I. Some studies on Boronium salts; II. the coordination chemistry of Beryllium borohydride

Banford, L.

I. Some Studies on Boronium Salts

II. The Coordination Chemistry of Beryllium Borohydride.

by

L. Banford.

A thesis submitted for the Degree of Doctor of Philosophy in the University of Durham.

June 1965.

ACKNOWLEDGEMENTS.

The author wishes to express his sincere thanks to Professor G.E. Coates, M.A., D.Sc., F.R.I.C., under whose direction this research was carried out, for his constant encouragement and extremely valuable advice.

The author is also indebted to the General Electric Company Limited for the award of a Research Scholarship.

MEMORANDUM

The work described in this thesis was carried out at the Science Laboratories of the University of Durham between October 1962 and May 1965, and has not been submitted for any other Degree. All the work described is the original work of the author, except that acknowledged by reference.

The work undertaken by the author consisted of two separate investigations, the results of which are incorporated in parts one and two of this thesis. Part of the work has been the subject of two publications in the Journal of the Chemical Society.(J.,1964,3564; J.,1965,5591).

SUMMARY.

PART I: Some studies on boronium salts.

Diphenylbipyridylylboronium salts and also the diphenyl-o-phenanthrolineboronium salts are relatively resistant to hydrolysis, and undergo metathetical reactions in aqueous solution. The colourless, very sparingly soluble hydrated nitrate, as well as the perchlorate and hydrogen sulphate, are readily precipitated from aqueous solution. The colours of the iodides and some other salts of the $(Ph_2bipyB)^+$, $(Ph_2phenanB)^+$, and $(n\text{-}Bu_2bipyB)^+$ cations are considered to be due to charge-transfer transitions between the anion and cation. The yellow colour of bipyridylyl-phenylenedioxyboronium perchlorate is attributed to intra-ionic charge-transfer, and the red colour of bisdimethylaminobipyridylyl-boronium tetraphenylborate may also be due in part to intra-ionic charge-transfer. The ultra-violet and visible spectra of several coloured boronium salts have been obtained in solvents of varying dielectric constant.

PART II: The coordination chemistry of beryllium borohydride.

Beryllium borohydride forms an isobutylamine complex, $(Be(Bu^iNH_2)_4)(BH_4)_2$, which can be sublimed at low pressure and is nearly insoluble in diethyl ether. Reactions of the borohydride with some ethers are discussed. Several liquid 1:1 adducts of the type, $L.BeB_2H_8$ (where L = Et_2O, Me_3P, Me_2PH, Et_3P, Me_3N, Me_2^iNH), have been prepared and their formation has been followed tensimetrically. The adducts are monomeric in benzene solution.

Triphenylphosphine forms a 1:1 adduct which is monomeric in benzene solution and decomposes when heated with the formation of triphenylphosphine-borane. Reaction with 2 moles of triphenylphosphine gives only the 1:1 adduct at room temperature, but between 100-180°, triphenylphosphine-borane is formed in high yield together with beryllium hydride, which is contaminated with some strongly held triphenylphosphine-borane. The main feature of the infrared spectrum of the best specimen of beryllium hydride prepared by this method consists of a broad absorption centred on 1758cm^{-1}.

Trimethylphosphine reacts rapidly at room temperature to form the liquid adduct, and then slowly reacts with a further mole of phosphine to give a solid product of overall composition $(Me_3P)_2BeB_2H_8$, from which trimethylphosphine-borane can be sublimed at room temperature.

TABLE OF CONTENTS.

Part I.

INTRODUCTION

INTRODUCTION.

Object of investigation.

The literature contains many references to boronium salts, but it is only recently that these salts have attracted serious study. In general, the unusual chemical stability shown by some of these compounds has not been realised, and in this present work a detailed study has been made of the preparation and properties of the bipyridylyldiphenylboronium salts.

During the course of this work it was found that several of these salts were coloured in the solid state, but in solvents of high dielectric constant the salts dissolved to give colourless solutions. The u.v. and visible spectra of these salts have been recorded in solvents of varying dielectric constant, and the results interpreted in terms of charge-transfer between the boronium cation and counter ion.

Cationic and anionic organo-boron compounds.

The outer electronic configuration of the boron atom in its ground state is $2s^2 2p^1$, with a first ionisation potential of 8.3e.v. Second and third ionisation potentials are 25.15 and 37.92e.v. respectively. Hence the large energy required for ionisation to B^{3+} precludes such cationic species from the chemistry of boron.

Covalent compounds of the type BX_3 are well established and all monomeric compounds are planar with X-B-X bond angles

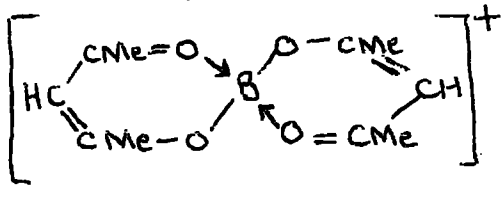
of 120°. However, in such compounds there remains a vacant low-lying orbital which confers pronounced Lewis acid behaviour allowing boron to achieve a coordination number of four. Anionic complexes of boron are well known, e.g. BF_4^-, BH_4^-, $(HB(OR)_3)^-$, and illustrate the tendency of boron to achieve this coordination number.

In this introduction a general review will be presented for cationic and the more important anionic species of boron, excluding the extensive and complex chemistry of borate anions containing only boron and oxygen. A full discussion of the borohydrides will be reserved for Part II of this thesis.

Cationic organo-boron compounds: Boronium salts.

Simple cationic species containing B^{4+} are unknown, and indeed in this state the boron would contain only two electrons in the valence shell. Boronium salts containing B^+ are only known in compounds containing coordinately saturated boron.

The history of boronium salts extends back to 1906, but from that date until quite recently the literature contains comparatively few examples of this type of compound. Probably the first example was reported by Dilthey and Schumacher[1] from the reaction of BCl_3 with acetylacetone or benzoylacetone. From acetylacetone, salts of the ion



were isolated in combination with various anions e.g. $AuCl_4^-$ and $FeCl_4^-$.

The 'diammoniate of diborane' prepared from diborane and

ammonia at low temperatures[2]. was believed to be the diammonium salt $(NH_4)_2^+B_2H_4^{2-}$. Schlesinger and Burg[3]. observed liberation of hydrogen from the 'diammoniate' by sodium in liquid ammonia, and suggested the compound would be better represented as the mono-ammonium salt NH_4^+ $(H_3BNH_2BH_3)^-$. It was further reported that a stable salt NaB_2H_8N was obtained from the reaction of 1mole sodium with 1mole 'diammoniate ' in liquid ammonia followed by careful removal of solvent. However, from X-ray diffraction studies[4]., the product NaB_2H_8N was shown to be a mixture of sodium borohydride and polymeric amino-borine. The structure $(NH_4)^+(BH_2NH_2BH_4)^-$ was proposed for the 'diammoniate'.

After considerable experimental work, Parry and co-workers[5]. provided strong evidence for a structure involving a boronium cation, $(H_2B(NH_3)_2)^+BH_4^-$. The more important evidence supporting this structure may be listed.

1) The Raman spectrum of a solution in liquid ammonia showed all the characteristic frequencies for the borohydride ion. Reaction of liquid ammonia solutions containing sodium, potassium, or lithium, gave the corresponding alkali-metal borohydride. Addition of magnesium ion to a liquid ammonia solution of the 'diammoniate' precipitated $(Mg(NH_3)_6)^{2+}(BH_4)_2^-$.

2) Ammonium chloride or bromide reacted with the 'diammoniate' to liberate hydrogen, and salts of the proposed boronium cation have been prepared e.g. $(H_2B(NH_3)_2)^+Cl^-$. The structure of this salt has been studied[6]., and the B-N distance

given as 1.58 ± 0.02Å, with the N-B-N angle nearly tetrahedral.

A 'diammoniate' of tetramethyldiborane has been prepared[7]. and found to have similar properties to those of the'diammoniate' of diborane, and hence may be expected to have a similar structure. Treatment of the tetramethyl derivative with trimethylamine[8]. displaced up to 1.6moles ammonia. This observation would be difficult to interpret if the addition compound existed as an ammonium salt, i.e. $NH_4^+((CH_3)_2BHNH_2BH(CH_3)_2)^-$ or $NH_4^+((CH_3)_2BNH_2BH_2(CH_3)_2)^-$, but is consistent with the boronium salt structure, $((CH_3)_2B(NH_3)_2)^+(H_2B(CH_3)_2)^-$.

It is of interest to note that the simple adduct $H_3B.NH_3$ has been prepared[5]., and shown to be quite distinct from the 'diammoniate'.

$$LiBH_4 + NH_4Cl \xrightarrow{Et_2O} LiCl + H_3B.NH_3 + H_2.$$

The adduct is soluble in ether, and cryoscopic measurements agree with a monomeric species. Ethereal solutions are reported slowly to deposit the 'diammoniate'.

Tetraborane has been shown to form a stable diammoniate[9]. $B_4H_{10}.2NH_3$, when allowed to react with ammonia in ether solution at -78°. No evidence was found for the existence of the reported tetra-ammoniate, $B_4H_{10}.4NH_3$, which was stated to decompose above -20° with loss of hydrogen and ammonia. The diammoniate of tetraborane has been assigned the salt structure $(H_2B(NH_3)_2)^+(B_3H_8)^-$.

With sodium in liquid ammonia, hydrogen is evolved, and sodium octahydrotriborate is formed.

$$(H_2B(NH_3)_2)^+(B_3H_8)^- + Na \xrightarrow{liq.NH_3} H_2 + NaB_3H_8 + (H_2BNH_2)_x.$$

With hydrogen chloride in ether, hydrogen is evolved according to the equation:

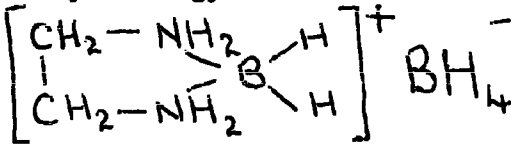
$$(H_2B(NH_3)_2)^+(B_3H_8)^- + HCl \xrightarrow{Et_2O} (H_2B(NH_3)_2)^+Cl^- + H_2 + Et_2OB_3H_7.$$

Ammonia will displace ether from the etherate at low temperature,

$$NH_3 + Et_2O.B_3H_7 \xrightarrow{Et_2O} H_3N.B_3H_7 + Et_2O.$$

In contrast to the unsymmetrical cleavage of diborane by ammonia, phosphine reacts to form the simple complex[10]. $H_3P.BH_3$.

The heterogenous adsorption of diborane by ethylenediamine in high vacuum apparatus, or reaction of ethylenediamine with the tetrahydrofuran complex of diborane, $THF.BH_3$, gave an air stable, white crystalline solid, $(CH_2NH_2.BH_3)_2$, decomposed by heat with liberation of two moles hydrogen per mole of starting material[11]. Two possible structures were suggested for the compound, a linear addition complex $H_3B.NH_2CH_2CH_2NH_2.BH_3$, or an ionic structure by analogy to the 'diammoniate'of diborane.



An alternative preparation for this compound and also for a 1:1 adduct has been described[12]. Ethylenediamine dihydrochloride with sodium borohydride in tetrahydrofuran at room temperature gave the 2:1 adduct, and this with ethylenediamine in tetrahydrofuran gave the 1:1 adduct, $en.BH_3$. By comparison of

i.r. spectra, en.2BH_3, (Co3en)Cl_3, and Hgen.Cl_2, it was concluded that the compound existed as represented by the ionic formula. However, the original authors[13.], after confirming the identity of the products prepared from the two methods, concluded from cryoscopic studies in water, solubility data, and the failure to precipitate thallium(I)borohydride after addition of thallous acetate, that the compound existed as represented by the open chain formula. In particular, a B^{11}n.m.r. spectrum of the complex in dimethoxyethane gave a single boron absorption, split into a quadruplet of relative intensity 1:3:3:1 indicating the equivalence of both boron atoms bound to three protons. The coupling constant 88c/s. agreed with J_{B-H} values for other amine-boranes.[14.] The structure involving a boronium cation should give two boron absorptions, one split into a triplet, and the second split into a quintuplet.

Several complexes obtained from reaction of diphenyl boron chloride with primary amines have been reported[15.], and the compounds, $Ph_2BCl.2L$ (L = Bu^iNH_2, $EtNH_2$, $MeNH_2$), were isolated from ether solution. In a later paper[16.] the complexes were discussed in terms of a salt structure, $(Ph_2B.2L)^+Cl^-$, and the compounds (L = $MeNH_2$, $EtNH_2$) were reported to form complex salts with stannic chloride in chloroform solution, $(Ph_2B.2L)_2^+ (SnCl_6)^{2-}$. Dibutyl boron chloride in ether solution reacted with hydrazine to give a salt like compound[17.], $(Bu_2B(N_2H_4)_2)^+Cl^-$.

Several boronium cations of the type, $(X_2B(NH_2R)_2)^+$, $(X_2B(NHR_2)_2)^+$, $(X_2B(NR_3)_2)^+$, X = H, alkyl, chlorine, were mentioned in a series of communications[18,19], but no details were given in these notes. Tris(dimethylamino)-borane with hydrogen chloride in ether solution[20] gave a compound of composition $BCl_3.2HNMe_2$, to which was assigned a salt structure $((Me_2NH)_2BCl_2)^+Cl^-$. Tris(diethylamino)-borane also reacted to give a similar product. The compound $((Me_2NH)_2BCl_2)^+Cl^-$ was also prepared from the reaction between boron trichloride and dimethylamine.[21] Evidence for the ionic structure was obtained, since with ferric chloride an ionic compound was isolated, $((Me_2NH)_2BCl_2)^+FeCl_4^-$. A similar compound, $((Me_2NH)_2B(OEt_2)_2)^+FeCl_4^-$, was prepared from boron trichloride and ferric chloride in ether.

The reduction of bis(dimethylamino)boron chloride by lithium hydride in ether solution to the hydrido compound $(Me_2N)_2BH$ has been reported.[22] The product with hydrogen chloride in ether solution at 0^o precipitated a compound of composition, $(Me_2N)_2BH.2HCl$, which by similarities in the i.r. spectrum with the salt $((Me_2NH)_2BCl_2)Cl$, and formation of a complex with ferric chloride, $((Me_2NH)_2B(H)Cl)^+FeCl_4^-$, was assigned the ionic structure, $((Me_2NH)_2B(H)Cl)^+Cl^-$.

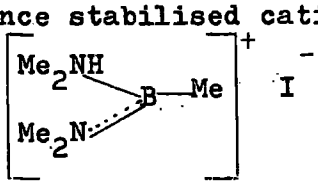
The preparation of alkyl-bis(dimethylamino)-boranes from alkylboron dichlorides and secondary amines, or alternatively from bis(dialkylamino)boron chloride and lithium alkyls in ether solution has been studied.[23] A salt like product,

$(Me_2NH)_2ClBMe)^+Cl^-$, was obtained from the methyl compound $MeB(NMe_2)_2$ and two moles of hydrogen chloride. Electrical conductivity studies in methylene chloride supported the ionic structure. Further, the absence of NH_2 bands in the i.r. spectrum excluded the alternative structure, $(Me_2NH_2)^+(Me_2N(Me)BCl_2)^-$. Complex salts of the type $((Me_2NH)_2ClBMe)_2^+X^-$, where X^- = $PtCl_6$, $FeCl_4$, $SbCl_6$, have been isolated from direct reaction in ether solution. In the series $RB(NMe_2)_2$, R = alkyl group, apart from the methyl and ethyl compounds, higher alkyl groups do not form the boronium salt, but give instead products of the type $Me_2NH.HCl$ and $RBClNMe_2$.

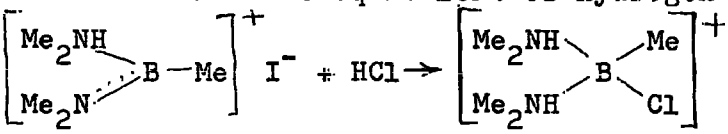
Methyl-bisdimethylaminoborane in pentane solution reacts with two moles of hydrogen bromide to give the analogous bromide $(MeBBr(NHMe_2)_2)^+Br^-$, and this with ferric chloride in ether solution gave the complex salt $(MeBBr(NHMe_2)_2)^+FeCl_3Br^-$. Only one equivalent of hydrogen iodide will react in toluene solution, but the product $(MeB(NHMe_2)NMe_2)^+I^-$ will react with a further equivalent of hydrogen chloride to give the normal salt $(MeBCl(NHMe_2)_2)^+I^-$.

$$MeB(NMe_2)_2 + HI \longrightarrow MeB(NMe_2)_2.HI$$

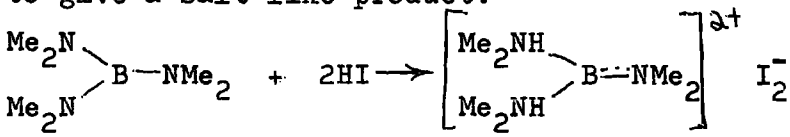
This compound readily forms a tri-iodide by reaction with iodine in pentane, and this would suggest the presence of iodide ion in the original compound. The authors suggested a structure involving a resonance stabilised cation,



A structure with a higher B-N bond order was inferred from i.r. evidence, and this band at 1576cm^{-1} disappears if the salt is reacted with one equivalent of hydrogen chloride.

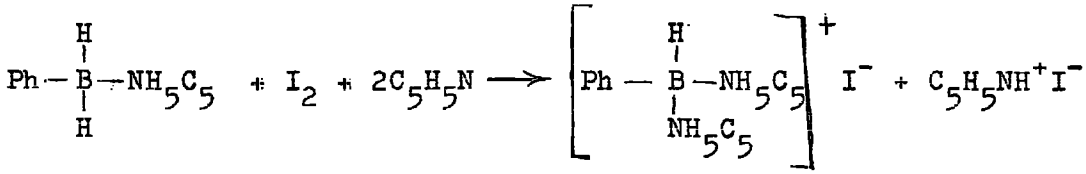


Tris(dimethylamino)borane reacts with two moles of hydrogen iodide to give a salt-like product.



Another mole of hydrogen iodide was slowly taken up at high concentrations of hydrogen iodide to give a compound of composition, $B(NMe_2)_3.3HI$. The i.r. spectrum of the salt contained a band at 1558cm^{-1} suggesting resonance stabilisation of the cation, $(Me_2NB(Me_2NH)_2)^{2+}$.

Pyridine phenylborane has been reported to react with excess pyridine and iodine in chloroform solution to give in addition to pyridinium iodide, a boronium salt.[24].



The white crystalline solid, phenylhydridobis(pyridine)-boron(III) iodide, was found to turn yellow in air. From the i.r. spectrum, the BH_2 bending mode present in the original compound at 1158cm^{-1}, was absent in the salt, but a B-H stretch was observed at

2427cm^{-1}. A tri-iodide salt was formed by reaction with iodine. The salt in chloroform slurry undergoes rapid metathesis with silver perchlorate, and the resulting salt was apparently air stable. It was subsequently found[24a.] that iodine reacted with a selected group of amine-boranes in the presence of amine to give iodide salts of bisamine-boronium cations.

$RBH_2.amine + I_2 + 2amine \longrightarrow RBH(amine)_2^+I^- + amineH^+I^-$.

The following salts have been prepared:

a) R = C_6H_5, Amine = C_5H_5N

b) R = cycloC_6H_{11}, Amine = C_5H_5N

c) R = H, Amine = Me_3N

d) R = H, Amine = C_9H_7N.

Metathesis of iodides (a-d) with silver perchlorate gave the corresponding perchlorates. A plausible two stage reaction sequence was proposed:

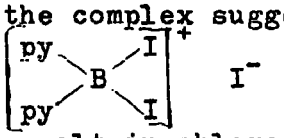
$RBH_2.amine + I_2 + amine \longrightarrow RBHIamine + amineH^+I^-$

$RBHIamine + amine \longrightarrow RBH(amine)_2^+I^-$.

Reference was made to the 2:1 complex[25.] formed from pyridine and n-dibutylboron chloride, and it was suggested that this compound may reasonably be considered as a boronium salt $((C_4H_9)_2Bpy_2)^+Cl^-$. The result of a preliminary investigation suggested that iodine reacted with pyridine-borane and pyridine to form a complex salt analagous to phenylhydrido-bis(pyridine)boron(III) iodide.

Boron tri-iodide will react with pyridine to give a yellow

solid of composition $BI_3.2py$.[26] Apart from chloroform and methylene chloride, the product was insoluble in non-polar solvents, and decomposition occurred with protonic solvents. The general properties of the complex suggested a salt structure:

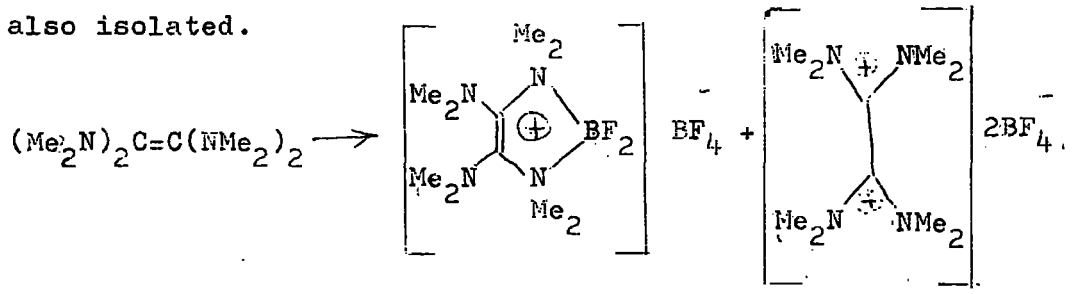


Iodine reacted with the salt in chloroform to give a tri-iodide.

$$(py_2BI_2)^+I^- + I_2 \longrightarrow (py_2BI_2)^+I_3^-$$

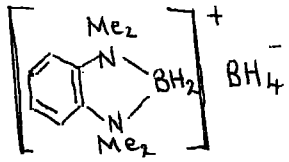
By analogy, the 1:1 complex from pyridine and boron trichloride may reasonably be formulated as a salt, $(py_2BCl_2)^+BCl_4^-$. However, the B^{11} n.m.r. spectra of $py.BCl_3$ and $py.BBr_3$ in acetonitrile consisted of a single resonance in the region characteristic of simple BX_3 addition compounds. Other workers[27] found no evidence for the bimolecular ionisation of this type of adduct in the molten complex.

A rather more complicated example of a boronium cation was obtained from the reaction of boron trifluoride etherate with tetrakis(dimethylamino)-ethylene in ether at -20°.[28] The main product from the reaction was tetrakis(dimethylamino)-ethylene-difluoroboron-tetrafluoroborate, readily recrystallised from methanol, m.p.217°(decomp.), and stable to air and water. A small amount of octamethyloxamidinium tetrafluoroborate was also isolated.



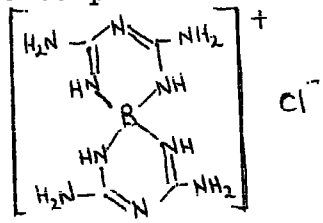
The assigned structure of the salt was found consistent with i.r., Raman, and n.m.r. spectra. Metathetical reactions with ammonium hexafluorophosphate or sodium tetraphenylborate in aqueous solution gave immediate precipitation of the boronium salt. Retention of the BF_2 structure in these derivatives was established from the conservation of the B^{11} triplet and F^{19} quartet in the n.m.r. spectra. The ease of formation and the stability of the cation was explained from the formation of a sterically favoured five membered ring.

A similar cationic species was isolated from the reaction between diborane and o-bis(dimethylamino)benzene.



Corresponding salts have been prepared containing other anions.

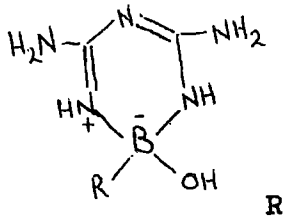
The transamination of biguanide with tris(dimethylamino)-borane gave a spiro compound isolated as a hydrochloride.[29]



Elemental analysis and molecular weight measurements in aqueous solution were consistent with a salt structure. The u.v. spectrum showed a band at 219mμ(ε 33,650) with approximately double the intensity of the biguanidinium ion ($\lambda_{max.}$ 231; 15,200).

Condensation reactions between biguanide and several boronic acids resulted in displacement of hydroxyl ion from the

boronic acid.



R = Phenyl, butyl, vinyl.

The existence of a diphenylboronium cation has been established[30] from u.v. absorption spectra, and conductivity measurements on nitrobenzene solutions of diphenylboron chloride and aluminium chloride. A nitrobenzene solution of the perchlorate, $(Ph_2B)^+ClO_4^-$, was prepared by addition of silver perchlorate to a solution of diphenylboron chloride. Conductivity measurements on this solution gave an equivalent conductance comparable to a nitrobenzene solution of diphenylboronium tetrachloroaluminate, suggesting the presence of the same cationic species, which may be solvated. A later report[31] described the preparation of 2-2'bipyridylyldiphenylboronium perchlorate, $(Ph_2Bbipy.)^+ClO_4^-$, by addition of bipyridyl to a solution of diphenylboronium perchlorate in nitromethane solution. The analogous salt, BB-2-2'bipyridylyl-9-oxa-10-boronia.anthracene perchlorate, has been prepared[32] from a similar series of reactions. Addition of bipyridyl to a nitrobenzene solution of diphenylboron chloride gave bipyridylyldiphenylboronium chloride. A dichlorodiphenylborate was isolated from the reaction of diphenylboron chloride (1mole) and bipyridyl(0.5mole) in petroleum benzene solution.

Quite recently a large number of boronium cations have

been reported,[33] and are of the type $(H_2BD_2)^+$, where D is a tertiary amine, phosphine, arsine, or dialkyl sulphide. The synthesis and chemical properties of the cations are dependent upon the size and basicity of the donor molecule. In particular the bisamine cations display remarkable hydrolytic, oxidative, and thermal stability, yet undergo facile substitution reactions at the B-H site to give mono and disubstituted derivatives.

One method of preparation of the cations involves the high temperature reaction of a base-borane with 'onium' salts of large anions.

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

The reaction is modified by changes in the anion X^- as well as changes in basicity and size of the donor molecule. Weak donor molecules (arsines, sulphides), for which 'onium' salts cannot be isolated, require the use of equivalent amounts of donor and hydrogen halide.

A second method involves displacement of a donor D in the cation, $(H_2BD_2)^+$ by a stronger donor, or a donor capable of chelate function.

$$(H_2BD_2)^+ + 2D' \longrightarrow (H_2BD'_2)^+ + 2D.$$

The order diamines$\rangle$amines$\rangle$ phosphines$\rangle$ arsines$\rangle$ sulphides roughly parallels the σ donor properties of these ligands.

Finally, the cationic species may be prepared by treating diborane with base-borane adducts to give salts of $B_{12}H_{12}^{2-}$ and $B_{12}H_{11}D^-$.[34] This method of preparation is

apparently still under investigation. I.r. and B^{11} n.m.r. spectra are found consistent with a tetrahedral configuration about the boron atom in the cation, $(H_2BD_2)^+$.

The chemical properties of the cation are governed by the nature of the base. Stability to hydrolysis and oxidation increase with base strength. Bisaminedihydridoboron(1^+) cations are particularly resistant to hydrolysis and oxidation, and salts may be recovered unchanged from concentrated sulphuric acid, nitric acid, and 10% sodium hydroxide, even after heating near 100° for prolonged periods. Aqua-regia converts the cation to the mono-chloro derivatives, $(HClB(NR_3)_2)^+$. Cations containing tertiary phosphines are quite stable to boiling acids, but are slowly degraded by hot aqueous bases. The cation $(H_2B(AsMe_3)_2)^+$ is hydrolysed by boiling water, and cations containing dialkyl sulphides are rapidly destroyed in cold water.

$$H_2BD_2^+ + 3H_2O \longrightarrow 2H_2 + H_3BO_3 + 2D + H^+$$

$$D = SR_2, \quad AsR_3.$$

Most of the salts are quite thermally stable. For some of the salts containing amines, decomposition is characterised by displacement of amine by the anion.

$$(H_2B(NMe_3)_2)^+Cl^- \xrightarrow{195^\circ} H_2BCl(NMe_3) + NMe_3.$$

Salts with larger anions are sparingly soluble in water and and usually crystallise in an anhydrous condition. Salts with smaller anions are water soluble and generally crystallise with water of hydration. Crystalline bases of the type

$(H_2BD_2)^+OH^-$ are prepared by stirring aqueous solutions of the chloride with silver oxide. Neutralisation of the strong bases with acids gives the appropriate salt.

Substitution reactions are observed in which the B-H hydrogen atoms are replaced by atoms or groups. Chlorine and bromine yield the monosubstituted derivatives, e.g. $(HXB(NR_3)_2)^+$. Monochlorination is also effected with SF_5Cl, NCl_3, and aqua-regia. Iodination is not observed with I_2, and iodine monochloride gives a dichloro derivative.

$$(H_2B(NMe_3)_2)^+ \xrightarrow{ICl} (Cl_2B(NMe_3)_2)^+.$$

Slow passage of fluorine diluted with nitrogen through aqueous solutions containing the cation at 0^o gave the disubstituted cation, $(F_2B(NMe_3)_2)^+$. A free radical mechanism was suggested for these substitution reactions.

Anionic compounds of boron.

Tri-aryl boron anions.

Early published work indicated that boron compounds, Ar_3B, react with alkali-metals to form salts containing negative tri-aryl boron ions. Such compounds are readily formed by direct reaction in a suitable solvent. Two series of salts may be formed, a 'mono sodium salt', $Na(Ar_3B^{\bullet -})$ isoelectronic with $Ar_3C^{\bullet}$, and 'disodium salts' of composition $Na_2(Ar_3B)^{2-}$.

Krause[35,36] observed the dissolution of sodium wire in an ethereal solution of triphenylborane to give a yellow solution from which an orange-yellow, oxygen sensitive salt, $Na^+(Ph_3B)^-$ crystallised. As indicated above, the triphenylborane anion-radical is iso-electronic with the triphenylmethyl radical, and it is found that the colours of the two series are similar.

Triphenylborane-sodium reacts with triphenylmethyl with the formation of a triphenylmethyl anion.

$$Ph_3B^{\bullet -}Na^+ + Ph_3C^{\bullet} \longrightarrow Ph_3B + Ph_3C^-Na^+.$$

A brilliant red coloured compound from $Ph_3C^{\bullet}$ and Ph_3B may be a radical of constitution $(Ph_3B\text{-}CPh_3)^{\bullet}$. A disodium salt,[37] $Na_2^+(Ph_3B)^{2-}$, may be obtained in tetrahydrofuran, and this salt is dark green in colour.

Tri-α- naphthylborane can add successively one atom of sodium to give a brown-yellow salt, $(C_{10}H_7)_3B^{\bullet -}Na^+$, and then a second to give the deep violet coloured salt, $(C_{10}H_7)_3B^{2-}Na_2^+$.

The chief interest in this series of compounds is in the

elucidation of their molecular constitution. Absorption spectra, paramagnetic resonance, and magnetic susceptibility have played an important role in clarifying the picture. The monosodium salt of triphenylborane should contain one unpaired electron, but several workers[37,38] reported the compound to be diamagnetic in tetrahydrofuran and the absorption spectrum in ether was quite different from that of the triphenylmethyl radical. This anomaly was explained[38,39] by association in solution and the solid state. With solvents of low dielectric constant, positive and negative ions must be completely associated as ion pairs, and then further association between pairs of anions takes place with spin-pairing and destruction of paramagnetism. Association is also favoured in the absence of steric hindrance in the aryl groups. Thus degrees of association fall in the order, benzene > ether > tetrahydrofuran, and in the order phenyl > α-naphthyl > β-methylnaphthyl > mesityl. The solid monosodium salts are diamagnetic and associated as far as is known.

The disodium salts have been much less investigated but as expected they have never been found to show paramagnetism. Triphenylborane with excess sodium amalgam (40%) in tetrahydrofuran gave the disodium salt.[37] Tri-arylborane-alkali metal compounds are very reactive, iodine in ether is immediately decolourised,

$$2Ph_3B^{\cdot -}Na^+ + I_2 \longrightarrow 2Ph_3B + 2NaI.$$

and with methanol[40] a boron hydride derivative is obtained.

$2Ph_3B^{\cdot-}Na^+ + MeOH \longrightarrow Na^+(Ph_3BOMe)^- + Na^+(Ph_3BH)^-$.

Sodium (or lithium) triphenylborohydride may also be prepared by addition of an ethereal solution of triphenylborane to sodium or lithium hydride. A better method involves heating the hydride and triphenylborane at 180° until the melt solidified.[41] The salt is hydrolysed by water.

$$Na^+(Ph_3BH)^- + H_3O^+ \longrightarrow Na^+ + Ph_3B + H_2 + H_2O.$$

Tri-alkylboranes do not react with alkali-metals to give salts[42] analogous to those discussed previously. Sodium[43] and calcium[44] salts of a dialkylboron anion, $(HB(CH_3)_2)^{2-}$, have been reported. Their method of preparation involves the reaction of tetramethyl diborane with sodium or calcium in liquid ammonia at -78°.

$(CH_3)_4B_2H_2 + 2Na + NH_3 \longrightarrow Na_2BH(CH_3)_2 + (CH_3)_2BH.NH_3$.

The ion, $HB(CH_3)_2^{2-}$ has a lone pair of electrons, and with trimethylborane forms a stable addition compound; $Na_2HB(CH_3)_2.BMe_3$.

Trimethylborane with ethyl-lithium in benzene reacts to give a salt, $Li^+(BMe_3Et)^-$ [45], and trimethylborane with methyl-lithium in ether solution gives the analogous compound $Li^+(BMe_4)^-$ [46]. The latter compound in aqueous solution conducts electricity, addition of acid liberates trimethylborane.

It is of interest to record that as long ago as 1862, alkaline solutions were found to absorb trimethylborane, but no crystalline product was isolated.[47] Triphenylborane however, reacts with tetramethylammonium hydroxide in alcoholic solution[48,49].

$$Ph_3B + Me_4N^+OH^- \longrightarrow Me_4N^+(Ph_3BOH)^-.$$

The product crystallises with water or ethanol, and has been shown to contain four covalent boron. Fusion of triphenylborane with sodium hydroxide yields the salt, $Na^+(Ph_3BOH)^-$, soluble in water but slowly hydrolysed by acetic acid with precipitation of triphenylborane. The slow reaction with ammonium chloride gives the ammine of triphenylborane.

$$Na(Ph_3BOH) + NH_4Cl \longrightarrow NaCl + Ph_3B.NH_3 + H_2O.$$

Heating with sodium cyanide gave sodium triphenylcyanoborate.[50] This compound may be obtained directly from triphenylborane and sodium cyanide.[51]

$$NaCN + Ph_3B \longrightarrow Na(Ph_3BCN).$$

The water soluble salt is more resistant to hydrolysis by acid than the corresponding hydroxy compound.

Tri-α-naphthylborane may be accurately titrated in alcoholic solution with sodium alkoxides using phenolphthalein as indicator.[52]

$$(C_{10}H_7)_3B + Na^+OR^- \longrightarrow Na^+(RO.B(C_{10}H_7)_3)^-.$$

Ammonia coordination compounds of the type, $R_3B.NH_3$ (R = Me, Bu^n) react with alkali-metals in liquid ammonia to give salts.[53,54]

$$R_3B.NH_3 + M \longrightarrow M^+(R_3B.NH_2)^- + \tfrac{1}{2}H_2.$$

The same salts are obtained by reaction with sodamide in liquid ammonia.

$$R_3B.NH_3 + NaNH_2 \longrightarrow Na^+(R_3B.NH_2)^- + NH_3.$$

Similar compounds are formed in ethylamine solution,

$$Me_3B.NH_2Et + Li \longrightarrow Li^+(Me_3B.NHEt)^- + \tfrac{1}{2}H_2.$$

Tetra-alkoxyborates and related compounds.

Tri-ethyl borate was observed to form a 1:1 complex with sodium ethoxide,[55] $Na^+(B(OEt)_4)^-$, and other tetra-alkoxyborate compounds of the type, $M(B(OR)_4)$ M = Na, K. R = Me, Et, Pr^i; M = Li, Ca. R = Me; M = Tl. R = Et, Pr^n; have been prepared by a similar method.[56] The method has been modified by preparing the metal-alkoxide in situ.[57]

$$M + 2ROH + 2B(OR)_3 \longrightarrow M(B(OR)_4)_2 + H_2.$$

M = Mg, Ca, Sr, Ba. R = Me, Et.

It is of interest to note that the corresponding beryllium compound, $Be(B(OMe)_4)_2$ could not be prepared by this or other methods.

The metal tetra-alkoxyborates are crystalline solids, soluble in alcohols or tetrahydrofuran, but sparingly soluble in other common organic solvents. They are generally thermally stable, but on strong heating decompose to the metal alkoxide and orthoborate.

Novel complexes,[58] $Li(C_6H_5B(OBu^i)_3)$ and $Li((C_6H_5)_2B(OBu^i)_2)$ were prepared from the corresponding orthoborate and phenyl-lithium.

Tri-alkoxyborates react with sodium hydride under reflux conditions to give tri-alkoxyborohydrides,[59] $(HB(OR)_3)^-$

R = Me, Et, Bu^n. Sodium trimethoxyborohydride may be obtained directly from sodium, hydrogen, and trimethylborate.[60]

$$2Na + H_2 + 2B(OMe)_3 \xrightarrow{250^\circ/press} 2Na(HB(OMe)_3).$$

The technique has been extended with tetrahydrofuran as solvent for sodium and lithium tri-alkoxyborohydrides.[61,62] They are stable white solids, and are powerful reducing agents. Borate ions containing different groups will disproportionate in certain instances, but this tendency is not usually a serious difficulty in their preparation.[63]

$$NaBH(OR)_3 \xrightarrow{reflux/THF} 3NaB(OR)_4 + NaBH_4.$$

R = Me, Et, but not Pr^i or Bu^t.

