0.0176 mol) was added to a suspension of sodium borohydride (8.0g, 0.211 mol) in 60 ml monoglyme. A solution of iodine (22.33g, 0.088 mol) in 80ml monoglyme was subsequently added. Recrystallisation afforded LXI (19.68g, 93.61%) as a white crystalline solid. Microanalytical and spectroscopic analyses were as for procedure (a).

Dicyclohexylamine-borane LXII: Procedure (a)

Sodium borohydride (1.1g, 0.0265 mol) was added to a solution of dicyclohexyl amine-hydrochloride (6.40g, 0.0265 mol) in 80 ml THF. Recrystallisation of the crude product from 95% ethanol afforded dicyclohexylamine-borane (3.35g, 98.9%) as a white crystalline solid. m.p. 101-102°C. Analysis: calcd. for $C_{12}H_{16}BN$: C, 73.84; H, 13.23; N, 7.18; B, 5.64% Found: C, 73.78, H, 12.92; N, 6.97; B, 5.74%. ν max (KBr) 3240 (m), 2930 (s); 2850 (s); 2650 (v.w); 2380 (s); 2340 (sh); 2320 (sh); 2270 (s); 1600 (w); 1570 (w); 1480 (sh); 1460 (sh); 1450 (s); 1380 (w); 1090 (w); 1055 (m); 1025 (w); 955 (m); 910 (w); 890 (v.w.); 870 (w); 840 (m); 800 (w); 790 (v.w.) cm^{-1} δ H (270 MHZ) 1.38-1.51 (br, m); 2.07 (br, s); 2.11 (br, d); 2.87-2.97 (br, m); 3.49 (br, s) p.p.m. δC (67.80 MHZ) 26.41 (s); 26.78 (s); 27.08 (d); 27.24 (s); 30.51 (s); 31.68 (s); 54.47 (s); 61.72 (s) p.p.m. δ B $\{^1H\}$ (86.55 MHZ) -21.6 (s) p.p.m.

Procedure (b):

Dicyclohexylamine (9.2 ml,0.046 mol) was added to a suspension of sodium borohydride (2.09 g,0.055 mol) in 80 ml monoglyme. A solution of iodine (5.88 g, 0.023 ml) in 80ml monoglyme was subsequently added. Recrystallisation of the crude product from 95% ethanol afforded LXII (11.30, 95.6%) spectroscopically and analytically identical to that from procedure (a).

Triethylamine-borane LXIII: Procedure (a)

Sodium borohydride (10.4g,0.28 mol)was added to a solution of triethylamine-hydrochloride (19.2g,0.14 mol)in 300ml THF. Glass beads were added to increase the vigour of the stirring. After filtration through a bed of celite to remove the precipitated sodium chloride and unreacted solids the THF was removed from the filtrate *in vacuo*. The residual liquid was distilled at 42-44°C/0.02 mmHg (lit 42°C/0.001 mmHg)[174] to produce triethylamine-borane (10.63g, 66.1%) as a clear, camphor-smelling liquid. ν max (Thin Film) 3610 (w), 3537 (m), 3430 (w), 3218 (m), 3005-2880 (br,s); 2738 (w), 2630 (w); 2350 (br,s); 2230 (s); 2030 (m); 1931 (w); 1818 (w), 1775 (w), 1720 (w); 1619 (m); 1463 (s), 1447 (s); 1385 (s); 1352 (w); 1332 (w); 1304 (m); 1259 (w); 1115 (s); 1220 (sh); 1109 (w); 1095 (m); 1065 (w); 1040 (m); 1028 (w); 1017 (w); 968 (m); 922 (w); 900 (w), 863 (m); 853 (sh); 808 (w); 790 (w); 769 (s); 709 (w); 680 (w)cm^{-1}. δH 1.15 (t, 9H, $\underline{CH_3}$-CH_2) 2.70 (q, 6H, CH_3-$\underline{CH_2}$) ppm.

Di-n-butylamine-borane LXIV Procedure (b):

Di-n-butylamine (14.98ml,0.088 mol)was added to a suspension of sodium borohydride (4.0g,0.105 mol)in 80ml monoglyme. A solution of iodine (11.16g,0.044 mol) in 80ml monoglyme was subsequently added. Benzene extraction led to a white semisolid which was further extracted with water /diethylether. The combined organic layers were dried over magnesium sulphate and cooled in an ice-bath. Large, needle crystals of di-n-

butylamine-borane (8.58g, 68.2%) were formed and readily liquefied above room temperature. mp 24-25°C. Analysis: calcd. for $C_8H_{22}NB$: C, 67.13; H, 15.38; N, 9.79; B, 7.69%. Found: C, 67.25; H, 15.36; N, 9.79; B, 7.45%. ν max (Thin Film) 3200 (s); 2950 (m); 2920 (w); 2860 (m); 2370 (s); 2360 (sh); 2320 (w); 2280 (m); 1460 (m); 1380 (m); 1160 (s); 1115 (m); 1070 (m); 880 (s); 730 (m) cm^{-1}. δH 0.97 (t, 6H $C\underline{H}_3$); 1.5 (m, 8H, $C\underline{H}_2$-$C\underline{H}_2$); 2.65 (m, 4H $C\underline{H}_2$-N) ppm.

Tri-n-butylamine-borane LXV Procedure (b) (ii)

A solution of iodine (8.7g, 0.034 mol) in 60ml monoglyme was added to a suspension of sodium borohydride (3.0g, 0.079 mol) in 30ml monoglyme and the mixture refluxed until colourless. A solution of tri-n-butylamine (18.7 ml, 0.079 mol) in 60ml monoglyme was added dropwise. Tri-n-butylamine-borane (10.05g, 63.8%) was obtained as a clear, colourless liquid by vacuum distillation b.p. 120° (1.5 mm Hg). Analysis: calcd. for $C_{12}H_{30}NB$: C, 72.36; H, 15.07; N, 7.03% Found: C, 72.56; H, 14.195; N, 7.09% . νmax (Thin Film) 2960-2860 (br, vs); 2380-2320 (br, vs); 2280 (s); 1465 (vs); 1375 (s); 1260 (w); 1235 (w); 1170 (vs); 1115 (m); 1070 (m); 1040 (m); 930 (w); 350 (s); 740 (m); 685 (m) cm^{-1}.

Dicyclohexylamine-cyanoborane LXVI Procedure (a)

Sodium cyanoborohydride (1.5g, 0.023 mol) was added to a solution of dicyclohexylamine-hydrochloride (7.74g, 0.0356 mol) in 80 ml THF. Recrystallisation from 95% ethanol furnished dicyclohexylamine-cyanoborane (2.4g, 45.8%) as a white crystalline solid. mp 196-197°C. Analysis: calcd. for $C_{13}H_{25}N_2B$: C, 70.90; H, 11.36; N, 12.72; B, 5.00%. Found: C, 70.74; H, 11.56; N, 12.62; B, 5.23% ν max (KBr) 3100 (s); 3060 (sh); 3000 (w); 2930 (s); 2850 (s); 2765 (w); 2740 (sh); 2705 (sh); 2665 (w); 2560 (w); 2530 (w); 2505 (sh); 2460 (sh); 2430 (w); 2360 (s); 2320 (br, s); 2280 (w); 2230 (w); 2180 (s); 1620 (w); 1600 (s); 1570 (m); 1433 (w); 1465 (sh);

1450 (s); 1385 (m); 1370 (w); 1360 (sh); 1350 (w); 1325 (w); 1310 (m); 1265 (w); 1250 (w); 1185 (m); 1150 (sh); 1125 (s); 1110 (w); 1045 (sh); 1040 (m); 1030 (m); 970 (m); 945 (w); 920 (w); 895 (m); 865 (m); 850 (w); 770 (w) cm^{-1}. δ H (270 MHZ) 3.1 (br, d); 3.20-3.38 (br, q); 3.63 (br, s); 3.79 (br, d); 4.0 (br, d); 5.05 (br, q); 8.99 (br, s) ppm. δ C (67.80 HZ) 25.35 (d); 29.75 (s) ppm. δ B {^{1}H} (86.55 MHZ) -40.0 ppm

Procedure (b):

Dicyclohexylamine (7.87g, 0.0396 mol) was added to a solution of sodium cyanoborohydride (3.0g, 0.0475 mol) in 70 ml monoglyme. A solution of iodine (5.0g, 0.0198 mol) in 50ml monoglyme was subsequently added. Recrystallisation of the crude solid from 95% ethanol afforded LXVI (7.57g, 86.9%) which analysed microanalytically and spectroscopically as above.

Aniline-cyanoborane LXVII Procedure (a)

Sodium cyanoborohydride (7.88g, 0.125 mol) was added to a solution of aniline-hydrochloride (22.0g, 0.169 mol) in 250ml THF. Recrystallisation from 95% ethanol afforded aniline-cyanoborane (16.54g, 78.88%) as colourless plates. mp 153-154°C (lit 152-154°C)[84]. Analysis: calcd, for $C_7H_9N_2B$: C, 63.71; H, 6.87; N, 21.23; B, 8.19% Found: C, 63.63; H, 6.74; N, 21.18; B, 8.07%. ν max (KBr) 3180 (br,s); 3100 (sh); 2400 (s); 2365 (m); 2305 (sh); 2180 (m); 1575 (s); 1480 (m); 1460 (m); 1290 (s); 1212 (m); 1170 (m); 1140 (w); 1100 (s); 1655 (m); 1010 (sh); 990 (m); 905 (sh); 885 (m); 830 (s); 740 (s); 680 (s); 655 (sh) cm^{-1}. δH 7.4 (m); 8.0 (m) ppm δB {^{1}H} (86.55 MHZ) -13.3 (s) ppm.

Procedure (b):

A solution of iodine (4.02g, 0.016 mol) in 20 ml monoglyme was added to a solution of aniline (2.45g, 0.026 mol) and sodium cyanoborohydride (2.0g, 0.032 mol) in 25 ml monoglyme. Recrystallisation from 95% ethanol afforded LXVII (2.87g, 82.4%) which analysed as above.

4-Dimethylaminopyridine-cyanoborane LXVIII Procedure (b) (ii):

A solution of iodine (5.28g,0.023 mol) in 40ml monoglyme was added dropwise to a solution of sodium cyanoborohydride (4.0g, 0.063 mol) in 40ml monoglyme and the solution refluxed until colourless. A solution of 4-dimethylaminopyridine (3.85g,0.031 mol) in 35ml monoglyme was subsequently added. Evaporation of the benzene extract resulted in a mixture of products. Preparative chromatography in dichloromethane: hexane (4 : 1) eluent, followed by recrystallisation from acetonitrile afforded 4-dimethylaminopyridine-cyanoborane (126g, 24.8%) as colourless crystals mp 126-128°C. Analysis: calcd, for $C_8H_{12}N_3B$: C, 59.56, H, 7.45; N, 26.08; B, 6.83%. Found: C, 59.42; H, 7.52; N, 26.12; B, 6.94%
ν max (KBr) 3060 (sh); 2990 (m); 2910 (br, s); 2820 (s); 2400 (s); 2360 (sh); 2280 (sh); 2245 (s); 2210 (m); 2100 (w); 2040 (w); 1640 (s); 1560 (br, s); 1540 (sh); 1500 (br, s); 1400 (w); 1370 (m); 1340 (m); 1300 (w); 1280 (m); 1245 (m); 1230 (m); 1210 (w); 1195 (m); 1100 (br,s); 1030 (s); 1000 (sh); 985 (m); 950 (m); 920 (sh); 860 (s); 845 (sh); 825 (w); 700 (w); 670 (w); 625 (w) cm^{-1}.

Crystals suitable for X-ray analysis were obtained from the acetonitrile mother liquor and sent to Professor Ferguson for structural analysis.

Pyrazabole LXIX Procedure (b) (i):

Pyrazole (7.28g,0.107 mol) was added to a suspension of sodium borohydride (4.85g,0.128 mol) in 90ml monoglyme. A solution of iodine (12.76g, 0.05 mol) in 120ml monoglyme was subsequently added. Recrystallisation from monoglyme: ethanol (1 : 1) furnished pyrazabole (7.63g, 80.1%) as colourless cubes. m.p. 78-80 (lit. 80-81°C).[170] Analysis: calcd. for $C_6H_{10}N_4B_2$: C, 45.00; H, 6.25; N, 35.00; B, 13.75%. Found: C, 45.26; H, 6.16; N, 35.27; B, 13.82%. ν max (KBr) 3140 (m); 3060 (m); 2980 (w); 2380 (s); 2340 (s); 1570 (s); 1400 (s); 1330 (s); 1220 (s);

1180 (s); 1135 (s); 1050 (m); 950 (w); 870 (br, s); 845 (w); 750 (s); 690 (w) cm^{-1}. δH (360 MHz) 6.21 (t); 7.60 (d) ppm δH {^{11}B} 3.62 (s); 6.21 (t); 7.60 (d) ppm. δC (90 MHz) 105.36 (d); 134.79 (s); ppm. δB (86.55 MHz) -7.7 (t, $\underline{B}H_2$) ppm δB {^1H} -7.7 (s, $\underline{B}H_2$) ppm.

1, 3, 5, 7- Tetramethylpyrazabole LXX Procedure (b):

3, 5-dimethylpyrazole (3.35g, 0.034 mol) was added to a suspension of sodium borohydride (1.58g, 0.041 mol) in 55 ml monoglyme. A solution of iodine (4.42g, 0.017 mol) in 45 ml monoglyme was added dropwise. Recrystallisation of the crude solid from monoglyme: ethanol (2:1) afforded 1, 3, 5, 7-tetramethylpyrazabole (3.1g, 80.8%) as a white, crystalline solid m.p. 172-174°C (lit. 172-174°C)[170]. Analysis: calcd. for $C_{10}H_{18}N_4B_2$: C 55.55; H, 8.33; N, 25.92; B, 10.18%. Found: C, 55.35, H, 8.43; N, 25.91; B, 10.22%; ν max (KBr) 3120 (m); 2980 (sh); 2960 (m); 2920 (m); 2450 (s); 2380 (s); 2320 (s); 2280 (sh); 2240 (sh); 2280 (sh); 1545 (v.s.); 1500 (w); 1455 (m); 1410 (br, s); 1375 (w); 1150 (br, s); 1095 (w); 1085 (w); 1030 (w); 985 (m); 920 (s); 870 (s); 810 (s); 790 (s); 670 (m); 645 (m) cm^{-1}. δH (360 MHz) 2.29 (s, 12H, $\underline{C}H_3$); 5.26 (s, 2H, $\underline{C}H$) ppm. δH {^{11}B} 2.29 (s, 12H, $\underline{C}H_3$); 3.44 (s, 4H, $\underline{B}H_2$); 5.86 (s, 2H, $\underline{C}H$) ppm. δC {^1H} (90 MHz) 11.85 (s, 4C, $\underline{C}H_3$); 105.67 (s, 2C, $\underline{C}H$); 143.67 (s, 2C, $\underline{C}$) ppm δC {^1H} DEPT $\frac{3\pi}{4}$ (90 MHz) 11.85 (s, 4C, $\underline{C}H_3$); 105.67 (s, 2C, $\underline{C}H$) ppm. δB (86.55 MHz) -11.7 (t, $\underline{B}H_2$) ppm δB {^1H} -11.72 (s, $\underline{B}H_2$) ppm.

Cyclohexylphenylketone LXXI

(i) From Attempted Synthesis of 4, 8-dicyano -1, 3, 5, 7-tetramethylpyrazabole Method b (i):

3, 5-dimethylpyrazole (3.80g, 0.039 mol) was added to a solution of sodium cyanoborohydride (3.00g, 0.047 mol) in 70ml monoglyme. A solution of iodine (5.0g, 0.019 mol) in 50 ml monoglyme was added dropwise according to procedure (b). Recrystallisation from diethylether furnished cyclohexylphenylketone (6.81g, 91.5%) as colourless crystals. m.p. 57°C. (lit. 55-

57°C). Analysis: calcd. for $C_{13}H_{16}O$: C, 82.97; H, 8.51; O, 8.51%. Found: C, 82.75; H, 8.35% ν max (KBr) 3310 (m); 3120 (w); 3080 (w); 3050 (m); 2930 (br, s); 2840 (s); 1980 (sh); 1975 (m); 1920 (m); 1830 (w); 1780 (w); 1670 (br, v.s.); 1585 (v.s.); 1445 (v.s.); 1370 (s); 1330 (m); 1315 (m); 1290 (m); 1250 (br, m); 1205 (m); 1170 (m); 1130 (s); 1070 (s); 1025 (sh); 10 20 (s); 1000 (s); 970 (s); 935 (m); 920 (m); 890 (s); 855 (s); 810 (s); 795 (s); 765 (s); 700 (s); 660 (s) cm^{-1}. δH (270 MHz) 1.19-1.54 (m, 6H, CH_2); 1.69-1.88 (m, 4H, CH_2) 7.38-7.53 (m, 3H, Ar); 7.95 (q, 2H, Ar) ppm. δC {'H} (90 MHz) 25.73 (d, CH_2); 29.26 (s, CH_2); 45.32 (s, CH); 128.17 (d, ArCH); 132.42 (s, Ar-C); 136.24 (s, Ar-C = O) ppm.

(ii) From Attempted Synthesis of N, N' -bis- (3-aminopropyl)-piperazine-bis-borane

Method b(i):

N, N' *-bis* - (3 amino-propyl)-piperazine (7.86g, 0.039 mol) was added to a suspension of sodium borohydride (3.0g, 0.039 mol) in 70ml monoglyme. A solution of iodine (8.7g, 0.034 mol) in 50 ml monoglyme waa added dropwise and the resulting solution stirred at room temperature overnight. The precipitated solid was removed by vacuum filtration through a bed of celite and washed with 30 ml monoglyme. The filtrates were combined and evaporated to dryness. The resulting solid was extracted with 3 x 30 ml portions of benzene. Evaporation of the benzene extractions followed by recrystallisation from diethylether yielded cyclohexylphenylketone (4.42g) as colourless crystals. m.p. 56-57°C. All analyses were as above.

In a separate experiment, the reaction mixture was refluxed for 20 hrs. The only product isolated and characterised was cyclohexylphenylketone.

(iii) From Attempted Synthesis of 3, 3' - Bis-aminopropylamine-triborane

Method b(i):

3, 3' *bis*-aminopropylamine (1.53g, 0.013 mol) was added to a suspension of sodium borohydride (1.5g, 0.039 mol) in 30 ml monoglyme. A solution

of iodine (4.35g,0.017 mol) in 30ml monoglyme was added dropwise and the solution stirred at room temperature for 20 hrs. Cyclohexylphenylketone (1.86g) was the only product from a similar work-up to (ii). All analyses were as above.

Refluxing the reaction mixture for 20 hrs furnished the same product.

Attempted Synthesis of Diphenylamine-borane LXXII Procedure (a):

Sodium borohydride (1.5g, 0.039 mol) was added to a solution of diphenylaminehydrochloride (8.15g, 0.039 mol) in 100ml THF. After 60 hrs reflux and standard work-up procedures, diphenylamine was recorded unchanged.

Procedure (b) i:

Diphenylamine (14.98, 0.088 mol) was added to a stirred suspension of sodium borohydride (4.0g, 0.105 mol) in 100ml monoglyme. A solution of iodine (11.16g 0.105 mol) was subsequently added. Recrystallisation from monoglyme: diethylether (1 : 1) furnished diphenylamine (10.93g, 75% recovery) as colourless crystals.

Attempted Synthesis of N, N'-bis-(3-aminopropyl) piperazine-bis-borane

Method (a):

Sodium borohydride (1.5g,0.039 mol) was added to a solution of N, N' - *bis* - (3-aminopropyl) piperazine-dihydrochloride (10.57, 0.039 mol) in 100ml THF. After standard work-up procedures no borane-containing material was isolated. T.l.C. (eluent acetone: pet. ether, 2 : 1) analysis showed that the product was a complex mixture.

Attempted Synthesis of 3, 3' - bis - (amino propyl) amine-tricyanoborane

Method (a):

Sodium cyanoborohydride (1.0g,0.016 mol) was added to a solution of 3, 3'-(aminopropyl)amine-trihydrochloride (3.8g,0.016 mol) in 50ml. Although infrared analysis of the crude product indicated the presence of both B-H

and C≡N absorption frequencies no such pure product could be isolated from this mixture.

Attempted Synthesis of 1, 2- Phenylenediamine - bis-cyanoborane

Method (a):

Sodium cyanoborohydride (1.5g, 0.024 mol) was added to a solution of 1, 2-phenylenediamine dihydrochloride (6.0g, 0.03 mol) in 70 ml THF. A purple precipitate separated from the reaction solution immediately. Evaporation of the THF *in vacuo* from the filtrate afforded an off-white solid which did not contain any cyanoborane. The purple precipitate was generally insoluble in most organic solvents. Infrared and analysis were not useful for identification purposes.

Attempted Synthesis of 1, 4-Phenylenediamine - bis cyanoborane

Method (b):

Sodium cyanoborohydride (1.5g, 0.024 mol) was added to a solution of 1, 4-diphenylamine-dihydrochloride (6.0g, 0.033 mol) in 70 ml THF. As with above, a purple precipitate resulted. No cyanoborane-containing material was isolated after work-up and purification procedures.

Attempted Synthesis of Histamine - bis cyanoborane

Method (a):

Sodium cyanoborohydride (1.98g, 0.032 mol) was added to a solution of histamine - dihydrochloride (2.90g, 0.016 mol) in 50 ml THF. Removal of the THF from the filtrate afforded a colourless oil. T.l.c. (CH_2Cl_2: hexane, 4 : 1) analysis suggested a complex mixture of products. Thin Film infrared indicated the presence of both B-H and C≡N peaks. No solid material was isolated from this oil.

Attempted Synthesis of Ephedrine-borane Method (a):

Sodium borohydride (2.0g, 0.032 mol) was added to a solution of ephedrine-hydrochloride (5.28g, 0.032 mol) in 70 ml THF. No borane containing pure solid was isolated after standard work-up and purification procedures.

Attempted Synthesis of 4-Dimethylaminopyridine-cyanoborane Method b(i):

4-Dimethylaminopyridine (3.87g, 0.032 mol) was added to a solution of sodium cyanoborohydride (2.0g, 0.032 mol) in 60ml monoglyme. A solution of iodine (4.02g, 0.016 mol) in 40ml monoglyme was added dropwise. Evaporation of the filtrate under reduced pressure furnished 2.79g of crude solid. No pure cyanoborane containing product was separable from this material.

Reaction with Mercuric Cyanide

Mercuric cyanide (3.78g, 0.015 mol) was added quickly to a solution of 4-dimethylaminopyridine-borane (4g, 0.029 mol) in 80ml THF. The ensuing vigorous reaction was stirred at room temperature until it had subsided. A grey solid precipitated from the THF and the mixture was refluxed for 12hrs. The solid was removed by filtration through a bed of celite and washed thoroughly with THF. However, no replacement of hydride by cyanide was detected in either the chemical analysis or the infrared spectrum of the product.

Attempted Synthesis of 4-Dimethylaminopyridine-bis-cyanoborane

Method b(i):

Sodium cyanoborohydride (4.0g, 0.063 mol) was added to a solution of 4-dimethylaminopyridine (3.8g, 0.032 mol) in 80ml monoglyme. A solution of

iodine (8.04g,0.032 mol) in 60ml monoglyme was added dropwise from a pressure equalised dropping funnel. Although there was evidence for reaction (t.l.c. and infrared spectroscopy) no pure cyanoborane-containing material was isolable from the products.

Triphenylphosphine-borane XXIII Procedure (b) (ii):

A solution of iodine (12.6g, 0.048 mol) in 140ml monoglyme was added to a suspension of sodium borohydride (4.36g, 0.116 mol) in 90ml monoglyme and refluxed until the iodine colour had disappeared. Triphenylphosphine (25.0g, 0.095 mol) was added followed by a further 40ml of monoglyme. Recrystallisation of the crude solid (found to be analytically pure) from 95% ethanol afforded triphenylphosphine-borane (25.52g, 97.9%) as a crystalline solid, m.p. 188-189°C (lit. 189°C).[36] Analysis: calcd. for $C_{18}H_{15}BP$: C, 76.72; H, 6.49, B, 3.97%. Found: C, 76.76; H, 6.32; B, 4.09%. ν max (KBr) 305 (s); 2350 (br, s); 2240 (m); 1930 (w); 1845 (w); 1820 (w); 1570 (s); 1540 (sh); 1475 (s); 1430 (s); 1385 (sh); 1325 (sh); 1305 (m); 1270 (sh); 1180 (s); 1155 (sh); 1120 (m); 1100 (s); 1055 (s); 1025 (m); 995 (m); 850 (w); 735 (s); 695 (s); 625 (w) cm^{-1}.

Triphenylphosphine-cyanoborane XXXX Procedure (b) (ii)

A solution of iodine (6.02g, 0.023 mol) in 70ml monoglyme was added dropwise to a stirred solution of sodium cyanoborohydride (3.0g, 0.047 ml) in 60ml monoglyme. Triphenylphosphine (10.37g, 0.039 mol) and a further 20ml monoglyme were added when the iodine colour had dissipated (1 hr). Recrystallisation of the crude solid from 95% ethanol furnished triphenylphosphine-cyanoborane (5.2g, 36.34%) as colourless plates m.p. 172-174°C (lit. 172-174°C).[149] Analysis: calcd. for $C_{19}H_{17}NBP$: C, 75.74; H, 5.64; N, 4.65; B, 3.65%. Found: C, 75.70; H, 5.47; N, 4.65; B, 3.71%. ν max (KBr) : 3070 (w); 3050 (s); 3030 (sh); 3010 (w); 2970 (m); 2380 (s); 2340 (sh); 2250 (m); 2200 (w); 1965 (m); 1900 (m); 1820 (m); 1770 (w); 1585 (s); 1570 (m); 1475 (s); 1430 (s); 1395 (w); 1380 (sh); 1330 (w);

1310 (m); 1270 (v.w); 1180 (m); 1160 (m); 1115 (sh); 1095 (s); 1070 (s); 1055 (s); 1025 (sh); 995 (s); 925 (v.w); 905 (s); 850 (m); 785 (m); 745 (s); 720 (w); 710 (sh); 690 (s); 625 (w) cm^{-1}. δH 7.42 (s, 15H, Ar-H) ppm.

Alternative Synthesis (i) Amine Displacement

Triphenylphosphine (3.96g, 0.015 mol) was added to a solution of aniline-cyanoborane (2.0g, 0.015 mol) in 60ml THF. The reaction was refluxed for 20hrs with vigorous stirring. Filtration of the cooled solution, under reduced pressure, removed 0.34g, of unreacted solid. The THF was evaporated from the filtrate and the crude solid washed three times with 30ml portions of diethylether to remove any remaining, unreacted triphenylphosphine. Recrystallisation from 95% ethanol afforded triphenylphosphine-cyanoborane (1.25g, 27.48%).

(ii) Reaction with Hg $(CN)_2$

Mercuric cyanide (2.28g, 0.009 mol) was added to a solution of triphenylphosphine-borane (5.0g, 0.018 mol) in 60ml THF resulting in vigorous gas evolution and the formation of a dark grey reaction mixture. When the hydrogen evolution had subsided the solution was refluxed for 3 hrs. Liquid mercury and precipitated grey solid were removed from the cooled solution by vacuum filtration through a bed of celite and thoroughly washed with THF. Evaporation of the combined filtrates and recrystallisation from 95% ethanol furnished triphenylphosphine-cyanoborane (4.15g, 76.4%).

Triphenylphosphine-ethoxycarbonylborane XXXXIII

Triphenylphosphine-cyanoborane (0.57g, 0.0018 mol) was added to an appropriate excess of triethyloxonium tetrafluoroborate in 20ml dichloromethane and the reaction mixture refluxed for 24 hrs. When the solution

had cooled the dichloromethane was removed under reduced pressure. The residue was treated with 10ml degassed H_2O and the resulting slurry stirred at room temperature for 44 hrs. Dichloromethane (4 x 25 ml portions) was used to extract the aqueous solution. The organic layers were combined, dried over magnesium sulphate and filtered to give a clear solution. Removal of the solvent produced a gummy solid which was dissolved in hot ethanol and precipitated with cooling by the addition of water. Triphenylphosphine-ethoxycarbonyl-borane (0.35g, 52.88%) was obtained as a white, crystalline solid. m.p. 76-78°C (lit. 77-79)[149]. Analysis: calcd. for $C_{22}H_{22}BO_2P$: C, 72.45; H, 6.37%. Found: C, 72.51; H, 6.50% ν max (KBr) 3075 (m); 2980 (m); 2940 (sh); 2880 (sh); 2410 (br, m); 2350 (sh); 1980 (m); 1920 (m); 1820 (w); 1780 (m); 1680 (m); 1580 (s); 1480 (s); 1450 (s); 1420 (sh); 1350 (w); 1320 (w); 1280 (w); 1200 (m); 1170 (w); 1125 (s); 1070 (br,s); 1000 (w); 950 (sh); 850 (w); 750 (s); 735 (w); 700 (s) cm^{-1}. δH 1.0 (t, 3H, CH_3); 3.85 (q, 2H, CH_2); 7.40 (s, 15H, Ar-H) ppm.

Crystallography for 4-Dimethylaminopyridine-cyanoborane

A colourless regular prism crystal of C8 H12 B N3 having approximate dimensions of 0.38 x 0.38 x 0.25 mm was chosen.

Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 21 reflections in the range $8 < \theta < 14°$, measured by the computer controlled diagonal slit method of centering. The monoclinic cell parameters and calculated volume are: a = 13.773(4), b = 9.635(3), c = 14.430(3) Å, β = 99.67(2)Å, v = 1887.88A.3. For Z = 8 and F.W. = 161.02 the calculated density is 1.13 g/cmÅ. From the systematic absences of: hkl h+k+l=2n+l and hOl h=2n+l and from subsequent least-squares refinement, the space group was determined to be $I2_1/a$ (No. 15).

A total of 2126 reflections were collected, of which 2052 were unique and not systematically absent.

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 0.7 cm-l for Mo-Kα radiation. No absorption correction was made.

The structure was solved by direct methods. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded.

Only the 809 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 109 variable parameters and converged (largest parameter shift was 0.01 times is esd) with unweighted and weighted agreement factors of; R = 4.7% and R_w = 6.4%. The final difference Fourier map

showed no significant residual electron density. The highest peak in the final difference Fourier had a height of 0.10 e/ $\AA^3$ with an estimated error based on wF of 0.03.

Molecular Dimensions

(a) Bond lengths (Å)

N1	C2	1.345(3)
N1	C6	1.342(4)
N1	B10	1.575(4)
C2	C3	1.355(4)
C3	C4	1.412(4)
C4	C5	1.404(4)
C4	N7	1.335(3)
C5	C6	1.353(4)
N7	C8	1.449(4)
N7	C9	1.448(4)
B10	C11	1.573(5)
C11	N12	1.130(4)

(b) Bond angles (°)

C2	N1	C6	116.5(2)
C2	N1	B10	122.0(2)
C6	N1	B10	121.4(2)
N1	C2	C3	123.9(3)
C2	C3	C4	120.3(2)
C3	C4	C5	114.9(2)
C3	C4	N7	123.0(2)
C5	C4	N7	122.2(2)
C4	C5	C6	121.2(3)
N1	C6	C5	123.3(3)
C4	N7	C8	121.4(2)
C4	N7	C9	121.6(2)
C8	N7	C9	116.9(2)
N1	B10	C11	109.4(3)
B10	C11	N12	178.2(3)

Torsional Angles

C6	N1	C2	C3	0.6
B10	N1	C2	C3	-179.4
C2	N1	C6	C5	-0.8
B10	N1	C6	C5	179.2
C2	N1	B10	C11	-74.4
C6	N1	B10	C11	105.6
N1	C2	C3	C4	0.1
C2	C3	C4	C5	-0.6
C2	C3	C4	N7	179.4
C3	C4	C5	C6	0.3
N7	C4	C5	C6	-179.7
C3	C4	N7	C8	0.5
C3	C4	N7	C9	-177.6
C5	C4	N7	C8	-179.5
C5	C4	N7	C9	2.4
C4	C5	C6	N1	0.4
N1	B10	C11	N12	-178.7

REFERENCES

1. A.B. Burg and H.I. Schlesinger, *J. Am. Chem. Soc., 1939,* 59, *780.*
2. G.W. Schaeffer and E.R. Anderson, *J. Am. Chem. Soc., 1949,* 71, *2143.*
3. H.C. Brown, H.I. Schlesinger and S.Z. Cadon, *J. Am. Chem. Soc., 1942,* 64, *325.*
4. R.A. Baldwin and R.M. Washburn, *J. Org. Chem., 1961,* 26, *3549.*
5. R. Koster, *Ange.Chem., 1957,* 69. 64.
6. E.C. Ashby and W.E. Foster, *J. Am. Chem. Soc., 1962,* 84, *3407.*
7. K. Lang and F. Schuber, *U.S. Patent, 3, 057, 985/1962.*
8. K.C. Nainan and R.E. Ryschkewitsch, *Inorg. Chem., 1969,* 8. *2671.*
9. J. Goubeau and H.M. Schneider, *Chem. Ber., 1961,* 94, *816.*
10. H.C. Kelly and J.O. Edwards, *Inorg. Chem., 1963,* 2, *226.*
11. C.J. Foret, M.A. Chiusano, J.D. O'Brien and D.R. Martin, *J. Inorg. Nucl. Chem., 1980,* 42, *165.*
12. D. Grec, L.G. Hubert-Pfalzfraf and J.G. Riess, *J. Am. Chem. Soc., 1980,* 102, *7133.*
13. R. Cassoux, R.L. Kuczkowski, P.S. Bryan and R.C. Taylor, *Inorg. Chem., 1975,* 14, *126.*
14. (a) D.R. Lide, R.W. Taft and P. Lowe, *J. Chem. Phys., 1959,* 31, *561.* (b) S. Geller, *ibid, 1960,* 32, *1569,* (c) D.R. Lide, *ibid, 1960,* 32, *1570.*
15. P.S. Bryan and R.L. Kuczkowski, *Inorg. Chem., 1971,* 10, *200.*
16. S.H. Bauer, *J. Am. Chem. Soc., 1937,* 59, *1804.*
17. L. Pierce, *J. Mol. Spectros., 1969,* 3, *575.*
18. H.G. Scherdewahn, *Doctoral Thesis, University of Freiburg, 1965.*
19. J.R. Durig, Y.S. Li and J.D. Odom, *J. Mol. Struct., 1973,* 16, *443.*

20. W. Horshborger, G.H. Lee, R.F. Porter and S.H. Bauer, *Inorg. Chem., 1969,* 8, *1683.*

21. F.B. Clippard and L.S. Bartell, *Inorg. Chem., 1969,* 8, *1677.*

22. A.G. Robiette, G.M. Sheldrick and W.S. Sheldrick, *J. Mol. Structure, 1970,* 5, *423.*

23. M.F. Lappert *et al., Metal and Metalloid Amides, Ellis Horwood, Chichester, 1980, Chapter 4.*

24. H. Noth and H. Beyer, *Chem. Ber., 1960,* 93, *928.*

25. E. Wiberg, *Naturwissenschaften, 1948,* 35, *212.*

26. N.E. Miller and E.L. Muetterties, *J. Am. Chem. Soc., 1964,* 86, *1033.*

27. W. Horshborger, G.H. Lee, R.F. Porter and S.H. Bauer, *Inorg. Chem., 1969,* 8, *382.*

28. G.E. Ryschkewitsch, *J. Am. Chem. Soc., 1966,* 88, *3145.*

29. C.W. Heitsch, *Inorg. Chem., 1965,* 4, *1019.*

30. H. Noth and B. Wrachemeyer, *Chem. Ber., 1974,* 107, *3070.*

31. (a) H.C. Brown and S. Krishnamurthy, *Tetrahedron, 1979,* 35, *567.* (b) C.F. Lane, *Chem. Rev., 1976,* 76, *766.*

32. R.O. Hutchins and F. Cistione, *Org. Prep. Proced. Int., 1981,* 13, *225.*

33. A. Hajos, *"Complex Metal Hydrides", Elsevier, New York, 1974.*

34. (a) R.O. Hutchins and N.R. Natale, *Org. Prep. Proced. Int., 1979,* 11, *201.* (b) C.F. Lane, *Synthesis, 1975, 135.*

35. (a) R.O. Hutchins *et al., Org. Prep. Proced. Int., 1984,* 16, *335.* (b) C.F. Lane, *Aldrichim. Acta., 1975,* 8, *20.* (c) E.R.H. Walker, *Chem. Soc. Rev., 1976,* 5, *23.* (d) C.F. Lane, *Aldrichim. Acta., 1973,* 6, *51.*

36. A. Pelter, R.M. Rosser and S. Mills, *J. Chem. Soc., Perkin-Trans. I, 1984,* 717.

37. D.M. Hrubowchak and F.X. Smith, *Tetrahedron Lett., 1982,* 23, *2293.*

38. G. Andrews and T.C. Crawford, *ibid, 1980,* 21, *693.*

39. *(a) S. Karady, J. Amato, R. Reamer and L. Weinstock, J. Am. Chem. Soc., 1981,* 103, *6765.* (b) P.J. Reider and E.J.J. Crabowski, *Tetrahedron Lett., 1982,* 22. *2293.*

40. H.C. Brown and L.T. Murray, *Inorg. Chem., 1984,* 23, *2746.*

41. J.H. Billman and J.W. McDowell, *J. Org. Chem., 1961,* 26, 1937.

42. W.G. Mixter, *Am. Chem. J., 1880,* 2, *153.*

43. S.H. Bauer, G.R. Finlay and A.W. Laubengayer, *J. Am. Chem. Soc., 1948,* 70, *2274.*

44. K. Niedenzu and J.W. Dawson, *ibid, 1960,* 32, *4233.*

45. "The Chemistry of Boron and Its Compounds", *E.L. Muetterties, (Ed.), Wiley, New York, 1966, Chapter 7.*

46. J.M. Van Paaschen and R.A. Geanangel, *J. Am. Chem. Soc., 1972,* 94, *2680.*

47. J.M. Van Paaschen, M.G. Hu, L.A. Peacock and R.A. Geanangel, *Syn. React. Inorg. Met.-Org. Chem., 1974,* 4, *11.*

48. M.G. Hu and R.A. Geannangel, *Inorg. Chem. Acta., 1974,* 10, *83.*

49. J.M. Van Paaschen and R.A. Geannangel, *Can. J. Chem., 1975,* 53, *723.*

50. G.E. Ryschkewitsch and V.R. Miller, *J. Am. Chem. Soc., 1973,* 95, *283.*

51. N.E. Paget and K. Smith, *J. Chem. Soc., Chem. Commun., 1980,* 1170.

52. H.C. Kelly, S.C. Yasuc and A.D. Twiss-Brooks, *Inorg. Chem., 1984,* 23, *2220.*

53. I. Wilson and H.C. Kelly, *Inorg. Chem., 1982,* 21, *6222.*

54. S. Ratajczak, *Bull. Soc. Chim. Fr., 1960, 487.*

55. J.E. Douglass, *J. Org. Chem., 1966,* 31, *962.*

56. (a) H.J. Dauben and L.L. McCoy, *J. Am. Chem. Soc., 1959,* 81, *4683,* (b) *J. Org. Chem., 1954,* 24, *1577.*

57. (a) F.L.J. Sixma and R.H. Riem, *Koninkl Ned., Akad, Netenschap Proc., 1958,* B61, *183.* (b) B.P. McGrath and J.M. Tedder, *Proc. Chem. Soc., 1961,* 80. (c) C. Walling, A.L. Rieyer and D.D. Tanner, *J. Am. Chem., Soc., 1963,* 85. *3129.* (d) G.A. Russell and K.M. Desmond, *ibid,* 85, *3142.*

58. O.T. Beachley and B. Washburn, *Inorg. Chem., 1975,* 14, *120.*

59. A.W. Laubengayer and O.T. Beachley, *Inorg. Chem., 1965,* 4, *578.*

60. B. Gyori and J. Emri, *J. Chem. Soc., Chem. Commun., 1983, 1303.*

61. O.T. Beachley and B. Washburn, *Inorg. Chem., 1976,* 15, *725.*

62. P.S. Bryan and R.L. Kuczkowski, *Inorg. Chem., 1971,* 10, *200.*

63. H. Noth, H. Bayer and J.H. Vetter, *Chem. Ber., 1964,* 97, *110.*

64. H. Noth, P. Schweizer and F. Ziegelgansberger, *ibid, 1966,* 99, *1089.*

65. G.E. Ryschkewitsch and J.M. Carret, *J. Am. Chem. Soc., 1967,* 89, *4240.*

66. K.C. Nainan and G.E. Ryschkewitsch, *Inorg. Chem., 1968,* 7, *1316.*

67. N.E. Miller, D.L. Reznicek, R.J. Rowatt and K.R. Lundberg, *Inorg. Chem., 1969,* 8, *862.*

68. D.L. Reznicek and N.E. Miller, *Inorg. Chem., 1972,* 11, *858.*

69. G.E. Ryschkewitsch and J.W. Wiggins, *J. Am. Chem. Soc., 1970,* 92, *1790.*

70. K.C. Nainan and G.E. Ryschkewitsch, *J. Am. Chem. Soc., 1969,* 91, *330.*

71. M.A. Mathur, *Ph.D. Dissertation, University of Florida, Gainesville, (1971).*

72. M.A. Mathur,and G.E. Ryschkewitsch, *Inorg. Syn., 1970,* 12, *139.*

73. J.R. Bergerud and G.E. Ryschkewitsch, *Unpublished date.*

74. G.E. Ryschkewitsch and T.E. Sullivan, *Inorg. Chem., 1970,* 9, *899.*

75. G.L. Smith and H.C. Kelly, *Inorg, Chem. 1969,* 8, *2000.*

76. G.E. Ryschkewitsch, *J. Am. Chem. Soc., 1969,* 91, *6535.*

77. P. Wisian-Nelson, M.K. Das and B.F. Spielvogel, *Inorg. Chem., 1978,* 17, *2327.*

78. C. Weidig, S.S. Uppal and H.C. Kelly, *Inorg. Chem., 1974,* 13, *1763.*

79. D.R. Martin, M.A. Chiusano, M.L. Denniston, D.J. Dye, E.D. Martin, and B.T. Pennington, *J. Inorg. Nucl. Chem., 1978,* 40, *9.*

80. B. Kemp, S. Kalbay and R.A. Geanangel, *Inorg. Chem., 1984,* 23.

81. B. Gyori and J. Emri, *J. Organomet Chem., 1982,* 238, *154.*

82. A.E. Martell, *"Stability Constants of Metal-ion Complexes", Section II, The Chemical Society, London 1964.*

83. J.R. Lowe, S.S. Uppal, C. Weidig and H.C. Kelly, *Inorg. Chem., 1970,* 9, *1423.*

84. B.F. Spielvogel, L. Wojnowich, M.K. Das, A.T. McPhail and K.D. Hargrave, *J. Am. Chem. Soc., 1976,* 98, *5702.*

85. *H.* Meerwein, *Org. Synth., 1966,* 46, *113.*

86. B.F. Spielvogel, M.K. Das, A.T. McPhail, K.D. Onan and I.H. Hall, *J. Am. Chem. Soc., 1980,* 102, *6343.*

87. B.F. Spielvogel, F.U. Ahmed, G.L. Silvey, P. Wisian-Nelson and A.T. McPhail, *Inorg. Chem., 1984,* 23, *4322.*

88. I.H. Hall, C.O. Starnes, A.T. McPhail, P. Wisian-Nelson, M.K. Das, F. Harchelroad and B.F. Spielvogel, *J. Pharm. Sci., 1980,* 69, *1025.*

89. I.H. Hall, M.K. Das, F. Harchelroad, P. Wisian-Nelson, A.T. McPhail and B.F. Spielvogel, *J. Pharm. Sci., 1981,* 70, *339.*

90. I.H. Hall, C.O. Starnes, B.F. Spielvogel, P. Wisian-Nelson, M.K. Das and L. Wojnowich, *J. Pharm. Sci., 1979,* 68, *685.*

91. A. Besson, *Compt. Rend., 1890, 110.*

92. E.L. Gamble and P. Gilmont, *J. Am. Chem., Soc., 1940,* 62, *717.*

93. (a) A.B. Burg and R. Wagner, *J. Am. Chem. Soc., 1953,* 75, *3872, 1954,* 76, *3307.* (b) F. Hewitt and A.K. Holliday, *J. Chem. Soc., 1953, 530.*

94. E.L. McGandy, *Diss. Abstr., 1961,* 22, *754.*

95. R.W. Rudolph, R.W. Parry and C.F. Favran, *Inorg. Chem., 1966,* 5, *723.*

96. (a) D.S. Bryan and R.L. Kuczkowski, *Inorg. Chem., 1972,* 11, *553; J. Chem. Phys., 1971,* 55, *3049.* (b) J.P. Pasinki and R.L. Kuczkowski, *Ibid, 1971,* 54, *1903.* (c) R.L. Kuczkowski and D.R. Lide, *ibid, 1967,* 46, *357.*

97. W.C. Hamilton, *Acta, Cryst., 1955,* 8, *199.*

98. P. Goldstein and R.A. Jacobson, *J. Am. Chem. Soc., 1962,* 84, *2457.*

99. (a) J.R. Durig, B.A. Hudgens, Y.S. Li and J.D. Odom, *J. Chem. Phys., 1974,* 61, *4890.* (b) J.R. Durig, Y.S. Li, L.A. Carrera and J.D. Odom, *J. Am. Chem. Soc., 1973,* 95, *2491.*

100. C.E. Nordman, *Acta. Cryst., 1960,* 13, *535.*

101. H.L. Carrell and J. Donohue, *Acta. Cryst. B, 1968,* 24, *699.*

102. G.W. Parshall in E.L. Muetterties (ed.), *"The Chemistry of Boron and Its Compounds", Wiley, New York 1967.*

103. J. Emsley and D.H. Hall, *"The Chemistry of Phosphorus", Harper and Row, London, 1976.*

104. (a) W.A.G. Graham and F.G.A. Stone, *J. Inorg. Nucl. Chem., 1956,* 3, *164.* (b) F.G.A. Stone, *Chem. Rev., 1958,* 58, *101; Adv. Inorg. Chem. Radiochem., 1960,* 2, *279.* (c) T.D. Coyle and F.G.A. Stone, *Progr. Boron Chem., 1964,* 1, *137.* (d) T.D. Coyle, H.D. Kaesz and F.G.A. Stone, *J. Am. Chem. Soc., 1959,* 81, *2989.*

105. (a) F.G.A. Stone and A.B. Burg, *ibid, 1954,* 76, *386.* (b) A.B. Burg, *Rec. Chem. Progr., 1954,* 65, *159.* (c) A.B. Burg and G. Rendel, *J. Am. Chem. Soc., 1958,* 80, *3198.* (d) A.B. Burg, *J. Chem. Educ., 1960,* 37, *482.*

106. A.J. Cowley and M.C. Damasco, *J. Am. Chem. Soc., 1971,* 93, *6815.*

107. M.A. Mathur, W.H. Myers, H.H. Sisler and G.E. Ryschkewitsch, *Inorg. Syn., 1974,* XV, *128.*

108. T. Imamoto, T. Kusomoto, N. Suzuki and K. Sato, *J. Am. Chem. Soc., 1985,* 107, *5301.*

109. D.C. Mente and Z.L. Mills, *Inorg. Chem., 1975,* 14, *1862.*

110. A. Peller, R. Rosser and S. Mills, *J. Chem. Soc., Chem. Commun.,* 1981, *1014.*

111. (a) W.A.G. Graham and F.G.A. Stone, *J. Inorg. Nucl. Chem., 1956,* 3, *164.* (b) T.D. Coyle, H.D. Kaesz and F.G.A. Stone, *J. Am. Chem. Soc., 1959,* 81, *2989.*

112. (a) F.G.A. Stone and A.B. Burg, *J. Am. Chem. Soc., 1954,* 76, *386.* (b) A.B. Burg, *Rec. Chem. Progr., 1954,* 15, *159.* (c) A.B. Burg and G. Brendel, *J. Am. Chem. Soc., 1958,* 80, *3198.*

113. A.M. Frisch, H.G. Hent, H. Mackle and I. Madden, *J. Chem. Soc., 1965, 899.*

114. H. Schmidbaur, E. Weiss and B. Zimmer-Gaussen, *Agen. Chem., Int. Eng. Ed., 1979,* 18, *782.*

115. R. Rosser and S. Mills, *J. Chem. Soc., Chem. Commun., 1981, 1041.*

116. N.T. Kuzneteor, *Zh Neorgan. Khim, 1964, 9, 1817.*

117. H. Schmidbaur, *J. Organomet. Chem., 1980,* 200, *287.*

118. C.A. Maryanoff, B.E. Maryanoff, R. Tang and K. Mislow, *J. Am. Chem. Soc., 1973,* 95, *5839.*

119. B.D. Vineyard, W.S. Knowles, M.J. Sabacky, G.L. Bachmar and D.J. Weinkanff, *J. Am. Chem. Soc., 1977,* 99, *5946.*

120. W.S. Knowles, M.J. Sabacky and B.D. Vineyard, *Adv. Chem. Ser., 1974,* 132, *274.*

121. A. Pelter and K. Smith, *"Comprehensive Organic Chemistry", Vol. III, Ed. D.N. Jones, Pergamon Press, Oxford, 1980, p. 695.*

122. H.C. Brown, *"Organic Synthesis via Boranes", Wiley, Interscience, New York, 1975.*

123. M.A. Frisch, H.G. Heal, H. Mackle and I.O. Madden, *J. Chem. Soc., 1965, 899.*

124. W.C. Davies and F.G. Mann, *J. Chem. Soc., 1944, 276.*

125. J.R. Von Wazer, *"Phosphorus and Its Compounds", Interscience, New York,* 19 *1958, p. 307.*

126. P.D. Bartlett and J. Merguerian, *J. Am. Chem. Soc., 1956,* 78, *3710.*

127. P.A. Tierney, D.W. Lewis and D. Berg, *J. Inorg. Nucl. Chem., 1962,* 24, *1163.*

128. D.R. Martin and R.E. Dial, *J. Am. Chem. Soc., 1950,* 72, *852.*

129. E.L. Gamble and P. Gilmont, *J. Am. Chem., 1940,* 62, *717.*

130. G.M. Phillips, J.S. Hunter and L.E. Sutton, *J. Chem. Soc., (London) 1945, 146.*

131. H.C. Brown, *J. Chem. Soc., 1956, 1248.*

132. W. Gee, R.A. Shaw and B.C. Smith, *J. Chem. Soc., 1964, 4180.*

133. E. Sirll and A. Adler, *Z. Naturforsch, 1061,* 16b, *403.*

134. R.I. Wagner, *U.S. Patent, 1963, 3, 092, 665.*

135. A.B. Burg and R.I. Wagner, *J. Am. Chem. Soc., 1953,* 75, *3872.*

136. H.S. Sisler and M.A. Mathur, *J. Inorg. Nucl. Chem., 1977,* 39, *1745.*

137. H. Noth and H. Beyer, *Chem. Ber., 1960,* 93, *2251.*

138. M.A. Mathur and G.E. Ryschkewitsch, *Inorg. Syntheses, 1970,* XII, *123.*

139. M.A. Mathur, *Doctoral Dissertation, University of Florida, 1970.*

140. J.W. Wigginsaand G.E. Ryschkewitsch, *Inorg. Chim. Acta., 1970,* 4, *33.*

141. B. Rapp and J.E. Drake, *Inorg. Chem., 1973,* 12, *2868.*

142. J.E. Drake and B. Rapp, *J. Chem. Soc., Dalton Trans., 1972, 2341.*

143. D.G. Mente and J.L. Mills, *Inorg. Chem., 1975,* 14, *1862.*

144. J.D. Odom, V.F. Kalasinsky and J.R. Durig, *Inorg. Chem., 1975,* 14, *2837.*

145. J.R. Durig, Y.S. Li, L.A. Carrera and J.D. Odom, *J. Am. Chem. Soc., 1973,* 95, *2491.*

146. J.R. Durig, B.A. Hudgens, Y.S. Li and J.D. Odom, *J. Chem. Phys., 1974,* 61, *4890.*

147. P.S. Bryan and R.L. Kuczkowski, *Inorg. Chem., 1972,* 11, *553.*

148. K.C. Nainan and G.E. Ryschkewitsch, *J. Am. Chem. Soc., 1969,* 91, *330.*

149. P. Wisian-Nelson, M.A. Wilkins, F.C. Weigel, C.J. Foret and D.R. Martin, *J. Inorg. Nucl. Chem., 1981,* 43, *457.*

150. M.K. Das and S. Roy, *Synth. React. Inorg. Met-Org. Chem., 1986,* 16, *67.*

151. J.R. Durig, B.A. Hudgens and J.D. Odom, *Inorg. Chem., 1974,* 13, *2306.*

152. F.G.A. Stone and A.B. Burg, *J. Am. Chem. Soc., 1954,* 76, *386.*

153. Y. Gushiken and F. Watori, *J. Chem. Soc., Dalton, 1980, 2016.*

154. M.L. Denniston and D.R. Martin, *J. Inorg. Nucl. Chem., 1974,* 36, *2175.*

155. M.L. Denniston and D.R. Martin, *J. Inorg. Nucl. Chem., 1974,* 36, *1461.*

156. D.C. Mente, J.L. Mills and R.E. Mitchell, *Inorg. Chem., 1975,* 14, *123.*

157. H. Noth and B. Wsackmeyer, *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds", Springer-Verlag, Berlin Heidelberg, 1978,* 89, *and references therein.*

158. T.L. Vidal and G.E. Ryschkewitsch *Inorg. Chem., 1977,* 16, *1898.*

159. R.C. Wade, E.A. Sullivan, J.R. Berschied and K.F. Purcell, *Inorg. Chem., 1970, 9, 2146.*

160. B.F. Spielvogel, F.U. Ahmed, K.W. Morse and A.T. McPhail, *Inorg. Chem., 1984, 23, 1776.*

161. S.S. Uppal and H.C. Kelly, *J. Chem. Soc., Dalton, 1970, 619.*

162. H. Noth and B. Wrackmeyer, *Chem. Ber., 1974, 107, 3070.*

163. H. Noth and B. Wrackmyer, *Chem. Ber., 1974, 107, 3089*

164. A.T. McPhail, K.D. Onan, B.F. Spielvogel and P. Wisian-Nelson *J. Chem. Res.(M), 1978, 2601.*

165. A.T. McPhail and D.L. McFadden, *J. Chem. Soc., Dalton, 1975, 1784.*

166. G. Ferguson, B. Kaitner, W.B. Whalley, D.A. Taylor and T.R. Liddell, *Acta Cryst., 1982,* B2253.

167. N.N. Greenwood and A. Earnshaw, *"Chemistry of the Elements", Pergamon Press, Oxford, 1984,* p. 337.

168. E.L. Muetterties (Ed.), *"The Chemistry of Boron and Its Compounds", Wiley, New York, 1967, p. 411.*

169. H. Noth and B. Wrackmeyer; *Chem. Ber., 1974,* 107, *3070.*

170. S. Trofimenko; *J. Am. Chem. Soc., 1967,* 89, *3165.*

171. H.C. Brown, *"Hydroboration", W.A. Benjamin, Inc., New York, N.Y., 1962,* p.*66.*

172. L.H. Toporcer, R.E. Deasy and W.I.E. Green, *J. Am. Chem. Soc., 1965,* 87, *1253.*

173. (a) J. Bielawski and K. Niedenzu; *Inorg. Chem., 1986,* 25, *1771.*
(b) J. Bielawski, M.K. Das, E. Hanecher, K. Niedenzu and H. Noth *Inorg. Chem., 1986,* 25, *4623.*

174. Aldrichimica Acta, *1987,* 20, *1, pp 9 - 27.*

175. H.C. Brown, M. Srebnik, R.K. Bakshi and T.E. Cole, *J. Am. Chem. Soc., submitted for publication at time of writing.*

176. B.F. Spielvogel, R.F. Bratton and C.G. Moreland, *J. Am. Chem. Soc., 1972,* 94, *8597.*

177. B.F. Spielvogel, F.U. Ahmed, M.K. Das and A.T. McPhail, *Inorg. Chem., 1984,* 23, *3263.*

178. D.D. Perrin, W.L.F. Armatego and D.R. Perrin, *"Purification of Laboratory Chemicals", Pergamon Press, 1966.*

179. C.M.D. Power, *Doctorial Thesis, University College, Cork, 1984.*

CHAPTER FIVE

FORMATION OF BH_2X ADDUCTS OF AMINOPHOSPHINES

5.1 INTRODUCTION

The basicity of the nitrogen atom adjacent to phosphorus in amino-phosphines has been the subject of much discussion.[1-7] Until recently,[8] the consensus was that in acyclic amino-phosphines the tricoordinate nitrogen atom assumed a planar configuration with respect to its substituents and thus demonstrates diminished basicity due to enhanced $N_{(p\pi)}$-$P_{(d\pi)}$ bonding.[2, 4, 7, 9.] Previous studies indicated that acyclic amino-phosphines behaved as "P-donors only" in their reactions with diborane.[10-13] On the other hand, *bis* (borane) adducts are known to form with amino-phosphines of the type $P(O\ CH_2\ CH_2)_2\ N$ (R, = H, Me)[9,14,15]. Here the nitrogen atom in the constrained bicyclic structure possesses a pyramidal geometry, which presumably weakens the $p\pi$-$d\pi$ interaction and enables nitrogen to exhibit a more basic character.[8, 13, 14.]