Sodium trimethoxyborohydride undergoes several interesting reactions.[59] Hydrogen chloride reacts to give dimethoxyborane,

$$Na(HB(OMe)_3) + HCl \longrightarrow NaCl + MeOH + HB(OMe)_2.$$

With diborane, trimethylborate and sodium borohydride were obtained. Dimethoxyborane reacted similarly.

$$B_2H_6 + 2Na(HB(OMe)_3) \longrightarrow 2NaBH_4 + 2B(OMe)_3.$$

$$3HB(OMe)_2 + Na(HB(OMe)_3) \longrightarrow NaBH_4 + 3B(OMe)_3.$$

Probably the most important reaction of sodium trimethoxyborohydride is with boron trifluoride etherate, which was originally the best preparation for diborane.

$$6Na(HB(OMe)_3) + 8Et_2O.BF_3 \longrightarrow B_2H_6 + 6NaBF_4 + 6B(OMe)_3 + 8Et_2O.$$

It has been claimed that the ethoxides of GroupII metals react with diborane in ethereal solution to give the corresponding

mono-ethoxyborohydride, $M(EtOBH_3)_2$. [57.]

Tetra-aryl and alkyl borates.

Lithium tetraphenylborate[64.] was obtained from triphenylborane and phenyl-lithium. An improved method involved the preparation of triphenylborane in situ, i.e. 1mole $BF_3.OEt_2$ and 4moles PhLi. Similarly, boron trifluoride etherate with excess phenylmagnesium bromide gave the compound, $(MgBr)^+(BPh_4)^-$, from which after removal of magnesium as carbonate, the addition of sodium chloride gave sodium tetraphenylborate.

The lithium salt has been found monomeric[65.] in ether solution over a wide range of concentrations. Sodium tetraphenylborate, soluble in water and ether, is a valuable analytical reagent[66.] particularly for potassium, rubidium, and caesium, as the salts of these cations are practically insoluble in water. Some indication of the versatility of the tetraphenylborate salts in analytical chemistry is given by the large volume of published material.[67.]

Other tetraphenylborates have been prepared from the lithium compound:

$$LiBPh_4 + Me_3NHCl \xrightarrow{H_2O} (Me_3NH)BPh_4 \xrightarrow{200^\circ} BPh_3 + Me_3N + C_6H_6$$

$$LiBPh_4 + Ph_4PI \xrightarrow{MeOH} (Ph_4P)BPh_4 \xleftarrow{2\ weeks} Ph_3B + PPh_5$$

$$AgBPh_4 \xleftarrow{AgNO_3/\ MeOH} LiBPh_4 \xrightarrow{CuBr_2} CuBPh_4$$

$$LiBPh_4 + PhN_2Cl \xrightarrow{MeOH} (PhN_2)BPh_4 \xrightarrow{55^\circ/H_2O} Ph\text{-}Ph + PhN\ NPh.$$

The reaction of the sodium salt with mercuric chloride is rapid and quantitative, and suitable for analytical purposes.

$$NaBPh_4 + 4HgCl_2 + 3H_2O \longrightarrow 4Ph.HgCl + NaCl + 3HCl + B(OH)_3$$

Although the potassium and ammonium salts are insoluble in water, cyclohexane, and benzene, they are soluble in chloroform, and addition of mercury to these solutions gave diphenylmercury and triphenylborane.[68] This was considered a free radical reaction involving the phenyl radical, particularly because mercury reacted neither with triphenylborane nor lithium tetraphenylborate in aqueous solution. However, with lithium chloride present, phenylmercury chloride was obtained in the latter instance.[69] Thermal decomposition of ammonium and amine tetraphenylborates[69] apparently proceeds by an ionic mechanism, with elimination of hydrocarbon.

$$(NH_4)^+(BPh_4)^- \xrightarrow{110^\circ} C_6H_6 + H_3N.BPh_3.$$

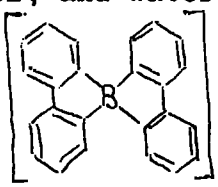
The hydrolysis of substituted borates has not been fully studied, and generally only qualitative observations have appeared in the literature.[70] Certainly the tetraphenylborates are among the most stable towards hydrolysis. A cold acid solution of $(BPh_4)^-$ does not easily decompose,[71] but at 80° it decomposes thus:

$$(B(C_6H_5)_4)^- + H^+ \longrightarrow C_6H_6 + (C_6H_5)_3B.$$

The cyanotriphenylborate anion is more resistant to hydrolysis than tetraphenylborate.

Aryl (o, m, p. $CH_3.C_6H_4$, p $(CH_3)_2NC_6H_4$-) analogues of the tetraphenylborate ion have been prepared from the appropriate

aryl-lithium and tri-alkylborane.[72] Lithium tetratolylborate was insoluble in non-polar solvents such as benzene, but soluble in acetone, ethanol, and water. The chelated anion,



from o,o'-dilithiobiphenyl and boron trifluoride etherate, is slowly hydrolysed to di(o-phenyl-phenyl)boronous acid. Anions containing heterocyclic rings have been prepared.[73]

Mixed aryl and aralkylborates are well established,[74] and are prepared for example from triphenylborane and aryl of alkyl-lithium.

$$Ph_3B + LiC{\equiv}CPh \xrightarrow{Et_2O/-80^\circ} Li(PhC{\equiv}CBPh_3).$$ [75]

This compound, with acids, generated phenyl acetylene, and with aqueous iodine gave phenylacetylyl iodide.

Triphenylborane with α-naphthyl-lithium gave, $Li(\alpha\text{-}C_{10}H_7BPh_3)$.[76] The ammonium or potassium salts are prepared by cationic exchange. Mercury causes fission of ammonium compounds in the manner shown below:

$$NH_4(\alpha\text{-}C_{10}H_7BPh_3) \longrightarrow C_{10}H_8 + Ph_3B.NH_3$$

$$NH_4(C_6H_5B(\alpha\text{-}C_{10}H_7)_3) \longrightarrow 2C_{10}H_8 + Ph(\alpha\text{-}C_{10}H_7)_2B.NH_3$$

$$NH_4(p\text{-}CH_3.C_6H_4.BPh_3) \longrightarrow CH_3.C_6H_5 + Ph_3B.NH_3.$$

p-Dimethylaminophenyl-lithium gave with triphenylborane, a complex which was converted to the potassium salt, and this on heating with methyliodide in acetone afforded a "zwitterion".[72]

$$(Me_2NC_6H_4B.Ph_3)K \xrightarrow{MeI} Me_3\overset{+}{N}C_6H_4\overset{-}{B}Ph_3$$

Lithium methyltriphenylborate decomposed on exposure to air, and fresh aqueous solutions gave no visible evidence of reaction with potassium or ammonium salts, but after a prolonged period ammonium tetraphenylborate precipitated from solution.

Lithium triphenylborohydride[77.] was obtained from triphenylborane and excess lithium hydride. It may be crystallised from dioxan, associated with five molecules of solvent. The salts $M(HBPh_3)$ M = Li, Na, K, may be obtained by three methods.[78.]

$$2Ph_3B + CH_3ONa + NaH \longrightarrow Na(HBPh_3) + Na(CH_3OBPh_3)$$

$$Ph_3B + MH \longrightarrow M(HBPh_3)$$

$$2Ph_3BM + CH_3OH \longrightarrow M(HBPh_3) + M(CH_3OBPh_3)$$

Triphenylborane with sodium hydroxide or sodium cyanide gave the sodium salt of hydroxytriphenylborate or cyanotriphenylborate respectively.

Sodium hydride will react with trimethylborane to give sodium trimethylborohydride,[59.] but the lithium salt is less stable and only known in ether solution. Lithium methylborohydride [79.] has been prepared from trimethylborane and lithium aluminium hydride.

$$Me_3B + LiAlH_4 \longrightarrow Li(MeBH_3) + Me_2AlH.$$

Substituted borohydrides may be obtained by direct replacement of hydrogen:

$$NaBH_4 + 4MeOH \longrightarrow Na(B(OMe)_4) + 4H_2.$$

or by reaction of organomagnesium halides with boron trifluoride[80.] However, the most widely used method involves assemblage of

the required radicals by coordination.

$$NaOMe + B(OMe)_3 \longrightarrow NaB(OMe)_4$$

$$NaH + B(OMe)_3 \longrightarrow Na(HB(OMe)_3)$$

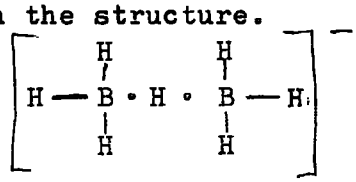
$$LiEt + BMe_3 \longrightarrow Li(EtBMe_3)$$ [45.]

$$2LiPh + B_2H_6 \longrightarrow 2Li(PhBH_3)$$ [81.]

Borohydride anions containing more than one boron atom.

Lipscomb predicted that a number of boron hydride anions, and some cations, would be stable, and indeed several anions apart from the borohydride anion, BH_4^- have been detected experimentally.

Lithium or sodium borohydride in diglyme solution[82.] readily absorb half a mole of diborane per mole of borohydride. The product is thought to contain the ion $B_2H_7^-$ with a single hydrogen bridge in the structure.



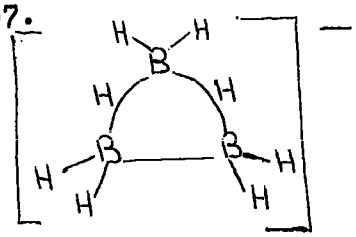
No direct proof of this structure is as yet available, and one can only suspect the B.H.B bond is present since the B^{11} n.m.r. spectrum shows all hydrogens to be equivalent.[83.] This effect is undoubtedly the result of fast intramolecular rearrangement. A single bridging hydrogen is suggested for the adduct formed from pyridine-borane and diborane.

A white salt obtained from the reaction of sodium with diborane[84.] was assigned the formula $Na_2B_2H_6$. It was subsequently

shown from X-ray diffraction studies[85] that the product was a mixture of sodium borohydride and an unknown compound. In ether solution, sodium borohydride was separated from an ether soluble salt of formula, NaB_3H_8.[86]

$$2Na + 2B_2H_6 \longrightarrow NaBH_4 + NaB_3H_8.$$

On the evidence of n.m.r. spectra, the structure shown below was suggested for the anion.[87]



Sodium octahydrotriborate is described as being thermally stable to 200°, soluble in ethers, liquid ammonia, methanol, and water. Dilute hydrochloric acid solutions are incompletely hydrolysed.

More recently[88], the ion has been prepared in good yield from hydroboration of alkali-metal addition compounds of naphthalene or triphenylborane with diborane in ether solutions. Alternatively, the ion may be prepared from reaction of metal borohydride with diborane in ether at 100°.

$$B_2H_6 + MBH_4 \xrightarrow{\text{ethers}} MB_3H_8 + H_2.$$

The diborane may be prepared <u>in situ</u> :

$$4BF_3 + 5MBH_4 \xrightarrow{\text{ether}} 3MBF_4 + 2MB_3H_8 + 2H_2.$$

The anion may be isolated in high yield by conversion to the tetramethylammonium salt. It has been suggested[9] that the addition compound of tetraborane with ammonia, $B_4H_{10}\cdot 2NH_3$, has the constitution, $(H_2B(NH_3)_2)^+(B_3H_8)^-$.

The observed B^{11} n.m.r. spectrum of sodium octahydrotriborate in heated solution was replaced by absorptions corresponding to the formation of more complex anionic species, $B_{11}H_{14}^-$, $B_{12}H_{12}^{2-}$, and the salt, $(Me_3NH)_2B_{12}H_{12}$, was isolated from a heated solution of sodium octahydrotriborate by the addition of trimethylammonium chloride.[89]

In suitable solvents, decaborane has been shown to ionise as a strong mono-protic acid.[90]

$$B_{10}H_{14} + OH^- \longrightarrow B_{10}H_{13}^- + H_2O .$$

The salt, $NaB_{10}H_{13}$, has been isolated as a slightly yellow solid from the reaction of sodium and $B_{10}H_{14}$ in ether.[91] Attempts to isolate a crystalline sodium salt from NaH and $B_{10}H_{14}$ in ether were unsuccessful,[92,93] but the triphenylmethylene phosphorane salt has been prepared.[94]

$$B_{10}H_{14} + Ph_3PCH_2 \longrightarrow Ph_3PCH_3(B_{10}H_{13}).$$

The diethylammonium and tetramethylammonium salts have recently been characterised.[95]

Substituted ions, $B_{10}H_{12}Z^-$ where Z^- = CN,CNO,CNS,OMe, are prepared in ether solution.

$$B_{10}H_{14} + Z^- \xrightarrow{0\text{-}25^\circ} B_{10}H_{12}Z^- + H_2.$$

Lipscomb predicted that the tetradecahydrodecaborate ion would exist as a stable ion, $B_{10}H_{14}^{2-}$, and indeed the sodium salt is produced in high yield from decaborane and sodium in liquid ammonia.

$$B_{10}H_{14} + e^- \longrightarrow B_{10}H_{14}^{\cdot -} \rightleftharpoons B_{10}H_{14}^{2-}$$
$$\downarrow$$
$$B_{10}H_{13}^- + \tfrac{1}{2}H_2$$

Titration of the disodium salt with acid results in the reversible uptake of one proton with formation of $B_{10}H_{15}^-$, and 'onium' salts of this anion have been isolated.

Neutral ligand molecules displace hydrogen from decaborane to give disubstituted products, $B_{10}H_{12}.2X$, and from such compounds the decahydrodecaborate salts have been characterised.[96] The salt $(Et_3NH)_2B_{10}H_{10}$ is obtained in near quantitative yields from $B_{10}H_{12}.2MeCN$ and excess Et_3N in refluxing benzene.

As indicated above, salts of the icosahedral ion, $B_{12}H_{12}^{2-}$, are prepared from hot aqueous solutions containing the octahydrotriborate ion.[89] The salt $(Et_3NH)B_{12}H_{12}$ was prepared in trace quantities from triethylamine and 2-iododecaborane-14 in refluxing benzene.[97] A further synthesis of the ion has been reported.[98] X-Ray studies[99] on the salt, $Cu_2B_{10}H_{10}$ confirm a polyhedral structure of D_{4d} symmetry, and indicate covalent interaction between Cu(I) and the $B_{10}H_{10}^{2-}$ polyhedron. The icosahedral structure has been confirmed by X-ray studies on the salt, $K_2B_{12}H_{12}$.[100]

The stability of salts containing the ions, $B_{10}H_{10}^{2-}$, and $B_{12}H_{12}^{2-}$, to heat, acids, bases, and oxidising agents has been investigated,[101] and found to be very high compared to that of other boron hydrides. No decomposition occurs with hot

alkaline solution, and $B_{10}H_{10}^{2-}$ reacts only slowly with hot acid. Stable solutions of the free acids, $H_2B_{10}H_{10}$, $H_2B_{12}H_{12}$, are obtained from acid ion-exchange resins and may be concentrated at room temperature to crystalline hydrates. $CsB_{12}H_{12}$ may be heated to 810° under vacuum without decomposition, and $Cs_2B_{10}H_{10}$ is unchanged at 600°. Large unipositive cations give relatively water insoluble salts, and spectroscopic results for salts containing polarising cations suggest interaction between the cation and anion.

Lipscomb has suggested[102.] that complex ions derived from $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ could be formed by linking single polyhedra by hydrogen bridges. For example, the species $B_{20}H_{19}^{3-}$ and $B_{20}H_{18}^{2-}$ are predicted from $B_{10}H_{10}^{2-}$, and regarding bridge hydrogen bonds as replacement of 2B-H bonds, one from each unit, by a single B.H.B bridge, an infinite chain of doubly linked B_{10} polyhedra would approach the composition $(B_{10}H_8)_n^{2-}$. Indeed, one such ion, $B_{20}H_{18}^{2-}$ has been reported from the oxidation of $B_{10}H_{10}^{2-}$ by an acidified ferric solution.[103.]

REFERENCES.

1) W.Dilthey and F.J. Schumacher — Annalen,1906,344,300,326.

2) A.Stock and E.Kuss — Ber.1923,56b,807.

A.Stock,E.Wiberg and H.N.Martini — Ber.1932,65,1711.

3) H.I.Schlesinger and A.B.Burg — J.Amer.Chem.Soc.,1938,60, 290.

40 G.W.Schaeffer,M.D.Adams,and F.J.Koenig — J.Amer.Chem.Soc.,1956,78,725.

5) S.G.Shore,R.W.Parry — J.Amer.Chem.Soc.,1955,77,6084.

R.W.Parry,D.R.Schultz, and P.R.Girardot — J.Amer.Chem.Soc.,1958,80,1,4.

6) C.E.Nordman and C.R.Peters — J.Amer.Chem.Soc.,1959,81,3551.

7) A.B.Burg and G.W.Campbell — J.Amer.Chem.Soc.,1952,74,3744.

8) Martincheck — Thesis,Univ.Houston Texas,1957.

9) G.Kodama and R.W.Parry — J.Amer.Chem.Soc.,1957,79,1007.

10) H.Brumberger and R.A.Marcus — J.Chem.Phys.,1956,24,741.

E.L.Gamble and P.Gilmont — J.Amer.Chem.Soc.,1940,62,717.

11) H.C.Kelly and J.O.Edwards — J.Amer.Chem.Soc.,1960,82,4842.

12) J.Goubeau and H.Schneider — Chem.Ber.,1961,94,816.

13) H.C.Kelly and J.O.Edwards — Inorg.Chem.,1963,2,226.

14) W.D.Phillips,H.C.Miller, and E.L.Muetterties — J.Amer.Chem.Soc.,1959,81,4496.

15) B.M.Mikhailov and N.S.Fedotov. — Izvest.Akad.Nauk S.S.S.R., Otdel.khim.Nauk 1959,1482.

16) ibid.,idem — 1961, 1913.

17) H.Noth Z.Naturforsch,1961,16b,471.

18) H.Noth Angew.Chem.,1960,72,638.

19) H.Noth and H.Beyer Angew.Chem.,1959,71,383.

20) H.Noth and S.Lukas Chem.Ber.,1962,95,1505.

21) B.M.Mikhailov,V.D.Shludyakov, and T.A.Shchegoleva Izvest.Akad.Nauk S.S.S.R. Otdel.khim.Nauk,1962,1698.

22) H.Noth,W.A.Dorochov,P.Fritz, and F.Pfab Z.anorg.Chem.,1962,318,293.

23) H.Noth and P.Fritz Z.anorg.Chem., 1963,322,297.

24a)J.E.Douglass J.Amer.Chem.Soc.,1962,84,121.

24b)J.E.Douglass J.Amer.Chem.Soc.,1964,86,5431.

25) I.W.Gerrard,M.F.Lappert and R.Shafferman J.,1957,3828.

26) E.L.Muetterties J.Inorg.Nuclear Chem.,1960,15,182.

27) N.N.Greenwood and K.Wade J.,1960,1130.

28) N.Wiberg and J.W.Buchler J.Amer.Chem.Soc.,1963,85,243.

29) J.E.Milks,G.W.Kennerly and J.H.Polevy J.Amer.Chem.Soc., 1962,84,2529.

30) J.M.Davidson and C.M.French J.,1958,114.

31) J.M.Davidson and C.M.French Chem.and Ind.,1959,750.

32) J.M.Davidson and C.M.French J.,1962,3364.

33) N.E.Miller and E.L.Muetterties J.Amer.Chem.Soc., 1964,86,1033.

34) H.C.Miller,N.E.Miller,E.L.Muetterties J.Amer.Chem.Soc., 1963,85,3885.

35) E.Krause Chem.Ber.,1924,57,216.

36) E.Krause and H.Polack Chem.Ber.,1926,59,777.

37) T.LChu J.Amer.Chem.Soc.,1953,75,1730.

38) C.W.Moeller and W.K.Wilmarth J.Amer.Chem.Soc.,1959,81,2638.

39) T.L.Chu and T.J.Weismann J.Amer.Chem.Soc.,1956,78,23.

40) G.Wittig,G.Keicher,A.Ruckert and P.Raff Annalen,1949,563,110.

41) G.Wittig and A.Ruckert Annalen,1950,566,101.

42) E.Krause and P.Nobbe Chem.Ber.,1930,63,934.

43) A.B.Burg and G.W.Campbell J.Amer.Chem.Soc.,1952,74,3744.

44) G.W.Campbell J.Amer.Chem.Soc.,1957,79,4023.

45) H.I.Schlesinger and H.C.Brown J.Amer.Chem.Soc.,1940,62,3429.

46) D.T.Hurd J.Org.Chem.,1948,13,711.

47) E.Frankland and D.Duppa Annalen,1862,124,129.

48) D.L.Fowler and C.A.Kraus J.Amer.Chem.Soc.,1940,62,1143.

49) C.A.Kraus and W.W.Hawes J.Amer.Chem.Soc.,1933,55,2776.

50) G.Wittig and P.Raff Annalen,1951,573,195.

51) G.Wittig and W.Herwig Chem.Ber.,1955,88,1962

52) H.C.Brown and Sei.Sujishi J.Amer.Chem.Soc.,1948,70,2793.

53) J.E.Smith and C.A.Kraus J.Amer.Chem.Soc.,1951,73,2751.

54) A.K.Holliday and N.R.Thompson J.,1960,2695.

55) H.Copaux Compt.rend.,1898,127,719.

56) L.Cambi Chem.Zentr.,1914,85,1412.

57) E.Wiberg and R.Hartwimmer Z.Naturforsch,1955,10b,290.

58) B.M.Mikhailov and P.M.Aronovich Doklady Akad.Nauk S.S.S.R. 1954,98,1791.

59) H.C.Brown,H.I.Schlesinger,I.Sheft, and D.M.Ritter J.Amer.Chem.Soc.,1953,75,192.

60) H.I.Schlesinger,H.C.Brown,A.E.Finholt J.Amer.Chem.Soc., 1953,75,205.

61) H.C.Brown and E.J.Mead J.Amer.Chem.Soc.,1953,75,6263.

62) E.J.Mead Diss.Abs.,1955,15,971.

63) H.C.Brown,E.J.Mead and C.J.Shoaf J.Amer.Chem.Soc., 1956,78,3616.

64) G.Wittig and G.Keicher Naturwiss.,1947,34,216.

65) G.Wittig,F.J.Meyer and G.Lange Annalen,1951,571,167.

66) H.Flaschka Z.Analyt.Chem.,1952,136,99.

67) See for example,'THE ORGANIC CHEMISTRY OF BORON', by W.Gerrard,(Academic Press,1961),p111,233.

68) G.A.Razuvaev and T.G.Brilkina Doklady Akad.Nauk S.S.S.R. 1952,85,815.

69) ibid.,idem 1953,91,861.

70) See for example,'RECENT STUDIES IN BORON CHEMISTRY', BY H.G.Heal, R.I.C. Monograph,1960,1,33.

71) G.Wittig,G.Keicher,A.Ruckert and P.Raff Annalen,1949,563,110.

72) G.Wittig and W.Herwig Chem.Ber.,1955,88,962.

73) V.A.Sazonova and L.P.Sorokina Doklady Akad.Nauk S.S.S.R. 1955,105,993;1957,113,1295.

74) G.A.Razuvaev and T.G.Brilkina Doklady Akad.Nauk S.S.S.R. 1953,91,861.

75) G.Wittig and P.Raff Annalen,1951,573,195.

76) G.A.Razuvaev and T.G.Brilkina Zhur.obshchei Khim., 1954,24,1415.

77) G.Wittig and A.RUckert Annalen,1950,566,101.

78) G.Wittig,G.Keigner,A.Ruckert, and P.Raff Annalen,1949,563,110.

79) T.Wartik and H.I.Schlesinger J.Amer.Chem.Soc.,1953,75,835.

80) Y.A.Sazinova,E.P.Serebryakov, and L.S.Kovaleva Doklady Akad.Nauk S.S.S.R.,1957,113,1295.

81) H.I.Schlesinger,H.C.Brown,B.Abraham,N.Davidson,A.E.Finholt, R.A.Lad,J.Knight and A.M.Schwartz J.Amer.Chem.Soc.,1953,75,191.

82) H.C.Brown,P.F.Stehle and P.A.Tierney J.Amer.Chem.Soc., 1957,79,2020.

83) R.E.Williams J.Inorg.Nuclear Chem.,1961,20,198.

84) A.Stock 'THE HYDRIDES OF BORON AND SILICON', Cornell University Press,1933.

85) J.S.Kasper,L.U.McCarty and A.E.Newkirk J.Amer.Chem.Soc., 1949,71,2583.

86) J.S.Hough,L.J.Edwards,A.D.McElroy J.Amer.Chem.Soc., 1956,78,689.

87) W.N.Lipscomb 'ADVANCES IN INORGANIC AND RADIOCHEMISTRY' Academic Books Ltd.,Vol1, 1959.

88) D.Gaines,R.Schaeffer and F.Tebbe Inorg.Chem.,1963,2,526.

89) I.A.Ellis,D.Gaines and R.Schaeffer J.Amer.Chem.Soc., 1963,85,3885.

90) G.A.Guter and G.W.Schaeffer J.Amer.Chem.Soc.,1956,78,3546.

91) R.H.Toeniskoetter Diss.Abs., 1959,20,879.

92) W.V.Hough and L.J.Edwards Abst.papers,133Meeting AC.S., San.Fran.Calif. 1958,p28L.

93) J.J.Miller and M.F.Hawthorne J.Amer.Chem.Soc.,1959,81,4501.

94) M.F.Hawthorne J.Amer.Chem.Soc.,1958,80,3480.

95) M.F.Hawthorne,A.R.Pitochelli, R.D.Strahm and J.J.Miller J.Amer.Chem.Soc.,1960,82,1825.

96) M.F.Hawthorne and A.R.Pitochelli J.Amer.Chem.Soc., 1959, 81,5519.

97) M.F.Hawthorne and A.R.Pitochelli J.Amer.Chem.Soc., 1960,82,3228.

98) H.C.Miller and E.L.Muetterties J.Amer.Chem.Soc.,1963,85,3885.

99) R.D.Dobrott and W.N.Lipscomb J.Chem.Phys.,1962,37,1779.

100) J.A.Wunderlich and W.N.Lipscomb J.Amer.Chem.Soc., 1960,82,4427.

102) W.N.Lipscomb Proc.Nat.Acad.Sci.U.S.A.,1961,47,1791.

103) M.F.Hawthorne and A.R.Pitochelli and W.N.Lipscomb J.Amer.Chem.Soc.,1959,81,5833; 1962,84,3026.

A.Kaczmarczyk,R.D.Dobrott and W.N.Lipscomb Proc.Nat.Acad.Sci.U.S.A.,1962,48,729.

Part I.

EXPERIMENTAL

EXPERIMENTAL.

Alkyl and arylboron chlorides, R_2BCl and $RBCl_2$, are extremely moisture sensitive, and were therefore prepared and handled under an atmosphere of dry, oxygen-free nitrogen.

Organic solvents, ethers and hydrocarbons, were dried over sodium wire for several days prior to use. Halogenated solvents were dried over anhydrous magnesium sulphate, and then distilled onto magnesium sulphate.

Nitrogen purification.

'White-spot' nitrogen was passed through a copper furnace heated to about 350° to remove oxygen, and then through a column of molecular sieve to remove water.

Periodically, the copper was regenerated by heating in a slow stream of hydrogen, and water removed from the molecular sieve by heating in vacuum for several hours.

Glove-box operations.

Occasionally it was necessary to handle air- or moisture-sensitive compounds within a glove-box. The box used throughout this work contained an atmosphere of dry, oxygen-free nitrogen. In addition to the purification system described above, it was found advantageous to pass the nitrogen gas from the molecular sieve through a trap cooled by liquid nitrogen to remove the last traces of water.

A small circulatory pump was positioned within the glove box to provide a continuous recycling process for the atmosphere

inside the box through the purification system.

Analysis of compounds.

The determination of carbon in the boronium compounds described in this work generally resulted in low figures. This effect has been widely observed, and is attributed to incomplete combustion with formation of boron carbide. Combustion in the presence of tungstic oxide gave improved results, but was still not altogether satisfactory.

Boron analysis.

A method of general applicability was developed, in which compounds were decomposed by the oxygen flask technique, and boric acid determined by titration against standard alkali in the presence of mannitol with bromo-thymol blue as indicator.

The compound (20mg.) was weighed into a gelatin capsule, and placed, with a filter paper fuse, into a platinum gauze container. The sample was ignited in a 2l. closed flask containing 50cc. water in an oxygen atmosphere.

After combustion the contents of the flask were shaken vigorously until all 'fog' dispersed, the solution washed into a conical flask and boiled for several minutes to remove carbon dioxide. The cooled solution was titrated against 0.01N. alkali to a blue end-point with bromo-thymol blue. Mannitol (2g.) was added, and the solution titrated to a blue end-point.

Determination of bipyridyl and o-phenanthroline.

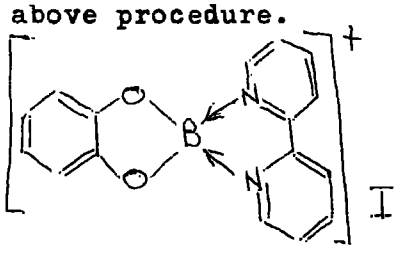
The unusual hydrolytic stability of the boronium salts

required the use of hot concentrated sulphuric acid for a quantitative liberation of either bipyridyl or o-phenanthroline. Quantitative studies confirmed the stability of both bases under the conditions required for decomposition of the boronium salts.

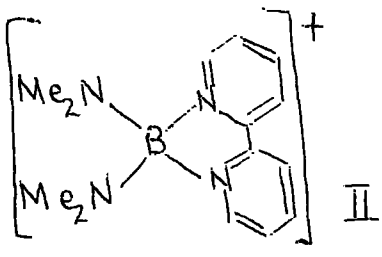
The bases were determined colorimetrically after addition of ferrous sulphate and ammonium citrate, and the instrument response compared to a calibration graph prepared from solutions of known strength.

A sample (30-50mg.) of the compound for analysis was dissolved in 1cc. concentrated sulphuric acid, and the solution heated to 180° for 20mins. The solution was diluted with water to 100cc., and a 20cc. aliquot buffered to pH 5 with a 20% ammonium citrate solution, 1cc.,7%, ferrous sulphate solution added, and the solution made to 100cc. with water. The absorption of the coloured solution was measured at 522mμ on an Eel-spectra spectrophotometer using a 1cm. cell.

Analysis for bipyridyl in salts containing either the bipyridylyl-o-phenylenedioxyboronium, (I), or bipyridylylbis-dimethylaminoboronium, (II), salts, required modification to the above procedure.



I



II

Salts containing the cation, I, were decomposed by sulphuric acid and the resulting solution made strongly alkaline with

sodium hydroxide solution. Free bipyridyl was removed by ether extraction, and then re-extracted into dilute sulphuric acid. The final solution was diluted to a known volume, and bipyridyl determined by the colorimetric method previously described.

Acid decomposition on compounds containing the cation, II, was found unsatisfactory. In these compounds, decomposition was effected after refluxing with 3N. sodium hydroxide. Bipyridyl was removed by ether extraction, and re-extracted into dilute sulphuric acid. After dilution to a known volume, bipyridyl was determined colorimetrically.

Potentiometric titrations.

Nitrogen gas, presaturated with water vapour, was introduced into the titration vessel contained in a thermostat. The glass and calomel electrode assemblies were connected to a Doran direct reading pH meter. Titrant was introduced into the titration vessel from a micro-burette.

Aqueous alcoholic solutions of 2-2', bipyridylyldiphenylboronium hydroxide, prepared from the chloride and freshly prepared silver oxide, were titrated against a standard acid solution. The resulting titration curve (Fig.1) is that expected for a strong base.

Aqueous solutions of 2-2',bipyridylyldiphenylboronium hydrogen sulphate titrated against standard sodium hydroxide solution (Fig.1) gave a titration curve that was consistent with the formulation as an acid salt.

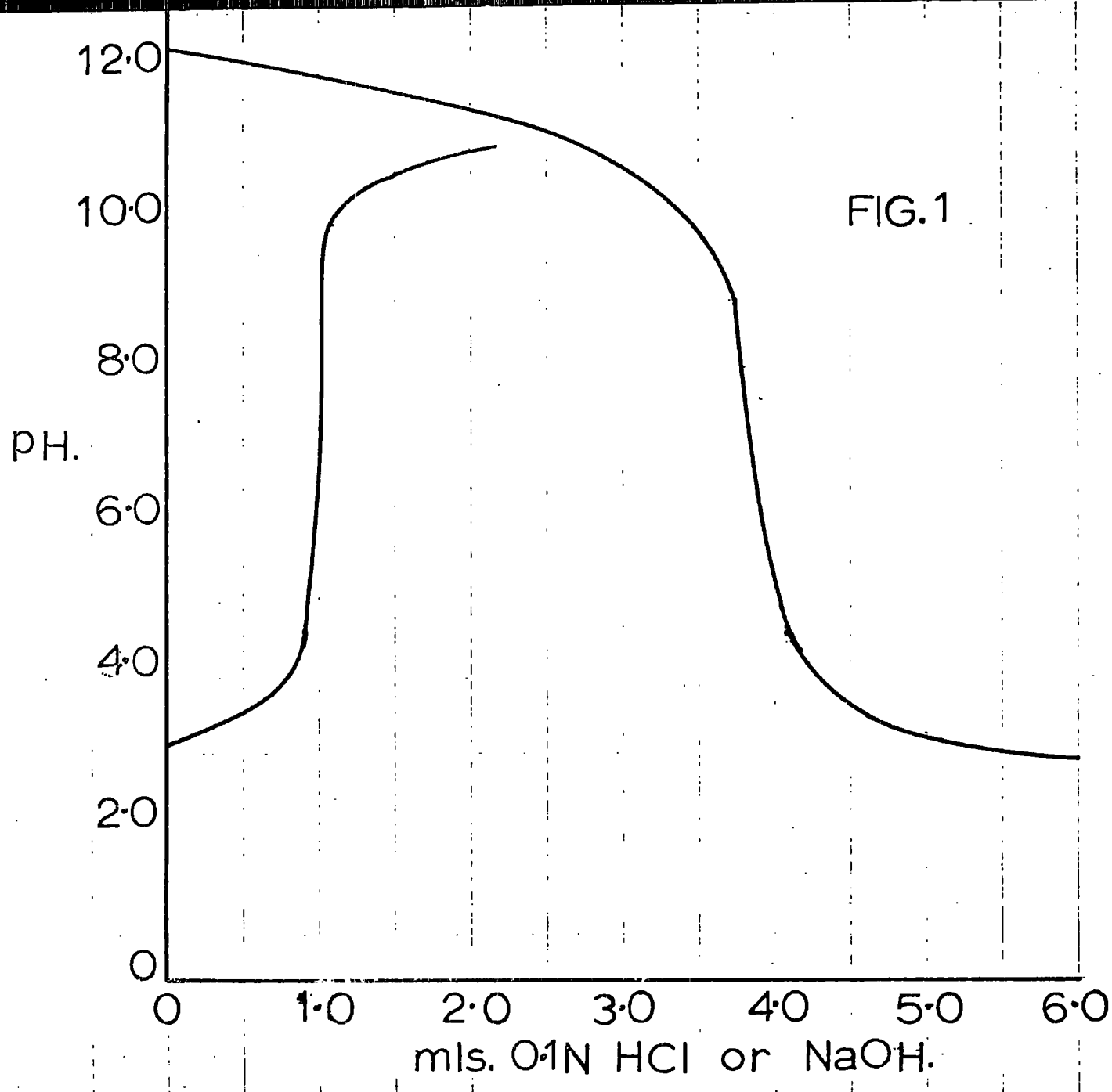


FIG. 1

Preparation of reagents.

2,2'-Bipyridyl.

The crude solid from I.C.I. Dyestuffs Division was available in the laboratory. Purification was effected by vacuum sublimation at 70-80° and 0.1mm.Hg pressure, m.p. 72°.

o-Phenanthroline.

The compound was available commercially as a mono-hydrate. Anhydrous o-phenanthroline was obtained from the hydrate by vacuum sublimation at 150° and 0.1mm.Hg pressure, m.p. 120°.

Diphenylboron chloride.

Diphenylborinic acid was converted to diphenylboronous anhydride, and this compound was reacted with boron trichloride in methylene chloride at -78° to give diphenylboron chloride.

Diphenylborinic acid. a) Prepared from trimethoxyboroxine and phenylmagnesium bromide.

Trimethoxyboroxine (8.7g., 0.05moles) in ether (90cc.) was added over a period of 2hrs. to an ether solution of phenylmagnesium bromide (0.48moles), maintaining the temperature between 24-26°. The mixture was stirred for a further 2hrs. after the addition of boroxine, and then hydrolysed by the slow addition of dilute hydrochloric acid (1:3 v.v.). The ether layer was separated, washed three times with water, and distilled to low volume.

Any boronic acid was removed by heating the crude product with water (25cc.) over a steam bath, and the liquid product,

diphenylborinic acid, purified by conversion to the monoethanolamine ester by the addition of aqueous ethanolamine (9cc. in 40cc. water). The ester collected after filtration was washed with water and finally crystallised from methylated spirits. (Yield of ester, 19g., 56%; m.p. 195°).

b) Prepared from dichlorodiphenylamino-borane and phenylmagnesium bromide.