Although Burg and Slota[12] claimed in 1960 to have synthesised the diborane adduct of Me_2PNMe_2 later workers excluded the possibility of the nitrogen atom being an active donor site in acyclic amino-phosphines.[9,11,15] However, recent reports showed that both As-BH_3 and N-BH_3 adducts form when BH_3.THF reacts with acyclic amino-arsines,[16,17] and a report in 1987 by Watkins and coworkers[8] has discussed evidence for the formation of (i) $Me_2(BH_3)PNMe_2$, (ii) $Me_2P\ N(BH_3)Me_2$ and (iii) $Me_2PN\ Me_2.2BH_3$ in the reaction of $Me_2PN\ Me_2$ with BH_3.THF.

5.1.1. *Synthesis of Dimethyl (Dimethylamino) Phosphine*

Dimethyl(dimethylamino)phosphine, I, was first synthesised by Burg and Slota[18] in 1957 by the action of CH_3 MgBr on $[(CH_3)_2N]PCl_2$ (1)

$$CH_3\ MgBr + [(CH_3)_2N]PCl_2 \longrightarrow \underset{\mathbf{I}}{(CH_3)_2\ P\text{-}N(CH_3)_2} \qquad (1)$$

The relatively low yield of 48% is accounted for by the fact that the Grignard reagent attacks the nitrogen-phosphorus bond almost as effectively as the phosphorus-chlorine bond.

5.1.2. *Reaction of Dimethyl(Dimethylamino)Phosphine with Borane*

The P-B bonded adduct, II, resulted from the gas phase reaction of diborane with I, (2).[12]

$$(CH_3)_2\,PN(CH_3)_2 + \tfrac{1}{2}\,B_2H_6 \xrightarrow{-196^\circ} \underset{II}{(CH_3)_2(BH_3)PN(CH_3)_2} \qquad (2)$$

Burg and Slota claimed that the reaction of I with diborane at 22°C for 14 hrs resulted in the diborane adduct $(CH_3)_2\,P.N(CH_3)_2.2BH_3$, III, (3).

$$(CH_3)_2\,PN(CH_3)_2 + B_2H_6 \xrightarrow[14\ hr]{22^\circ} \underset{III}{(CH_3)_2\,PN(CH_3)_2.2BH_3} \qquad (3)$$

However, no proof other than thermal decomposition data was offered by authors in support of the existence of III.

In direct contradiction of (3), Jugie and coworkers,[11] reported reactions (4) and (5).

$$4(C_2H_5)_3\,N.BH_3 + (CH_3)_2\,PN(CH_3)_2 \xrightarrow[I]{\text{reflux}} (CH_3)_2\underset{II}{(BH_3)}\,PN(CH_3)_2 + Et_3N + 3(C_2H_5)_3\,N.BH_3 \qquad (4)$$

$$(CH_3)_2\,PN(CH_3)_2 + (X-1)\,\tfrac{1}{2}\,B_2H_6 \longrightarrow \underset{II}{(CH_3)_2(BH_3)PN(CH_3)_2} + (X-1)\,\tfrac{1}{2}B_2H_6 \qquad (5)$$

(X = large excess)

Despite having used a large excess of both diborane and coordinated borane[$(C_2H_5)_3N.BH_3$] no indication of the formation of an N-B adduct was obtained. ^{31}P, ^{11}B and ^{1}H nmr data provided unequivocal confirmation that compound II was the sole adduct from reactions (4) and (5). The ^{31}P signal for the product consisted of a 1 : 1 : 1 : 1 quartet at -51 ppm as opposed to a singlet at -73 ppm for the free ligand. The ^{11}B spectrum showed a 1 : 3 : 3 : 1 quartet at -37 ppm with each member of

the quartet being further split into a doublet by ^{31}P. The chemical shift and splitting pattern are characteristic of four coordinate P-BH_3 compounds.

Recently the reaction of $(CH_3)_2P.N(CH_3)_2$ with BH_3.THF was re-investigated as a function of time and for mole ratios of 1 : 0.5 and 1 : 3.0, by Watkins and coworkers.[8] In a typical experiment, the appropriate amount of $(CH_3)_2$ $PN(CH_3)_2$ was condensed at -196°C onto a toluene-d_8 solution of BH_3.THF-d_8 [16,17] in an nmr tube. After sealing and agitation of the tube at -95°C it was inserted into a precooled (-90°C) probe of an n.m.r. spectrometer. ^{11}B, ^{31}P and ^{13}C spectra were then recorded (Table 1). At -90°C, only small amounts of $(CH_3)_2PN(BH_3)$ $(CH_3)_2$(IV) and $(CH_3)_2P.N(CH_3)_2.2BH_3$ (III) are observed initially, suggesting that the formation of $(CH_3)_2(BH_3)P.N(CH_3)_2$ (II) is kinetically favoured at low temperature. On completion of a reaction from -150 to 25°C, with mole ratios > 1 : 1, only II and $(CH_3)_2$ $P.N(CH_3)_2$ are observed. Completion of reactions with mole ratios greater than 1 : 1 yielded mixtures of II and III, with the relative amounts of each being dependent on the initial mole ratio of the starting materials. In a reaction with a 1 : 2 mole ratio of $(CH_3)_2P.N(CH_3)_2$: BH_3.THF, the reaction mixture initially contained 79%, 10%, 5.5% and 5.1% of II, III, IV and $(CH_3)_2P.N(CH_3)_2$ respectively (6),

$$(CH_3)_2P.N(CH_3)_2 + 2\ BH_3.THF \longrightarrow \underset{\text{II}}{(CH_3)_2(BH_3)P.N(CH_3)_2} + \underset{\text{III}}{(CH_3)_2P.N(CH_3)_2.2\ BH_3} + \underset{\text{IV}}{(CH_3)_2P.N(BH_3)(CH_3)_2} + (CH_3)_2\ P.N(CH_3)_2 \qquad (6)$$

at -90°C, as determined from the ^{31}P nmr spectrum. Raising the temperature increased the intensities of the peaks associated with the *bis* (borane) adduct at the expense of those of unreacted $(CH_3)_2P$ $N(CH_3)_2$ and

TABLE 1. *Multinuclear Nmr Data for Borane Adducts of Acyclic Aminophosphines*[a]

CHEMICAL SHIFT, ppm

Compound	temp °C	^{11}B	^{31}P	^{13}C		Coupling Constant, Hz	
				$(CH_3)_2P$	-*C - N - P	$^1J_{P-B}$	$^1J_{P-C}$
$(CH_3)_2P\ N(CH_3)_2$	25		39.7	14.2(d)	39.2(d)		18.3
$(CH_3)_2P\ N(BH_3)(CH_3)_2$	-70	-15.8	83.7	12.9(d)	46.9(d)		25.6
$(CH_3)_2(BH_3)P\ N(CH_3)_2$	25	-38.3	63.7	11.8(d)	37.3(d)	68.7	40.6
$(CH_3)_2P\ N(CH_3)_2.2BH_3$	25	-11.8(B-N) -40.7(B-P)	104.4	10.3(d)	48.0(d)	49.4	36.3

(a) ^{11}B, ^{13}C and ^{31}P were recorded on a Nicolet 300 - MHz multinuclear F T nmr spectrometer operating at 96.3, 121.5 and 75.4 MHz respectively $\delta(^{11}B)$, $\delta(^{31}P)$ and $\delta(^{13}C)$ were measured relative to $BF_3.OEt_2$, 85% H_3PO_4 and Me_4 Si (internal) respectively. (b) Negative δ values indicate upfield shift from BF_3OEt_2.

the NBH_3 compound. At -10°C the peaks assigned to IV and the starting amino-phosphine have disappeared and only peaks due to II and III are observed. The authors claim that maintaining the reaction at -60°C for 24 hrs produced $(CH_3)_2P.N(CH_3)_2.2\ BH_3$ in quantitative yields and that the ^{11}B nmr spectrum only contained two resonances of equal intensity associated with B - N and B - P coordination in III.

5.1.3. *Alternative Synthesis of An Acyclic Amino-Phosphine-Borane Adduct*

An alternative synthetic route to an $R_2(BH_3)PNR'_2$ type complex was reported by Schmidbaur *et al*[19] in 1985. These authors synthesised dimethyl (amino)phosphine-borane, $(CH_3)_2(BH_3)PNH_2$ V as a colourless crystalline solid melting at 29°C. The first step in the synthesis is the reaction of chlorodimethylphosphine with BH_3.THF to give the borane adduct, VI in 96% yield (7)

$$(CH_3)_2P\text{-}Cl + BH_3.THF \xrightarrow{R.T} \underset{\textbf{VI}}{(CH_3)_2P\ Cl.BH_3} + THF \qquad (7)$$

Subsequent reaction of VI with sodium amide or gaseous ammonia[20,21] results in the formation of V (8).

$$\underset{\textbf{VI}}{(CH_3)_2P.Cl.BH_3} + 2NH_3 \xrightarrow[Et_2O]{R.T} \underset{\textbf{V}}{(CH_3)_2P\ NH_2.BH_3} + [NH_4]Cl \qquad (8)$$

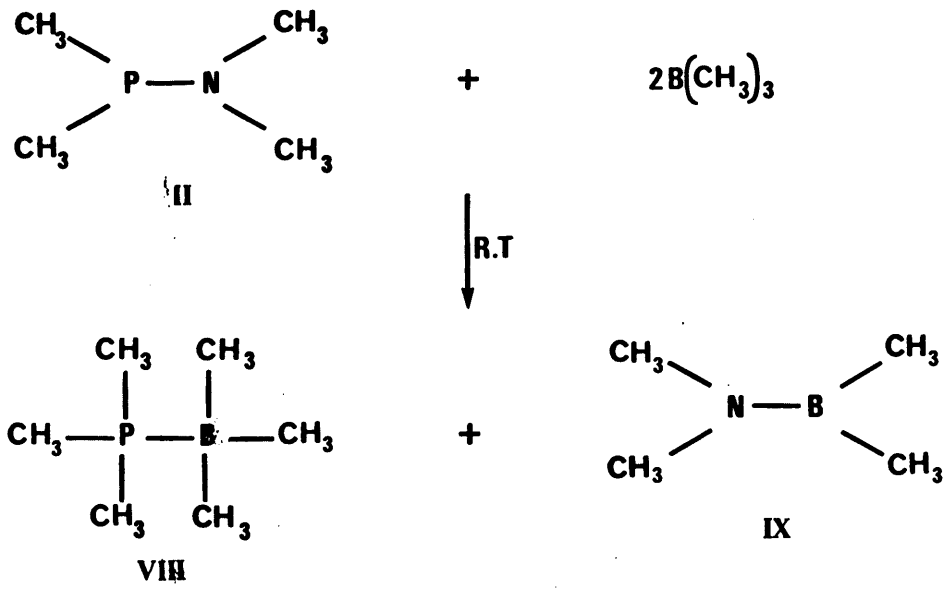
The last method gives higher yields (98%) and avoids handling of the air sensitive sodium amide.

It is interesting to note that, as Schmidbaur *et al* have pointed out, the $Me_2(BH_3)P$- group is isoelectronic and isostructural with the versatile Me_3 Si- group and may have an equally interesting chemistry.

5.1.4. *Reactions of Me_2P-NMe_2 Involving Cleavage of the P-N Bond*

The reaction of dimethyl(dimethylamino)phosphine with trimethyl-borane at -46°C results in the adduct $(CH_3)_2P\ N(CH_3)_2.B(CH_3)_3$, VII[22]

This adduct was not isolated but rather the authors claimed that VII acts as an intermediate in the room temperature reaction (9) leading to compounds VIII and IX.



A second example of P-N bond cleavage was reported by Burg and Slota.[12] These authors reported that both the amino-phosphine, $(CH_3)_2P$ $N(CH_3)_2$ and the aminophosphine-borane adduct decompose thermally to form the diphosphine X, Figure 1.

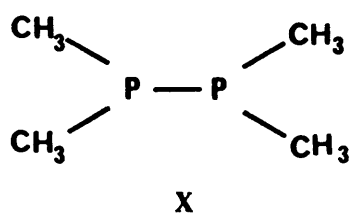


Figure 1 $[(CH_3)_2P]_2$

5.1.5. *More Complex P-N Systems*

The majority of recent research into borane adducts of aminophosphines is centred on those derived from phosphoranes, e.g. $P(OCR_2CH_2)_2$ N. Because of the constraints imposed by these cyclic systems, the nitrogen atom is forced into a pyramidal position, which in turn facilitates borane absorption. The discussion below is structured to deal with compounds in order of increasing numbers of P-N bonds. Compounds with a single phosphorus atom are discussed before those with two, three or more phosphorus atoms.

5.1.5.1. *Compounds with one P-N Bond*

Riess and coworkers[23] have studied the reactions of the bicycloaminophosphines, XI and XII, Figures 2 and 3, with diborane.

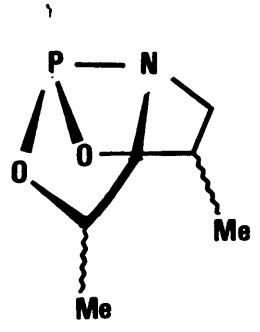


Figure 2: Bicycloaminophosphine XI

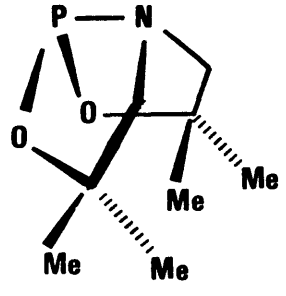


Figure 3: Bicycloaminophosphine XII

The bicyclic structure and the pyramidal phosphorus atom force the nitrogen atom to stay pyramidal. This hinders the pπ-dπ interaction and restores the nitrogen atom's donor properties. When XI and XII were reacted with

0.5 molar equivalent of diborane at room temperature, the expected P-B bonded borane adduct was obtained in each case and identified by n.m.r.[9] Reaction with one molar equivalent of diborane under the same conditions yields *bis* (borane) adducts of both XI and XII. The isolation of stable crystals of the *bis* (borane) adduct of XII made it possible for the first X-ray diffraction data on a P-bound N atom coordinated to borane to be recorded, XIII. (Figure 4)

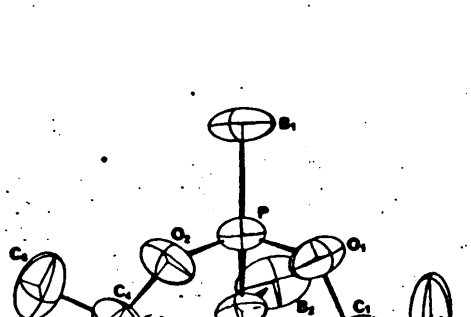
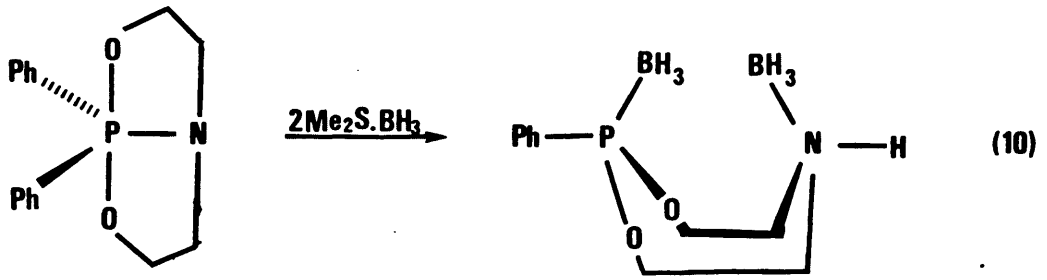


Figure 4 Molecular Structure of XIII

The N - B bond length [1.655(8) Å] is comparable to that of $(CH_3)_3N.BH_3$ [1.638(01) Å], the structure of which was determined by microwave spectroscopy.[24] The P - B bond length [1.873 Å] is short but comparable to those obtained for other adducts in which phosphorus has electonegative substituents.[7] The P - N bond length [1.757(4) Å] is as expected in the absence of π bonding.

For compound XIV, reaction with borane involved cleavage of the phosphorus-nitrogen bond (10).



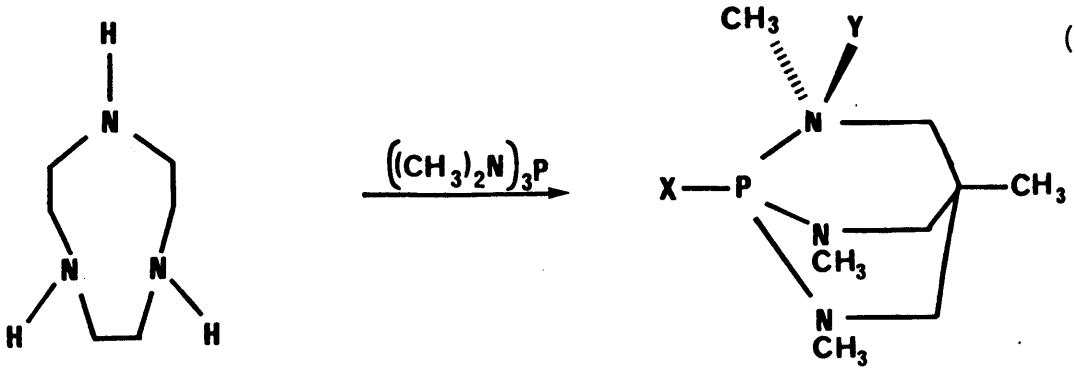
(10)

XIV

5.1.5.2. *Compounds of the Type* $-P(N-)_3$

Verkade and coworkers[26] have reported several examples of borane absorption by cyclic aminophosphines of this type.

The aminophosphine, 2,6,7- trimethyl-4-methyl -2,6,7-triaza-1-phospha -bicyclo [2, 2, 2] octane, XVI, was prepared[26] by the reaction of the triamine, 1, 3 *bis*(methylamino)-2-(methylaminomethyl)-2-methylpropane XV,[28] with $[(CH_3)_2N]_3$ P. (11). Derivatives[29,30] of XV and XVI were made by reaction of XV with Cl_3P = O, XVII, and by the reaction of XVI with elemental sulphur, XVIII, and selenium, XIX.



(11)

XV

X = lone pair, XVI; O, XVII; S, XVIII; Se, XIX

Diborane was condensed at -196° onto frozen solutions of compounds XVI to XIX. These solutions were then stirred at an equilibration temperature until a constant pressure was obtained. The products of the reactions are listed in Table 2.

TABLE 2. *Borane-Adducts of XVI, XVII and XVIII*

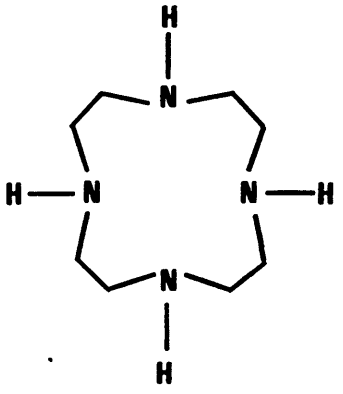
	Compound			*Product*	
	x	y		x	y
XVI	lp	lp	XX	BH_3	BH_3
			XXI	BH_3	lp
XVII	O	lp	XXII	O	BH_3
XVIII	S	lp	XXIII	S	BH_3

The solid compound, XX, filtered cold from the reaction mixture of XVI and diborane was found to lose borane readily in moist air to produce the white, sublimable compound XXI. The adduct XX was stable, however, on purging a chloroform solution for 2 hrs with dry nitrogen.

Concentrating the solutions from the reactions of XVII and XVIII with diborane and cooling to -78°C yielded the colourless adducts XXII and XXIII, respectively. Both compounds were stable in halogenated hydrocarbons.

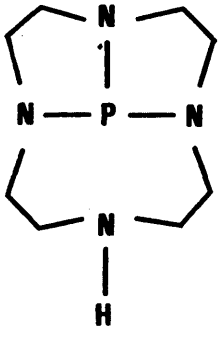
5.1.5.3. *Compounds of the Type P-(N-)$_4$*

Atkins and Richman,[31] reacted stoichiometric amounts of 1, 4, 7, 10-tetrazocyclodecane,[32] XXIV, and hexamethylphosphorustriamide. This reaction led to the synthesis of the cyclic phosphorane, XXV, (12), which was isolated as a white crystalline solid. From the strong P - H stretch in the infrared spectrum and P - H coupling in both the ^1H and ^{31}P n.m.r.s, the authors concluded that the phosphorane tautomer, XXV, predominated rather than the tricyclic phosphorus triamide, XXVa.[33]

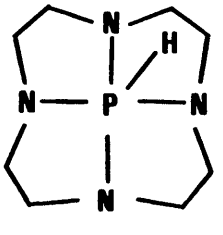


XXIV

+ $\left((CH_3)_2N\right)_3P$



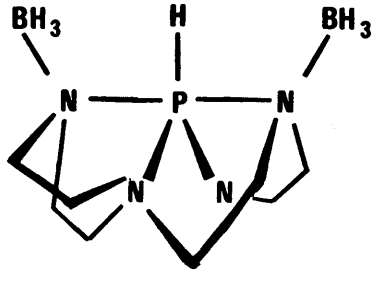
XXVa



XXV

(12)

Riess and coworkers,[23] investigated the possibility of stabilising the open form XXVa, by displacement of the tautomeric equilibrium, (12), under the action of a Lewis Acid capable of coordinating both the phosphorus and nitrogen sites. Cyclenphosphorane, XXV, reacted readily with diborane to add two equivalents of diborane. The reaction product isolated, in near quantitative yield, as a white crystalline powder, proved unexpectedly to be the *bis* adduct, XXVI, in which no rearrangement of the initial structure had occurred, (Figure 5)



XXVI

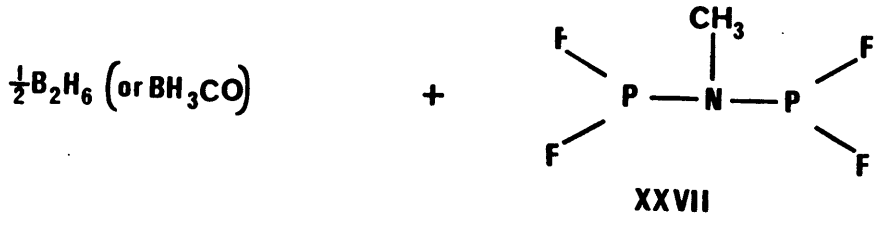
Figure 5: Cyclenphosphorane *bis* borane

The ^{11}B nmr spectrum of XXVI consisted of two signals of equal intensity at δ + 41.2 and 50.2 ppm; consistent with the presence of two BH_3 groups on two nitrogen atoms symmetrically located in the macrocycle. Compounds such as fluorocyclenphosphorane[34] and *bis* cyclenphosphorane[35]

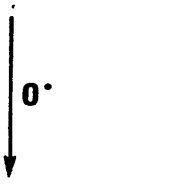
both show the tendency of pentavalent phosphorus atoms to adopt a nearly perfect triagonal bipyramidal arrangement despite the constraints imposed by the cyclic structures. Riess and coworkers[23] proposed that XXVI adopts a similar arrangement. The BH_3 groups are then likely, both on kinetic and thermodynamic grounds, to be co-ordinated to the apical nitrogen atoms. Muetterties *et al*[36] have shown that these undergo less $p\pi$-$d\pi$ interaction with phosphorus than those in equatorial positions. Because of this the apical nitrogens are likely to manifest greater basicity.[21] Thus, even if the BH_3 groups did attack the equatorial nitrogen atoms, it is expected that the structure would rearrange itself so as to bring the uncoordinated nitrogen atoms into the equatorial plane in which $p\pi$-$d\pi$ interactions are favoured and the BH_3 coordinated nitrogen atoms, which have no electron left for back donation, into the apical positions.[23]

5.1.6. *Aminophosphines with two Phosphorus Atoms*

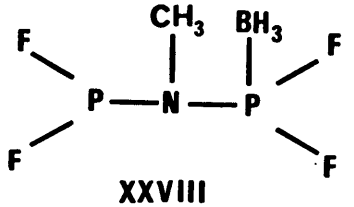
Reactions with methylamine *bis*(difluorophosphine), $F_2PN(CH_3)PF_2$, XXVII, have been used to prepare the mono -, XXVIII, and *bis* -, XXIX, borane adducts (13), (14).[37]



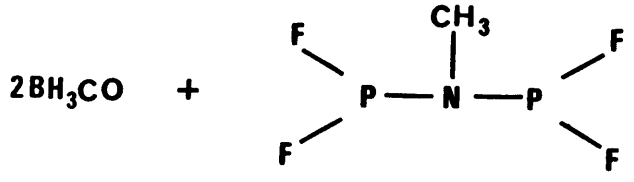
XXVII



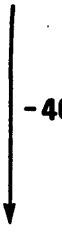
(13)



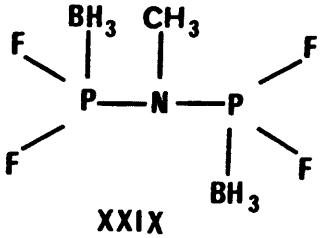
XXVIII



XXVII



(14)



XXIX

Compound XXVIII is stable but the *bis*(borane) adduct readily undergoes irreversible decomposition.

Martin *et al*[38] have reported similar borane absorption studies on cyclic aminophosphines containing two phosphorus atoms. These authors reported that compound, XXX, Figure 6, added one or two equivalents of borane depending on the stoichiometry.[39] Similarly, XXXI, Figure 7, also added two equivalents of BH_3,[40] as will compound XXXII,[41] (Figure 8). In all of these cases the borane groups were coordinated solely to phosphorus.

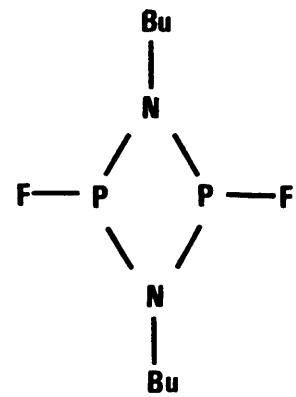


Figure 6: XXX

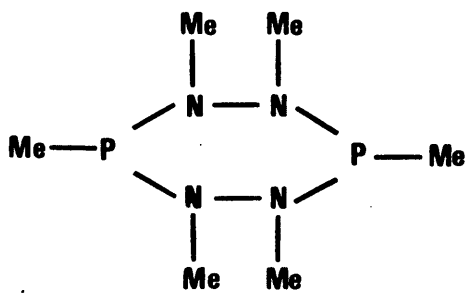


Figure 7: XXXI

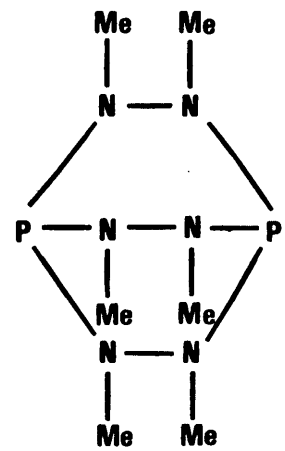


Figure 8: XXXII

5.1.7. *Systems with Four Phosphorus Atoms*

Phosphorus tri-N methylimide, $P_4(NCH_3)_6$, XXXIII, reacts with diborane in solution[42] to give the complexes $P_4(NCH_3)_6(BH_3)n$ with n = 1 - 4. The BH_3 groups are affixed to the phosphorus atoms without rupture of the original symmetric cage structure. This addition occurred almost at random at first, then the distribution of the molecular species present in the solution was seen to change with time and finally reached an equilibrium after ca. 4 days. This system of complexes is formally treated as an exchange of borane groups versus electron pairs around the $P_4(NCH_3)_6$ core.

In $P_4(NCH_3)_6(BH_3)_4$, XXXIV, the BH_3 groups can be displaced by trimethylamine, on the other hand $(CH_3)_3$ N.BH_3 can be used as a source of BH_3 groups for complexing $P_4(NCH_3)_6$, (15).

$$4(CH_3)_3N.BH_3 + \underset{\text{XXXIII}}{P_4(NCH_3)_6} \rightarrow \underset{\text{XXXIV}}{P_4(NCH_3)_6(BH_3)_4} + 4(CH_3)_3N \qquad (15)$$

The relative affinity of BH_3 towards $P_4(NCH_3)_6$ and trimethylamine was measured by Riess and Van Wazer.[42]

5.1.8. *Related Systems with No Direct P - N Bond*

Miller and coworkers[43] studied the reactions of the *gem*-dibasic ligand, dimethyl phosphine methyldimethylamine, $[(CH_3)_2PCH_2N(CH_3)_2]$, XXXVI, Figure 9.

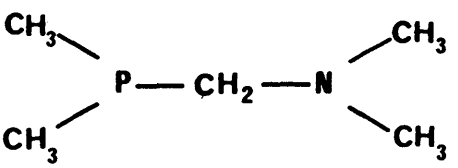


Figure 9: $[(CH_3)_2PCH_2\ N(CH_3)_2]$

with 0.5 molar and 1 molar equivalents of diborane. Both the monoborane and *bis*(borane) adducts were isolated as stable solids. The authors claimed that the simple *bis*(borane) adduct structure, XXXVII, Figure 10

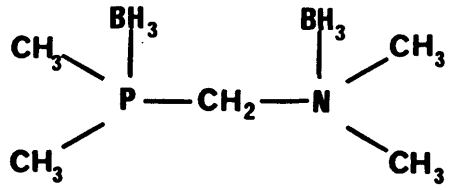


Figure 10: $(CH_3)_2PCH_2N(CH_3)_2 \cdot 2BH_3$

was favoured for this compound as opposed to the symmetrical salt structure, XXXVIII, Figure 11,

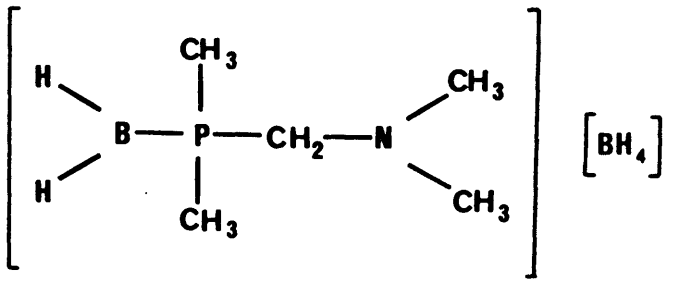
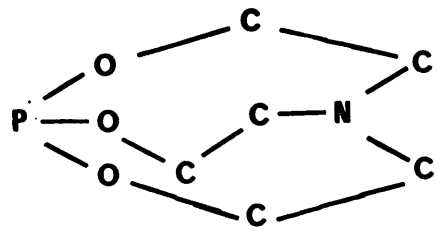


Figure 11: XXXVIII

since the infrared spectrum did not contain the strong bending absorption of $[BH_4]^-$ in the 1070-1170 cm^{-1} region.

Verkade and coworkers[26] studied the reaction of unstable $P(OCH_2CH_2)_3N$, XXXIX, Figure 12,

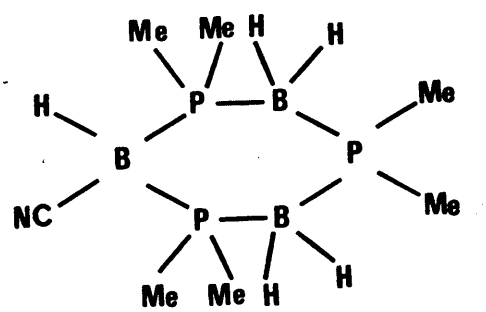


(22)

Figure 12: XXXIX

with BH_3.THF at room temperature in toluene to obtain a stable, phosphorus-boron bonded, solid adduct $H_3B.P(OCH_2CH_2)_3N$, whose structure was confirmed by X-ray analysis. One interesting feature of XXXIX is its increased basicity. This is conferred by the twisting of the OCH_2CH_2 bridges with respect to the P-N axis, thus putting the largely unhybridised 2p lone pair orbital on each oxygen in $P(OCH_2CH_2)_3N$ in a position to interact repulsively with the phosphorus lone pair in this preferred molecular conformation.

To date no cyanoborane adducts of aminophosphines of the type $R_2PNR'_2$ have been reported. However the cyclic system

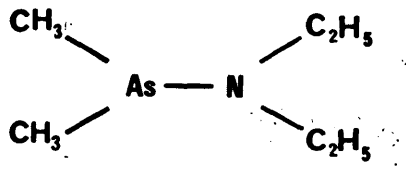


has been reported as well as some halogenated adducts such as $(Me_2N)_3P$ BH_2Cl and $(Me_2N)_3PBHCl_2$.

Cyanoborane adducts have not been reported in aminoarsine chemistry either *(vide infra)*

5.1.9. *Aminoarsines and Their Reactions with Borane*

Borane absorption studies were performed on aminoarsines by Krannich and coworkers.[44] The reaction of BH_3.THF with diethylaminodimethylarsine, $(CH_3)_2AsN(CH_2CH_3)_2$, XL Figure 13, was followed by temperature



XL

Figure 13: Dimethylaminodimethylarsine

dependent ^{11}B, ^{13}C and ^{1}H n.m.r. spectroscopic studies. Both N - B, XLI, and the As - B adducts, XLII, were formed by a 1 : 1 : 1 reaction of XL with BH_3.THF in THF/toluene at -90°C, in comparable yields (Figures 14 and 15).

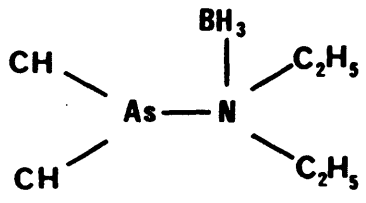


Figure 14: XLI

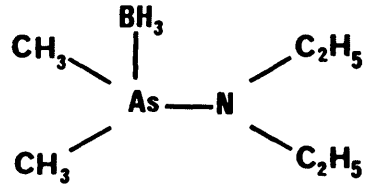


Figure 15: XLII

As the reaction mixture is gradually allowed to warm up, compound XLII undergoes rearrangement to XLI with some decomposition, the disappearance of XLII being complete at -10°C. These findings indicated that XLI is more stable than XLII or that boron-nitrogen bond formation is favoured over boron-arsenic bond formation in the above system. This is consistent with the results of previous studies which suggest that the order of adduct stability is

$$(CH_3)_3P.BH_3 \; > \; (CH_3)_2N.BH_3 \; > \; (CH_3)_3As.BH_3$$ [45,46,47]

Since at -10°C the reaction mixture contained primarily XLI, with trace amounts of $(CH_3)_2As.BH_2$ and $(CH_3CH_2)_2NH.BH_3$ these authors suggested that the following reactions occur (16), (17), (18).

$$(CH_3)_2As(BH_3)N(CH_2CH_3)_2 \longrightarrow (CH_3)_2As\,N(CH_2CH_3)_2.BH_3 \qquad (16)$$

XLI XLII

$$(CH_3)_2AsN(BH_3)(CH_2CH_3)_2 \longrightarrow (CH_3)_2AsBH_2 + (CH_3CH_2)_2NH \qquad (17)$$

XLII

$$(CH_3CH_2)_2NH + BH_3.THF \longrightarrow (CH_3CH_2)_2NH.BH_3 + THF \quad (18)$$

At 20°C, ^{11}B signals at δ 36.2 and -19.4 ppm were noted indicating the presence of $(CH_3)_2AsBH_2$,[46,47] $(CH_3CH_2)_2NH.BH_3$[48,49,50] and the μ-hydrido-bridged species, μ-$[CH_3CH_2N]B_2H_5$[48,51,52,53] decomposition products of XLII. The formation of these substances is thought to take place by the following reactions (19), (20), (21).

$$(CH_3)_2AsN(BH_3)(CH_2CH_3)_2 \longrightarrow (CH_3)_2AsH + (CH_3CH_2)_2NBH_2 \quad (19)$$

$$(CH_3CH_2)_2NBH_2 + BH_3.THF \longrightarrow (CH_3CH_2)_2NB_2H_5 + THF \quad (20)$$

$$(CH_3)_2AsH + BH_3.THF \longrightarrow (CH_3)_2AsH.BH_3 + THF \quad (21)$$

Krannich and coworkers[44] have also shown that the diarsine compound, $(CH_3)_2AsAs(CH_3)_2$, XLIII, is formed by the decomposition of $(CH_3)_2AsN(BH_3)(CH_3)_2$. The first step is the formation of $(CH_3)_2AsH$, (22).

$$(CH_3)_2AsN(BH_3)(CH_3)_2 \longrightarrow (CH_3)_2AsH + (CH_3)_2NBH_2 \quad (22)$$

$(CH_3)_2AsH$ then reacts with undecomposed adduct, (23),

$$(CH_3)_2AsH + (CH_3)_2AsN(BH_3)(CH_3)_2 \longrightarrow \underset{\text{XLIII}}{(CH_3)_2AsAs(CH_3)_2} + (CH_3)_2NH.BH_3 \quad (23)$$

These reactions occur irreversibly and good yields of the diarsine product, XLIII, are obtained.

5.2 RESULTS AND DISCUSSION

The objective of this work was the synthesis of novel BH_2X (X = H, CN) complexes of aminophosphines of the type $Ph_2P\ NR_2$. The preparation of both P-BH_2X and N-BH_2X compounds was attempted. Three different approaches were employed (a) aminophosphines were reacted with BH_2X -ether (THF or mono-glyme) complexes to generate mono- and di-BH_2X adducts, (24), (25).

$$Ph_2PNR_2 + BH_2X\text{-ether} \longrightarrow Ph_2(BH_2X)\ PNR_2 + \text{ether} \qquad (24)$$

$$Ph_2PNR_2 + 2BH_2X\text{-ether} \longrightarrow Ph_2P\ NR_2.2BH_2X + \text{ether} \qquad (25)$$

(b) the second approach involved the reaction of Ph_2PCl (BH_2X) complexes with amines (primary or secondary) to afford phosphorus-mono-boron bonded aminophosphine adducts (26).

$$Ph_2PCl\ (BH_2X) + R_2NH \xrightarrow{Et_3N} Ph_2(BH_2X)\ PNR_2 \qquad (26)$$

(c) Since it was anticipated that routes (a) and (b) would generate only phosphorus-boron bonded adducts, amine-boranes and -cyanoboranes were reacted with chlorodiphenylphosphine in an attempt to furnish nitrogen-boron bonded adducts, (27).

$$R_2NH.BH_2X + Ph_2PCl \xrightarrow{Et_3N} Ph_2\ PN(BH_2X)R_2 + [Et_3NH]\ [Cl] \qquad (27)$$

5.2.1. *Method (a): Reactions of $Ph_2PN\ (C_6H_{11})_2$*

Firstly, the preparation and characterisation of the new aminophosphine, $Ph_2PN\ (C_6H_{11})_2$, XLVIII will be described.

Two syntheses of XLVIII were utilised. Initially, chlorodiphenyl-phosphine was reacted with two equivalents of dicyclohexylamine (28), method (i).

$$Ph_2P\ Cl + 2(C_6H_{11})_2NH \xrightarrow[\text{reflux}]{THF} Ph_2PN(C_6H_{11})_2 + [(C_6H_{11})_2\ NH_2][Cl] \qquad (28)$$

Diphenyl(dicyclohexylamino)phosphine was isolated in 80% yield from this reaction. The second method (ii) involved the reaction between equivalent

quantities of chlorodiphenyl-phosphine, dicyclohexylamine and triethylamine in refluxing THF (29) (91% yield).

$$Ph_2PCl + (C_6H_{11})_2NH + Et_3N \xrightarrow[\text{reflux}]{\text{THF}} Ph_2PN(C_6H_{11})_2 + [Et_3NH][Cl] \qquad (29)$$

Compound XLVIII is thermally and hydrolytically stable and has a melting point of 177-178°C. It is soluble in polar, aprotic solvents and aromatic hydrocarbons. The compound's formula was confirmed by chemical analysis and by its mass spectrum which exhibits a molecular ion, M/Z = 365, and a fragmentation pattern showing loss of both phenyl and cyclohexyl groups. The infrared spectrum of XLVIII clearly indicates phenyl and CH_2^- containing groups with aromatic absorptions at 3060 and 3000 cm^{-1} and also at 1580 and 1480 cm^{-1}, and aliphatic CH_2- absorptions at 2930 and 2840 cm^{-1}. A sharp peak at 1440 cm^{-1} is characteristic of phosphorus phenyl group absorption.

Although halogen-exchange reactions are known to occur in systems such as (30)[17]

$$Ph_2PCl + (C_6H_{11})_2NH \longrightarrow Ph_2PH + (C_6H_{11})_2NCl \qquad (30)$$

there was no evidence of either P-H (2440-2350 cm^{-1}) or N-Cl (805-690 cm^{-1}) absorptions.[54]

Multinuclear (^1H, ^{13}C, ^{31}P) n.m.r. spectra of XLVIII showed the expected H and C signals and a phosphorus resonance at δP = 23.8 ppm.

5.2.1.1. *Reaction of XLVIII with BH_3.THF in a 1: 2 Mole Ratio*

In 1958, Burg and Slota[18] claimed to have synthesised $(CH_3)_2P\,N(CH_3)_2 .2BH_3$ with borane groups bonded to both phosphorus and nitrogen, but offered no evidence in their report for that compound's isolation other than that based on the products of thermal decomposition. However, later Jugie and coworkers[11] on attempting the same reaction reported that evidence for only P ⟶B adduct formation was found by using ^1H, ^{11}B and ^{31}P n.m.r. techniques.

Even using a large excess of borane (either gaseous B_2H_6 or a BH_3 -ether adduct) addition at both nitrogen and phosphorus could not be obtained.[11] Diphenyl(dicyclohexylamino)phosphine, XLVIII, reacted smoothly with two equivalents of borane-THF XLIV in refluxing THF to furnish diphenyl(dicyclohexylamino)-phosphine-*bis* borane LIII in 42% yield (31).

$$Ph_2\,PN(C_6H_{11})_2 + 2BH_3\text{-}THF \xrightarrow[THF]{reflux} Ph_2P.N(C_6H_{11})_2 \cdot 2BH_3 \qquad (31)$$

XLVIII LIII

At the time of its preparation (1986) compound LIII was apparently the first *bis*-borane adduct of a simple aminophosphine to be isolated at room temperature. In a paper published in 1987, Krannich and coworkers[8] reported the preparation of dimethyl(dimethylamino)-phosphine-*bis* borane (III) by the reaction of $Me_2PN\,Me_2$ with gaseous diborane at -10°C (32).

$$Me_2PNMe_2 + B_2H_6(g) \xrightarrow[THF/toluene]{-10^{\circ}C} Me_2PNMe_2.2BH_3 \qquad (32)$$

I III

Dimethyl(dimethylamino)phosphine-*bis* borane melted at 117°C and was reported to be moderately air stable. Compound, LIII (m.p. 217-218°C) was initially characterised by its chemical analysis: C, 72.99; H, 9.74; N, 3.72; B, 5.60%; ($C_{24}H_{38}NB_2P$ requires C, 73.28; H, 9.67; N, 3.56; B, 5.59%) and was found to be moderately thermally and air stable in solid form. However, compound LIII was unstable in solution and a sample recrystallised from monoglyme solvent analysed differently from LIII giving a reduced boron content relative to nitrogen and phosphorus *i.e.* changing from 2 : 1 to 1.2 : 1. The analysis figures were suggestive of the presence of oxygen in the recrystallised material. Preliminary ^1H and ^{13}C n.m.r. spectra of the recrystallised material did not indicate any major structural changes from LIII with the signals for cyclohexyl and phenyl groups being retained. Crystals of this new compound were sent to Professor G. Ferguson in Guelph for X-ray crystallographic structural analysis but unfortunately it was

found that the crystals were twinned and a full characterisation was not possible.

The infrared spectrum of LIII showed typical aromatic and cyclohexyl (CH_2) absorptions. The B-H absorptions at 2515 and 2420 cm^{-1} are relatively weak with others at 2365 and 2330 cm^{-1} even weaker. There is a strong absorption at 1440 cm^{-1} which may be due to a phosphorus bonded phenyl group but could possibly also be associated with aromatic CH vibrations. No infrared data have been reported for previous *bis* borane adducts so general comparisons are not possible.

As may be expected both the ^{1}H (Figure 16) and ^{13}C. (Figure 17) n.m.r. spectra for LIII were similar to those of the parent aminophosphine. A corresponding observation was also made by Krannich and coworkers in the case of the ^{1}H n.m.r. spectrum of $Me_2PN\ Me_2.2BH_3$. Due to lack of facilities at U.C.C. to obtain ^{11}B and ^{31}P n.m.r. spectra, samples had to be sent to either University College, Galway or Edinburgh University. The resulting ^{11}B and ^{31}P n.m.r. spectra of LIII were unsatisfactory and contained peaks which suggested decomposition of the original compound. It is probable that these spectra correspond to the previously mentioned product obtained on recrystallisation. Instability in solution is a feature of aminophosphine-borane chemistry and is further emphasised in the attempted synthesis of diphenyl (dicyclohexylamino) phosphine-borane (*vide infra*).

5.2.2.2. *Reaction of XLVIII with BH_3-THF in a 1 : 1½ Mole Ratio*

Diphenyl(dicyclohexylamino)phosphine reacted smoothly in refluxing THF, with one equivalent of borane-THF. However, although exactly the same conditions were used as for the *bis* borane adduct above, the product isolated was not the anticipated diphenyl(dicyclohexylamino)phosphine-borane (10).

$$Ph_2\ PN(C_6H_{11})_2 + BH_3\text{-}THF \xrightarrow[THF]{\text{reflux}} Ph_2P\ N(C_6H_{11})_2.BH_3 \qquad (10)$$

Figure 16: ^{1}H n.m.r. spectrum of Diphenyl(dicyclohexylamino)phosphine-*bis* borane

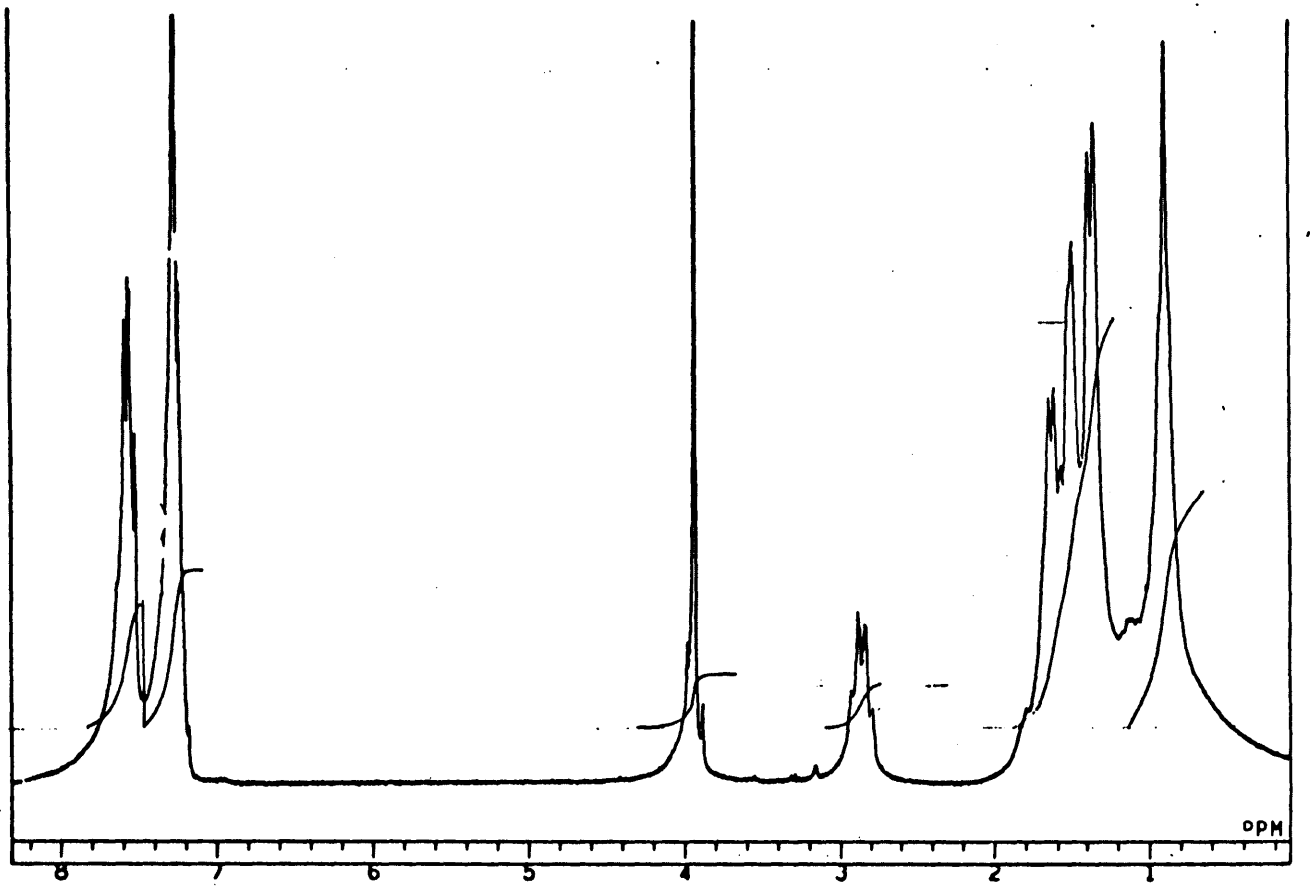
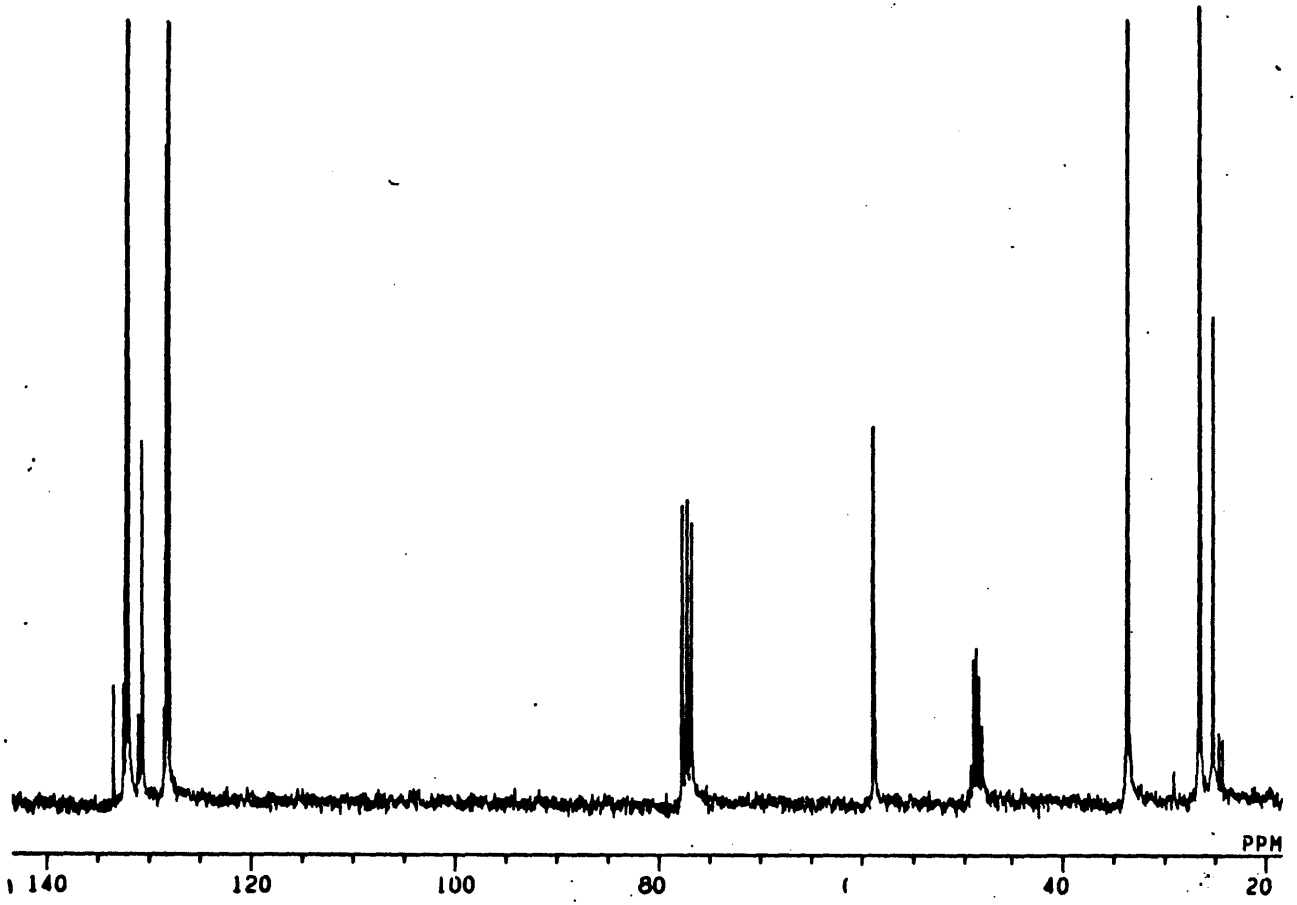


Figure 17: ^{13}C n.m.r. spectrum of Diphenyl(dicyclohexylamino)phosphine-*bis* borane



During the work-up procedure oxygen was incorporated into the system and the product which was isolated as a colourless, crystalline solid, was a biphosphine monoxide derivative, [Ph_2(O)P-P Ph_2] complexed with two diphenylamine molecules LIV (Figure 18). This compound was characterised by i.r., n.m.r., mass spectroscopic and X-ray crystallographic techniques.