Diphenylamine (191g., 1.13moles), purified by vacuum distillation, was dissolved in benzene (900cc.), and the solution slowly added over 3hrs. to boron trichloride (140g., 1.19moles) dissolved in benzene (1800cc.) under an atmosphere of nitrogen, and the temperature maintained at 6°. The resulting solution was refluxed under a nitrogen atmosphere for about 1hr., during which time hydrogen chloride was released.

Finally, the solution was concentrated by distillation to a volume of about 1500cc., and the strength of the solution determined by analysis.

Phenylmagnesium bromide (0.5moles) in ether (400cc.) was added slowly with stirring, to an aliquot of the above dichlorodiphenylamino-borane solution (325cc.=50g. Ph_2NBCl_2,) under a nitrogen atmosphere. The mixture was refluxed for ½hr., and then hydrolysed with dilute hydrochloric acid to pH 6.0-7.0. The organic layer was separated and solvent removed at the pump to leave crude borinic acid which was heated with water (100cc.) on a water bath to remove boronic acid.

The borinic acid was dissolved in ether (100cc.) and precipitated as the monoethanolamine ester by the addition of ethanolamine (44cc. in an equal volume of water), and crystallised free of diphenylamine from methylated spirits.(Yield of ester, 30g.,67%; m.p. 195°).

Hydrolysis of the ester to diphenylborinic acid.

The monoethanolamine ester was dissolved in a mixture containing equal volumes of acetone and methanol, and hydrolysed with dilute hydrochloric acid (12%). The borinic acid was ether extracted and the solution dried with anhydrous magnesium sulphate before removal of ether at reduced pressure from pure diphenylborinic acid.

Preparation of diphenylboronous anhydride.

The borinic acid, prepared as described above, was pumped (0.01mm.Hg) at room temperature with frequent agitation for 3-4hrs. The resulting pale yellow solid was transferred under nitrogen to a Soxhlet extractor, and extracted with hexane. The coloured solution on cooling deposited white crystals of pure diphenylboronous anhydride (m.p. 142°).

Preparation of diphenylboron chloride.

A solution of diphenylboronous anhydride (50g.,0.276moles) in methylene chloride (160cc.), was added dropwise, with stirring and under nitrogen, to a cooled (-78°) solution of boron trichloride (16.8g.,0.143moles) in methylene chloride (60cc.). Excess solvent was removed by distillation under nitrogen, and

the last trace of solvent was removed at the pump. Diphenylboron chloride was vacuum distilled from a crust of boron oxychloride and purified by a further vacuum distillation.(b.p.82°/0.05mm.Hg, Yield, 42g.,76%).

The methylene chloride used as solvent in this preparation was purified by washing with successive portions of water, 10% aqueous sodium carbonate, water, dried with anhydrous magnesium sulphate, and finally distilled.

The transfer of solutions containing methylene chloride or boron trichloride should be made through an all glass pourer, and not poly-vinyl chloride tubing. Greased joints should not be exposed to hot diphenylboron chloride, and are best replaced by teflon sleeves, perhaps lightly greased with a fluorocarbon grease.

Preparation of o-phenylenedioxyboron chloride.

A suspension of catechol (8.0g., 0.072moles), purified by sublimation, in methylene chloride (50cc.) was added dropwise, with stirring under nitrogen, to a solution of boron trichloride (10g., 0.085moles) in methylene chloride at -78°. The mixture was warmed to room temperature and the liberated hydrogen chloride and excess boron trichloride were absorbed by moist sodium hydroxide pellets. Excess solvent was removed by distillation under nitrogen, and the last trace of solvent was removed at the pump.

The crude product was vacuum distilled, and purified by

a further vacuum distillation.(b.p.64°/10mm.Hg, Yield,10g.,91%).

Bisdimethylaminoboron chloride.

A sample of this compound was kindly supplied by Dr.M.F. Lappert, and was used without further purification.

EXPERIMENTAL RESULTS.

The preparation of 2,2'-bipyridylyldiphenylboronium chloride.

A solution of bipyridyl (6.2g., 0.04moles) in benzene (40cc.) was added dropwise to a stirred solution of diphenylboron chloride (8g., 0.04moles) in benzene (40cc.) under a nitrogen atmosphere. A viscous yellow liquid separated from the benzene solution, but after stirring for a few minutes the liquid was replaced by a fine white powder. The solid product was washed with ether, and pumped dry to give 2,2'-bipyridylyldiphenylboronium chloride, (14g.,100%, m.p.333°(decomp.) lit.329°).

The monohydrate was obtained by crystallising the chloride from boiling water, and collected as fine needles, (Found: B,3.0; bipy,41.2; Cl,9.4. $C_{22}H_{20}BClN_2O$ requires B,2.9; bipy,41.7; Cl,9.5%).

The reaction between diphenylborinic acid and bipyridyl.

A small amount of an equimolecular mixture of diphenylborinic acid and bipyridyl was heated to 200° for a few minutes. The resulting melt was cooled and extracted with hot water and addition of dilute mineral acid (hydrochloric, nitric, and sulphuric acid) resulted in precipitation of the respective salts

containing the bipyridylyldiphenylboronium cation. Yields from this preparation were extremely low.

The reaction was repeated in nitrobenzene and also in benzene under reflux conditions, and after removal of solvent by distillation, the concentrated solution was extracted with hot water. Addition of dilute mineral acids resulted in precipitation of the boronium salts, but the yield was again extremely low.

The preparation of bipyridylyldiphenylboronium chloride from diphenylborinic acid, bipyridyl, and hydrochloric acid.

Diphenylborinic acid,(1.8g., 0.01moles), was refluxed with a solution containing bipyridyl (1.5g., 0.01moles), in 50% hydrochloric acid (50cc.), for about 2hrs. During this period, the upper layer of borinic acid gradually diminished, and after cooling the colourless solution the hydrated chloride slowly crystallised (1.5g.,50%).

The monoethanolamine ester of diphenylborinic acid may be used instead of the free acid, and was found not to affect the yield of the boronium chloride.

Diphenylborinic acid, bipyridyl, and hydriodic acid.

The ethanolamine ester of the borinic acid (4.5g, 0.02moles) was refluxed for about 3hrs. with a solution of bipyridyl (3.1g., 0.02moles),in 40% hydriodic acid (100cc.). Bipyridylyl-diphenylboronium iodide separated as the yellow crystalline hydrate (5.5g.,60%).

Diphenylborinic acid, bipyridyl, and sulphuric acid.

Diphenylborinic acid was observed to decompose on refluxing with 50% sulphuric acid, and consequently no boronium salt was isolated from this reaction.

Attempted preparation of 2,2'-bipyridylyldiphenylboronium hydroxide.

A freshly prepared suspension of silver oxide in alcohol was made from silver nitrate (3g.) dissolved in water to which was added a dilute solution of sodium hydroxide. The resulting precipitate was repeatedly washed with water to remove excess alkali, and finally washed with alcohol.

The alcoholic suspension of silver oxide was added to a solution of bipyridylyldiphenylboronium chloride (1g.) in alcohol (10cc.), and the mixture shaken for about 10mins. Excess silver oxide and precipitated silver chloride were removed by filtration, and the colourless filtrate was found to be strongly alkaline (pH 12). Removal of solvent by flash distillation left a yellow residue, which on pumping darkened to a brown tar.

This tar redissolved in alcohol to give a neutral, brown coloured solution, and addition of excess dilute nitric acid did not precipitate the nitrate, nor was free bipyridyl detected in the alcoholic solution.

Preparation of bipyridylyldiphenylboronium salts from the base.

Addition of excess mineral acids to aqueous or alcoholic solutions of bipyridylyldiphenylboronium hydroxide generally resulted in the immediate precipitation of the corresponding

salt. The salts were readily recovered by crystallisation from water in which they are sparingly to moderately soluble.

Analytical data for several salts prepared by this method, or by direct metathesis from the chloride in aqueous solution, are presented in TABLE 1.

TABLE 1.

Z, denotes the 2,2'-bipyridylyldiphenylboronium cation, (Ph_2Bbipy).

Compound	m.p.°C (decomp.)	Found(%)	Molecular formula	Required(%).
(Z)ClO_4	320	- ;bipy36.5	$C_{22}H_{18}BClN_2O_4$	-;bipy37.1
(Z)Br,H_2O	370	B,2.6;bipy37.3	$C_{22}H_{20}BBrN_2O$	B,2.6;bipy37.3
*(Z)I,H_2O	345	B,2.5;bipy34.0	$C_{22}H_{20}BIN_2O$	B,2.3;bipy33.6
*(Z)CNS	273	B,3.0;bipy41.1	$C_{23}H_{18}BN_3S$	B,2.9;bipy41.2
*(Z)N_3	217	B,3.0;bipy43.1	$C_{22}H_{18}BN_5$	B,3.0;bipy43.0
*(Z)$SSPMe_2$	228	-;bipy35.5	$C_{24}H_{24}BN_2PS_2$	-;bipy35.1
*(Z)BPh_4	204	B,3.4;bipy25.0	$C_{46}H_{38}B_2N_2$	B,3.4;bipy24.5
(Z)NO_3,$\frac{1}{2}H_2O$	263	B,2.8;bipy40.2	$C_{22}H_{19}BN_3O_{3.5}$	B,2.8;bipy39.9
(Z)HSO_4H_2O	275	B,2.7;bipy35.3	$C_{22}H_{21}BN_2O_5S$	B,2.5;bipy35.9

Salts marked by asterisk are isolated as yellow solids.

Preparation of 2,2'-bipyridylyldibutylboronium iodide.

Impure bipyridylyldibutylboronium chloride was prepared from dibutylboron chloride and bipyridyl in benzene solution.

The chloride was dissolved in water, and to the solution was added an aqueous solution of potassium iodide. The yellow iodide was precipitated and recrystallised from water. (Found: B,2.7 ; bipy,37.5. $C_{18}H_{26}BIN_2$ requires B,2.7; bipy,38.3%. m.p.226°decomp.)

Preparation of o-phenanthrolinediphenylboronium chloride, $(Ph_2Bo\text{-phenan})Cl.H_2O$.

o-Phenanthroline (3.6g., 0.02moles) in benzene (60cc.) was added dropwise with stirring, under nitrogen, to diphenylboron chloride (4g., 0.02moles) in benzene (100cc.).

A viscous yellow liquid separated, but this changed to a fine white powder after a few minutes stirring. No appreciable increase in the temperature of the reaction mixture was observed. The solid was collected by filtration, washed with ether, and finally pumped dry to give o-phenanthrolinediphenylboronium chloride (7.7g.,100%), recrystallised from boiling water (Found: B,2.7; phenan,46.0. $C_{24}H_{20}BClN_2O$ requires B,2.7; phenan,45.3%. m.p.275° decomp.).

The corresponding nitrate, $(Ph_2Bo\text{-phenan})NO_3.\frac{1}{2}H_2O$, (Found: B,2.7; phenan,43.7. $C_{24}H_{19}BN_3O_{3.5}$ requires B,2.6; phenan,43.3%, m.p. 209° decomp.), and iodide, $(Ph_2Bo\text{-phenan})I.H_2O$, (Found: B,2.3; phenan,37.3 $C_{24}H_{20}BIN_2O$ requires B,2.2; phenan,36.9%, m.p. 330° decomp.), precipitated from aqueous solution after addition of the appropriate acid to an aqueous solution of the chloride. Both the colourless nitrate and yellow iodide were recrystallised from hot water.

Attempted preparation of o-phenanthrolinediphenylboronium hydroxide.

o-Phenanthrolinediphenylboronium chloride (2g.) was dissolved in alcohol, and shaken with a freshly prepared slurry of silver oxide in the same solvent. A purple-red colour developed almost immediately, and after filtration, the solution was found to be just alkaline (pH8.0). Addition of excess dilute nitric or hydriodic acid failed to precipitate the nitrate or iodide.

In a further experiment the chloride (2g.) and silver oxide were shaken in a water slurry, and no colour developed in the solution. Excess silver oxide and silver chloride were removed by filtration, and the filtrate was found to be strongly alkaline (pH 12). Addition of excess dilute nitric or hydriodic acid caused immediate precipitation of the boronium salt.

The aqueous solution of base was observed to thicken to almost a jelly after standing for several hours, and was then found to be neutral (pH 7). Addition of dilute nitric acid to this 'jelly' failed to precipitate the boronium salt.

It was noted that addition of o-phenanthrolinediphenylboronium chloride to an alcoholic potassium hydroxide solution gave an immediate mauve solution, but o-phenanthroline under the same conditions gave no colour.

The reaction between diphenylboron chloride and ethylenediamine

Ethylenediamine (1.2g., 0.02moles) in benzene(40cc.) was added dropwise with stirring to diphenylboron chloride

(4g., 0.02moles) in benzene (50cc.) under nitrogen. A white solid separated immediately, and an increase in the temperature of the mixture was noted. The solid was collected by filtration, washed with ether, and pumped dry to give the product (5g.,100%), (Found: B,4.1; Cl,13.6 $C_{14}H_{18}BClN_2$ requires B,4.2; Cl,13.6%, m.p. 322° decomp.). The product was soluble in water, but could not be recovered from solution. Addition of dilute nitric acid, or potassium iodide, to the solution did not precipitate an insoluble salt.

The reaction between diphenylboron chloride and N,N,N',N'-tetramethylethylenediamine.

The amine (1.2g., 0.01moles) in benzene was added dropwise and with stirring to diphenylboron chloride (2g., 0.01moles) in benzene (15cc.) under nitrogen. The final pale yellow solution was cloudy, and after refluxing for about 1hr., a small amount of white solid separated from solution. The solid was collected by filtration, washed with ether, and pumped dry. Prolonged exposure to air or solution in water resulted in hydrolysis of the solid.

The reaction between o-phenylenedioxyboron chloride and bipyridyl.

Bipyridyl (8.5g., 0.054moles) in benzene (100cc.) was added dropwise to a stirred solution of o-phenylenedioxyboron chloride (8.2g., 0.054moles) in benzene (50cc.) under nitrogen.

Initial addition of the bipyridyl solution gave a red precipitate which quickly turned yellow, and after addition of

one half of the bipyridyl solution the precipitate was mostly yellow, but did contain some red material. The product after addition of the second half of the bipyridyl solution was an intense orange coloured solid.

The air sensitive product was Soxhlet extracted with benzene to remove any unreacted reagents, and then with methylene chloride in an attempt to separate the mixture of products. Early extractions were apparently richer in the red constituent, but the final solution gave only the original orange mixture.

In subsequent reactions, considerable attention was paid to the exclusion of air and moisture, but in all instances, the final product was an orange solid. In one experiment, o-phenylenedioxyboron chloride was added to the bipyridylsolution, and in this case a yellow solid formed initially, but the final product was the usual orange mixture.

The mixture in water gave a yellow solution in which chloride and free bipyridyl were detected. Concentration of such solutions to low volume did not give a solid product.

Preparation of bipyridylyl-o-phenylenedioxyboronium iodide and perchlorate.

A sample of the above mixture was dissolved in water to give a yellow solution, which was filtered from a small amount of an insoluble red solid. To the solution was added an aqueous solution of potassium iodide and the mixture set aside for several hours, during which time orange crystals of bipyridylyl-

o-phenylenedioxyboronium iodide tetrahydrate separated from solution (Found: B,2.3; bipy,33.0; I,26.6. $C_{16}H_{20}BIN_2O_6$ requires B,2.3; bipy,33.0; I,26.8%). The salt is rapidly hydrolysed by boiling water, and decomposes when heated.

The corresponding perchlorate was obtained as yellow needles from aqueous solutions of the iodide and sodium perchlorate (Found: bipy,41.1. $C_{16}H_{12}BClN_2O_6$ requires bipy,41.8%).

The reaction between bisdimethylaminoboron chloride and bipyridyl.

Bipyridyl (6.3g., 0.04moles) in benzene solution was added dropwise with stirring to a benzene solution of bisdimethylaminoboron chloride (5.3g., 0.04moles) under nitrogen. The initial yellow solution deposited an orange solid with the continued addition of the bipyridyl solution.

The mixture was filtered under nitrogen and the orange solid (7.8g.) washed several times with ether before pumping off solvent. The yellow filtrate was discarded.

A small sample of the orange solid quickly decomposed on exposure to air with liberation of free bipyridyl and dimethylamine. The solid was found to be soluble in a variety of polar and non-polar solvents to give coloured solutions, and in particular, addition of silver nitrate solution to a yellow aqueous solution gave an immediate precipitate of silver chloride. Analysis of the orange solid suggested a mixture of products (Found: Cl,13.8; bipy,58.7. $(bipyB(Me_2N)_2)Cl$ requires Cl,12.3; bipy,53.7%).

Preparation of bipyridylylbisdimethylaminoboronium tetraphenylborate. $(bipyB(NMe_2)_2)BPh_4$.

An isopropanol solution of the impure chloride, prepared as described above, was mixed with a solution of sodium tetraphenylborate in the same solvent. An orange precipitate was formed immediately and this was collected by filtration.

Exposure of this solid to air did not cause any apparent decomposition, and in particular, no free bipyridyl nor dimethylamine was detected. The solid was insoluble in water, alcohol, and acetone, but very soluble in chloroform to give a red solution.

The solid was recrystallised from ether-chloroform* mixtures as red rhombic crystals contaminated with dimethylammonium tetraphenylborate (identified from m.p. and comparison of the i.r. spectrum with that for an authentic sample of dimethylammonium tetraphenylborate). A pure sample of bipyridylylbisdimethylaminoboronium tetraphenylborate was obtained after several recrystallisations from the chloroform-ether solvent, (Found: C,78.8; H,7.5; B,3.6; bipy,26.9. $C_{38}H_{40}B_2N_4$ requires C,79.4; H,7.0; B,3.8; bipy,27.2%).

* The chloroform-ether mixture was prepared as follows:- A strong chloroform solution of the impure salt was prepared, and to this was added ether just to the point of precipitation. The solution was set aside in a closed flask until precipitation occured.

Ultraviolet and visible absorption spectra for some boronium salts.

Spectra were recorded with an OPTICA CF_4 recording grating spectrophotometer.

In the series of salts $(Ph_2Bbipy)^+X^-$, where X = Cl, Br, NO_3, HSO_4, ClO_4, the compounds are white solids. However, where X = I, CNS, N_3, $SSPMe_2$, BPh_4, the salts are yellow solids, dissolving in water to give colourless solutions. Solutions of these salts in solvents of low dielectric constant are strongly coloured. Similar observations hold for the series, $(Ph_2Bphen)^+X^-$, and $(Bu^n_2Bbipy)^+I^-$.

In contrast, the salts, bipyridylyl-o-phenylenedioxy-boronium iodide and perchlorate, give coloured aqueous solutions.

These colours are considered due to charge-transfer transitions from the anion to the π-electron system of the bipyridyl or phenanthroline. Such a transition will require the anion and cation to be in fairly close proximity. In solutions of polar solvents the ions will be separated and no transfer of charge is to be expected.

In the following tables are to be found details of the u.v. and visible absorption spectra for several boronium salts in solvents of varying dielectric constant.

TABLE 2.

Molar extinction coefficients for several boronium salts, (Z = (Ph_2Bbipy); C = (Ph_2Bphenan).), obtained in methanol solution (10^{-5}mol/l).

λ(mμ)	log E.				
	ZI	ZCNS	ZN_3	$ZBPh_4$	CI
199	4.2355	4.4011	4.3532	4.3643	4.3389
209	4.7040	4.6412	4.6081	5.0055	4.6849
219	4.5821	4.3945	4.3740	4.7245	4.7184
229	4.4314	4.2720	4.2290	4.5725	4.6672
239	4.3849	4.3389	4.3129	4.5437	4.2355
249	4.1453	4.1358	4.1066	4.2644	3.7993
259	3.3655	3.3909	3.3747	3.7324	3.9791
269	3.2480	3.2148	3.1644	3.5705	4.2904
279	3.4728	3.4440	3.3909	3.4983	4.4723
289	3.8028	3.7745	3.7404	3.7443	4.0802
299	4.0656	4.0331	4.0103	3.9983	3.8325
309	4.1066	4.0965	4.0592	3.9274	3.6875
319	3.8910	3.9217	3.8579	3.8938	2.9868

TABLE 3.

Molar extincion coefficients for bipyridylyldiphenylboronium chloride in chloroform (10^{-3}mol/l), and bipyridylyl-o-phenylene-dioxyboronium iodide in methanol (10^{-3}mol/l).

$(Ph_2Bbipy)Cl$		$(C_6H_4O_2Bbipy)I$	
λ(mμ)	log E	λ(mμ)	log E
319	-	327	-
329	-	337	2.6588
339	2.8245	347	1.8938
349	2.3459	357	1.7818
359	1.9070	377	1.7251
369	1.5866	397	1.7042
379	1.4298	417	1.6128
389	1.3483	437	1.4654
		457	1.3010
		477	1.0414
		497	0.6435

TABLE 4.

Molar extinction coefficients for (Ph_2Bbipy)I in solvents of varying dielectric constant.(10^{-3}mol/l).

λ(mμ)	log E					
	$CHCl_3$	CH_2Cl_2	$Cl.CH_2.CH_2Cl$	C_4H_9OH	C_2H_5OH	CH_3OH
319	3.2477	-	-	-	-	-
329	-	-	-	-	3.1294	2.8580
339	3.2477	3.1911	3.1294	2.7923	2.6175	2.3489
349	3.0671	3.0195	2.9693	2.5035	2.2720	1.8162
359	2.8311	2.7986	2.7923	2.1934	1.6609	1.1206
369	2.6471	2.6353	2.6294	2.0149		
379	2.4911	2.4849	2.4723	1.9217		
389	2.4210	2.3945	2.3532	1.8325		
399	2.3740	2.3389	2.2720	1.7251		
409	2.3600	2.3098	2.2106	1.5866		
419	2.3389	2.2720	2.1987	1.3483		
429	2.3098	2.2485	2.1812	1.1903		
439	2.2797	2.2274	2.1724	1.0414		
449	2.2106	2.1724	2.1358	0.8195		
459	2.1262	2.0867	2.0867	0.3424		
469	2.0216	1.9741	2.0103			
479	1.8488	1.8325	1.8938			
489	1.6693	1.6609	1.7634			
499	1.3483	1.4298	1.5966			
509	0.8195	1.0414	1.4983			
519	-	-	1.1206			

TABLE 5.

Molar extinction coefficients for several boronium salts, (Z = Ph_2Bbipy; D = $C_6H_4O_2$Bbipy; E = $(Me_2N)_2$Bbipy) in chloroform solution (10^{-3}mol/l).

λ(mμ)	log E.				
	ZCNS	ZN_3	$ZSSP(Me)_2$	DI	$EBPh_4$
337	2.9907	3.0237	3.2610	-	3.3619
347	2.7366	2.7672	3.0923	3.1632	3.2303
357	2.4911	2.5211	2.9190	3.0298	3.1523
367	2.4038	2.3643	2.7759	2.8513	3.1000
377	2.4077	2.3025	2.6648	2.6353	3.0511
387	2.4275	2.3025	2.6057	2.4404	3.0216
397	2.4038	2.3318	2.5701	2.2949	2.9907
407	2.3054	2.3459	2.5401	2.2156	2.9474
417	2.1987	2.3532	2.5217	2.2073	2.8994
427	2.0216	2.3432	2.5035	2.2485	2.8513
437	1.7993	2.3129	2.4533	2.2874	2.7859
447	1.3655	2.2644	2.3807	2.3025	2.7257
457	-	2.1953	2.2874	2.3098	2.6660
467	-	2.1165	2.1635	2.3098	2.6033
477	-	2.0103	1.9983	2.2797	2.5279
487	-	1.8938	1.8062	2.2400	2.4469
497	-	1.7443	1.5866	2.1635	2.3532
507	-	1.6128	1.2695	2.0965	2.2402
517	-	1.4440	-	1.9983	2.1066
527	-	1.3010	-	1.8639	1.9538
537	-	1.0414	-	1.7251	1.7520
547	-	0.6435	-	1.5302	1.3979
557	-	-	-	1.3010	-

TABLE 6:- INFRA-RED SPECTRA.

$(Ph_2Bbipy)Cl.H_2O$.

3472; 3413s(sh); 3077m; 2994m; 1626vs; 1600m; 1567w; 1508m; 1475s; 1453s; 1431m; 1316s; 1258w; 1205w; 1193s; 1183w; 1152s; 1120m; 1087w; 1078s; 1030vw; 995vw; 909vw; 895vw; 881w; 873w; 814w; 781vs; 775m(sh); 749m; 733s; 725vs; 704vs; 633w; 614m.

$(Ph_2Bbipy)Br.H_2O$.

3472s; 3413s(sh); 3077m; 3040m; 2994m; 1618vs; 1592s; 1563m; 1504s; 1471vs; 1449s; 1311vs; 1261m; 1250m; 1205m; 1190vs; 1179m; 1149vs; 1117s; 1087m; 1075s; 1026w; 995w; 907vw; 893vw; 881m; 873m; 834vw; 816m; 803vw; 775vs; 769s(sh); 748s; 732vs; 721vs; 704vs; 630m; 614s.

$(Ph_2Bbipy)I.H_2O$.

3401vs; 3049m; 2994m; 1618vs; 1563w; 1499; 1466s; 1449vs; 1429s; 1422s; 1309m; 1261w(sh); 1250w; 1208w; 1192s; 1179w; 1149vs; 1114s; 1087w; 1072vs; 1028w; 995w; 898w; 877m; 833vw; 813w; 803w; 772vs; 763m(sh); 752vs; 741m; 732s; 721vs; 709s(sh); 704vs; 647vw; 634w; 626vw; 614s.

$(Ph_2Bbipy)ClO_4$.

3448m; 3058w; 3012vw; 1623vs; 1567w; 1504m; 1471s; 1453vs; 1433m; 1429m; 1316s; 1253m; 1212w; 1198s; 1183w; 1152s; 1107vs; 1087vs; 1075vs; 1031m; 1000w; 971vw; 930vw; 899w; 881m; 836vw; 814m; 772vs; 752s; 741s; 735s; 725s; 704vs; 635m; 623vs; 614s;

$(Ph_2Bbipy)CNS$.

3077m; 3049m; 2994m; 2062vs; 1618s; 1563m; 1502m; 1471s; 1449s; 1429s; 1312s; 1250m; 1208w; 1193s; 1179m; 1149s; 1117s; 1089w; 1075s; 1031m; 995w; 897w; 877m; 836vw; 816w; 806vw; 770vs; 763m(sh); 749s; 732s; 721vs; 699vs; 667vw; 647vw; 634w; 626w; 612s.

$(Ph_2Bbipy)N_3$.

3390s; 3058m; 3003m; 2119m; 2033s(sh); 2012vs; 1626vs; 1567w; 1511m; 1471s; 1456vs; 1433s; 1429s; 1312s; 1256m; 1209m; 1195s; 1182m; 1149s; 1119m; 1089w; 1075s; 1029w; 995w; 895w; 877m; 873m; 833vw; 814w; 772vs; 749s; 741s(sh); 732vs; 721vs; 703vs; 647vw; 633w; 626w; 614s.

$(Ph_2Bbipy)SSPMe_2$.

3030m; 2959w; 2882w; 1618vs; 1590w; 1563m; 1497s; 1464s; 1453vs; 1433m; 1429s; 1408s; 1397m; 1346w; 1311s; 1277w; 1263s; 1250m; 1209m; 1193s; 1149s; 1111s; 1083m; 1070vs; 1026m; 995m; 936s; 897vs; 889vs; 877s; 870s; 835s; 813m; 773vs; 763s; 752s; 735vs; 723vs; 704vs; 698vs; 633m; 602vs; 501s.

$(Ph_2Bbipy)BPh_4$.

3030m; 2986w; 1709w; 1626s; 1575m; 1504w; 1473s; 1453s; 1429s; 1316m; 1258w; 1220w; 1198m; 1182w; 1163w; 1149m; 1120m; 1091w; 1075m; 1031m; 1000vw; 880w; 867m; 846w; 810w; 769s; 742s; 731vs; 735s; 702vs; 633w; 624w; 613s; 604s.

$(Ph_2Bbipy)NO_3.\frac{1}{2}H_2O$.

3448m; 3077w; 3003w; 1621vs; 1567m; 1506m; 1471s; 1456vs; 1439vs; 1385vs; 1362vs; 1316vs; 1261m; 1209m; 1198s; 1183m; 1153s; 1120m; 1092w; 1076s; 1031w; 1000w; 909m(sh); 901m; 885m; 838w; 828m; 815m; 775vs; 753s; 743s(sh); 735s; 724vs; 709vs; 648w; 634m; 627w; 614s.

$(Ph_2Bbipy)HSO_4.H_2O$.

3413s; 3333m(sh); 3077w; 1626s; 1570w; 1508m; 1471m; 1456vs; 1429m; 1314s; 1294w; 1255m; 1211vs; 1198vs; 1163s(sh); 1153vs; 1124m; 1090w; 1076m; 1045vs; 893m(sh); 886s; 866s; 858s(sh); 816w; 775s(sh); 772vs; 760m; 746s; 735s; 722vs; 702vs; 633m; 612s; 592m; 578s.

$(Ph_2Bphenan)Cl.H_2O$.

3390s; 3030m; 2994m; 1653m; 1626s; 1605m; 1575m; 1520s; 1471m; 1439vs; 1403m; 1346vw; 1325w; 1316w; 1266w; 1224m; 1198s; 1147s; 1120w; 1098vw; 1068vw; 1031w; 995vw; 941m; 965m; 885w; 852vs; 840m; 784m; 758s; 732vs; 714vs; 690vs; 639m; 618m.

$(Ph_2Bphenan)I.H_2O$.

3448m; 3030w; 3003w; 1653w; 1626s; 1580m; 1527s; 1481vw; 1439vs; 1429m(sh); 1408w; 1370w; 1319w; 1266w; 1220w; 1205s; 1149s; 1117m; 1031vw; 995vw; 947w; 943m; 926w; 885w; 847vw; 800w; 787w; 760s; 738s; 729s; 709vs; 643w; 632vw; 617m.

$(Ph_2Bphenan)NO_3.\frac{1}{2}H_2O$.

3448s; 3049m; 3003w; 1653w; 1626s; 1575w; 1522s; 1475w; 1431s; 1422m(sh); 1403m; 1372vs; 1342vs; 1316s; 1261w; 1227w; 1215m; 1200s; 1149s; 1139m; 1119m; 1089vw; 1065vw; 1029vw, 995vw; 947w; 940m; 921w; 885w; 847s(sh); 841vs; 836s(sh); 826m; 757m; 735s; 709vs; 705vs; 641w; 633w; 617m.

$(Bu_2Bbipy)I$.

3040m; 3003m; 2941m; 2899m; 1618vs; 1563m; 1499s; 1471vs; 1449vs; 1439vs; 1418s; 1376m; 1370m; 1316m; 1304m(sh); 1277w; 1266m; 1250m; 1220m; 1205m; 1190w(sh); 1163m; 1151vs; 1133w; 1111s; 1096m; 1072vs; 1053m; 1028m; 1010w; 963m; 923m; 901w; 803m; 781vs; 732vs; 690m; 646m; 590m.

$(C_6H_4O_2Bbipy)I.4H_2O$.

3497vs; 3425vs; 3096m; 3058m; 3012m; 1626s; 1618s; 1600w; 1570m; 1506s; 1477vs; 1456vs; 1439m; 1429m; 1361m; 1348w; 1316s; 1261s; 1230vs; 1205m(sh); 1200m; 1176s; 1149vs; 1124vs; 1111s; 1099s; 1078s; 1032vs; 1015s; 1000m; 922w; 865w; 843m; 817s; 800s; 779m; 763vs; 758s(sh); 746s; 721s.

$(C_6H_4O_2Bbipy)ClO_4.4H_2O$.

3448m; 3106m; 3067m; 1639s; 1626s; 1600m; 1575s; 1515s; 1477vs; 1460vs; 1439s; 1370m; 1353m; 1319s; 1266s; 1235vs; 1198vs; 1149vs; 1093vs; 1026vs; 925s; 865s; 840m; 814s; 800s; 769vs; 763vs; 725s; 618vs;

$(bipyB(NMe)_2)BPh_4$.

3049; 2976m; 2867; 2825m; 2762m; 1616s; 1575m; 1555w(sh); 1497m; 1471s; 1449s; 1418s; 1330s; 1307s; 1290m; 1263w; 1255w; 1200m; 1176s; 1163m; 1156m; 1111m; 1089s; 1064s; 1053s; 1029m; 1010s; 961w; 901w; 862m; 840m; 769s; 748s; 735vs; 728vs; 714s; 704vs; 666m; 629w; 621w; 608s.

Abbreviations:- vs = very strong; s = strong; m = medium w = weak; vw = very weak; sh = shoulder.

Part I.

DISCUSSION

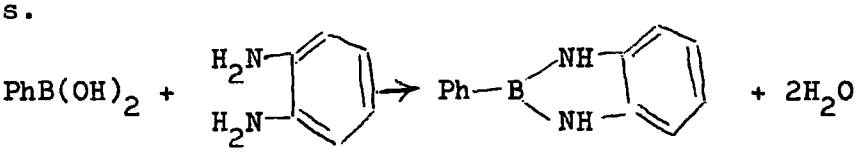
DISCUSSION.

The boronium salts described in this work, and those described by other workers, contain a coordinately saturated boron ion, and this fact is reflected in the overall stability exhibited by many of the reported boronium salts. In particular, the bipyridylyldiphenylboronium cation displays marked hydrolytic stability to boiling water, and even hot solutions of strong acids.

It is perhaps of interest to compare the original preparation[1.] of bipyridylyldiphenylboronium chloride from bipyridyl and diphenylboron chloride in nitrobenzene solution , with that for the same reactants in benzene solution. Conductivity measurements of diphenylboron chloride in nitrobenzene solution show the existence of a diphenylboronium ion, and this will certainly be associated with solvent. The addition of bipyridyl to this solution results in an exothermic reaction, presumably as the bidentate ligand replaces the solvate molecules. In benzene solution however, no ionisation of the boron chloride is to be expected and the first stage of reaction with bipyridyl must be initial donation from a single nitrogen atom to the boron. This stage of the reaction probably corresponds to the observed viscous liquid product separating from benzene solution. The onset of salt formation requires displacement of chloride ion with chelation by the second nitrogen atom of the bipyridyl.

Formation of bipyridylyldiphenylboronium halides from diphenylborinic acid and bipyridyl in acid solution necessarily

requires displacement of a hydroxyl group from the borinic acid. This rather unusual reaction holds some similarities to the reactions of alkyl and aryl boronic acids or their esters, with aromatic diamines.[2,3,4] In particular, boronic acids with o-phenylenediamine in refluxing toluene form dihydrobenzoboradiazoles.



It appears that the spatial relationship of amino groups in o-phenylenediamine, and the formation of a five membered ring in the product are important factors in this reaction. A low melting 1:1 adduct has been isolated from aqueous methanol solution, and i.r. examination of this complex displayed the presence of amino groups as well as the hydroxyl group of the boronic acid. Subsequent melting of the adduct resulted in cyclisation.

The attempted preparation of boronium cations containing ethylenediamine or N,N,N¦N',tetramethylethylenediamine must be regarded as unsuccessful. Reaction of diphenylboron chloride with ethylenediamine in benzene solution gave an insoluble product with a composition in agreement to that for the boronium salt. However, this reaction was found to be exothermic, and the general properties of the salt-like product suggest an amine-hydrochloride. The very small amount of salt-like solid obtained from the reaction with N,N,N¦N'-tetramethylethylenediamine was

found to be readily hydrolysed in aqueous solution. The small yield of product and its hydrolytic instability suggest that steric overcrowding may prevent the formation of a stable boronium salt.

Reaction of e-phenylenedioxyboronchloride or bisdimethylaminoboron chloride with bipyridyl in benzene solution give products from which the boronium salts may be isolated, but there can be no doubt that the initial product is a mixture containing at least two constituents. The unexpected complexity of this reaction, compared to that with diphenylboron chloride is difficult to explain, but may involve a 1:1 adduct with only one nitrogen from bipyridyl donating to the boron atom.

The free bases, $(Ph_2Bbipy)OH$ and $(Ph_2Bphenan)OH$, could not be isolated, but aqueous solutions were prepared from the corresponding chlorides and freshly prepared silver oxide, and these solutions were found to be strongly alkaline, pH ~12. Alcoholic solutions of the strong base, $(Ph_2Bbipy)OH$, were apparently stable at room temperature, but attempts to concentrate the solution gave only a brown-tar, neutral to litmus paper, and contained neither the boronium cation, $(Ph_2Bbipy)^+$, nor free bipyridyl. Reaction of the salt, $(Ph_2Bphenan)Cl$, with silver oxide in alcoholic solution yielded a neutral, (pH 8), deep purple-red solution which contained no boronium ions, $(Ph_2Bphenan)^+$. Aqueous solutions of the base, $(Ph_2Bphenan)OH$, became viscous after several hours at room temperature, and were no longer alkaline.

It was noted that addition of o-phenanthrolinediphenylboronium chloride to an alcoholic potassium hydroxide solution gave an immediate mauve coloured solution, but o-phenanthroline under the same conditions produced no colour.

These observations suggest decomposition of the boronium cation following nucleophilic attack by hydroxyl or alkoxide ion on the heterocyclic nucleus.

Metathetical reactions.