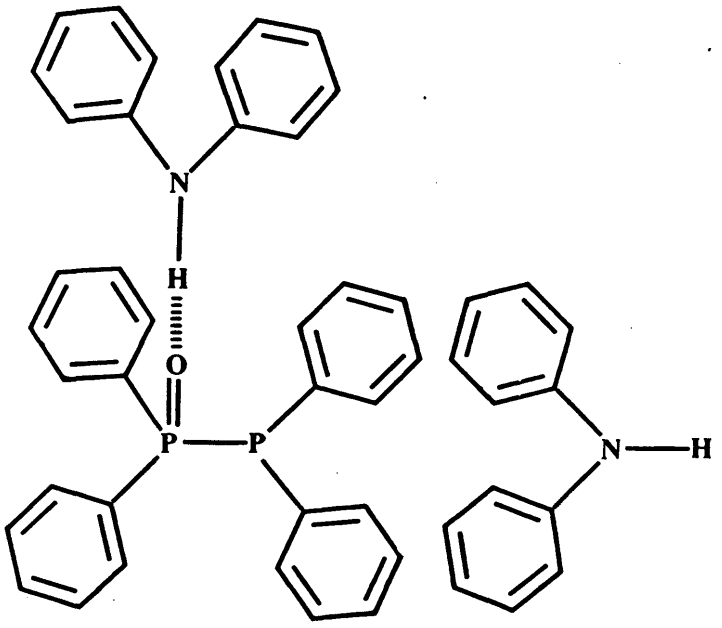
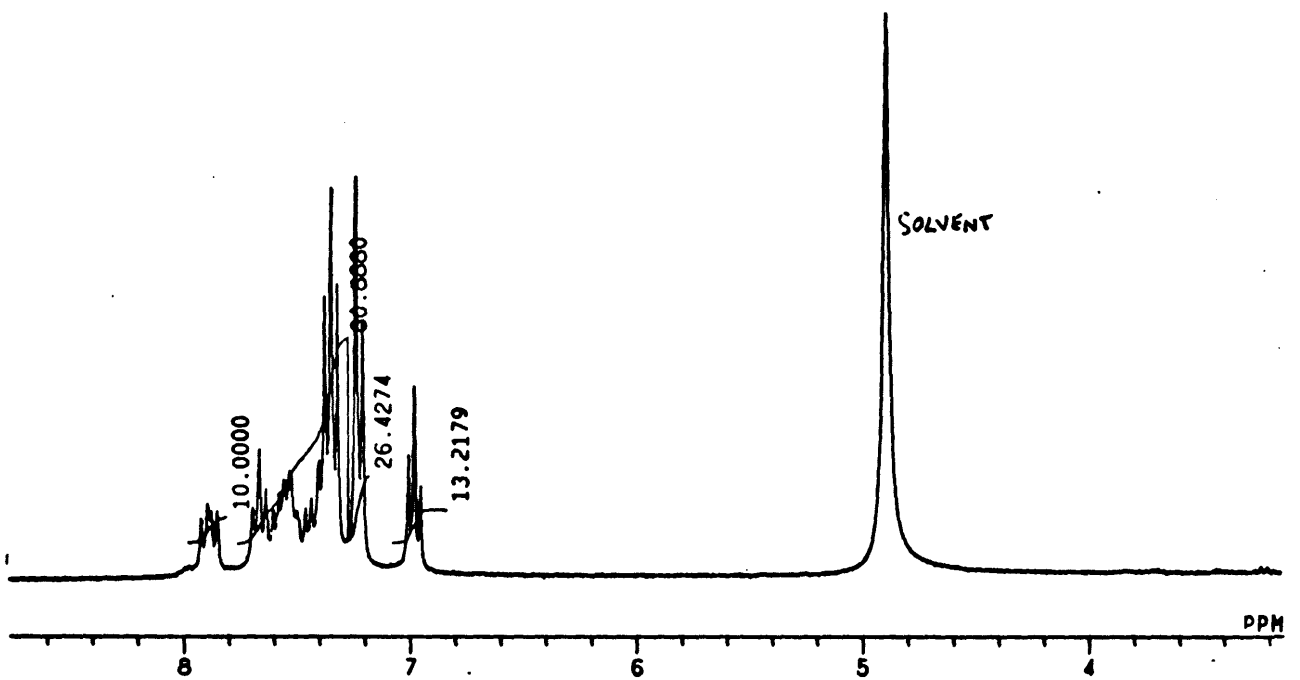


Figure 18: [Ph_2 (O) P-P Ph_2] .$(Ph_2NH)_2$

The infrared spectrum of LIV showed strong C-H aromatic absorptions (2960-3180 cm^{-1} and 1580 cm^{-1}); a P = O absorption (1300 cm^{-1}) and a strong absorption (1455 cm^{-1}) which is suggestive of phosphorus bonded phenyl groups. There was no evidence in the infrared spectrum for cyclohexyl methylene group absorptions. The ^{1}H (270 MHz) n.m.r. spectrum of LIV (Figure 19) emphasised the completely aromatic nature of the compound. All signals were between 6.97 and 7.88 ppm in a series of complex multiplets and no detailed assignements were made. The ^{13}C n.m.r. spectrum of LIV (Figure 20) showed clearly the diphenylamine species but the phosphorus-containing moiety produced a more complex spectral pattern which was difficult to analyse. However, the ^{31}P (109.25 MHz) n.m.r. spectrum of

Figure 19: ^1H n.m.r. spectrum of $[Ph_2(O)\ PPPh_2]\ (Ph_2NH)_2$



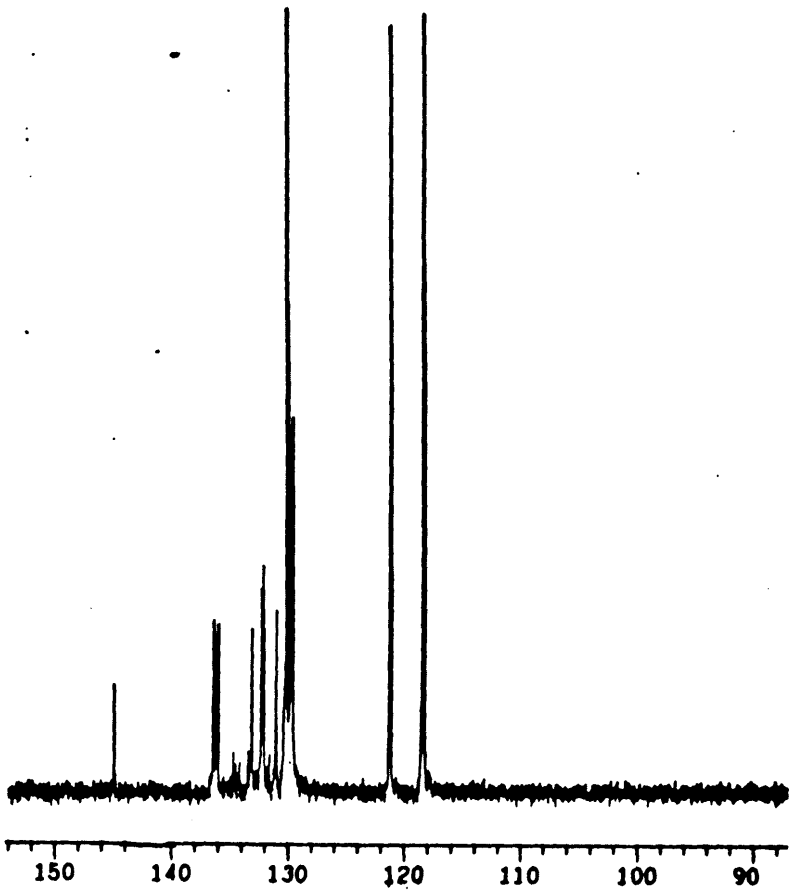


Figure 20: ^{13}C n.m.r. spectrum of $[Ph_2(O)PP\ Ph_2]\ (Ph_2NH)_2$

compound LIV (Figure 21) was much more informative and showed two doublets centred at $\delta^{31}P$ = -21.6 and 39.2 ppm. The doublet at -21.6 ppm corresponded exactly with that reported by Fluck and Binder for the P^{III} atom in $Ph_2(O)P\ PPh_2$.[55] However, the signal for the P^V atom (39.2 ppm) was shifted upfield from 36.9 ppm in $Ph_2(O)PP\ Ph_2$. This was possibly the result of the interaction with a diphenylamine molecule (*vide infra*). The $^1J(^{31}P-^{31}P)$ coupling constant was 98 Hz. Mass spectral analysis of LIV confirmed the presence of diphenylamine. The parent molecular ion $[M]^+$ and fragment ions $[M-H]^+$, and $[M-2H]^+$ were observed as the most abundant peaks. No ions at higher mass were observed which agrees with the suggestion of weakly bound diphenylamine species being present in the compound, *(vide infra)*.

Compound LIV was isolated from reaction (10) on seven different occasions. In order to obtain some information as to how it was formed an n.m.r. study of reaction (10) in solution at room temperature was undertaken. Ten minutes after the addition of the borane-THF solution to the suspension of diphenyl(dicyclohexylamino)phosphine, the cyclohexyl methylene group signals had become very weak in comparison to the aromatic protons (relative ratio of the sum of $C\underline{H}_2$: $C\underline{H}$ signals originally 2 : 1 was reduced to 1 : 8). Within thirty minutes of the addition the ^1H n.m.r. spectrum of an aliquot of the reaction solution exhibited only aromatic signals. The only other product of the reaction was an intractable, air-unstable semi-solid. No information about this material would be obtained because of its reactivity. To ascertain the structure, crystals which were suitable for X-ray diffraction study were grown from a monoglyme-diethyl ether (2 : 1) and sent to Professor G. Ferguson. The crystals were found to have monoclinic space group P_{21}/n. The structure was solved using the Patterson heavy atom method which resolved the position of one phosphorus atom, with

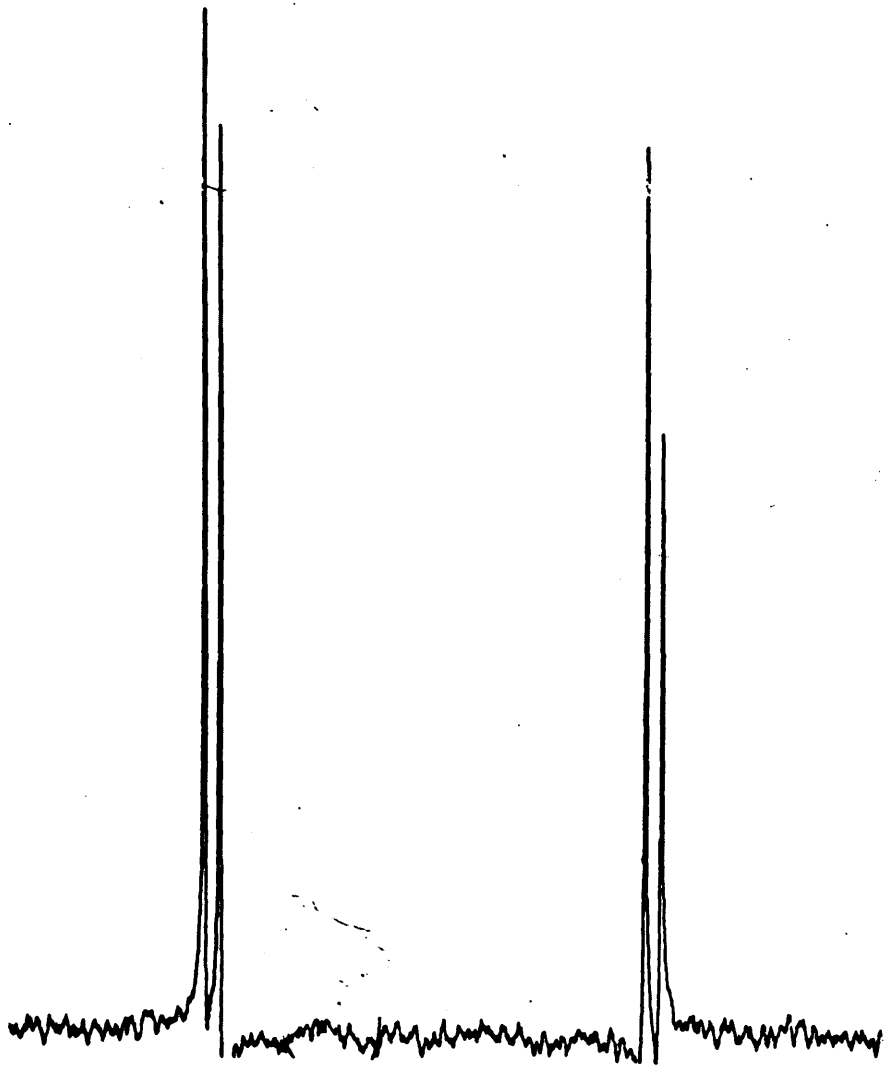


Figure 21: ^{31}P n.m.r. of $[Ph_2(O)\ PP\ Ph_2]\ (Ph_2NH)_2$

the remaining atoms being located in successive difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was resolved in full matrix least squares calculations. A drawing of a single molecule showing 25% probability ellipsoids is illustrated in Figure 22.

The crystal structure of LIV is quite unusual in that it is disordered about the inversion centre (in the middle of the phosphorus-phosphorus bond). The oxygen atom position is only 'half occupied' and is equally disordered over the two phosphorus atoms, which are thus identical due to this space group induced disorder. The structure also has (a) a hydrogen bonded diphenylamine group and (b) a second diphenylamine group which is part of the compound but which, unlike the first, does not appear to be hydrogen bonding in the structure.

The complete structural data for compound LIV is in the Experimental section. Table 3 lists the principal bond lengths and bond angles.

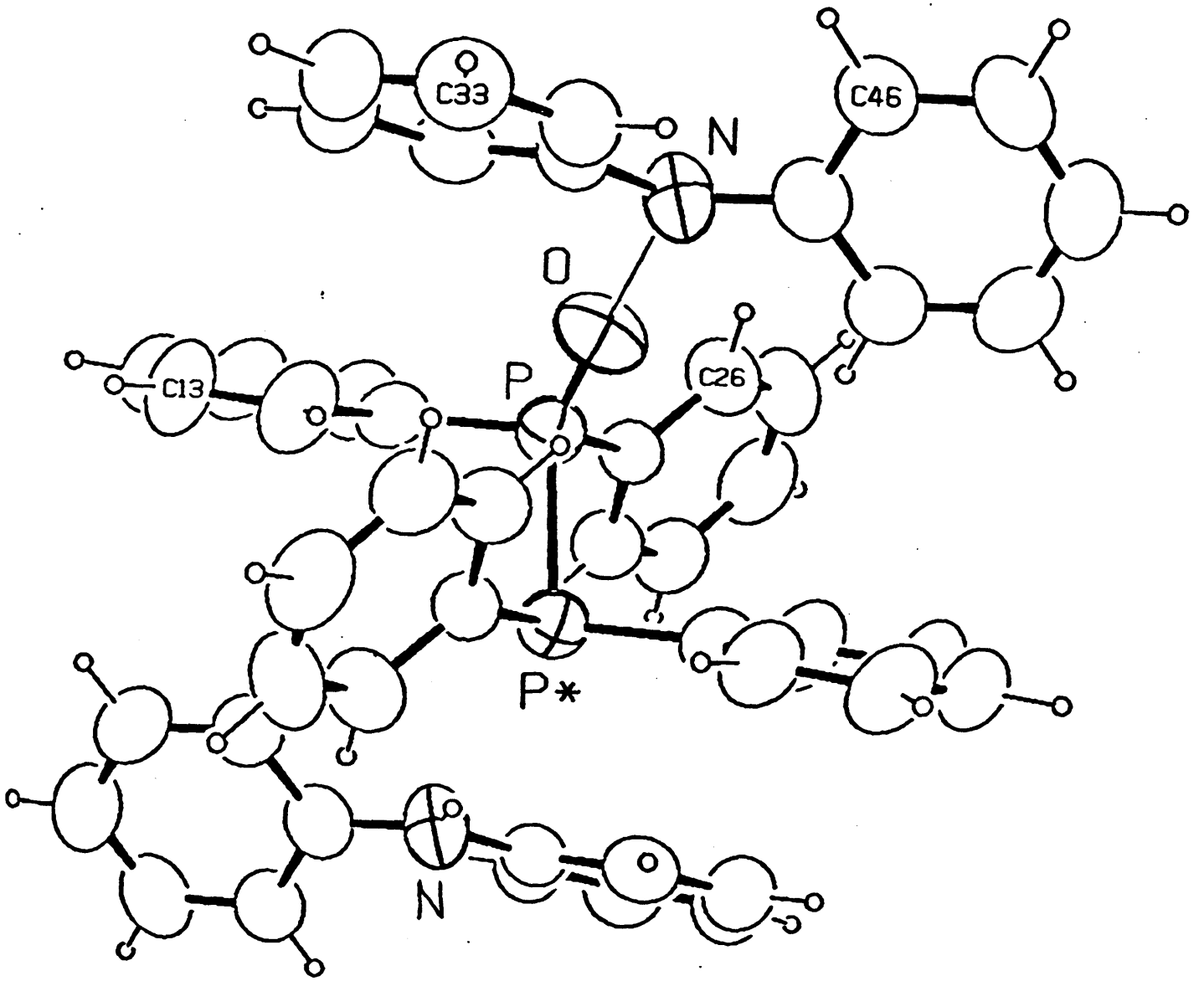


Figure 22: Structure of $[Ph_2(O)PP\ Ph_2]\ (Ph_2NH)_2$

TABLE 3. *Bondlengths and Bond Angles for* $[Ph_2(O)PP\ Ph_2]2(Ph_2NH)_2$

Bond	Bondlength Å	Bond Angles (Degree)	
P-P*	2.228 (2)	P* - P - O	120.5 (3)
P=O	1.345 (6)	P* - P - C11	102.2 (1)
P-C11	1.817 (4)	P* - P - C21	102.0 (1)
P-C12	1.812 (4)	O - P - C11	116.0 (3)
N-C31	1.386 (5)	O - P - C21	109.3 (3)
N-C41	1.396 (5)	N - H(N) ...O	15
N....O	2.690 (6)		
H(N) O	1.79		

* refers to the equivalent position 1 - X, 1 - Y, 1 - Z

The P - P bondlengths in compound LIV is quite similar to the majority of the P - P bonds in black phosphorus (from 2.20 to 2.28 Å)[56]. It is also quite similar to that in P_2I_4(2.21 Å)[57]. The structure of hypophosphoric acid has been established (Figure 23) by X-ray diffraction studies.[57]

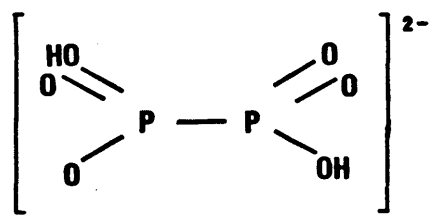


Figure 23: $H_4P_2O_6$

The phosphorus-phosphorus bondlength in the oxoacid is 2.17 Å, that is 0.058 Å shorter than in compound LIV. Other organic species with P - B bonds are hexa(methylimido) tetraphosphorus (2.996 Å)[58], *bis* (cyclenphosphorane)

(2.264 Å),[35] both of which are longer than that in compound LIV. (The single bond covalent radius of phosphorus has been reported as 1.10 Å ,[59] the bondlength in LIV is approximately twice that value). The P = O bondlength at 1.345 (0) Å is significantly shorter than that in hypophosphoric acid (1.50 and 1.57 Å) and that in phosphorous acid (Figure 24) (1.47 and 1.54 Å).

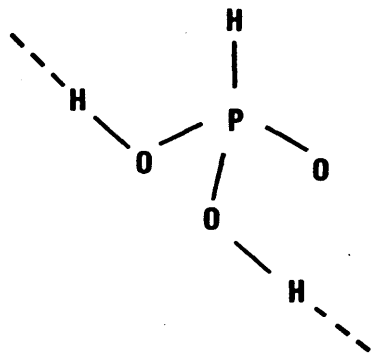


Figure 24: Phosphorous Acid

The longer bondlengths in the acids are clearly due to the partial double bond character found among the oxygen atoms of P-oxyacids. Perhaps a more meaningful comparison is with d(P = O) in P_4O_{10}, 1.43 Å. Crystalline phosphoric acid has a hydrogen bonded layer structure in which each $PO(OH)_3$ molecule is linked to six others by H-bonds which are of two lengths, 2.53 and 2.84 Å. The shorter bonds link OH and O = P groups (Figure 25a) whereas the longer hydrogen bonds are between two OH groups on adjacent molecules (Figure 25b).

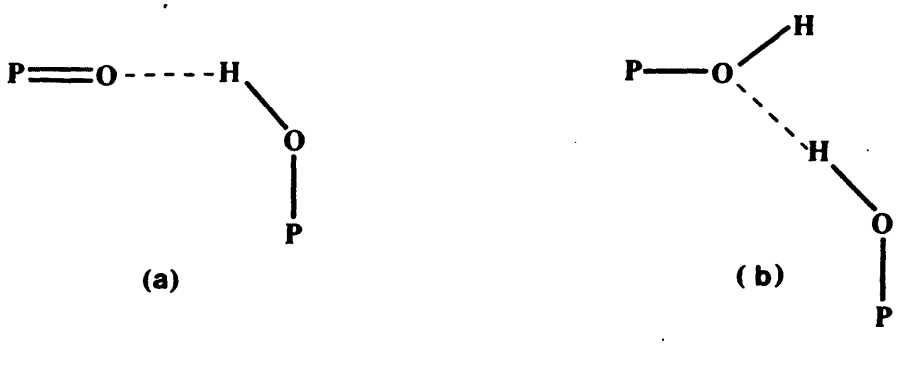


Figure 25: H-bonds in Phosphoric Acid

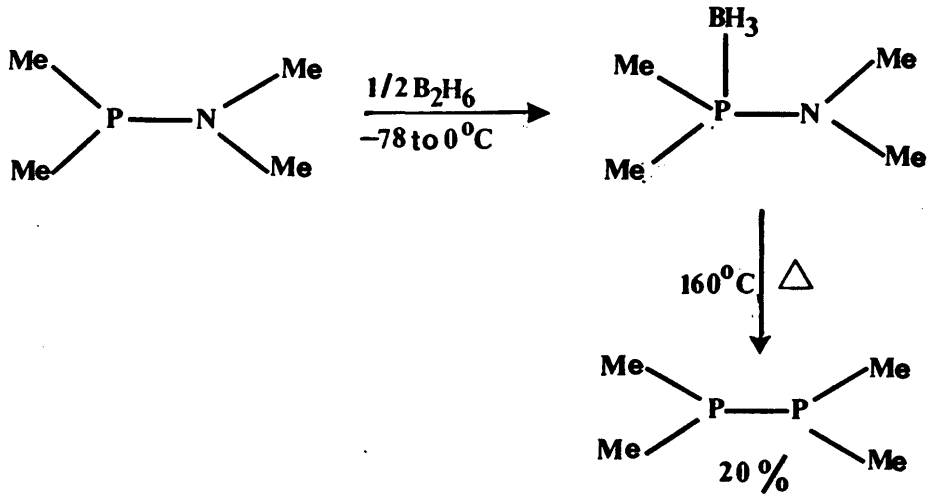
The hydrogen bond in compound LIV at 1.79 Å is significantly shorter than both types in phosphoric acid.

5.2.1.3. *Mode of Formation of LIV*

The generation of compound LIV from the reaction between diphenyl (dicyclohexylamino)phosphine and borane-THF involves (i) cleavage of the phosphorus-nitrogen bond in LIV, (ii) reaction of two Ph_2P- containing species followed by oxidation of the P-P compound formed and (iii) formation of diphenylamine either via oxidation of the N-cyclohexyl groups or reaction with another species (possibly diphenylphosphine).

(i) and (ii):Cleavage of the Phosphorus-Nitrogen Bond and Formation of $Ph_2(O)PPh_2$

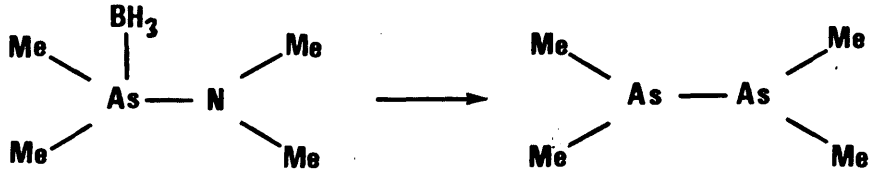
The thermally induced cleavage of phosphorus-nitrogen bonds in simple aminophosphines is well documented in the chemical literature. In 1960, Burg and Slota,[12,18] reported that heating dimethyl(dimethylamino)phosphine to 160°C with borane generated the phosphorus-phosphorus compound, P_2Me_4 (34).



(34)

Other products of the reaction included H_2, "aminoborane", Me_2PH, $(Me_2PBH_2)_n$, and $B_3H_5(Me_2P)_2$. It is noteworthy that the *bis* borane adduct (III), did

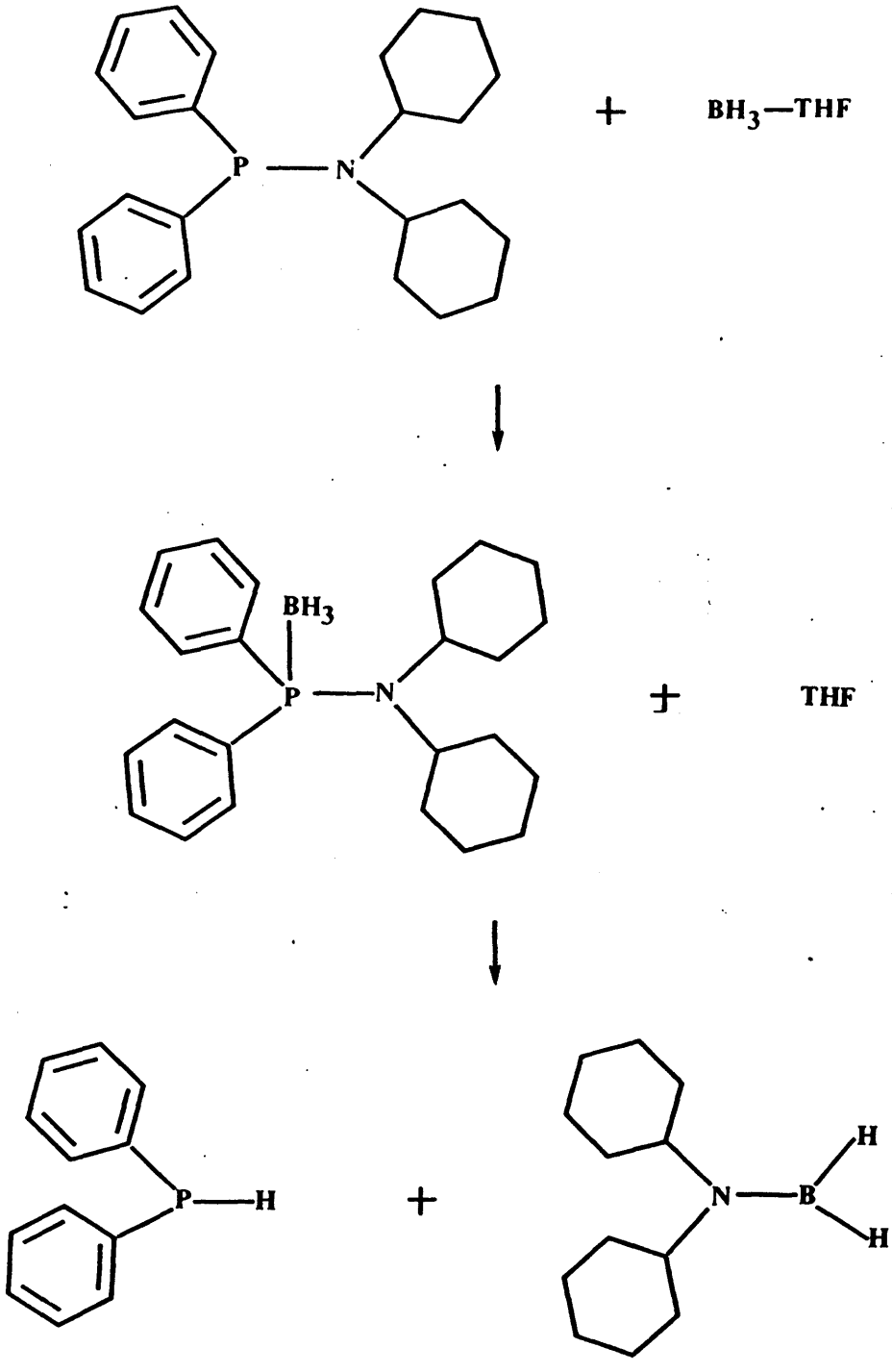
not furnish Me_2PPMe_2 on thermal decomposition. In an analogous reaction to that reported by Burg and Slota, Krannich and coworkers[17], studied the generation of Me_4As_2 from the decomposition of dimethyl(dimethylamino) arsine-borane (35).



(35)

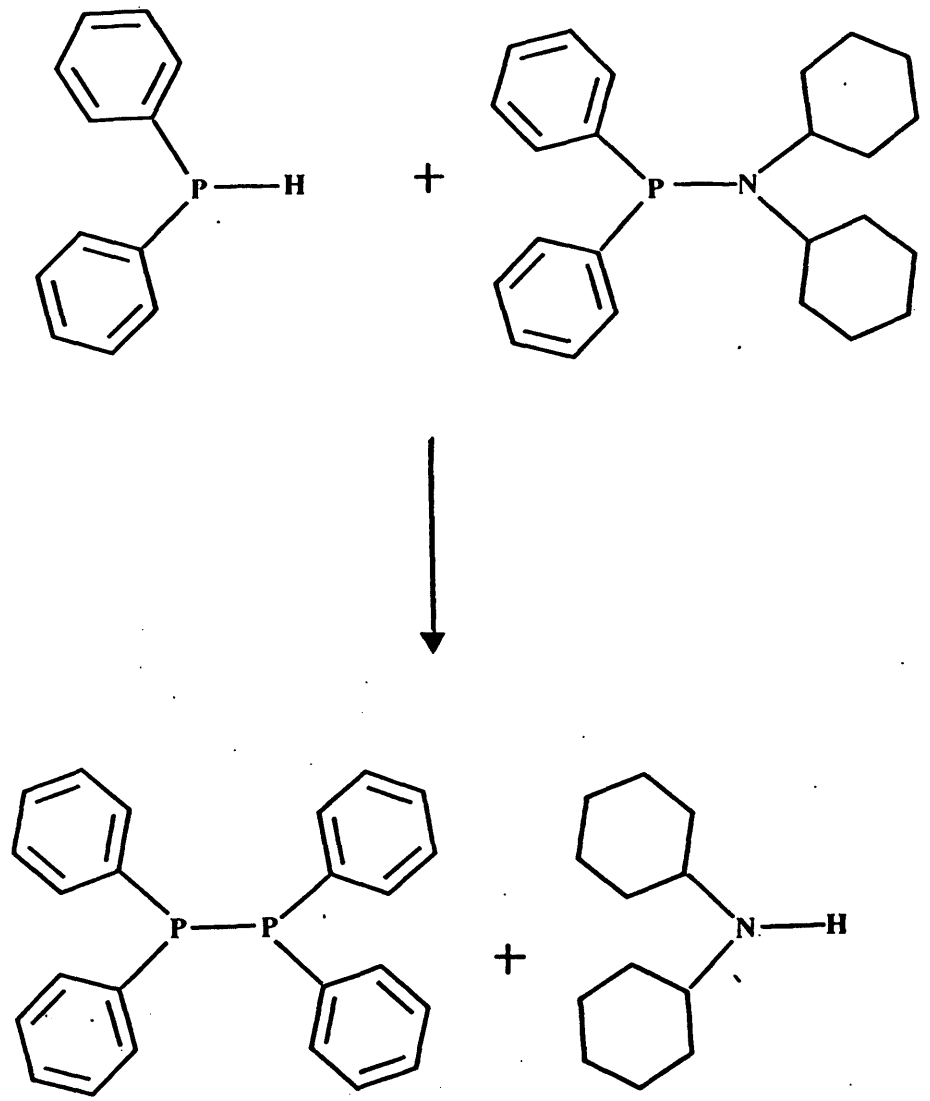
These authors reported that the generation of dimethyl-arsine, Me_2AsH, from dissociation of the aminoarsine-borane complex is the crucial step in the reaction. Using these systems as models, the generation of the phosphine -phosphine portion of LIV may occur as follows. The initial step of the reaction may be the formation of the phosphorus-boron aminophosphine-borane adduct. This could then decompose to form diphenyl-phosphine and dicyclo-hexylamino borane (Scheme 1).