The yellow iodide, $(Ph_2Bbipy)I$, is only sparingly soluble in water, and is precipitated when potassium iodide is added to an aqueous solution of the boronium chloride. The colourless bromide is a little more soluble. The thiocyanate, azide, tetraphenylborate, and dimethyldithiophosphinate, are all formed as yellow precipitates in aqueous solution; the dimethylphosphinate in contrast, is colourless and very soluble in water (it was prepared from the hydroxide and dimethylphosphinic acid, and not purified). The colourless perchlorate and nitrate are very sparingly soluble, and are precipitated at once from aqueous solutions of the chloride: the solubility of the nitrate in water at 25°, 3.6×10^{-3} moles l^{-1}., was calculated from the conductance of its saturated solution. The conductance of the chloride, $(Ph_2Bbipy)Cl$, in water at 25° was appropriate for a 1:1 salt, the molar conductance varied linearly with $C^{\frac{1}{2}}$ over the range from 2×10^{-4} to 0.01M, whence the conductance at zero concentration is 100.0 and the mobility of the boronium ion found

to be 23.7.

A sparingly soluble acid sulphate, $(Ph_2Bbipy)HSO_4.H_2O$, is precipitated when dilute sulphuric acid is added to an aqueous solution of the chloride. This was identified as an acid sulphate by potentiometric titration, and the water could be removed by heating at $140^{\circ}/0.01$mm.Hg. for 2hrs. The normal sulphate is evidently much more soluble, since no precipitate results when aqueous sodium sulphate is added to a neutral solution of the chloride, but addition of hydrochloric or sulphuric acid causes immediate precipitation of the hydrogen sulphate. It is surprising that not only the acid sulphate, but also the nitrate,chloride, bromide, and iodide crystallise from water as hydrates. Similarly the halides, $(Ph_2Bphenan)X.H_2O$, crystallised as monohydrates, and all absorb in the infra-red spectrum near $3470cm^{-1}$.

If the yellow iodide, $(Ph_2Bbipy)I.H_2O$, is kept at room temperature for several hours at a pressure of less than 0.01mm.Hg, the colour changes to orange, and the absorption at $3470cm^{-1}$ of a Nujol-mull prepared in a dry-box disappears. If a potassium iodide disc is prepared from this material in the usual way, the presence of water is then apparent from the spectrum. The anhydrous orange iodide takes up water when exposed to the air, reverting to yellow, and the absorption at $3470cm^{-1}$ returns. The yellow iodide, $(Ph_2Bphenan)I.H_2O$, is observed to undergo the same colour change during pumping at room temperature, and exposure of the orange solid to air results in a colour change

back to the original yellow solid.

The yellow bipyridylyldibutylboronium iodide, (Bu^n_2Bbipy)I, crystallises from water, after addition of potassium iodide to an aqueous solution of the chloride, in an anhydrous condition and prolonged evacuation of the crystals at less than 0.01mm.Hg., results in no colour change. Of the salts prepared, only the perchlorate, thiocyanate, azide, dimethyldithiophosphinate, and tetraphenylborate, crystallise in anhydrous form.

Addition of excess dilute acid (hydrochloric, hydrobromic, hydriodic, nitric, sulphuric, perchloric acid) to an aqueous solution of either (Ph_2Bbipy)OH, or (Ph_2Bphenan)OH, results in immediate precipitation of the corresponding salt.

Light absorption.

Since the coloured salts give colourless solutions in water (hot water in many instances), the colours are considered due to charge-transfer transitions from the anion to the π-electron system of the bipyridyl or phenanthroline. This behaviour is similar to that of the methiodides of several heterocyclic bases (e.g. quinoline methiodide), and has been discussed by Kosower and Burbach[5]. who made a detailed study of methylpyridinium iodide and showed that the absorption at about 300mμ was greater in ethanol than in water. These authors were able to explain on this basis Hantzsch's observations[6]. that the colour of ethylpyridinium iodide changes from colourless in water, in which the salt would be ionised and the ions well separated to deep yellow

in chloroform in which the salt would exist mainly in the form of ion-pairs or more complex aggregates.

The salts, $(Rh(bipy)_3)X_3$ and $(Rh(2,2';2'' \text{ terpy})_2)X_3$, where X = Cl, Br, I, SCN, ClO_4, have been prepared.[7] In these compounds, colours increase with increasing polarisability of the anion, ranging from colourless for the perchlorate and hydrated chloride, through various shades of yellow to a deep orange-red for the anhydrous iodide. Interionic charge transfer is considered and the increase in colour on dehydration, indicating a shift of the absorption to longer wavelength, is a result of the closer approach of the ions, lowering the energy required for charge transfer. The authors suggest charge transfer may occur by donation of charge from the anion to either the central metal atom, or the aromatic ring system of the ligand.

It is also of interest to note that colourless salts, $(Ga(phenan)_3)Cl_3$, $(Ga(phenan)_3)Br_3$, and orange-yellow $(Ga(phenan)_3)I_3$ are precipitated from ethereal solutions of gallium halides with phenanthroline.[8] The complexes are apparently stable in aqueous solution, but unfortunately the reference does not indicate the colour of the iodide in solution.

The bipyridylyldiphenylboronium salts discussed in this work were found to have strong absorption (log E, 4.5-5.0) at about 210mμ, with a shoulder or subsidiary peak at 235-240mμ, and less intensely (log E 4) at about 300-310mμ. Phenanthroline-boronium complexes have quite different spectra in this region

and the absorptions are no doubt due to π-π^* transitions within the heterocyclic system. The absorptions at longer wavelength, causing visible colour, are shown in FIG 2., which refers to 10^{-3} M. solutions of bipyridylyldiphenylboronium iodide in four solvents.

The absorptions in the polar solvents (curve A methanol, curve B ethanol) are the long wavelength tail of the 300-310mμ band already mentioned, but in butanol (dielectric constant 17 at 25°, curve C), an inflection due to the charge-transfer is apparent, and in chloroform (dielectric constant 4.8, curve D), the broad charge transfer band extends to about 500mμ. Spectra in methylene dichloride and ethylene dichloride (dielectric constants 9.1, and 10.4) are similar to curve D. These results are therefore in agreement with increasing charge-transfer as the dielectric constant of the solvent decreases. It is perhaps pertinent to observe that Winstein[9.] has shown that the dielectric constant is not a quantitative measure of solvent polarity, and proposed a series of Y values for solvents which give a kinetic measure for the ionising power of a solvent. Since charge-transfer bands are often measured in solvents for which Y values would be difficult to obtain, Kosower[10.] proposed a series of Z values as empirical measures of solvent polarity.

Rather broad absorption bands attributed to charge-transfer transitions are observed in the spectra of the neutral bipyridyl complexes, Me_2bipyBe and Et_2bipyBe.[11.] The colours of the

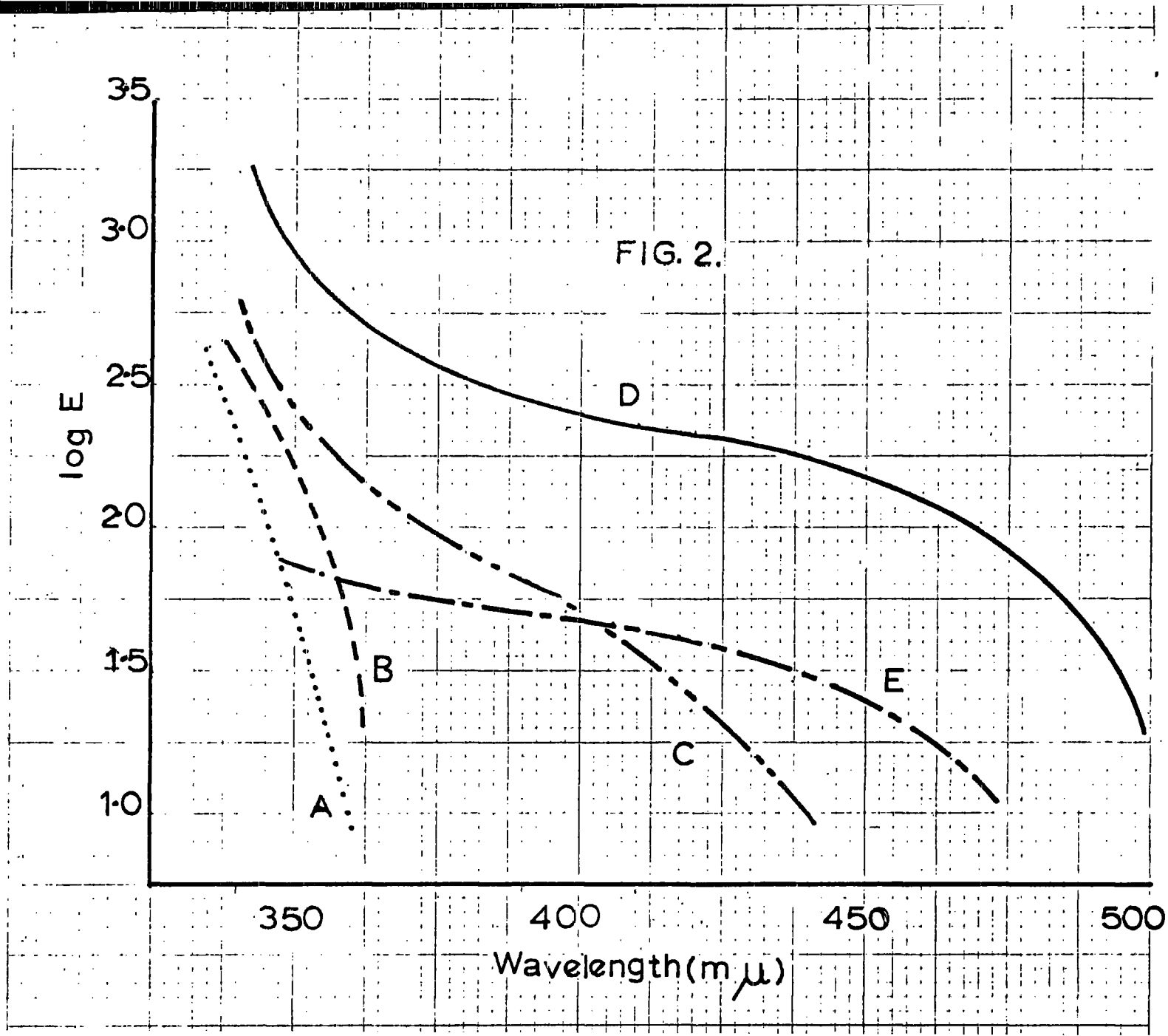


FIG. 2.
3·5
3·0
2·5
2·0
1·5
1·0
log E
A
B
C
D
E
350
400
450
500
Wavelength (mμ)

complexes, R_2bipyBe, deepen as the group R becomes less electronegative, and the colour is ascribed to a charge-transfer transition from a Be-C bond to the bipyridyl group. Most coordination complexes of dialkyl and diarylzinc with mono- and bidentate ligands are colourless, but certain complexes with bipyridyl and phenanthroline are coloured.[11,12] Dialkyl and diphenylzinc compounds with bipyridyl or phenanthroline in inert solvents give coloured solutions from which crystalline 1:1 complexes are isolated. The colour depends on the nature of the group bound to the zinc, being red for Pr^i, pale yellow for Ph., and colourless for Br and C_6F_5. Since the more electronegative groups on zinc increase the energy required for transition, this suggests that in the excited state of complex, the group R_2Zn acts as donor. For beryllium complexes, the values of $\lambda_{max.}$ and extinction coefficient decrease as the electron attraction of the group R increases. A similar relationship is found with the zinc complexes except for a reversed trend in absorption intensity, and this has been explained by interaction of the filled 3d electron shell with orbitals on the ligand molecule. The bipyridyl and phenanthroline complexes of several transition metal ions (including the d^{10} ion Cu^+) display long wavelength charge-transfer bands arising from transition of d electrons to vacant type ligand orbitals,[13] but Zn^{2+} complexes failed to show such bands.

The tendency of d^{10} transition metal ions to d_π bond

formation has been correlated with ionisation energy,[14] and in ditertiary arsine complexes of $\underline{d}^{10}$ ions, including Zn^{2+}, $\underline{d}_{\pi}$-$\underline{d}_{\pi}$ bonding is considered unimportant in view of the high I.P. of the non-bonding $\underline{d}^{10}$ shell.[15] However, the Zn-C bond is largely covalent and the formal positive charge of the metal and the ionisation energy of a $3\underline{d}$ electron is considerably less for organozinc complexes than for Zn-Br which probably has no charge-transfer band in the spectrum.

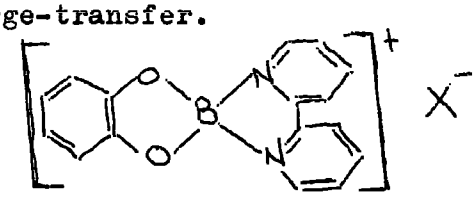
The absence of charge-transfer in bipyridylyldiphenylboronium chloride and bromide must be related to the higher electron affinities of these anions. To a first approximation, the energy required for the transition $M^+A^- \rightarrow MA$ is of the form, $W = E - I + \Delta$[16], where E is the electron affinity of the halogen, I the ionisation potential of the cation, and Δ the difference in energy between formation of a normal crystal and the crystal with a pair of adjacent atoms substituted for a pair of ions.

The spectrum of bipyridylyldiphenylboronium dimethyldithiophosphinate closely resembles that of the iodide, but above 360mμ, the extinction is a little greater (2.55 and 2.35 resp. at 400mμ). That of the azide is similar, but displays a broad maximum at about 420mμ instead of an inflection. That of the thiocyanate differs markedly in that the charge-transfer band (maximum at 300-400mμ) is much narrower, and the extinction coefficient falls rapidly above 410mμ, whereas those of the other salts just mentioned do not drop significantly until about

480-500mμ.

If the colours of these salts in the solid stat or in solvents of relatively low dielectric constant are due to charge-transfer between anion and cation, then it should be possible to prepare coloured bipyridylylboronium salts that retain their colour even in polar solvents if the charge-transfer takes place within the cation. This could occur if the boron were bound to nitrogen or oxygen atoms instead of to carbon (as in the dibutyl- and diphenylboronium salts already discussed), since there may be electron transfer from the 'lone pairs' of the nitrogen or oxygen into the π-electron system of the bipyridyl.

The preparation of coloured salts containing the bipyridylyl-o-phenylenedioxyboronium cation from the boron chloride and bipyridyl, indicate that 'lone pairs' of electrons can participate in such a charge-transfer.



The chloride (X = Cl) has not been isolated in a pure state, but aqueous solutions containing the salt are yellow. The colour of the anhydrous iodide (X = I) was similar in water, ethanol, and chloroform, but charge-transfer could take place both from oxygen and from the iodide anion. Intra-ionic charge-transfer occurs in the yellow perchlorate (X = ClO_4), which should be compared with the colourless salt, $(Ph_2Bbipy)ClO_4$. Salts containing the bipyridylyl-o-phenylenedioxyboronium cation

are found to be stable to warm water, but are rapidly hydrolysed when their aqueous solutions are heated to boiling.

The absorption spectrum of the iodide in methanol is shown in FIG.2, (curve E). Comparison with the spectrum of $(Ph_2Bbipy)I$ in the same solvent (curve A) indicates the absorption due to intra-ionic charge-transfer in the o-phenylenedioxy-boronium salt.

Reaction between bipyridyl and bisdimethylaminoboron chloride gave an orange-yellow product, which was quickly hydrolysed in air liberating dimethylamine and bipyridyl, and becoming dark red. However, the tetraphenylborate , $(bipyB(NMe_2)_2)^+Ph_4B^-$, was obtained in the form of ruby red rhombic crystals. The deep colour of this is probably mainly due to intra-ionic charge-transfer, but is not necessarily so, since the tetraphenylborate ion could act as an electron source, $(Ph_2Bbipy)^+Ph_4B^-$ being yellow like the iodide.

REFERENCES.

1) J.M.Davidson and C.M.French J.,1962,3364.

2) R.L.Letsinger and S.B.Hamilton J.Amer.Chem.Soc.,1958,80,5411.

3) R.J.Brotherton and H.Steinberg J.Org.Chem.,1961,26,4632.

4) B.M.Mikhailov and P.M.Aronovich Zhur.obshchei Khim.,1959,29,3124.

5) E.M.Kosower and J.C.Burbach J.Amer.Chem.Soc.,1956,78,5838.

6) A. Hantzsch Ber.,1919,52,1544.

7) C.M.Harris and E.D.McKenzie J.Inorg.Nuclear Chem.,1963,25,171.

8) B.N.Ivanov and L.A.Niselson Zhur.neorg.Khim.,1961,6,1142.

9) F.Grunwald and S.Winstein J.Amer.Chem.Soc.,1948,70,846,
1951,73,2700.

10) E.M.Kosower J.Amer.Chem.Soc.,1958,80,3253.

11) G.E.Coates and S.I.E.Green J.,1962,3340.

12) J.G.Noltes and J.W.G.Hurk J.Organometal.Chem.,1965,3,222.

13) A.Kiss and J.Czaszar Acta Chim.Acad.Sci.Hung.,1963,38,405,421.

14) R.S.Nyholm Proc.Chem.Soc.,1961,273.

15) J.R.Lewis,R.S.Nyholm and D.J.Philips J.,1962,2177.

16) L.E.Orgel Quart.Rev.,1954,8,422.

Part II.

INTRODUCTION

INTRODUCTION.

Object of investigation.

The preparation of beryllium borohydride was reported some 25 years ago, but apart from the one complex, trimethylamineberyllium borohydride, the coordination chemistry of beryllium borohydride has not been explored. This early work indicated that the 1:1 adduct, $Me_3N.BeB_2H_8$, reacted with more amine to give trimethylamine-borane and a compound, $(BeBH_5.NMe_3)_x$.

The object of this investigation is to study the coordination chemistry of beryllium borohydride in rather more detail. In particular, the pyrolysis at moderate temperatures of 1:1 adducts of beryllium borohydride and excess ligand has been studied in an attempt to effect removal of borane units from the borohydride since this could provide a novel preparation for beryllium hydride.

Metal borohydrides.

In this review the term 'borohydride' denotes salts containing the discrete ion, BH_4^-, and covalent compounds containing boron-hydrogen-metal bonds from BH_4 units. One electron bonds will be represented diagramatically by a dot, e.g. B.H.Be, and normal two electron bonds by a line, e.g. B-H. The I.U.P.A.C. nomenclature, tetrahydro borate, has found little usage in the current literature.

General preparative methods for metal borohydrides may be considered as primary, requiring synthesis of the borohydride

unit, or secondary, where metathetical reactions are used for the preparation. The alkali-metal borohydrides have attracted interest since they offer good routes to diborane, and find considerable application as reducing agents.

Preparation of alkali-metal borohydrides.

Three principal methods have been developed for the preparation of these borohydrides, and may be represented by the following equations.

$$3MX + 2B_2H_6 \longrightarrow 3MBH_4 + BX_3 \quad (X = H,R,OR,NH_2)$$

$$4MH + BX_3 \longrightarrow MBH_4 + 3MX \quad (X = H,F,Cl,OR)$$

$$MX + M'BH_4 \longrightarrow M'X + MBH_4 \quad (X = Cl,OH,OR)$$

In principle the reaction of diborane and alkali-metal hydride provides the most direct route to the borohydride, and indeed lithium hydride and diborane react at room temperature in the presence of ether.[1] The reaction does not proceed in the absence of solvents, even at high temperature and pressure.[2,3,4] The method is not general and neither sodium nor potassium hydride will react with diborane even in the presence of ether. Ethyl-lithium with diborane gives lithium borohydride.[5]

Good yields of alkali-metal borohydrides result from diborane with the metal-alkoxide,[2] -trimethoxyborate, and -tetramethylborate.[1,2,6,7,8,9]

$$3NaOMe + 2B_2H_6 \xrightarrow{\text{room temp.}} 3NaBH_4 + B(OMe)_3$$

Sodium trimethoxyborate from sodium hydride and trimethylborate reacts with diborane at room temperature.

$$2NaBH(OMe)_3 + B_2H_6 \longrightarrow 2NaBH_4 + 2B(OMe)_3$$

$$3NaB(OMe)_4 + 2B_2H_6 \longrightarrow 3NaBH_4 + 4B(OMe)_3$$

In most cases the reaction proceeds quantitatively with the ester acting as solvent, and may be considered as displacement of the weaker Lewis acid, trimethylborate, by the stronger acid, diborane.

Since the alkali-metal borohydrides are extensively used as a source of diborane, preparative methods not involving diborane are of considerable value. In these methods the metal hydride is used as a source of hydridic hydrogen.[10,11].

$$4LiH + BF_3.OEt_2 \xrightarrow{125^\circ} LiBH_4 + 3LiF + Et_2O.$$

Diborane, from the hydride and boron trifluoride etherate, reacts with more hydride to give the borohydride.[6,12,13].

Sodium hydride and boron trifluoride in the absence of solvent gives only the trifluoroborohydride,[6]. but in the presence of sodium ethoxide, the reaction proceeds to give sodium borohydride.[14].

$$4NaH + BF_3 \xrightarrow{NaOEt,\ 180/400^\circ} NaBH_4 + 3NaF$$

A method involving displacement of methoxide ions from the methoxyborates by hydride ion involves a thermal redistribution,

$$NaH + B(OMe)_3 \longrightarrow Na(HB(OMe)_3)$$

The trimethoxyborate disproportionates at 250°, [15].

$$4Na(HB(OMe)_3) \rightleftharpoons NaBH_4 + 3Na(B(OMe)_4)$$

$$\Downarrow$$

$$3NaOMe + 3B(OMe)_3$$

Good yields of borohydride were obtained by slow addition of

ester to an excess of well-stirred powdered hydride at 250°. The overall reaction may be represented by the equation.

$$4NaH + B(OMe)_3 \longrightarrow 3NaOMe + NaBH_4$$

The ethyl or n-butyl ester may be used in place of trimethylborate. Sodium borohydride is extracted from the reaction products by liquid ammonia or isopropylamine. Lithium borohydride is formed in reduced yield, and the separation is difficult. In an industrial process the sodium hydride, prepared from hydrogen and finely dispersed sodium in mineral oil, is treated with the ester.[16].

Sodium hydride and boric oxide at 330-350° give a 60% yield of the borohydride.[15].

$$4NaH + 2B_2O_3 \longrightarrow 3NaBO_2 + NaBH_4$$

Sodium metaborate may be converted to the borohydride by a high pressure reaction.[17].

Metal borohydrides are obtained in good yield from the hydride and amine-borane.[18].

$$H_3B.NR_3 + MH \xrightarrow{100^\circ} MBH_4 + NR_3$$

The amine-boranes may be prepared without using diborane:

$$Et_3B + NEt_3 + 3H_2 \xrightarrow{200/300^\circ + press.} H_3B.NEt_3 + 3C_2H_6$$

It is claimed that the method is the only technically feasible one that gives the product unmixed with solid contaminants.

An elementary, but low yield,process involves hydrolysis of magnesium boride in strongly alkaline solution.[19].

$$2B + Mg \xrightarrow{Ar/950^\circ} MgB_2 \xrightarrow{3M.KOH} KBH_4 \text{ (13\% on boron).}$$

As will be evident in the following sections, lithium borohydride is extensively used in the preparation of other metal borohydrides, and is conveniently prepared from sodium borohydride by metathesis in non-aqueous solution.[20,21].

$$NaBH_4 + LiCl \xrightarrow{Pr^iNH_2} NaCl + LiBH_4.$$

Preparation of other metal borohydrides.

Metal borohydrides, other than those of the alkali-metals, are not required in tonnage quantities, and hence, direct preparations involving diborane are of some importance. Several borohydrides have been prepared from diborane and the metal hydride, alkyl, or alkoxide. Other borohydrides result from reactions between metal halides and either lithium or aluminium borohydride, and these exchange reactions may be performed either in the presence or absence of non-aqueous solvent. Metal borohydrides of predominantly ionic character may be isolated from metathetical reactions with sodium or potassium borohydride in aqueous or alcoholic solution.

Methods involving diborane.

The original preparation of aluminium and beryllium borohydrides[22,23]. involved reaction of diborane with trimethyl-aluminium or dimethylberyllium. These reactions are complex and proceed through several intermediates.

$$(Be(Me)_2)_x + B_2H_6 \longrightarrow MeBeBH_4 \xrightarrow{B_2H_6} (HBeBH_4)_x \xrightarrow{B_2H_6} BeB_2H_8.$$

Beryllium hydride reacts slowly with diborane to give the borohydride[24,30].

Trimethylgallium[25.] and indium[26.] react with diborane at low temperature in ether solution. At -45° trimethylgallium yields dimethylgallium borohydride, Me_2GaBH_4, (m.p.1.5°), which melts to a clear liquid slowly decomposing at room temperature. In the absence of ether, and at higher temperature, trimethylgallium reacts with diborane, but the product $Ga(BH_4)_3$, if formed at all, rapidly decomposes with deposition of gallium. The reaction is thought to proceed:

$$2Me_3Ga + 9B_2H_6 \longrightarrow 2Ga(BH_4)_3 + 6MeB_2H_5$$

$$2Ga(BH_4)_3 \longrightarrow 2Ga + 3B_2H_6 + 3H_2$$

Trimethylindium and diborane react in the proportions 1:10 in ether/tetrahydrofuran solvent at -40° to give indium borohydride, isolated as the ether complex, $In(BH_4)_3.3C_4H_8O$. The etherate loses one molecule of solvent at -30°, and the remainder at -10° with simultaneous decomposition of the borohydride to the elements.

Diethylmagnesium [27,28.] and excess diborane react in ether solution to give ultimately magnesium borohydride. The reaction apparently proceeds through formation of ethylmagnesium borohydride. In the presence of aluminium alkyls, introduced by preparing diethylmagnesium from a magnesium-aluminium alloy, further disproportionation of diethylmagnesium occurs with the formation of an ether insoluble compound, $MgH_2.BEt_3$. This compound is thought to have the structure, $MgH.(Et_3BH)$. Magnesium borohydride has been obtained in good yield from the hydride and diborane[29.] in glycol ether/benzene mixture at 80°.

Zinc hydride in ether suspension (and beryllium hydride contaminated with ether) absorbs diborane to give the borohydride which was not isolated.[30] Recently, methylzinc borohydride has been prepared from dimethylzinc and diborane at room temperature.[31]

$$2Me_2Zn + B_2H_6 \longrightarrow MeZnBH_4 + Me_3B + ZnH_2$$

The alkaline earth borohydrides are prepared in good yield from diborane and the tetramethoxyborates or alkoxides. In the absence of solvent, yields are less than in the presence of ether, which in turn gives smaller yields than those obtained using tetrahydrofuran as solvent. The borohydrides are isolated as solvates, $M(BH_4)_2 \cdot 2THF$.[32]

Titanium(IV)alkoxides and diborane in tetrahydrofuran solution react to give titanium(III)borohydride in good yield, and is isolated as the monosolvate.[33] Similarly, stannous methoxide in ether at -78° reacts with diborane to give stannous borohydride,[34] decomposing above -65° to tin, diborane, and hydrogen.

$$SnBr_2 + NaOMe \xrightarrow{MeOH} Sn(OMe)_2 \xrightarrow{B_2H_6} Sn(BH_4)_2 \xrightarrow{-65^\circ} Sn, B_2H_6, H_2$$

Exchange reactions involving other borohydrides.

Neither tetramethyltin nor the lead compound react with diborane under various experimental conditions, but are found to react vigorously with aluminium borohydride.[35] The resulting solid products decompose to Sn(Pb), H_2, methylated boranes, and methylaluminium borohydride, and on the basis of the decomposition products, the formation of intermediate compounds is suggested:

$$2Al(BH_4)_2 + SnMe_4 \longrightarrow Me_2Sn(BH_4)_2 + MeAl(BH_4)_2$$

Aluminium borohydride has also been used for the preparation of U,[36] Th, Zr, Hf[37] borohydrides.

$$UF_4 + 2Al(BH_4)_3 \longrightarrow U(BH_4)_4 + 2Al(BH_4)F_2$$

$$U(BH_4)_4 \xrightarrow{100^\circ} U(BH_4)_3 + \tfrac{1}{2}H_2 + \tfrac{1}{2}B_2H_6$$

$$ThF_4 + 2Al(BH_4)_3 \longrightarrow Th(BH_4)_4 + 2Al(BH_4)F_2$$

Although aluminium borohydride failed to react with the fluorides, HfF_4, and ZrF_4, the reaction with double salts, $NaHfF_5$, and $NaZrF_5$, was rapid at room temperature.

$$NaHfF_5 + 2Al(BH_4)_3 \longrightarrow Hf(BH_4)_4 + 2AlF_2(BH_4) \pm NaF$$

These compounds are low melting solids, and are readily purified by vacuum sublimation. The fluorides of titanium, TiF_4, TiF_3, and the double salt, $NaTiF_4$, all failed to react with aluminium borohydride, but with the tetrachloride, a chloroborohydride was formed:

$$2TiCl_4 + 3Al(BH_4)_3 \longrightarrow 2TiCl(BH_4)_2 + 3AlCl_2(BH_4) + B_2H_6 + H_2$$

The similar volatilities of the chloroborohydrides made isolation of pure compounds very difficult. Titanium(III)borohydride was obtained from the tetrachloride and lithium borohydride,

$$2TiCl_4 + 8LiBH_4 \longrightarrow 2Ti(BH_4)_3 + 8LiCl + B_2H_6 + H_2.$$

Isolation of the pure borohydride, $Zr(BH_4)_4$, from the chloride and aluminium borohydride is difficult, but with lithium borohydride the compound is obtained pure and in good yield.[33]

$$ZrCl_4 + 4LiBH_4 \longrightarrow Zr(BH_4)_4 + 4LiCl$$

Both beryllium and aluminium borohydrides are readily

prepared from the halides and lithium borohydride.[20] An intimate mixture of the reactants is heated in vacuo, and the volatile borohydrides are trapped at low temperature.

Exchange reactions in the presence of solvents.

Borohydrides of predominantly ionic character are conveniently prepared in aqueous solution:

$$NaBH_4 + KOH \xrightarrow{\text{aq.soln.}} KBH_4 + NaOH$$

$$TlNO_3 + KBH_4 \xrightarrow{\text{cold water}} TlBH_4 + KNO_3$$

Quaternary ammonium borohydrides[38] are obtained by direct metathesis in aqueous solution,

$$R_4NX + NaBH_4 \longrightarrow R_4NBH_4 + NaX$$

(R = Me,Et, Benzyltrimethyl; X = halide, hydroxide, etc.)

as are also the trimethyl[39] (or phenyl) sulphonium, diphenyliodonium and tetraphenylphosphonium borohydrides.[40]

$$(Ph_4P)F + KBH_4 \longrightarrow (Ph_4P)BH_4 + KF$$

Exchange reactions in non-aqueous solution are useful for preparations of borohydrides which are either unstable in aqueous solution, or unstable at room temperature.

Both calcium and magnesium borohydride are prepared by metathesis in cold ethanol,[41] and the salt, $Ca(BH_4)_2.2THF$, has been prepared from metathesis in pyridine solution followed by extraction with tetrahydrofuran.[42] The reaction of zinc or cadmium chloride with lithium borohydride in ether solution is apparently complex and involves the formation of intermediate salts.

$$ZnCl_2 + 2LiBH_4 \longrightarrow Li(ZnCl(BH_4)_2)$$

After removal of excess solvent and lithium chloride, an ethereal solution of zinc borohydride is obtained.[43]. The salt, $Li(ZnCl(BH_4)_2)$, has been isolated as a white solid, decomposed at 120°. Similarly, cadmium chloride with lithium borohydride at 0° in ether solution gives the borohydride, $Cd(BH_4)_2$, and the reaction proceeds through formation of a complex salt, $Li(CdCl(BH_4)_2)$. Ethereal solutions of cadmium borohydride decompose at room temperature.

Many complex borohydrides are mentioned in the literature, but unfortunately a large number are reported without characterisation and as "unpublished observations".[44]. By varying proportions in the system, $BeCl_2/LiBH_4$, in ether solution, the following complexes are obtained, $Li(BeCl(BH_4)_2)$, $Li(Be(BH_4)_3)$, and $Li_2(Be(BH_4)_4)$.

A complex salt, $Li_2(Mg(BH_4)_2I_2)$, is obtained from magnesium iodide and lithium borohydride in ether solution, and a complex salt of composition, $Li(EtMgXBH_4)$, from the borohydride and ethylmagnesium halides.[27].

Complex borohydrides of general composition, $Li(X_3AlBH_4)$, are claimed to be present in ethereal mixtures of $AlCl_3$ and $LiBH_4$, (X = halide, borohydride), and dichloroalane with lithium borohydride in ether gives the salt, $Li(AlCl_2(H)BH_4)$. The gallium compound, $Li(Cl_3GaBH_4)$, reacts rapidly with excess borohydride to give the normal borohydride.[45].

$$GaCl_3 + 3LiBH_4 \xrightarrow{15^\circ} Ga(BH_4)_3 + 3LiCl$$

No stable compound was obtained from indium trichloride and lithium borohydride in ether solution at room temperature, and immediate reduction to the element was observed. Similarly, thallium(III) chloride was reduced by the borohydride at -100°.

$$TlCl_3 + 2LiBH_4 \longrightarrow TlCl + 2LiCl + H_2 + B_2H_6$$

Lithium diborohydridodihalogenomanganese(II) salts are reported as products from the chloride or iodide and lithium borohydride.

$$2LiBH_4 + MnCl_2 \longrightarrow Li_2(Mn(BH_4)_2Cl_2)$$

Additional complexes varying in composition between $Li_3(Mn(BH_4)_3I_2)$ and $Li(BH_4.4MnI_2)$ are obtained from the iodide. Complex salts of nickel, $Li(Ni(BH_4)_3)$ and $Li_2(Ni(BH_4)_4)$, were obtained from the chloride and lithium borohydride in ether solution at -40°.

Since the borohydride group is a powerful reducing agent, it is not surprising to find that halides of metals in a high oxidation state are reduced during formation of the borohydrides. Thus, ferric chloride reacts with lithium borohydride in a two-stage process[46]. involving initial reduction of Fe(III), and then formation of the borohydride, $Fe(BH_4)_2$. The product is a non-volatile solid, fairly soluble in ether, and decomposes rapidly at 0° into diborane, hydrogen, and a pyrophoric residue containing iron and boron. Cobalt(II) chloride is reduced to the metal[47]. in ether solution at room temperature.

$$CoCl_2 + 2LiBH_4 \longrightarrow Co + 2B + 4H_2 + 2LiCl$$

Cupric or cuprous chloride react with an ethereal solution of

lithium borohydride at -20° to give cuprous borohydride,[48,49] decomposing at 0° into diborane, hydrogen, boron, and copper hydride.

$$2CuCl_2 + 4LiBH_4 \xrightarrow{-20^\circ} CuBH_4 + 4LiCl + H_2 + B_2H_6$$

Cuprous borohydride reacts with pyridine to form a stable complex. Silver borohydride is precipitated from ether at -80°, and deposits metallic silver at -30°. Gold(III) and thallium(III) chloride are reduced by lithium borohydride at low temperatures, and an intermediate chloroborohydride,[50] $TlCl(BH_4)_2$, decomposes above -95° into thallium(I) chloride, hydrogen, and diborane.

The reaction between lead chloride and lithium borohydride in ether solution at room temperature results in deposition of lead. Trimethyl lead chloride and potassium borohydride deposit potassium chloride from liquid ammonia at -33°, presumably leaving trimethyl lead borohydride[35,51] in solution.

$$Me_3PbCl + KBH_4 \xrightarrow{liq.NH_3} Me_3PbBH_4 + KCl$$

This compound decomposes in the presence of ammonia with formation of trimethyl lead hydride, and a substance of empirical formula, $H_3B.NH_3$.

$$Me_3PbBH_4 \xrightarrow{NH_3} Me_3PbH + H_3B.NH_3$$

Several chloroborohydrides have been prepared from metathetical reactions between the rare-earth chlorides and lithium borohydride in tetrahydrofuran.[51]

$$MCl_3 + 2LiBH_4 \longrightarrow MCl(BH_4)_2 + 2LiCl$$

Several examples have been cited of reduction of metals

in a high oxidation state by the borohydride group. In liquid ammonia however, several borohydrides are isolated as ammines and in which the cation retains its original oxidation state. For example, Cr(III) and Co(III) borohydrides[52.] are isolated as ammines from metathesis in liquid ammonia with sodium borohydride.

$$(Cr(NH_3)_6)F_3 + 3NaBH_4 \longrightarrow 3NaF + (Cr(NH_3)_6)(BH_4)_3$$

It is of interest to note that ammonium borohydride has been isolated by this method.

$$NH_4F + NaBH_4 \xrightarrow[-45.]{liq.NH_3} NH_4BH_4 + NaF \xrightarrow{20^\circ} H_2 + (BNH_6)_x$$

Both hexammine cobalt(II) borohydride, and hexammine nickel(II) borohydride have been prepared by metathesis in liquid ammonia,[53.] but silver salts are unstable and deposit metallic silver.

Compounds of the type, $NiABH_4ClO_4$, $NiA(BH_4)_2$, where A is a cyclic tetramine or non-cyclic tetradentate Schiffs base, are prepared from soluble salts, $(NiA)X_2$, and sodium borohydride in aqueous solution.[54.] The salts are stable indefinitely in closed containers, and thermally stable to about 120°.