Scheme 1: Generation of Diphenylphosphine



That the *bis* borane LIII adduct did not decompose in this fashion may be due to the addition of the second borane group to nitrogen precluding decomposition to the diphenylphosphine and the aminoborane.

Diphenylphosphine could then react with aminophosphine to generate the biphosphine species and dicyclohexylamine (36).



(36)

Similar reactions for Me_2PH and Me_2PNMe_2 have been reported by Burg.[60,61] It is envisaged that since the addition of BH_3 to $Ph_2P\text{-}N(Cy)_2$ is carried out under inert atmosphere conditions, the oxidation to phosphine oxide occurs during the workup procedure in air (37).

$$Ph_2P\text{-}P\ Ph_2 \xrightarrow[\text{workup}]{\text{air}} Ph_2(O)\ P\text{-}P\ Ph_2 \qquad (37)$$

Krannich and coworkers[62] observed broadening of peaks assigned to Me_2AsNMe_2 and Me_2NH in the ^1H n.m.r. of (38).

$$Me_2AsH + Me_2AsNMe_2 \longrightarrow Me_2AsAsMe_2 + Me_2\ NH \qquad (38)$$

They suggested that exchange of Me_2N groups between Me_2AsNMe_2 and Me_2AsH (what they termed "self-transamination") was occurring equation (38).

These authors noted that this was not unexpected since such reactions are a known synthetic pathways to dialkylaminosubstituted arsines.[63,64] Alder and Kober[65], have established the dimethyl-amino group exchange in the Me_2NH/Me_2AsNMe_2 system through n.m.r. studies using isotopic labelling. Krannich and coworkers investigated the $Me_2AsNMe_2/Et_2AsAsEt_2$ system as a function of temperature (-80°C to -10°C) and time using equimolar ratios of the reactants in a toluene-d_8 solution. From -80 to -30°C the ^{13}C n.m.r. spectrum contained only peaks associated with Me_2AsNMe_2 and $Et_2As.AsEt_2$. Thus exchange of Et_2As and Me_2As groups did not occur over this temperature range. At -25°C, very low intensity peaks corresponding to $Me_2AsAsEt_2$ and Et_2AsNMe_2 appeared (39).

$$Me_2AsNMe_2 + Et_2AsAsEt_2 \longrightarrow Me_2AsAsEt_2 + Et_2AsNMe_2 \qquad (39)$$

At -10°C the intensities of these peaks increase with time as those of the starting materials peaks decrease. After 5 hrs at this temperature, a peak assignable to $Me_2AsAsMe_2$ appears and increases in intensity with time. Thus the unsymmetrical diarsine undergoes symmetrisation. After 5 days at -10°C, the reaction reached equilibrium. The ^1H n.m.r. spectral data at equilibrium indicated the presence of 18% Me_2AsNMe_2, 34% $Et_2AsAsEt_2$, 24% Et_2AsNMe_2, 20% $Me_2AsAsEt_2$ and 4% $Me_2AsAsMe_2$. This study suggested that the following equilibria were established in solution (40), (41).

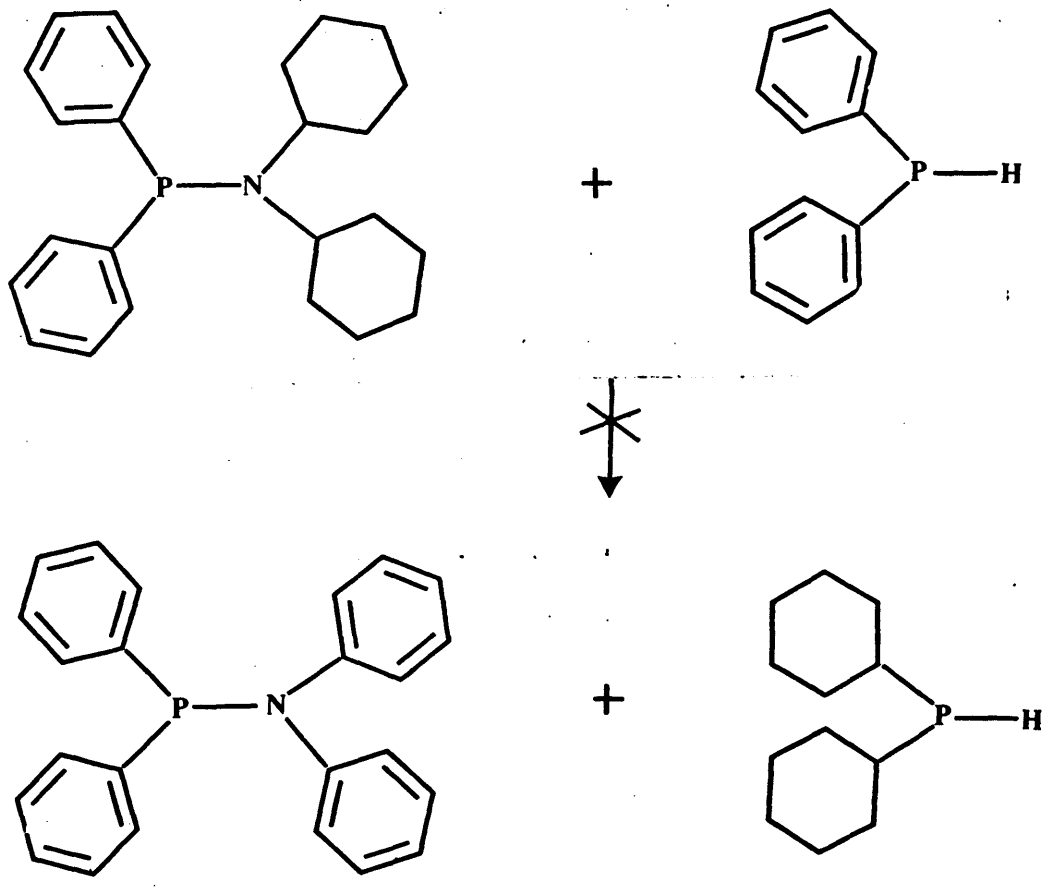
$$Et_2AsAsEt_2 + Me_2AsNMe_2 \rightleftharpoons Et_2AsNMe_2 + Me_2AsAsEt_2 \qquad (40)$$

$$2Me_2AsAsEt_2 \rightleftharpoons Et_2AsAsEt_2 + Me_2ASAsMe_2 \qquad (41)$$

Since the line widths of all the peaks in the ^1H and ^{13}C n.m.r. spectra remained very narrow over the entire temperature range, the authors concluded that the exchange of Me_2As and Et_2As moieties is very slow on the n.m.r. time scale.

(iii): Formation of Diphenylamine

The formation of diphenylamine is not readily explicable. The reaction conditions are apparently not conducive to oxidation of the N-cyclohexyl groups to N-phenyl groups. Also such reactions appear to be unknown in the chemical literature. Moreover, since the yield of LIV is 75% based on diphenyl(dicyclohexylamino)phosphine and thus most of the nitrogen in the system must be retained in LIV, a possible phenyl group exchange between the aminophosphine or dicyclohexylamine and diphenylphosphine (see Scheme 1 above) has to be ruled out (42).

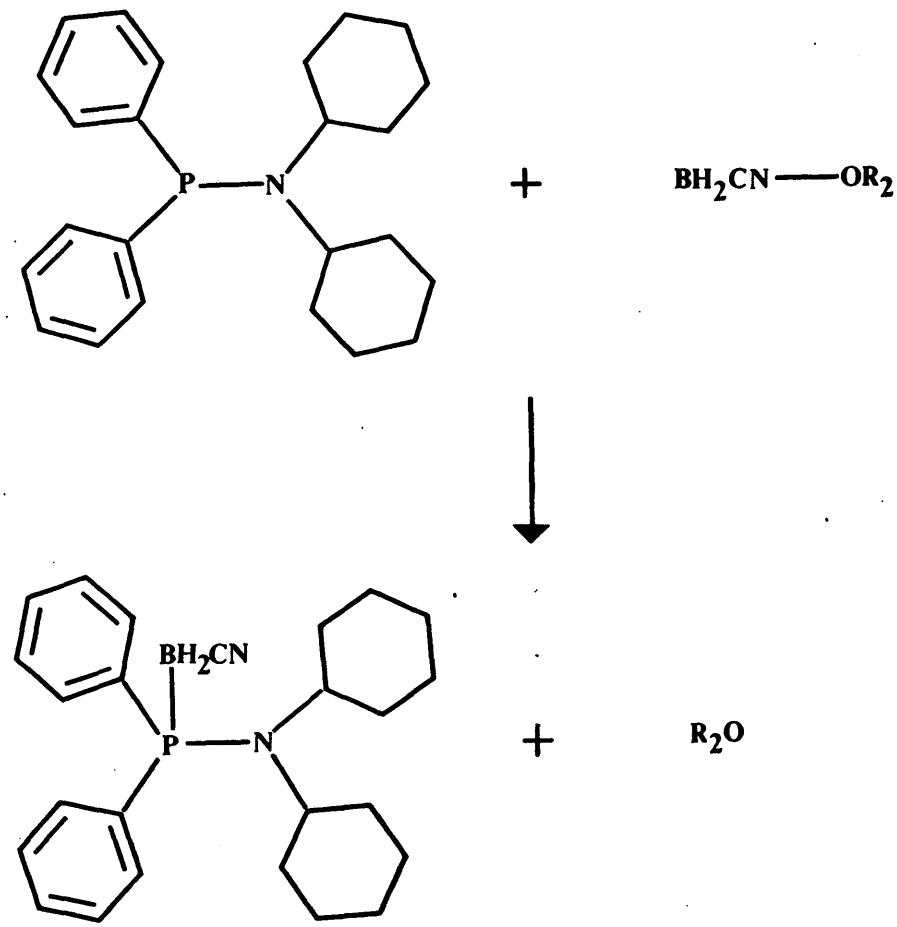


(42))

Since if this were the case the maximum yield of LIV possible by this method would be 50%. Hence the formation of diphenylamine is unexpected and cannot be explained at this time. Clearly this reaction requires further study, however such study would be outside the realm designated as of primary importance in this thesis, i.e. borane and pseudohalo-borane chemistry, and was not pursued.

5.2.1.4. *Reaction of XLVIII with Cyanoborane-monoglyme Complex*

Apparently no cyanoborane adducts of aminophosphines have been previously reported. In an attempt to prepare such adducts diphenyl(dicyclohexylamino)phosphine was reacted with cyanoborane-ether complexes in both 1 : 1 and 1 : 2 stoichiometry e.g. (43).



(43)

R_2O = THF or monoglyme

In the present work, the reaction of diphenyl(dicyclohexylamino)phosphine with BH_2CN -THF in a 1 : 2 ratio did not yield any isolable, pure, products. Instead, highly air-unstable, intractable semisolids were formed for which no satisfactory chemical or spectroscopic analysis was obtained. In contrast, however, the reaction of the aminophosphines with one equivalent of

BH_2CN-monoglyme, while not yielding the anticipated aminophosphine-cyanoborane adduct (or the biphosphine monoxide species) did, however, furnish high yields of a stable boron containing product (m.p. 202-203°C) LV. Chemical analysis of LV showed that it contained carbon, hydrogen, boron and phosphorus but not nitrogen. The ^{1}H (360 MHz) and ^{13}C (90 MHz) n.m.r. data suggested that the organic groups present were aromatic. However, since little structural information could be derived from both i.r. and n.m.r. spectroscopic analyses, single crystals were grown from an ethanol: diethylether (1 : 1) mixture and sent to Professor G. Ferguson for an X-ray crystallographic diffraction study. At the time of writing the results of this analysis were not available.

5.2.1.5. *Syntheses of Other Aminophosphines*

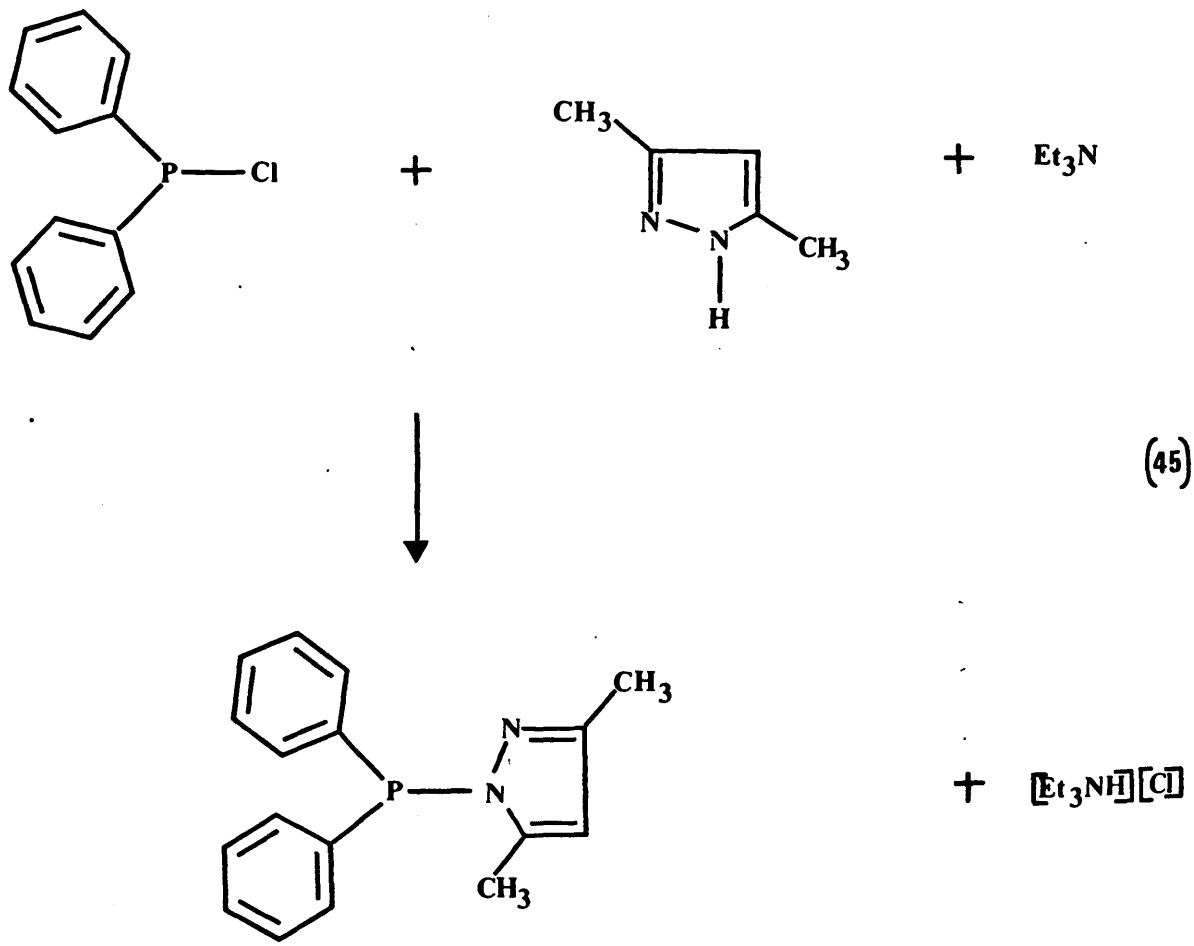
In anticipation of studying the reactions of other aminophosphines with BH_3- and BH_2CN- ether complexes the synthesis of several other aminophosphines was attempted. However, these preparations were unsuccessful *(vide infra)* and further work was curtailed. A brief account of these reactions is given below.

Four amines were reacted with chlorodiphenylphosphine using procedures (a) and (b). The amines used were t-butylamine, di-n-butylamine, 3, 5-dimethylpyrazole and diphenylamine. From these reactions using general method (ii) (compare $Ph_2 PN(C_6H_{11})_2$, reaction (29)) both t-butylamine and di-n-butylamine afforded novel aminophosphine oxides of the type $Ph_2(O)\ PNR_1R_2$ (44).

$$Ph_2PCl + R_1R_2NH \xrightarrow[\text{air/workup}]{Et_3N} Ph_2(O)\ PN\ R_1R_2 + [Et_3NH]\ Cl \qquad (44)$$

(a) $R_1 = R_2 = C_4\ H_9$; (b) $R_1 = (CH_3)_3C$, $R_2 = H$

The reaction of 3, 5-dimethylpyrazole with chlorodiphenylphosphine furnished an unusual product and diphenylamine apparently failed to react. The aminophosphine oxides, $Ph_2(O)\ PN(Bu^n)_2$ L and $Ph_2(O)\ PNH(Bu^t)$ IL were initially identified as such by their chemical analyses and infrared spectra. Both showed the presence of strong P = O absorptions (1230 cm^{-1} for L and 1225 cm^{-1} for IL). ^1H and ^{13}C n.m.r. spectra established the presence of the phenyl and alkyl groups. Both aminophosphine oxides were air-stable, crystalline solids soluble in halogenated hydrocarbons. However, since these compounds were not those required for reaction with BH_2X- adducts, further work was stopped. Chlorodiphenylphosphine was reacted with 3, 5-dimethylpyrazole in an attempt to synthesise diphenyl (3,5-dimethylpyrazolyl) phosphine (45).



(45)

However, the product isolated LI was an aromatic(i.r. and ^{1}H and ^{13}C n.m.r.) phosphorus containing species which had no nitrogen. Since this product was not an aminophosphine further reactions were not pursued.

The synthesis of diphenyl(diphenylamino)phosphine LII was attempted using both procedures (i) and (ii) . Under reflux conditions for up to two weeks both ^{1}H n.m.r. and chromotographic analysis (t.l.c., eluent acetone, pet.ether, 3 : 1) indicated that only a small portion of starting material had reacted and diphenylamine was recovered (~ 73%) after workup. (The unreactivity of diphenylamine has previously been noted in relation to its inability to form amine-borane or -cyanoborane adducts by the methods outlined in Chapter 4).

5.2.2 *Method (b): Reactions of $Ph_2PCl(BH_2X)$ (X= H, LIII, X =CN, LIV) with Amines*

5.2.2.1. *Preparation of $Ph_2PCl(BH_2X)$*

Both $Ph_2PCl(BH_3)$ XLVI and Ph_2PCl (BH_2CN) XLVII are apparently novel complexes. They were prepared by the reaction of chlorodiphenylphosphine with either BH_3-THF or BH_2CN-THF (prepared *in situ)* (46).

$$Ph_2PCl + BH_2X\text{-}THF \xrightarrow{-20^{\circ}C} Ph_2PCl(BH_2X) + THF \qquad (46)$$

The complexes were characterised by infrared and ^{1}H n.m.r. spectroscopy and used *in situ.* Both XLVI and XLVII are air sensitive oils. Schmidbaur *et al*[19] prepared Me_2P (Cl) BH_3 by a reaction similar to (21) and reported that it is highly air sensitive. To date no cyanoborane adducts of organo-phosphine chlorides appear to have been reported.

According to Schmidbaur *et al*[19] reaction of organo-phosphine chloride boranes with water or alcohol takes place at the P-Cl function and the evolved hydrogen chloride chlorinates the borane group generating a complex mixture of products (47).

$$R_2P(Cl)BH_3 + H_2O \longrightarrow R_2P(OH)BH_3 + HCl \quad (47)$$

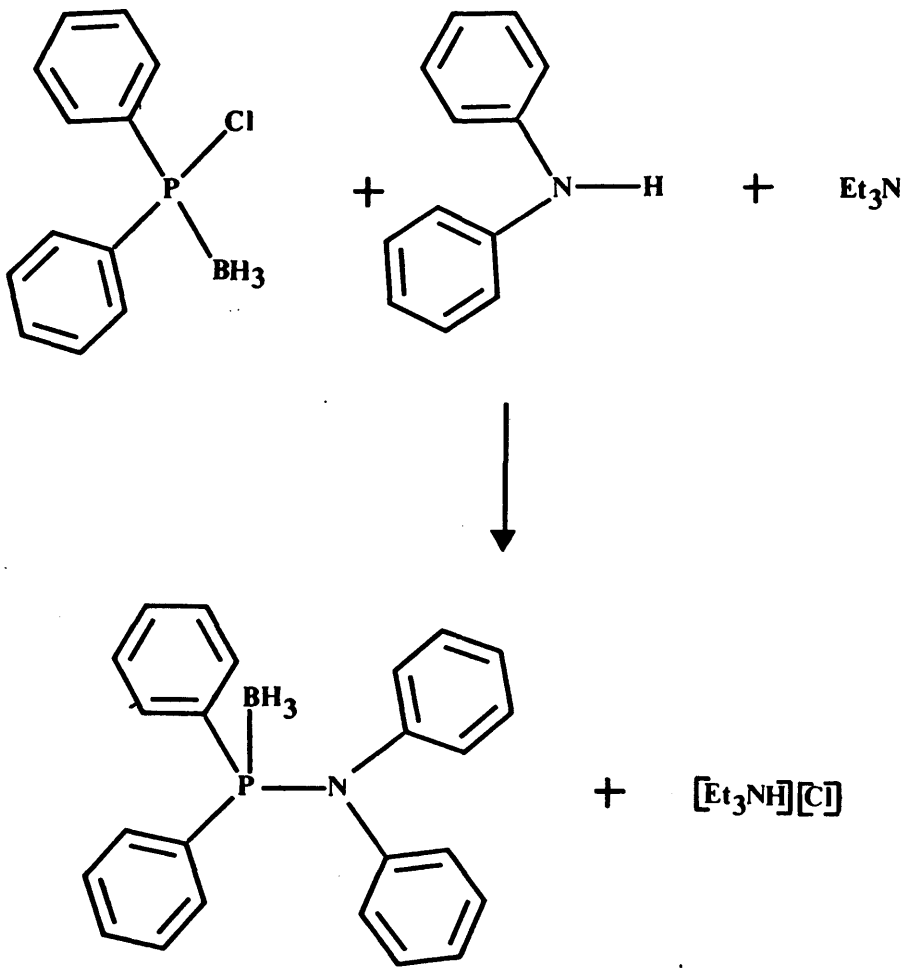
$$\downarrow + HCl$$

Mixture of products

Purity and yield of the $R_2P(Cl)BH_3$ adducts depends critically on the exact reaction of stoichiometry and on the purity of the reactants used.

5.2.2.2. *Reaction of $Ph_2P(Cl)BH_3$ with Diphenylamine*

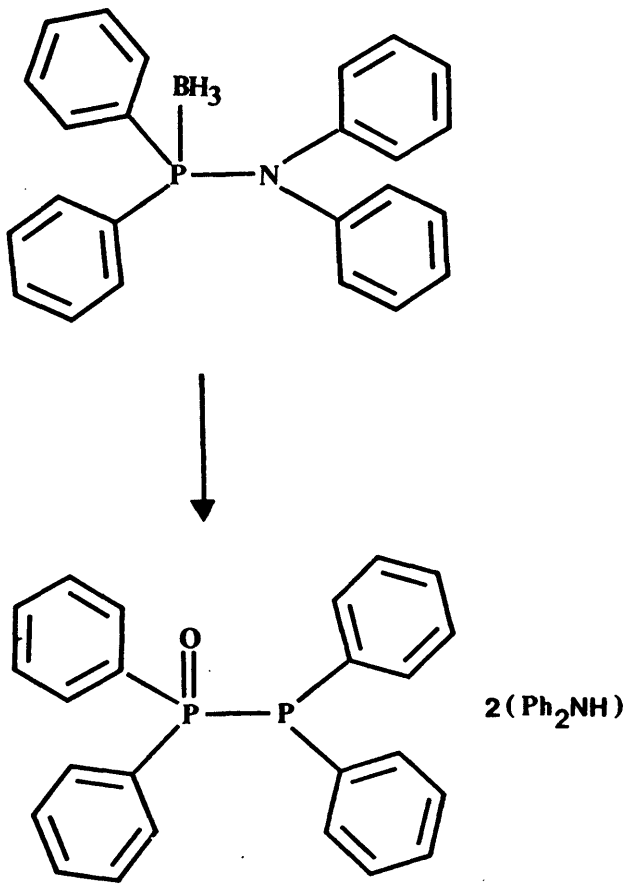
The reaction between chlorodiphenylphosphine-borane XLVI and diphenylamine afforded diphenyl(diphenylamino)phosphine-borane LVI in 45% yield (48).



(48)

Diphenyl(diphenylamino)phosphine-borane was obtained as an analytically pure solid which was moderately air stable when crystalline (m.p. 95-

96°C). This increased stability over the chlorophosphine-borane adduct was also noted by Schmidbaur *et al* for $Me_2(BH_3)PNH_2$, which is also only moderately air and moisture sensitive compared to the highly sensitive $Me_2P(Cl)BH_3$. Data from infrared spectroscopy and mass spectrometry were consistent with the formulation $Ph_2(BH_3)PNPh_2$. The infrared spectrum exhibited aromatic CH absorptions at 3040, 3010, 2940, 2850, 1580, and 1490 cm^{-1}. There were B-H absorptions at 2380 and 2340 cm^{-1}. The mass spectrum of LVI showed a molecular ion M/Z at 367 and fragmentation patterns due to loss of one and two phenyl groups. However, compound LVI decomposes slowly in air and when recrystallised samples were sent for high field n.m.r. spectra (University of Edinburgh) and X-ray crystallographic structural analysis (University of Guelph), they were found to have decomposed to $[Ph_2(O)PPPh_2]$ $2(Ph_2NH)$ (49).



(49)

The decomposition reaction would probably be somewhat analogous to that which produced $[Ph_2(O)PPh_2]$ $2(Ph_2NH)$ previously (Section 5.2.2.2 above) but in this case oxidation/hydrolysis could have been responsible for cleavage of the P-N bond. Possibly $Ph_2P(O)H$ may have been an intermediate (50).

$$Ph_2(BH_3)PNPh_2 \xrightarrow{O_2/H_2O} Ph_2P(O)\,H + Ph_2NH + B(OH)_3 \qquad (50)$$

Further reaction of the secondary phosphine-oxide with compound LVI could generate the biphosphine monoxide produce (51).

$$\begin{array}{l} Ph_2P\ NPh_2.BH_3 \ + \ Ph_2P(O)\ H \\ \qquad\qquad \downarrow \\ Ph_2(O)\ PPPh_2 \ + \ Ph_2NH \ + \ B(OH)_3 \end{array} \qquad (51)$$

Although hyrdolysis of phosphinous chlorides leading to dimerisation products (52) is well documented in the chemical literature[66,67]

$$Ph_2PCl \xrightarrow{H_2O} Ph_2\ P(O)H \xrightarrow[Et_3N]{Ph_2PCl} Ph_2(O)\ P\ P\ Ph_2 + [Et_3NH][Cl] \qquad (52)$$

no such reports of the hydrolysis of aminophosphines followed by dimerisation to phosphorus-phosphorus bonded species appear to have been reported.

Diphenyl(diphenylamino)phosphine-borane represents the first simple aminophosphine-borane adduct where both nitrogen and phosphorus have aromatic groups. Previously reported amino-phosphine-borane adducts were of the type $Me_2P(BH_3)\ NR_2$ where R = H, Me, Et. For example, in 1985, Schmidbaur *et al*[19] reported the synthesis of dimethyl(dimethylamino)-phosphine -borane in 98% yield (53).

$$Me_2P(Cl)BH_3 \ + \ 2NH_3 \longrightarrow Me_2(BH_3)P.NH_2 + [NH_4][Cl] \qquad (53)$$

5.2.2.3. *Reaction of $Ph_2P(Cl)BH_2CN$ XLVII with Dicyclohexylamine*

The reaction between chlorodiphenylphosphine-cyanoborane and dicyclohexylamine was attempted in order to synthesise the phosphorus-boron bonded aminophosphine-cyanoborane adduct (55).

$$Ph_2P(Cl)BH_2CN + (C_6H_{11})_2NH + Et_3N \xrightarrow[\text{reflux}]{\text{THF}} Ph_2(BH_2CN)PN(C_6H_{11})_2 + [Et_3NH][Cl] \qquad (55)$$

However, the only product isolated from this reaction was a hydrolytically stable crystalline solid (m.p. 222-223°C), LVII. Evidence from the infrared spectrum suggested that this product contained B-H, alkyl and aromatic C-H and possibly C ≡ N absorptions (Table 4) of the type expected for the anticipated product. However, the microanalysis was not consistent with the expected product (Table 4).