Dicyclopentadienyltitanium borohydride[55.] and dicyclopentadienylzirconium diborohydride[56.] are prepared from the appropriate chloride and lithium borohydride in ether.

$$(\pi\text{-}C_5H_5)_2TiCl_2 + 2LiBH_4 \longrightarrow 2LiCl + (\pi\text{-}C_5H_5)_2TiBH_4 + \tfrac{1}{2}H_2 + \tfrac{1}{2}B_2H_6$$

$$(\pi\text{-}C_5H_5)_2ZrCl_2 + 4LiBH_4 \longrightarrow (\pi\text{-}C_5H_5)_2Zr(BH_4)_2$$

A chloroborohydride, $(\pi\text{-}C_5H_5)_2ZrClBH_4$, is obtained using only a ~~two equivalents~~ two-fold molar excess of lithium borohydride. Both zirconium compounds are readily purified by vacuum sublimation. Dicyclopentadienylniobium chloroborohydride has been prepared.[56b.]

Structure and reactions of the metal borohydrides.

The borohydrides range in character between the typically ionic compounds exemplified by the alkali-metal borohydrides, to those of aluminium and beryllium which are predominantly covalent in character.

The alkali-metal borohydrides are stable, involatile, crystalline solids with ionic structures, and those of the heavier alkali-metals form face-centred cubic lattices,[57,58.] with the ionic radius of the borohydride ion given as 2.04Å. Infra-red,[59,60.] Raman,[61,62,63.] and n.m.r. studies,[64.] are in agreement with a boron atom tetrahedrally surrounded by four hydrogen atoms. Raman examination of potassium borohydride in liquid ammonia shows a single polarised shift, $\nu = 2270^{+}\text{-}3cm^{-1}$, attributed to a totally symmetric vibration ν_1 of the regular tetrahedral BH_4^- ion. The borohydride ion has two i.r. active fundamentals, ν_3 observed in the region $2300cm^{-1}$, and ν_4 at about $1100cm^{-1}$. A slight lowering in these values observed in the spectrum of $TlBH_4$, (ν_3 $100cm^{-1}$, ν_4 $60cm^{-1}$) is suggested as indicating the onset of multicentre bonding, or perhaps, a small covalent contribution to the bonding in the crystal lattice.

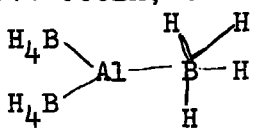
The alkali-metal borohydrides are stable in cold alkaline

aqueous solution, and indeed sodium borohydride may be recovered as a dihydrate. Lithium borohydride, unlike other members of its group, is soluble in ether and in tetrahydrofuran. Most borohydrides are soluble in liquid ammonia and amines. No decomposition is observed after prolonged exposure to dry air, and thermal decomposition to hydrogen, metal and boron or boride, occurs only at temperatures above 300°. The borohydrides are strong reducing agents as indicated by the redox potential of -1.24v.[65,66].

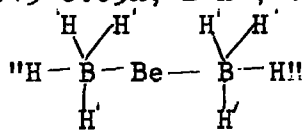
In contrast to the ionic compounds, the borohydrides of beryllium and aluminium are covalent in character. The mobile liquid, $Al(BH_4)_3$, is volatile, m.p.-64.5; v.p. given by the equation, log p = 7.808 - 1565/T, H_v = 7160cals./mole, and Trouton constant 22.5, b.p.(extrapolated) 44°, and the vapour detonates in contact with moist air. Beryllium borohydride is a volatile solid, v.p. given by the equation, $\log p_{mm} = 11.772-3240/T$, H_v = 14810cals./mole, m.p.123°(decomp.), spontaneously igniting on contact with air, and violently decomposed by water. The borohydrides of these elements are the most volatile compounds formed by the metals.

The result of an electron diffraction study of the aluminium compound[67]. was interpreted as indicating the following configuration, in which the Al atom is bonded to three BH_4 groups at angles of 120° making the molecule planar except for the H atoms. The boron atoms are located near the centre of trigonal bipyramids formed by the four H atoms of each BH_4 group and the

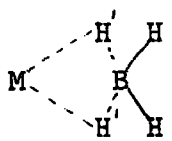
central Al, Al-B 2.14±0.02Å, B-H 1.27±0.04Å.



A similar study of beryllium borohydride[68] indicated that the configuration H''-B-Be-B-H'' was linear, with three hydrogen atoms (H') uniformly spaced in the girdle of each boron atom, B-Be, 1.66±0.04Å; B-H'',1.15±0.05Å; B-H',1.19±0.05Å; BeBH', 85±5°.



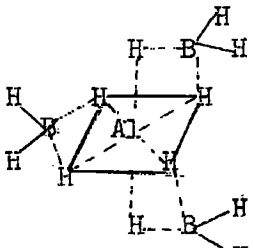
Although symmetrical hydrogen bridges were eliminated from the structure, it was later shown that highly unsymmetrical bridges, in which the H' atoms are considerably closer to the boron than to the metal atom M, were in good agreement with the experimental results.[69]

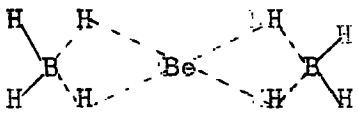


Infra-red and Raman spectra of both aluminium and beryllium borohydrides[70,71] indicate structures involving bridging hydrogen. For example, the i.r. spectrum of the aluminium compound contains two bands at 2559 and 2493cm^{-1} corresponding to terminal BH_2 groupings (2614,2522cm^{-1}) in diborane. Bands at 2031 and 1500cm^{-1} are analogous to BH_2B bridge vibrations in diborane, (1860 and 1604cm^{-1}). The shift of one to shorter, and the other to longer wavelength is related to the fact that as bonding of boron to metal becomes more ionic, the higher frequency vibration becomes a stretching vibration of the BH_4^- group, and the lower

one becomes a deformation vibration of the same group. Bands at 1114 and 978cm^{-1} are by analogy, associated with in-plane and out-of-plane vibrations of a terminal BH_2 group. The vibrational analysis was in good agreement with a molecular symmetry D_{3h} (prismatic), in which the bridge hydrogens are located at corners of an equilateral triangular prism, with Al, 3B, and six terminal hydrogens located in a plane lying midway between the two end faces of the prism.

In the spectrum of beryllium borohydride, bands at 2465 and 2440cm^{-1} are clear evidence of terminal BH_2, and those at 2180 and 1450cm^{-1} are vibrational bands of BH_2Be which is probably slightly ionic. A band at 1196cm^{-1} corresponds to a BH_2 deformation.





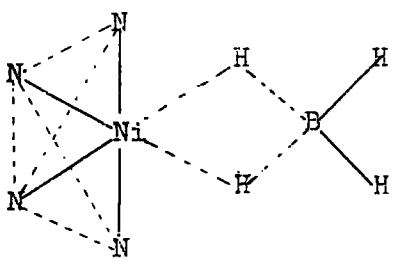
The p.m.r. spectrum of aluminium borohydride[72] gave the unexpected result of all protons having an equivalent electronic arrangement, with no differentiation between bridge and terminal hydrogens. A fast proton 'tunnelling' mechanism was suggested, giving time-average identity of enviroment. During this investigation it was found that the borohydride was in equilibrium with a second compound.

$$2AlB_3H_{12} \rightleftharpoons Al_2B_4H_{18} + B_2H_6$$

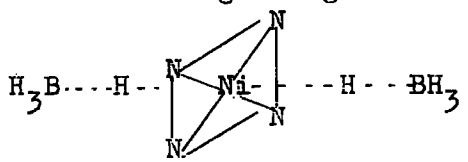
At 20° the equilibrium was well to the left, but at 80° the new compound was the dominant species. Such behaviour is reminiscent of the thermal equilibria found amongst the boron hydrides.

Other metal borohydrides are intermediate in character between the extreme cases of ionic and covalent compounds just described. In certain cases (Zr,Hf,U(IV)) the borohydrides are the most volatile compounds known for the metals.

Very little information is available on the structure of metal borohydrides in general, but several compounds show in their i.r. spectra, absorptions associated with a bridging hydrogen structure. The i.r. spectrum for $(\pi\text{-}C_5H_5)_2Zr(BH_4)_2$[56] shows terminal and bridging hydrogen vibrations, but that for the compound, $(\pi\text{-}C_5H_5)_2TiBH_4$,[55] suggests the compound contains a metal-hydrogen bond and a coordinated BH_3 group. The recently described nickel salts,[54] $NiABH_4ClO_4$ and $NiA(BH_4)_2$ (A = cyclic tetramine or non-cyclic tetradentate Schiffs base), show terminal B-H vibrations (2200-2400cm^{-1}), and bridging hydrogen vibrations (2000-2200cm^{-1}). The perchlorate salts are thought to contain two sets of three centre Ni.H.B orbitals involving two octahedral hybrid orbitals of the nickel ion.



One isomer of a diborohydride, $NiA(BH_4)_2$, is thought to contain a trans configuration for the borohydride groups, each interacting with the nickel ion through single three-centre bonds.



The physical properties of $LiBH_4$, $Be(BH_4)_2$, $Al(BH_4)_3$, and B_2H_6, show a gradual transition from a relatively high melting, non-volatile, ionic compound, to a very low melting, very volatile and non-polar compound.

	Mol.Wt.		m.p.	b.p.	v.p.(mm)	Ref.
	obs.	calc.				
$LiBH_4$			275°(d)		0	23
BeB_2H_8	38.5	38.7	123°(d)	91.3	5.2(20°)	5
AlB_3H_{12}	71.4	71.5	-65.4°	44.5	119.5(0)	22
B_2H_6	27.7	27.69	-165°	-92.5	225(-112°)	73.

A similar transition is observed in the chemical properties of this series.[74] For example, diborane reacts rapidly with trimethylamine at -110° to give trimethylamine-borane, $Me_3N.BH_3$, aluminium borohydride above 0°, and beryllium borohydride about 100°. Lithium borohydride and trimethylamine do not give the adduct, $Me_3N.BH_3$, at 100°.[5,75] Conversely, as ease of formation of borane derivatives decreases, the ease of formation of the ion, BH_4^-, increases. Thus diborane reacts rapidly with trimethyl-

amine, but reacts slowly with ethyl-lithium to give lithium borohydride. Aluminium borohydride reacts rapidly with ethyl-lithium in benzene solution.[5]

$$6EtLi + 2AlB_3H_{12} \longrightarrow 6LiBH_4 + Al_2Et_6$$

The increasing covalent character from lithium to aluminium borohydride may be explained by the increasing charge density of the metal ion. Schrauzer[76] has calculated the 'percentage ionic character' of a number of actual and hypothetical metal borohydrides by means of Sanderson's 'stability ratio' method.[77] The ionic character for isolated gas molecules is given by the equation:

$$I.C. = 10^2(\Delta SR_{M(BH_4)_n} - M \,/\, \Delta SR_{M^{n+}} - M)$$

$$= 10^2(\Delta SR_{BH_4} - M(BH_4)_n \,/\, \Delta SR_{BH_4} - BH_4^-)$$

where $\Delta SR_{M(BH_4)_n} - M$ gives the change in electronegativity from the metal atom to the molecular stability ratio of the metal borohydride.

Main groups.

Li 37	Be 27	B 4.3*	C 0	N neg.
Na, K, Rb, Cs >45	Mg 36.5	Al 17	Si 3.6	P 1.2
	Ca 45	Ga 2	Ge 0.4	As neg.
	Sr 52	In 4	Sn 1.8	Sb 1.8
	Ba 55	Tl 0	Pb 0.2	Bi 0

Sub-groups.

Cu 31	Zn 11	Sc 23		Mn 6
Ag 34	Cd 15	Ti 17	Zr 12	Ni 3
Au 3	Hg 2	Y 24	Hf 12	Fe 5

* calculated for diborane.

There is a fair correlation between these values and certain properties of the borohydrides. The melting points increase approximately linearly with the percentage ionic character. Borohydrides with less ionic character than diborane itself are, on Schrauzer's view, expected to be unknown or highly unstable. The observed instability of borohydrides of Ga,In,Tl,Sn,Pb,Hg, Au, etc. is in good agreement with theory. Borohydrides with more than about 40% ionic character are insoluble in ether. As previously indicated, reaction between trimethylamine and metal borohydride to give trimethylamine-borane, is confined to the covalent compounds of beryllium and aluminium. The borohydrides of lithium[5.75.] and magnesium[78.] form addition compounds with the amine, which may be recovered by heating to about 100°. Schrauzer pointed out that the tendency to form addition compounds between borohydrides and ethers, or amines, decreases with increasing ionic character.

Cold aqueous solutions of the alkali-metal borohydrides are reasonably stable in the presence of alkali, but are immediately decomposed by acid.

$$BH_4^- + H^+ + 3H_2O \longrightarrow H_3BO_3 + 4H_2.$$

The slight decomposition in neutral solution is reported to involve formation of a hydroxyborohydride ion, and indeed the sodium salt,[79.] $Na(BH_3OH)$, has been isolated and characterised from its i.r. spectrum.

The alkali-metal borohydrides are thermally decomposed

about 300° into hydrogen, metal, boron or metal boride.[80] 'Onium' borohydrides[38,39,40] decompose at lower temperatures with elimination of hydrogen or hydrocarbon, and formation of diborane or a borane coordination compound.

$$(Me_4N)BH_4 \xrightarrow{150^\circ} Me_3N.BH_3 + CH_4$$

$$(Me_3S)BH_4 \xrightarrow{90^\circ} Me_2S.BH_3 + CH_4$$

$$2(Ph_2I)BH_4 \longrightarrow B_2H_6 + 2PhI + 2C_6H_6.$$

The pyrolysis of 'onium' borohydrides is thought to involve nucleophilic attack by the anion on the 'onium' cation.

$$BH_4^- + Me\ldots\overset{+}{S}(Me)_2 \longrightarrow BH_3 + CH_4 + SMe_2$$

$$BH_3 + SMe_2 \longrightarrow Me_2S.BH_3$$

Ammonium borohydride probably decomposes in this way, but the resulting ammonia-borane is unstable and decomposes further into borazole.[81] The covalent compound, $Al(BH_4)_3$, is much less thermally stable, and indeed some decomposition is reported at room temperature[20] with formation of diborane.

Reactions of the alkali-metal borohydrides.

Reactions with sulphur and halogens.

Boron halides are obtained from reduction of the halogens by the alkali-metal borohydrides, and in particular, boron triiodide is obtained in good yield from lithium borohydride and iodine in cyclohexane,[82]

$$LiBH_4 + 4I_2 \longrightarrow LiI + BI_3 + 4HI.$$

The reaction with sulphur in ether or tetrahydrofuran apparently proceeds by a step-wise reduction.[83]

$$8LiBH_4 + S_8 \longrightarrow 8Li(H_3B.SH)$$

$$Li(H_3B.SH) \longrightarrow Li(BSH_2) + H_2$$

$$2Li(BSH_2) \longrightarrow Li_2S + S(BH_2)_2$$

The diborane sulphide is not isolated as such, but as a complex salt, $Li(B_3S_2H_6)$. At higher temperatures the metal metathioborate is obtained.

$$MBH_4 + 2S \xrightarrow{250/350^\circ} MBS_2 + 2H_2$$

Reactions with alkyl and hydrogen compounds.

The partial charge carried by hydrogen in binary compounds, AH_n, depends upon the electronegativity of the element A. Since the hydrogen in a borohydride group carries a partial negative charge, reaction with the binary compound will eliminate hydrogen if the element A is sufficiently electronegative.

Hydrogen halides.

Hydrogen chloride and bromide react at -80° with alkali-metal borohydrides,[2].

$$MBH_4 + HX \longrightarrow MX + H_2 + \tfrac{1}{2}B_2H_6$$

Further reaction between diborane and hydrogen chloride is very slow in the absence of ethers or amines. If the anion X^- is sufficiently basic, substitution in the borohydride ion occurs.

Lithium cyanoborohydride is obtained with hydrogen cyanide in ether solution.[84].

$$LiBH_4 + HCN \longrightarrow Li(H_3BCN) + H_2$$

At low temperatures, hydrazoic acid will replace one hydrogen of the borohydride group, but all the hydrogen is replaced at

room temperature.[85]

$$LiBH_4 + 4HN_3 \xrightarrow{Et_2O/20^\circ} Li(B(N_3)_4) + 4H_2$$

Alkyl and hydrogen compounds of Group VI.

As previously mentioned, very little hydrolysis of lithium borohydride in aqueous solution is observed at 0°, but with increasing temperature, hydrogen is released corresponding to step-wise hydrolysis through hydroxyborates.[86]

$$LiBH_4 \rightarrow Li(H_3BOH) \rightarrow Li(H_2B(OH)_2) \rightarrow Li(HB(OH)_3) \rightarrow Li(B(OH)_4).$$

Tetra-alkoxyborates are formed with alcohols,

$$LiBH_4 + 4ROH \longrightarrow Li(B(OR)_4) + 4H_2$$

and in the presence of acetic acid, the reaction has been found suitable for the preparation of boric esters.[87]

$$MBH_4 + 3ROH + H\bar{A}c \longrightarrow \bar{M}Ac + B(OR)_3 + 4H_2$$

Substitution reactions are reported with thio-alcohols.[88]

Alkyl and hydrogen compounds of Group V.

Alkali- metal borohydrides are soluble in liquid ammonia, and lithium borohydride has been found to form definite solvates, $LiBH_4.nNH_3$ (n = 1-4).[89] Substitution in the borohydride group by ammonia occurs only at high temperature.

$$LiBH_4 + NH_3 \longrightarrow Li(H_2BNH_2) + H_2$$

In contrast, ammonia reacts rapidly with lithium tetrahydroaluminate at room temperature.[90] Lithium borohydride forms complexes with methylamine[91] and trimethylamine,[75] which are precipitated from ether solution.

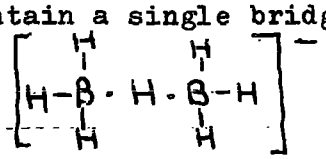
Alkyl and hydrogen compounds of Group III.

As previously indicated, hydrides are not expected to undergo substitution reactions with alkali-metal borohydrides. However, the hydrides of Group III are strong Lewis acids, and reaction with the nucleophilic borohydride group occurs through bridging-hydrogen.

Lithium borohydride does not react with diborane in ether solution as shown by measurement of electrical conductivity, but similar measurements in tetrahydrofuran indicate formation of a complex.[92]

$$LiBH_4 + B_2H_6 \xrightarrow{THF} Li(BH_4.BH_3)$$

The complex is decomposed by removal of solvent. The sodium salt, $Na(BH_4.BH_3)$, is formed in diglycoldimethylether,[93] and the anion is thought to contain a single bridging hydrogen.



The existence of this and other compounds containing a single hydrogen bridge, $C_5H_5N.BH_3.BH_3$, $Et_3N.BH_3.BH_3$,[93] suggests a possible reaction mechanism for diborane with neutral and anionic donors.

$$X: + B_2H_6 \longrightarrow XBH_3.BH_3 \xrightarrow{X:} 2XBH_3$$

rather than,

$$B_2H_6 \rightarrow 2BH_3 \qquad 2BH_3 + 2X: \rightarrow 2XBH_3.$$

The activation energy for the first mechanism is considerably less than the dissociation energy of diborane.[94]

A complex anion is formed from lithium borohydride and

alane.[92].

$$LiBH_4 + AlH_3 \longrightarrow Li(BH_4.AlH_3)$$

Lithium borohydrido-alanate is not stable in ether solution, but crystals of a solvate, $Li(BH_4.AlH_3).2THF$, are isolated from tetrahydrofuran. The compound is obtained from diborane and a tetrahydroaluminate,

$$2MAlH_4 + B_2H_6 \longrightarrow 2M(BH_4.AlH_3).$$

A complex salt, $Li(Me_3Al.BH_4)$, is obtained from lithium borohydride and trimethylaluminium in ether solution.

In contrast to the easy addition of borane and alane to alkali-metal borohydrides, tetraborane and decaborane react to give substitution products.[95].

$$NaBH_4 + B_4H_{10} \longrightarrow NaB_3H_8 + B_2H_6$$

Lithium or sodium borohydride react with decaborane in ether solution to give a salt of decaborane.[96].

$$MBH_4 + B_{10}H_{14} \longrightarrow MB_{10}H_{13} + H_2 + \tfrac{1}{2}B_2H_6.$$

Reaction with non-metallic halides.

The preparation of borohydrides from metal halides and an alkali-metal borohydride has been discussed and may be related to Schrauzer's predictions. Elements with an electronegativity greater than two do not form borohydrides, but generally react to give the hydride and diborane.

$$M(BH_4)_n \longrightarrow MH_n + nBH_3.$$

If the hydride, MH_n, is itself a Lewis base, reaction may proceed with the formation of a borane adduct.

Phosphine, alkyl, and aryl phosphines are obtained from the corresponding halide and alkali-metal borohydrides.[97,98,99]

$$PCl_3 + 3LiBH_4 \longrightarrow PH_3 + 3/2\ B_2H_6 + 3LiCl.$$

Borane adducts of the type, $PR_{3-n}H_nBH_3$, formed in this type of reaction, may be converted directly into the alkylphosphino-borane by working in a high boiling solvent.[99]

$$3R_2PH.BH_3 \xrightarrow{60/180^\circ} (R_2P.BH_2)_3 + 3H_2.$$

Reduction of the pentachloride to phosphine is effected by lithium borohydride at -80° in ether solution.[100]

Borane adducts are obtained from alkoxyphosphorus chloride[101] $(RO)_{3-n}PCl_n$ (n = 1,2), or dialkylaminophosphorus chlorides,[102] $(R_2N)_{3-n}PCl_n$ (n = 1,2).

$$(RO)PCl_2 + 2LiBH_4 \longrightarrow (RO)PH_2.BH_3 + \tfrac{1}{2}B_2H_6 + 2LiCl$$

$$(R_2N)_2PCl + LiBH_4 \longrightarrow (R_2N)_2PH.BH_3 + LiCl$$

The trichlorides of arsenic and antimony give the hydrides with lithium borohydride in ether, but bismuth trichloride is reduced to the metal.[103] Similarly, alkyl and aryl arsenic[103] or antimony[104] halides are reduced to the corresponding arsine and stibine derivatives, and in part to borane adducts.

$$R_{3-n}MX_n + nLiBH_4 \longrightarrow R_{3-n}MH_n + nLiX + n/2\ B_2H_6$$

Polyphenyl bismuth is precipitated from ether by reaction of phenylbismuth dibromide and lithium borohydride.[103]

$$PhBiBr_2 + 2LiBH_4 \longrightarrow 2LiBr + 1/x\ (PhBi)_x + B_2H_6$$

Halides of As(V) and Sb(V) are reduced at low temperature.[105]

$$SbCl_5 + 5LiBH_4 \xrightarrow{Et_2O} SbH_3 + H_2 + 5/2\ B_2H_6 + 5LiCl.$$

$$R_{5-n}MX_n + nLiBH_4 \longrightarrow R_{5-n}MH_n + H_2 + nLiX + n/2\ B_2H_6$$

The reaction with silicon tetrachloride is complex,[106] and several reaction products are formed depending upon temperature and molecular ratios of the reactants. Silane is obtained from the reaction,

$$SiCl_4 + 4LiBH_4 \longrightarrow SiH_4 + 2B_2H_6 + 4LiCl.$$

Hydrogen is produced by a side reaction:

$$2LiBH_4 + SiCl_4 \rightarrow \left[Li_2(Cl_4Si(BH_4)_2)\right] \xrightarrow{-60^\circ} LiCl + H_2 + \tfrac{1}{2}B_2H_6 + Li(H_3B.SiCl_3)$$

The complex salt, $Li(H_3B.SiCl_3)$, isolated as the trisether complex, decomposes at 20°, and reacts with trimethylamine.

$$Li(H_3BSiCl_2.Cl) + Me_3N \longrightarrow LiCl + H_3B.SiCl_2.NMe_3$$

Alkoxysilanes are obtained from reaction of the chloro compounds with lithium borohydride.

The reaction between alkali-metal borohydrides and boron halides is of importance for the preparation of diborane and higher boron hydrides.

$$3LiBH_4 + BF_3 \xrightarrow{Et_2O} 3LiF + 2B_2H_6.$$

The reaction is only quantitative in the presence of ether, and may be considered as displacement of the weaker Lewis acid, BH_3, from the borohydride ion, by the stronger Lewis acid, BF_3.

$$BF_3 + BH_4^- \longrightarrow BH_3 + (HBF_3)^-$$

Derivatives of borane, $X_{3-n}BH_n$, are prepared from reduction of the corresponding halides.

$$\rangle B\text{-}Cl + MH.BH_3 \longrightarrow \rangle B\text{-}H + MCl + BH_3$$

$$2Ph_2BCl + 2LiBH_4 \longrightarrow 2LiCl + (Ph_2BH)_2 + B_2H_6 \quad 44a.$$

$$2PhBCl_2 + 4LiBH_4 \longrightarrow 4LiCl + (PhBH_2)_2 + 2B_2H_6$$

Excellent yields of borazole are obtained from the B-halogen borazole and lithium borohydride in n-butyl ether.[107]

$$(-ClB{=}NH-)_3 + 3LiBH_4 \longrightarrow (-HB{=}NH-)_3 + 3LiCl + 3/2\ B_2H_6$$

Several boron heterocyclic compounds have been prepared in this way.[108]

In general then, non-metallic halides react with alkali-metal borohydrides to give diborane and hydrogen compounds. The borohydride group is considered as a nucleophile, and this is supported by the isolation of complex salts, $Li_2(Cl_4Si(BH_4)_2)$, $Li_2(Cl_3(H)Si(BH_4)_2)$. Nucleophilic attack probably involves a transition state with a bridging hydrogen.

$$H_3B\text{-}\bar{H} + \underset{X}{\overset{|}{M}}\text{-}X \longrightarrow \left[H_3B..H..\underset{X}{\overset{|}{M}}\text{-}X\right]^- \longrightarrow H_3B + H\text{-}\underset{X}{\overset{|}{M}} + X^-$$

The extensive applications of borohydrides as selective reducing agents in organic chemistry[109,110] are not considered here. The reducing properties of the borohydride group are modified by the solvent employed in the reduction, and by the cation associated with the borohydride group.

Rate of reaction is influenced by the solvent medium, and suggests solvent participation in transfer of hydride. The reducing ability of solutions containing sodium borohydride is markedly affected by the addition of various metal halides, and for example, the reducing strength of several borohydrides increase in the order: $K < Na < Li < Ca < Al$.[41] In particular, the

reducing solution formed by the addition of aluminium chloride to sodium borohydride in diglyme reduces esters, lactones, and carboxylic acids to alcohols, and nitriles to primary amines.[111]. Replacement of hydrogen by alkoxy substituents has a profound effect upon the reducing properties of the borohydride group.[112]. The greater reactivity of a trialkoxyborohydride is attributed to the more facile removal of a hydride ion from the weaker Lewis acid of an alkylborate.

A mechanism has been postulated for the reduction of the carbonyl group by the borohydride ion,[112,113].

$$4R_2C{=}O + NaBH_4 \longrightarrow NaB(OCHR_2)_4 \xrightarrow{H_2O/NaOH} Na_3BO_3 + 4R_2CHOH.$$

It is suggested that the adduct is formed in four successive stages, the initial stage being the rate determining step, and subsequent adducts are formed faster in accordance with the weakening Lewis acid function of the boron.

$$R_2C{=}O + BH_4^- \xrightarrow{r.d.s.} (R_2CHOBH_3)^- \xrightarrow{R_2CO} (H_2B(OHCR_2)_2)^- \text{ etc.}$$

An alternative mechanism, applicable to aqueous solution, does not involve four molecules participating in the reaction intermediate complex, and does not require the borohydride adducts to react faster with carbonyl than the borohydride group itself. The formation of the 1:1 complex is the rate-determining step, and then the complex is hydrolysed to alcohol and a mono-substituted hydroxyborohydride which undergoes rapid reaction with another ketone molecule.[114].

$$R_2C{=}O + NaBH_4 \longrightarrow Na(R_2CHO)BH_3 \xrightarrow{H_2O} R_2CHOH + NaBH_3OH$$

$$\text{etc.} \xleftarrow{R_2CO} R_2CHOH + NaBH_2(OH)_2 \xleftarrow{H_2O} Na(R_2CHOBH_2OH) \quad (\downarrow R_2CO)$$

Hydroboration of olefins by diborane[115,116] assumed importance as a synthetic route to trialkylboron compounds when it was found that ethers, used as solvents, catalysed the addition of boron-hydrogen groups across multiple bonds.[117] The reaction is conveniently carried out in diglyme (diethyleneglycol-dimethyl ether), and the diborane produced in situ.

$$12RCH{=}CH_2 + 3NaBH_4 + 4BF_3.OEt_2 \longrightarrow 4(RCH_2CH_2)_3B + 3NaBF_4 + 4Et_2O.$$

Diglyme is a convenient solvent since both diborane and sodium borohydride are readily soluble in it, and because it is miscible with water, allowing easy separation of the products.

Alternatively the diborane may be bubbled in a stream of nitrogen through a solution of the olefin dissolved in an appropriate ether. Tri-n-hexylborane, for example, may be obtained in a 90% yield by bubbling diborane through a solution of 1-hexene in tetrahydrofuran.[118]

$$6Bu^nCH{=}CH_2 + B_2H_6 \longrightarrow 2(C_6H_{13})_3B.$$

Although these two methods are of general applicability, variations on them are possible. The essential ingredients are a hydride, which need not contain boron (e.g. $LiBH_4$, $LiAlH_4$, LiH, NaH, $C_5H_5N.BH_3$ or $Me_3N.BH_3$), an acid, which must contain boron if the hydride does not, (e.g. BF_3, BCl_3, $AlCl_3$, $AlCl_3 + B(OMe)_3$, HCl or H_2SO_4), and a suitable weak base as solvent, most often

an ether, having a boiling point which allows easy separation of the products. Amine-boranes, $R_3N.BH_3$, are less convenient as sources of boron hydride than metal hydrides for the hydroboration of olefins because they require higher temperatures, (100-200°).

The alkali-metal borohydrides have proved useful in the preparation of hydrides. Stannane was obtained in 84% yield from stannous chloride and sodium borohydride.[119] Similarly, arsine,[103] stibine,[120] and germane,[121,122] are obtained in good yield from the appropriate chloride and an alkali-metal borohydride. Dropwise addition of an alkaline solution containing arsenite, antimonite, germanate, or stannite, and a borohydride to aqueous solutions of acid gave good yields of AsH_3, SbH_3, GeH_4, SnH_4, and small amounts of As_2H_4, Ge_2H_6, Sn_2H_6 were also isolated.[123]

The preparations of several dicyclopentadienylmetal borohydrides have already been considered, but it is of interest to note that other dicyclopentadienylmetal borohydrides are apparently unstable at room temperature. Dicyclopentadienyltitanium dichloride is reduced by lithium borohydride to dicyclopentadienyltitanium(III) borohydride.[55] The reduction of dicyclopentadienylcobalt and rhodium halides by sodium borohydride (or $LiAlH_4$)[124] forms a neutral compound in which one cyclopentadienyl ring has been converted into a cyclopentadiene group, π-$C_5H_5(C_5H_6)M$. Infra-red and high resolution

nuclear magnetic resonance spectra indicate one π-cyclopentadienyl ring bound to the metal, and that the rhodium compound was not a dicyclopentadienylrhodium hydride as previously suggested.[125] Reduction of the dicyclopentadienyl halides of molybdenum and tungsten by sodium borohydride[126] gives the corresponding dihydrides, $(\pi\text{-}C_5H_5)_2MH_2$, readily sublimed at 120° in vacuum. A similar reduction of cyclopentadienyliron - dicarbonyl chloride yields the hydride, $\pi\text{-}C_5H_5Fe(CO)_2H$, decomposing at room temperature to the compound, $(\pi\text{-}C_5H_5Fe(CO)_2)_2$.

The transition metal carbonyls of Group VI, are reduced by sodium borohydride in liquid ammonia to decacarbonyl metallates.[127]

$$2M(CO)_6 + 2NaBH_4 + 2NH_3 \longrightarrow Na_2(M_2(CO)_{10}) + 2CO + 2H_3BNH_3 + H_2$$

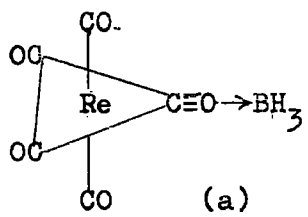
Crystalline complexes containing the borane group, BH_3, as an electron-accepting ligand have been obtained by reaction of borane etherates with Group VII metal carbonyl anions.[128] Salts of $(Re(CO)_5)^-$, $(Mn(CO)_5)^-$, and $(Ph_3PMn(CO)_4)^-$, give monoborane complexes in which the group, BH_3, is coordinated to the metal, and a bisborane complex , $(Re(BH_3)_2(CO)_5)^-$, has been isolated.

$$NaRe(CO)_5 + R_2OBH_3 \longrightarrow (ReBH_3(CO)_5)^- + R_2O$$

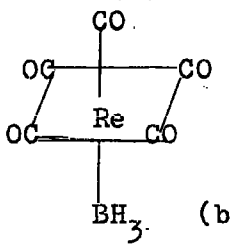
$$(ReBH_3(CO)_5)^- \xrightarrow{R_2OBH_3} (Re(BH_3)_2(CO)_5)^- + R_2O.$$

Two structures, (a) and (b), were considered for the monoborane complex. The structure (a), involving BH_3 coordinated to the

oxygen of a carbonyl group, would be expected to show a substantial shift in the C≡O stretching frequency. On the other hand, a structure such as (b) in which the BH_3 group is coordinated to the metal should show only a slight increase in the C=O stretching frequency as compared to the ion, $(Re(CO)_5)^-$. The great similarity in the spectra of $(Re(CO)_5BH_3)^-$, and $(Re(CO)_5)^-$, strongly supports the structure (b).



(a)



(b)

Reactions of the covalent metal borohydrides.

The borohydrides of beryllium and aluminium, prepared from the metal alkyl and diborane[5,22]. are the final products of a complex series of reactions. The initial reaction between dimethylberyllium and diborane at 95° gives a non-volatile liquid which on subsequent reaction with diborane gives a product with the empirical formula, $MeBeBH_4$. This volatile product reacts rapidly with additional diborane to give the borohydride and small amounts of a non-volatile white solid, thought to be $(BeBH_5)_x$. Intermediates formed during the preparation of the aluminium compound have not been isolated. A non-volatile zinc compound, $(ZnBH_5)_x$, is reported[74]. from the reaction between dimethylzinc and diborane, and more recently the volatile solid $MeZnBH_4$ (v.p.1.1mm.at 25°,m.p.55-56°), has been shown to be a product in this reaction.[31].

Coordination chemistry of the borohydrides.

Both beryllium and aluminium borohydrides form 1:1 addition compounds with trimethylamine. The compound, $Me_3N.BeB_2H_8$ (v.p. $\log_{10} p = 8.353 - 2909/T$, b.p. 260°), is sufficiently stable to permit determination of molecular weight from vapour density measurements, and the analogous compound, $Me_3N.Al(BH_4)_3$ m.p. 79°, may be sublimed in vacuum, but at 100°, decomposes into trimethylamine-borane and an oily liquid, 'AlB_2H_9', which was not obtained pure. Aluminium borohydride also reacts with other Lewis bases to form 1:1 adducts, $L.Al(BH_4)_3$ (L = NH_3, Me_2O, Et_3N, Me_3P, Me_3As, Et_2O, Me_2S), which are reported to decompose slowly at room temperature and rapidly above 50°. [22,129]. The etherate, $Me_2O.Al(BH_4)_3$, decomposes at 60° with evolution of methane, and the compound, $Et_2O.Be(BH_4)_2$, monomeric in benzene, is decomposed at 100° according to the equation:

$$BeB_2H_8.OEt_2 \longrightarrow C_2H_6 + 2H_2 + 'BeB_2H_3.OEt'$$

The reaction of aluminium borohydride with ammonia has been studied in some detail, [131]. and at low temperatures a hexammine is formed, which loses ammonia at room temperature to give a compound of composition, $AlB_3H_{12}.(NH_3)_{5.3-5.7}$. This product is soluble in water with only slight decomposition, and is insoluble in hydrocarbons, ethers, and ketones.

All adducts of the type, $L.Al(BH_4)_3$, have i.r. spectra very similar to aluminium borohydride over the region 4000-1100cm^{-1}, and the B^{11} n.m.r. spectra show all boron atoms

to be equivalent, and surrounded by four hydrogen atoms.[129.] This evidence suggests that in these adducts the ligand is bound directly to the aluminium.

Further reaction of the adduct, $Me_3N.Al(BH_4)_3$, with trimethylamine at slightly elevated temperatures resulted in the formation of almost exactly one mole of trimethylamine-borane per mole of borohydride, and left a product of empirical composition $Me_3N.AlB_2H_9$. Removal of trimethylamine-borane from the analogous beryllium compound, $Me_3N.BeB_2H_8$, occurs at higher temperatures, and the residual material, $Me_3N.BeBH_5$, reversibly loses some trimethylamine.

$$Me_3N.BeB_2H_8 + Me_3N \longrightarrow Me_3N.BH_3 + Me_3N.BeBH_5$$

The product, $Me_3N.BeBH_5$, will react with diborane to give beryllium borohydride, but the adduct, $Me_3N.Be(BH_4)_2$, with diborane at 70° failed to give the amine-borane.

It is not certain that the residues ,$Me_3N.BeBH_5$,$Me_3NAlB_2H_9$, are single compounds. Attempts to remove all of the boron from these products, and so form addition compounds of alane or beryllium hydride have not been successful. However, treatment of the monoammine, $H_3N.AlB_3H_{12}$, with trimethylamine resulted in removal of 93% of the total boron, but the reaction was accompanied by loss of hydrogen and formation of a non-volatile solid of composition, $(AlH_2N)_x$. Tensimetric titration of aluminium borohydride[129.] with nitrogen or phosphorus ligands showed that four equivalents of ligand reacted with the borohydride.