TABLE 4. *Microanalytical and Infrared Data for LVII*

Microanalysis %					*Found* (theory)	*Infrared* cm^{-1}	
C	H	N	B	P	ν C-H	ν B-H	ν C≡N
72.33	8.58	4.00	2.62	5.25	3060(sh)	2500(m)	2180(w)
					3040(w)	2440(m)	
(76.4)	(6.09)	(7.10)	(2.79)	(7.62)	2950(m)	2380(w)	
					1610(m)		
					1500(w)		

From these analysis figures there appears to be one nitrogen present per boron instead of the two expected in the aminophosphine-cyanoborane adduct. The analysis figures give a formula of $C_{24}H_{34}NBP$ compared to $C_{25}H_{34}N_2BP$ for the expected molecule. It is noteworthy here that these figures suggest the loss of the cyano group. The 60 MHz ^1H n.m.r. spectrum indicated the presence of both phenyl and methylene groups and these are confirmed in the 15 MHz $^{13}C\{^1H\}$ n.m.r. spectrum. Further evidence for the absence of B-CN was seen in the $^{13}C\{^1H\}$ spectrum which failed to show the expected ^1J C-B quartet in the region p.p.m. with coupling constant of the order of 100 Hz.[68] Since the structure of this compound could not be elucidated with the data above, X-ray diffraction quality crystals were sent to Professor G. Ferguson for analysis. No results were available at the time of writing.

5.2.2.4. *Reaction of $Ph_2PCl(BH_2CN)$ with Di-n-butylamine*

The reaction of XLVII with di-n-butylamine in refluxing THF proceeded in a similar manner to the previous reaction. Once more the stable, crystalline solid obtained LVII was not the anticipated product i.e. diphenyl (di-n-butylamine)phosphine-cyanoborane. As before the CHNB analysis showed a notably reduced nitrogen content. However, the infrared spectrum was again consistent with a cyanogroup (ν C≡N 2180 cm^{-1}) being present. The microanalytical and infrared data are listed in Table 5.

TABLE 5. *Microanalytical and Infrared Data for LVIII*

Microanalysis %			*Found (theory)*		*Infrared* cm^{-1}		
C	*H*	*N*	*B*	*P*	*ν CH*	*ν BH*	*ν CN*
78.44 (71.54)	*6.93* (8.52)	*4.78* (7.95)	*3.94* (3.12)	*6.86* (8.82)	*3040(w)* 2950(s) 2920(s)	*2410(m)*	*2180(w)*

The analysis figures correspond to the formulation $C_{18.5}H_{20}$ NP as opposed to C_{21} H_{28} N_2BP for the anticipated product. Proton (200.13 MHz), ^{11}B (64.2 MHz), ^{13}C(15 MHz) and ^{31}P (81.02 MHz) n.m.r. data were obtained for LVIII (Table 6).

TABLE 6. *Multinuclear n.m.r. Data for LVIII*

δ H *p.p.m.*	δ B *p.p.m.*	δ B $\{^1H\}$ *p.p.m.*	δ P *p.p.m.*
0.83(m)	-13.48(t)	-13.38(s)	18.41(s)
1.29(quin)			22.10(s)
1.62(m)			31.71(s)
2.77(m)			
7.35-7.77(m)			

The ^{1}H and ^{13}C data show the presence of phenyl and alkyl groups. The triplet signal in the ^{11}B spectrum is indicative of a BH_2X group and it collapsed to a singlet on proton decoupling. However, there was no ^{1}J (B-P) coupling indicating that any BH_2X group present was not attached to phosphorus. Also the chemical shift is more indicative of an N-BH_2CN group. The three ^{31}P singlet resonances (ratios 3 : 3 : 1) may suggest a mixture of products or an unsymmetrical single product. Suitable quality crystals of this compound have been sent to Professor G. Ferguson for X-ray analysis.

5.2.3 *Method (c): Reaction of Amine-boranes/cyanoboranes with chlorodiphenylphosphine*

To date no formal routes to nitrogen-boron bonded aminophosphine adducts have been reported. Competition between nitrogen and phosphorus sites in simple aminophosphines for a single BH_3 moeity generates the phos-

phorus-borane bonded adduct preferentially (56).

$$R_2PN\ R^1_2 + \tfrac{1}{2}B_2H_6 \longrightarrow R_2(BH_3)\ PNR_2{}^1 \qquad (56)$$

With this in mind a series of amine-boranes/cyanoboranes were reacted with chlorodiphenylphosphine according to equation (57).

$$\begin{array}{l} R_2NH(BH_2X) + Ph_2PCl + Et_3N \\ \qquad\qquad \Big\downarrow \text{ THF} \\ Ph_2PNR_2(BH_2X) + [Et_3NH]\,[Cl] \end{array} \qquad (57)$$

X = H, CN; R = H, alkyl.

However, none of the anticipated products were isolated and in each case (regardless of the choice of amine) the products obtained were aromatic consisting of carbon, hydrogen phosphorus, boron (and possibly oxygen). There was no nitrogen present in any of the isolated species. The micro-analysis results for the products and the theoretical values for the anticipated compounds are listed in Table 7.

TABLE 7. *Analysis Results for Reactions with Chlorodiphenylphosphines*

Reactant Adduct	% Found (theory)	C	H	N	B		Product Number
$(C_6H_{11})_2NH.BH_3$		71.73	5.35	0	5.15	5.31	LIX
		(75.99)	(9.23)	(3.69)	(2.90)	8.19	
$(C_6H_{11})_2NH.BH_2CN$		65.00	5.17	0	5.29	3.26	LX
		(74.25)	(8.41)	(6.93)	(2.72)	(7.69)	
$(CH_3)_3CNH_2\ BH_3$		67.53	5.09	0	5.90	6.47	LXI
		(70.85)	(8.48)	(5.16)	(4.06)	11.45	
$(C_4H_9)_2NH.BH_3$		66.49	5.11	0	5.04	12.75	LXII
		(73.33)	(9.48)	(4.28)	(3.36)	(9.55)	

All compounds were thermally stable , had a melting range of 1-2° and melted between 118 and 197°C. The compounds were also apparently pure. The absence of nitrogen and the presence of B-H absorptions in the infrared spectra (Table 8) suggests the presence of $P-BH_3$ or $P-BH_2X$ groups.

TABLE 8. *Infrared Absorptions*

Compound No.	$\frac{\delta\ C-H}{cm^{-1}}$	$\frac{\delta\ B-H}{cm^{-1}}$
LIX	2960 (sh)	2520 (m)
	2930 (s)	2410 (m)
	2850 (m)	
	2820 (m)	
LX	2940 (s)	2480 (s)
	2790 (sh)	2340 (w)
LXI	3050 (m)	2460 (s)
	3010 (sh)	
LXII	3040 (m)	2440 (m)
	2960 (w)	
	2850 (m)	

The aromaticity of the products was indicated by the ^{1}H (60 MHz) and ^{13}C (15 MHz) n.m.r. spectra. Unfortunately, it was not possible to assign these data in detail. Samples of compounds LXX to LXII were sent to the University of Edinburgh for ^{11}B and ^{31}P n.m.r. However, these results were not available at the time of writing. Suitable crystals of the products of the dicyclohexylamine-borane and -cyanoborane reactions have been sent to Professor G. Ferguson for X-ray crystallographic structural analysis.

5.2.4. *Conclusions*

The results outlined in this chapter illuminate the unexpected complexity of the systems studied. Of the compounds synthesised many are apparently novel but a lot of them were (structurally) unassignable with the available spectroscopic data.

Method (a) successfully generated the *bis* borane adduct, $Ph_2PN(C_6H_{11})_2 .2BH_3$ but when this method was used to prepare the monoborane adduct an unusual product, $[Ph_2(O)P\ Ph_2]\ 2(Ph_2NH)$, resulted. The structure of this compound was solved by X-ray crystallographic analysis. It is noteworthy too that the only aminophosphine isolated was $Ph_2PN\ (C_6H_{11})_2$. Attempted syntheses of other aminophosphines resulted in the generation of aminophosphine oxides ($Bu_2^n NH$, $Bu^t NH_2$), an unusual product (3, 5-dimethylpyrazole), or failed to react (Ph_2NH). The stability of $Ph_2PN(C_6H_{11})_2$ to oxidation and hydrolysis may be due to the steric inhibition of such reactions by the cyclohexyl groups.

Method (b) generated the novel monoborane adduct, $Ph_2(BH_3)\ PNPh_2$. Unfortunately, this compound was found to decompose in solution to $[Ph_2(O)P\ PPh_2]_2\ (Ph_2NH)_2$, so full structural analysis could not be completed. The reaction of chlorodiphenylphosphine-cyanoborane with dicyclohexylamine and di-n-butylamine generated unusual products which were thermally and hydrolytically stable. Analysis of these compounds showed that they were quite similar to the anticipated $Ph_2\ P(BH_2CN)NR_2$ type products.

Since method (c) generated only unusual non-nitrogen containing products it clearly did not provide a route to nitrogen-boron bonded BH_2X adducts of aminophosphines. The results presented here are indicative of the tendency of nitrogen-boron bonds to cleave even under room temperature reaction conditions.

5.3 EXPERIMENTAL

Borane-THF XLIV

Borane-THF was prepared in accordance with the literature by the dropwise addition of a solution of freshly distilled boron trifluoride etherate (8.2 ml) in 28 ml THF to a suspension of a sodium borohydride (2.0g, 0.052mol) in 71 ml THF. The mixture was maintained at $0^{o}C$ by an ice-bath and stirred for 1 hour at room temperature. When the solution had warmed to ambient temperature, the precipitated sodium tetrafluoroborate was removed by vacuum filtration under a blanket of nitrogen and washed with 25 ml THF. Borane-THF was isolated quantitatively as a colourless solution and used immediately. ν max (Thin Film) 2380 (w, B-H)cm^{-1}.

Cyanoborane-THF XLV

In a similar manner cyanoborane-THF was prepared by the dropwise addition of boron trifluoride etherate (7.49 ml) in 26 ml THF to a stirred solution of sodium cyanoborohydride (3.0g, 0.047 mol) in 64.2 ml THF and reacted as above. Cyanoborane-THF was isolated as a clear colourless liquid. ν max (Thin Film) 2400 (s, B-H); 2210 (m, C≡N)cm^{-1}.

Chlorodiphenylphosphine-borane XLVI

A solution of borane-THF (0.042 mol) in 60 ml THF was added dropwise over a 20 minute period to a solution of chlorodiphenylphosphine (7.52 ml, 0.042 mol) in 60 ml THF at $-20^{o}C$. The solution was warmed gradually to room temperature and stirred for 1 hr. Evaporation of the THF under reduced pressure afforded chlorodiphenylphosphine-borane as a colourless oil which was used immediately. ν max (Thin Film) 2980 (s, ArCH); 2880 (m, ArCH); 2380 (br, s, B-H), 1120 (s, P-Ph)cm^{-1}. δH 7.6 (m, Ar-H), 7.85 (m, Ar-H) ppm.

Chlorodiphenylphosphine-cyanoborane XLVII

A solution of cyanoborane-THF (0.047 mol) in 60 ml THF was added to a solution of chlorodiphenylphosphine (8.11 ml, 0.047 mol) in 70 ml THF and reacted as above. Upon evaporation of the THF, chlorodiphenylphosphine-cyano-

borane was obtained as a colourless oil which was used immediately. ν max (Thin Film) 2970 (s, ArCH); 2880 (s, ArCH); 2420 (s, BH); 2240 (m, C≡N); 1130 (s, P-Ph) cm^{-1}. δH 7.6 (br, m, Ar C-H) ppm.

Aminophosphines/Aminophosphineoxides General Procedure (a)

A solution of chlorodiphenylphosphine in THF was added to a stirred solution of two equivalents of primary or secondary amine resulting in the immediate precipitation of amine-hydrochloride. After reflux for 16 hrs the amine-hydrochloride was separated from the cooled solution by vacuum filtration through a bed of celite and thoroughly washed with THF. The combined filtrates were evaporated to dryness *in vacuo*. Recrystallisation of the crude solid from an appropriate solvent system afforded high yields of aminophosphine or aminophosphineoxide.

General Procedure (b)

A solution of chlorodiphenylphosphine in THF was added to an equivalent amount of both amine (primary or secondary) and triethylamine in THF. After 16 hrs reflux the precipitated triethylamine-hydrochloride was separated from the cooled solution by vacuum filtration through a bed of celite and washed thoroughly with THF. Evaporation of the combined filtrates followed by re-crystallisation from an appropriate solvent system afforded high yields of aminophosphine or aminophosphineoxide. Usually procedure (b) gave higher yields than (a).

Diphenyl(dicyclohexylamino)phosphine XLVIII Procedure (a)

A solution of chlorodiphenylphosphine (3.25 ml, 0.018 mol) was added dropwise to a stirred solution of dicyclohexylamine (7.15 ml, 0.036 mol) in 80 ml THF. The precipitated dicyclohexylamine-hydrochloride was removed by vacuum filtration. Recrystallisation of the crude product from a mixture of monoglyme : diethylether (2 : 1) furnished diphenyl(dicyclohexylamino) phosphine (8.2g, 79.9%) as a white crystalline solid m.p. 177-178°C. Analysis:

calcd. for $C_{24}H_{32}NP$: C, 78.88; H, 8.76; N, 3.83%. Found: C, 78.68; H, 8.68; N, 3.96% νmax (KBr) 3060 (sh); 3050 (m); 3010 (w); 2990 (w); 2840 (s); 1580 (m); 1475 (m); 1460 (w); 1450 (m); 1440 (m); 1435 (s); 1380 (m); 1370 (m); 1345 (w); 1330 (w); 1305 (w); 1295 (w); 1270 (w); 1250 (m); 1240 (sh); 1200 (m); 1130 (w); 1160 (m); 1155 (s); 1100 (s); 1085 (w); 1065(sh); 1055 (s); 1025 (m); 990 (w); 970 (s); 920 (w); 890 (s); 860 (m); 810 (m); 790 (w); 750 (s); 740 (s); 720 (sh); 695 (s); 660 (s) cm^{-1}. δH (270 MHz) 1.1 (m, 16H, -CH_2); 2.86 (m, 4H, -CH -N); 7.26 (d, 6H, Ar-H); 7.48 (t, 4H, Ar-CH -P) ppm. δ C (68.75 MHz) 24.32 (t, 6C, -CH_2); 28.78 (t, 4C, -CH_2); 52.43 (d, 2C, CH -N); 127.60 (d, 6C, Ar-CH); 129.39 (d, 4C, -CH); 131.34 (s, 2C, AR -C-P) ppm. Mass Spec M^+ = 3 65 ($C_{24}H_{32}NP$ = 365).

Procedure (b)

A solution of chlorodiphenylphosphine (5.84 ml, 0.034 mol) in 50 ml THF was added dropwise to a stirred solution of dicyclohexylamine (8.0 ml, 0.034 mol) and triethylamine (4.76 ml, 0.034 mol) in 80 ml THF. Recrystallisation from monoglyme: diethyl ether (2 : 1) afforded diphenyl (dicyclohexylamino) phosphine (11.41g, 91.5%) as a crystalline solid.

Diphenyl(t-butylamino)phosphineoxide IL Procedure (b)

A solution of chlorodiphenylphosphine (7.00 ml, 0.041 mol) in 50 ml THF was added to a mixture of t-butylamine (4.28 ml, 0.041 mol) and triethylamine (5.70 ml, 0.041 mol) in 70 ml THF. Recrystallisation from chloroform: THF (1 : 1) furnished diphenyl(t-butylamino)phosphineoxide (10.47g, 93.6%) as colourless crystals m.p. 126-128°. Analysis: calcd. for $C_{10}H_{20}NOP$: C, 70.32; H, 7.39; N, 5.12%. Found: C, 70.37; H, 7.32, N, 4.99%. ν max (KBr) 3360 (m, N-H); 3080 (m, ArCH); 3050 (s, ArCH); 2960 (s); 2920 (sh); 2900 (sh); 2860 (s); all alkyl CH) 1950 (m); 1880 (m); 1810 (m); 1725 (m); 1660 (w); 1580 (s); 1570 (sh); 1480 (s); 1460 (sh); 1430 (s); 1360 (s); 1300 (s); 1200 (vs, P=O); 1190 (s); 1065 (m); 1025 (m); 980 (s); 910 (m); 840 (s); 730 (s); 700 (s) cm^{-1}.

δH 1.37 (s, 9H, ($\underline{CH}_3$)$_3$C); 7.25 (d, 6H, Ar-H); 7.50 (m, 4H, Ar-H) ppm.
δC 7.63 (q, 3C, ($\underline{CH}_3$)$_3$C); 42.19 (s, 1C, (CH_3)$_3$S); 127.58 (d, 6C, Ar$\underline{C}$H); 129.39 (d, 4C, Ar$\underline{C}$H); 131.34 (s, 2C, Ar-$\underline{C}$-P) ppm.

Diphenyl (di-n-butylamino)phosphineoxide L Procedure (b)

A solution of chlorodiphenylphosphine (8.0 ml, 0.047 mol) in 60 ml THF was added dropwise to a stirred solution of di-n-butylamine (7.9 ml, 0.047 mol) and triethylamine (6.56 ml, 0.047 mol) in 60 ml THF. Recrystallisation of the crude product from a chloroform : THF (1 : 1) mixture furnished diphenyl(di-n-butylamino)phosphineoxide (10.58g, 69.3%) as colourless crystals m.p. 133-136°C. Analysis: calcd. for $C_{20}H_{28}NOP$: C, 72.94; H, 8.51; N, 4.25%. Found: C, 73.05; H, 8.34; N, 4.44% νmax (KBr) 3060 (s, ArCH);2940 (s); 2860 (m); (both alkyl CH); 1580 (m, ArCH); 1475 (sh); 1460 (m); 1430 (m); 1360 (m); 1300 (w); 1185 (s, P=O); 1120 (m); 1090(m); 1060 (w); 1030 (m); 990 (w); 920 (w); 740 (s); 720 (w); 695 (s) cm^{-1}. δH 0.7 (t, 6H, CH_3); 0.92-1.46 (m, 8H, -CH_2-$\underline{CH}_2$-$\underline{CH}_2$-CH_3) 2.85 (t, 4H, $\underline{CH}_2$ -N); 7.27 (d, 6H, Ar-$\underline{H}$); 7.46 (m, 4H, Ar-$\underline{H}$) ppm.

Procedure (a)

A solution of chlorodiphenylphosphine (3.25 ml, 0.018 mol) in 35 ml THF was added dropwise to a solution of di-n-butylamine (6.16 ml, 0.036 mol) in 65 ml THF. Evaporation of the combined filtrates yielded a viscous yellow-oil from which a white solid precipitated on washing with diethylether. The crude solid was isolated by filtration, washed thoroughly with diethylether and recrystallised from a chloroform: THF (1 : 1) mixture to afford diphenyl (di-n-butylamino)phosphineoxide (3.30g, 55.8%) as colourless crystals.

3, 5-Dimethylpyrazole Reaction with Chlorodiphenylphosphine LI Procedure (b)

A solution of chlorodiphenylphosphine (8.88 ml, 0.052 mol) in 60 ml THF was added to a solution of 3, 5-dimethylpyrazole (5.0g, 0.052 mol) and triethylamine (7.23 ml, 0.052 mol) in 60 ml THF. Recrystallisation from a chloroform

: diethylether: THF (1 : 1 :1) mixture furnished 6.40g of colourless crystals m.p. 160-162°C. Analysis: Found: C, 65.10, H, 5.05%. ν max (KBr) 3050 (m, ArCH); 1840 (m); 1570 (m, ArCH); 1550 (w); 1480 (s, ArCH); 1430 (s); 1340 (w); 1310(m); 1230 (w); 1180 (s, P=O); 1160 (sh); 1110 (m); 1090 (m); 1070 (m); 1040 (m); 1025 (m); 1000 (m); 920 (m); 740 (s); 715 (m); 690 (s) cm^{-1}. δH 7.45 (m, Ar-H); 7.90 (m, Ar-H) ppm. δ C 129.23 (s); 130.08 (s); 131.90 (s); 132.62 (s); 133.16 (s); 139.11 (s); (Ar Ar-C) ppm. Crystals suitable for X-ray analysis were grown and sent to Professor G. Ferguson (University of Guelph) in Canada.

Attempted Synthesis of Diphenyl(diphenylamino)phosphine LII Procedure (a)

A solution of chlorodiphenylphosphine (3.25 ml, 0.018 mol) in 35 ml THF was added to a stirred solution of diphenylamine (6.13g, 0.036 mol) in 65 ml THF. The solution remained colourless on completion of the addition with no evidence of precipitation of diphenylamine-hydrochloride. After 96 hrs reflux no precipitate was present in the cooled solution. Evaporation of the THF solvent afforded a white solid. This was extracted with chloroform. Evaporation of the chloroform, followed by recrystallisation from diethylether afforded diphenylamine (4.48g, 73% recovery) as colourless plates. Chromatographic (t.l.c. eluent acetone: pet. ether 2:1) and spectral analyses were identical with an authentic sample of diphenylamine.

(Procedure (b)

A solution of chlorodiphenylphosphine (8.06 ml, 0.047 mol) in 60 ml THF was added dropwise to a stirred solution of diphenylamine (8.0g, 0.047 mol) and triethylamine (6.57 ml, 0.047 mol) in 80ml THF. Recrystallisation from diethylether afforded diphenylamine (5.45g,76.82%). No other product was isolated.

Diphenyl(dicyclohexylamino)phosphine-bis *borane LIII*

A solution of freshly prepared borane-THF (0.022 mol) in 100 ml THF was added dropwise to a stirred suspension of diphenyl(dicyclohexylamino)-phosphine (4.00g, 0.011 mol) in 40 ml THF and the resulting reaction mixture refluxed for 14 hrs. Trace amounts of unreacted solid were isolated from the THF solution by suction filtration and the solvent was evaporated. The resulting white, semisolid was washed thoroughly with diethylether to furnish diphenyl (dicyclohexylamino)phosphine-*bis* borane as an analytically pure, white crystalline solid m.p. 217-213°C. Analysis: calcd. for $C_{24}H_{38}NB_2P$: C, 73.28; H, 7.67; N, 3.56; B, 5.59%. Found: C, 72.99; H, 9.74; N; 3.72; B, 5.60%. νmax (KBr) 3060 (m); 3040 (m) (both Ar$\underline{C}$H); 2920 (s); 2840 (s); 2800 (sh); (all cyclohexyl CH); 2405 (w); 2380 (s); 2250 (m); 2220 (sh); (all B-H); 1470 (m); 1955 (m); 1905 (w); 1880 (w); 1815 (w); 1765 (w); 1680 (w); 1590 (m, ArCH); 1570 (w); 1480 (s, ArCH); 1460 (sh); 1450 (sh); 1430 (s); 1395 (w); 1380 (m); 1345 (m); 1330 (m); 1310 (w); 1260 (m); 1250 (s); 1220 (w); 1170 (w); 1155 (m); 1120 (m); 1100 (s); 1060 (w); 1045 (m); 1010 (w); 995 (w); 980 (w); 920 (w); 890 (s); 880 (s); 850 (s); 820 (m); 795 (m); 770 (sh); 760 (sh); 750 (s); 735 (sh); 700 (s); 625 cm^{-1}. δ H (270 MHz) 0.88 (s, 4H, $\underline{CH}_2$); 1.34 (d, 8H, $\underline{CH}_2$); 1.54 (m, 8H, $\underline{CH}_2$); 2.85 (d, 2H, $\underline{CH}$ -N); 7.24 (d, 2H, Ar-$\underline{H}$); 7.51-7.58 (m, 8H, Ar-$\underline{H}$) ppm. δ C (67.80 MHz) 25.14 (s, 2C, $\underline{CH}_2$); 26.42 (s, 4C, $\underline{CH}_2$); 33.51 (s, 4C, $\underline{CH}_2$); 58.70 (d, 2C, $\underline{CH}$-N); 128.11 (t, 2C, Ar$\underline{C}$H); 130.70 (t, 4C, Ar$\underline{C}$H); 131.22 (t, 4C, Ar$\underline{C}$H); 133.29 (s, 2C, Ar-$\underline{C}$-P) ppm A sample of LIII was recrystallised from monoglyme. The colourless crystals obtained were not LIII. Analysis: Found: C, 71.96; H, 8.20, N, 3.45; B, 3.63; P, 5.61% Crystals were sent to Professor Ferguson in Canada for X-ray analysis. Unfortunately, it was discovered that the crystals were twinned and thus structural analysis could not be performed.

$[Ph_2(O)P\ P\ Ph_2]\ (Ph_2NH)_2$ *LIV*

A solution of freshly prepared borane-THF (0.011 mol) in 60 ml THF was added dropwise to a stirred suspension of diphenyl(dicyclohexylamino)phosphine (4.0g, 0.011 mol) in 40 ml THF and the resulting reaction mixture refluxed for 16 hrs. Trace amounts of unreacted solid were removed from the cooled solution by vacuum filtration and the THF evaporated. Recrystallisation from a mixture of monoglyme: diethylether (2 : 1) afforded 3.02g, of colourless crystals. Several attempts using a variety of reaction conditions and purification procedures generated the same product. The structure and identity of LIV was identified by X-ray crystallography. m.p. 98-99°C. Analysis: calcd. for $C_{42}H_{42}N_2OP_2$: C, 79.55, H, 5.80; N, 3.86%. Found: C, 79.40, H, 5.88; N, 3.90%. νmax (KBr) 3180 (vs); 3120 (m); 2935 (vs); 2860 (vs) (all ArCH); 1600 (s); 1455 (s); 1380 (m); 1360 (w); 1350 (w); 1335 (w); 1310 (m); 1290 (w); 1270 (w); 1250 (w); 1210 (s, P=O); 1050 (s); 915 (w); 850 (w); 840 (sh); 765 (w); 750 (w); 725 (m); 695 (m); 650 (m) cm^{-1}. δH (270 MHz) 6.97 (t); 7.21 (t); 7.32 (d); 7.42 (t); 7.55 (m); 7.65 (t); 7.88 (t) ppm. (All ArC<u>H</u>). δC (67.80 MHz); 118.43 (s); 121.26 (s); 124.77 (q); 130.18 (s); 131.07 (s); 131.22 (t); 133.19 (s); 132.26 (q); 144.99 (s) ppm. (All Ar-<u>C</u>). δP (109.25 MHz); -21.58 (d, P-P=O), + 39.22 (d, P-P=O) ppm. Mass. Spec. M/Z cut off 169 ($^{12}C_{12}{}^{1}H_{11}{}^{14}N$ = 169).

Crystallography

A colourless small plate crystal of $C_{48}H_{42}N_2OP_2$ having approximate dimensions of 0.18 x 0.30 x 0.45 mm was mounted on a glass fiber with its long axis roughly parallel to the phi axis of the goniometer. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $10 < \theta < 14°$, measured by the computer controlled diagonal slit method of centering. The monoclinic cell parameters and calculated volume are: a = 10.587(2), b = 18.485 (6), c = 10.026 (2) A, β = 90.59 (3)°, V = 1962.0Å^3. For Z = 2

and F.W. = 724.83 the calculated density is 1.23 g/cm^3. From the systematic absences of: h0l h+l=2n+1 and 0k0 k=2n+1 and from subsequent least-squares refinement, the space group was determined to be P21/n (No. 14).

A total of 4824 reflections were collected, of which 4277 were unique and not systematically absent. As a check on crystal and electronic stability 3 representative reflections were measured every 240 min. The slope of the least-squares line through a plot of intensity versus time was -25 ± 2 counts/hour which corresponds to a total loss in intensity of 14.0%. A linear decay correction was applied. The correction factors on I ranged from 1.000 to 1.079 with an average value of 1.038. Lorentz and polarisation corrections were applied to the data. The linear absorption coefficient is 1.4 cm^{-1} for Mo-Kδ radiation. No absorption correction was made.

The structure was solved using the Patterson heavy-atom method which revealed the position of one P atom. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. Only the 1466 reflections having intensities greater than 9.0 times their standard deviation were used in the refinements. The final cycle of refinement included 245 variable parameters and converged (largest parameter shift was 0.00 times is esd) with unweighted and weighted agreement factors of $R = 4.2\%$ and $R_n = 7.1\%$. The standard deviation of an observation of unit weight was 1.76. The highest peak in the final difference Fourier had a height of 0.17 e/Å^3 with an estimated error based on W of 0.04.