$Al(BH_4)_3 + 4MR_3 \longrightarrow 3R_3M.BH_3 + R_3M.AlH_3$ (M = N,P; R = alkyl)

Only trimethylamine reacted rapidly at 25° to cleave all the bridging structure in the borohydride, triethylamine reacted over a period of hours, and trimethylphosphine over several days. Trimethylarsine, and oxygen or sulphur ligands, all reacted rapidly to form the corresponding 1:1 adduct, but did not react beyond this point.

Hydrido-aluminium borohydride complexes with amines have been obtained from metathetical reactions between the corresponding chloro compounds and lithium borohydride.[132] Trimethylamine chloroalanes reacted smoothly with a benzene suspension of lithium borohydride.

$$H_2AlCl.NMe_3 + LiBH_4 \longrightarrow H_2AlBH_4.NMe_3 + LiCl$$

$$HAlCl_2.NMe_3 + 2LiBH_4 \longrightarrow HAl(BH_4)_2.NMe_3 + 2LiCl$$

$$AlCl_3.NMe_3 + 3LiBH_4 \longrightarrow Al(BH_4)_3.NMe_3 + 3LiCl.$$

Dimethylaminochloroalanes reacted similarly:

$$HAlCl.NMe_2 + LiBH_4 \longrightarrow HAlBH_4.NMe_2 + LiCl$$

$$Cl_2AlNMe_2 + 2LiBH_4 \longrightarrow (BH_4)_2AlNMe_2 + 2LiCl$$

These compounds react violently with water, less violently with oxygen. They are stable at room temperature, and most are sufficiently volatile for purification by sublimation or vacuum distillation. However, trimethylamineborohydrido-alane is decomposed at 90° according to the equation:

$$H_2AlBH_4.NMe_3 \longrightarrow Me_3NBH_3 + Al + 3/2H_2$$

The i.r. spectra of the complex borohydrides in the region

2500-1650cm^{-1} closely resemble that of aluminium borohydride. Doublets at 2560 and 2440cm^{-1}, and broad bands at 2170 and 2130cm^{-1} are assigned to terminal B-H stretching and asymmetric bridge stretching respectively. A band at 1890-1820cm^{-1} has been assigned as Al-H stretch.[133] The B^{11} n.m.r. spectra of the hydridoaluminium borohydride complexes indicate four equivalent hydrogen atoms bound to the boron, and in complexes containing two or more borohydride groups, all boron atoms are equivalent. The presence of four equivalent hydrogens bound to the boron, eliminates configurations involving B-N and Al-B bonds. Dimethylaminohydrido-aluminium borohydride and the diborohydride have been shown, from tensimetric titrations, to react rapidly with trimethylamine.

$$HAlBH_4.NMe_2 + NMe_3 \longrightarrow H_2AlNMe_2 + Me_3NBH_3$$

$$(BH_4)_2AlNMe_2 + 2NMe_3 \longrightarrow H_2AlNMe_2 + 2Me_3N.BH_3$$

The B^{11} n.m.r. spectrum of the crude product gave a quadruplet, consistent with destruction of the borohydride group, and trimethylamine-borane was isolated from the reaction products.

Reactions of trimethylamine with trimethylamine complexes of dihydridoaluminium borohydride and hydridoaluminium diborohydrides have been reported.[134] The tensimetric titration of the compound, $H_2AlBH_4.NMe_3$ with trimethylamine showed rapid addition of one mole of amine, and a much slower reaction with a second mole of amine. The product corresponding to the composition, $H_2AlBH_4.2NMe_3$, solid at 0°, was observed to liquify

at 25° and the B^{11}n.m.r. spectrum showed a quadruplet, δ_4 = 26.0 J_{BH} = 100c/s, and a quintuplet, δ_5 = 56.6 J_{BH} = 86c/s, indicating cleavage of the borohydride to the amine-borane, $Me_3N.BH_3$. The initial reaction with amine did not cause cleavage of the hydride bridge, since the liberated alane adduct, $Me_3N.AlH_3$, would have reacted rapidly with more amine to give the bisamine complex, $H_3Al.2NMe_3$.[135] Further, the B^{11}n.m.r. spectrum of a 1:1 mixture of the reactants showed only the quintuplet indicating that the second amine molecule was coordinated to the aluminium. The decomposition of the 2:1 adduct is thought to proceed:

$$H_2AlBH_4.2NMe_3 \rightleftharpoons H_3Al.NMe_3 + Me_3N.BH_3$$

and at appreciable concentrations of trimethylamine-alane, a second reaction is likely,

$$H_2AlBH_4.2NMe_3 + H_3Al.NMe_3 \longrightarrow H_3Al.2NMe_3 + H_2AlBH_4.NMe_3$$

Apparently the first reaction is reversible since the B^{11}n.m.r. spectrum of mixtures containing $H_3Al.NMe_3$ and $Me_3N.BH_3$, originally a quadruplet, eventually contained a quintuplet. However, addition of two moles of amine to one mole of borohydride resulted in direct conversion to the borane, and no evidence was found for the original equilibrium.

$$H_2AlBH_4.NMe_3 + 2Me_3N \longrightarrow H_3Al.2NMe_3 + Me_3N.BH_3.$$

The reaction between the compound, $HAl(BH_4)_2.NMe_3$ and trimethylamine approached the equation:

$$HAl(BH_4)_2.NMe_3 + 3Me_3N \longrightarrow H_3Al.2NMe_3 + 2Me_3N.BH_3$$

although some hydrogen gas was evolved. Complete conversion of

borohydride to the borane adduct was confirmed by B^{11}n.m.r. spectrum. Tensimetric titration at 0° showed a break at a 1:1 ratio, corresponding to the formation of the compound, $HAl(BH_4)_2.2NMe_3$, but this is much less stable than the dihydridoaluminium borohydride.

Preparation and reactions of tetrahydroaluminate, gallate, indate, and thallate.

The hydride ion can also act as an electron donor to the remaining elements of Group III.

$$H^- + MH_3 \longrightarrow MH_4^-$$

The complex hydrides are prepared from the corresponding metal halide and lithium hydride in the presence of ether, or in the case of aluminium, from sodium hydride, hydrogen, and activated aluminium powder.[136,137].

Both lithium tetrahydroaluminate and the corresponding gallium compound are prepared at room temperature, although the second compound is reported to decompose slowly at room temperature,[138]. and ethereal solutions of the compounds, $LiInH_4$, $LiTlH_4$, are only stable at low temperatures.[26]. As anticipated, the stability of the complex hydrides, MH_4^-, decreases from boron to thallium, and for the ion, AlH_4^-, the most stable salts are those containing a cation of low deforming power. The tetrahydroaluminates of the metals, Ca,Mg, and Be are known, and the salt, $Tl(GaH_4)_3$, is reported to decompose above -90° into thallium, hydrogen and gallane.[139]. It has been suggested that the compound

$Be(AlH_4)_2$, contains bridging hydrogen.[140]

Ethereal solutions of the complex hydrides, $LiMH_4$, react with the metal chloride, MCl_3, to give the metal hydride.[26,138]

$$3LiMH_4 + MCl_3 \xrightarrow{Et_2O} 3LiCl + 4MH_3$$

The complex hydrides of boron, aluminium, and gallium, have been used for the preparation of amine derivatives of borane,[141] alane,[142] and gallane,[143] by reaction with alkylammonium halides.

$$LiMH_4 + R_3NHCl \longrightarrow H_2 + LiCl + R_3N.MH_3$$

Reactions of lithium tetrahydroaluminate.

The compound is less thermally stable than the corresponding borohydride,[138] and unlike the borohydride, reacts rapidly with primary and secondary amines.

$$LiAlH_4 + 4RNH_2 \longrightarrow LiAl(RNH)_4 + 4H_2$$

A trimethylamine addition compound, $LiAlH_4.NMe_3$, is obtained in ether solution.[144]

The hydrides of zinc, cadmium, beryllium, and magnesium, have been prepared from the metal alkyls and the hydride, $LiAlH_4$, in ether solution.[145] Those of zinc and cadmium were obtained pure, but those of beryllium and magnesium could not be obtained free of solvent. Attempts to prepare a hydride of mercury, even at -80°, gave only the metal and hydrogen.

Dialkylaluminium hydride is formed from lithium aluminium hydride and the trialkyls of boron, aluminium, and gallium.[146]

$$LiAlH_4 + R_3M \longrightarrow LiMH_3R + R_2AlH.$$

The reaction is thought to proceed in two steps:

$$LiAlH_4 + R_3B \longrightarrow LiH + R_xBH_{3-x} + R_yAlH_{3-y}$$

(where x + y = 3, but neither x nor y are zero.)

$$R_2BH + RAlH_2 \rightleftharpoons RBH_2 + R_2AlH$$

It is then proposed that the mono-alkylboron compound reacts preferentially with lithium hydride.

No reaction between lithium tetrahydroaluminate and the alkyls of Group IV,V,VI, was observed. It would appear that the more electropositive the element with which the alkyl group is associated, the more readily are they replaced by hydrogen.

Halides of Group III,IV,V, react with lithium tetrahydroaluminate in ether solution to give the corresponding hydride.

$$LiAlH_4 + SiCl_4 \longrightarrow LiCl + AlCl_3 + SiH_4$$

$$LiAlH_4 + 2Me_2SnCl_2 \longrightarrow LiCl + AlCl_3 + 2Me_2SnH_2.$$

REFERENCES.

1) H.I.Schlesinger and H.C.Brown J.Amer.Chem.Soc.,1953,75,186.

2) H.I.Schlesinger,H.C.Brown,H.R.Hoekstra, and L.R.Rapp J.Amer.Chem.Soc.,1953,75,199.

3) H.Noth and H.Beyer Chem.Ber.,1960,93,928.

4) H.C.Brown and P.A.Tierney J.Amer.Chem.Soc.,1957,79,5400; 1958,80,1552.

5) H.I.Schlesinger and H.C.Brown J.Amer.Chem.Soc.,1940,62,3425, 3429.

6) H.I.Schlesinger,H.C.Brown,J.J.Katz, and J.R.Gilbreath J.Amer.Chem.Soc.,1953,75,195.

7) E.Wiberg,H.Noth,and R.Hartwimmer Z.Naturforsch,1954,10b,292.

8) E.Wiberg and R.Hartwimmer Z.Naturforsch,1954,10b,193.

9) E.Zange Chem.Ber.,1960,93,652.

10) G.Wittig and P.Hornberger Annalen,1952,577,18.

11) J.Goubeau and R.Bergmann Z.anorg.Chem.,1950,263,369.

12) J.R.Elliot,E.M.Boldebuck, and G.F.Roedel J.Amer.Chem.Soc.,1952,74,5047.

13) H.I.Schlesinger and H.C.Brown A.P.2543511,1946.

14) E.I.Dupont A.P.2684888,1954.

15) H.I.Schlesinger,H.C.Brown, and A.E.Finholt J.Amer.Chem.Soc.,1953,75,205.

16) Amer.Potash Chem Co. A.P.2898184,1959.

17) Farbenfabriken Bayer D.A.S.1053476,1957.

18) R.Koster Angew.Chem.,1957,69,94.

19) A.King,F.A.Kanda,V.A.Russell,
and W.Katz J.Amer.Chem.Soc.,1956,78,4176.

20) H.I.Schlesinger,H.C.Brown,
and E.K.Hyde J.Amer.Chem.Soc.,1953,75,209.

21) R.Paul and N.Joseph Bull.Soc.chim.France,1953,758.

22) H.I.Schlesinger,R.T.Sanderson,
and A.B.Burg J.Amer.Chem.Soc.,1940,62,3421.

23) A.B.Burg and H.I.Schlesinger J.Amer.Chem.Soc.,1940,62,3425.

24) G.E.Coates and F.Glockling J.,1954,2526.

25) H.I.Schlesinger,H.C.Brown.
and G.W.Schaeffer J.Amer.Chem.Soc.,1943,65,1786.

26) E.Wiberg and M.Schmidt Z.Naturforsch,1957,12b,54.

27) E.Wiberg and R.Bauer Z.Naturforsch,1950,5b, 397.

28) R.Bauer Z.Naturforsch,1961,16b,839.

29) H.D.Batha,E.D.Whitney,T.L.Heying,
J.P.Faust and S.Papeti J.Appl.Chem.,1962,12,478.

30) G.D.Barbaras,C.Dillard,A.E.Finholt,T.Wartik,
K.E.Wilzbach and H.I.Schlesinger J.Amer.Chem.Soc.,1951,73,4585.

31) G.E.Coates and D.Ridley Personal.comm.

32) E.Wiberg,H.Noth and R.Hartwimmer Z.Naturforsch,1955,10b,292.

33) W.E.Reid,J.M.Bish and A.Brenner Trans.Electrochem.Soc.,
1957,104,21.

34) E.Amberger and M.R.Kula Chem.Ber.,1963,96,2556:
Angew.Chem.,1963,75,476.

35) A.K.Holliday and W.Jeffers J.Inorg.Nuclear Chem.,1958,6,134.

36) H.I.Schlesinger and H.C.Brown J.Amer.Chem.Soc.,1953,75,219.

37) H.R.Hoekstra and J.J.Katz J.Amer.Chem.Soc.,1949,71,2488.

38) M.D.Banus,R.W.Bragdon and T.R.P.Gibbs J.Amer.Chem.Soc., 1952,74,2347.

39) H.G.Heal J.Inorg.Nuclear Chem.,1960,12,255.

40) H.G.Heal J.Inorg.Nuclear Chem.,1960,16,208.

41) J.Kollonitsch,O.Fuchs, and V.Gabor Nature,1954,173,125; 1955,175,346.

42) L.V.Titov Doklady Akad.Nauk S.S.S.R.,1964,154,654.

43) E.Wiberg and W.Henle Z.Naturforsch,1952,7b,579.

44a) H.Noth Angew.Chem.,1961,73,371.

44b) E.Wiberg Experienta,SuppVII,ICPAC,Paris,1957.

45) E.Wiberg,O.Dittmann,H.Noth, and M.Schmidt Z.Naturforsch,1957,12b,56.

46) G.W.Schaeffer,J.S.Roscoe, and A.C.Stewart J.Amer.Chem.Soc.,1956,78,729.

47) A.C.Stewart and G.W.Schaeffer J.Inorg.Nuclear Chem., 1956,3,194.

48) E.Wiberg and W.Henle Z.Naturforsch, 1952,7b,582.

49) E.Wiberg Angew.Chem.,1953,65,16.

50) E.Wiberg,O.Dittmann and M.Schmidt Z.Naturforsch,1957,12b, 62,63.

51) A.Brukl and K.Rossmanith Mh.Chem.,1959,90,481.

52) R.W.Parry,D.R.Schultz and P.R.Girardot J.Amer.Chem.Soc., 1958,80,1.

53) P.W.Schenk and W.Muller Angew.Chem.,1959,71,457.

54) N.F.Curtis J.,1965,924.

55) R.Noth and R.Hartwimmer Chem.Ber.,1960,93,2238.

56a) R.K.Nanda and M.G.H.Wallbridge Inorg.Chem.,1964,3,1798.

56b) R.B.King Z.Naturforsch,1963,18b,157.

57) S.C.Abrahams and J.Kalnajs. J.Chem.Phys.,1954,22,434.

58) P.T.Ford and H.M.Powell Acta cryst.,1954,7,604.

59) W.C.Price J.Chem.Phys.,1949,17,1044.

60) T.C.Waddington J.,1958,4783.

61) L.A.Woodward and H.L.Roberts J.,1956,1170.

62) R.C.Taylor,D.R.Schultz and A.R.Emery J.Amer.Chem.Soc.,1958,80,27.

63) J.Goubeau and M.Kallfass Z.anorg.Chem.,1959,299,160.

64)R.A.Ogg J.Chem.Phys.,1954,22,1933.

65) W.A.Stockmayer,D.W.Rice, and C.Stephenson J.Amer.Chem.Soc.,1955,77,1980.

66) R.L.Pescsok J.Amer.Chem.Soc.,1953,75,2862.

67) J.Y.Beach and S.H.Bauer J.Amer.Chem.Soc.,1940,62,3440.

68) G.Silbiger and S.H.Bauer J.Amer.Chem.Soc.,1946,68,314.

69) S.H.Bauer J.Amer.Chem.Soc.,1950,72,622.

70) W.C.Price J.Chem.Phys.,1949,17,1044.

71) A.R.Emery and R.C.Taylor Spectrochim.Acta,1960,16,1455.

72) R.A.Ogg and J.D.Ray Discuss.Faraday Soc.,1955,19,239.

73) A.Stock HYDRIDES OF BORON AND SILICON, Cornell Univ.Press, Ithaca New York,1933.

74) H.I.Schlesinger and A.B.Burg Chem.Rev.,1942,31,35.

75) E.Wiberg and A.Jahn Z.Naturforsch,1956,11b,489.

76) G.N.Schrauzer Naturwiss.,1955,42,438.

77) R.T.Sanderson J.Amer.Chem.Soc.,1952,74,438.

78) E.Wiber and R.Bauer Z.Naturforsch,1952,7b,58.

79) J.Goubeau and H.Kallfass Z.anorg.Chem.,1959,299,160.

80) A.G.Ostroff and R.T.Sanderson J.Inorg.Nuclear Chem.,1957,4, 230.

81) S.G.Shore and R.W.Parry J.Amer.Chem.Soc.,1955,77,6084.

82) Th.Renner Angew.Chem.,1957,69,478.

83) H.Nothe and G.Mikulaschek unpublished observation.

84) G.Wittig and P.Raff Z.Naturforsch,1951,6b,225.

85) E.Wiberg and H.Michaud Z.Naturforsch,1954,9b,499.

86) W.I.Michejewa and J.W.Fednewa Ber.Akad.Wiss.VdSSSR,1955,99, 101.

87) H.C.Brown,E.J.Mead and C.J.Shoaf J.Amer.Chem.Soc.,1956, 78,3613.

88) H.Noth Dissert.Univ.Munich,1954.

89) E.A.Sullivan and S.Johnson J.Phys.Chem,1959,93,233.

90) A.E.Finholt,A.C.Bond, and H.I.Schlesinger J.Amer.Chem.Soc.,1956,78,3613.

91) G.W.Schaeffer and D.J.Hunt Abstracts of papers,139th. Meeting ACS,1959,28M.

92) G.N.Schrauzer Dissert.Univ.Munich,1956.

93) H.C.Brown,P.F.Stehle , and P.A.Tierney J.Amer.Chem.Soc.,1957,79,2020, 1958,80,1552.

94) R.E.McCoy and S.H.Bauer J.Amer.Chem.Soc.,1956,78,2061,3613.

95) L.J.Edwards,W.V.Hough and M.D.Ford Abstract of papers, 16th.,IUPAC Kongress,1957,1,158.

96) H.Noth unpublished observation.

97) E.Wiberg and H.Noth Z.Naturforsch,1955,12b,125.

98) L.D.Freeman and G.O.Doak J.Amer.Chem.Soc.,1952,74,3414.

99) A.B.Burg and J.P.Slota J.Amer.Chem.Soc.,1960,82,2145.

100) E.Wiberg and K.Modritzer Z.Naturforsch,1956,11b,747.

101) G.Muller Dissert.Univ.Munich,1959.

102) H.Noth unpublished observation.

103) E.Wiberg and K.Modritzer Z.Naturforsch,1957,12b,123.

104) A.B.Burg and L.B.Grant J.Amer.Chem.Soc.,1959,81,1.

105) E.Wiberg and K.Modritzer Z.Naturforsch,1956,11b,748.

106) G.Hockele Dissert.Univ.Munich,1960.

107) R.Schaeffer J.Amer.Chem.Soc.,1954,76,3303.

108) G.Dahl and R.Schaeffer J.Inorg.Nuclear Chem.,1960,12,380.

109) N.G.Gaylord REDUCTION WITH COMPLEX METAL HYDRIDES, Interscience Publishers Ltd.,1956.

110) W.Gerrard THE ORGANIC CHEMISTRY OF BORON,Academic Press, 1961,134.

111) H.C.Brown and B.C.Subba Rao J.Amer.Chem.Soc.,1956,78,2582.

112) H.C.Brown,E.J.Mead and C.J.Shoaf J.Amer.Chem.Soc., 1956,78,3616.

113) S.W.Chaikin and W.G.Brown J.Amer.Chem.Soc.,1949,71,122.

114) E.R.Garrett and D.A.Lyttle J.Amer.Chem.Soc.,1953,75,6051.

115) E.Stock and E.Kuss Chem.Ber.,1923,56,789.

116) D.T.Hurd J.Amer.Chem.Soc.,1948,70,2053.

117) H.C.Brown and B.C.Subba Rao J.Amer.Chem.Soc.,1959,81,6428.

118) H.C.Brown and B.C.Subba Rao J.Org.Chem.,1957,22,1136.

119) G.W.Schaeffer and M.Emilius J.Amer.Chem.Soc.,1954,76,1203.

120) L.Berka,T.Briggs,M.Millard, and W.Jolly J.Inorg.Nuclear Chem.,1960,14,190.

121) T.S.Piper and M.K.Wilson J.Inorg.Nuclear Chem.,1957,4,22.

122) E.D.Macklen J.,1959,1989.

123) W.L.Jolly J.Amer.Chem.Soc.,1961,83,335.

124) M.L.H.Green,L.Pratt and G.Wilkinson J.,1959,3753.

125) A.D.Liehr Naturwiss.,1957,44,61.

126) M.L.H.Green,C.N.Street, and G.Wilkinson Z.Naturforsch,1959,14b,738.

127) H.Behrens and W.Haag Z.Naturforsch,1959,14b,600.

128) G.W.Parshall J.Amer.Chem.Soc.,1964,86,361.

129) P.A.Bird and M.G.H.Wallbridge J.1965. In press.

130) R.H.Kratzer and K.L.Paciorek NAVWEPS Report,8204,Aug.,1964.

131) L.Taylor U.S.Dept.Comm.Office Tech.Serv.,1961, 256,887, p30.

132) J.K.Ruff Inorg.Chem.,1963,2,515.

133) G.Schomberg and E.G.Hoffmann Z.Elektrochem.,1957,61,110.

134) J.K.Ruff ADVANCES IN CHEMISTRY,Series No.42, BORON-NITROGEN CHEMISTRY.

135) J.K.Ruff and M.F.Hawthorne J.Amer.Chem.Soc.,1961,83,535.

136) E.C.Ashby,G.J.Brendel and H.E.Redman Inorg.Chem.,1963,2,499.

137) E.C.Ashby Chem.and Ind.,1962,208.

138) H.I.Schlesinger,A.E.Finholt, A.C.Bond J.Amer.Chem.Soc.,1947,69,1199.

139) E.Wiberg and M.Schmidt Z.Naturforsch,1951,6b,335.

140) E.Wiberg and R.Bauer Z.Naturforsch,1951,6b,171, 1950,5b,397.

141) G.W.Schaeffer and E.J.Anderson J.Amer.Chem.Soc.,1949,71,2143.

142) J.K.Ruff and M.F.Hawthorne J.Amer.Chem.Soc.,1960,82,2141.

143) N.N.Greenwood,E.J.F.Ross and A.Storr J.,1965,1400.

144) E.Wiberg,H.Noth and R.U.Lacal Z.Naturforsch,1956,11b,486.

145) G.D.Barbaras,C.Dillard,A.E.Finholt,T.Wartik, K.E.Wilzbach and H.I.Schlesinger J.Amer.Chem.Soc.,1951,73,4585.

146) T.Wartik and H.I.Schlesinger J.Amer.Chem.Soc.,1953,75,835.

Part II.

EXPERIMENTAL

EXPERIMENTAL.

Many of the compounds described in this work are extremely air and moisture sensitive. Beryllium borohydride spontaneously ignites on contact with air, and although many of the adducts are rather more stable towards dry air, they are explosively decomposed on contact with water.

The purification of commercial nitrogen and the maintenance of a glove-box have been described in the first part of this thesis.

Vacuum line.

A general purpose vacuum line was constructed (PHOTO.1), and consisted of three main sections.

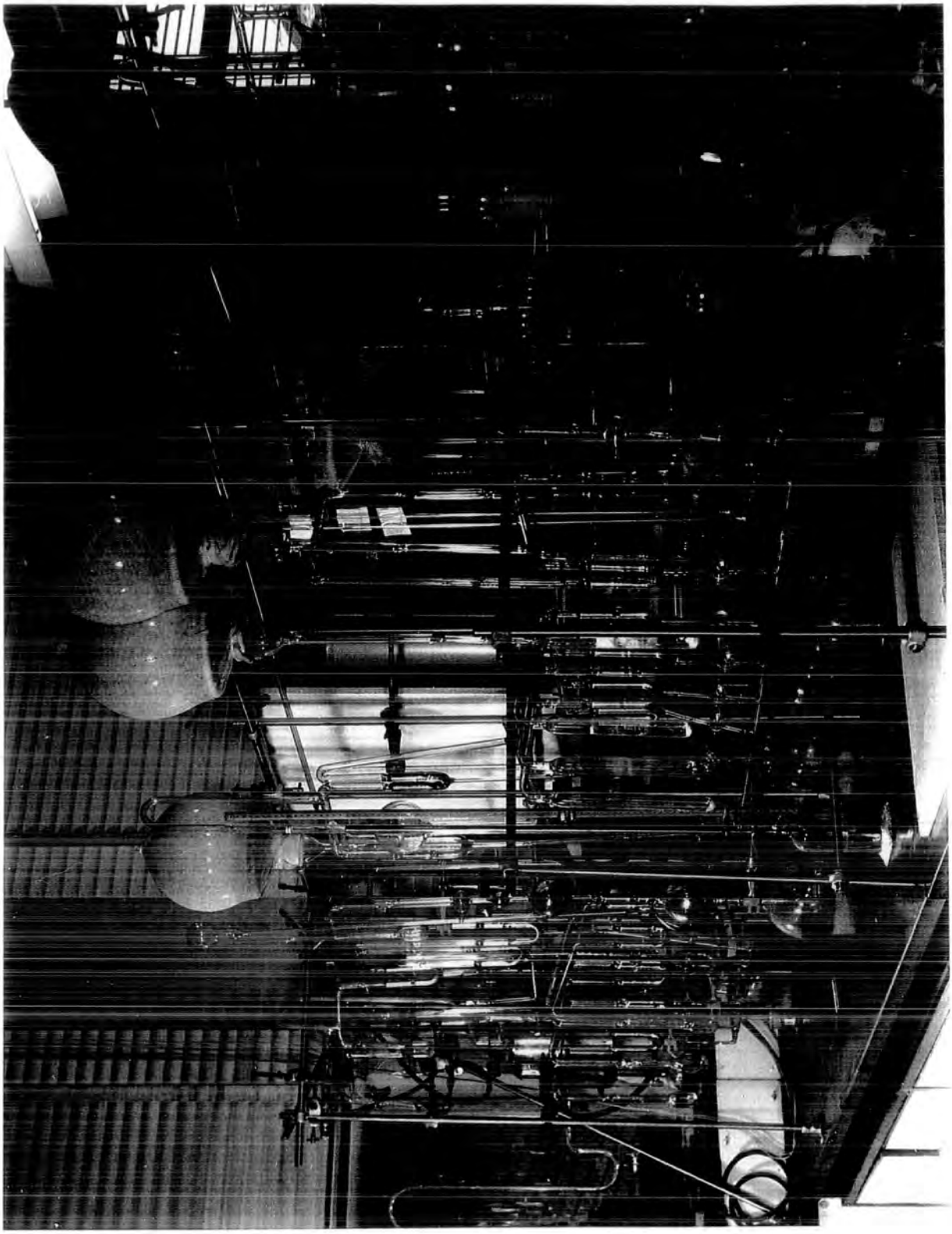
Storage section.

Volatile liquids and solids were stored in small tubes, and gaseous reactants were stored in large (31.) bulbs fitted with manometer and cold-finger. The storage tubes were connected through mercury float-valves to the main line.

Gas analysis section.

A Töpler pump was used for the measurement of gases not condensed by liquid nitrogen. The calibration marks on the pump correspond to volumes of 11.52cc. and 151.8cc.

Condensable gases were measured in calibrated bulbs connected to a manometer. The volume of each bulb was found by condensing known quantities of carbon dioxide into the apparatus.



PHOTOGRAPH 1.

Vol. small bulb, 505.6cc.; Vol. large bulb, 4613cc.

Internal radius of manometer tube, 0.5cm.

Internal radius of mercury reservoir, 2.9cm.

For a 1cm. drop in the manometer level, the reservoir level increases by 0.0298cm.

Fractionation section.

Three small U-traps were interconnected by mercury float-valves, and each trap could be connected directly to the main line through a separate float valve.

Tensimetric titration apparatus.

A small volume (60cc.) constricted reaction tube, and single limb manometer were connected through a mercury float-valve to the main vacuum line. Volatile reactants were measured on the vacuum line and condensed onto a known weight of beryllium borohydride contained in the reaction tube. The float valve was closed and the reactants allowed to equilibrate at room temperature before measuring the pressure in the apparatus.

Molecular weight measurements.

Molecular weights were measured cryoscopically in benzene solution. The cryoscopic constant of sodium dried benzene was determined using freshly sublimed diphenyl. A benzene solution of the compound, prepared under nitrogen, was introduced into the Beckmann apparatus against a counter flow of nitrogen. A slow flow of nitrogen was passed continuously throughout the determination to prevent back diffusion of air.

Infra-red spectra.

These were kindly recorded by Mr.G.Collier of this department on either a Grubb-Parsons G.S.2A or a Grubb-Parsons prism-grating Spectromaster. Air sensitive materials were handled in a glove-box and submitted as nujol-mulls, or in the case of liquids as a contact film between potassium bromide discs. Spectra were recorded over the range, $4000-400cm^{-1}$.

B^{11} magnetic resonance spectra.

These were kindly recorded by Mr.J.W.Akitt of the University of Newcastle on a A.E.I. RS2 spectrometer operating at 20Mc/s.

Liquid samples were used undiluted, and sealed in 9mm. bore soda-glass tubing under a slightly reduced pressure of nitrogen. Solid and viscous liquid samples were dissolved in the minimum volume of benzene. Chemical shifts were measured against trimethylborate as an external reference.

Preparation of starting materials.

Ethyl ether and tetrahydrofuran were sodium dried for several days and then distilled from lithium tetrahydroaluminate. 1,2-Dimethoxyethane (monoglyme) was dried by refluxing with potassium for several hours and was then distilled. Final purification was carried out just before use by refluxing with, and distillation from, lithium tetrahydroaluminate.

Hydrocarbon solvents were dried over sodium wire, and after distillation, were stored over sodium wire.

Samples of trimethylamine, dimethylamine, isopropylamine, isobutylamine, trimethylphosphine, triethylphosphine, and dimethylphosphine were available in the laboratory and were dried by distillation from sodium hydroxide pellets.

Commercial triphenylphosphine was purified by recrystallisation from benzene-hexane solution followed by vacuum sublimation. The purified material was stored under an atmosphere of nitrogen.

Beryllium chloride.

Anhydrous beryllium chloride was prepared in good yield (90-95%) by heating beryllium powder in a stream of chlorine. The rate of reaction was controlled by dilution of the chlorine with nitrogen. The product was sublimed into a suitable flask which was evacuated to remove excess chlorine, and the compound stored under nitrogen.

Lithium borohydride.

Commercial samples of lithium borohydride were extracted with ether in a Soxhlet-apparatus. The ether solution was concentrated by distillation, and the solid mono-etherate decomposed by heating in vacuo for several hours at 120°. The purified compound was stored under nitrogen.

The compound has been prepared from anhydrous lithium chloride and sodium borohydride in isopropylamine. It was found convenient to Soxhlet extract the sodium borohydride into an isopropylamine solution of the lithium chloride, since this

gave a coarse and easily filtered precipitate of sodium chloride. After filtration and removal of solvent, the lithium borohydride was purified by the method just described.

Beryllium borohydride.

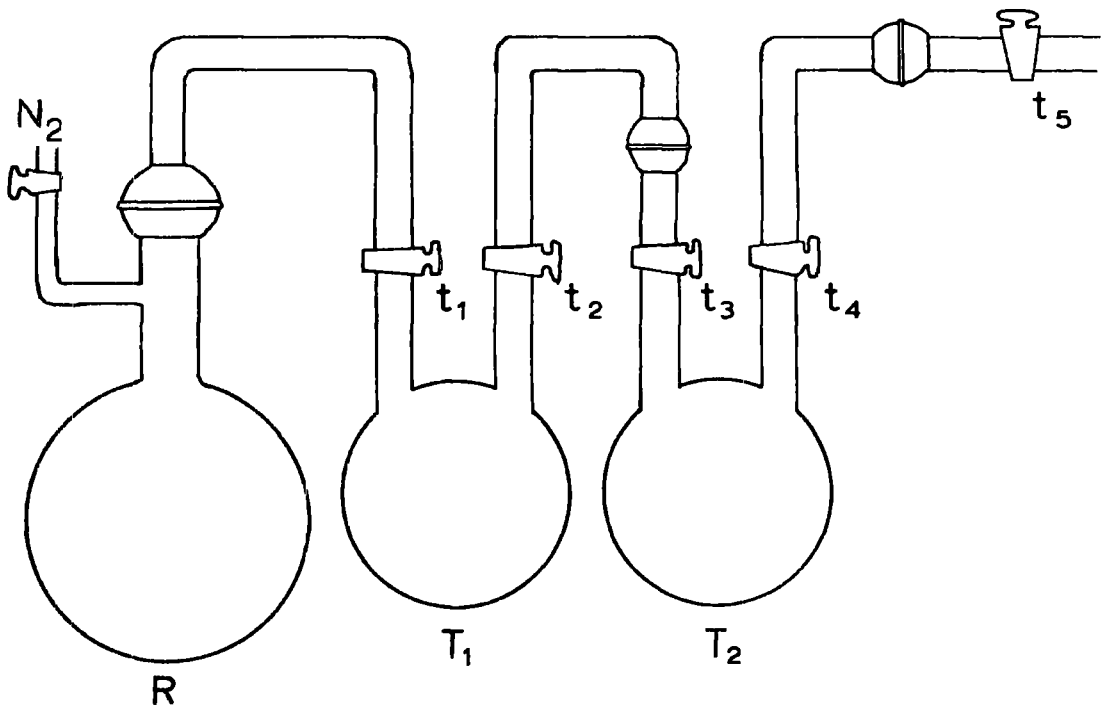
An intimate mixture of beryllium chloride and lithium borohydride was heated in vacuo(0.001mm.Hg.) to 140° over a period of 8hrs. in the apparatus shown in FIG.3. The volatile product was collected in traps cooled by liquid nitrogen.

Method.

A mixture of beryllium chloride,(49g.,0.613moles), and lithium borohydride,(6.3g.,0.29moles), was introduced into the reaction flask against a counter flow of nitrogen. The flask was stoppered and shaken for about 10mins. to ensure intimate mixing of the reactants. During this period there was a perceptible temperature increase, suggesting that the reaction was spontaneous at room temperature. The flask was attached to the apparatus and evacuated through taps t_1,t_2,t_3,t_4, and t_5. Traps T_1 and T_2 were cooled by liquid nitrogen, and the reaction flask heated to a maximum temperature of 140° over a period of 8hrs. The reaction flask was cooled to room temperature, and taps t_1 and t_4 were closed.

Trap T_2 was warmed to room temperature, and all volatile material was collected in trap T_1 which was then warmed to -78° (acetone/CO_2) and with tap t_4 open, was pumped at this temperature to remove any diborane produced from thermal decomposition of

FIG. 3



APPARATUS FOR THE PREPARATION OF
BERYLLIUM BOROHYDRIDE

beryllium borohydride. The cooling bath was removed from T_1, and with tap t_4 closed, the product was sublimed into trap T_2, which was cooled by liquid nitrogen. A small amount of a white involatile residue remained in trap T_1.

With taps t_2, t_3, t_4, and t_5 closed, the trap T_2 was removed from the apparatus and weighed before connecting to the vacuum line and storing the product, (4.3g.,75% on $LiBH_4$), in a suitable storage tube.

Beryllium borodeuteride.

The compound was prepared from excess beryllium chloride and lithium borodeuteride, (obtained as 98.99% $LiBD_4$,D-purity 98.69%,from the Czechoslovak Academy of Science. Prague, and used without further purification), by the method described above.

Storage of beryllium borohydride,

Freshly prepared samples of aluminium borohydride are reported to decompose spontaneously at room temperature with formation of diborane and unknown compounds. The stability of beryllium borohydride at room temperature was investigated by storing a freshly prepared sample in a tube attached to a bulb and manometer.

After several hours, a pressure of about 2cm. developed within the system, (v.p. BeB_2H_8 at 20° 5mm.) and the gas was condensed by liquid nitrogen suggesting the formation of diborane. The borohydride was cooled by acetone/CO_2, and the system evacuated. No further excess pressure developed in the apparatus,

even after standing for several months, and it was concluded that beryllium borohydride is only slowly decomposed at room temperature. It should be noted however, that after about 6-7months a little white involatile residue remained in the storage tube after removal of beryllium borohydride.

Measurement of beryllium borohydride.

Samples of the borohydride were weighed in a tube fitted with a side-arm containing a small amount of mercury. After condensing the borohydride into the tube from the vacuum line, the grease on the glass tap was protected by mercury by inverting the apparatus.

Analytical methods.

Hydrolysis.

Many of the compounds to be described are conveniently decomposed by low temperature hydrolysis with 2-methoxy ethanol and finally with dilute sulphuric acid at room temperature.

However, the amount of hydrogen released in the hydrolysis is generally less than that required by the equation:

$$L.BeB_2H_8 + 8H_2O \longrightarrow Be(OH)_2 + 2B(OH)_3 + 8H_2 + L$$

In such cases, depending on the nature of the base L, borane adducts of the type, $L.BH_3$, are present in the final solution. In the extreme case, ($L = Ph_3P$), exactly 5/8 the total hydrolysable hydrogen is released in accordance with the equation:

$$Ph_3P.BeB_2H_8 + 5H_2O \longrightarrow Be(OH)_2 + B(OH)_3 + 5H_2 + Ph_3P.BH_3$$

The amount of hydrogen released by other compounds, ($L = Me_3P, Et_3P$)

is found to be intermediate between that required from either of these equations. This suggests either partial hydrolysis of the borane adduct, or only partial formation of the borane adduct. In either case, analysis for hydrolysable hydrogen or boric acid in the hydrolysate is of little practical significance.

Analysis for beryllium and boron.

A method was developed for the simultaneous determination of beryllium and boron following decomposition by hydrolysis. If necessary, the final solution was benzene-extracted to remove borane adducts, and then diluted to a known volume.

Beryllium was determined by titrating the alkaline solution formed on addition of excess potassium fluoride to beryllium hydroxide.

$$Be(OH)_2 + 4F^- \longrightarrow BeF_4^{2-} + 2OH^-$$

The method requires standardisation under fairly closely controlled conditions, and the calibration procedure about to be described should be strictly adhered to.

Aliquots of a standard beryllium solution, (0.01M $BeSO_4$), were taken to cover the range 0-6mg. Be^{2+}. To each was added 5cc. of a 0.5M potassium sodium tartrate solution, 2drops of a 0.1% alcoholic solution of bromo thymol blue, and the solution titrated with dilute sodium hydroxide to a green end point. Then was added 5cc. of a 1M potassium fluoride solution, and the resulting blue solution set aside for about 2mins. before titrating with 0.1N sulphuric acid to a green end point. A linear calibration graph of beryllium concentration against volume of

acid titrant was plotted.

Boron was then determined by titrating the solution to a blue end point with 0.1N sodium hydroxide, and after the addition of excess mannitol, the acid solution was titrated with 0.1N sodium hydroxide to a blue end point.

Experimental results.

Ether complexes of beryllium borohydride.

Diethyl ether was evaporated under reduced pressure, (finally 0.01mm.Hg.) from a solution obtained by dissolving the borohydride (0.1g) in the ether (10cc.). The product was a colourless, slightly viscous liquid involatile at room temperature. (Found: hydrolysis of 0.0136g. gave 20.8cc.H_2, Calc. for the 1:1 adduct $C_4H_{18}B_2BeO$, 21.6cc.H_2).

Tetrahydrofuran vapour was allowed to equilibrate at room temperature with beryllium borohydride (0.1g.) and then excess tetrahydrofuran was removed at reduced pressure giving crystalline tetrakistetrahydrofuranberyllium borohydride. (Found: hydrolysis of 0.0586g. gave 29.9cc.H_2, Calc. for $C_{16}H_{40}B_2BeO_4$, 32.0cc.H_2). The solid does not melt sharply,(sealed tube under nitrogen), but slowly melts,evolving gas at about 90°.

1,2-Dimethoxyethane was added in excess to the borohydride (0.1g.), and the sparingly soluble product was recrystallised from the solvent before removing the excess ether under reduced pressure. (Found: hydrolysis of 0.0367g. gave 40.3cc.H_2, Calc. for the complex, $(C_2H_4(OMe)_2)_3$ $(Be(BH_4)_2)_2$, 37.9cc.H_2.). The

compound does not melt sharply, (sealed tube under nitrogen), but slowly liquified about 120°.

Preparation of beryllium borohydride etherate from beryllium chloride and lithium borohydride in ether solution.

Lithium borohydride,(2.1g.,0.097mole) in ether (150cc.), was added dropwise to a stirred solution of beryllium chloride, (3.5g.,0.044mole), in ether (150cc.) under a nitrogen atmosphere. The solution was separated from lithium chloride by filtration under nitrogen, and solvent removed by distillation under reduced pressure. The liquid product was dissolved in benzene (20cc.) and the solution filtered from insoluble material. Solvent was removed at the pump to leave the product, $Et_2O.BeB_2H_8$ (4.4g.,90%) as a colourless liquid.

Solubility of beryllium borohydride in benzene.

A saturated solution of the borohydride in benzene at room temperature was prepared in one limb of a double Schlenk-tube. The solution was filtered into the second limb of the Schlenk, and a known volume was removed for hydrolysis. From the volume of hydrogen released on hydrolysis, the solubility of beryllium borohydride in benzene at room temperature was found to be 0.8g./l.

Tetrakisisobutylamineberyllium borohydride.

Addition of the amine in excess to a solution of beryllium borohydride in ether solution resulted in immediate precipitation of the colourless complex, which was washed several times with

ether and dried under reduced pressure. (Found: hydrolysable H,2.38; isobutylamine,88.8, $C_{16}H_{52}B_2BeN_4$ requires hydrolysable H,2.43; isobutylamine,88.3%). The product melted with decomposition at 187°, and was found to sublime at 145° in a good vacuum.

Triphenylphosphineberyllium borohydride.

Beryllium borohydride,(0.2659g.,0.00687mole), was condensed onto a frozen (-196°) solution of triphenylphosphine, (1.75g.,0.0067mole) in benzene (20cc.). When the mixture had warmed to room temperature, the borohydride slowly dissolved in the phosphine solution. Solvent and any excess of the borohydride was then removed at reduced pressure leaving the colourless crystalline complex,(1.9g.,100%).(Found: Be,2.9%, and hydrolysis of 0.1105g. gave H_2,40.8cc.; H_3BO_3,0.0234; $Ph_3P.BH_3$,0.1000g.; M, cryoscopically in 0.79,1.58 wt.% benzene solution,310,323. $C_{18}H_{23}B_2BeP$ requires Be,3.0% and hydrolysis according to the equation:

$$Ph_3P.BeB_2H_8 + 5H_2O \longrightarrow Be(OH)_2 + B(OH)_3 + Ph_3P.BH_3 + 5H_2$$

requires H_2,41.1cc.; H_3BO_3,0.0228g.; $Ph_3P.BH_3$,0.1013g.; M,301.).

The compound, $Ph_3P.BH_3$ was separated from the hydrolysate by extraction with benzene, m.p.189°,(Found: C,78.8; H,6.59. $C_{18}H_{18}BP$ requires C,78.3; H,6.53%).

The complex, $Ph_3P.BeB_2H_8$, did not melt sharply (sealed tube under nitrogen), but was mostly liquid at 122°, resolidified above this temperature and again melted at 163°.

Attempted preparation of bistriphenylphosphineberyllium borohydride.

Beryllium borohydride,(0.4848g.,0.0125mole) was condensed onto a frozen (-196°) solution of triphenylphosphine,(6.57g., 0.0251mole) in benzene (40cc.). After warming the mixture to room temperature, benzene was removed at reduced pressure to leave a crystalline solid. (Found: Be,1.6% and hydrolysis of 0.4338g., gave H_2, 77.6cc.; M, cryoscopically in 2.9 wt.% benzene solution,277. Calc. for a 1:1 mixture(Ph_3P + $Ph_3P.BeB_2H_8$) Be,1.7%, hydrolysable H_2,86.2cc.; M(apparent),281).

It was concluded that beryllium borohydride does not form a bistriphenylphosphine complex at room temperature.

Triethylphosphineberyllium borohydride.

Beryllium borohydride,(1.10g.,0.0284mole) was condensed onto a frozen(-196°) solution of triethylphosphine,(3.4g.,0.0288 mole), in benzene (20cc.). The mixture was warmed to room temperature, and benzene removed from the clear solution under reduced pressure. The colourless, slightly viscous liquid was purified by vacuum distillation, b.p.68°/ 0.01mm.Hg. (Found: Be,5.3% and hydrolysis of 0.0682g., gave H_2,53.2cc.; M, cryoscopically in 1.12,0.56 wt.% benzene solution, 169,162.7. $C_6H_{23}B_2BeP$ requires Be,5.7%; and hydrogen assuming formation of one mole $Et_3P.BH_3$, 48.8cc.; M,156.9).

The compound, $Et_3P.BH_3$ was separated from the hydrolysate by extraction with benzene,m.p.49° (Found: C,54,9; H,14.0.

$C_6H_{18}BP$ requires C,54.5; H,13.9%0.

Triethylphosphineberyllium borohydride from beryllium borohydride etherate and triethylphosphine.

Triethylphosphine,(1.48g.,0.0125mole) was syringed onto a cooled (-196°) sample of beryllium borohydride etherate,(1.415g., 0.0125mole). The mixture was allowed to warm to room temperature and volatile material removed at the pump. The product was purified by vacuum distillation and shown by its i.r.spectrum to be identical to the compound prepared above.

Trimethylphosphineberyllium borohydride.

Trimethylphosphine,(254cc.,0.0113mole), was condensed onto a cooled (-196°) sample of beryllium borohydride,(0.4048g., 0.0105mole) contained in a reaction tube attached to the vacuum line. On warming to room temperature, there was a rapid reaction with the formation of a liquid product which was involatile at room temperature.(Found: Be,7.9%; M,cryoscopically in 0.66 and 0.33 wt.% benzene solution 120,118.1. $C_3H_{17}B_2BeP$ requires Be,7.9%; M,114.8).

Hydrolysis of 0.0538g., gave H_2, 58.1cc.; Me_3P,2.1cc., and the compound, $Me_3P.BH_3$ m.p.99°, was isolated from the hydrolysate. The latter compound was identified by melting point and comparison of the i.r. spectrum with that for an authentic sample of trimethylphosphine-borane,m.p.102°, prepared from trimethylphosphine and diborane. Assuming the trimethylphosphine to be formed from partial hydrolysis of the phosphine-borane,

the observed hydrogen figure,(58.1cc.), may be corrected as follows:

1 mole Me_3P = 3 moles H_2,

Then 2.1cc.Me_3P = 6.3cc.H_2.

Thus corrected hydrogen figure = (58.1-6.3) = 51.8cc.

Hydrolysis of 0.0538g., assuming formation of 1mole Me_3PBH_3, requires H_2,52.5cc.

Dimethylphosphineberyllium borohydride and dimethylamineberyllium borohydride.

The liquid adducts were prepared quantitatively by a similar method to that described for the preparation of trimethylphosphineberyllium borohydride.

Dimethylphosphineberyllium borohydride. (Found: Be,8.9%; M, cryoscopically in 0.445,0.223 wt.% benzene solution 101.3,101. $C_2H_{15}B_2BeP$ requires Be,8.9%; M,100.8).

Dimethylamineberyllium borohydride. (Found: Be,10.6%; M, cryoscopically in 0.55 and 0.27 wt.% benzene solution 89.5,86.6. $C_2H_{15}B_2BeN$ requires Be,10.7%; M,83.7).

Displacement of ether in beryllium borohydride etherate by other donor molecules.

The preparation of triethylphosphineberyllium borohydride from triethylphosphine and beryllium borohydride etherate showed that the coordinated ether molecule could be replaced by other donor molecules.

Displacement by triphenylphosphine. Beryllium borohydride etherate

(0.467g.,0.00417mole) and triphenylphosphine,(1.09g.,0.00416mole), were heated in vacuo to 80°, and volatile material was trapped at -196°. Diethyl ether (45cc., required 93cc.) was identified by comparing the i.r. spectrum with that for diethylether.

Displacement by trimethylphosphine. Trimethylphosphine (28cc.) was condensed onto a frozen (-196°) sample of the etherate, and the mixture was allowed to equilibrate at room temperature for 4hrs. before removing volatile material (27cc.) which was identified as diethylether from its i.r.spectrum.

Displacement of trimethylphosphine by trimethylamine. Trimethylamine (16.2cc) was condensed onto a frozen (-196°) sample of trimethylphosphineberyllium borohydride, and the mixture equilibrated at room temperature for about 1hr. before removing volatile material (6.0cc.) identified as trimethylphosphine from its i.r. spectrum.

The preparation of beryllium hydride from phosphine adducts of beryllium borohydride.

The attempted preparation of a bistriphenylphosphine-beryllium borohydride complex at room temperature, gave only a mixture of triphenylphosphineberyllium borohydride and triphenylphosphine. Similarly, triethylphosphine could be recovered from a 1:1 mixture of the phosphine and triethylphosphineberyllium borohydride by pumping at room temperature.

However, it was found that on heating these mixtures at about 100°, a reaction occured with the formation of beryllium

hydride.

Pyrolysis of a 2:1 mixture of triphenylphosphine and beryllium borohydride.

The borohydride,(0.8465g.,0.022mole), was condensed onto a frozen (-196°) solution of triphenylphosphine (11.48g., 0.044mole) in xylene (mixed isomers,100cc.) contained in one limb of a double Schlenk-tube fitted with a reflux condenser. After the mixture had warmed to room temperature and the borohydride had dissolved, it was heated to 150°(oil-bath temperature) for 6hrs. under a nitrogen atmosphere, during which time a white precipitate formed. The reaction mixture was filtered while still hot into the second limb of the Schlenk-tube, and the residue was boiled with two 40cc. portions of dry benzene, the filtrate each time being added to the xylene solution from which the adduct, $Ph_3P.BH_3$ (11.6g.,97%), was recovered (identified by m.p, and i.r. spectrum).

The insoluble residue (0.25g.) consisted mainly of beryllium hydride (Found: Be,63.2%; hydrolysis of 0.0193g., gave 63.3cc.H_2. Calc. for BeH_2, Be,81.9%; H_2,78.4cc. Sample corresponds to 80.7 wt.% BeH_2). From the hydrolysate was extracted $Ph_3P.BH_3$(0.0032g., required,0.0037g.) identified by its i.r. spectrum. Hence, the molar purity of the beryllium hydride was found to be 99.1mole%.

The main feature of the i.r. spectrum of the best specimen of beryllium hydride prepared by this method consists of a broad absorption centred on 1758cm^{-1}.

Pyrolysis of a 2:1 mixture of triethylphosphine and beryllium borohydride in the absence of solvent.

Triethylphosphine (1.2g.,0.010mole), was added to triethylphosphineberyllium borohydride (1.5g.,0.0096mole), contained in one limb of a double Schlenk-tube fitted with a reflux condenser. The mixture was heated under nitrogen without apparent reaction until at 120°, a small amount of white solid appeared in the solution which quickly set to a glassy-solid, and the product was heated at 145° for about 4hrs. The product was refluxed with benzene, and after filtration the adduct, $Et_3P.BH_3$ m.p.49°(1.4g.) was recovered from the benzene solution. Impure beryllium hydride was removed from the Schlenk and heated in vacuum to remove the last traces of the borane-adduct. (Found: Be,29.8%, and hydrolysis of 0.0235g., gave H_2,33.6cc. BeH_2 requires Be,81.9%, H_2,95.6cc. Sample corresponds to 35.1 wt.% BeH_2, and boron was not detected as H_3BO_3 in the hydrolysate.)

Pyrolysis of a 2:1 mixture of triethylphosphine and beryllium borohydride in xylene solution.

Triethylphosphine (1.3g.,0.011mole) and triethylphosphineberyllium borohydride (1.2g.,0.0076mole) were dissolved under nitrogen in xylene (mixed isomers,30cc.), contained in one limb of a double Schlenk-tube fitted with a reflux condenser. The mixture was heated by oil-bath, and at about 140-150° a slight precipitate of beryllium hydride separated from the solution. The oil-bath temperature was increased to 170° over 3hrs. after

which time the hot solution was filtered and the beryllium hydride washed with hot benzene before heating in vacuo to remove the last trace of the borane-adduct, $Et_3P.BH_3$. The impure beryllium hydride, (0.077g.) was recovered from the Schlenk.(Found: Be,55%; and hydrolysis of 0.008g. gave H_2,19.1cc. BeH_2 requires Be,81.9%, H_2,32.6cc. Sample corresponds to 58.6 wt.% BeH_2, and boron was not detected as H_3BO_3 in the hydrolysate). After distillation of the hydrocarbon solvent, the triethylphosphine-borane, (identified from m.p. and i.r. spectrum) was isolated with a small amount of involatile solid, which was found to contain 1.7% of the original beryllium content.

Pyrolysis of a 2:1 mixture of trimethylphosphine and beryllium borohydride in benzene solution.

Beryllium borohydride (0.2857g.,0.0074mole) and trimethylphosphine (337cc.,0.015mole), were condensed onto benzene (10cc.) in a cooled (-196°) reaction tube. The tube was sealed under vacuum, and heated at 60° for 65hrs. during which time a precipitate of beryllium hydride separated from the solution. Heating was continued for a total of 9days to allow complete reaction.

The tube was opened on the vacuum line and benzene removed at -10°. Trimethylphosphine-borane (0.737g., reqd.1.33g.,56%) was removed by pumping at room temperature. A small volume of liquid was removed from the beryllium hydride by 'flaming' the reaction tube while pumping at 0.001mm.Hg. Sufficient liquid was

recovered to record the i.r. spectrum, which closely resembled that for trimethylphosphineberyllium borohydride. The reaction tube was transferred to a glove-box and the beryllium hydride recovered,(0.051g.,required,0.081g.,63%). (Found: Be,58.6%, and hydrolysis of 0.0157g. gave H_2,47.7cc. BeH_2 requires Be,81.9%; H_2,63.9cc. Sample corresponds to 74.8 wt.% BeH_2, and boron was not detected as H_3BO_3 in the hydrolysate).

Tensimetric titration of beryllium borohydride with donor molecules.

To investigate the possible formation of adducts other than the 1:1 compounds described above, samples of beryllium borohydride were titrated tensimetrically at room temperature with volatile donor molecules in the apparatus previously described. The equilibrium pressure (p_{mm}) at room temperature was plotted against the mole ratio of donor to beryllium borohydride.

Titration of beryllium borohydride with diethyl ether.

Weight of beryllium borohydride = 0.1065g.(61.6cc.)

Vol.Et_2O(cc.)	Total vol.Et_2O	p_{mm}.	Et_2O/BeB_2H_8
0.0	0.0	8.2	-
10.7	10.7	8.0	0.174
12.7	23.4	7.4	0.380
9.6	33.0	9.3	0.536
11.9	44.9	8.2	0.728
16.4	61.3	20.1	0.996
14.9	76.2	107.2	1.238
12.8	89.0	167.0	1.446
14.0	103.0	218.4	1.672
14.8	117.8	263.0	1.910
14.9	132.7	296.8	2.150
12.3	145.0	314.7	2.350

On completion of the titration excess ether was recovered from the apparatus,(86.2cc.). Thus, combined ether = 145-86.2 = 58.8cc. corresponding to a mole ratio of 0.96/1.0.(v.p. of product, 0.05mm. Hg. at 22°). FIG.4, curve A.

Titration of beryllium borohydride with trimethylamine.

Weight of beryllium borohydride = 0.0525g.(30.4cc.)

Vol.Me_3N(cc.)	Total vol.Me_3N	$p_{mm.}$	Me_3N/BeB_2H_8
0.0	0.0	12.5	-
6.6	6.6	5.4	0.217
7.6	14.2	6.5	0.467
10.4	24.6	3.6	0.810
9.9	34.5	27.5	1.135
14.9	49.4	149.6	1.626
9.0	58.4	237.6	1.923
9.8	68.2	327.7	2.245

Consistent pressure readings for ratios $Me_3N/BeB_2H_8 > 1.0$ were obtained after about 17hrs. On completion of the titration excess trimethylamine was recovered from the apparatus,(31.1cc.). Thus combined amine = 37.1cc., corresponding to a mole ratio of 1.22/1.0.(v.p. of product,1.07mm. at 21°). A small amount of volatile solid was recovered from the apparatus, but was not identified. FIG.4, curve B.

Titration of beryllium borohydride with dimethylamine.

Weight of beryllium borohydride = 0.0731g.(42.3cc.)

FIG.4, curve E.

Vol.Me_2NH(cc.)	Total vol.Me_2NH	$p_{mm.}$	Me_2NH/BeB_2H_8
0.0	0.0	5.7	-
9.2	9.2	2.9	0.218
8.3	17.5	3.6	0.414
10.1	27.6	0.7	0.653
10.2	37.8	1.2	0.942
8.9	46.7	10.6	1.110
10.2	56.9	16.3	1.35
13.2	70.1	23.1	1.66
13.6	83.7	30.3	1.98
18.6	102.3	41.5	2.42
13.7	116.0	54.2	2.75
16.9	132.9	128.0	3.14
10.9	143.8	266.0	3.40

Consistent pressure readings for the ratios $Me_2NH/BeB_2H_8 > 1.0$ were obtained after about 17hrs. During the titration, a small volume of hydrogen ($\sim$ 3cc.) was liberated. The product corresponding to a ratio Me_2NH/BeB_2H_8 = 3.0/1.0, was completely solid, and a sample (0.1137g.) melted about 94° with evolution of dimethylamine,(19.7cc.), and hydrogen,(18.2cc.). On completion of the titration, excess amine was recovered from the apparatus (19.5cc.).Combined amine = 124.3cc., corresponding

to a ratio of 2.94/1.0.(v.p. of product, 0.4mm. at 22°).

Titration of beryllium borohydride with dimethylphosphine.

Weight of beryllium borohydride = 0.0544g.(31.5cc.)

FIG.4, C.

Vol.Me_2PH(cc.)	Total vol.Me_2PH	$p_{mm.}$	Me_2PH/BeB_2H_8
0.0	0.0	7.3	-
4.3	4.3	7.1	0.137
7.9	12.2	7.8	0.388
10.7	22.9	4.1	0.726
11.3	34.2	32.0	1.085
13.9	48.1	80.8	1.530
9.7	57.8	152.6	1.83
12.3	70.1	211.9	2.23

Consistent pressure readings for ratios $Me_2PH/BeB_2H_8 > 1.0$ were obtained after about 17hrs. During the titration, a total of 2.3cc.H_2 was liberated, and the final product was a clear mobile liquid. The i.r. spectrum of this liquid contained absorptions due to terminal and bridging B-H, and in particular, a strong absorption centred on 1758cm^{-1} indicating Be.H.Be bridging. On completion of the titration, excess phosphine was recovered from the apparatus (26.4cc.) together with a small amount of a slightly volatile liquid (v.p. 2mm.Hg. at 25°) identified by i.r. spectrum and analysis as dimethylphosphine-borane.(Found: C,31.1; H,13.4. $C_2H_{10}BP$ requires C,31.7; H,14.2%). Thus, dimethylphosphine (43.7cc.) reacted with beryllium

borohydride (31.5cc.), corresponding to a ratio, Me_2PH/BeB_2H_8 of 1.39/1.0. (v.p.of liquid product 0.4mm.Hg. at 26°).

Titration of beryllium borohydride with trimethylphosphine.

Weight of beryllium borohydride = 0.0664g.(38.4cc.)

FIG.4, D.

Vol.Me_3P(cc.)	Total vol.Me_3P	$p_{mm.}$	Me_3P/BeB_2H_8
0.0	0.0	10.2	-
7.2	7.2	5.5	0.187
9.5	16.7	5.2	0.435
9.3	26.0	3.6	0.676
10.6	36.6	0.8	0.954
14.6	51.2	13.3	1.334
12.5	63.7	24.8	1.663
9.2	72.9	30.2	1.900
12.8	85.7	159.0	2.230
11.1	96.8	279.0	2.520
7.7	104.5	326.0	2.720

Consistent pressure readings for ratios, $Me_3P/BeB_2H_8 > 1.0$ were obtained after about 17hrs. A solid product separated after 4hrs. at the point Me_3P/BeB_2H_8 = 1.7, and the final product was completely solid. On completion of the titration, excess phosphine was recovered from the apparatus,(28.8cc.). Thus, trimethylphosphine,(75.7cc.) reacted with beryllium borohydride,(38.4cc.), corresponding to a ratio, Me_3P/BeB_2H_8 of 1.97/1.0.(v.p. of solid product, 2mm. at 21°). The i.r. spectrum of this solid

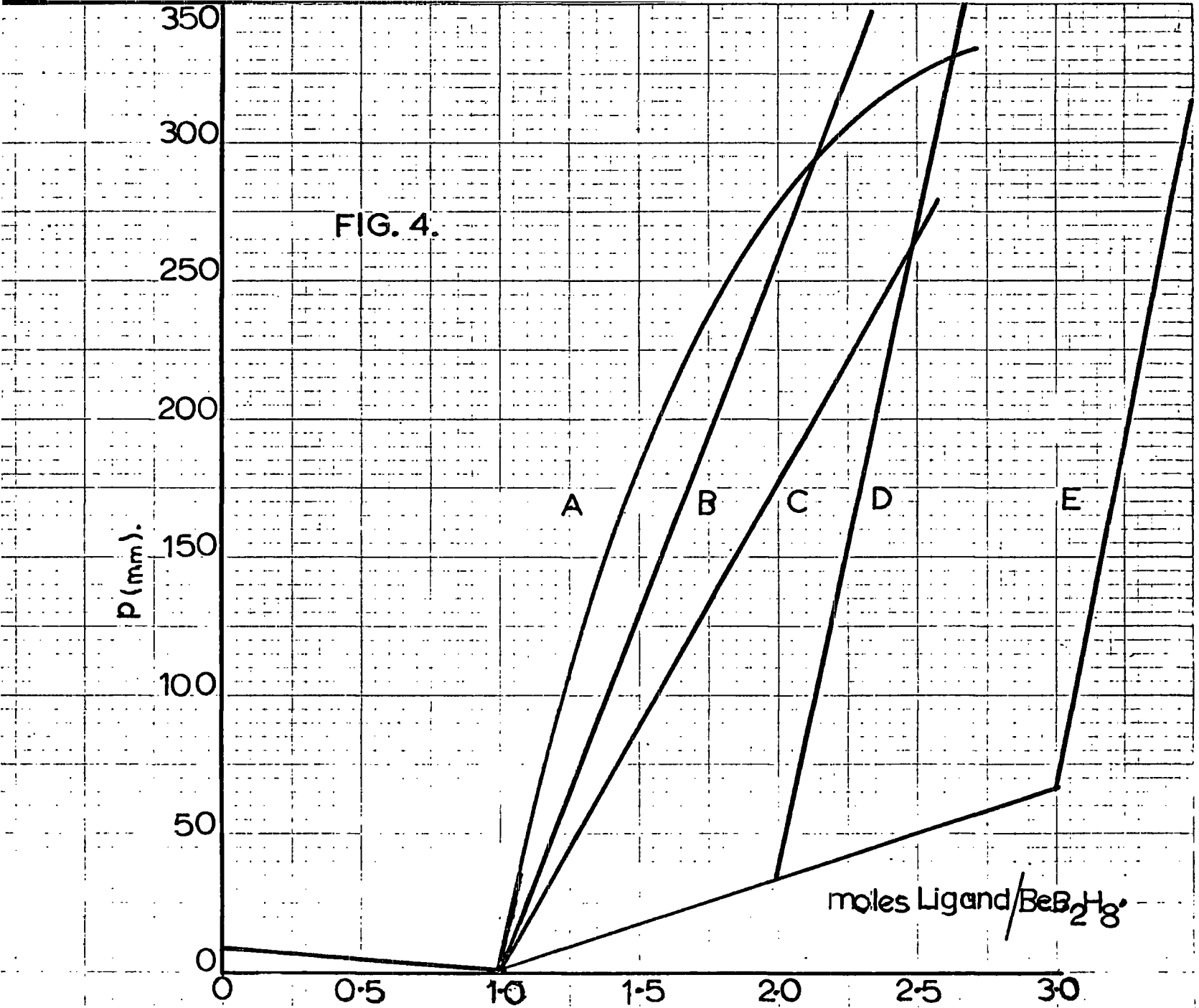


FIG. 4.
P (mm).
350
300
250
200
150
100
50
0
0
0·5
1·0
1·5
2·0
2·5
3·0
A
B
C
D
E
moles Ligand/BeB2H8

corresponded very closely to that of the liquid adduct, $Me_3P.BeB_2H_8$.

The results of this and the other tensimetric titrations are illustrated in FIG.4.

Attempted preparation of bistrimethylphosphineberyllium borohydride.

The result from the tensimetric titration of beryllium borohydride with trimethylphosphine indicates rapid formation of the 1:1 adduct, $Me_3P.BeB_2H_8$, followed by slow reaction with a second mole of phosphine to give a solid product of overall composition, $2Me_3P + BeB_2H_8$. The nature of this product will now be examined in detail.

Trimethylphosphine,(168.8cc.,0.00755mole), was condensed onto beryllium borohydride,(0.1406g.,0.00364mole), contained in a reaction tube attached to the vacuum line through a mercury float-valve. The valve was closed and the mixture allowed to react at room temperature. White crystals suddenly appeared in the liquid adduct after about $3\frac{1}{2}$hrs.,and the contents of the tube solidified after a further $\frac{1}{2}$hr. The 'damp' appearance of the solid disappeared after about 45hrs.,and with the reaction tube cooled to -20°, excess phosphine (7.5cc.),was recovered from the apparatus. Hence, trimethylphosphine,161.3cc., reacted with beryllium borohydride,81.4cc., corresponding to a mole ratio of 1.99/1.0. (v.p. of solid product, 2.3mm.Hg. at 21°).

On pumping the product at room temperature, a volatile solid and condensable gas were collected in a cooled (-196°)

trap, and the solid product slowly assumed a 'damp' appearance and eventually gave a viscous liquid product. The reaction tube was warmed to 40° to ensure complete removal of volatile material, sealed at a constriction, and transferred to a glove-box.

Examination of volatile material collected at -196°.

The contents of the trap were separated by fractionation at -20° and the gas, trimethylphosphine,(24.5cc.), and the solid, trimethylphosphine-borane,(0.2g.), were identified from their i.r. spectra. This weight of trimethylphosphine-borane corresponds to removal of 30.6% of the boron content of the borohydride.

Examination of the liquid product remaining in the reaction tube.

The i.r. spectrum of this product compared closely to that of the 1:1 adduct, $Me_3P.BeB_2H_8$, except for a broad band centred on 1758cm^{-1} indicating the presence of Be.H.Be units. Hydrolysis of 0.0481g., gave H_2,49.8cc.; Me_3P,3.3cc.; and Be,9.8%.

It was concluded from these results, that if a 2:1 adduct is formed, it is readily decomposed at room temperature into trimethylphosphine, trimethylphosphine-borane, and an unknown liquid closely resembling the 1:1 adduct, $Me_3P.BeB_2H_8$, but containing Be.H.Be units.

In a further experiment, trimethylphosphine,(262cc.,0.0117 mole), and beryllium borohydride,(0.2065g.,0.00534mole), were allowed to react at room temperature, and after removal of excess

phosphine,(27cc.), it was found that trimethylphosphine-borane could be sublimed from the solid product simply by cooling the upper part of the reaction tube with solid CO_2.

After pumping the solid product at room temperature, trimethylphosphine,(32.3cc.), and phosphine-borane,(0.521g.), were isolated, and the residual product was a glassy-solid. The recovered phosphine was condensed back onto the glassy-solid, and over a period of 80hrs. the pressure within the apparatus decreased and a further sample of the phosphine-borane,(0.0176g.), and phosphine,(10.7cc.), was recovered. The total trimethyl-phosphine-borane,(0.539g.) recovered, corresponded to removal of 56.5% of the total boron content in the borohydride.

The material remaining in the reaction tube, was a cloudy, viscous paste, and the i.r. spectrum showed in addition to absorptions found in the 1:1 adduct, a broad absorption centred on 1768cm^{-1}.

The removal of trimethylphosphine-borane from the borohydride has been studied at elevated temperatures.

The solid product from beryllium borohydride,(0.1373g., 0.00355mole), and trimethylphosphine, (159.3cc.,0.0071mole), was heated at 65° for a few minutes and then cooled to room temperature, when it was found that an appreciable pressure, (>9cm.Hg.), of trimethylphosphine was present above the solid. The tube was heated at 70° for 5hrs., and towards the end of this period a white precipitate separated from the liquid.

Trimethylphosphine-borane,(0.5175g.), and unreacted trimethylphosphine, (13.1cc.), were separated from the solid which was contaminated with a small amount of liquid which could not be removed by pumping at 120°.

On the basis of the equation:

$$BeB_2H_8 + 2Me_3P \longrightarrow BeH_2 + 2Me_3P.BH_3$$

the recovered phosphine-borane, (0.5175g.), corresponds to removal of 81.5% of the boron content in the borohydride. Further,since 89.92g.$Me_3P.BH_3$ = 22400cc.Me_3P, the phosphine accounted for,(142.1cc) corresponds to 89% of the phosphine originally used.

Attempted alkyl-hydrogen exchange reaction between trimethylborane and beryllium borohydride.

By analogy with the exchange reaction exemplified by trimethylborane and diborane, and more specifically to the reported exchange between trimethylborane and uranium borohydride, it was thought possible for exchange to occur between trimethylborane and beryllium borohydride.

No evidence was obtained for such a reaction after trimethylborane was equilibrated with beryllium borohydride at room temperature for 90hrs., nor after equilibration for 45hrs. at 75°. The unchanged borane was recovered from the borohydride at -20°, and the i.r. spectra of both compounds compared exactly to those for the original reactants.

Attempted preparation of chloroberyllium borohydride etherate.

Lithium borohydride,(0.298g.,0.0137mole), in ether (150cc.) was added dropwise to a stirred solution of beryllium chloride, (1.1g.,0.0138mole), in ether (100cc.) under a nitrogen atmosphere. The precipitated lithium chloride was separated by filtration and solvent removed at reduced pressure. Benzene,(20cc.) was added to the liquid product and the solution filtered from a slight precipitate of lithium chloride, and solvent removed at reduced pressure to leave a slightly viscous liquid from which some solid separated on standing. The liquid product was filtered from the solid.(Found: Be,6.6; B,6.6; H,2.0; Cl,26.8. $ClBeBH_4.OEt_2$ requires Be,6.8; B,8.1; H,3.0; Cl,26.7%).

The compound was distilled in vacuum,(oil-bath, 80-90° at 0.01mm.Hg.), to give a clear distillate,(Found: Be,6.85; B,10.1; Cl,16.8%). A thick viscous liquid remained in the distillation flask and slowly solidified at room temperature. Repeated distillation left more solid in the flask, and was shown to contain beryllium and chloride.

It was concluded that the product disproportionated on heating according to the equation:

$$2ClBeBH_4.OEt_2 \longrightarrow BeCl_2.OEt_2 + Et_2O.BeB_2H_8$$

TABLES OF INFRA-RED SPECTRA. (cm^{-1})

BeB_2H_8: 2475s.sh; 2427s; 2283s; 2222w; 2169s; 2101s; 2079ssh; 2000w; 1515m; 1299s; 1190s; 1124s; 1010w; 714sb.

BeB_2D_8: 1852s; 1779s; 1733s; 1647w; 1587s; 1563msh; 1527m; 1458s; 1376s; 1342wsh; 1299w; 1261w; 1149msh; 1072s; 1015m; 680sb; 617sb.

$Et_2O.BeB_2H_8$: 2451s; 2410s; 2347w; 2257msh; 2212msh; 2174ssh; 2137s; 2028m; 1515m; 1479s; 1447s; 1451s; 1397s; 1335m; 1294m; 1198m; 1155m; 1134s; 1095m; 1010sb; 901s; 855s; 787s; 714sb.

$Et_2O.BeB_2D_8$: 2457m; 2151m; 1869s; 1786s; 1701m; 1639s; 1575s; 1515s; 1475m; 1468s; 1445s; 1389s; 1359m; 1330m; 1285m; 1193s; 1149s; 1081s; 1000s; 890s; 841s; 828msh; 784s; 690sb; 538wb; 492msh; 472mb.

$Ph_3P.BeB_2H_8$: 2500m; 2481m; 2427s; 2375s; 2347msh; 2252w; 2155m; 2114s; 1484msh; 1464s; 1437s; 1379s; 1333w; 1312w; 1185w; 1160w; 1131m; 1103m; 1064msh; 1058m; 1029m; 1022wsh; 1000m; 753ssh; 746s; 735s; 704m; 694s; 623m; 604m; 510ssh; 500s.

$Et_3P.BeB_2H_8$: 2469s; 2421s; 2381msh; 2347wsh; 2252m; 2155s; 2114s; 2000w; 1515m; 1460s; 1414s; 1387s; 1299mb; 1176w; 1131s; 1075m; 1042ssh; 1036s; 1012s; 855w; 778s; 763s; 709sb; 671s; 606sb.

$Me_3P.BeB_2H_8$: 2475s; 2421s; 2353msh; 2257m; 2160msh; 2114s; 1502ssh; 1460s; 1437s; 1425s; 1319m; 1299s; 1133s; 1013m; 980s; 952s; 893w; 852w; 781msh; 750s; 714sb; 633sb.

$Me_2PH.BeB_2H_8$: 2469s; 2421s; 2247m; 2141ssh; 2114s; 1531m; 1471s; 1427s; 1311m; 1295m; 1135s; 1011m; 993s; 966m; 769msh; 761m; 714sb; 630sb.

$Me_3N.BeB_2H_8$: 2475s; 2421s; 2398msh; 2262w; 2222wsh; 2174ssh; 2141s; 2028w; 1515msh; 1486s; 1466s; 1418msh; 1274m; 1250m; 1242m; 1176m; 1136s; 1111m; 1031w; 988s; 946w; 855wsh; 833s; 714sb.

$Me_2NH.BeB_2H_8$: 2994m; 2941m; 2817w; 2475s; 2421s; 2283s; 2222s; 2174ssh; 2137s; 2024m; 1515s; 1471s; 1408s; 1282s; 1230m; 1136s; 1124s; 1064s; 1020s; 900s; 833w; 749sb; 714sb; 471wb.