TABLE 9 *Interatomic Distances and Angles: (a) Interatomic Distances (Å)*

P	P*	2. 228(2)	C24	C25	1.374(7)
P	O	1.345 (6)	C25	C26	1.358(6)
P	C11	1.817 (4)	C31	C32	1.406(6)
P	C21	1.812 (4)	C31	C36	1.372(6)
N	C31	1.386 (5)	C32	C33	1.367(7)
N	C41	1.396 (5)	C33	C34	1.375(7)
C11	C12	1.385 (6)	C34	C35	1.364(8)
C11	C16	1.354 (6)	C35	C36	1.355(7)
C12	C13	1.383 (7)	C41	C42	1.383(6)
C13	C14	1.340 (8)	C41	C46	1.401(6)
C14	C15	1.367 (7)	C42	C43	1.362(6)
C15	C16	1.361 (7)	C43	C44	1.378(7)
C21	C22	1.396 (6)	C44	C45	1.365(7)
C21	C26	1.368(6)	C45	C46	1.377(7)
C22	C23	1.363 (6)	N...	O	2.690(6)
C23	C24	1.367 (7)	H(N)	O	1.79

(b) Bond Angles (°)

P*	P	O	120.5(3)	C23	C24	C25	119.3(4)
P*	P	C11	102.2(1)	C24	C25	C26	120.5(5)
P*	P	C21	102.0(1)	C21	C26	C25	121.2(4)
O	P	C11	116.0(3)	N	C31	C32	124.0(4)
O	P	C21	109.3(3)	N	C31	C36	118.3(4)
C11	P	C21	105.0(2)	C32	C31	C36	117.7(4)
C31	N	C41	128.1(3)	C31	C32	C33	119.1(4)
P	C11	C12	118.7(3)	C32	C33	C34	121.3(5)
P	C11	C16	124.1(3)	C33	C34	C35	119.8(5)
C12	C11	C16	116.9(4)	C34	C35	C36	119.1(5)
C11	C12	C13	120.4(4)	C31	C36	C35	122.9(4)
C12	C13	C14	121.1(5)	N	C41	C42	119.8(4)
C13	C14	C15	118.8(4)	N	C41	C46	122.2(4)
C14	C15	C16	120.3(4)	C42	C41	C46	117.9(4)
C11	C16	C15	122.5(4)	C41	C42	C43	121.0(4)
P	C21	C22	123.3(3)	C42	C43	C44	121.0(5)
P	C21	C26	118.7(3)	C43	C44	C45	118.7(4)
C22	C21	C26	118.0(4)	C44	C45	C46	121.0(4)
C21	C22	C23	120.7(4)	C41	C46	C45	120.3(4)
C22	C23	C24	120.3(4)	N---	H(N)..	O	157

The * refers to equivalent position 1-x, -y, 1-z.

TABLE 10 Deposition Data: Torsional Angles

O	P	C11	C12	-65.4	P	C21	C22	C23	-177.2
O	P	C11	C16	109.2	C26	C21	C22	C23	-0.5
C21	P	C11	C12	174.0	P	C21	C26	C25	177.9
C21	P	C11	C16	-11.5	C22	C21	C26	C25	1.0
P*	P	C11	C12	67.8	C21	C22	C23	C24	-0.9
P*	P	C11	C16	-117.7	C22	C23	C24	C25	1.7
O	P	C21	C22	176.2	C23	C24	C25	C26	-1.1
O	P	C21	C26	-0.5	C24	C25	C26	C21	-0.3
C11	P	C21	C22	-58.7	N	C31	C32	C33	-178.3
C11	P	C21	C26	124.6	C36	C31	C32	C33	-0.7
P*	P	C21	C22	47.6	N	C31	C36	C35	178.0
P*	P	C21	C26	-129.1	C32	C31	C36	C35	0.2
C41	N	C31	C32	-9.5	C31	C32	C33	C34	-0.7
C41	N	C31	C36	172.9	C32	C33	C34	C35	2.6
C31	N	C41	C42	140.5	C33	C34	C35	C36	-3.1
C31	N	C41	C46	-42.3	C34	C35	C36	C31	1.7
P	C11	C12	C13	176.0	N	C41	C42	C43	177.8
C16	C11	C12	C13	1.0	C46	C41	C42	C43	0.5
P	C11	C16	C15	-175.0	N	C41	C46	C45	-178.4
C12	C11	C16	C15	-0.4	C42	C41	C46	C45	-1.2
C11	C12	C13	C14	-1.1	C41	C42	C43	C44	0.8
C12	C13	C14	C15	0.4	C42	C43	C44	C45	-1.4
C13	C14	C15	C16	0.3	C43	C44	C45	C46	0.8
C14	C15	C16	C11	-0.3	C44	C45	C46	C41	0.5

Reaction of XLVIII with BH_2CN-Monoglyme Complex LV

Sodium cyanoborohydride (0.62g, 0.009 mol) was added to a stirred solution of diphenyl(di cyclohexylamino)phosphine (3.0g, 0.008 mol) in 40 ml monoglyme and the resulting solution stirred at room temperature for 10 minutes. A solution of iodine (1.25g, 0.005 mol) in 20 ml monoglyme was added dropwise from a pressure equalised dropping funnel and the reaction mixture refluxed for 16 hrs. The precipitated sodium iodide was removed from the cooled solution by vacuum filtration through a bed of celite and washed with 20 ml monoglyme. The combined filtrates were evaporated and the resulting semisolid washed with diethylether to yield a white crystalline solid. The crude solid was isolated by vacuum filtration, dried *in vacuo* and recrystallised from an ethanol: diethylether (1 : 1) mixture. Colourless crystals (1.89g) of an unidentified product were isolated m.p. 202-203°C. Analysis: diphenyl(di cyclohexylamino)phosphine-cyanoborane. $C_{25}H_{24}N_2BP$ requires: C, 76.4, H, 6.09; N, 7.10; B, 2.79; P, 7.62%. Found: C, 65.46; H, 5.02; N, 0.0; B, 2.71; P, 6.86%. νmax (KBr) 3060 (sh); 3040 (w); 3000 (w); 2520 (m); 2440 (m); 2380 (w); 1610 (m); 1500 (m); 1470 (m); 1450 (s); 1430 (s); 1170 (s); 1135 (s); 1065 (s); 1040 (s); 1020 (s); 995 (w); 760 (s); 730 (s); 695 (s); cm^{-1}. δH 7.45 (m); 7.93 (m); (both Ar-H) p.p.m. δ C $\{^1H\}$ 128.4 (s); 128.83 (s); 129.62 (s); 131.88 (s); 136.19 (s) ppm.

Reactions of XLVI and XLVII with Amines

Diphenyl (diphenylamino)phosphine-borane LVI

A freshly prepared solution of chlorodiphenylphosphine-borane (0.069 mol) in 80 ml THF was added dropwise from a pressure equalised dropping funnel to a stirred solution of diphenylamine (11.72g, 0.069 mol) and triethylamine (9.4 ml, 0.069 mol) in 120 ml THF. The reaction mixture was refluxed for 48 hrs with constant t.l.c. analysis (acetone: pet. ether (3 : 2) eluent). After 48 hrs approx., 70% of the diphenylamine had reacted, further reflux for a second 48 hr period did not improve this percentage. When the

solution had cooled, the precipitated triethylamine-hydrochloride [δ H 1.54 (t, 9H, CH_3); 3.30 (q, 6H, CH_2) ppm] was isolated by vacuum filtration through a bed of celite and washed thoroughly with THF. The filtrates were combined and the THF evaporated to yield a semisolid. Washing with diethylether precipitated a white, analytically pure, crystalline solid, m.p. 95-96°C. Analysis: calcd. for $C_{24}H_{23}NBP$: C, 78.47, H, 6.26; N, 3.82; B, 3.60%. Found: C, 78.49; H, 5.95; N, 3.90; B, 8.78%. ν max (KBr) 3040 (m); 3010 (sh); 2940 (sh); 2850 (s); (all CH); 2380 (m); 2340 (m); (both B-H); 1580 (vs ,ArCH); 1560 (sh); 1490 (s, ArCH); 1455 (w); 1435 (m); 1420 (m); 1370 (w); 1310 (s); 1260 (m); 1110 (br, s); 1025 (w); 940 (w); 920 (w); 875 (m); 750 (s); 720 (sh); 690 (s); 645 (w)cm^{-1}. Mass. spec. M/Z 367 ($C_{24}H_{23}NBP$ = 367). A sample was recrystallised from a diethylether: ethanol (2 : 1) mixture for both X-ray analysis and high field nmr. The X-ray analysis showed that the compound had oxidised to $[(C_6H_5)_2P]_2O$ $[(C_6H_5)_2NH]_2$ m.p. 98-99°C.

Reaction of XLVII with Dicyclohexylamine LVII

A solution of chlorodiphenylphosphine-cyanoborane XLVII, (0.063 mol) in 60 ml THF was added dropwise to a stirred solution of dicyclohexylamine (12.6 ml, 0.063 mol) and triethylamine (8.99 ml, 0.063 mol) in 80 ml THF. A white solid immediately precipitated from the reaction solution. The mixture was refluxed for 16 hrs on completion of the addition. The precipitated solid was isolated from the cooled solution by vacuum filtration through a bed of celite and washed thoroughly with THF. The combined filtrates were evaporated yielding a sticky, white semisolid from which a white, crystalline solid was obtained on washing with diethylether. Recrystallisation from a mixture of monoglyme: diethylether (2 : 1) afforded 6.14g of colourless crystals mp. 222-223°C. Analysis: (diphenyl(di-cyclohexylamino)phosphine-cyanoborane $C_{25}H_{24}NBP$ requires: C, 76.4; H, 6.09; N, 7.10; B, 2.79; P, 7.62%. Found: C, 72.33; H, 8.58; N, 4.00; B, 2.62;

P, 5.25%. ν max (KBr) 3060 (sh); 3040 (w); 2930 (s); 2850 (m); (all ArCH); 2440 (m); 2380 (w); (both B-H); 2180 (w, C≡N; 1610 (m); 1500 (m, ArCH); 1450 (s); 1430 (s); 1310 (w); 1190 (vs, P = 0); 1120 (s); 1060 (w); 1035 (s); 1020 (m); 915 (w); 740(s); 720 (s); 690 (s) cm^{-1}. δ H 1.06-2.0 (br, m, unresolved $C\underline{H}_2$); 7.43 (m); 7.32 (m); (both Ar$C\underline{H}$) ppm. δ C 24.82 (t, $C\underline{H}_2$); 28.78 (t, $C\underline{H}_2$); 52.43 (d, $C\underline{H}$); 127.22 (s); 127.91 (s); 129.30 (s); 129.49 (s); 131.05 (s); 131.64 (s); 136.45 (s); 145.08 (s) ppm (all Ar-S). Crystals suitable for X-ray crystallographic analysis were grown from the solvent system and sent to Professor Ferguson in Canada.

Reaction of XLVII with Di-n-butylamine LVIII

A solution of chlorodiphenylphosphine-cyanoborane (0.063 mol) in 60 ml THF was added dropwise to a stirring solution of triethylamine (8.99 ml, 0.063 mol) and di-n-butylamine (10.77 ml, 0.063 mol) in 120 ml THF. The resulting solution was refluxed for 24 hrs. When the solution had cooled the precipitated solid was removed by vacuum filtration through a bed of celite and thoroughly washed with THF. Evaporation of the combined filtrates afforded a sticky semisolid. Repeated washing with THF furnished a white, crystalline solid. Recrystallisation of the crude solid from a mixture of monoglyme: diethylether (1:1) yielded 7.2g of an unidentified product mp. 188-190°C. Analysis: (diphenyl(di-n-butylamino)phosphine-cyanoborane; $C_{21}H_{30}N_2BP$ requires: C, 71.59; H, 8.52; N, 4.95; B, 3.12; P, 8.82%. Found: C, 78.44; H, 6.93; N, 4.78; B, 3.94, P, 6.26%. ν max (KBr) 3040 (w); 2950 (s); 2920 (s); 2890 (s); (all CH); 2410 (m, BH); 2180 (w, C ≡ N); 1670 (s); 1590 (ArCH); 1575 (sh); 1435 (s); 1370 (m); 1250 (w); 1200 (m, P = O); 1170 (w); 1110 (m); 1030 (w); 995 (w); 830 (m); 740 (s); 695 (s); cm^{-1}. δ H (CD_3CN, 200.13 Hz) 0.83 (m, $C\underline{H}_3$); 1.29 (quin, $C\underline{H}_2$); 1.62 (m, $C\underline{H}_2$); 2.77 (m, $C\underline{H}_2$); 7.35-7.88 (m, Ar$C\underline{H}$) ppm. δ B (CD_3CN, 6.42 MHz) -13.43 (t, $B\underline{H}_2CN$) ppm δ B $\{^1H\}$ -13.48 (s, $B\underline{H}_2CN$) ppm. δ P (CD_3CN, 81.02 MHz) 18.41 (s); 22.10 (s); 31.71 (s) ppm.

Reactions of Amine-borane/cyanoboranes with Chlorodiphenylphosphine: General Procedure

A solution of chlorodiphenylphosphine in THF was added dropwise from a pressure equalised dropping funnel to a stirring solution of an equal quantity of amine-borane/cyanoborane in THF. The resulting mixture was stirred at ambient temperature for 10 minutes when an equal quantity of triethylamine solution in THF was added dropwise. The reaction mixture was subsequently stirred at room temperature or alternatively refluxed, both for 16 hrs. The precipitated solid was removed by vacuum filtration and thoroughly washed with THF. The combined filtrates were evaporated to dryness. Recrystallisation from various solvent mixtures consistently furnished large yields of crystalline material. In each reaction attempted, whether amine-borane or cyanoboranes were used and irrespective of the reaction conditions, none of the products contained nitrogen. All were found to be aromatic compounds containing carbon, hydrogen, boron and phosphorus. The products had high melting points and generally similar microanalyses.

The following amine-boranes/cyanoboranes were thus reacted.

Dicyclohexylamine-borane LIX

Dicyclohexylamine-borane (5.30g, 0.027 mol) was added to 60ml THF and stirred. A solution of chlorodiphenylphosphine (4.85 ml, 0.027 mol) in 40 ml was added followed by a solution of triethylamine (3.77 ml, 0.027 mol) in 30 ml THF and the resulting mixture was stirred for 16 hrs in accordance with the general procedure. Recrystallisation of the crude solid from a mixture of monoglyme: ethanol: chloroform (1:1:1) furnished 4.18g, of colourless crystals. mp. 118-120°C. Analysis: Found: C, 71.73; H, 5.35; B; 5.15; P, 5.3%. νmax (KBr) 2960 (sh); 2930 (s); 2850 (m); 2820 (m); 2740 (w); 2720 (w); 2640 (m); 2620 (w); 2520 (m); 2410 (m); 1580 (s); 1440 (s); 1380 (w); 1320 (w); 1270 (w); 1240 (w); 1160 (s);

1130 (w); 1110 (w); 1060 (m); 1000 (w); 990 (s); 840 (m); 740 (s); 690 (s) cm^{-1}. δ_H 7.47 (br, m); 8.05 (br, m) ppm (Both Ar-H). δ_C 127.93 (s); 128.84 (s); 130.92 (s); 131.57 (s); 131.90 (s); 137.75 (s) ppm. (All Ar-C).

Dicyclohexylamine-borane (3.35g, 0.027 mol) was added to 35 ml THF and stirred at room temperature. A solution of chlorodiphenylphosphine (2.9ml, 0.017 mol) in 25 ml THF was added dropwise followed by a solution of triethylamine (2.39 ml, 0.017 mol) in 20 ml THF. The resulting mixture was refluxed for 16 hrs in accordance with the general procedure. Recrystallisation of the crude solid from a monoglyme: chloroform mixture (3:1) afforded 1.8g of colourless crystals. All analyses were identical to above. Crystals suitable for X-ray analysis were grown and sent to Professor G. Ferguson.

Dicyclohexylamine-cyanoborane LX

Dicyclohexylamine-cyanoborane (3.0g, 0.013 mol) was added to 30 ml THF and stirred at room temperature. A solution of chlorodiphenylphosphine (2.32 ml,0.013 mol) in 20 ml THF was added followed by a solution of triethylamine (1.89 ml, 0.013 mol) in 20 ml THF. The reaction mixture was refluxed for 16 hrs in accordance with the general procedure. Recrystallisation of the crude solid in a mixture of monoglyme: diethylether (2:1) yielded 2.44g, of colourless needles m.p. 189-191°C. Analysis: found: C, 65.00; H, 5.17, B, 4.29; P, 7.69%. ν max (KBr) 2940 (s); 2790 (sh); 2760 (m); 2680 (m); 2480 (s); 2340 (w); 1460 (s); 1460 (s); 1390 (s); 1320 (w); 1180 (w); 1180 (sh); 1165 (s); 1125 (w); 1060 (w); 1035 (s); 850 (s); 800 (s); 700 (s); cm^{-1}. δ_H 7.45 (br, m); 7.95 (br, m); ppm (Both Ar-C-H).

t-Butylamine-borane LXI

t-Butylamine-borane (2.0g, 0.023 mol) was added to 20 ml THF and stirred at room temperature. A solution of chlorodiphenylphosphine (3.92 ml. 0.023 mol) in 30 ml THF was added dropwise followed by a solution of triethyl-

amine (3.19 ml, 0.023 mol) in 25 ml THF. The reaction mixture was refluxed for 16 hrs in accordance with the general procedure. Recrystallisation of the crude solid from a mixture of monoglyme: ethanol (2:1) furnished 2.40g, of a white solid m.p. 197-198 °C. Analysis: Found: C, 67.53; H, 5.09; B, 5.9; P, 6.47%. νmax (KBr) 3050 (m); 3010 (sh); 2460 (s); 1585 (m); 1570 (sh); 1480 (s); 1430 (s); 1330 (w); 1310 (w); 1235 (m); 1200 (sh); 1175 (vs); 1110 (s); 1085 (w); 1065 (m); 1025 (m); 995 (m); 920 (w); 855 (w); 750 (s); 735 (s); 715 (s); 690 (s) cm^{-1}. δH (CD_3OD); 7.65 (m); 8.05 (m) ppm (Ar-H). δC (CD_3OD); 129.04 (s); 129.88 (s); 131.90 (s); 132.61 (s); 132.81 (s); 134.43 (s); 140.28 (s) ppm (Ar-C). Crystals suitable for X-ray analysis were subsequently grown and sent to Professor Ferguson.

Di-n-butylamine-borane LXII

Di-n-butylamine-borane (2.43g, 0.017 mol) was added to 35 ml THF and stirred at room temperature. A solution of chlorodiphenylphosphine (2.9 ml. 0.017 mol) in 25 ml THF was added dropwise followed by a solution of triethylamine (2.39 ml, 0.017 mol) in 20 ml THF. The reaction mixture was refluxed for 16 hrs in accordance with the general procedure. Recrystallisation of the crude solid from a monoglyme: chloroform (2:1) mixture afforded 3.38g, of colourless, cubic crystals. mp. 124-125°C. Analysis: found: C, 66.54; H, 5.16; B, 5.00, P, 2.75%. νmax (KBr) 3040 (m); 2960 (w); 2850 (m); 2440 (m); 1585 (m); 1480 (s); 1455 (m); 1395 (m); 1330 (w); 1310 (w); 1240 (m); 1175 (vs); 1110 (s); 1080 (m); 1050 (w); 1025 (s); 990 (w); 940 (s); 885 (m); 855 (w); 770 (w); 765 (w); 710 (s); 690 (s) cm^{-1}. δH (CD_3OD) 7.60 (m); 8.15 (m) ppm. (both ArCH); δC (CD_3OD) 128.51 (s); 129.90 (s); 132.0 (s); 133.05 (s); 134.57 (s); 139.98 (s) ppm (all Ar-C).

1. D. Dakternicks and R. Di Giacomo, *Phosphorus Sulphur, 1985,* 24, *217.*
2. D.E. Schiff, J.W. Richardson, R.A. Jacobson, A.H. Cowley, and J. Lasch, *Inorg. Chem., 1984,* 23, *3373* and references therein.
3. D. Gonbeau, M. Sanchez and G. Pfister-Guillonzo, *Inorg. Chem., 1981,* 20, *1966.*
4. D.W. White, B.A. Karcher, R.A. Jacobson and J.G. Verkade, *J.Am. Chem. Soc., 1974,* 101, *4921.*
5. C. Romming and J. Songstad, *Actu. Chem. Scand., Ser.A, 1978, A* 32, *689.*
6. A. Cowley, *Phosphorus Sulphur, 1976,* 2, *283.*
7. J.G. Verkade, *Co-Ord. Chem. Rev., 1972/73,* 9, 1.
8. R.K. Kanjolia, C.L. Watkins and L.K. Krannich, *Inorg. Chem., 1987,* 26, *223.*
9. D. Grec, L.G. Hubert-Pfalzgraf, J.G. Riess and A. Grand, *J. Am. Chem. Soc., 1980,* 102, *7134.*
10. J.P. Laurent, G. Jugie and G. Commenges, *J. Inorg. Nucl. Chem., 1969,* 31, *1353.*
11. C. Jouany, J.P. Laurent and G. Jugie, *J. Chem. Soc., Dalton Trans., 1974, 1510.*
12. A.B. Burg, and P.J. Slota, *J. Am. Chem. Soc., 1960,* 82, *2145.*
13. (a) J.S. Jessup, R.T. Paine and C.F. Campana, *Phosphorus Sulphur, 1981,* 9, *279.* (b) R.T. Paine, *Inorg. Chem., 1977,* 16, *2996.*
14. J. Febray, F. Casablanca and J.G. Riess, *Inorg. Chem., 1985,* 24, *3235.*
15. D. Grec, L.G. Hubert-Pfalzgraf, A. Grand and J.F. Riess, *Inorg. Chem., 1985,* 24, *4642.*
16. R.K. Kanjolia, L.K. Krannich and C.L. Watkins, *Inorg. Chem., 1985,* 24, *445.*
17. R.K. Kanjolia, L.K. Krannich and C.L. Watkins, *J. Chem. Soc., Dalton Trans., 1986, 2345.*
18. A.B. Burg and P.J. Slota, *J. Am. Chem. Soc., 1958,* 80, *1107.*
19. H. Schmidbaur, E. Weiss and G. Müller, *Synth. React. Inorg. Met-Org. Chem., 1985,* 15, *415.*
20. E. Weiss, *Dissertation, Technische Universität München, 1981.*
21. H. Schmidbaur, E. Weiss, *Angew. Chem. Int. Eng. Ed., 1979,* 19, *781.*
22. R.R. Holmes and P.P. Wagner, *J. Am. Chem. Soc., 1962,* 84, *357.*
23. J.M. Dupart, S. Pace and J.G. Riess, *J. Am. Chem. Soc., 1983,* 105, *1051.*

24. P. Cassoux, R.L. Kuczkowski, P.S. Bryan and R.C. Taylor, *Inorg. Chem., 1975,* 14, *126.*

25. D.E.C. Corbridge, Ed., *The Structural Chemistry of Phosphorus, Elsevier, Amsterdam, 1974.*

26. J.C. Clardy, D.S. Milbrath and J.G. Verkade, *Inorg. Chem., 1977,* 16, *2135.*

27. R. Burgada, *Ann. Chim. (Paris), 1963,* 8, *347.*

28. (a) J.G. Verkade, R.W. King and C.W. Heitsch, *Inorg. Chem., 1964,* 3, *1884.* (b) G. Jugie and J.P. Laurent, *Bull, Soc. Chim. France, 1970, 838.*

29. B.L. Laube, R.D. Bertra, G.A. Casedy, R.D. Compton and J.G. Verkade, *Inorg. Chem., 1967,* 6, *173.*

30. D.W. White, B.A. Karcher, R.A. Jacobson and J.G. Verkade, *J. Am. Chem. Soc., 1979,* 101, *4921.*

31. J.E. Richman and T.J. Atkins, *Tetrahedran Lett., 1978, 4333.*

32. J.E. Richman, D.D. Gupta and R.B. Flay, *J. Am. Chem. Soc., 1983,* 101, *1291.*

33. T.J. Atkins, *Tetrahedran Lett., 1978, 4334.*

34. J. Guggenber, *Unpublished Results.*

35. J.E. Richman, R.O. Day and R.R. Holmes, *Inorg. Chem., 1981,* 20, *3378.*

36. R. Hoffmann, J.M. Howell and E.L. Muetterties, *J. Am. Chem. Soc., 1972,* 94, *3407.*

37. R.T. Paine, *Inorg. Chem., 1977,* 16, *2996.*

38. D.R. Martin, C.M. Merkel, J.P. Ruîz and J.U. Mondal, *Inorg. Chim. Actu., 1985,* 100, *293.*

39. J.S. Jessup, R.T. Paine and C.F. Campana, *Phosphorus Sulphur, 1981,* 9, *274.*

40. H. Nöth and R. Ullman, *Chem. Ber., 1976,* 109, *1942.*

41. R. Goetzee, H. Nöth and D.S. Payne, *Chem. Ber., 1972,* 105, *2637.*

42. J.G. Riess and J.R. Van Wazer, *Bull. Soc., Chim. France, 1968, 3087.*

43. K.L. Lundberg, R.J. Rowatt and N.E. Miller, *Inorg. Chem., 1969,* 8, *1336.*

44. R.K. Kanjola, L.K. Krannich and C.L. Watkins, *Inorg. Chem., 1985,* 24, *445.*

45. D.C. Mente, and J.L. Mills, *Inorg. Chem., 1975,* 14, *1862.*

46. F.G.A. Stone, *Chem. Rev., 1958,* 14, *101.*

47. D.C. Mente, J.L. Mills and R.E. Mitchell, *Inorg. Chem., 1975,* 14, *123.*

48. H. Nöth and B. Wrachemeyer, *NMR Spectroscopy of Boron Compounds; Springer-Verlag: New York, 1978.*

49. F.G.A. Stone and A.B. Burg, *J. Am. Chem. Soc., 1954,* 76, *386.*

50. H. Nöth and H. Vahrenkamp, *Chem. Ber., 1967,* 100, *3353.*

51. D.F. Gaines and R. Schaeffer, *J. Am. Chem. Soc., 1964,* 86, *1505.*

52. L.D. Schwartz and P.C. Keller, *J. Am. Chem. Soc., 1972,* 94, *3015.*

53. W.D. Phillips, H.C. Miller and E.L. Muetterties, *J. Am. Chem. Soc., 1959,* 81, *4496.*

54. G. Socrates, *Infrared Characteristic Group Frequencies, John Wiley & Sons, 1980,* p. 107.

55. E. Fluck and H. Binder, *Inorg. Nucl. Chem. Letters, 1967,* 3, *307.*

56. H. Von Thurn and H. Krebs, *Acta Cryst; 1969,* B25, *125.*

57. N.N. Greenwood and A. Earnshaw, *"Chemistry of the Elements", Pergamon Press, Oxford, 1984,* p. 568 and references therein.

58. F.A. Cotton, J.M. Troup, F. Casablanca and J.G. Riess, *Inorg. Chim, Acta; 1974,* 11, *L33.*

59. L. Pauling. *"The Nature of the Chemical Bond", 3rd Ed., Cornell University Press, Ithaca, N.Y., 1960,* p. 25.

60. A.B. Burg, *J. Am. Chem. Soc., 1961,* 83, *2226.*

61. A.B. Burg, *Topics in Modern Inorganic Chemistry, Proceedings of the Robert A. Welch Foundation Conferences on Chemical Research, 1962,* Vol. VI, *Houston Texas,* S. *133.*

62. V.K. Gupta, L.K. Krannich and C.L. Watkins, *Inorg. Chem., 1986,* 25, *2553.*

63. F. Kober, Z. Anorg, *Allg. Chem., 1973,* 400, *285.*

64. L.K. Krannich, *Inorg. Chem., 1980,* 19, *3300.*

65. O. Alder and F. Kober, *J. Am. Chem., Soc., 1966,* 88, *1842.*

66. K. Issleib and B. Walter, *Angew. Chem., 1967,* 59, *79.*

67. K. Issleib and B. Walther, *J. Organometal. Chem., 1970,* 22, *375.*

68. C. Weidig, S.S. Uppal and H.C. Kelly, *Inorg. Chem., 1974,* 13, *1763.*

PUBLICATIONS

(i) The Structure of 4-Dimetheylaminopyridine-cyanoborane.
G. Ferguson, M. Myers and T.R. Spalding; Acta Cryst., Section C (in preparation).

(ii) The Structure of Tetraphenyldiphosphine monoxide-*bis*(diphenylamine).
G. Ferguson, M. Myers and T.R. Spalding; Acta Cryst., Section C (in preparation).

(iii) Synthesis and characterisation of Selenaborane Clusters, 12-X-I-$SeB_{11}H_{10}$(I) (X = Cl, Br, I); X-ray Diffraction Structure of I (X = I). Experimental (P.E.S.) and Theoretical (M.N.D.O.) Analysis of the electronic Structures.
P. Brint, G. Ferguson, P. Hayes, J. MacCurtain, M. Myers and T.R. Spalding; J. Chem. Soc., Dalton. (In preparation).