$Ph_3P.BH_3$: 2381s; 2342ssh; 2247w; 1484s; 1433s; 1389w; 1311w; 1183w; 1134m; 1103s; 1066msh; 1055s; 1026m; 997m; 763w; 743s; 733s; 701s; 690s; 623m; 602m; 500ssh; 491s; 472m.

$Et_3P.BH_3$: 2370s; 2342ssh; 2257w; 1460m; 1416m; 1385m; 1274m; 1263m; 1250w; 1136m; 1087m; 1047ssh; 1041s; 1002m; 781sb; 726m; 680w; 667m; 546m; 539wb.

$Me_3P.BH_3$: 2370s; 2342ssh; 2257w; 1429s; 1316w; 1295s; 1139m; 1085m; 1073s; 976s; 949s; 889m; 759s; 709s; 581m; 570m;

$Me_2PhP.BH_3$: 2370s; 2342ssh; 2257m; 1488m; 1433s; 1418s; 1337w; 1312m; 1302m; 1290s; 1189w; 1134s; 1115s; 1064s; 1000w; 946s; 918s; 857s; 752ssh; 738s; 691s; 578sb; 474mb.

$Me_2PH.BH_3$: 2381s; 2347msh; 2257w; 1418m; 1312w; 1295m; 1136m; 1070s; 1010msh; 998s; 952s; 885m; 765m; 721m; 633w; 564w.

Solid corresponding to '$(Me_3P)_2BeB_2H_8$' - nujol mull.

2545w; 2469ssh; 2404s; 2347msh; 2299msh; 2252s; 2174s; 2119s; 2049w; 2008w; 1464s; 1429s; 1383s; 1316m; 1295s; 1136m; 1085ssh; 1072s; 1020msh; 971ssh; 947s; 889m; 758m; 722wsh; 708s; 633w; 578w; 568m.

$(Be(Bu^iNH_2)_4)(BH_4)_2$: 3175s; 3096s; 2410wsh; 2381wsh; 2299ssh; 2247s; 2174msh; 1590m; 1466s; 1393m; 1374; 1348w; 1319w; 1261ssh; 1242s; 1220ssh; 1174m; 1117ssh; 1093s; 1020s; 943m; 907m; 826m; 793m.

Abbreviations: s = strong; m = medium; w = weak; b = broad; sh = shoulder.

Part II.

DISCUSSION

DISCUSSION.

Ether complexes and the isobutylamine complex of beryllium borohydride.

Beryllium borohydride has been reported[1] to be soluble in anisole, diethyl ether, diphenyl ether, but insoluble in tetrahydrofuran, 1,2-dimethoxyethane, and some other ethers. The present work finds that beryllium borohydride reacts exothermically with diethyl ether, tetrahydrofuran, and 1,2-dimethoxyethane. Diethyl ether can be evaporated from an ethereal solution of the borohydride at low pressure, and the ether-to-beryllium ratio was only a little more than one, leaving a slightly viscous liquid product. The result was confirmed by a tensimetric titration which clearly indicated the formation of a 1:1 adduct. The compound is reported[2] to be monomeric in benzene solution, and a B^{11} n.m.r. spectrum shows a quintuplet of relative intensity 1:4:6:4:1. A convenient preparation of the etherate is by a metathetical reaction between beryllium chloride and lithium borohydride in ether solution.

Tetrahydrofuran vapour is absorbed by beryllium borohydride to give a crystalline complex of approximate composition, $Be(BH_4)_2 \cdot 4THF$, which may be reasonably be formulated as a salt, $(Be(THF)_4)\ (BH_4)_2$. The compound has negligible vapour pressure at room temperature and is quite soluble in tetrahydrofuran, but evaporation of solvent under reduced pressure yields only glassy material.

1,2-Dimethoxyethane did not give the analogous chelate, $(Be(MeOC_2H_4OMe)_2)(BH_4)_2$, but unexpectedly gave a crystalline complex, moderately soluble in the ether, in which the O/Be ratio was about 3:1. This compound has not been further investigated, and the structure remains quite unclear.

Addition of excess isobutylamine to an ethereal solution of beryllium borohydride resulted in immediate precipitation of tetrakisisobutylamineberyllium borohydride which is formulated as a salt, $(Be(Bu^iNH_2)_4)(BH_4)_2$. The complexes formulated as salts have i.r. spectra which in the region 2200-2300cm^{-1} are typical of those compounds containing the borohydride ion.[3.]

The i.r. spectrum of the diethyl ether adduct is more complex in the 2500-2000cm^{-1} region, and very similar to that of beryllium borohydride, suggesting the presence of both terminal B-H (2451, 2410cm^{-1}) and a bridged hydrogen group, BH_2Be (2257,2212,2174,2138cm^{-1}). Since the B^{11}n.m.r. spectrum shows only a quintuplet, then both boron atoms are equivalent, and each is coupled with four equivalent hydrogen atoms. These observations are consistent with the ether molecule coordinated to the beryllium atom, and this result would be anticipated from the unequal charge distribution of the Be.H.B bond, which would favour nucleophilic attack at the beryllium atom.

Substituted amine and phosphine adducts of beryllium borohydride.

That the complex, $Et_2O.BeB_2H_8$, contains strongly coordinated ether is illustrated by the reported[2.] decomposition

at about 80° with evolution of ethane.

$$Et_2O.BeB_2H_8 \longrightarrow C_2H_6 + 2H_2 + 'BeB_2H_3.OEt'$$

It is of interest however to observe that the ether can be displaced by other donor molecules. For example, isobutylamine immediately displaces ether with formation of the tetrakis complex described above. Trimethylphosphine and triethylphosphine quantitatively displace ether with formation of the corresponding 1:1 phosphine adducts. The reaction between triethylphosphine and the ether complex at room temperature was exothermic, and crystalline triethylphosphine-borane was recovered from the reaction product. Triphenylphosphine displaced some ether from the ether complex at room temperature, and more at 40°, but did not quantitatively displace the ether, presumably due to the reaction mixture solidifying. In no reaction was there obtained evidence for the formation of a mixed complex of the type, $Et_2O(L)BeB_2H_8$, where L is a donor molecule other than ether.

Trimethylamine displaced the phosphine from trimethylphosphineberyllium borohydride, and so the donor strength of the ligands investigated would appear to be in the order:

$Me_3N > Me_3P(Et_3P, Ph_3P) > Et_2O$.

Trimethylamineberyllium borohydride was described[4] as a glassy product decomposing about 140°, but was sufficiently volatile to allow vapour pressure measurements to be made, (v.p. = $\log_{10}p_{mm} = 8.353 - 2909/T$, b.p.260°). The compound reacted with trimethylamine at 95° for 30hrs. with formation of

trimethylamine-borane.

$$Me_3N.BeB_2H_8 + Me_3N \longrightarrow Me_3N.BH_3 + Me_3N.BeBH_5$$

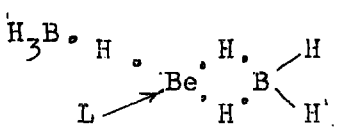
The second product, $Me_3N.BeBH_5$, reacted with diborane to give pure beryllium borohydride, but no such reaction was observed with the original adduct. Some trimethylamine could be removed from the compound, $Me_3N.BeBH_5$, at 100°, which was found to react reversibly with the product.

The 1:1 complexes, $L.BeB_2H_8$ (where L = Ph_3P, Et_3P, Me_3P, Me_2PH, Me_2NH) described in this work were found to be monomeric in benzene solution, and with the exception of the triphenylphosphine complex, were all slightly viscous liquids at room temperature. The i.r.spectra of the adducts are very similar in the region 2500-2000cm^{-1}, and contain two main groups of absorption bands, one about 2450cm^{-1} due to terminal B-H stretching vibrations and the second about 2150cm^{-1} attributed to bridging hydrogens. These conclusions are based on similarities to the spectrum of beryllium borohydride examined as a nujol-mull, which contains two intense absorptions at 2463 and 2415cm^{-1}, and one even more intense absorption at 2174cm^{-1} with shoulders at 2141,2096, and 2053cm^{-1}. The spectrum of gaseous beryllium borohydride previously examined[3], showed absorptions at 2440 and 2465cm^{-1} attributed to terminal BH_2 groups, and those at 2180 and 1450cm^{-1} to BH_2Be bridges. The absorptions in the region 2500-2000cm^{-1} are absent in the i.r. spectrum of beryllium borodeuteride

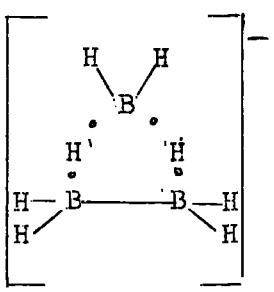
examined as a nujol-mull, and reappear in the region 1852-1520cm^{-1}.

The B^{11}n.m.r. spectra of the adducts, $Me_3P.BeB_2H_8$ (δ = 995c/s, J_{B-H} = 84c/s) and $Me_3N.BeB_2H_8$ (δ = 892c/s, J_{B-H} = 86c/s), show a well defined quintuplet of relative intensity, 1:4:6:4:1, which suggests, as for the ether complex, that both borons are equivalent and each coupled with four equivalent hydrogen atoms. The B^{11}n.m.r. spectra of the triphenylphosphine complex, (ca. 30wt.% solution in benzene), and triethylphosphine complex were very much less well defined, and that of $Ph_3P.BeB_2H_8$ consisted of a poorly defined broad band at 916c/s to the high field of trimethoxyborane used as external reference. For these compounds it is less certain that the ligand is attached directly to the beryllium, but this may be inferred since only one boron signal was observed in the spectrum.

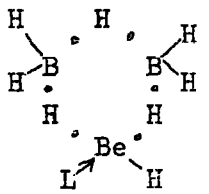
From this evidence, the structure of the 1:1 adducts of beryllium borohydride described above, may be represented:

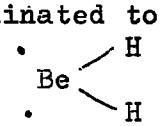


Since these adducts are iso-electronic with the octahydrotriborate ion, $B_3H_8^-$, which on the evidence of its n.m.r. spectrum has been assigned the structure:[5]



an alternative structure for the beryllium borohydride adducts may be written.

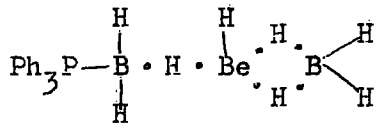


No final selection between these structures has been made, but since no compound containing a terminal beryllium-hydrogen bond is known, the first structure would appear to be the more likely of the two. Indeed, in a later part of this discussion it is proposed that formation of a polymeric material containing Be.H.Be units is sufficient to displace ligand coordinated to beryllium from an intermediate structure containing  units.

Single bridged hydrogen structures of the type B.H.B are fairly well known, and are thought to occur for example in the heptahydrodiborate ion, $B_2H_7^-$, and the complex formed between pyridine-borane and diborane.[6]

Two experimental observations are difficult to reconcile with the ligand being bound to beryllium. The triphenylphosphine-beryllium borohydride complex, $Ph_3P.BeB_2H_8$, heated under nitrogen became semi-liquid at about 122°, solidified above this temperature and finally melted with apparent decomposition at 163°. After benzene extraction, triphenylphosphine-borane was identified as one of the decomposition products. It should be noted that the adducts, triethylphosphine-, trimethylphosphine-,

and diethyletherberyllium borohydride, have been found to distil unchanged <u>in vacuo</u>. Secondly, the quantitative recovery (98.5%) of triphenylphosphine-borane following hydrolysis of the 1:1 adduct, $Ph_3P.BeB_2H_8$, would suggest that the phosphine is coordinated to boron rather than beryllium.



Hydrolysis of this compound would liberate 5/8 of the total hydrolysable hydrogen according to the equation.

$$Ph_3P.BeB_2H_8 + 5H_2O \longrightarrow Ph_3P.BH_3 + Be(OH)_2 + B(OH)_3 + 5H_2$$

Hydrolysis of the triethylphosphine and trimethylphosphine complexes release rather more than 5/8 of the hydrolysable hydrogen but considerably less than the total. The corresponding phosphine-borane has been identified as a hydrolysis product in both cases. If it is accepted that the phosphine is coordinated to beryllium, the mechanism of the reaction leading to the formation of phosphine-borane remains unknown.

Aluminium borohydride with trimethylamine or dimethyl ether gives 1:1 adducts,[7] and the amine adduct,(m.p.79°), decomposes at 100° to give trimethylamine-borane as one product, and an oily liquid corresponding to 'AlB_2H_9' which was not isolated as a pure compound. With excess amine, 3moles of amine react per mole of borohydride and on warming from -80° to room temperature the product separates into a crystalline solid and liquid. Trimethylamine-borane and trimethylamine were removed

in vacuo, and the residue corresponding to '$AlB_2H_9.NMe_3$' reacted with diborane according to the equation:

$$'AlB_2H_9.NMe_3' + B_2H_6 \longrightarrow AlB_3H_{12} + Me_3N.BH_3$$

With trimethylamine at room temperature, aluminium borohydride reacts with four moles of amine to give a product consisting of a solid and liquid. Trimethylamine quantitatively displaces ether from the complex, $Me_2O.AlB_3H_{12}$. Finally, the reaction between trimethylamine and the ammine complex, $H_3N.AlB_3H_{12}$, removed 93% of the total boron content as trimethylamine-borane together with a small amount of hydrogen. The remaining non-volatile solid corresponded to a composition, $(AlH_2N)_x$.

Several 1:1 adducts of aluminium borohydride, $L.AlB_3H_{12}$ where L = $Me_3N, Et_3N, Me_3P, Me_3As$, Me_2O, Et_2O, Me_2S, have recently been reported,[8] and on the basis of i.r. and B^{11} n.m.r. spectra it is suggested that coordination of ligand occurs to the aluminium atom. A ligand-acceptor bond strength order was proposed using the measured proton shift as an indication of relative strength of donor-acceptor bonds:

$$Me_3P \sim Me_3As > Me_3N,\ Et_2O > Me_2O > Me_2S.$$

Tensimetric titrations between aluminium borohydride and amine or phosphine compounds showed a break after addition of four equivalents of ligand, and the B^{11} n.m.r. spectrum of the product, 1:3:3:1 quartet, confirmed complete destruction of the borohydride.

$$Al(BH_4)_3 + 4R_3M \longrightarrow 3R_3M.BH_3 + R_3M.AlH_3 \quad (M = N,P;\ R = alkyl).$$

Only trimethylamine reacted rapidly at room temperature to cleave all the bridged hydrogen structure in the borohydride, trimethylphosphine reacted over several days, and the remaining ligands did not react beyond the formation of a 1:1 adduct.

Dimethylaminohydrido-aluminium borohydride and dimethylamino-aluminium diborohydride react rapidly with trimethylamine to give one and two equivalents respectively of amine-borane.[9]

$$HAlBH_4.NMe_2 + Me_3N \longrightarrow H_2Al.NMe_2 + Me_3N.BH_3$$

$$(BH_4)_2Al.NMe_2 + 2Me_3N \longrightarrow H_2AlNMe_2 + 2Me_3N.BH_3$$

Trimethylaminedihydrido-aluminium borohydride reacted rapidly with one mole of trimethylamine followed by a much slower reaction with a second mole of amine. The product corresponding to $H_2AlBH_4.2Me_3N$, solid at 0°, melted at 25° and the B^{11} n.m.r. spectrum showed a quadruplet, $\delta_4 = 26.0$, $J_{B-H} = 100c/s$, and a quintuplet, $\delta_5 = 56.6$, $J_{B-H} = 86c/s$, indicating cleavage of borohydride to amine-borane. The initial rapid reaction with amine did not cleave the borohydride to produce trimethylamine-alane, since if this had been formed it would have reacted with excess amine to give bistrimethylamine-alane.[10] The tensimetric titration between trimethylamine and trimethylaminehydrido-aluminium diborohydride indicated formation of a compound corresponding to $HAl(BH_4)_2.2NMe_3$, but in this case further reaction with amine was rapid and proceeded according to the equation:

$$HAl(BH_4)_2.NMe_3 + 3Me_3N \longrightarrow H_3Al.2NMe_3 + 2Me_3N.BH_3$$

Attempts to prepare triphenylphosphine or triethylphosphine

adducts of beryllium borohydride with P/Be ratios greater than one were unsuccessful. Triphenylphosphine and beryllium borohydride in benzene solution at room temperature gave an equimolar mixture of the 1:1 adduct and unreacted phosphine. The freezing points of dilute benzene solutions prepared from one mole of borohydride and two moles of phosphine, were those expected for the equimolar mixture of a 1:1 adduct and the phosphine.

Diethyl ether does not react with beryllium borohydride beyond the formation of a 1:1 adduct as shown by the tensimetric titration of the reactants, and after removal of excess ether, the ratio of ether combined per mole of borohydride was 0.96/1.0. Similarly, tensimetric titrations of the borohydride with various amine and phosphine compounds all indicated rapid formation of the corresponding 1:1 adduct. However, although the titration curve for trimethylamine indicates formation of only a 1:1 adduct, the ratio of amine reacting per mole of borohydride was 1.22/1.0, and for dimethylphosphine the ratio was 1.39/1.0. In both cases, constant pressure readings were only obtained after about 17hrs. beyond the formation of the 1:1 adduct. With dimethylphosphine, dimethylphosphine-borane was identified as a reaction product, and this suggests that the 1:1 adduct slowly reacts with excess phosphine to give the borane adduct. If the reaction involves formation of a 2:1 adduct, $(Me_2PH)_2BeB_2H_8$, it must be concluded that the product is decomposed at room temperature.

$Me_2PH.BeB_2H_8 + Me_2PH \rightarrow [(Me_2PH)_2BeB_2H_8] \rightarrow Me_2PH.BH_3 + Me_2PH.BeBH_5$

The i.r. spectrum of the liquid product after removal of dimethylphosphine-borane was found to be similar to that of the 1:1 adduct, $Me_2PH.BeB_2H_8$, except for the presence of a strong broad band centred on 1758cm^{-1}.

The titration curve obtained with trimethylphosphine indicates a break at a mole ratio of 2.0/1.0, and the ratio of reacted trimethylphosphine to borohydride was found to be 1.97/1.0. Addition of the phosphine to the borohydride was rapid up to the formation of the liquid 1:1 adduct, and this reacted slowly with excess phosphine to give ultimately a solid product corresponding to the composition, $(Me_3P)_2BeB_2H_8$. However, it was established that trimethylphosphine-borane could be sublimed from the solid product at room temperature, and this suggested that the product was a mixture of trimethylphosphine-borane and '$Me_3P.BeBH_5$'. The i.r. spectrum of the solid product, obtained as a nujol-mull, was similar to that of the 1:1 adduct, $Me_3P.BeB_2H_8$, but after removal of trimethylphosphine-borane, by vacuum sublimation at room temperature, the residue contained a strong broad band centred on 1758cm^{-1}. For reasons that will become apparent in a later part of this discussion, the broad absorption centred on 1758cm^{-1} is associated with a stretching mode of the $(Be.H.Be)_n$ group.

Dimethylamine reacts rapidly with beryllium borohydride up to the formation of a 1:1 adduct, but beyond this point

constant pressure readings were obtained only after about 17hrs., and the original liquid product gradually solidified to give a product corresponding to a mole ratio of amine to borohydride of 2.94/1.0. This product has not been examined in any great detail, but the i.r. spectrum does not contain an absorption band at 1758cm^{-1}. The product melts with evolution of hydrogen and dimethylamine at 94°, and after standing for several hours, the liquid product deposits solid of unknown composition and which was not further studied.

The reaction between trimethylphosphine and beryllium borohydride in a mole ratio of phosphine to borohydride of 2.0/1.0 has been investigated in rather more detail. At room temperature, the liquid product becomes completely solid after about 48hrs., and both trimethylphosphine-borane and trimethylphosphine were recovered by vacuum sublimation at room temperature. In one such experiment, 30.6%, of the total boron content of the borohydride was recovered as the phosphine-borane, together with trimethylphosphine corresponding to 15.2% of that originally added. It was established, in a separate experiment, that the recovered phosphine reacted slowly with the glassy-residue to give a product from which more phosphine-borane could be recovered together with a small amount of trimethylphosphine. A total of 56.5% of the boron content of the borohydride was removed as the phosphine-borane. The i.r. spectrum of the residual cloudy viscous paste was very similar to that of the 1:1 adduct,

$Me_3P.BeB_2H_8$, except for a strong absorption centred on 1758cm.$^{-1}$

On warming (60°) the solid material corresponding in composition to $(Me_3P)_2BeB_2H_8$, considerable dissociation occurred with liberation of trimethylphosphine. After heating to 100° for several hours, trimethylphosphine and trimethylphosphine-borane were recovered corresponding to removal of 81.5% of the total boron content of the borohydride.

It is of interest at this stage to observe that although trimethylamine will displace trimethylphosphine from the complex, $Me_3P.BeB_2H_8$, in which the phosphine is bonded to the beryllium atom, trimethylphosphine is more efficient than trimethylamine[4]. in removing boron from the borohydride as the borane adduct. This is in agreement with the greater donor strength of trimethylphosphine to boron in the adduct, $Me_3P.BH_3$, compared to that of the amine adduct, $Me_3N.BH_3$.[11] For example, it has been found that trimethylamine is displaced from the adduct, $Me_3N.BH_3$, by trimethylphosphine. Considering the stability of the adduct, $L\text{-}BH_3$, purely from the strength of the σ bond between the donor and acceptor molecules, it would appear that this order is just the reverse of what would be expected since in general, the donor strength to a given acceptor molecule decreases in the order, N > P > As > Sb. However, it is postulated that in adducts of the type, $L\text{-}BH_3$, the σ bond is reinforced by back coordination from BH_3 in a π type interaction with a vacant $\underline{d}_\pi$ orbital on the donor atom. This interaction is of course absent when N is the

donor atom, but is presumably quite important with P as the donor atom. The stability of borane adducts with ligands of Group VI atoms is considerably less than that of the analogous ligands of Group V. For example, neither diethyl ether nor dimethyl ether form a stable adduct of the type $R_2O.BH_3$, and this would account for the fact that diethyl ether does not react with beryllium borohydride beyond the formation of a 1:1 adduct, $Et_2O.BeB_2H_8$.

There would appear to be little evidence for the formation of a stable phosphine complex, '$Me_3P.BeBH_5$', corresponding to the reported[4] amine compound, $Me_3N.BeBH_5$. The sublimation of trimethylphosphine-borane from the mixture corresponding to the composition, $(Me_3P)_2BeB_2H_8$, resulted in removal of trimethylphosphine which slowly reacted with the involatile residue to form more phosphine-borane. The i.r. spectrum of the final involatile material contained a strong absorption at 1758cm^{-1} which is consistent with the formation of polymeric material containing (Be.H.Be) units. A 2:1 mixture of trimethylphosphine and beryllium borohydride in benzene solution after heating for several hours at 65° slowly precipitated beryllium hydride, and after heating for 9days, the hydride was recovered in about 63% yield after removal of trimethylphosphine-borane (corresponding to 56% of the total boron content) and a small volume of an unknown liquid. The beryllium hydride so prepared contained 74.8 wt.% BeH_2, and the impurities could not be removed by solvent extraction or vacuum sublimation. The overall reaction may be

written:

$$BeB_2H_8 + 2Me_3P \longrightarrow 2Me_3P.BH_3 + BeH_2$$

and it is perhaps significant that even in the presence of excess ligand, no evidence was obtained for the formation of beryllium hydride adducts, L_2BeH_2. This is in complete contrast to similar reactions with aluminium borohydride:

$$Al(BH_4)_3 + 4R_3M \longrightarrow 3R_3M.BH_3 + H_3Al.MR_3$$

Before describing further preparations of beryllium hydride by the above type of reaction, and indicating a possible reaction path, a brief outline of alternative methods for the preparation of beryllium hydride will be presented. In particular, i.r. assignments for compounds containing beryllium-hydrogen bonds will be indicated.

Beryllium hydride.

Beryllium hydride has been prepared in varying degrees of purity by several methods.

The white, insoluble, and involatile hydride obtained from lithium tetrahydroaluminate and dimethylberyllium in ether solution[12]. decomposed on heating at 125° and reacted vigorously with water. It was subsequently reported[13]. that the hydride so prepared was inseperably contaminated with aluminium and lithium. Dimethylberyllium was found to react with dimethylaluminium hydride in the absence of solvent,[12].

$$2Me_2AlH + Me_2Be \longrightarrow 2Me_3Al + BeH_2$$

but even in isopentane solution, a product free from methyl

groups could not be obtained.

Pyrolysis of ethereal ditert-butylberyllium at 150° gave a product corresponding to 89mole % BeH_2, and that from pyrolysis at 210° to 96.3mole % BeH_2, the rest being Bu^t groups.[14] This product decomposed at 300°, and was incompletely hydrolysed by water at room temperature. Ether free ditert-butylberyllium[15] at 200° gave 97mole % BeH_2, density 0.51g./cc., and an X-ray powder photograph contained no lines attributable to a crystalline hydride.

Direct synthesis from the metal and both molecular or atomic hydrogen at high temperatures and pressures have been unsuccessful.[16,17] A surface reaction between lithium hydride and beryllium chloride has been reported,[18] but no product was isolated.

Beryllium hydride was reported[14] to react with two moles of dimethylamine at 160° liberating hydrogen and forming bis-dimethylaminoberyllium, and with diborane at 95° to give beryllium borohydride. The compound did not react with trimethylamine even at 210°. Apparently the heat of polymerisation of the hydride is too great to allow depolymerisation which must precede coordination to trimethylamine.

Sodium hydridodiethylberyllate[19] and sodium hydridodimethylberyllate[20] react with beryllium chloride to give a complex alkylberyllium hydride:

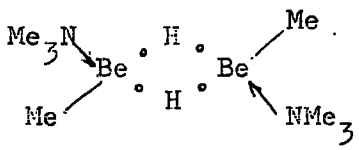
$$2NaBeEt_2H + BeCl_2 \longrightarrow 2NaCl + 'Et_4Be_3H_2'$$

Pyrolysis of this material at 110-120° in vacuo gave a residue containing 17.8% hydride hydrogen suggesting the reaction,

$$'Et_4Be_3H_2' \longrightarrow 2Et_2Be + BeH_2$$

since the hydrogen content of beryllium hydride is 18.3%. However, this result was misleading since a small amount of the salt, $NaBeEt_2H$, contaminated the alkylberyllium hydride. This was removed by the addition of the calculated amount of beryllium chloride. Pyrolysis of the product at 180°gave an amorphous product corresponding to the composition $Na_2Be_2H_6 + 65BeH_2$ (or $Na_2BeH_4 + 66BeH_2$) or 91 wt.% BeH_2. The i.r. spectrum showed a strong absorption centred on 1754cm^{-1}.[21].

The trimethylamine complex of methylberyllium hydride[22]. is dimeric in benzene solution.



The compound is thought to contain a hydride bridge since the complex is not decomposed by excess amine, whereas methyl bridges in dimethylberyllium are cleaved by trimethylamine.[22]. Studies[23]. of reactions between dialkylaluminium hydrides and donor molecules have shown that hydride bridges in these compounds are less readily cleaved than are methyl bridges in trimethylaluminium.

Attempts to prepare monomeric complexes, L_2BeMeH, by donor molecules which readily form chelate complexes were not successful.[20].

Infra-red Spectra.[20]

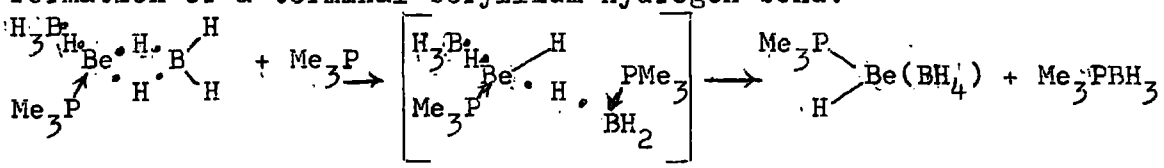
Since the 0-1 vibrational transition of the ground state of the BeH molecule is at 2058.6cm^{-1},[24] a terminal Be-H group would be expected to cause absorption near 2100cm.$^{-1}$ The vibrational modes of mainly stretching character of the bridging hydrogen atoms in a BeH_2Be group should cause absorption at frequencies well below 2100cm^{-1}, by analogy with the vibrational modes of the BH_2B groups in diborane and the various methyl- and ethyl-diboranes. Whereas terminal B-H bonds usually cause absorption in the 2200-2500cm^{-1} region, the two modes due to the BH_2B bridge in diborane are at 1915 (ν_{13}, symmetrical out-of-phase) and 1606cm^{-1}(ν_{17}, asymmetric in-phase).

The i.r. spectrum of the compound, $(MeHBe.NMe_3)_2$, contains a strong absorption at 1344cm^{-1} which is due to one of the BeH_2Be stretching modes since in the spectrum of the deutero-analogue, $(MeDBe.NMe_3)_2$, it moves to about 1020cm.$^{-1}$ Absorption due to $\nu(BeH_2Be)$ occurs at 1333cm^{-1} in the spectrum of the ethyl derivative $(EtHBe.NMe_3)_2$. Absorptions at 1328cm^{-1} and 1165cm^{-1} observed in the spectrum of $Na_2(Me_4Be_2H_2)$ are due to BeH_2Be bridge vibrations.

The spectrum of $(MeHBe.NMe_3)_2$ as saturated vapour showed $\nu(BeH_2Be)$ at 1342cm^{-1}, and at 80° a sharp absorption at 2141cm^{-1} appeared. It is thought that this absorption is due to terminal ν(Be-H) in the monomer, $(MeHBe.NMe_3)$.

Proposed mechanism for the formation of beryllium hydride from beryllium borohydride and trimethylphosphine.

There can be little doubt that the initial reaction involves formation of the liquid 1:1 adduct, $Me_3P.BeB_2H_8$, which is followed by a slower reaction with a second mole of phosphine to remove borane units from the borohydride as trimethylphosphine-borane. This must necessarily involve cleavage of a hydride bridge and coordination of the ligand to a boron atom with formation of a terminal beryllium-hydrogen bond.



During removal of the borane adduct by vacuum sublimation at room temperature from the solid material of overall composition, $(Me_3P)_2BeB_2H_8$, or by gently heating this solid material, trimethylphosphine was liberated. Now since this is unlikely to be formed by dissociation of the borane adduct, it must be liberated from the intermediate, $Me_3P.Be(H)BH_4$, presumably with formation of a Be.H.Be bond. This suggestion would appear to be consistent with the appearance of an absorption band at $1758cm^{-1}$ in the i.r. spectrum of the solid after removal of trimethylphosphine-borane and trimethylphosphine. It would appear then that the heat of formation of a single hydride bridge, Be.H.Be, is sufficient to compensate for the removal of phosphine coordinated to beryllium. This does not appear unreasonable since the hydride bridge in the

dimeric compound, $(MeHBe.NMe_3)_2$, is not cleaved by trimethylamine, which itself is a considerably stronger donor to beryllium than trimethylphosphine, and neither is the hydride bridge in beryllium hydride depolymerised by trimethylamine. On the basis of this argument, it is apparent that the earlier proposed structures for the 1:1 adducts of beryllium borohydride containing a terminal beryllium-hydrogen bond are unacceptable.

Removal of trimethylphosphine from the intermediate material '$Me_3P.BeBH_5$' may be represented by the equation.

$$n(Me_3P.BeBH_5) \longrightarrow xMe_3P + (Me_3P)_{n-x}.(BeBH_5)_n$$

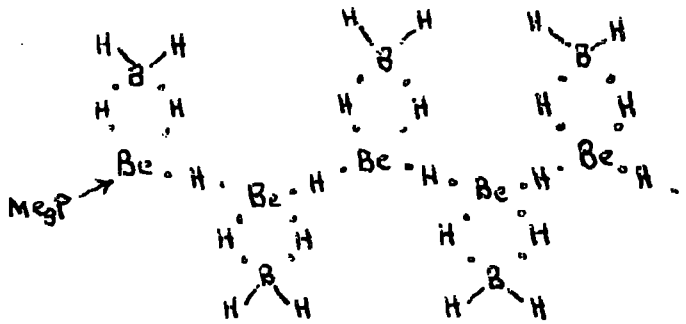
It has been established that the recovered phosphine will react with the material $(Me_3P)_{n-x}.(BeBH_5)_n$ to give more trimethylphosphine-borane as indicated in the equation:

$$xMe_3P + (Me_3P)_{n-x}.(BeBH_5)_n \longrightarrow xMe_3P.BH_3 + (Me_3P)_{n-x}Be_nB_{n-x}H_{5n-3x}$$

The continued displacement of trimethylphosphine and abstraction by this of borane units, would give ultimately a polymeric beryllium hydride.

A possible intermediate structure, shown below, does not show random cross-linking by Be.H.Be bonds between adjacent chains. However, and especially with the possibility of cross-linking, it is apparent that in material approaching the composition of beryllium hydride it will become increasingly difficult for the phosphine to react with available borane units. Further, it will become more difficult to remove the borane adduct formed within the beryllium hydride structure. This may account for the

observation that the impurities in beryllium hydride prepared by this method could not be removed by either solvent extraction or vacuum sublimation.



Preparation of beryllium hydride from beryllium borohydride and triphenylphosphine.

Pyrolysis of a mixture of beryllium borohydride with two moles of triphenylphosphine at 180° in a sealed tube under nitrogen results in the formation of a mixture of liquid and solid products. In one experiment, extraction of the cooled solid mixture with benzene gave triphenylphosphine-borane in 98.5% yield, and left a white insoluble residue consisting mainly of beryllium hydride, (78 wt.% or 98.6mole%). The hydride so prepared is only slowly hydrolysed by water, but dissolves readily in dilute acid solutions to give a slightly cloudy solution from which enough solid material could be separated to allow its identification by i.r. spectrum as the phosphine-borane, $Ph_3P.BH_3$. The hydride obtained from pyrolysis at 100° was much less pure, and indeed, was found to fire on exposure to air.

If reaction is carried out in solution, the beryllium hydride content of the insoluble product is a little higher.

Solutions of the 1:1 adduct in benzene containing an additional mole of triphenylphosphine slowly became turbid at 100°, and it was better to use xylene as solvent since reaction then was apparently complete after 6hrs. at 150°. At this temperature the density of the hydride appeared very close to that of the solution. After extraction of the borane adduct from the insoluble product with benzene, the residue contained 83wt.% BeH_2, or 99mole % on the assumption that the rest is triphenylphosphine-borane. Attempts to separate the impurity by prolonged benzene extraction, or high temperature (200°) sublimation in a good vacuum were quite unsuccessful. The i.r. spectrum of the hydride as a nujol-mull, showed only one major feature which was a broad band, (width 313cm^{-1} at half-height), centred on 1758cm^{-1}.

Beryllium borohydride and two moles of triethylphosphine deposited beryllium hydride at 120°, and the liquid reactants immediately set to a glassy-solid. After heating at 145° for several hours, the triethylphosphine-borane was removed by benzene extraction to leave impure beryllium hydride,(35.1wt.%). Impurities could not be removed by either solvent extraction or vacuum sublimation. A slightly purer product,(58.6wt.%), was prepared from working in xylene solution, but again attempts to purify the product were unsuccessful.

REFERENCES.

1) A.Brenner and B.Wood J.Electrochem.Soc.,1957,104,33.

2) R.H.Kratzer and K.L.Paciorek NAVWEPS Report,8204,Aug.,1964.

3) W.C.Price J.Chem.Phys.,1949,17,1044.

4) A.B.Burg and H.I.Schlesinger J.Amer.Chem.Soc.,1940,62,3425.

5) W.N.Lipscomb ADVANCES IN INORGANIC CHEMISTRY AND RADIOCHEMISTRY.(Academic Books Ltd.) Vol.1,1959.

6) H.C.Brown,P.F.Stehle and P.A.Tierney J.Amer.Chem.Soc.,1957,79,2020.

7) H.I.Schlesinger,R.T.Sanderson, and A.B.Burg J.Amer.Chem.Soc.,1940,62,3421.

8) R.H.Bird and M.G.H.Wallbridge J.,1965, in press.

9) J.K.Ruff Inorg.Chem.,1963,2,515.

10) J.K.Ruff ADVANCES IN CHEMISTRY,SERIES No.42, BORON-NITROGEN CHEMISTRY.

11) F.G.A.Stone Chem.Rev.,1958,58,101.

12) G.D.Barbaras,C.Dillard,A.E.Finholt,T.Wartik, K.E.Wilzbach and H.I.Schlesinger J.Amer.Chem.Soc.,1951,73,4585.

13) E.L.Head,C.E.Holley, and S.W.Rabideau J.Amer.Chem.Soc.,1957,79,3687.

14) G.E.Coates and F.Glockling J.,1954,2526.

15) G.E.Coates and F.Glockling J.,1954,22.

16) J.C.Poweres,D.W.Vose,and E.A.Sullivan Chem.Abs.,1963,58,219.

17) E.Pietsch Z.Elektrochem.,1933,577,39.

18) E.Wiberg and R.Bauer Z.Naturforsch,1951,6b,171.

19) G.E.Coates and G.F.Cox Chem.and Ind.,1962,269.

20) N.A.Bell and G.E.Coates J.,1965,692.

21) N.A.Bell Ph.D. Thesis,Durham, 1964.

22) G.E.Coates and N.D.Huck J.,1952,4501.

23) E.G.Hoffmann and G.Schomburg Z.Elektrochem,1957,61,1101,1110.

24) G.Herzberg MOLECULAR SPECTRA AND MOLECULAR STRUCTURE, Van Nostrand, Princeton,1950, Vol.1, 508.